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**VAIRĀKU IZMEKLĒTU ORGANISKO REAKCIJU
PĒTĪJUMI AR MOLEKULĀRĀS MODELĒŠANAS
METODĒM**
MAGISTRA DARBS

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CHEMISTRY

**INVESTIGATION OF SOME ORGANIC
REACTIONS WITH THE HELP OF MOLECULAR
MODELLING METHODS**
MASTER'S THESIS

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ANOTĀCIJA

Vairāku izmeklētu organisko reakciju pētījumi ar molekulārās modelēšanas metodēm. Balodis M., darba vadītāji profesors Actiņš A. un profesors Farkas Ö. Maģistra darbs, 191 lappuses, 35 attēli, 15 tabulas, 110 literatūras avoti, 76 pielikumi. Angļu valodā.

Šajā darbā ir pētītas un analizētas butadiēna un etēna Dīlsa-Aldera reakcija, 1,5-heksadiēna Koupa reakcija, 2,3-diazabīciklo(2.2.1)hept-2-ēna deacetizēšana un N-neopentilmaleisoimīda un 2,3-dimetilbutadiēna Dīlsa-Aldera reakcijas katalīze. Nosauktajās reakcijās atrasti un optimizēti svarīgākie stacionārie punkti. Modelēta Dīlsa-Aldera, Koupa un 2,3-diazabīciklo(2.2.1)hept-2-ēna deacetizēšana reakciju dinamika un secināts par UB3LYP funkcionāla nelietderību pēdējā no šīm reakcijām. Ir izvērtēti vairāki potenciālie N-neopentilmaleisoimīda un 2,3-dimetilbutadiēna Dīlsa-Aldera reakcijas katalizatori kā arī optimālākie piedāvāti tālākiem laboratorijas eksperimentiem. Molekulārās modelēšana analīzes metodes, kas sevī ietver stacionārās un dinamiskās, ir izmantotas izdevīgāko konformāciju meklējumos, struktūru optimizācijā kā arī pārejas stāvokļu un kopējā reakcijas ceļa aprēķinos.

MOLEKULĀRĀ DINAMIKA, DEACETIZĒŠANA, DĪLSA-ALDERA REAKCIJA, IZOMALEIMĪDS, TRĪS ŪDEŅRAŽA SAIŠU KATALĪZE.

ABSTRACT

Investigation of some organic reactions with the help of molecular modelling methods. Balodis M., supervisors professor Actins A. and professor Farkas Ö. Master's thesis, 191 pages, 35 figures, 15 tables, 110 literature references, 76 appendices. In English.

Diels-Alder reaction of butadiene and ethene, Cope reaction of 1,5-hexadiene, 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization and catalysis of N-neopentylmaleisomide reaction with 2,3-dimethylbutadiene have been investigated and analyzed in this work. Main stationary points for these reactions have been found, optimized and characterized. Diels-Alder, Cope and 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization reaction dynamics have been simulated and inferred about unsuitableness of UB3LYP functional in the latter one. Some possible catalysts for catalysis of N-neopentylmaleisomide reaction with 2,3-dimethylbutadiene have been looked at and the most optimal ones have been introduced for further work in the laboratory. Methods of molecular modeling that included stationary and dynamic methods have been used for conformational search, optimization of structures, and transition state and reaction path calculations.

MOLECULAR DYNAMICS, DEAZETIZATION, DIELS-ALDER REACTION, ISOMALEIMIDE, THREE HYDROGEN BOND CATALYSIS.

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ABBREVIATIONS

<i>ab initio</i>	– “from the first principles of the quantum mechanics”
AcDAP	– Molecular complex of 2,6-diacetylaminopyridinium ion and N-neopentylisomaleimide
AIMD	– <i>ab initio</i> molecular dynamics
B_n	– n-molecular complex of biuret and N-neopentylisomaleimide
B3LYP	– Becke three-parameter Lee-Yang-Parr exchange-correlation functional
BOMD	– Born-Oppenheimer molecular dynamics
CASSCF	– Complete active space self-consistent field theory
CASPT2N	– Complete active space self-consistent field second-order perturbation theory
CBS	– Complete basis set method
CC	– Coupled cluster theory
CCSD(T)	– Coupled cluster, full singles and doubles, estimate triples
CI	– Configuration interaction
COSMO	– Conductor-like screening model
COSMO-RS	– Conductor-like screening model for real solvents
CPMD	– Car-Parrinello molecular dynamics
DA	– Diels-Alder reaction
DAP	– Molecular complex of 2,6-diaminopyridinium ion and N-neopentylisomaleimide
DB	– 2,3-Dimethylbutadiene
DBH	– 2,3-Diazabicyclo(2.2.1)hept-2-ene
DFT	– Density functional theory
HF	– Hartree Fock theory
HOMO	– Highest occupied molecular orbital
G2 (G3)	– Gaussian 2 (Gaussian 3) methods
GD3BJ	– Grimme’s dispersion with Becke-Johnson damping
GTO	– Gaussian type orbitals
IPCM	– Isodensity polarizable continuum model
IRC	– Intrinsic reaction coordinate

LUMO	– Lowest unoccupied molecular orbital
MM	– Molecular mechanics
MMFF94	– Merck molecular force field 94
MP	– Møller-Plesset perturbation theory
MCSCF	– Multiconfigurational self-consistent field theory
NI	– N-neopentylisomaleimide
PCM	– Polarizable continuum model
PES	– Potential energy surface
PM3	– Parameterized model number 3
QCI	– Quadratic configuration interaction
R_{ij}	– Distance between atoms i and j
RRKM	– Rice–Ramsperger–Kassel–Marcus
SchrThioB_n	– n th -molecular molecular complex of Schreiner’s-like thiobiuret catalyst and N-neopentylisomaleimide
SchrThioU_n	– n th -molecular molecular complex of Schreiner’s catalyst and N-neopentylisomaleimide
SCIPCM	– Self-consistent isodensity polarizable continuum model
SCRf	– Self-consistent reaction field
STQN	– Synchronous transit-guided quasi-Newton
ThioB_n	– n th -molecular complex of dithiobiuret and N-neopentylisomaleimide
ThioU_n	– n th -molecular complex of thiourea and N-neopentylisomaleimide
TS	– Transition state
TST	– Transition state theory
U_n	– n th -molecular complex of urea and N-neopentylisomaleimide
Zn-ThioB	– Complex of Zn ²⁺ , dithiobiuret and N-neopentylisomaleimide

INTRODUCTION

A geometric increase in the performance of computers over past few decades has led to the birth of a new way of doing science that is at the intersection of theory and experiment. Many theories now are incorporated in computer software and readily usable to pursue problems in chemistry before actually exploring them in laboratory. They help to separate out possible paths that should be followed and also paths that should be avoided in practice. And they also provide means to deepen our mechanistic understanding of reactions and the ways in which they are happening. Static calculations help to evaluate stationary points on potential energy surface whereas molecular dynamic calculations, to see reaction and conformation evolution in the course of time. The field of molecular modeling is still growing and finding new ways how to improve itself. New algorithms are implemented and improved all the time and software that contains them needs to be tested.

One of the implicit goals of this thesis is to test a new computational software, called Cool Molecular Dynamics, which is still under development, but shows promise because of the conceptually new algorithm that is implemented in it. To test it and also to get used to using computational tools for molecular modeling calculations, first some simple reactions will be chosen. Diels-Alder and Cope reactions are natural choice; because they have been extensively studied and therefore results can be compared with the literature. These reactions are important in the context of the organic chemistry and also simplest systems that can be simulated are conveniently small. After probing these, something bigger and not adequately described with static molecular modeling tools needs to be chosen. It is deazetization of 2,3-diazabicyclo(2.2.1)hept-2-ene (DBA). While being one of the cornerstones for dynamically controlled reactions, nobody has tried to use the most popular density functional B3LYP in hands with molecular dynamics to study it. As the density functional theory nowadays is the default choice for using *ab initio* molecular dynamics, it is important to evaluate its robustness by applying it to different types of reactions. Last but not least of the chemical processes that will be studied in this work will be catalysis of Diels-Alder reaction of symmetrical diene and isomaleimide with three hydrogen bond donor organic catalysts. Organic catalysts are more eco-friendly and cheaper than conventional metal-organic catalysts. In many cases these catalysts serve as

hydrogen bond donors for the substrate and henceforth help to speed up the reaction. Many examples are known where two hydrogen donor acts this way. However, almost nothing can be found about cases where three hydrogen bond donors would be applied in the same way. By adding one additional interaction they could enhance the catalytic effect even further, at least there, in those cases where all three hydrogen bond donors could be applied. One of the substrates that could gain from it is isomaleimide in Diels-Alder reaction with diene, with its three, in almost straight line positioned heteroatoms that could serve as hydrogen bond acceptors. Besides, because of the complexity of this study, possibility to perform molecular dynamics conformational search will come handy and will be tested to find suitable conformers for in-depth studies.

Objective of the work is to simulate Diels-Alder reaction, Cope reaction and deazetization of DBA using Cool Molecular Dynamics, to evaluate the results and to explore suitability of different three hydrogen bond donor catalysts for N-neopentylisomaleimide reaction with 2,3-dimethylbutadiene.

Tasks of the work:

1. to simulate Diels-Alder and Cope reactions with the help of molecular dynamics and to test molecular dynamics suitability for finding transition states;
2. to investigate the suitability of UB3LYP functional for molecular dynamics calculations of 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization;
3. to assess and improve biuret, dithiobiuret and their derivative catalytical activity for N-neopentylisomaleimide and 2,3-dimethylbutadiene Diels-Alder reaction and to propose potentially effective three hydrogen bond forming catalyst for this reaction.

1. LITERATURE REVIEW

In the first subsection theories that are the most important for calculations made in this work have been listed and shortly described. The second subsection continues theme of the first one, introducing molecular dynamics which expands theme developed in the first section by adding a time factor. The third section tells about transitional and conformational search. The last subsection of the literature review is dedicated to the reactions which have been studied in this work.

1.1. Electronic structure theories in computational chemistry

Thermodynamic, conformational, kinetic and other data that concern chemical reactions and molecular systems are of interest to any chemist. Obtaining these data, however, sometimes is hard and time-consuming. Quantum chemistry provides access to these data via use of the nonrelativistic Schrodinger equation and thus they can be obtained with the help of theoretical computations [1].

Hartree-Fock (HF) theory is both the starting point on which other, much more advanced *ab initio* methods have had been built and also of great conceptual importance [2, 3]. In the HF theory we introduce Born-Oppenheimer approximation (nuclei are fixed in their positions) and reduce the many-electron problem to one-electron problems by considering the interactions between individual electrons with the mean field of the remaining electrons. HF theory is variational, i. e. the calculated energies are equal or bigger than the ground state energy of the system. Biggest drawback of the HF theory is that it doesn't take into account electron correlation (except exchange correlation) and gives energies which are typically 90-99% the exact energy [4-7]. Post-HF methods try to fix this drawback by calculating the correlation energy; energy due to the electron correlation. Some notes about the correlation energy. It is partitioned in two parts, static and dynamic. Static correlation is so called long-range correlation which arises from near-degeneracies between occupied and unoccupied orbitals. Dynamic correlation accounts for instantaneous changes in short-range interactions between electrons which "feel" each other's presence because of the Coulomb repulsion [8]. While being one of the first, HF method is still used, e.g. as a cheap way to calculate occupied orbital energies [9], as a

method for comparison of calculated properties [10] or as a base on which to make more efficient algorithms for other methods that share similarity with it [4, 11].

Configuration interaction (CI) method, being direct extension of HF, corrects the mean-field approach of the latter. Correlation is included by describing wavefunction as a linear combination of Slater determinants. Method is very computationally demanding and full CI (“full” standing for inclusion of all possible electron excitations) calculations scale factorially with the basis set size [12]. For medium and large sized systems practically only truncated versions are used where included are only single (CIS), double (CID) or single-double (CISD) excitations [13]. Full CI is size consistent, i. e. for system $A \cdots B$, where A and B are non-interacting species, energy of this system is the sum of separately calculated energies of A and B. Truncated versions lack the size consistency that being the greatest shortcoming of them. Extension of CI – quadratic configuration interaction (QCI) theory corrects the problem with the size-inconsistency [5, 6, 13]. Nowadays a role of the CI theory has mostly been replaced by the theories that are discussed further.

Multiconfigurational self-consistent field (MCSCF) theory is used in quasi-degenerate molecular orbital cases or in bond breaking situations. To do it, MCSCF theory refines basis functions, which are included in the Slater determinants. MCSCF methods only take into account static electron correlation [8]. Variation of MCSCF is complete active space self-consistent field theory (CASSCF), where orbitals which makes various CI determinants, are chosen beforehand [5, 6]. Before calculation one needs to choose orbitals and electrons that will be included in the active space [14]. CASSCF nowadays is a gold standard for static electron correlation computations [8]. It can be size-consistent if the active space is chosen properly. However, it is not variational [5]. Complete active space perturbational theory second order (CASPT2N), which is an extension of the CASSCF, uses perturbational calculations (mentioned later in this text) to include the dynamic correlation [5, 6].

Most used quantum mechanical methods in computational chemistry currently are based on Kohn–Sham Density Functional Theory (DFT). It is because of the fact that typically their accuracy are similar with low level post-HF methods and can be achieved in time consistent with HF calculations [15]. The biggest difference between these and the *ab initio* methods are that DFT uses total electron density $\rho(\mathbf{r})$ in the place of $3N$ variables (x, y and z coordinates) for each electron. For a similar computational cost as HF method,

DFT includes the electron correlation [5, 6]. The major problem with DFT is that the exact functionals that describe exchange and correlation are not known, so, approximations are used [16]. DFT methods are not the best choice for calculations involving excited and degenerate states [17]. But they are considered as standard for probing pericyclic reactions [18]. Most widely used functional is Becke three-parameter Lee-Yang-Parr exchange-correlation functional (B3LYP). It includes Hartree-Fock exchange, local exchange, gradient exchange correction, local correlation, and gradient correlation correction [19]. B3LYP excels in geometry determination and thermochemical quantity calculations and is fast compared with more sophisticated functionals [20]. If one wants to take into account situations where main contributions to interactions are given by the dispersion then one can use Grimme's dispersion correction. One of the latest versions of it is GD3BJ (Grimme's dispersion with Becke-Johnson damping) [21].

CASSCF and CASPT2N have shown their superiority over various DFT methods in calculations where di-radical character have been investigated [22]. And for ionization potential calculations even HF method is considered to be better than DFT [23].

There are other important electronic structure calculation theories, which are widely used and will be shortly mentioned. For example, Moller-Plesset (MP) perturbation theory which uses perturbative expansion to describe electron correlation [24]. Or coupled-cluster theory (CC), which is related (and superior) to the CI. Latters variation is CCSD(I), which is considered to be the "gold standard" in terms of its capability to predict accurate energies [13]. For accurate assessment of thermochemical properties composite energy methods are available, with most commonly used ones being gaussian-2 (G2), gaussian-3 (G3) and complete basis set (CBS) methods [25].

To use appropriate theory one beforehand also needs to choose mathematical description of the starting atomic orbitals, called, a basis set. 6-31G++(d,p) is an example of Pople-style basis set. Here six Gaussian type orbitals (GTO's) are used for inner core functions and valence space is split in two functions (called double-zeta), where three GTO's are used for the first (inner) function and one GTO is used for second (outer) function [26]. Plus sings designates addition of additional diffuse functions, which are needed when looking at anions or molecular properties related to electron densities not localized in the valence space [27]. (d,p) designates additional d polarization functions on non-hydrogen atoms and p polarization functions on hydrogen atoms. Alternative to

these Pople-style split-valence basis sets are Dunning correlation-consistent basis sets [5, 6]. Choice of the basis set sometimes is very important, for example, medium sized 6-31G(d) is too small to give accurate unoccupied orbital energies. Also, the bigger the basis set, the more reliable it is and better energies can be gained by the use of it [28].

It can be concluded that for practical purposes the most useful theory nowadays is DFT with moderate sized size basis set, because it gives reasonable results without using too much of computational resources. Although slowly losing its reign amongst others, B3LYP functional is still a good starting point for any calculation, especially, if one doesn't know what would be the best for the studied system. For really precise results one would want to use the composite energy methods or CCSD(T), but they are not immune to serious errors. CASSCF is good for systems where static correlation is important and CASPT2N can improve CASSCF results by correcting for the dynamical correlation. However, each examined case is different, so it's a good practice to do calculations and comparison using different methods. When that is done, last, but no least, obtained results should be compared with the experimental results.

1.2. *Ab initio* molecular dynamics

Ab initio molecular dynamics (AIMD), also called direct dynamics [29] is a semiclassical method which unifies both molecular dynamics and electronic structure theory [30]. AIMD is the numerical solution of Hamilton's equation of motion, which allows both thermodynamic and dynamic properties of a system at finite temperature to be computed [31]. In AIMD interatomic forces acting on the nuclei (which is the most challenging computation) are calculated on-the-fly as the molecular dynamics trajectory is generated. Electronic structure theory can give significantly more accurate potential energy surface (PES) than classical force fields, particularly for systems exhibiting strong polarization, charge transfer, and bond rearrangements [32]. Methodology of the AIMD simulations is still in the stage of development and its application has become active only in the last 20 years [32, 33]. Quantum mechanical nature of the electrons usually is described with DFT, but nuclei are treated classically (although for low temperatures nuclear quantum effects can be important) [31]. Methods other than DFT are used too, e.g. HF [32], MPn [34, 35] and CASSCF [36]. Very high-level theories, like, CCSD(T) are

not feasible because of the computational cost they involve and by the lack of analytical gradients for the most of them [37].

There are two main AIMD approaches: Born-Oppenheimer molecular dynamics (BOMD) and Car-Parrinello molecular dynamics (CPMD). The main difference between these two is that in the latter explicit electronic energy minimization at each step is not necessary, which saves time [31]. In BOMD version of AIMD at each step of trajectory integration the potential energy $V(\mathbf{q})$ and gradient $\delta V(\mathbf{q})/\delta q_i$ are obtained by optimizing the electronic wavefunction for fixed nuclear positions [30, 37]. CPMD explicitly includes the electrons as active degrees of freedom and prevents the need to calculate self-consistent field at each step opposed to BOMD [31]. Recently there have been developed a second generation of CPMD, which combines the accuracy and long timesteps of BOMD with the efficiency of CPMD [38]. Older than the discussed two approaches is the Ehrenfest molecular dynamics, but nowadays it is typically used only for a few-body collision and scattering problems [30, 39]. Sometimes degrees of freedom are constrained in AIMD [40] but it comes with the cost of imprecise PES. Temperature usually is controlled by a simulated thermostat, like Nose-Hoover [41]

DFT provides a useful way to challenge problems associated with reliable potential energy surface calculations [42]. Unfortunately, conventional functionals suffer from some notorious failures, like, underestimation of heights of reaction energy barriers and incapability to reproduce long-range van der Waals interactions. For example, inadequacy of B3LYP to describe dynamics was shown in a $\text{H} + \text{H}_2$ exchange reaction [42]. In this case, recently developed doubly hybrid functional XYG3 [43], which had already shown its superiority to the B3LYP, was much better descriptor [42]. CASSCF is frequently utilized in AIMD studies where it gives a reliable description of the mixing of electronic states in the surface crossings, called conical intersections [44]. It is important in studying electronically excited states [45]. Because of the large computational demand typically no more than 10 electrons and 10 orbitals can be included in the active space [44].

AIMD can help to probe cases where conventional computational chemistry methods don't give the correct answer [33]. AIMD correctly suggested that intramolecular heterolysis of pinacolyl alcohol occurs through stepwise route, while intrinsic reaction coordinate calculations were predicting concerted pathway [46]. Molecular dynamics trajectory calculations showed that enyne-allene conversion from starting material to

product cannot be adequately described by a single minimum-energy path [47]. AIMD investigation with MP2 theory gave negative answer whether methanol forms $\text{CH}_3\text{OH}\cdots\text{F}^-$ intermediate in $\text{S}_{\text{N}}2$ reaction $\text{OH}^- + \text{CH}_3\text{F} \rightarrow \text{F}^- + \text{CH}_3\text{OH}$ [35]. These and many more other examples [34, 36, 48, 49] show the need to incorporate the AIMD in theoretical chemical investigations, especially if different mechanism types are possible.

1.3. Aspects of transitional and conformational search

When we are talking about reactions and particularly, about their kinetics, we usually are concerned with transition states. A transition state (TS) is a saddle point of first order on the potential energy surface that possesses a negative curvature in one principle direction and positive in all others [50]. For the first order saddle point there can be only one negative eigenvalue (harmonic force constant) for the Hessian (matrix of the second derivatives of the energy) [51]. Species residing on these points are called activated complexes. They connect reactants and products each with other [52]. Transition state theory (TST) [53] and its extension Rice–Ramsperger–Kassel–Marcus (RRKM) theory [54], studies the reaction rates of elementary chemical reactions by examining activated complexes lying near the saddle points of PES. They assume thermodynamic equilibrium throughout the entire studied system for all degrees of freedom and neglects effects that result from deviation from thermal equilibrium distribution. Also, initial distribution of species must be strictly random [54]. Reaction rates and product selectivity of kinetically controlled reactions are not always sufficiently described by standard RRKM or TST theories [33, 55]. Many examples show that kinetic selectivity is not always determined by simple choice of different barrier heights and dynamical effects come into play [33, 55]. In cases like these molecular dynamics come handy [33].

Geometry optimization for minima begins by computing the energy and forces acting on a guess structure and then exploring a local approximation to the PES with the goal of locating a structure where the forces are zero. Optimization of a transition state is more cumbersome and typically requires both a good initial guess of the molecular structure and one or more computationally demanding Hessians for calculations to converge reliably [51]. For transition state searches nowadays most popular is synchronous transit-guided quasi-Newton (STQN) method. It uses input of both reactant and product and in

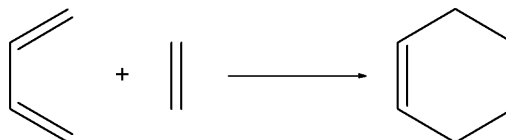
some cases also a guess for the transition state to find the corresponding first-order saddle point [56].

Normally quantum chemical calculations go into a vacuum and may give correct prediction of the vacuum PES. But as most of the chemical reactions occur in solvent, solvation must be taken into account. Addition of methoxide anion to methyl acetate illustrates this with drastic changes in the energy of products relative to the reactants and impossibility to calculate TS without inclusion of the solvation [57]. Inclusion of several explicit solvent molecules is computationally expensive, so in many cases continuum model for the solvent surrounding investigated species is being used [58]. Solute is placed in a cavity surrounded by a solvent reaction field. Practically used models are polarizable continuum model (PCM) which creates cavity by overlapping spheres [59], isodensity polarizable continuum model (IPCM) [60], self-consistent isodensity PCM (SCIPCM) [60] and the Onsager model [61], latter being the simplest one of these and placing solute in a spherical cavity. Also conductor-like screening model (COSMO) [62] and conductor-like screening model for real solvents (COSMO-RS) [63], which use van der Waals-like molecular surface in the approximation of conductor, are available.

Wrong choice of conformers can sometimes lead to big errors, as it has been shown in the case of Suzuki-Miyaura cross-coupling [64]. Because of that it is important to invest some time in the conformational study, before studying the reaction. Target accuracy of conformational energies usually is about $0.1 \text{ kcal} \cdot \text{mol}^{-1}$ [1]. Conformational analysis could be done in different ways. One is to explicitly consider all possible, most important bond and torsional angles, optimize corresponding structures and compare energies as was done in the case of leucine conformational search [65]. This approach can be time consuming, especially, if the molecule is big. In the case of leucine, 324 trial structures were considered and firstly studied with PM3 semi-empirical method and here only 5 bond rotations have been considered [65]. Molecular mechanics (MM) gives great contribution to this context [64]. By using MM approach through a framework of classical molecular dynamics, they can give reasonable conformations in a fairly quick time. To use the MM one needs to represent global potential surface and it usually is approximated by a truncated expansion of many-body contributions called “force field” [66]. MMFF94 [67] is one of the best known implemented force fields and it can also describe non-covalent interactions like hydrogen bonds [68].

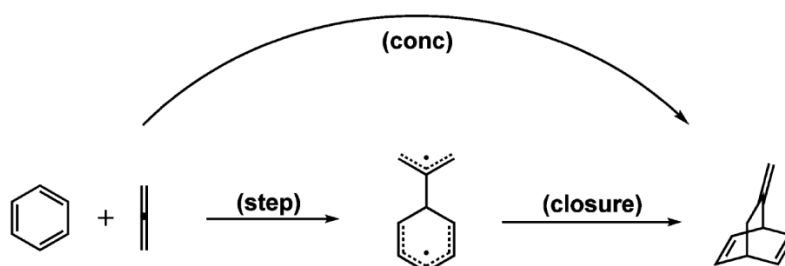
1.4. Reactions

Diels-Alder reaction. Diels-Alder (DA) reaction (Figure 1.1) is one of the most important reactions in organic chemistry, as it had been shown by the Nobel Prize in Chemistry (1950) for its discovery.



1.1. Fig. Diels-Alder reaction of butadiene and ethene

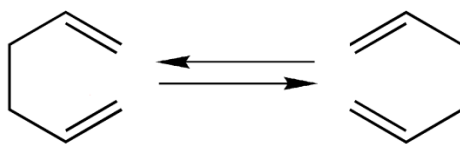
In DA structural complexity is efficiently increased by creating two new single bonds, a six-membered ring and four potential stereocenters [69]. DA reaction between butadiene and ethene to yield cyclohexene (Figure 1.1) is considered to be the prototype of a thermally allowed $4s+2s$ cycloaddition [70]. It was the first reaction where aromaticity in a transition state was recognized, by comparing transition state with its six delocalized electrons with benzene [71]. According to Dieter Cremer et. al. [72], DA reaction of butadiene and ethene possesses three transition states – TS_1 , TS_2 and TS_3 . TS_1 and TS_3 correspond to the points of the reaction path, at which the C_S -symmetrical reaction complex converts breaks symmetry. At TS_1 C_{2v} -symmetrical *cis*-butadiene converts to C_{2h} -symmetrical *trans*-butadiene and at TS_3 cyclohexene isomerizes from boat to twist structure. TS_2 is the transition state between TS_1 and TS_3 . While usually DA reaction is considered to happen through concerted pathway, there are computations that show possibility of a stepwise mechanism too. For example, in the reaction of allene with benzene there is a ambimodal transition state from which it is possible to follow both concerted or stepwise reaction path (Figure 1.2) [22].



1.2. Fig. DA of allene and benzene, stepwise vs. concerted pathway [22]

Also, concerted to stepwise pathway can change by the influence of the temperature [69].

Cope rearrangement. The Cope rearrangement, the simplest case being a formal (3,3)-sigmatropic reaction of a 1,5-hexadiene moiety to its degenerate isomer (Figure 1.3), has been one of the most mechanistically discussed reactions in the course of the last 40 years [18].



1.3. Fig. **Cope rearrangement**

Main discussions were whether the mechanism is stepwise or concerted and which one of the transition state resonance contributors specify the Cope reaction (aromatic, diyl or diallyl, Figure 1.4.) [73]. Also, “centauric” or “chameleonic” models for mechanism of substituted Cope reactions have been in a highlight [18, 74].

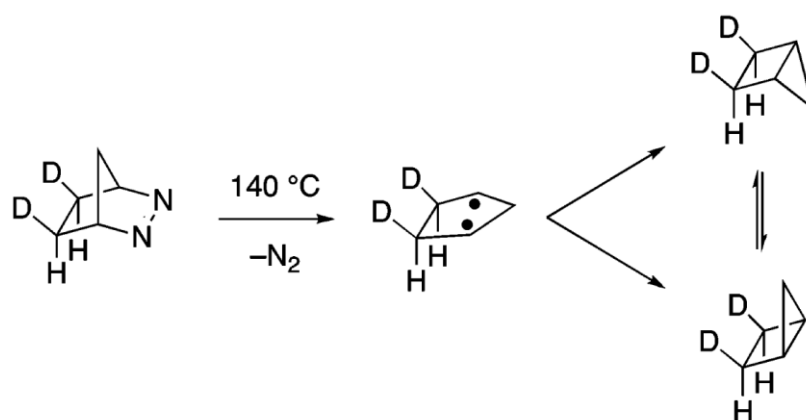


1.4. Fig. **Possible TS's for Cope rearrangement** [18]

A wide range of computational methods have been utilized to compute Cope activation barriers [18]. The key element for correct determination of TS has been considered dynamic electron correlation amongst all of the electrons, which means, that, for example, HF or CASSCF are not the best methods of choice. The best results by far have been given by CASPT2N [75] and B3LYP [76] computations, which predict the activation enthalpy of the Cope rearrangement within 1 kcal · mol⁻¹ in the case of the parent system. From these the method of choice is B3LYP (for other reactions, which isn't the parent reaction, unrestricted version could be better, because it takes into

account the di-radical contribution to the TS), because it's not as resource-intensive as the other [18]. The choice of the basis sets also influence the results, and not surprisingly, larger basis sets usually gives better energies [18]. The general result after years of studies is that the parent Cope system proceeds via a single TS with a chair-like C_{2h} symmetry, have no intermediates and TS has some aromatic character [18]. Last statement has been shown to be true by nucleus independent chemical shift (NICS) value, which had been calculated as -25.4 ppm [73].

Deazetization of 2,3-diazabicyclo(2.2.1)hept-2-ene (DBH). The reaction mechanism of the denitrogenation of DBH derivatives has been studied and discussed since 1967 [77], but light have been shed on this question only recently [78-80]. DBH deazetization is one of the most known examples of dynamically controlled reactions which cannot be explained by the transition state theory, because TST predicts ratio of the products as 1:1. DBH gives stereoisomeric bicyclopentanes in a ratio that favors the exo isomer by about 5:1 in the gas phase (Figure 1.5), and many studies have been conducted to explain the prevalence of the inverted product [81-83].



1.5. Fig. Deazetization of DBH [84]

Explanation is that prior to the product formation internal energy of the intermediate is not randomized and one of the two stereoisomers is preferred as the product [81]. PES surface topology of this reaction is such that there is a high entrance TS that leads into a shallow minimum and reaction leads to product ratios that fail to conform to the symmetry of PES (forward reaction happens without any visible intermediate, but backward reactions reveals it) [81]. It falls into a class of reactions with “reactive

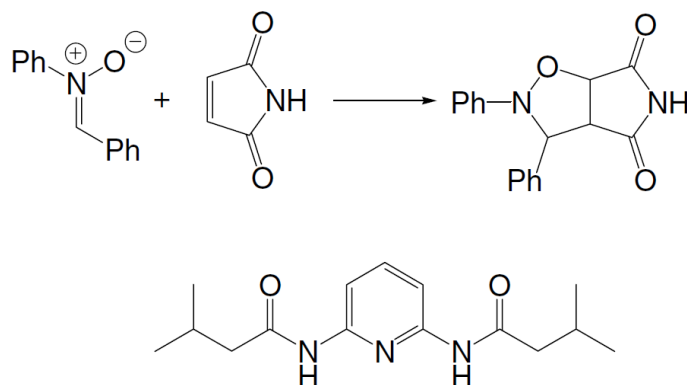
intermediate” which is a specie residing in a shallow minima where the activation barrier for the product side is very low [84].

It is important to use computational methods that include nondynamic electron correlation for the electrons in two C–N σ bonds and N=N π bond, as it was shown by Reyes and Carpenter [78]. Natural choice of theirs was to use CASSCF in calculations and improve energies by CASPT2. CASPT2 has shown a very good agreement with experiment in a number of reactions involving singlet biradicals [85, 86]. They revealed that rate-limiting step in this reaction corresponds to synchronous C–N bond cleavage which leads to a singlet diradical species. This conclusion was also shown experimentally, using 5 fs pulse laser [78, 80]. U3BLYP calculations contradict previous results, predicting one-bond cleavage path being energetically more favorable. In this case U3BLYP overestimates stability of both the diazenyl diradical and subsequent one-bond cleavage transition structure [82]. Calculations and experiment also have shown that by changing substituents on the methano bridge from electron donors (like SiR₃ or H) to electron acceptors (like F or OR) concerted deazetization changes to the stepwise one [79, 80]. These changes have been attributed to the substituent effects on the electronic configuration of the lowest singlet state of the 1,3-diradicals. Reactivity of the 1,3-diradical also is influenced by substituents and it can yield cyclopentene or bicyclo(2.1.0)pentane derivatives [87].

Dynamical investigations have been made for this reaction using semiempirical and *ab initio* calculations [83, 84]. It has been shown that the ratio of the rate constants between two isomeric bicyclopentane products exhibits no statistically significant temperature dependence in ~50 °C interval [83]. Product ratios have been predicted to be 2.2-2.3, thus predicting correctly the preference for the stereochemical outcome [83]. AIMD investigation showed that after crossing first transition state most of the energy goes into mode that corresponds to the out-of-plane bending of methylene group and leads to the product, in most cases without going through the intermediate [84].

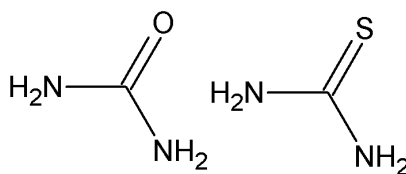
Catalysis of N-neopentylmaleisomide reaction with 2,3-dimethylbutadiene. Interplay between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in Diels-Alder cycloaddition is the main contributor to the reaction rate. One can enhance the reactivity by decreasing the energy gap between them [88]. In α,β -unsaturated carbonyl compounds, which can be used as dienophiles in DA

reaction, one can improve reactivity by lowering the energy of LUMO [88, 89]. If we are looking at maleisoimides, one way how to theoretically do it is by coordinating O and N atoms through hydrogen bonds. Similar example of it has been shown by Domingo et. al. by catalyzing 1,3-dipolar cycloaddition between diphenylnitrone and maleimide by bisamide (Figure 1.6) [88].



1.6. Fig. DA reaction of diphenylnitrone and maleimide

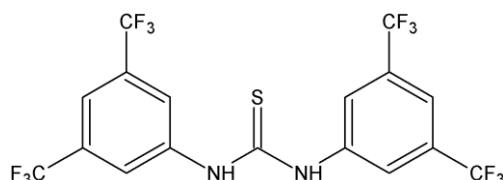
When looking at possible catalysts, field of organocatalysts presents many good possible choices. Organocatalysts are more eco-friendly than conventional organometallic catalysts, less toxic and also cheaper in general [90]. Within the field of organocatalysis hydrogen-bonding catalysts represents an ever growing class [91]. Dominant wave of non-specific hydrogen-bonding catalysts are based on the urea/thiourea (Figure 1.7) motif and they have been utilized in catalysis of the DA reaction [92, 93].



1.7. Urea and thiourea

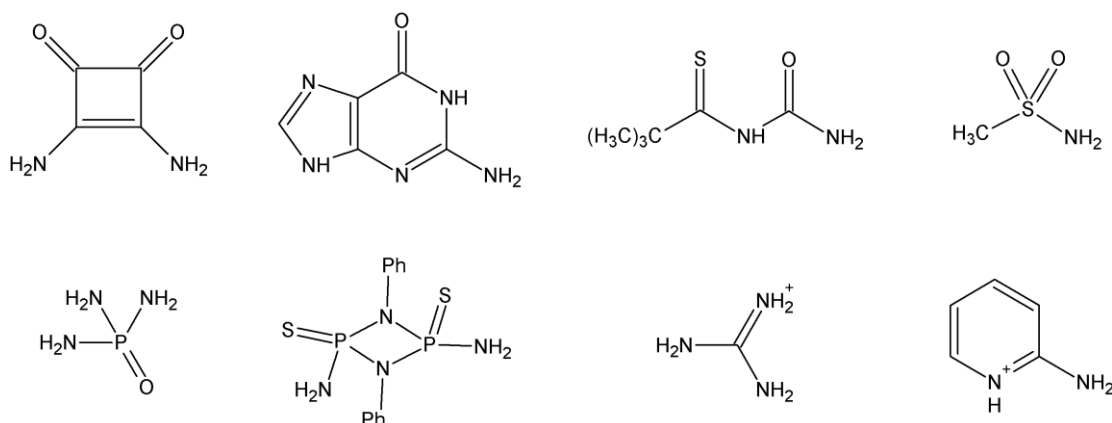
Hydrogen bonds are characterized as strong, moderate and weak, which corresponds to bond lengths of 1.2-1.5 Å (strong), 1.5-2.2 Å (moderate) and 2.2-3.2 Å (weak). Thioureas usually fall into the last two categories [94].

Thioureas have been used as catalysts in DA reaction [95, 96]. Linear correlation have been found between ^{31}P NMR chemical shifts of thiourea complexed phosphine oxides and $\ln(k_{\text{rel}})$ of DA reaction between cyclopentadiene and methyl vinyl ketone catalyzed by the same thiourea [95]. Catalytic activity of thioureas is more strongly dependent on their substituents than solvent [96] and Schreiner's thiourea (Figure 1.8) is found to have the highest catalytical activity [97].



1.8. Fig. **Schreiner's thiourea**

Problems with (thio)ureas are that they form aggregates between themselves in the solution and they tend to degrade under elevated temperatures [98, 99]. Schreiner's thiourea is good, because it tends not to self-associate, as simple thioureas do. It is also more soluble in variety of solvents and is easier to prepare [97]. Complementary motif to (thio)urea have recently emerged in the form of squaramides [100]. Other, not so popular, but still used, are guanines [101], N-sulfinyl ureas [102], sulfonamides [103], P-triamides [91], cyclodiphosphazanes [91] and some protonated catalysts like ammonium salts [104], guanidinium [105] and 2-aminopyridinium [106]. They all can be seen in Figure 1.9.



1.9. Fig. **Some selected organocatalysts**

Most catalysts can form two hydrogen bonds to a reactant which enhances the activity more if compared to the catalysts which can form only one bond.[91]. Literature lacks of many examples with catalysts that forms three hydrogen bonds, one example provided by Domingo et. al. [88]. There is a chance that they could even further enhance the reactivity in cases, where formation of all three hydrogen bonds is possible.

2. COMPUTATIONAL DETAILS

Calculations were carried out using Gaussian 09 rev. D.01 [107] quantum chemistry software and Cool Molecular Dynamics software, latter still being under development and being improved in the course of the work. Visualization and molecule building was done using GaussView 5.0 [108]. Relevant data of optimized structures, which include coordinates and energies, can be found in appendices.

Diels-Alder reaction of butadiene and ethylene and Cope rearrangement of 1,5-cyclohexadiene. *Gaussian 09 part.* Optimization of reactants, products and transition states were done by using B3LYP exchange-correlation functional and 6-31G(d), 6-31G(d,p) and aug-cc-pVTZ basis sets in gas phase. Transition state optimizations were carried out using Berny and QST2 algorithms and frequency calculations were performed at 298.15 K and 1.0 atm to verify and characterize transition state by one and only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed to check whether transition states connect associated reactants and products. *Molecular dynamics part.* With Gaussian 09 optimized reactants were used as an input for molecular dynamics calculation. Born-Oppenheimer molecular dynamics algorithm was used and forces were calculated with B3LYP/6-31G(d) method. Starting energy was given to the modes that correspond to the reaction trajectory and simulations were carried out at 298.0 K. Simulation was stopped after visual inspection of generated structures and their potential energy curves, and conclusion that products have been reached.

Deazetization of 2,3-diazabicyclo(2.2.1)hept-2-ene. *Gaussian 09 part.* Optimization of reactants, products and transition states were done by using B3LYP exchange-correlation functional and CASSCF(6,6) with 6-31G(d) basis set. Transition state optimizations were carried out using Berny, QST2 and QST3 algorithms and frequency calculations were performed at 450.0 K and 1.0 atm to verify and characterize transition state by one and only one imaginary frequency. *Molecular dynamics part.* Structures of optimized reactants were used as an input for Born-Oppenheimer molecular dynamics calculation, using both B3LYP and CASSCF(6,6) with 6-31G(d) basis set. Starting energy was given to the modes that correspond to the reaction trajectories and simulations were carried out at 450.0 K. Simulation was stopped after visual inspection of generated

structures and their potential energy curves, and conclusion that products have been reached.

Catalysis of N-neopentylmaleisomide reaction with 2,3-dimethylbutadiene.

Gaussian 09 part. Optimization of reactants, products and transition states were done by using B3LYP exchange-correlation functional with 6-31G(d) basis set. In some cases semi-empirical AM1 and PM6 methods were used to optimize geometries for quadratic synchronous transit searches. Transition state optimizations were carried out using Berny, QST2 and QST3 algorithms and frequency calculations were performed at 298.15 K and 1.0 atm to verify and characterize transitions state by one and only one imaginary frequency. Solvent effects were considered by including in calculations self-consistent reaction field (SCRF) based on polarizable continuum model (PCM). *Molecular dynamics part.* Conformer search was done by molecular dynamics using MMF94 force field. Search was done at 200.0 K with hydrogen atoms cooled.

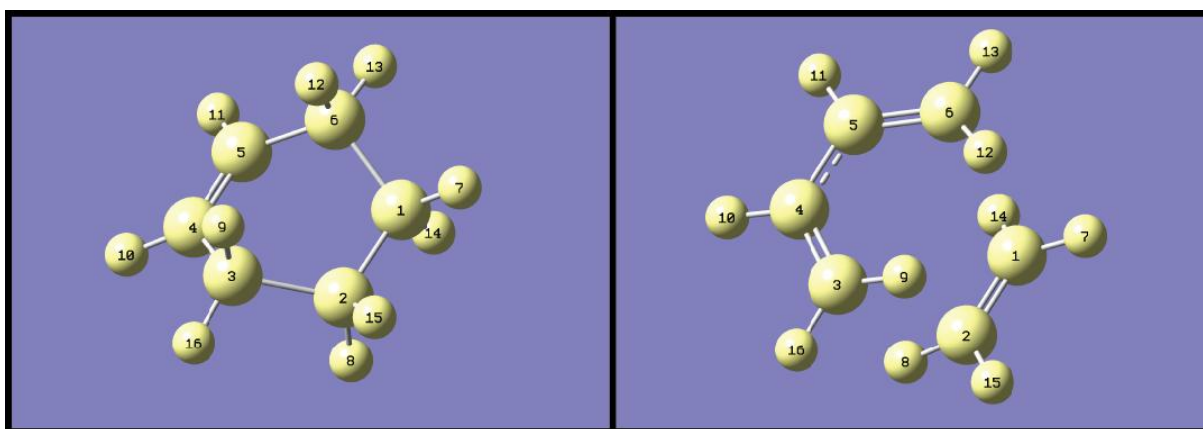
3. RESULTS AND DISCUSSION

3.1. Diels-Alder reaction

The reaction between butadiene and ethene was chosen as the representative of the Diels-Alder reaction. Both the simplicity and symmetrical nature of the reactants makes it a good starting point for the DA investigation.

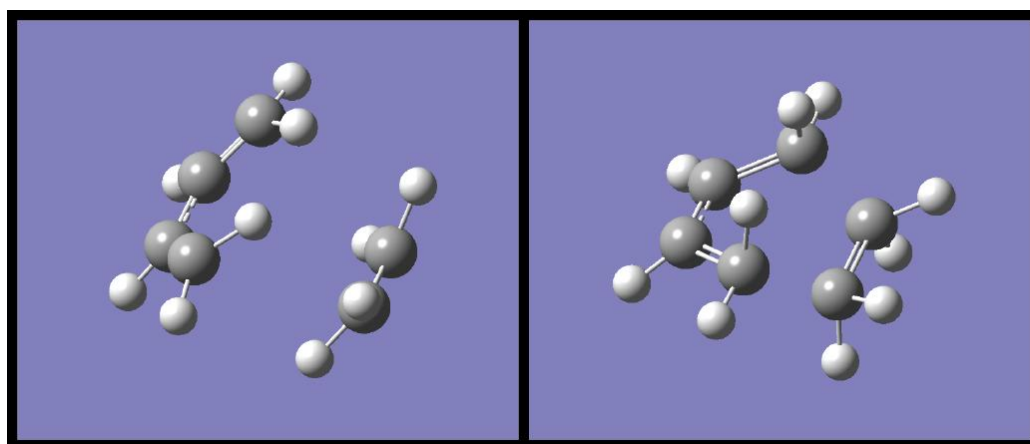
All reactants, product and transition states were optimized at B3LYP/6-31G(d) level of theory. This method was chosen because it has been known to give good results for this reaction [6].

First, structures of reactants and product were obtained. Cyclohexene was optimized in its C_s -symmetrical boat's conformation (first structure in Figure 3.1). To make one of the structures for QST2 search algorithm, obtained conformer was taken and bonds between atoms 2-3 and 1-6 elongated (second structure in Figure 3.1) until they were 2.5 Å long.



3.1. *Fig.* Input structures for QST2 transition state search

Then these two bonds were frozen and the molecule was optimized. Optimization yielded complex that together with cyclohexene's boat's conformation was taken as the input for calculation using QST2 algorithm (Figure 3.1). Structure with one imaginary frequency was found, with normal mode that corresponded to the first transition state (TS_1). In Figure 3.2 you can see two snapshots of vibration that corresponds to this normal mode and leads to the reactants in the first case and to the product in the second one.



3.2. Fig. First transition state of Diels-Alder reaction

The obtained structure was constrained in the C_s point group [72] and re-optimized with Berny algorithm. Calculated enthalpies of transition, bond lengths between atoms C_1 and C_6 (R_{16}) and corresponding imaginary frequencies for transition states can be looked at in Table 3.1.

3.1. Table

Enthalpies with respect to reactants and products, R_{16} , and TS imaginary frequencies

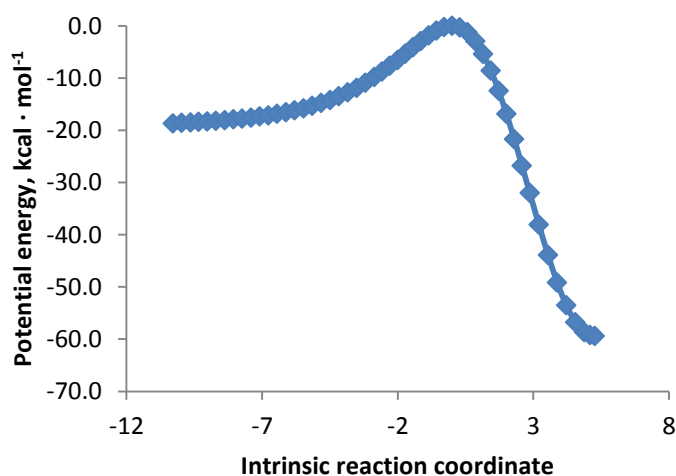
Transition state	Basis set	Forward enthalpy $\Delta H^\ddagger$, $\text{kcal} \cdot \text{mol}^{-1}$	Backward enthalpy $\Delta H^\ddagger$, $\text{kcal} \cdot \text{mol}^{-1}$	Imaginary frequency, cm^{-1}	R_{16} , Å
TS ₁	6-31G(d)	23.4	62.0	525i	2.27
	6-31G(d,p)	23.4	61.2	528i	2.27
	aug-cc-pVTZ	27.2	55.8	546i	2.24
	Experimental [72]	23.5	63.1	-	-

Structures were re-optimized with the two other basis sets. One, where the only change was an addition of p orbitals to hydrogen atoms, and second, correlation consistent aug-cc-pVTZ, which is much bigger than the other two.

Theoretically calculated transition enthalpies for TS₁ are close to the experimental ones. Addition of additional p orbitals on hydrogens doesn't change enthalpy much.

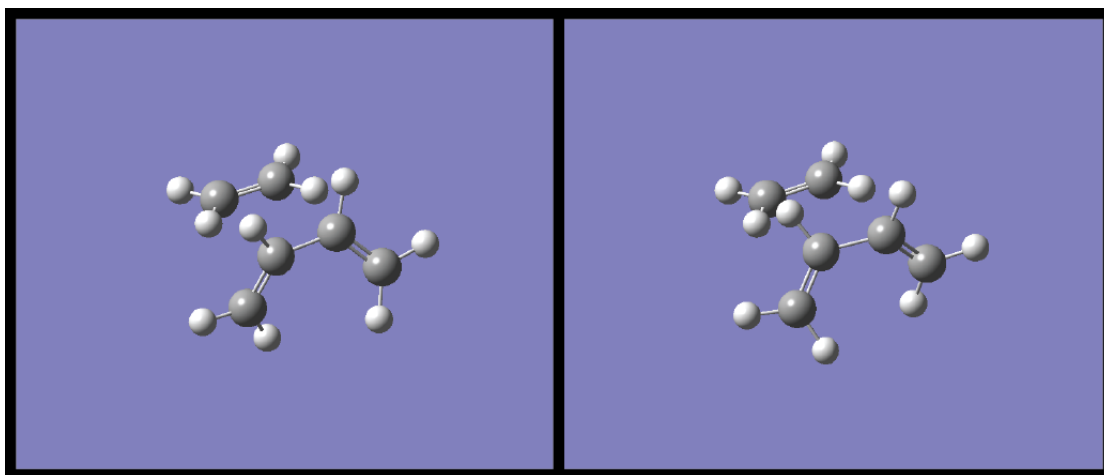
Interestingly, using bigger aug-cc-pVTZ basis set, results are worse than using much smaller 6-31G basis sets. Explanation would be that a good correspondence of 6-31G(d) and experimental values are partly because of the tendency of error cancelation in B3LYP calculations. Bigger basis set reduces error in one direction and allows other errors to manifest themselves.

Intrinsic reaction coordinate (IRC) calculation was made from TS₁ until it stopped in vicinities of second transition state (TS₂) for the reactant side and third transition state (TS₃) for the product side. Result of the calculation is shown in Figure 3.3. As expected, reactants are higher in energy than product.



3.3. *Fig.* **Potential energy against IRC to both sides from TS₁ for butadiene reaction with ethene**

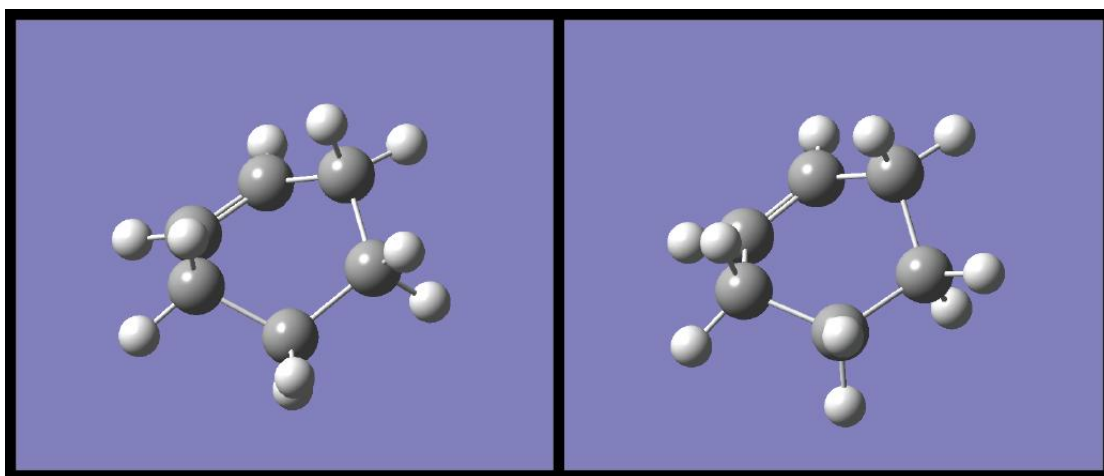
Both farthest-right and farthest-left points of IRC were taken and Berny transition state optimizations were made. These two points correspond to the places where C_s symmetry is broken and reaction falls to one of the mirror images of reactants or product. Transition state optimizations were successful. Snapshots of TS₂, which corresponds to the one closest to the reactants, can be seen in Figure 3.4.



3.4. *Fig.* **Second transition state of Diels-Alder reaction**

At TS₂ C_{2v}-symmetrical *cis*-butadiene breaks symmetry and converts to the more stable C_{2h}-symmetrical *trans*-butadiene; TS₂ connects mirror images of *trans*-butadiene.

TS₃, which corresponds to the transition state which is the closest to the products, can be seen in Figure 3.5.



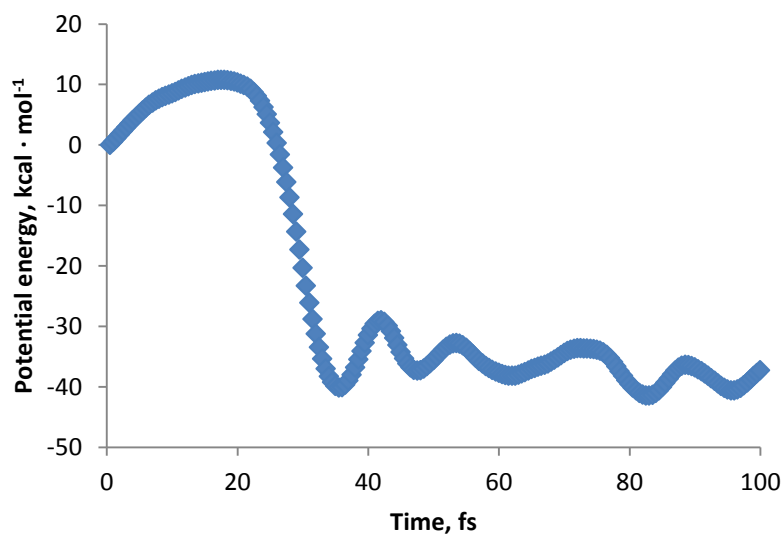
3.5. *Fig.* **Third transition state of Diels-Alder reaction**

Here you can see that C_s-symmetrical cyclohexene converts to its more stable C₂-symmetrical twist conformation; TS₃ connects mirror images of *twist*-cyclohexene. Calculated energetical and conformational data can be seen in Table 3.2

Enthalpies with respect to reactants, R_{16} , and TS imaginary frequencies

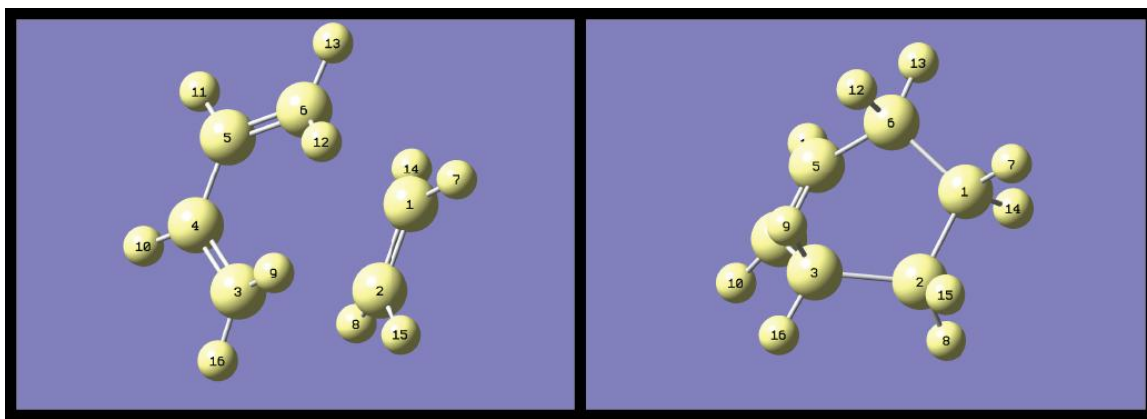
Transition state	Method	Enthalpy with respect to reactants $\Delta H^\ddagger$, kcal $\cdot$ mol $^{-1}$	Imaginary frequency, cm $^{-1}$	R_{16} , Å
TS ₂	B3LYP/6-31G(d,p)	1.72	121i	4.242
	Literature [72]	3.0	130i	-
TS ₃	B3LYP/6-31G(d,p)	-32.7	30i	1.549
	Literature [72]	-32.7	28i	-

When all important stationary points for the reaction were found with Gaussian 09, it was further investigated using molecular dynamics. C_s-symmetrical reactants were taken as an input. Reaction was thermostated at 298 K and starting energy of 20 kcal $\cdot$ mol $^{-1}$ was given to the bonds between atoms 2-3 and 1-6. In Figure 3.6 you can see potential energy against time for the reaction.



3.6. Fig. MD simulation of DA reaction potential energy curve

At 17.5 fs reaction reaches maximum potential energy value and structure at that point resembles TS₁ (Figure 3.7).



3.7. Fig. Structures at 17.5 fs and 36.0 fs for MD simulation of DA

R_{16} here is 2.24 Å, which, compared to 2.27 Å of optimized TS at the same level of theory is close. Corresponding transition state was obtained by optimizing this structure.

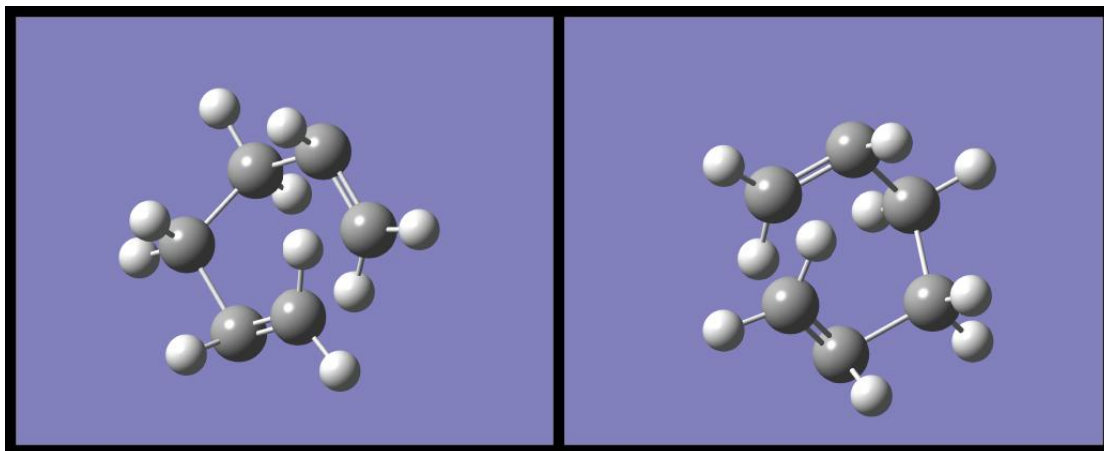
After maximum potential energy goes down and reaches minimum, after which you can see slow oscillation in energy. That is due to the residual kinetic energy. Structures at minima resemble C_s -symmetrical cyclohexene. In the structure at 36.0 fs (Figure 3.7) bonds R_{16} and R_{45} are 1.59 Å and 1.32 Å. Optimized values are 1.56 Å and 1.33 Å respectively. Here too, values are close.

These results show that *ab initio* MD can successfully simulate DA reaction between ethene and butadiene and MD gives alternative way how to get to the TS_1 and the product. Two more transition states were successfully found for DA reaction using Gaussian 09, but they represent only conformational changes to get to the more stable forms of reactants and products, so, the main one that represents bond making is TS_1 . Both molecular dynamics and static approach, using different transition state search algorithms, can give TS_1 for DA reaction at more or less the same time. The main point in MD approach is that it is an alternative that can be used for cases when the static approach fails to give a reasonable result.

3.2. Cope rearrangement

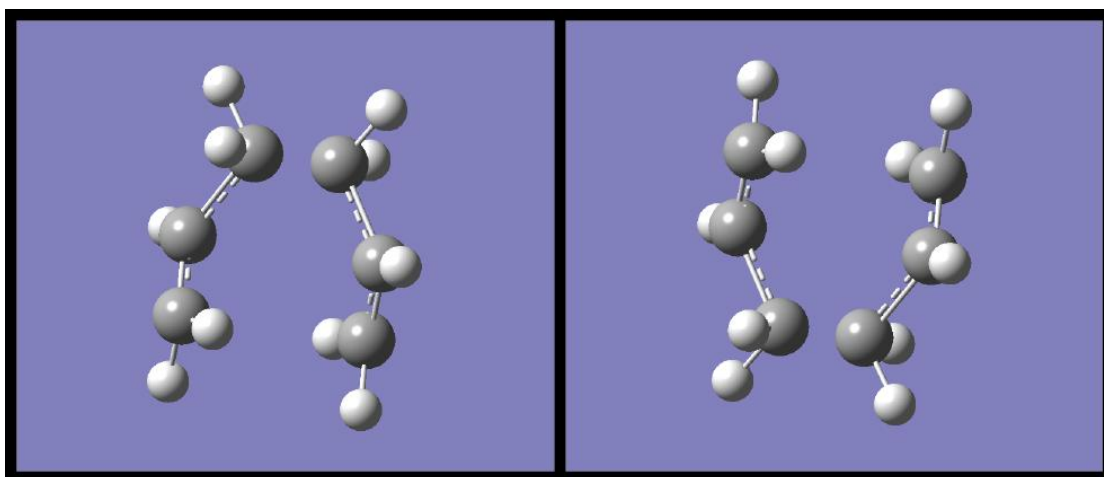
For the Cope rearrangement the parent molecule, 1,5-cyclohexadiene, was taken for the investigation. 1,5-cyclohexadiene's structure was made from benzene in Gaussview 5.0. One bond was erased, two hydrogens added and quick molecular mechanics

optimization made. In this way approximate structure of the reactant was gained and by mirror inversion of it, also that of the product (Figure 3.8).



3.8. *Fig.* **Input structures for the Cope rearrangement transition state calculation**

Both structures were taken as the input for calculations with QST2 algorithm. Transition state was found. It was constrained to C_{2h} point group re-optimized once more with Berny algorithm. Snapshots of the corresponding vibration for the normal mode that leads to product and reactant can be seen in Figure 3.9.



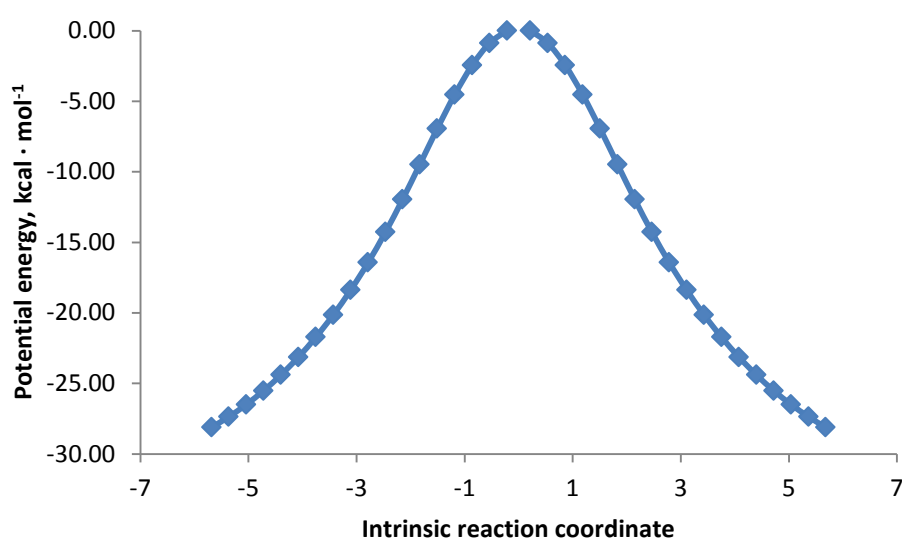
3.9. *Fig.* **Transition state for the Cope rearrangement**

Corresponding imaginary frequency, bond length between atoms C_2 and C_4 and transition enthalpy are shown in Table 3.3.

Calculated reaction data for the Cope rearrangement

Method	Transition enthalpy $\Delta H^\ddagger$, kcal $\cdot$ mol $^{-1}$	R ₂₄ , Å	Imaginary frequency, cm $^{-1}$
B3LYP/6-31G(d)	32.6	1.96	566i
Experimental [6]	33.5	-	-

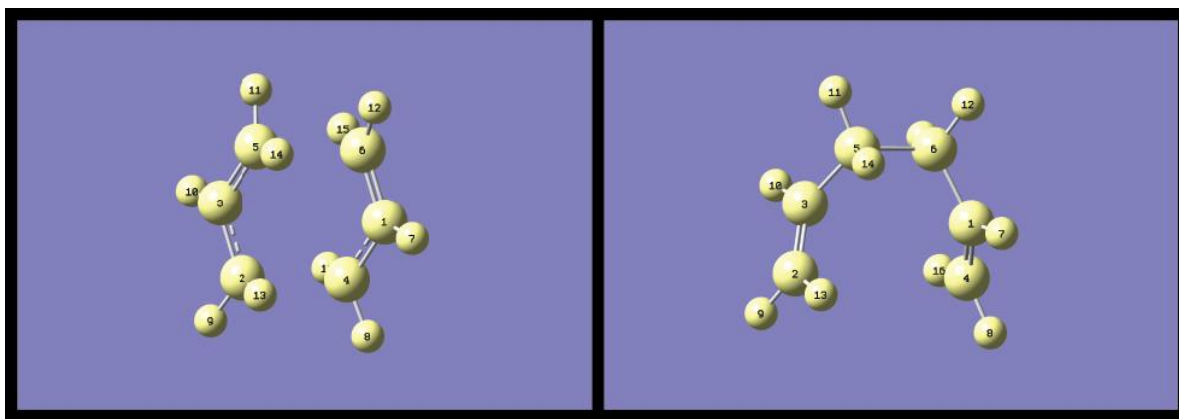
IRC calculation that was made from the transition state can be seen in Figure 3.10.



3.10. Fig. Potential energy against IRC from TS for Cope rearrangement

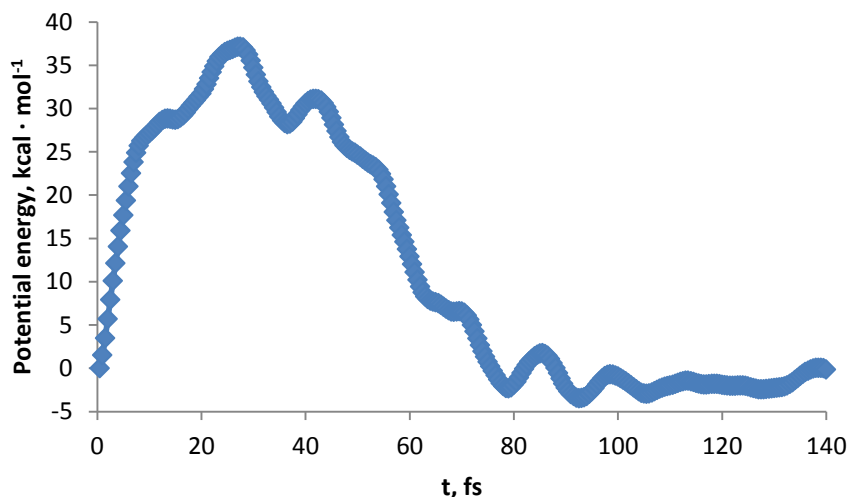
Energy path on both sides is completely symmetrical as it should be. By taking and optimizing one of the points that yield the lowest energy, reactant/product can be gained.

Lowest energy structure of previous IRC calculation was taken for MD calculations. Reaction was thermostated at 298 K and starting energy of 50.0 kcal $\cdot$ mol $^{-1}$ given to bonds between atoms 2-4 and 5-6 (Figure 3.11).



3.11. *Fig.* Structures at 27.0 fs and 79.0 fs for MD simulation of Cope

In Figure 3.11 you can see two structures from MD simulation. First is the maximum of the potential energy curve (Figure 3.12). It resembles transition state and if taken as an input for TS optimization with Gaussian 09, transition state can be located from this structure. Bonds between atoms 2-4 and 5-6 are 2.09 Å and 2.08 Å long. That is 0.12-0.13 Å longer than calculated value with Gaussian 09 and is an acceptable difference. Second structure corresponds to local minimum in potential energy curve (Figure 3.12) and resembles product with bond length between atoms 5-6 being 1.56 Å long, that falls under typical length of C-C single bond.

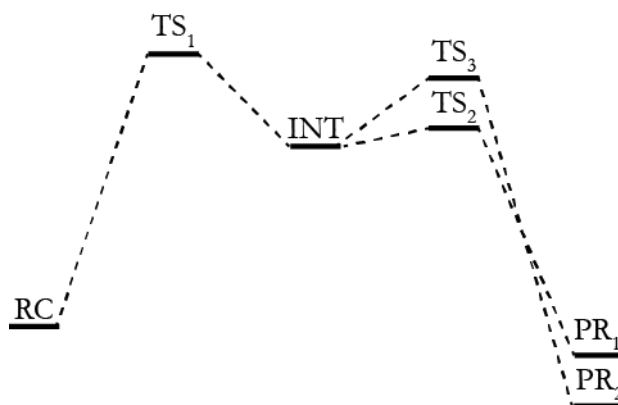


3.12. *Fig.* MD simulation of Cope rearrangement potential energy curve

In conclusion, also Cope reaction can be successfully simulated with ab initio MD using only starting reactant and transition state and product can be found.

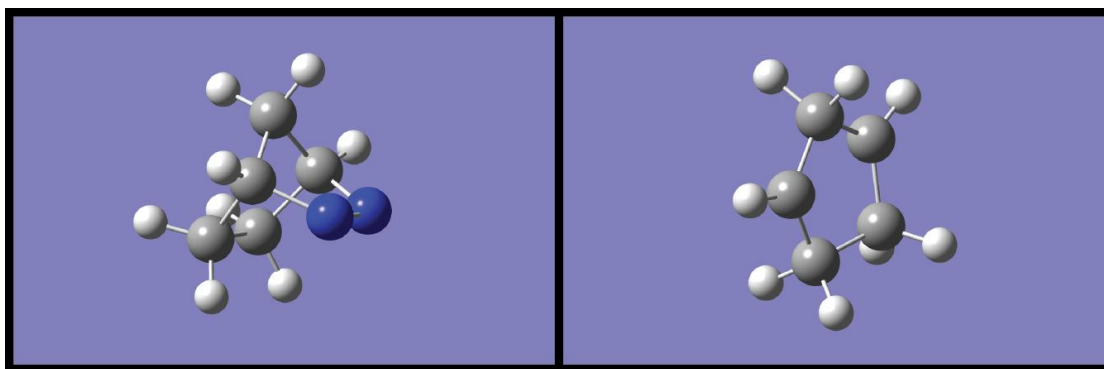
3.3. Deazetization of 2,3-diazabicyclo(2.2.1)hept-2-ene

This reaction was chosen as one of the cornerstones of dynamically controlled reactions, mainly to test and improve Cool Molecular Dynamics software. Firstly, UB3LYP level of theory was chosen for the investigation with moderate-sized 6-31G(d) basis set. B3LYP was chosen because of its generality, good compatibility with molecular dynamics and because for this reaction there haven't been any MD investigation with it. Unrestricted version was used because of the biradical-like character of some stationary points on potential energy surface. In Figure 3.13 you can see scheme of main stationary points for DBH deazetization looked at in this section. **RC** and **INT** are for reactants and intermediate, **TS_n** stands for transitions states, **PR₁** for main product, bicyclo(2.1.0)pentane and **PR₂** for side product, cyclopentene.



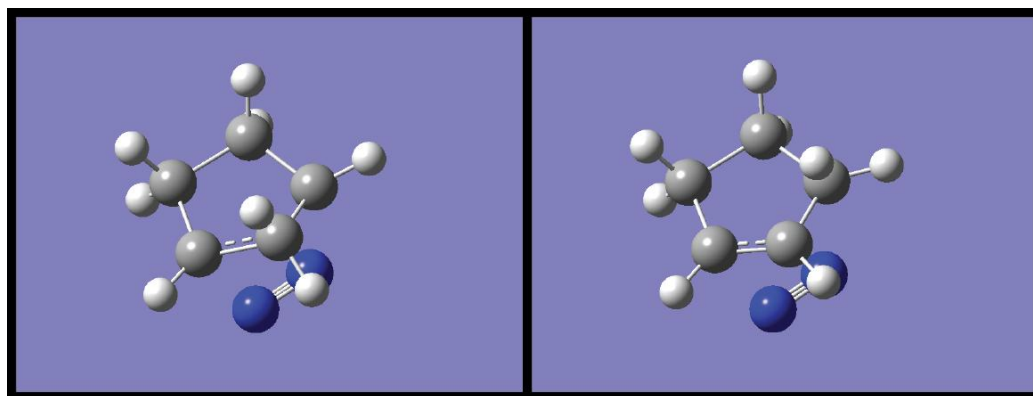
3.13. *Fig.* Scheme with main stationary points for deazetization of DBH

Firstly, first transition state (**TS₁**) was searched to use it as an input for molecular dynamics, as was done by Carpenter in his investigation [109]. Reactant (**RC**) and intermediate (**INT**) (Figure 3.14) were optimized and used as inputs for QST2 algorithm to perform the transition state search. Reactant is C_s -symmetrical and intermediate C_2 -symmetrical, as stated in literature [78].



3.14. *Fig.* **Reactant and intermediate for 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization**

Frequencies were calculated at 445 K, to compare activation enthalpy values with the experimental ones which have been determined as $36.5 \pm 0.3 \text{ kcal} \cdot \text{mol}^{-1}$ (404-453 K) and $36.0 \pm 0.2 \text{ kcal} \cdot \text{mol}^{-1}$ (444-475 K) [82]. This approach and also approach just by using Berny search algorithm failed, because the obtained resultant structure was later in this work discussed third transition state (**TS₃**) (Figure 3.15), which connects intermediate and reaction's byproduct, cyclopentene (**PR₂**). In Figure 3.15 you can see two images of normal mode that corresponds to the hydrogen migration to neighboring carbon atom and formation of double bond in **TS₃**.



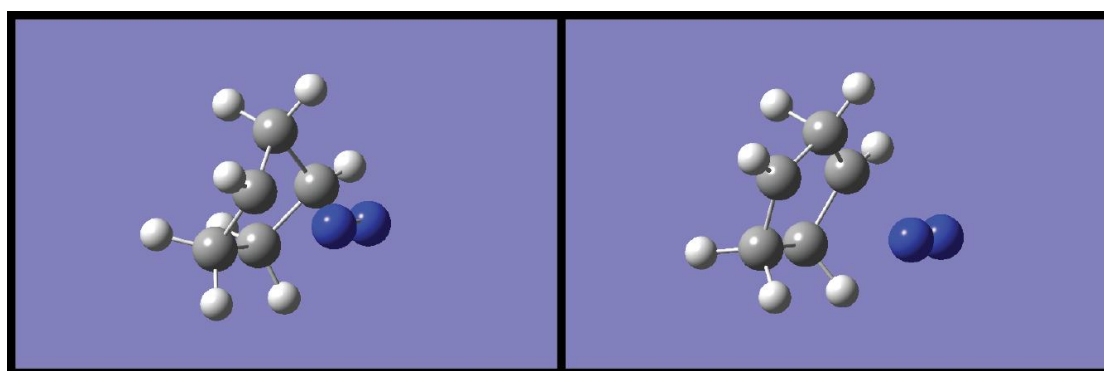
3.15. *Fig.* **Transition state 3 for 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization**

Corresponding energy and frequency can be seen in Table 3.4, where are also data for other structures that have been calculated in this work with UB3LYP/6-31G(d) method are presented.

Data from optimization using UB3LYP/6-31G(d) at 445 K

Name	Enthalpy H_{445} , hartree	ΔH_{445} in comparison with reactant, kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
RC	-304.6507	0	-
TS₁	-304.5880	39.4	348i
INT	-304.7055	55.0	-
TS₂	-304.5791	45.0	355i
TS₃	-304.5752	47.3	701i
PR₁	-304.6716	-9.5	-
PR₂	-304.7119	-38.4	-

To find **TS₁**, both C-N bonds were constrained to calculated value of 2.16 Å [82] and structure to C_s symmetry point group [109]. In this way **TS₁** was finally found and corresponding reaction transition normal mode can be surmised from the Figure 3.16.

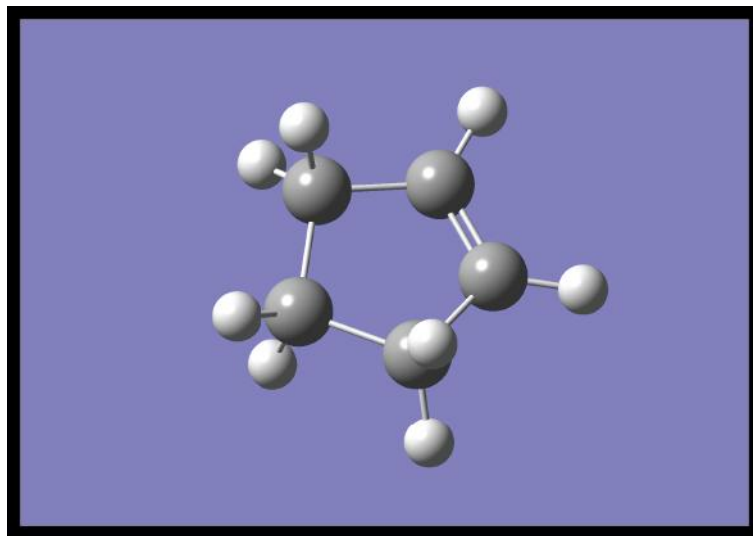


3.16. Fig. Transition state 1 for 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization

The obtained transition structure was semi-stable because when constraints were released and structure optimized once more, N₂ drifted away and structure once more optimized to **TS₃**. Because of this instability intrinsic reaction coordinate calculation wasn't possible.

With constraints optimized **TS₁** structure was taken as an input for molecular dynamics calculation. Starting energy was given to both C-N bonds and reaction thermostated at 445 K. At this temperature only intermediate-like (**INT**) structure was reached and none of the products were obtained. Simulation was repeated once more,

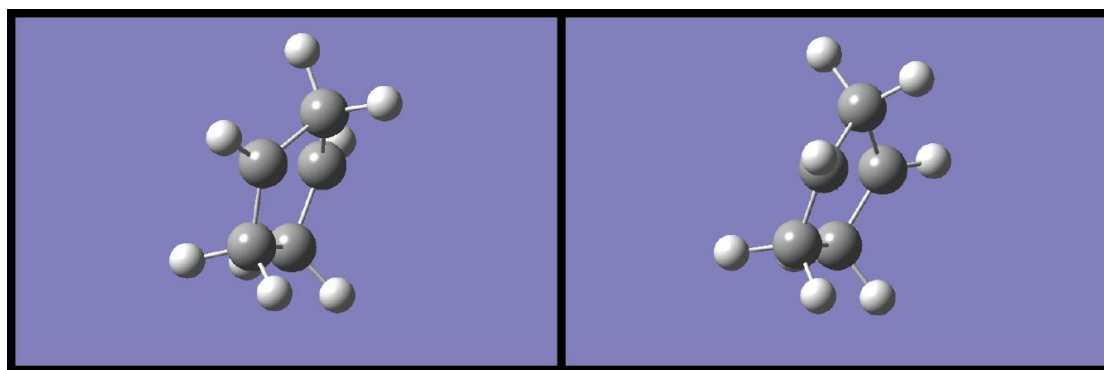
only this time without temperature constraint (allowing temperature to reach approximately 2000 K). In the Figure 3.17 given product was reached.



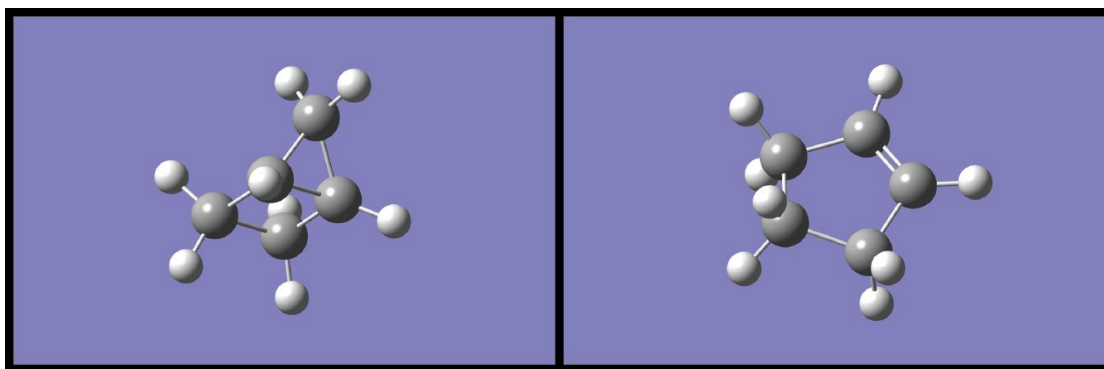
3.17. *Fig.* **Product of deazetization calculated with MD, UB3LYP**

One of the hydrogens is migrated from the methylene bridge to neighboring carbon atom and one of the bonds is shortened, resembling double bond in its length. That means the simulation gives not the expected bicyclo(2.1.0)pentane (**PR₁**), but **PR₂** which is a minor byproduct in this reaction. The same product was reached if simulation was started with reactant as an input.

These results stimulated to make further investigations. Transition state that leads from intermediate to **PR₁** (**TS₂**) (Figure 3.18) and also both products (Figure 3.19) were calculated.



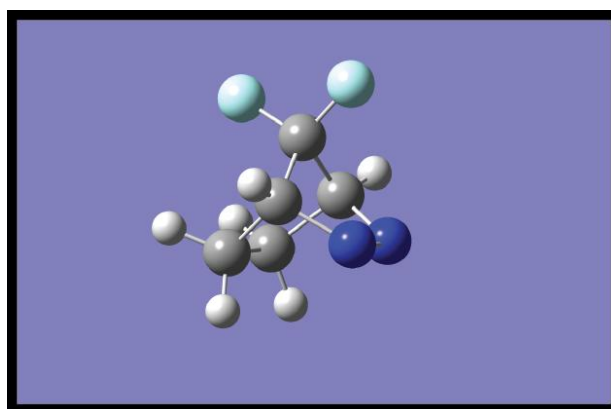
3.18. *Fig.* **Transition state 2 for 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization**



3.19. *Fig.* **Product 1 and 2 for 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization**

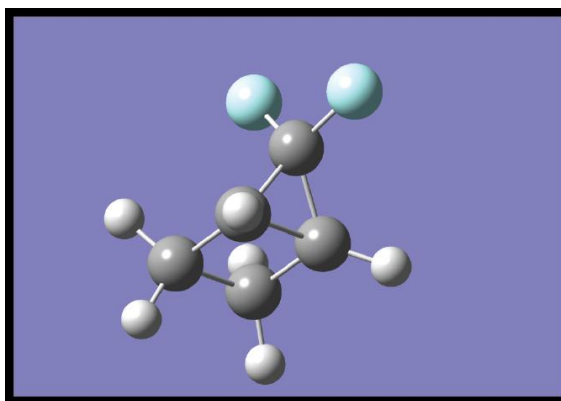
Comparing the relative energies of both **TS₂** and **TS₃** with intermediate (Table 3.4), surprising result was found. Intermediate has higher energy than both transition states. It appears that intermediate, as calculated with UB3LYP, sits on an inflection point which further leads down to one of the transition states. Intrinsic reaction coordinate doesn't give a definite answer about intermediate, because in both cases path from both **TS₂** and **TS₃** leads down to one of the pairs of possible mirror image products.

To see whether it is possible to reach bicyclo product at all, the following was done. It is known that replacing methylene hydrogens with more electron-withdrawing groups the formation of bicycle product is stimulated [79]. Also, the migration is cancelled. So both methylene hydrogens were replaced with fluorine and the obtained structure optimized (Figure 3.20).



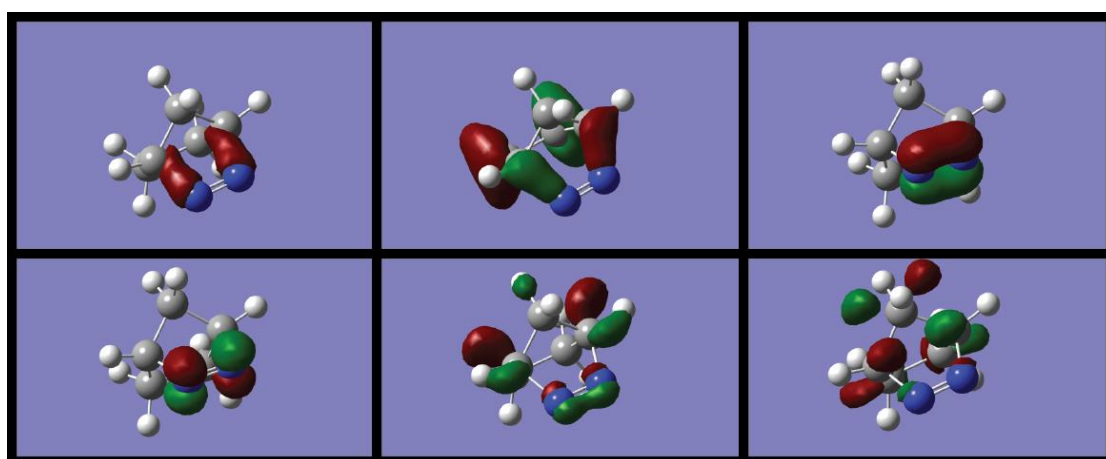
3.20. *Fig.* **Optimized 2,3-Diaza-7,7-difluorobicyclo(2.2.1)hept-2-ene**

This compound was further put in use with molecular dynamics. Energy was given to both C-N bonds at 445 K and soon, after denitrogenation step, formation of bicyclo-product was observed (Figure 3.21).



3.21. *Fig.* **1,1-Difluorobicyclo(2.1.0)pentane**

This proves that the bicyclo-product formation is possible. Further calculations were done with CASSCF, because it is known that molecular dynamics simulation goes well with this level of theory [109]. 6 electrons and 6 orbitals were included in the active space, correlating the two σ C-N bonds that are broken and N=N π bond, including both bonding and corresponding antibonding orbitals. Orbitals were chosen by visual inspection through GaussView 5.0 and trial-and-error until energies that were the same or lower as in literature were gained [78]. Chosen orbitals for reactant are shown in Figure 3.22. Upper three ones are bonding and lower three, anti-bonding orbitals.



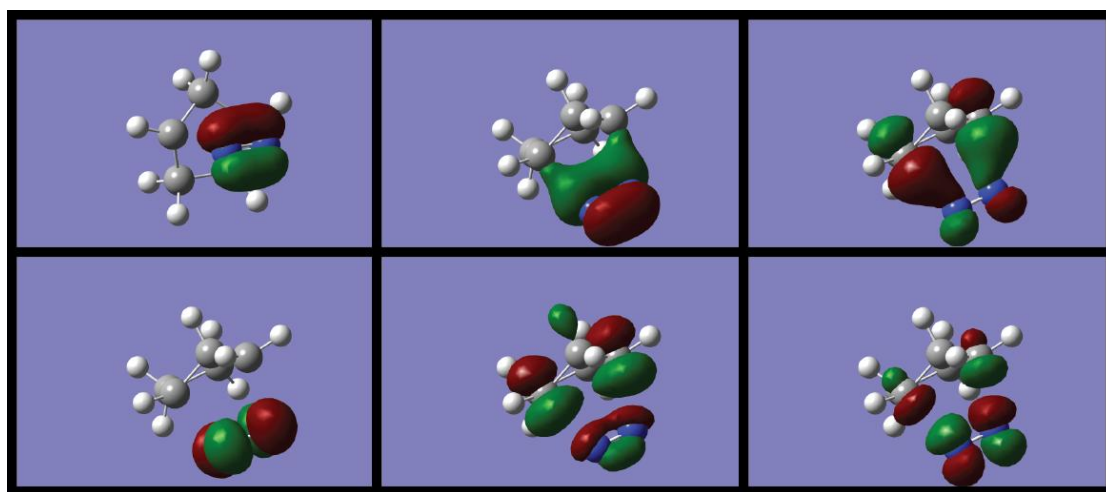
3.22. *Fig.* **Chosen orbitals for optimization of the reactant with CASSCF**

Gained energies for corresponding optimized structures and imaginary frequencies for transition states are shown in Table 3.5.

Data from G09 calculations using CASSCF(6,6)/6-31G(d) at 445 K

Name	Enthalpy H_{445} , hartree	ΔH_{445} in comparison with reactant, kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
RC	-302.7814	0	-
TS₁	-302.7375	27.5	706i
INT	-302.7396	26.4	-
TS₂	-302.7372	27.7	355i
TS₃	-	-	-
PR₁	-302.7787	1.6	-
PR₂	-302.8383	-35.7	-

Transition state was optimized using UB3LYP structure as an input, but here optimization went smoothly and without using constraints. Activation enthalpy poorly corresponds to the experimental one (~ 9 kcal · mol⁻¹ difference). It could be further improved by correction of some theory that includes dynamic correlation, like CASSPT, if that would be needed [78]. Chosen orbitals for **TS₁** are shown in Figure 3.23. Comparing this Figure with Figure 3.22, you can see that molecular orbitals corresponding to the π bond are not changed at all, but orbitals which correspond to the σ bond, have changed their shape and one of them starts to take the shape of the second π bond in N₂.

3.23. Fig. Chosen orbitals for optimization of the TS₁ with CASSCF

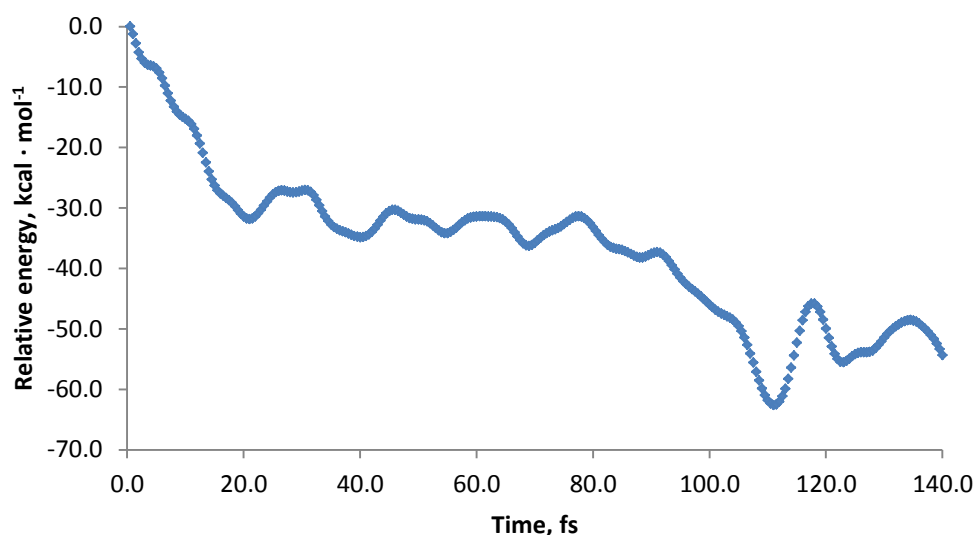
For other structures N₂ was calculated with CASSCF(4,4), where active space includes both π bonding and anti-bonding orbitals. Its energy was added to the energies of the structures that lack it, to make a comparison between them. Intermediate, both products and transition states were calculated with CASSCF(2,2) and inclusion of both bonding and anti-bonding orbitals for electrons that are active in this reaction.

In CASSCF case intermediate was lower in enthalpy than transition state 2, making it a true intermediate. Also, activation enthalpy being 1.3 kcal · mol⁻¹ is close to the experimental value of 3.1 kcal · mol⁻¹ measured at 413 K [78].

Using many different approaches locating the **TS**₃ failed. If with UB3LYP method **TS**₃ was gained even when it was not searched, here it was the other way around.

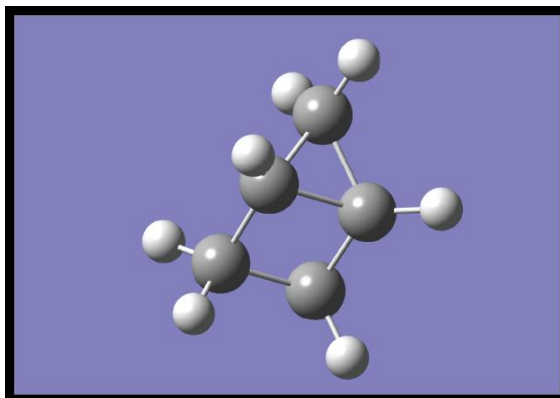
PR₁ is higher in enthalpy than reactant, but after inspecting Gibbs free-energy difference, where entropy kicks in, it can be seen that it is actually thermodynamically lower in energy by 17.7 kcal · mol⁻¹.

Molecular dynamics calculations were done both from transition structure and reactant in 445 K. After giving the starting energy to both C-N bonds, reaction was followed and cut off after formation of the product. Formation of product can be followed by visual inspection and also by a drop in potential energy, as can be seen in Figure 3.24.



3.24. Fig. MD calculation potential energy curve of formation of bicyclo(2.1.0)pentane from **TS**₁

Steep drop can be seen after 100 fs and structure at 111 fs corresponds to bicyclo(2.1.0)pentane that can be seen in Figure 3.25.



3.25. Fig. Bicyclo(2.1.0)pentane gained from MD using CASSCF(6,6) forces

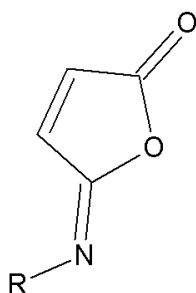
Main reaction product **PR₁** is formed in this simulation.

It has been shown that molecular dynamics with CASSCF(6,6) can correctly predict formation of the main product, starting both from reactant and first transition state. From these results also crystallizes conclusion that B3LYP functional is not only unable to correctly describe relative energies for transition states [82] and intermediate, but even qualitatively fails to describe this reaction using molecular dynamics. DBH deazetization involves degenerate states and it is known that B3LYP have problems with describing them properly [17]. This shows that proper choice of method that generates the potential energy surface is crucial when using AIMD, at least, in probing this reaction.

3.4. Catalysis of N-neopentylmaleisomide reaction with 2,3-dimethylbutadiene

Many examples are known where two hydrogen bond donors serve as organocatalysts. Nevertheless, scientific community is fairly silent about cases, where the same could be said about three hydrogen bond donors. One of the rare examples that can be found in literature is maleimide's DA reaction with diphenylnitrone, where authors choosed bisamide for the catalyst (Figure 1.6) [88].

To further investigate catalytical possibilities of three hydrogen bond donors for DA reaction, isomaleimide (Figure 3.26) was chosen as the substrate.

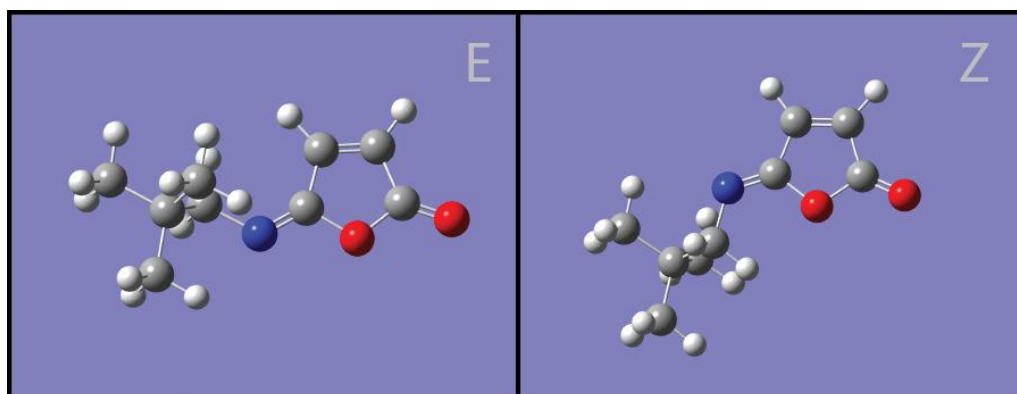


3.26. Fig. Isomaleimide

Isomaleimide has three heteroatoms in convenient positions to serve as hydrogen bond acceptors and in comparison with its isomeric analog maleimide, it is asymmetric. Asymmetry eliminates problem noticed in maleimide's case, where symmetrical nature of substrate possibly lowered catalytical activity [88]. Catalysis of isoimides with dienes in mild temperature and with mild catalyst would be a valuable gain by itself and it also would give a chance to test capability of Cool Molecular Dynamics conformational search.

2,3-Dimethylbutadiene (**DB**) was chosen as the diene and N-neopentylisomaleimide (**NI**) as the dienophile. Future experiments in the laboratory will be made with these two reagents, so, choices were influenced by practical reasons. Solvation was taken into account knowing that experiments will be done in dimethylsulfoxide (DMSO). As algorithms which look at the solvation and basis set superposition error are incompatible one with each other, there were no calculations made that would correct energies for the latter. But as systems that were compared with each other were approximately the same size, one could predict that basis set superposition error (which usually is not too big) would mostly cancel.

Firstly, reactants were optimized. Because N-neopentylisomaleimide can exist in both E (**NI_E**) and Z (**NI_Z**) conformations, both were calculated (Figure 3.27).



3.27. Fig. N-neopentylisomaleimide in E and Z conformations

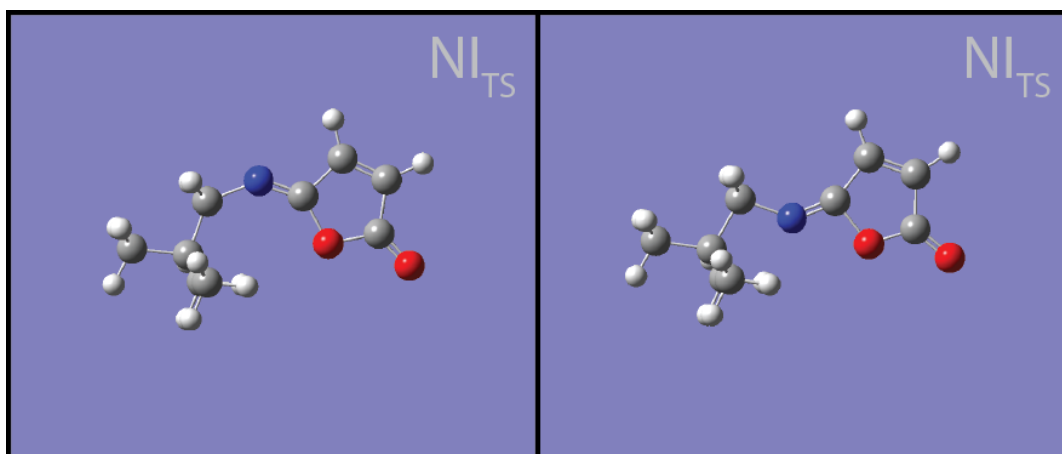
NI in solution prefers to adopt Z conformation, as Table 3.6 confirms, Z conformation being lower in Gibbs free energy by 2.2 kcal · mol⁻¹. In Table 3.6 you can also see that difference in enthalpy with respect to **NI_Z** is almost the same as the difference in Gibbs free energy. From that follows that both structures have similar number of degrees of freedom.

3.6. Table

Thermodynamic data for optimized structures that are involved in reaction without catalysts

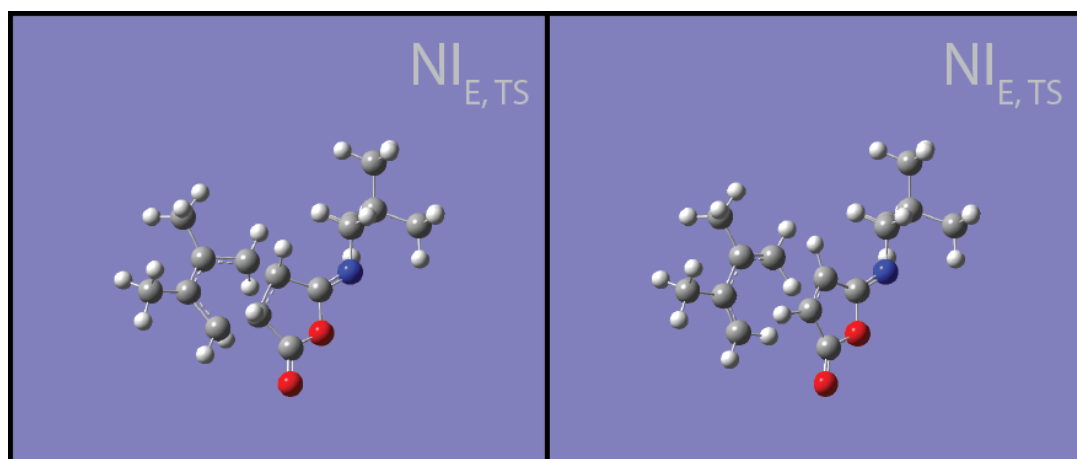
Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
NI_E	2.0	2.2	-
NI_Z	0	0	-
NI_{TS}	17.8	18.2	182i

Both gained structures were taken as inputs for QST2 algorithm to calculate isomerization energy barrier. Activation Gibbs energy that needs to be added to convert from **NI_Z** to **NI_E** is 18.2 kcal · mol⁻¹ (Table 3.6). Unpublished isomerization data for docecylisomaleimide and benzylisomaleimide are in agreement with calculations for isopentylmaleimide. In both cases activation Gibbs free energy was around 20 kcal · mol⁻¹ and difference between both isomers were around 1 kcal · mol⁻¹, so similar results would be expected from homologue of these compounds. Gained transition state (**NI_{TS}**) can be seen in Figure 3.28.



3.28. *Fig.* **Transition state from conversion from NI_E to NI_Z**

When isomerization barrier was calculated, uncatalyzed reaction transition states for both (E and Z) isomers were optimized by adding **DB**. Forming bonds between two fragments were set to 2.3 Å (as in the previously calculated ethene with butadiene DA transition state's case) and then frozen. With frozen bonds structures were optimized to get rid of unwanted negative eigenvalues. When that was done, constraints were relaxed and transition state found using Berny algorithm. Transition state in the case of E isomer ($\text{NI}_{E, \text{TS}}$) can be seen in Figure 3.29.



3.29. *Fig.* **Transition state for uncatalyzed reaction, E isomer**

Bond lengths between atoms that make the new single bonds are 2.23 Å and 2.29 Å in E isomers case and 2.37 Å and 2.15 Å in Z isomers case. Asynchronicity arises from asynchronous nature of the dienophile. In E isomers case both bonds lengths are more

alike. From data in Table 3.7 you can also see that more synchronous E isomers transition state is a bit more energetically favorable than the TS of the Z isomers, by 0.5 kcal · mol⁻¹.

3.7. Table

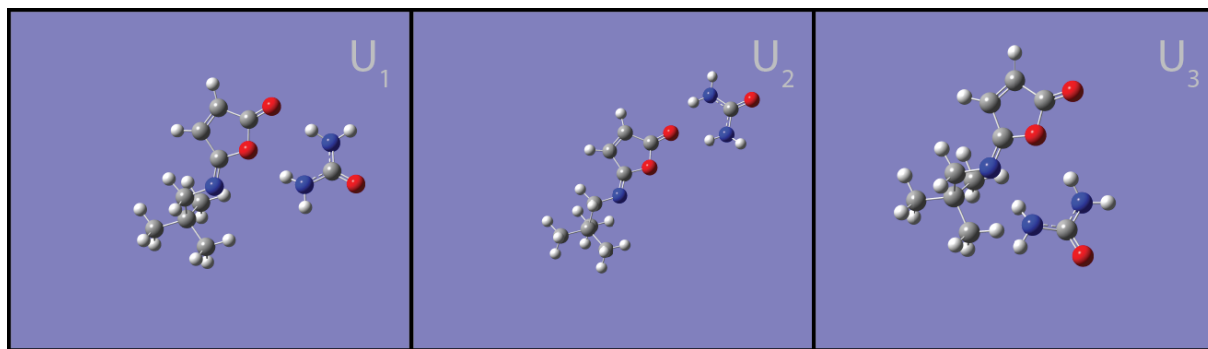
Thermodynamic data for uncatalysed reaction

Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
NI_E , TS	17.2	30.9	470i
NI_Z , TS	17.5	31.4	467i

Because in Z conformation it is not possible to make three hydrogen bonds from one side with **NI**, it is crucial that conversion between both forms is much faster than the main reaction. If one compares transition states' Gibbs free energies for **NI** isomerization (3.6. Table) and for Diels-Alder reaction between **NI** and **BD** (3.7. Table) then one can see that barrier for DA reaction is almost by 13 kcal · mol⁻¹ bigger. It can be concluded that isomerization happens relatively fast in comparison with the main reaction and the rate determining step is the DA reaction.

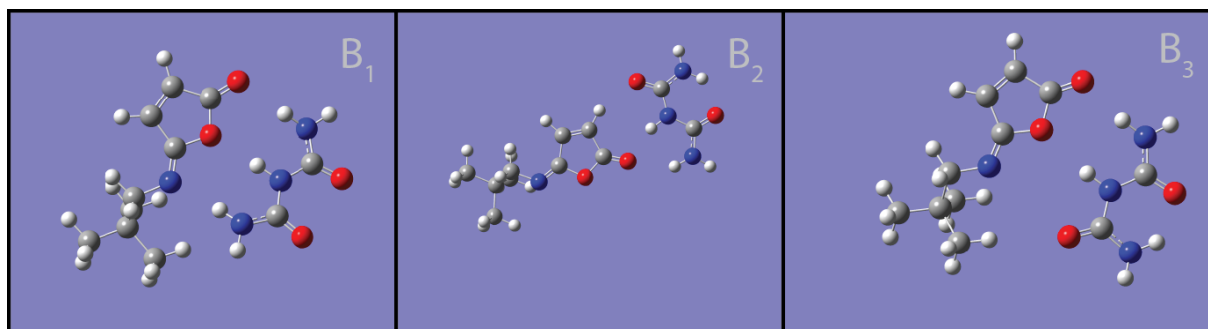
Further, catalysts were chosen. First ones, that were investigated, were two similar pairs of two and three hydrogen bond donors. First pair was urea and biuret. Second pair was thiourea and dithioubiuret. As mentioned in literature review, urea and thiourea and their derivatives are one the most popular hydrogen bond donor-type catalysts, so these were the first obvious choices. Also their three hydrogen bond donor analogs, biuret and dithiobiuret are commonly available, especially the former.

As systems which provide wide and rich variety of possible conformers and molecular complexes, they were first investigated with molecular dynamics, using molecular mechanics with MMFF94 force field. For urea/thiourea molecular complexes with **NI** three low-lying energy conformations were found. First, where hydrogen bonds are made with two oxygens (**U₁/ThioU₁**), second, where both hydrogen bonds are made with one oxygen (**U₂/ThioU₂**) and third, where both hydrogen bonds are made with oxygen and nitrogen (**U₃/ThioU₃**). **U₁**, **U₂** and **U₃** can be seen in Figure 3.30.



3.30. *Fig.* Three low-lying energy conformations for urea and NI complex

Also three low-lying energy conformations were found for biuret/dithioubiuret molecular complexes. First, where all three hydrogen bonds are made with **NI** (**B₁**/**ThioB₁**), second, where two hydrogen bonds are made with one oxygen of **NI**, while third hydrogen bond being intramolecular (**B₂**/**ThioB₂**) and the last complex, where two hydrogen bonds are made with two oxygens and third hydrogen bond is intramolecular (**B₃**/**ThioB₃**). **B₁**, **B₂** and **B₃** can be seen in Figure 3.31.



3.31. *Fig.* Three low-lying energy conformations for biuret and NI complex

First conformation (**B₁**/**ThioB₁**), where all three hydrogen bonds are made between dienophile and catalyst, is the main in which we are interested. Relative energies for all conformations with respect to the main one are shown in Table 3.8.

Relative energies for different **NI**:catalyst complexes

Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹
U₁	0	0
U₂	0.6	-0.4
U₃	-0.3	1.3
ThioU₁	0	0
ThioU₂	0.5	0.0
ThioU₃	-0.4	0.6
B₁	0	0
B₂	-4.7	-5.5
B₃	-3.8	-3.8
ThiouB₁	0	0
ThioB₂	-5.9	-8.3
ThioB₃	-4.6	-6.2

From data in Table 3.8 we can draw some conclusions about main conformations in which molecular complexes between the **NI** and the catalyst exist in the solution. First we can see that all three conformers for urea and thiourea molecular complexes with **NI** are with approximately the same energy. For urea the second conformer is a bit more stable and for thiourea the first one and the second one are more stable, but they are close in their relative energies and we can expect to see all three of them in the solution. With biuret and thiobiuret segregation in energies occurs. Second conformer is the dominant one, in the biuret's case being lower in energy more than 5 kcal · mol⁻¹ and in the dithiobiruret's case more than 8 kcal · mol⁻¹. Third one rests energetically closer to the second one with being 3.8 kcal · mol⁻¹ (for biuret) and 6.2 kcal · mol⁻¹ (for dithiobiruret) more stable than the first molecular complex.

To explore what it means with respect to the activation energies in all cases, transition states were optimized. Thermodynamic data for urea and biuret molecular complexes with **NI** can be seen in Table 3.9.

Thermodynamic data for urea and biuret catalysed reaction

Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
U₁, TS	16.0	28.5	461i
U₂, TS	16.2	31.1	456i
U₃, TS	16.0	29.5	460i
B₁, TS	15.1	29.8	449i
B₂, TS	16.2	30.6	454i
B₃, TS	15.9	29.9	456i

Gibbs free energy of uncatalyzed reaction was calculated to be 30.9 kcal · mol⁻¹ (Table 3.7) and one can compare it with data for catalyzed reactions in Table 3.9.

First, urea and **NI** molecular complexes. Here, the second conformation for urea and **NI** complex, which is the most stable one according to Table 3.8, has activation barrier of 31.1 kcal · mol⁻¹. That's more than for uncatalyzed reaction. Other two conformations give increase in reactivity by 1.4 and 2.4 kcal · mol⁻¹ respectively. One could predict that there exist multiple pathways if urea is used as the catalyst and reaction could even go through uncatalyzed pathway.

Second, biuret and **NI** molecular complexes. Data show that here also the second complex has the highest energy barrier for the activation. If one compares 30.9 kcal · mol⁻¹ and 30.6 kcal · mol⁻¹, then one can conclude that reaction's speed will be almost the same. The first complex lowers the activation barrier by 1.1 kcal · mol⁻¹, but it is unlikely that reaction goes through it. Third one lowers it by 1.0 kcal · mol⁻¹, but it too is not the most stable one.

As urea/biuret pair seems to give no improvement in reaction's speed, further investigation of thiourea and dithiobiuret was made. Calculated activation data for thiourea and dithiobiuret can be seen in Table 3.10.

Thermodynamic data for thiourea and thiobiuret catalysed reaction

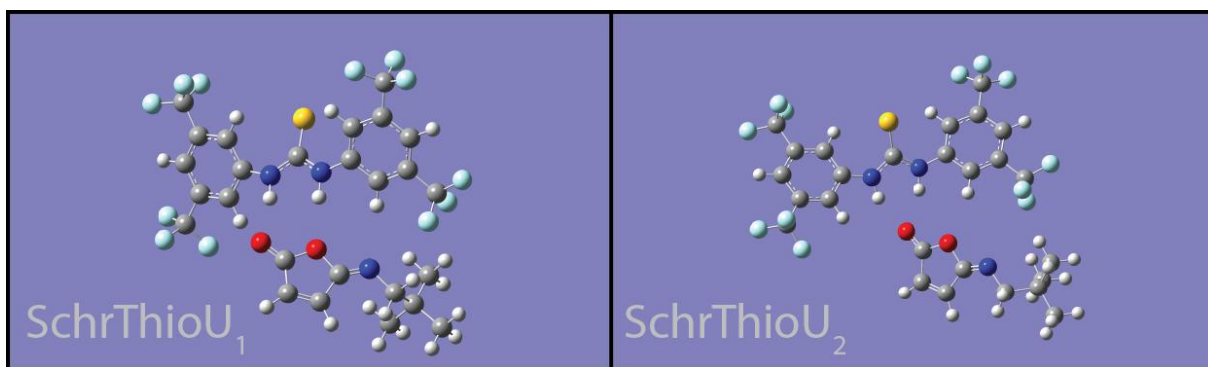
Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
ThiouU₁, TS	15.7	29.4	455i
ThiouU₂, TS	16.2	29.6	457i
ThiouU₃, TS	15.7	29.4	458i
ThiouB₁, TS	14.3	28.0	441i
ThiouB₂, TS	15.9	29.7	451i
ThiouB₃, TS	15.4	29.5	450i

In thiourea's case all three complexes show increase in reactivity by 1.3-1.5 kcal · mol⁻¹. That was expected because thiourea's generally are better catalysts than urea's [110].

In thiobiuret's case, the second molecular complex, which also is the most energetically favorable one, too has the highest activation Gibbs free energy. But it gives 1.2 kcal · mol⁻¹ of speeding up the reaction. Activation is a bit weaker than in the case when thiourea is used. First complex, where all three hydrogen bonds are involved with substrate, activation reaches 2.9 kcal · mol⁻¹, but unfortunately this form is not the most stable one, as can be seen by inspecting Table 3.8. Third molecular complex gives almost the same lowering in Gibbs free energy as the second one, by 1.4 kcal · mol⁻¹.

Some conclusions. First, both urea and biuret are not usable by themselves as catalysts for this reaction. From thioure/dithiobiuret pair thiourea is the best and dithiobiuret follows it in catalytical activity. One could see the general problem that three hydrogen bond catalysts tend to make intramolecular hydrogen bonds. Problem, because complexes with this intramolecular hydrogen bond has higher activation barriers than complexes where all three hydrogen bonds are made between catalyst and substrate. To see whether it is true for other thiourea derivatives, Schreiner-type thioureas catalysts were explored. They were chosen because they usually have the highest catalytical activity from thiourea family [97].

Both optimized complexes with Schreiner's thiourea (**SchrThioU₁** and **SchrThioU₂**) can be seen in Figure 3.32.

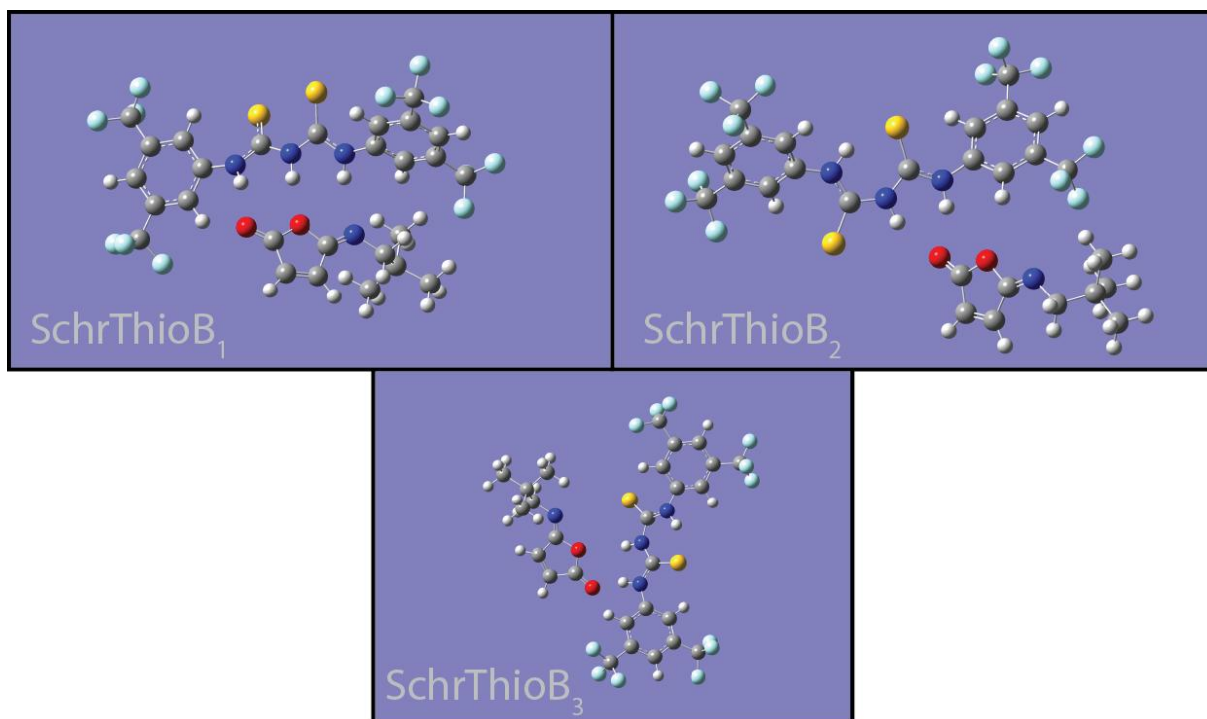


3.32. *Fig.* NI molecular complexes with Schreiner's thiourea

Schreiner's thiourea is quite large molecule in comparison with N-eneptylmaleisoimide. Big bis(trifluoromethyl)phenyl groups act as electron withdrawing groups and make N-H bonds a bit better electron donors, at least in theory. But one could also guess by looking at the picture, that they could negatively influence rate, because of the steric hindrances when both molecules come together.

One could hypothesize on sterical assumptions that for both molecules it is easier to make **SchrThioU₂** than **SchrThioU₁**. Third complex where hydrogen bonds are made with O and N atoms wasn't calculated. Reason was because in urea's and thiourea's case we could see that this complex between with O and N atoms was highest in energy and so, it was assumed that this would be the case in this situation too. Especially, if we take into notice that bis(trifluoromethyl)phenyl groups would have even bigger problems to fit in this complex.

Dithiobiuret's analogs of Schreiner's can be seen in Figure 3.33, **SchrThioB₁**, **SchrThioB₂** and **SchrThioB₃**.



3.33. Fig. **NI** molecular complexes **Schreiner's dithiobiuret**

Partial reason why Shreiner's catalyst is so effective is ascribed to entropic reasons. *Ortho*-hydrogens on phenyls' make hydrogen bonds with sulphur atoms and this rigidifying interaction minimizes the entropy loss upon binding of the substrate. When looking at **SchrThioB₁**, one can see that, even if there is this type of interaction, it is very weak. Orto-hydrogens and sulphur atoms rest in different planes and S-H_{phenyl} distances are 2.7 Å and 2.8 Å long. In the second complex too, both S-H_{phenyl} distances are weak, both 2.8 Å long. In comparison, S-H_{nitrogen} distance is 2.1 Å long. Also in the third complex S-H_{nitrogen} distance is 2.1 Å long. Both S-H_{phenyl} distances are 2.9 and 2.7 Å long. Relative energies for all optimized Shreiner's-type complexes can be seen in Table 3.11.

Relative energies for different conformations of Schreiner's urea/biuret and NI complexes

Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹
SchrThioU₁	0	0
SchrThioU₂	0.0	-0.3
SchrThioB₁	0	0
SchrThioB₂	-6.9	-9.3
SchrThioB₃	-3.8	-6.9

Both Schreiner's thiourea complexes are approximately the same as far as the energetic considerations go. Their enthalpies are the same and Gibbs free energy difference of 0.3 kcal · mol⁻¹ is negligible. Different situation appears when one looks at Shreiner's dithiobiuret complexes. Second complex is much lower in the energy and both enthalpic and entropic factors come into the play.

Energies and frequencies for transition states of Schreiner's thiourea, dithiobiuret and **NI** molecular complexes can be seen in Table 3.12.

Thermodynamic data for Schreiner's urea/biuret catalysed reaction

Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
SchrThioU_{1,TS}	15.0	27.9	445i
SchrThioU_{2,TS}	15.5	29.9	446i
SchrThioB_{1,TS}	14.2	27.2	436i
SchrThioB_{2,TS}	15.5	30.4	446i

SchrThioU_{1,TS} gives the best change in Gibbs free energy seen so far and decreases the barrier by 3.0 kcal · mol⁻¹. **SchrThioU_{2,TS}** is much worse, giving decrease only by 1.0 kcal · mol⁻¹. Still, as both complexes are almost the same in energy, one could predict substantial increase in the reaction's speed.

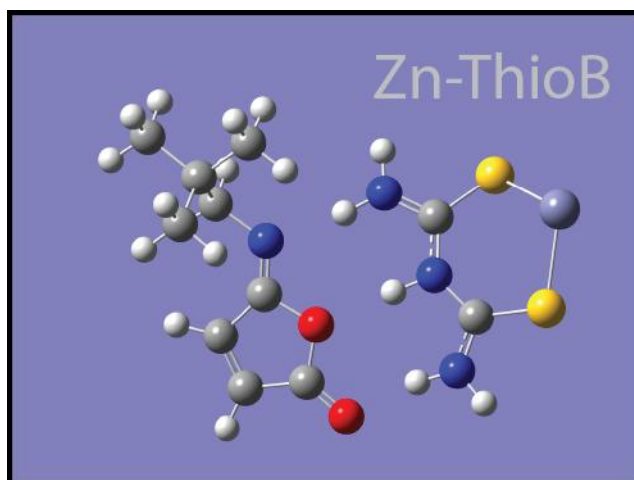
In the case of Shreiner's dithiobiuret one can see that **SchrThioB_{1,TS}** lowers energy barrier even more than the catalysts looked before at, by 3.7 kcal · mol⁻¹. But

unfortunately it is not the most stable one of the both complexes. Second one, which is more stable than the first, lowers the barrier only by $0.5 \text{ kcal} \cdot \text{mol}^{-1}$ and because of that one can predict that increase in the reaction's speed will not be significant.

In conclusion it can be said that both biuret, dithiobiuret and their derivatives are not the best three hydrogen bond-donor choice for catalysis of N-neopentylisomaleimide reaction with 2,3-dimethylbutadiene. In all cases they tend to make complexes with the **NI** with single oxygen atom, at the same time making intramolecular hydrogen bond with one the O or S atoms in the molecule. They are relatively bad catalysts. Complexes where all three hydrogen bonds are made between catalyst and **NI** show greater catalytical possibility but unfortunately they are not as stable as the formerly mentioned ones where intramolecular hydrogen bond forms in the catalyst's molecule.

Two further options were looked at. First was to incorporate some divalent metal ion that could bind to it both O/S atoms in biuret/dithiobiuret derivatives and not let intramolecular hydrogen bond to form. Also, as this binding would mean drawing electron density from carbonyl group's carbon, it would mean better hydrogen bond formation and possible increase in catalytical activity. Second was to model and to try out molecule based on different skeleton than before mentioned urea-like species.

First approach was tried out with dithiobiuret and Zn^{2+} ion in molecular complex. Dithiobiuret was chosen as the perspective catalyst because it showed better catalytical activity than biuret, but was simpler than Shreiner-analogs (faster calculations). Zn^{2+} ion was chosen because salts of it shows good solubility in dimethyl sulfoxide and easily binds with S. Optimized complex (**Zn-ThioB**) can be seen in Figure 3.34.



3.34. *Fig.* **NI**, dithiobiuret and Zn^{2+} molecular complex

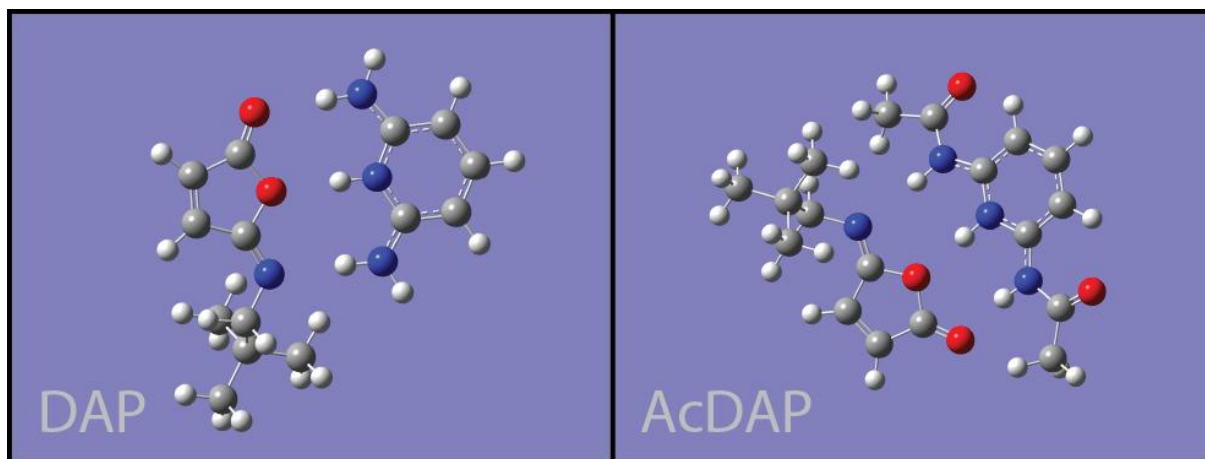
One thing that is noticeable is that both lateral O $\cdots$ H and N $\cdots$ H hydrogen bonds are shorter when there is Zn²⁺ ion. In molecular complex with Zn²⁺ they are 1.92 and 1.93 Å long, respectively, but without Zn²⁺ their lengths are 2.07 and 2.10 Å. This mean stronger hydrogen bond and possibly better catalytical activity. Catalytical activity was explored by optimizing **Zn-ThioB's** and 2,3-dimethylbutadiene's transition state. Thermodynamic energies for it are shown in Table 3.13 where for comparison **ThioB₁,_{TS}** energies are put too.

3.13. Table

Thermodynamic data for Zn ²⁺ and dithioubiuret catalysed reaction			
Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
Zn-ThioB_{TS}	13.2	27.7	436i
ThioB₁,_{TS}	14.3	28.0	441i

One can conclude from this table that **Zn-ThioB** as catalyst lowers reaction Gibbs free energy barrier even more than dithiobiuret's first molecular complex without zinc ions. It lowers activation barrier by 3.2 kcal · mol⁻¹ and that comes without allowing dithiobiuret to make intramolecular hydrogen bond.

Second approach was tried out with 2,6-diaminopyridinium ion and after that with N,N'-diacetyl-2,6-diaminopyridinium, where acetyl-groups were added. Molecular complexes of 2,6-diaminopyridinium and N,N'-diacetyl-2,6-diaminopyridinium with **NI** (**DAP**, **AcDAP**) can be seen in Figure 3.35.



3.35. Fig. 2,6-diaminopyridinium and NI molecular complex

Thermodynamic data for reaction which is catalyzed by **DAP** and **AcDAP** are shown in Table 3.14.

3.14. Table

Thermodynamic data for DAP and AcDAP catalysed reaction			
Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹	Imaginary frequency, cm ⁻¹
DAP _{TS}	14.3	28.4	437i
AcDAP _{TS}	13.0	25.9	429i

Use **DAP** lowers activation Gibbs free energy by 2.5 kcal · mol⁻¹. That inspired thought that catalyst on basis of this one could be effective. So, acetyl-groups were added to **DAP** resulting in **AcDAP**.

Looking at Table 3.14, it can be seen that **AcDAP** obviously is the best by far from all catalysts that have been looked at in this work. It lowers activation Gibbs free energy by 5.0 kcal · mol⁻¹. For comparison, dithiobiuret and Zn²⁺ ions decreased activation barrier by only 3.2 kcal · mol⁻¹.

Comparison of all activation enthalpies and Gibbs free energies can be seen in Table 3.15. Only the energies for the most stable forms are shown, as being the best representatives for the reactivity.

3.15. Table

Summary of thermodynamic data for different catalyst		
Name	ΔH_{298} , kcal · mol ⁻¹	ΔG_{298} , kcal · mol ⁻¹
Uncatalyzed _{TS}	17.2	30.9
U _{TS}	16.2	31.1
ThioU _{TS}	16.2	29.6
B _{TS}	16.2	30.6
ThiouB _{TS}	15.9	29.7
SchrThioU _{TS}	15.5	29.8
SchrThioB _{TS}	15.5	30.4
Zn-ThioB _{TS}	13.2	27.8
DAP _{TS}	14.3	28.4
AcDAP _{TS}	13.0	25.9

In summary one can conclude following things. Two hydrogen bond donors (urea and thiourea derivatives) are not good catalysts, they improve reaction speed only a little or doesn't improve it at all. Three hydrogen bond donors from biuret and dithiobiuret family are perspective catalysts, if we are looking only at molecular complexes that make all hydrogen bonds between substrate and catalyst. To suppress the tendency for them to form intramolecular hydrogen bonds some divalent metal cation, like Zn^{2+} , should be introduced. Catalysts from 2,6-diaminopyridinium family are perspective too as was shown with the example of N,N'-diacetyl-2,6-diaminopyridinium ion which gave the lowest so far calculated activation Gibbs free energy.

CONCLUSIONS

1. Molecular dynamics can adequately simulate Diels-Alder and Cope parent reactions and can help to find their transition states.
2. DFT method using UB3LYP functional is not suitable for molecular dynamics calculations of 2,3-diazabicyclo(2.2.1)hept-2-ene deazetization, while CASSCF is.
3. Biuret and dithiobiuret and their derivatives tend to form intramolecular hydrogen bonds instead of forming all three hydrogen bonds with N-neopentylisomaleimide. These complexes also show decreased catalytical activity with respect to catalytical complexes that form all three hydrogen bonds with N-neopentylisomaleimide. To suppress intramolecular hydrogen bonding in biuret and dithiobiuret derivatives, and to improve their catalytical activity Zn^{2+} ions could be added.
4. Theoretically calculated best possible three hydrogen bond forming catalyst is N,N'-diacetyl-2,6-dimethylaminopyridinium ion that lowers Gibbs free energy of activation by $5 \text{ kcal} \cdot \text{mol}^{-1}$.

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APPENDICES

1. appendix

Coordinates for ethene optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0	0.665429	0
2	1	0.923691	1.239533	0
3	1	-0.923650	1.239576	0
4	6	0	-0.665430	0
5	1	-0.923690	-1.23953	0
6	1	0.923653	-1.23958	0

Thermodynamic data for ethene optimized at B3LYP/6-31G(d) level

Zero-point correction, Hartree	0.051226
Thermal correction to energy, Hartree	0.054268
Thermal correction to enthalpy, Hartree	0.055212
Thermal correction to Gibbs free energy, Hartree	0.029696
Sum of electronic and zero-point energies, Hartree	-78.536232
Sum of electronic and thermal energies, Hartree	-78.533191
Sum of electronic and thermal enthalpies, Hartree	-78.532246
Sum of electronic and thermal Gibbs free energies, Hartree	-78.557762

Coordinates for ethene optimized at B3LYP/6-31G(d,p) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0	0.677600	0
2	1	0.924521	1.216266	0
3	1	-0.927705	1.210764	0
4	6	0	-0.677600	0
5	1	-0.924521	-1.216266	0
6	1	0.927705	-1.210764	0

Thermodynamic data for ethene optimized at B3LYP/6-31G(d,p) level

Zero-point correction, Hartree	0.051124
Thermal correction to energy, Hartree	0.054167
Thermal correction to enthalpy, Hartree	0.055111
Thermal correction to Gibbs free energy, Hartree	0.029596
Sum of electronic and zero-point energies, Hartree	-78.542683
Sum of electronic and thermal energies, Hartree	-78.539641
Sum of electronic and thermal enthalpies, Hartree	-78.538697
Sum of electronic and thermal Gibbs free energies, Hartree	-78.564211

Coordinates for ethene optimized at B3LYP/aug-cc-pVTZ level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0	0.662444	0
2	1	0.920466	1.231890	0
3	1	-0.920246	1.231955	0
4	6	0	-0.662444	0
5	1	-0.920466	-1.231890	0
6	1	0.920246	-1.231955	0

Thermodynamic data for ethene optimized at B3LYP/aug-cc-pVTZ level

Zero-point correction, Hartree	0.050895
Thermal correction to energy, Hartree	0.053934
Thermal correction to enthalpy, Hartree	0.054879
Thermal correction to Gibbs free energy, Hartree	0.029378
Sum of electronic and zero-point energies, Hartree	-78.573170
Sum of electronic and thermal energies, Hartree	-78.570130
Sum of electronic and thermal enthalpies, Hartree	-78.569186
Sum of electronic and thermal Gibbs free energies, Hartree	-78.594686

Coordinates for *trans*-butadiene optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.107129	-1.484654	0
2	1	2.099989	-1.039868	0
3	1	1.059957	-2.569406	0
4	6	-0.000011	-0.728770	0
5	1	-0.978112	-1.211048	0
6	6	0	0.728758	0
7	1	0.978110	1.211018	0
8	6	-1.107123	1.484663	0
9	1	-2.099997	1.039911	0
10	1	-1.059916	2.569414	0

Thermodynamic data for *trans*-butadiene optimized at B3LYP/6-31G(d) level

Zero-point correction, Hartree	0.085491
Thermal correction to energy, Hartree	0.090134
Thermal correction to enthalpy, Hartree	0.091079
Thermal correction to Gibbs free energy, Hartree	0.059049
Sum of electronic and zero-point energies, Hartree	-155.906647
Sum of electronic and thermal energies, Hartree	-155.902004
Sum of electronic and thermal enthalpies, Hartree	-155.901060
Sum of electronic and thermal Gibbs free energies, Hartree	-155.933089

Coordinates for *trans*-butadiene optimized at B3LYP/6-31G(d,p) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.106746	-1.484066	0
2	1	2.098212	-1.038194	0
3	1	1.058972	-2.567932	0
4	6	-0.000010	-0.728637	0
5	1	-0.97745	-1.210973	0
6	6	0	0.728625	0
7	1	0.977449	1.210945	0
8	6	-1.106741	1.484074	0
9	1	-2.098220	1.038234	0
10	1	-1.058934	2.567940	0

Thermodynamic data for *trans*-butadiene optimized at B3LYP/6-31G(d,p) level

Zero-point correction, Hartree	0.085320
Thermal correction to energy, Hartree	0.089965
Thermal correction to enthalpy, Hartree	0.090909
Thermal correction to Gibbs free energy, Hartree	0.058878
Sum of electronic and zero-point energies, Hartree	-155.916342
Sum of electronic and thermal energies, Hartree	-155.911697
Sum of electronic and thermal enthalpies, Hartree	-155.910753
Sum of electronic and thermal Gibbs free energies, Hartree	-155.942784

Coordinates for *trans*-butadiene optimized at B3LYP/aug-cc-pVTZ level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.101973	1.478360	0
2	1	2.089463	1.033298	0
3	1	1.053027	2.558031	0
4	6	0	0.726377	0
5	1	-0.973239	1.207689	0
6	6	-0.000048	-0.726394	0
7	1	0.973159	-1.207671	0
8	6	-1.101939	-1.478353	0
9	1	-2.089361	-1.033360	0
10	1	-1.052963	-2.557928	0

Thermodynamic data for *trans*-butadiene optimized at B3LYP/aug-cc-pVTZ level

Zero-point correction, Hartree	0.084920
Thermal correction to energy, Hartree	0.089565
Thermal correction to enthalpy, Hartree	0.090510
Thermal correction to Gibbs free energy, Hartree	0.058479
Sum of electronic and zero-point energies, Hartree	-155.972569
Sum of electronic and thermal energies, Hartree	-155.967924
Sum of electronic and thermal enthalpies, Hartree	-155.966980
Sum of electronic and thermal Gibbs free energies, Hartree	-155.999011

Coordinates for *twist*-cyclohexene optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.698358	-1.192273	0.318574
2	6	0.698358	-1.192274	-0.318572
3	6	1.498901	0.047906	0.110988
4	6	0.666054	1.306046	0.057279
5	6	-0.666054	1.306046	-0.057282
6	6	-1.498901	0.047906	-0.110988
7	1	-1.244745	-2.105926	0.053921
8	1	1.244745	-2.105926	-0.053918
9	1	2.386480	0.163840	-0.526627
10	1	1.199473	2.254634	0.112885
11	1	-1.199472	2.254634	-0.112889
12	1	-1.889185	-0.090088	-1.132259
13	1	-2.386480	0.163842	0.526627
14	1	-0.593386	-1.192531	1.412572
15	1	0.593386	-1.192533	-1.412570
16	1	1.889185	-0.090086	1.132259

Thermodynamic data for *twist*-cyclohexene optimized at B3LYP/6-31G(d) level

Zero-point correction, Hartree	0.146987
Thermal correction to energy, Hartree	0.152477
Thermal correction to enthalpy, Hartree	0.153421
Thermal correction to Gibbs free energy, Hartree	0.118350
Sum of electronic and zero-point energies, Hartree	-234.501308
Sum of electronic and thermal energies, Hartree	-234.495818
Sum of electronic and thermal enthalpies, Hartree	-234.494874
Sum of electronic and thermal Gibbs free energies, Hartree	-234.529945

Coordinates for *twist*-cyclohexene optimized at B3LYP/6-31G(d,p) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.698376	-1.192376	-0.318167
2	6	-0.698402	-1.192364	0.318165
3	6	-1.498322	0.047978	-0.110582
4	6	-0.665898	1.305835	-0.057058
5	6	0.665928	1.305821	0.057057
6	6	1.498323	0.047946	0.110585
7	1	1.244342	-2.105175	-0.053599
8	1	-1.244387	-2.105149	0.053590
9	1	-2.385240	0.164397	0.526287
10	1	-1.198233	2.254200	-0.112680
11	1	1.198284	2.254175	0.112676
12	1	1.888574	-0.088695	1.131143
13	1	2.385246	0.164342	-0.526280
14	1	0.593840	-1.193245	-1.411366
15	1	-0.593867	-1.193243	1.411364
16	1	-1.888581	-0.088653	-1.131138

Thermodynamic data for *twist*-cyclohexene optimized at B3LYP/6-31G(d,p) level

Zero-point correction, Hartree	0.146498
Thermal correction to energy, Hartree	0.152003
Thermal correction to enthalpy, Hartree	0.152947
Thermal correction to Gibbs free energy, Hartree	0.117856
Sum of electronic and zero-point energies, Hartree	-234.516184
Sum of electronic and thermal energies, Hartree	-234.510678
Sum of electronic and thermal enthalpies, Hartree	-234.509734
Sum of electronic and thermal Gibbs free energies, Hartree	-234.544825

Coordinates for *twist*-cyclohexene optimized at B3LYP/aug-cc-pVTZ level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.697139	-1.189842	0.315825
2	6	0.697138	-1.189843	-0.315823
3	6	1.493324	0.048514	0.109617
4	6	0.662523	1.302034	0.057045
5	6	-0.662522	1.302035	-0.057047
6	6	-1.493324	0.048515	-0.109617
7	1	-1.240791	-2.097962	0.048397
8	1	1.240789	-2.097964	-0.048393
9	1	2.374598	0.166602	-0.527087
10	1	1.191741	2.247137	0.112942
11	1	-1.191739	2.247138	-0.112945
12	1	-1.884529	-0.085931	-1.125347
13	1	-2.374598	0.166605	0.527085
14	1	-0.595526	-1.194082	1.405204
15	1	0.595524	-1.194086	-1.405201
16	1	1.884530	-0.085931	1.125346

Thermodynamic data for *twist*-cyclohexene optimized at B3LYP/aug-cc-pVTZ level

Zero-point correction, Hartree	0.145850
Thermal correction to energy, Hartree	0.151360
Thermal correction to enthalpy, Hartree	0.152304
Thermal correction to Gibbs free energy, Hartree	0.117211
Sum of electronic and zero-point energies, Hartree	-234.588283
Sum of electronic and thermal energies, Hartree	-234.582773
Sum of electronic and thermal enthalpies, Hartree	-234.581829
Sum of electronic and thermal Gibbs free energies, Hartree	-234.616922

**Coordinates for the first transition state of butadiene and ethene Diels-Alder
reaction optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.57835	0.68985	-0.22604
2	6	1.57538	-0.69612	-0.22856
3	6	-0.45056	-1.43643	0.48988
4	6	-1.32475	-0.70083	-0.28952
5	6	-1.32129	0.70635	-0.28998
6	6	-0.44323	1.43793	0.48903
7	1	2.07789	1.22999	0.57317
8	1	1.47085	-1.23719	-1.16227
9	1	-0.12805	-1.06798	1.45700
10	1	-1.87438	-1.20953	-1.08025
11	1	-1.86787	1.21723	-1.08141
12	1	-0.12441	1.06918	1.45729
13	1	-0.38757	2.51810	0.37767
14	1	1.47840	1.23456	-1.15813
15	1	2.07215	-1.24188	0.56850
16	1	-0.40043	-2.51694	0.37949

Thermodynamic data for the first transition state of butadiene and ethene Diels-Alder reaction optimized at B3LYP/6-31G(d) level

Zero-point correction, Hartree	0.140573
Thermal correction to energy, Hartree	0.146991
Thermal correction to enthalpy, Hartree	0.147935
Thermal correction to Gibbs free energy, Hartree	0.111007
Sum of electronic and zero-point energies, Hartree	-234.403323
Sum of electronic and thermal energies, Hartree	-234.396905
Sum of electronic and thermal enthalpies, Hartree	-234.395961
Sum of electronic and thermal Gibbs free energies, Hartree	-234.432889

Coordinates for the first transition state of butadiene and ethene Diels-Alder**reaction optimized at B3LYP/6-31G(d,p) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.26092	1.56920	0.69308
2	6	-0.26092	1.56920	-0.69308
3	6	0.49839	-0.43428	-1.43613
4	6	-0.26092	-1.32839	-0.70305
5	6	-0.26092	-1.32839	0.70305
6	6	0.49839	-0.43428	1.43613
7	1	0.52471	2.08699	1.23428
8	1	-1.19092	1.44647	-1.23506
9	1	1.45793	-0.09308	-1.06682
10	1	-1.03742	-1.89530	-1.21315
11	1	-1.03742	-1.89530	1.21315
12	1	1.45793	-0.09308	1.06682
13	1	0.38638	-0.38422	2.51560
14	1	-1.19092	1.44647	1.23506
15	1	0.52471	2.08699	-1.23428
16	1	0.38638	-0.38422	-2.51560

Thermodynamic data for first transition state of butadiene and ethene Diels-Alder**reaction optimized at B3LYP/6-31G(d,p) level**

Zero-point correction, Hartree	0.140220
Thermal correction to energy, Hartree	0.146648
Thermal correction to enthalpy, Hartree	0.147592
Thermal correction to Gibbs free energy, Hartree	0.110649
Sum of electronic and zero-point energies, Hartree	-234.419509
Sum of electronic and thermal energies, Hartree	-234.413082
Sum of electronic and thermal enthalpies, Hartree	-234.412137
Sum of electronic and thermal Gibbs free energies, Hartree	-234.449080

**Coordinates for the first transition state of butadiene and ethene Diels-Alder
reaction optimized at B3LYP/aug-cc-pVTZ level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.258898	1.551385	0.692469
2	6	-0.258898	1.551385	-0.692469
3	6	0.494864	-0.424294	-1.429735
4	6	-0.258898	-1.320725	-0.699132
5	6	-0.258898	-1.320725	0.699132
6	6	0.494864	-0.424294	1.429735
7	1	0.523393	2.071758	1.22715
8	1	-1.187542	1.440638	-1.230967
9	1	1.454212	-0.088721	-1.067185
10	1	-1.027931	-1.890248	-1.208192
11	1	-1.027931	-1.890248	1.208192
12	1	1.454212	-0.088721	1.067185
13	1	0.375462	-0.371623	2.50396
14	1	-1.187542	1.440638	1.230967
15	1	0.523393	2.071758	-1.22715
16	1	0.375462	-0.371623	-2.50396

**Thermodynamic data for first transition state of butadiene and ethene Diels-Alder
reaction optimized at B3LYP/ aug-cc-pVTZ level**

Zero-point correction, Hartree	0.139565
Thermal correction to energy, Hartree	0.145985
Thermal correction to enthalpy, Hartree	0.146930
Thermal correction to Gibbs free energy, Hartree	0.110005
Sum of electronic and zero-point energies, Hartree	-234.500234
Sum of electronic and thermal energies, Hartree	-234.493813
Sum of electronic and thermal enthalpies, Hartree	-234.492869
Sum of electronic and thermal Gibbs free energies, Hartree	-234.529793

**Coordinates for the second transition state of butadiene and ethene Diels-Alder
reaction optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.32647	2.68097	0.66624
2	6	0.32647	2.68097	-0.66624
3	6	0.32647	-1.49187	-1.54751
4	6	-0.73407	-1.35897	-0.73654
5	6	-0.73407	-1.35897	0.73654
6	6	0.32647	-1.49187	1.54751
7	1	0.45052	3.59620	1.24111
8	1	0.20219	1.76273	-1.23590
9	1	1.33879	-1.61851	-1.17087
10	1	-1.71564	-1.23943	-1.19376
11	1	-1.71564	-1.23943	1.19376
12	1	1.33879	-1.61851	1.17087
13	1	0.21092	-1.48178	2.62732
14	1	0.20219	1.76273	1.23590
15	1	0.45052	3.59620	-1.24111
16	1	0.21092	-1.48178	-2.62732

**Thermodynamic data for the second transition state of butadiene and ethene
Diels-Alder reaction optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.137024
Thermal correction to energy, Hartree	0.146236
Thermal correction to enthalpy, Hartree	0.147180
Thermal correction to Gibbs free energy, Hartree	0.099149
Sum of electronic and zero-point energies, Hartree	-234.440820
Sum of electronic and thermal energies, Hartree	-234.431608
Sum of electronic and thermal enthalpies, Hartree	-234.430664
Sum of electronic and thermal Gibbs free energies, Hartree	-234.478694

**Coordinates for the third transition state of butadiene and ethene Diels-Alder
reaction optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.77675	-1.21941	-0.19103
2	6	-0.77844	-1.22071	-0.19109
3	6	-1.40210	0.09260	0.34335
4	6	-0.66710	1.30214	-0.17993
5	6	0.66963	1.30357	-0.17984
6	6	1.40343	0.09467	0.34333
7	1	1.15956	-2.06146	0.39444
8	1	-1.13597	-1.37364	-1.21648
9	1	-1.35486	0.09007	1.44421
10	1	-1.23499	2.15641	-0.54295
11	1	1.23697	2.15863	-0.54283
12	1	1.35626	0.09250	1.44432
13	1	2.46833	0.13121	0.08770
14	1	1.13359	-1.37325	-1.21601
15	1	-1.16409	-2.06387	0.39304
16	1	-2.46697	0.12811	0.08760

**Thermodynamic data for the third transition state of butadiene and ethene Diels-
Alder reaction optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.146535
Thermal correction to energy, Hartree	0.151537
Thermal correction to enthalpy, Hartree	0.152481
Thermal correction to Gibbs free energy, Hartree	0.118262
Sum of electronic and zero-point energies, Hartree	-234.492619
Sum of electronic and thermal energies, Hartree	-234.487617
Sum of electronic and thermal enthalpies, Hartree	-234.486673
Sum of electronic and thermal Gibbs free energies, Hartree	-234.520892

**Coordinates for the third transition state of butadiene and ethene Diels-Alder
reaction optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.77675	-1.21941	-0.19103
2	6	-0.77844	-1.22071	-0.19109
3	6	-1.40210	0.09260	0.34335
4	6	-0.66710	1.30214	-0.17993
5	6	0.66963	1.30357	-0.17984
6	6	1.40343	0.09467	0.34333
7	1	1.15956	-2.06146	0.39444
8	1	-1.13597	-1.37364	-1.21648
9	1	-1.35486	0.09007	1.44421
10	1	-1.23499	2.15641	-0.54295
11	1	1.23697	2.15863	-0.54283
12	1	1.35626	0.09250	1.44432
13	1	2.46833	0.13121	0.08770
14	1	1.13359	-1.37325	-1.21601
15	1	-1.16409	-2.06387	0.39304
16	1	-2.46697	0.12811	0.08760

**Thermodynamic data for the third transition state of butadiene and ethene Diels-
Alder reaction optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.146535
Thermal correction to energy, Hartree	0.151537
Thermal correction to enthalpy, Hartree	0.152481
Thermal correction to Gibbs free energy, Hartree	0.118262
Sum of electronic and zero-point energies, Hartree	-234.492619
Sum of electronic and thermal energies, Hartree	-234.487617
Sum of electronic and thermal enthalpies, Hartree	-234.486673
Sum of electronic and thermal Gibbs free energies, Hartree	-234.520892

Coordinates 1,5-hexadiene optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.492734	-0.104408	-0.468581
2	6	-2.252288	-0.976909	0.193942
3	6	2.252365	-0.976742	-0.193890
4	6	1.492745	-0.104342	0.468693
5	6	0.760039	1.056836	-0.146399
6	6	-0.760232	1.056968	0.146302
7	1	-1.375639	-0.217823	-1.548282
8	1	-2.761542	-1.793213	-0.311430
9	1	2.762314	-1.792753	0.311272
10	1	1.376041	-0.217424	1.548468
11	1	1.177698	1.997585	0.242731
12	1	-1.177799	1.997664	-0.243020
13	1	2.394734	-0.908388	-1.270841
14	1	0.927239	1.066944	-1.231678
15	1	-0.927469	1.067260	1.231575
16	1	-2.394955	-0.908269	1.270793

Thermodynamic data 1,5-hexadiene optimized at B3LYP/6-31G(d) level

Zero-point correction, Hartree	0.142401
Thermal correction to energy, Hartree	0.149718
Thermal correction to enthalpy, Hartree	0.150662
Thermal correction to Gibbs free energy, Hartree	0.110669
Sum of electronic and zero-point energies, Hartree	-234.468284
Sum of electronic and thermal energies, Hartree	-234.460967
Sum of electronic and thermal enthalpies, Hartree	-234.460023
Sum of electronic and thermal Gibbs free energies, Hartree	-234.500016

**Coordinates for transition state of 1,5-hexadiene Cope reaction optimized at
B3LYP/6-31G(d level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.256614	1.432053	0.000000
2	6	-0.256614	-0.949827	1.218645
3	6	0.256614	-1.432053	0.000000
4	6	0.256614	0.949827	1.218645
5	6	-0.256614	-0.949827	-1.218645
6	6	0.256614	0.949827	-1.218645
7	1	-1.273317	1.826439	0.000000
8	1	-0.188210	1.312214	2.145261
9	1	0.188210	-1.312214	2.145261
10	1	1.273317	-1.826439	0.000000
11	1	0.188210	-1.312214	-2.145261
12	1	-0.188210	1.312214	-2.145261
13	1	-1.333242	-0.810965	1.299878
14	1	-1.333242	-0.810965	-1.299878
15	1	1.333242	0.810965	-1.299878
16	1	1.333242	0.810965	1.299878

**Thermodynamic data for transition state of 1,5-hexadiene Cope reaction optimized
at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.146535
Thermal correction to energy, Hartree	0.151537
Thermal correction to enthalpy, Hartree	0.152481
Thermal correction to Gibbs free energy, Hartree	0.118262
Sum of electronic and zero-point energies, Hartree	-234.492619
Sum of electronic and thermal energies, Hartree	-234.487617
Sum of electronic and thermal enthalpies, Hartree	-234.486673
Sum of electronic and thermal Gibbs free energies, Hartree	-234.520892

Coordinates for DBH optimized at UB3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.226138	-0.778351	-0.328453
2	6	0.167965	-1.098765	0.288539
3	6	0.168558	1.098445	0.289265
4	6	-1.225630	0.779171	-0.328124
5	1	-1.324023	-1.208170	-1.328773
6	1	-2.023035	-1.191211	0.297917
7	1	-1.323141	1.209504	-1.328266
8	1	-2.022327	1.192253	0.298345
9	6	0.319678	-0.000579	1.348990
10	1	1.298593	-0.001046	1.838191
11	1	-0.474630	-0.000645	2.101145
12	1	0.348106	-2.139418	0.556873
13	1	0.349220	2.138821	0.558311
14	7	1.138721	-0.625447	-0.758410
15	7	1.139085	0.625501	-0.758024

Thermodynamic data for DBH optimized at UB3LYP/6-31G(d) level

Zero-point correction, Hartree	0.129984
Thermal correction to energy, Hartree	0.141331
Thermal correction to enthalpy, Hartree	0.142740
Thermal correction to Gibbs free energy, Hartree	0.083304
Sum of electronic and zero-point energies, Hartree	-304.663491
Sum of electronic and thermal energies, Hartree	-304.652145
Sum of electronic and thermal enthalpies, Hartree	-304.650735
Sum of electronic and thermal Gibbs free energies, Hartree	-304.710172

**Coordinates for the first transition state of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.447170	-1.224672	0.787817
2	6	-0.447170	0.245936	1.171040
3	6	-0.447170	0.245936	-1.171040
4	6	-0.447170	-1.224672	-0.787817
5	1	0.416912	-1.747318	1.213688
6	1	-1.337352	-1.738830	1.179122
7	1	0.416912	-1.747318	-1.213688
8	1	-1.337352	-1.738830	-1.179122
9	6	-0.955681	0.999343	0.000000
10	1	-0.806608	2.081337	0.000000
11	1	-2.049253	0.806934	0.000000
12	1	-0.588460	0.573580	2.195402
13	1	-0.588460	0.573580	-2.195402
14	7	1.595701	0.620402	0.577697
15	7	1.595701	0.620402	-0.577697

**Thermodynamic data for the first transition state of DBH deazetization optimized
at UB3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.121893
Thermal correction to energy, Hartree	0.135314
Thermal correction to enthalpy, Hartree	0.136723
Thermal correction to Gibbs free energy, Hartree	0.072177
Sum of electronic and zero-point energies, Hartree	-304.602850
Sum of electronic and thermal energies, Hartree	-304.589429
Sum of electronic and thermal enthalpies, Hartree	-304.588020
Sum of electronic and thermal Gibbs free energies, Hartree	-304.652566

**Coordinates for the intermediate of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.317423	0.703403	-0.983778
2	6	0.000000	1.204181	0.391487
3	6	0.000000	-1.204181	0.391487
4	6	-0.317423	-0.703403	-0.983778
5	1	0.014877	1.341886	-1.820705
6	1	1.426803	0.574603	-1.054262
7	1	-1.426803	-0.574603	-1.054262
8	1	-0.014877	-1.341886	-1.820705
9	6	0.000000	0.000000	1.245772
10	1	-0.861543	-0.095512	1.931951
11	1	0.861543	0.095512	1.931951
12	1	0.391248	2.150207	0.759449
13	1	-0.391248	-2.150207	0.759449

**Thermodynamic data for the intermediate of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.110066
Thermal correction to energy, Hartree	0.120090
Thermal correction to enthalpy, Hartree	0.121499
Thermal correction to Gibbs free energy, Hartree	0.066705
Sum of electronic and zero-point energies, Hartree	-195.071339
Sum of electronic and thermal energies, Hartree	-195.061315
Sum of electronic and thermal enthalpies, Hartree	-195.059906
Sum of electronic and thermal Gibbs free energies, Hartree	-195.114700

**Coordinates for the second transition state of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.032841	-0.763970	0.000689
2	6	-0.391659	-1.122239	-0.000356
3	6	-0.391638	1.122259	0.000432
4	6	1.032847	0.763961	-0.000798
5	1	1.583087	-1.165462	0.875150
6	1	1.585284	-1.168104	-0.871034
7	1	1.584966	1.168036	0.871239
8	1	1.583449	1.165421	-0.874987
9	6	-1.406732	0.000005	-0.000104
10	1	-2.097095	-0.000126	0.877285
11	1	-2.097153	0.000123	-0.877463
12	1	-0.698272	-2.167981	-0.001140
13	1	-0.698224	2.167996	0.001773

**Thermodynamic data for the second transition of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.111729
Thermal correction to energy, Hartree	0.121379
Thermal correction to enthalpy, Hartree	0.122789
Thermal correction to Gibbs free energy, Hartree	0.066684
Sum of electronic and zero-point energies, Hartree	-195.071105
Sum of electronic and thermal energies, Hartree	-195.061455
Sum of electronic and thermal enthalpies, Hartree	-195.060046
Sum of electronic and thermal Gibbs free energies, Hartree	-195.116151

**Coordinates for the third transition state of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.032841	-0.763970	0.000689
2	6	-0.391659	-1.122239	-0.000356
3	6	-0.391638	1.122259	0.000432
4	6	1.032847	0.763961	-0.000798
5	1	1.583087	-1.165462	0.875150
6	1	1.585284	-1.168104	-0.871034
7	1	1.584966	1.168036	0.871239
8	1	1.583449	1.165421	-0.874987
9	6	-1.406732	0.000005	-0.000104
10	1	-2.097095	-0.000126	0.877285
11	1	-2.097153	0.000123	-0.877463
12	1	-0.698272	-2.167981	-0.001140
13	1	-0.698224	2.167996	0.001773

**Thermodynamic data for the third transition of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.109798
Thermal correction to energy, Hartree	0.120200
Thermal correction to enthalpy, Hartree	0.121609
Thermal correction to Gibbs free energy, Hartree	0.065064
Sum of electronic and zero-point energies, Hartree	-195.073681
Sum of electronic and thermal energies, Hartree	-195.063280
Sum of electronic and thermal enthalpies, Hartree	-195.061870
Sum of electronic and thermal Gibbs free energies, Hartree	-195.118416

**Coordinates for the first product of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.016888	0.782952	0.136991
2	6	0.409863	0.766290	-0.425617
3	6	0.410353	-0.765689	-0.426583
4	6	-1.016268	-0.783386	0.137094
5	1	-1.144498	1.280140	1.106752
6	1	-1.750978	1.193319	-0.562690
7	1	-1.141573	-1.279879	1.107497
8	1	-1.751060	-1.195188	-0.560964
9	6	1.323463	-0.000129	0.491508
10	1	1.151503	-0.001065	1.569016
11	1	2.374508	0.000851	0.211641
12	1	0.799712	1.450079	-1.174648
13	1	0.799249	-1.448490	-1.176961

**Thermodynamic data for the first product of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.116866
Thermal correction to energy, Hartree	0.126440
Thermal correction to enthalpy, Hartree	0.127849
Thermal correction to Gibbs free energy, Hartree	0.073043
Sum of electronic and zero-point energies, Hartree	-195.163368
Sum of electronic and thermal energies, Hartree	-195.153794
Sum of electronic and thermal enthalpies, Hartree	-195.152385
Sum of electronic and thermal Gibbs free energies, Hartree	-195.207191

**Coordinates for the second product of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.236785	-0.317375	0.101120
2	6	0.667179	1.076245	-0.045443
3	6	-1.236564	-0.318354	0.101361
4	6	0.000551	-1.227425	-0.132872
5	1	2.049359	-0.525637	-0.606717
6	1	1.663160	-0.456127	1.106726
7	1	0.000457	-1.576971	-1.171483
8	1	0.000896	-2.115176	0.507315
9	6	-0.668197	1.075693	-0.046108
10	1	-1.293751	1.962794	-0.102949
11	1	-1.661940	-0.457123	1.107456
12	1	1.292381	1.963575	-0.102618
13	1	-2.049079	-0.528040	-0.606077

**Thermodynamic data for the second product of DBH deazetization optimized at
UB3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.117305
Thermal correction to energy, Hartree	0.127114
Thermal correction to enthalpy, Hartree	0.128524
Thermal correction to Gibbs free energy, Hartree	0.072568
Sum of electronic and zero-point energies, Hartree	-195.209833
Sum of electronic and thermal energies, Hartree	-195.200024
Sum of electronic and thermal enthalpies, Hartree	-195.198615
Sum of electronic and thermal Gibbs free energies, Hartree	-195.254570

Coordinates for nitrogen optimized at UB3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	7	0	0	0.552751
2	7	0	0	-0.552751

Thermodynamic data for nitrogen optimized at UB3LYP/6-31G(d) level

Zero-point correction, Hartree	0.005599
Thermal correction to energy, Hartree	0.009166
Thermal correction to enthalpy, Hartree	0.010591
Thermal correction to Gibbs free energy, Hartree	-0.024301
Sum of electronic and zero-point energies, Hartree	-109.518530
Sum of electronic and thermal energies, Hartree	-109.514963
Sum of electronic and thermal enthalpies, Hartree	-109.513538
Sum of electronic and thermal Gibbs free energies, Hartree	-109.548430

Coordinates for DBH optimized at CASSCF(6,6)/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.188854	-1.248680	0.776984
2	6	-0.188854	0.264197	1.091388
3	6	-0.188854	0.264197	-1.091388
4	6	-0.188854	-1.248680	-0.776984
5	1	0.677783	-1.741235	1.199523
6	1	-1.074286	-1.723401	1.183160
7	1	0.677783	-1.741235	-1.199523
8	1	-1.074286	-1.723401	-1.183160
9	6	-1.096811	0.826559	0.000000
10	1	-1.150888	1.909021	0.000000
11	1	-2.095649	0.407202	0.000000
12	1	-0.370869	0.535169	2.119886
13	1	-0.370869	0.535169	-2.119886
14	7	1.135332	0.742653	0.633980
15	7	1.135332	0.742653	-0.633980

Thermodynamic data for DBH optimized at CASSCF(6,6)/6-31G(d) level

Zero-point correction, Hartree	0.138664
Thermal correction to energy, Hartree	0.149125
Thermal correction to enthalpy, Hartree	0.150534
Thermal correction to Gibbs free energy, Hartree	0.092466
Sum of electronic and zero-point energies, Hartree	-302.793298
Sum of electronic and thermal energies, Hartree	-302.782837
Sum of electronic and thermal enthalpies, Hartree	-302.781428
Sum of electronic and thermal Gibbs free energies, Hartree	-302.839496

**Coordinates for the first transition state of DBH deazetization optimized at
CASSCF(6,6)/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.188854	-1.248680	0.776984
2	6	-0.188854	0.264197	1.091388
3	6	-0.188854	0.264197	-1.091388
4	6	-0.188854	-1.248680	-0.776984
5	1	0.677783	-1.741235	1.199523
6	1	-1.074286	-1.723401	1.183160
7	1	0.677783	-1.741235	-1.199523
8	1	-1.074286	-1.723401	-1.183160
9	6	-1.096811	0.826559	0.000000
10	1	-1.150888	1.909021	0.000000
11	1	-2.095649	0.407202	0.000000
12	1	-0.370869	0.535169	2.119886
13	1	-0.370869	0.535169	-2.119886
14	7	1.135332	0.742653	0.633980
15	7	1.135332	0.742653	-0.633980

**Thermodynamic data for the first transition state of DBH deazetization optimized
at CASSCF(6,6)/6-31G(d) level**

Zero-point correction, Hartree	0.138664
Thermal correction to energy, Hartree	0.149125
Thermal correction to enthalpy, Hartree	0.150534
Thermal correction to Gibbs free energy, Hartree	0.092466
Sum of electronic and zero-point energies, Hartree	-302.793298
Sum of electronic and thermal energies, Hartree	-302.782837
Sum of electronic and thermal enthalpies, Hartree	-302.781428
Sum of electronic and thermal Gibbs free energies, Hartree	-302.839496

**Coordinates for the intermediate of DBH deazetization optimized at
CASSCF(2,2)/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.223409	0.738115	-1.020382
2	6	0.000000	1.185769	0.400704
3	6	0.000000	-1.185769	0.400704
4	6	-0.223409	-0.738115	-1.020382
5	1	-0.319531	1.341602	-1.741356
6	1	1.279778	0.809699	-1.282118
7	1	-1.279778	-0.809699	-1.282118
8	1	0.319531	-1.341602	-1.741356
9	6	0.000000	0.000000	1.338076
10	1	-0.871440	0.005799	1.993029
11	1	0.871440	-0.005799	1.993029
12	1	0.253777	2.175928	0.734282
13	1	-0.253777	-2.175928	0.734282

**Thermodynamic data for the intermediate of DBH deazetization optimized at
CASSCF(2,2)/6-31G(d) level**

Zero-point correction, Hartree	0.120083
Thermal correction to energy, Hartree	0.130468
Thermal correction to enthalpy, Hartree	0.131878
Thermal correction to Gibbs free energy, Hartree	0.075610
Sum of electronic and zero-point energies, Hartree	-193.782558
Sum of electronic and thermal energies, Hartree	-193.772173
Sum of electronic and thermal enthalpies, Hartree	-193.770764
Sum of electronic and thermal Gibbs free energies, Hartree	-193.827031

**Coordinates for the second transition state of DBH deazetization optimized at
CASSCF(2,2)/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.223409	0.738115	-1.020382
2	6	0.000000	1.185769	0.400704
3	6	0.000000	-1.185769	0.400704
4	6	-0.223409	-0.738115	-1.020382
5	1	-0.319531	1.341602	-1.741356
6	1	1.279778	0.809699	-1.282118
7	1	-1.279778	-0.809699	-1.282118
8	1	0.319531	-1.341602	-1.741356
9	6	0.000000	0.000000	1.338076
10	1	-0.871440	0.005799	1.993029
11	1	0.871440	-0.005799	1.993029
12	1	0.253777	2.175928	0.734282
13	1	-0.253777	-2.175928	0.734282

**Thermodynamic data for the second transition state of DBH deazetization
optimized at CASSCF(2,2)/6-31G(d) level**

Zero-point correction, Hartree	0.120083
Thermal correction to energy, Hartree	0.130468
Thermal correction to enthalpy, Hartree	0.131878
Thermal correction to Gibbs free energy, Hartree	0.075610
Sum of electronic and zero-point energies, Hartree	-193.782558
Sum of electronic and thermal energies, Hartree	-193.772173
Sum of electronic and thermal enthalpies, Hartree	-193.770764
Sum of electronic and thermal Gibbs free energies, Hartree	-193.827031

**Coordinates for the first product of DBH deazetization optimized at
CASSCF(2,2)/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.010685	0.778509	0.134211
2	6	0.411689	0.773778	-0.422434
3	6	0.411689	-0.773697	-0.422581
4	6	-1.010685	-0.778534	0.134064
5	1	-1.138702	1.268137	1.094721
6	1	-1.737132	1.184890	-0.559167
7	1	-1.138701	-1.268345	1.094480
8	1	-1.737132	-1.184784	-0.559392
9	6	1.309007	-0.000046	0.486955
10	1	1.136672	-0.000148	1.553125
11	1	2.351819	-0.000020	0.216953
12	1	0.798543	1.464265	-1.150868
13	1	0.798543	-1.464046	-1.151146

**Thermodynamic data for the first product state of DBH deazetization optimized
at CASSCF(2,2)/6-31G(d) level**

Zero-point correction, Hartree	0.124663
Thermal correction to energy, Hartree	0.133539
Thermal correction to enthalpy, Hartree	0.134948
Thermal correction to Gibbs free energy, Hartree	0.081222
Sum of electronic and zero-point energies, Hartree	-193.820191
Sum of electronic and thermal energies, Hartree	-193.811314
Sum of electronic and thermal enthalpies, Hartree	-193.809905
Sum of electronic and thermal Gibbs free energies, Hartree	-193.863631

**Coordinates for the second product of DBH deazetization optimized at
CASSCF(2,2)/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.010685	0.778509	0.134211
2	6	0.411689	0.773778	-0.422434
3	6	0.411689	-0.773697	-0.422581
4	6	-1.010685	-0.778534	0.134064
5	1	-1.138702	1.268137	1.094721
6	1	-1.737132	1.184890	-0.559167
7	1	-1.138701	-1.268345	1.094480
8	1	-1.737132	-1.184784	-0.559392
9	6	1.309007	-0.000046	0.486955
10	1	1.136672	-0.000148	1.553125
11	1	2.351819	-0.000020	0.216953
12	1	0.798543	1.464265	-1.150868
13	1	0.798543	-1.464046	-1.151146

**Thermodynamic data for the second product state of DBH deazetization
optimized at CASSCF(2,2)/6-31G(d) level**

Zero-point correction, Hartree	0.124404
Thermal correction to energy, Hartree	0.133721
Thermal correction to enthalpy, Hartree	0.135130
Thermal correction to Gibbs free energy, Hartree	0.080011
Sum of electronic and zero-point energies, Hartree	-193.880216
Sum of electronic and thermal energies, Hartree	-193.870899
Sum of electronic and thermal enthalpies, Hartree	-193.869490
Sum of electronic and thermal Gibbs free energies, Hartree	-193.924609

Coordinates for nitrogen optimized at CASSCF(2,2)/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	7	0	0	0.54457
2	7	0	0	-0.54457

Thermodynamic data for nitrogen optimized at CASSCF(2,2)/6-31G(d) level

Zero-point correction, Hartree	0.005995
Thermal correction to energy, Hartree	0.009520
Thermal correction to enthalpy, Hartree	0.010930
Thermal correction to Gibbs free energy, Hartree	-0.023476
Sum of electronic and zero-point energies, Hartree	-108.973772
Sum of electronic and thermal energies, Hartree	-108.970247
Sum of electronic and thermal enthalpies, Hartree	-108.968838
Sum of electronic and thermal Gibbs free energies, Hartree	-109.003243

Coordinates for 2,3-dimethylbutadiene optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.426287	1.189066	-0.475778
2	1	-2.513375	1.200570	-0.494075
3	1	-0.919594	2.074196	-0.848677
4	6	-0.745154	0.124959	-0.026950
5	6	0.745154	0.124991	0.026883
6	6	1.426245	1.189096	0.475791
7	1	2.513332	1.200595	0.494208
8	1	0.919514	2.074202	0.848689
9	6	1.459953	-1.129031	-0.427535
10	1	1.217164	-1.986774	0.212762
11	1	1.169854	-1.405347	-1.449819
12	1	2.545203	-0.992655	-0.405479
13	6	-1.459916	-1.129064	0.427548
14	1	-1.217161	-1.986808	-0.212755
15	1	-1.169730	-1.405371	1.449811
16	1	-2.545174	-0.992713	0.405589

**Thermodynamic data for 2,3-dimethylbutadiene optimized at B3LYP/6-31G(d)
level**

Zero-point correction, Hartree	0.142130
Thermal correction to energy, Hartree	0.149411
Thermal correction to enthalpy, Hartree	0.150356
Thermal correction to Gibbs free energy, Hartree	0.111436
Sum of electronic and zero-point energies, Hartree	-234.480614
Sum of electronic and thermal energies, Hartree	-234.473333
Sum of electronic and thermal enthalpies, Hartree	-234.472389
Sum of electronic and thermal Gibbs free energies, Hartree	-234.511308

Coordinates for *E*-N-neopentylisomaleimide optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	2.855208	1.216092	0.097382
2	6	1.544363	1.329146	-0.159304
3	6	3.199835	-0.222023	0.111974
4	6	0.987728	-0.027859	-0.322814
5	8	2.040924	-0.932471	-0.147205
6	8	4.255464	-0.775541	0.302802
7	7	-0.156126	-0.498264	-0.574418
8	6	-1.299535	0.380219	-0.769898
9	1	-1.585049	0.294304	-1.827251
10	1	-1.071420	1.438448	-0.578137
11	6	-2.515214	-0.039623	0.098941
12	6	-3.666316	0.932753	-0.218845
13	1	-4.555484	0.679699	0.370293
14	1	-3.392547	1.968600	0.016552
15	1	-3.943333	0.888734	-1.279429
16	6	-2.149504	0.061243	1.590799
17	1	-1.333780	-0.623799	1.847305
18	1	-1.832641	1.078564	1.853325
19	1	-3.012412	-0.192853	2.217534
20	6	-2.944347	-1.477698	-0.242660
21	1	-3.229424	-1.563658	-1.298752
22	1	-2.134103	-2.188115	-0.052172
23	1	-3.809340	-1.773498	0.362835
24	1	3.584793	1.995098	0.272277
25	1	0.963202	2.236920	-0.241678

**Thermodynamic data for *E*-N-neopentylisomaleimide optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.209354
Thermal correction to energy, Hartree	0.221534
Thermal correction to enthalpy, Hartree	0.222478
Thermal correction to Gibbs free energy, Hartree	0.170474
Sum of electronic and zero-point energies, Hartree	-555.774363
Sum of electronic and thermal energies, Hartree	-555.762183
Sum of electronic and thermal enthalpies, Hartree	-555.761239
Sum of electronic and thermal Gibbs free energies, Hartree	-555.813243

Coordinates for Z-N-neopentylisomaleimide optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	2.855208	1.216092	0.097382
2	6	1.544363	1.329146	-0.159304
3	6	3.199835	-0.222023	0.111974
4	6	0.987728	-0.027859	-0.322814
5	8	2.040924	-0.932471	-0.147205
6	8	4.255464	-0.775541	0.302802
7	7	-0.156126	-0.498264	-0.574418
8	6	-1.299535	0.380219	-0.769898
9	1	-1.585049	0.294304	-1.827251
10	1	-1.071420	1.438448	-0.578137
11	6	-2.515214	-0.039623	0.098941
12	6	-3.666316	0.932753	-0.218845
13	1	-4.555484	0.679699	0.370293
14	1	-3.392547	1.968600	0.016552
15	1	-3.943333	0.888734	-1.279429
16	6	-2.149504	0.061243	1.590799
17	1	-1.333780	-0.623799	1.847305
18	1	-1.832641	1.078564	1.853325
19	1	-3.012412	-0.192853	2.217534
20	6	-2.944347	-1.477698	-0.242660
21	1	-3.229424	-1.563658	-1.298752
22	1	-2.134103	-2.188115	-0.052172
23	1	-3.809340	-1.773498	0.362835
24	1	3.584793	1.995098	0.272277
25	1	0.963202	2.236920	-0.241678

**Thermodynamic data for Z-N-neopentylisomaleimide optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.209136
Thermal correction to energy, Hartree	0.221355
Thermal correction to enthalpy, Hartree	0.222299
Thermal correction to Gibbs free energy, Hartree	0.169886
Sum of electronic and zero-point energies, Hartree	-555.777561
Sum of electronic and thermal energies, Hartree	-555.765341
Sum of electronic and thermal enthalpies, Hartree	-555.764397
Sum of electronic and thermal Gibbs free energies, Hartree	-555.816811

**Coordinates for uncatalyzed DA reaction of *E*-N-neopentylisomaleimide with
2,3-dimethylbutadiene optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.800303	2.470652	-0.255423
2	6	-0.370096	3.088965	-0.037609
3	1	1.775361	2.924126	-0.366466
4	1	-0.573372	4.145445	0.070581
5	6	-1.423380	2.059688	0.043738
6	8	-2.615402	2.163305	0.229966
7	6	0.554735	1.019328	-0.330402
8	7	-2.865963	-1.537461	-0.771740
9	6	-4.011646	-1.549568	-0.001768
10	8	-4.801442	-2.498344	-0.007757
11	7	-4.205460	-0.425118	0.767694
12	1	-5.149173	-0.314415	1.112793
13	1	-3.723535	0.439215	0.531587
14	1	-2.103836	-0.920096	-0.513286
15	8	-0.825601	0.829255	-0.134852
16	6	2.698472	0.107106	-0.736942
17	1	3.078557	1.126471	-0.580790
18	1	2.881139	-0.153350	-1.788227
19	7	1.262454	-0.004058	-0.526055
20	6	3.496810	-0.878217	0.157171
21	6	3.231829	-0.569771	1.641895
22	1	3.495667	0.467063	1.885862
23	1	2.176837	-0.719499	1.897343
24	1	3.829830	-1.227442	2.283525
25	6	4.990926	-0.673521	-0.155183
26	1	5.604272	-1.354276	0.446466
27	1	5.208496	-0.871498	-1.211954
28	1	5.310078	0.351585	0.069881
29	6	3.095267	-2.329820	-0.159712
30	1	3.301045	-2.575692	-1.209045
31	1	3.662579	-3.028902	0.466024
32	1	2.029129	-2.495223	0.023703
33	1	-2.580051	-2.449824	-1.100751

**Thermodynamic data for uncatalyzed DA reaction of *Z*-N-neopentylisomaleimide
with 2,3-dimethylbutadiene optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.353095
Thermal correction to energy, Hartree	0.372855
Thermal correction to enthalpy, Hartree	0.373799
Thermal correction to Gibbs free energy, Hartree	0.304712
Sum of electronic and zero-point energies, Hartree	-790.229640
Sum of electronic and thermal energies, Hartree	-790.209881
Sum of electronic and thermal enthalpies, Hartree	-790.208936
Sum of electronic and thermal Gibbs free energies, Hartree	-790.278024

Coordinates for the first NI complex with urea optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.800303	2.470652	-0.255423
2	6	-0.370096	3.088965	-0.037609
3	1	1.775361	2.924126	-0.366466
4	1	-0.573372	4.145445	0.070581
5	6	-1.423380	2.059688	0.043738
6	8	-2.615402	2.163305	0.229966
7	6	0.554735	1.019328	-0.330402
8	7	-2.865963	-1.537461	-0.771740
9	6	-4.011646	-1.549568	-0.001768
10	8	-4.801442	-2.498344	-0.007757
11	7	-4.205460	-0.425118	0.767694
12	1	-5.149173	-0.314415	1.112793
13	1	-3.723535	0.439215	0.531587
14	1	-2.103836	-0.920096	-0.513286
15	8	-0.825601	0.829255	-0.134852
16	6	2.698472	0.107106	-0.736942
17	1	3.078557	1.126471	-0.580790
18	1	2.881139	-0.153350	-1.788227
19	7	1.262454	-0.004058	-0.526055
20	6	3.496810	-0.878217	0.157171
21	6	3.231829	-0.569771	1.641895
22	1	3.495667	0.467063	1.885862
23	1	2.176837	-0.719499	1.897343
24	1	3.829830	-1.227442	2.283525
25	6	4.990926	-0.673521	-0.155183
26	1	5.604272	-1.354276	0.446466
27	1	5.208496	-0.871498	-1.211954
28	1	5.310078	0.351585	0.069881
29	6	3.095267	-2.329820	-0.159712
30	1	3.301045	-2.575692	-1.209045
31	1	3.662579	-3.028902	0.466024
32	1	2.029129	-2.495223	0.023703
33	1	-2.580051	-2.449824	-1.100751

**Thermodynamic data for the first NI complex with urea optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.274400
Thermal correction to energy, Hartree	0.292828
Thermal correction to enthalpy, Hartree	0.293773
Thermal correction to Gibbs free energy, Hartree	0.224785
Sum of electronic and zero-point energies, Hartree	-780.991628
Sum of electronic and thermal energies, Hartree	-780.973200
Sum of electronic and thermal enthalpies, Hartree	-780.972256
Sum of electronic and thermal Gibbs free energies, Hartree	-781.041243

**Coordinates for the second NI complex with urea optimized at B3LYP/6-31G(d)
level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.813657	1.901389	-0.141120
2	6	-0.499971	2.099465	0.044763
3	1	1.602941	2.639753	-0.119174
4	6	-1.175680	0.793887	-0.078862
5	8	-2.351537	0.509486	0.017705
6	6	1.032399	0.465290	-0.394306
7	7	-5.351980	0.673560	0.471866
8	6	-5.672860	-0.611688	0.086993
9	7	-4.614873	-1.495250	0.096851
10	1	-3.673953	-1.126562	0.000850
11	1	-4.795477	-2.367520	-0.380453
12	1	-4.392917	0.986871	0.367190
13	8	-0.226438	-0.158875	-0.341575
14	6	3.371636	0.302450	-0.711927
15	1	3.409932	1.365218	-0.433625
16	1	3.682715	0.227949	-1.762770
17	7	2.032618	-0.261601	-0.636654
18	6	4.386729	-0.489036	0.155177
19	6	3.976919	-0.416199	1.637265
20	1	3.920446	0.623658	1.983291
21	1	2.999133	-0.881920	1.803814
22	1	4.709167	-0.938208	2.264313
23	6	5.765454	0.170472	-0.033525
24	1	6.524278	-0.353976	0.558702
25	1	6.080649	0.141401	-1.083801
26	1	5.755503	1.219003	0.288300
27	6	4.448066	-1.957347	-0.302455
28	1	4.756833	-2.031207	-1.352702
29	1	5.174179	-2.515340	0.300513
30	1	3.473655	-2.445328	-0.201819
31	1	-1.029548	3.019199	0.251842
32	1	-6.061508	1.361117	0.259351
33	8	-6.831335	-0.962256	-0.156165

**Thermodynamic data for the second NI complex with urea optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.274547
Thermal correction to energy, Hartree	0.293016
Thermal correction to enthalpy, Hartree	0.293960
Thermal correction to Gibbs free energy, Hartree	0.223275
Sum of electronic and zero-point energies, Hartree	-780.990639
Sum of electronic and thermal energies, Hartree	-780.972170
Sum of electronic and thermal enthalpies, Hartree	-780.971225
Sum of electronic and thermal Gibbs free energies, Hartree	-781.041911

**Coordinates for the third NI complex with urea optimized at B3LYP/6-31G(d)
level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.020557	-2.782804	-0.368824
2	6	1.148137	-3.383597	-0.102607
3	1	-0.974356	-3.252322	-0.564090
4	1	1.368452	-4.439834	-0.030477
5	6	2.174867	-2.339649	0.095519
6	8	3.347867	-2.417593	0.355980
7	6	0.196833	-1.324418	-0.357458
8	7	2.373549	1.811384	0.869402
9	6	2.002454	2.777199	-0.045699
10	7	1.107436	2.352326	-1.000969
11	1	0.542202	1.519838	-0.830448
12	1	0.640236	3.100735	-1.494720
13	1	2.267230	0.835573	0.613163
14	8	1.547533	-1.108358	-0.073718
15	6	-1.953426	-0.448611	-0.837533
16	1	-2.272501	-1.497313	-0.899521
17	1	-2.112594	0.001409	-1.825893
18	7	-0.533016	-0.309505	-0.542828
19	6	-2.852080	0.292268	0.190571
20	6	-2.652952	-0.309106	1.593407
21	1	-2.878023	-1.383046	1.601610
22	1	-1.623426	-0.175178	1.943492
23	1	-3.318260	0.177425	2.316076
24	6	-4.312220	0.089084	-0.256809
25	1	-4.996531	0.591224	0.436692
26	1	-4.484063	0.504549	-1.257356
27	1	-4.580040	-0.974247	-0.280755
28	6	-2.525968	1.796324	0.211749
29	1	-2.659295	2.244530	-0.780720
30	1	-3.192604	2.319383	0.907494
31	1	-1.495181	1.980457	0.530013
32	1	3.224192	2.026869	1.372086
33	8	2.439380	3.931000	-0.003484

**Thermodynamic data for the third NI complex with urea optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.274808
Thermal correction to energy, Hartree	0.293089
Thermal correction to enthalpy, Hartree	0.294033
Thermal correction to Gibbs free energy, Hartree	0.225835
Sum of electronic and zero-point energies, Hartree	-780.991916
Sum of electronic and thermal energies, Hartree	-780.973635
Sum of electronic and thermal enthalpies, Hartree	-780.972691
Sum of electronic and thermal Gibbs free energies, Hartree	-781.040889

**Coordinates for transition state of the first NI complex with urea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.250779	0.007955	0.662301
2	6	-1.043903	-1.288931	1.161008
3	1	-1.940867	0.715986	1.098606
4	1	-1.581489	-1.755098	1.972749
5	6	0.334746	-1.666247	0.865943
6	8	0.975430	-2.665194	1.131830
7	6	0.047939	0.467186	0.115630
8	7	3.693870	-1.265292	-1.202005
9	6	4.550885	-2.028768	-0.435878
10	8	5.728202	-2.222360	-0.755913
11	7	3.992924	-2.557644	0.704988
12	1	4.524579	-3.311663	1.117935
13	1	2.980162	-2.634555	0.791602
14	1	2.864309	-0.873482	-0.769343
15	8	0.920287	-0.637920	0.137908
16	6	-0.320253	2.742793	-0.397382
17	1	-1.282262	2.620877	0.120300
18	1	-0.544128	2.922532	-1.458448
19	7	0.514485	1.551310	-0.328095
20	6	0.396449	3.996419	0.168321
21	6	0.725919	3.781878	1.656573
22	1	-0.183105	3.586965	2.239990
23	1	1.403919	2.932145	1.793159
24	1	1.209824	4.671291	2.077466
25	6	-0.564633	5.190170	0.017642
26	1	-0.104134	6.105965	0.406613
27	1	-0.820415	5.365130	-1.034821
28	1	-1.498177	5.024758	0.569547
29	6	1.688811	4.273361	-0.620390
30	1	1.473288	4.440814	-1.683242
31	1	2.189616	5.169541	-0.234773
32	1	2.385564	3.432907	-0.544804
33	6	-3.507305	-0.886931	-0.804927
34	6	-3.332203	-2.223618	-0.345233
35	6	-2.065376	-2.782899	-0.318097
36	6	-2.401069	-0.137462	-1.198708
37	1	-1.298759	-2.489173	-1.023903
38	1	-1.545839	-0.611965	-1.665449
39	1	-2.544653	0.901084	-1.483756
40	1	-1.906495	-3.750585	0.149136
41	1	4.159596	-0.657299	-1.862129
42	6	-4.479969	-2.944882	0.326585
43	1	-4.171183	-3.931295	0.682275

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-4.875328	-2.381778	1.181617
45	1	-5.315258	-3.087117	-0.370282
46	6	-4.842779	-0.202488	-0.629240
47	1	-5.634826	-0.745406	-1.159323
48	1	-5.144755	-0.159979	0.425842
49	1	-4.818393	0.819366	-1.016276

**Thermodynamic data for transition state of the first NI complex with urea
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.417998
Thermal correction to energy, Hartree	0.444141
Thermal correction to enthalpy, Hartree	0.445085
Thermal correction to Gibbs free energy, Hartree	0.357084
Sum of electronic and zero-point energies, Hartree	-1015.446216
Sum of electronic and thermal energies, Hartree	-1015.420073
Sum of electronic and thermal enthalpies, Hartree	-1015.419129
Sum of electronic and thermal Gibbs free energies, Hartree	-1015.507129

**Coordinates for transition state of the second NI complex with urea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	0.656463	0.455863	-1.045037
2	6	-0.726152	0.297291	-1.239930
3	1	1.281638	1.096516	-1.650602
4	6	-1.077514	-1.056293	-0.818392
5	8	-2.143033	-1.650963	-0.843533
6	6	1.164059	-0.852056	-0.571234
7	7	-4.942309	-0.618624	-0.552028
8	6	-5.407162	-1.492469	0.410516
9	7	-4.418147	-2.168778	1.092248
10	1	-3.514892	-2.285928	0.644418
11	1	-4.745710	-2.955591	1.635289
12	1	-4.025120	-0.796599	-0.952890
13	8	0.046535	-1.670439	-0.309714
14	6	3.507914	-0.595881	-0.671030
15	1	3.341681	0.489261	-0.601194
16	1	3.805330	-0.806363	-1.708763
17	7	2.301476	-1.367302	-0.395734
18	6	4.678990	-0.991637	0.261637
19	6	4.296839	-0.717090	1.727199
20	1	4.076497	0.346128	1.887968
21	1	3.411350	-1.293304	2.017197
22	1	5.117339	-0.992467	2.400570
23	6	5.898499	-0.134747	-0.125044
24	1	6.760557	-0.383965	0.504859
25	1	6.187993	-0.302597	-1.169945
26	1	5.691413	0.935368	0.000201
27	6	5.017348	-2.482311	0.079474
28	1	5.321304	-2.693673	-0.953686
29	1	5.844248	-2.773649	0.738267
30	1	4.154083	-3.113164	0.312902
31	1	-1.335550	0.830123	-1.954400
32	6	-1.823260	1.395988	0.481750
33	6	-1.245118	2.648307	0.340963
34	1	-2.873703	1.247560	0.246903
35	6	0.161896	2.798532	0.492916
36	6	-2.071265	3.794330	-0.199723
37	6	0.953582	1.684135	0.761917
38	6	0.822154	4.106457	0.122538
39	1	-3.121891	3.510079	-0.300667
40	1	-2.022284	4.662798	0.468613
41	1	-1.713287	4.131882	-1.181012
42	1	0.572197	0.859996	1.352942
43	1	2.031565	1.805764	0.812938

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	0.622896	4.384196	-0.920971
45	1	0.441910	4.927588	0.742632
46	1	1.905373	4.056379	0.259605
47	1	-1.398645	0.648612	1.140601
48	1	-5.650845	-0.294367	-1.196063
49	8	-6.603030	-1.592121	0.698466

**Thermodynamic data for transition state of the second NI complex with urea
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.418662
Thermal correction to energy, Hartree	0.444572
Thermal correction to enthalpy, Hartree	0.445516
Thermal correction to Gibbs free energy, Hartree	0.359557
Sum of electronic and zero-point energies, Hartree	-1015.444596
Sum of electronic and thermal energies, Hartree	-1015.418686
Sum of electronic and thermal enthalpies, Hartree	-1015.417742
Sum of electronic and thermal Gibbs free energies, Hartree	-1015.503701

**Coordinates for transition state of the third NI complex with urea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.289423	0.294681	0.684077
2	6	-1.873026	-0.865643	1.216234
3	1	-1.520172	1.296509	1.014885
4	1	-2.626714	-0.895001	1.989314
5	6	-0.895864	-1.953359	1.100037
6	8	-0.913699	-3.101856	1.472923
7	6	0.075803	-0.069926	0.256176
8	7	3.097497	-2.685928	0.393444
9	6	3.803461	-2.325014	-0.737353
10	7	3.253169	-1.287922	-1.453575
11	1	2.580333	-0.658708	-1.009197
12	1	3.885649	-0.856679	-2.113903
13	1	2.115105	-2.436915	0.450493
14	8	0.208988	-1.457001	0.395740
15	6	1.025740	2.005691	-0.362628
16	1	0.056670	2.428799	-0.064678
17	1	1.145998	2.198084	-1.437469
18	7	1.085448	0.560112	-0.177287
19	6	2.150499	2.758941	0.396456
20	6	2.020659	2.510086	1.909802
21	1	1.040203	2.832990	2.282410
22	1	2.140634	1.447904	2.149685
23	1	2.787952	3.068184	2.459326
24	6	1.975155	4.261101	0.103320
25	1	2.751032	4.844561	0.612593
26	1	2.051059	4.468653	-0.971260
27	1	1.000370	4.626206	0.449638
28	6	3.535683	2.300832	-0.094176
29	1	3.650585	2.475916	-1.171392
30	1	4.327374	2.857662	0.421252
31	1	3.695609	1.234630	0.093338
32	6	-3.580622	0.629729	-1.009407
33	6	-4.152868	-0.563889	-0.485110
34	6	-3.356490	-1.685531	-0.297712
35	6	-2.227807	0.668676	-1.327603
36	1	-2.512671	-1.891464	-0.945048
37	1	-1.707705	-0.214619	-1.677738
38	1	-1.783511	1.607107	-1.646974
39	1	-3.760520	-2.558135	0.207747
40	6	-5.550732	-0.538155	0.091140
41	1	-5.828640	-1.514303	0.496924
42	1	-5.651199	0.205718	0.892221
43	1	-6.287153	-0.273043	-0.677580

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	6	-4.377231	1.914461	-0.991698
45	1	-5.292243	1.817269	-1.588728
46	1	-4.692906	2.186159	0.024252
47	1	-3.796883	2.745576	-1.400482
48	1	3.324809	-3.607178	0.742983
49	8	4.849275	-2.890618	-1.072417

**Thermodynamic data for transition state of the third NI complex with urea
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.418696
Thermal correction to energy, Hartree	0.444563
Thermal correction to enthalpy, Hartree	0.445507
Thermal correction to Gibbs free energy, Hartree	0.360026
Sum of electronic and zero-point energies, Hartree	-1015.446449
Sum of electronic and thermal energies, Hartree	-1015.420583
Sum of electronic and thermal enthalpies, Hartree	-1015.419638
Sum of electronic and thermal Gibbs free energies, Hartree	-1015.505119

**Coordinates for the first NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.469711	2.485293	-0.232953
2	6	0.396175	3.248717	0.022631
3	1	2.495547	2.807166	-0.345772
4	1	0.339091	4.318937	0.165498
5	6	-0.784980	2.369426	0.087742
6	8	-1.951624	2.625015	0.292674
7	6	1.031397	1.082782	-0.343626
8	7	-2.520983	-1.189974	-0.243837
9	6	-3.797221	-0.848173	0.006930
10	7	-4.043933	0.443255	0.280020
11	1	-4.996447	0.722099	0.459162
12	1	-3.319136	1.160970	0.288719
13	1	-1.758087	-0.520318	-0.227256
14	8	-0.361954	1.076935	-0.136289
15	6	3.023105	-0.112073	-0.796440
16	1	3.537943	0.852703	-0.687438
17	1	3.152038	-0.437402	-1.837335
18	7	1.588598	-0.023330	-0.569193
19	6	3.698877	-1.157812	0.130884
20	6	3.539685	-0.732808	1.601890
21	1	3.969232	0.261647	1.777320
22	1	2.484882	-0.703177	1.897194
23	1	4.053175	-1.440602	2.263045
24	6	5.193868	-1.196669	-0.237467
25	1	5.723842	-1.919165	0.393895
26	1	5.338949	-1.495045	-1.283011
27	1	5.667967	-0.217657	-0.095939
28	6	3.075667	-2.548140	-0.086498
29	1	3.190189	-2.873899	-1.127797
30	1	3.567120	-3.290661	0.553180
31	1	2.007551	-2.545744	0.151836
32	16	-5.055084	-2.018341	-0.021272
33	1	-2.307366	-2.154908	-0.443499

**Thermodynamic data for the first NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.272012
Thermal correction to energy, Hartree	0.290998
Thermal correction to enthalpy, Hartree	0.291942
Thermal correction to Gibbs free energy, Hartree	0.220857
Sum of electronic and zero-point energies, Hartree	-1103.956701
Sum of electronic and thermal energies, Hartree	-1103.937715
Sum of electronic and thermal enthalpies, Hartree	-1103.936771
Sum of electronic and thermal Gibbs free energies, Hartree	-1104.007856

**Coordinates for the second NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.980556	2.282499	-0.485835
2	6	1.432119	3.474095	-0.208072
3	1	3.002638	2.077461	-0.771260
4	1	1.893378	4.452086	-0.213622
5	6	0.009639	3.266498	0.131466
6	8	-0.857689	4.040458	0.442429
7	6	0.939367	1.248925	-0.339413
8	7	-2.936411	0.424394	0.488722
9	6	-3.027030	-0.808863	-0.041569
10	7	-1.903704	-1.335197	-0.556074
11	1	-1.941481	-2.275378	-0.919585
12	1	-0.991551	-0.871477	-0.508393
13	1	-2.090157	0.981246	0.419826
14	8	-0.238063	1.897429	0.037098
15	6	2.086070	-0.757302	-0.871232
16	1	2.944906	-0.106333	-1.079584
17	1	1.832614	-1.274297	-1.805331
18	7	0.897953	-0.006819	-0.480181
19	6	2.502966	-1.820671	0.182655
20	6	2.864589	-1.135184	1.512467
21	1	3.674735	-0.407243	1.379488
22	1	2.002999	-0.610647	1.940270
23	1	3.200252	-1.878174	2.245188
24	6	3.741021	-2.546159	-0.378419
25	1	4.083154	-3.314928	0.323900
26	1	3.516008	-3.038989	-1.332082
27	1	4.572429	-1.850309	-0.544235
28	6	1.370710	-2.838706	0.407543
29	1	1.088980	-3.331524	-0.531349
30	1	1.694484	-3.615982	1.109490
31	1	0.476647	-2.363720	0.823449
32	16	-4.513837	-1.669597	-0.051073
33	1	-3.777539	0.871211	0.819977

**Thermodynamic data for the second NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.272280
Thermal correction to energy, Hartree	0.291094
Thermal correction to enthalpy, Hartree	0.292038
Thermal correction to Gibbs free energy, Hartree	0.222381
Sum of electronic and zero-point energies, Hartree	-1103.957085
Sum of electronic and thermal energies, Hartree	-1103.938271
Sum of electronic and thermal enthalpies, Hartree	-1103.937327
Sum of electronic and thermal Gibbs free energies, Hartree	-1104.006984

**Coordinates for the third NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.304464	-1.869899	-0.115950
2	6	0.012785	-2.058312	0.054658
3	1	-2.090812	-2.609289	-0.056543
4	1	0.548968	-2.969168	0.282750
5	6	0.680428	-0.756044	-0.124196
6	8	1.858844	-0.466458	-0.058042
7	6	-1.532037	-0.443554	-0.411143
8	7	4.763468	-0.930392	0.289860
9	6	5.206324	0.320189	0.072425
10	7	4.273115	1.248778	-0.199474
11	1	3.285386	1.012969	-0.233231
12	1	4.561217	2.200723	-0.363662
13	1	3.773831	-1.156409	0.249906
14	8	-0.272564	0.184960	-0.400609
15	6	-3.876701	-0.292935	-0.691767
16	1	-3.906271	-1.351376	-0.396812
17	1	-4.212215	-0.234253	-1.735982
18	7	-2.537325	0.274250	-0.657568
19	6	-4.872825	0.509752	0.187335
20	6	-4.431873	0.453778	1.661214
21	1	-4.369073	-0.582035	2.018152
22	1	-3.450584	0.920627	1.802072
23	1	-5.150435	0.983820	2.297251
24	6	-6.255079	-0.151935	0.035171
25	1	-7.001063	0.378432	0.638270
26	1	-6.592757	-0.133455	-1.008345
27	1	-6.237917	-1.197167	0.367183
28	6	-4.943795	1.972592	-0.285981
29	1	-5.271830	2.034215	-1.331112
30	1	-5.659219	2.536762	0.323935
31	1	-3.968185	2.462399	-0.208628
32	1	5.429822	-1.658110	0.495820
33	16	6.876844	0.710190	0.137992

**Thermodynamic data for the third NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.271864
Thermal correction to energy, Hartree	0.290983
Thermal correction to enthalpy, Hartree	0.291927
Thermal correction to Gibbs free energy, Hartree	0.220072
Sum of electronic and zero-point energies, Hartree	-1103.956116
Sum of electronic and thermal energies, Hartree	-1103.936997
Sum of electronic and thermal enthalpies, Hartree	-1103.936053
Sum of electronic and thermal Gibbs free energies, Hartree	-1104.007908

**Coordinates for transition state of the first NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.557616	-0.194278	0.644606
2	6	-1.113253	-1.426044	1.154547
3	1	-2.374167	0.371174	1.070533
4	1	-1.567252	-1.987197	1.957172
5	6	0.315718	-1.530285	0.889060
6	8	1.133035	-2.383515	1.181037
7	6	-0.363382	0.503156	0.113784
8	7	3.684649	-0.025631	-0.536686
9	6	4.525607	-1.020090	-0.202200
10	7	4.001279	-2.075913	0.439771
11	1	4.617984	-2.829110	0.703381
12	1	3.010533	-2.150752	0.680256
13	1	2.688117	-0.059197	-0.339599
14	8	0.706019	-0.415650	0.157388
15	6	-1.149486	2.663579	-0.424859
16	1	-2.086369	2.359157	0.064147
17	1	-1.370429	2.799181	-1.492964
18	7	-0.103901	1.653674	-0.329981
19	6	-0.701165	4.028977	0.157106
20	6	-0.391574	3.880167	1.657740
21	1	-1.267729	3.514614	2.208391
22	1	0.431036	3.176226	1.825546
23	1	-0.103235	4.845559	2.090310
24	6	-1.863555	5.020978	-0.034111
25	1	-1.597475	6.006357	0.366178
26	1	-2.109652	5.146256	-1.095869
27	1	-2.768710	4.682525	0.485170
28	6	0.543297	4.543623	-0.588253
29	1	0.334888	4.677404	-1.657317
30	1	0.859854	5.513042	-0.184946
31	1	1.378811	3.843553	-0.491928
32	6	-3.580529	-1.517786	-0.837925
33	6	-3.145561	-2.795594	-0.383036
34	6	-1.792786	-3.090194	-0.344334
35	6	-2.643224	-0.561492	-1.222832
36	1	-1.092026	-2.643133	-1.038126
37	1	-1.709057	-0.856138	-1.686594
38	1	-2.987369	0.429336	-1.505736
39	1	-1.448557	-4.009739	0.120336
40	6	-4.132497	-3.736518	0.272223
41	1	-3.642208	-4.656727	0.600187
42	1	-4.618522	-3.279606	1.143935
43	1	-4.932607	-4.012902	-0.425195

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	6	-5.026955	-1.115562	-0.669358
45	1	-5.688644	-1.791125	-1.225411
46	1	-5.343928	-1.162021	0.380935
47	1	-5.201621	-0.099807	-1.033050
48	16	6.200767	-0.936723	-0.581329
49	1	4.051197	0.773239	-1.030553

**Thermodynamic data for transition state of the first NI complex with thiourea
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.415811
Thermal correction to energy, Hartree	0.442374
Thermal correction to enthalpy, Hartree	0.443319
Thermal correction to Gibbs free energy, Hartree	0.355128
Sum of electronic and zero-point energies, Hartree	-1338.411701
Sum of electronic and thermal energies, Hartree	-1338.385137
Sum of electronic and thermal enthalpies, Hartree	-1338.384193
Sum of electronic and thermal Gibbs free energies, Hartree	-1338.472384

**Coordinates for transition state of the second NI complex with thiourea optimized
at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.113885	0.597270	-1.002572
2	6	-0.269249	0.796398	-1.150878
3	1	1.861502	1.059692	-1.631106
4	6	-0.936004	-0.422204	-0.702086
5	8	-2.119487	-0.722513	-0.685534
6	6	1.288975	-0.795154	-0.532009
7	7	-4.964191	-0.054773	-0.520395
8	6	-5.399494	-1.160639	0.108122
9	7	-4.472275	-2.090405	0.395058
10	1	-3.494274	-1.950663	0.152887
11	1	-4.752950	-2.931309	0.874766
12	1	-3.983568	0.059388	-0.765158
13	8	0.007409	-1.300955	-0.224766
14	6	3.615317	-1.146518	-0.707438
15	1	3.728063	-0.053224	-0.664505
16	1	3.822642	-1.447964	-1.744607
17	7	2.261526	-1.584074	-0.387739
18	6	4.674813	-1.803634	0.211387
19	6	4.412474	-1.414820	1.677533
20	1	4.465677	-0.327301	1.815951
21	1	3.421142	-1.749271	2.002709
22	1	5.158475	-1.871338	2.338998
23	6	6.058274	-1.284806	-0.222222
24	1	6.847299	-1.725649	0.398303
25	1	6.270778	-1.543038	-1.267206
26	1	6.125817	-0.194183	-0.123858
27	6	4.627053	-3.334769	0.060536
28	1	4.836470	-3.635907	-0.973816
29	1	5.375819	-3.809416	0.706020
30	1	3.641935	-3.726046	0.332928
31	1	-0.747640	1.462216	-1.853353
32	6	-0.993167	2.146879	0.582668
33	6	-0.114634	3.206201	0.415582
34	1	-2.050708	2.279091	0.372319
35	6	1.286726	2.987608	0.534955
36	6	-0.628359	4.523537	-0.121928
37	6	1.769198	1.706778	0.793315
38	6	2.253281	4.080384	0.141585
39	1	-1.718243	4.517510	-0.205128
40	1	-0.347563	5.353285	0.538365
41	1	-0.211463	4.753167	-1.110950
42	1	1.200173	1.007004	1.393617
43	1	2.842636	1.543919	0.818906

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	2.114206	4.392816	-0.901889
45	1	2.105816	4.975313	0.758530
46	1	3.289847	3.755855	0.263228
47	1	-0.764282	1.319702	1.243102
48	16	-7.052720	-1.373764	0.521859
49	1	-5.627419	0.664017	-0.764170

**Thermodynamic data for transition state of the second NI complex with thiourea
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.415796
Thermal correction to energy, Hartree	0.442464
Thermal correction to enthalpy, Hartree	0.443408
Thermal correction to Gibbs free energy, Hartree	0.353829
Sum of electronic and zero-point energies, Hartree	-1338.410157
Sum of electronic and thermal energies, Hartree	-1338.383490
Sum of electronic and thermal enthalpies, Hartree	-1338.382546
Sum of electronic and thermal Gibbs free energies, Hartree	-1338.472125

**Coordinates for transition state of the third NI complex with thiourea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.607356	0.287592	0.660019
2	6	-2.040626	-0.883834	1.300745
3	1	-2.025556	1.266849	0.839609
4	1	-2.839446	-0.947493	2.024799
5	6	-0.898822	-1.799876	1.383357
6	8	-0.762613	-2.887035	1.889264
7	6	-0.169892	0.114676	0.375472
8	7	2.980742	-2.381444	0.349133
9	6	3.793923	-1.701048	-0.479445
10	7	3.365791	-0.502320	-0.905343
11	1	2.488402	-0.068898	-0.591127
12	1	3.979960	0.037707	-1.495883
13	1	2.038170	-2.064324	0.558954
14	8	0.170301	-1.204127	0.694810
15	6	0.486801	2.241701	-0.425973
16	1	-0.572935	2.503369	-0.306256
17	1	0.727972	2.347584	-1.492084
18	7	0.761080	0.854749	-0.062503
19	6	1.342368	3.262900	0.371881
20	6	1.041487	3.145523	1.876752
21	1	-0.022869	3.313050	2.084280
22	1	1.310512	2.155306	2.260677
23	1	1.613028	3.891375	2.441656
24	6	0.951790	4.668301	-0.124342
25	1	1.531422	5.435730	0.401691
26	1	1.145089	4.779986	-1.198382
27	1	-0.111608	4.872706	0.051044
28	6	2.842930	3.031290	0.118738
29	1	3.079783	3.104242	-0.950294
30	1	3.439437	3.786047	0.644975
31	1	3.163780	2.045799	0.470672
32	6	-3.763271	0.028727	-1.214061
33	6	-4.195117	-1.161932	-0.564166
34	6	-3.260897	-2.111891	-0.173507
35	6	-2.408247	0.240283	-1.443494
36	1	-2.347571	-2.266588	-0.735080
37	1	-1.734180	-0.587604	-1.626526
38	1	-2.082200	1.186310	-1.866257
39	1	-3.572569	-2.963931	0.423950
40	6	-5.624373	-1.282359	-0.085366
41	1	-5.789205	-2.231525	0.430920
42	1	-5.897586	-0.469238	0.599771
43	1	-6.325540	-1.232496	-0.927472

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	6	-4.740375	1.160572	-1.435983
45	1	-5.565378	0.844122	-2.085981
46	1	-5.194273	1.500429	-0.495893
47	1	-4.252682	2.017853	-1.906989
48	16	5.315888	-2.340806	-0.960279
49	1	3.245122	-3.314796	0.624333

**Thermodynamic data for transition state of the third NI complex with thiourea
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.416283
Thermal correction to energy, Hartree	0.442605
Thermal correction to enthalpy, Hartree	0.443549
Thermal correction to Gibbs free energy, Hartree	0.356762
Sum of electronic and zero-point energies, Hartree	-1338.411987
Sum of electronic and thermal energies, Hartree	-1338.385664
Sum of electronic and thermal enthalpies, Hartree	-1338.384720
Sum of electronic and thermal Gibbs free energies, Hartree	-1338.471508

**Coordinates for the first NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.503687	2.701493	-0.460903
2	6	0.482959	3.558140	-0.301547
3	1	2.548965	2.939910	-0.598135
4	1	0.499655	4.638922	-0.277278
5	6	-0.756945	2.774527	-0.146980
6	8	-1.903451	3.114871	0.028402
7	6	0.968817	1.328979	-0.423914
8	7	-2.471780	-0.835248	-0.049716
9	6	-3.717990	-0.522778	0.509888
10	6	-2.064887	-2.078793	-0.553779
11	8	-2.774706	-3.076508	-0.603458
12	8	-4.622267	-1.328826	0.693094
13	7	-0.783809	-2.052823	-1.040876
14	1	-0.106377	-1.330320	-0.798348
15	1	-0.403423	-2.957287	-1.281938
16	7	-3.808711	0.793225	0.888931
17	1	-4.738505	1.092440	1.148361
18	1	-3.200420	1.514815	0.510460
19	1	-1.792938	-0.082683	-0.099929
20	8	-0.414896	1.435818	-0.230475
21	6	2.876694	-0.045807	-0.723885
22	1	3.439798	0.895407	-0.771392
23	1	2.985855	-0.545117	-1.694989
24	7	1.448040	0.166275	-0.527682
25	6	3.498923	-0.955284	0.371123
26	6	3.337462	-0.300424	1.754706
27	1	3.793650	0.697150	1.778359
28	1	2.281410	-0.197779	2.028151
29	1	3.824743	-0.909658	2.524714
30	6	4.996340	-1.099578	0.038986
31	1	5.490002	-1.740416	0.778519
32	1	5.144511	-1.551720	-0.949229
33	1	5.503444	-0.127063	0.046781
34	6	2.834160	-2.343498	0.363995
35	1	2.940597	-2.828324	-0.614468
36	1	3.303520	-2.992943	1.112184
37	1	1.766578	-2.280027	0.596942

**Thermodynamic data for the first NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.301869
Thermal correction to energy, Hartree	0.323098
Thermal correction to enthalpy, Hartree	0.324042
Thermal correction to Gibbs free energy, Hartree	0.248954
Sum of electronic and zero-point energies, Hartree	-949.678632
Sum of electronic and thermal energies, Hartree	-949.657402
Sum of electronic and thermal enthalpies, Hartree	-949.656458
Sum of electronic and thermal Gibbs free energies, Hartree	-949.731547

**Coordinates for the second NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.134299	1.074590	-0.482761
2	6	-0.182483	0.833468	-0.391096
3	1	1.628618	2.035334	-0.521092
4	1	-1.020026	1.520303	-0.334208
5	6	-0.365938	-0.630270	-0.372821
6	8	-1.386750	-1.288203	-0.299881
7	6	1.841533	-0.218665	-0.529259
8	7	-4.000611	0.030124	-0.003899
9	6	-4.208882	1.415260	0.026411
10	6	-4.912554	-0.990106	0.250395
11	8	-6.102328	-0.796635	0.523166
12	8	-3.249218	2.175454	-0.134028
13	7	-4.373423	-2.236136	0.131184
14	1	-3.370446	-2.369696	0.095059
15	1	-4.933211	-3.004802	0.471371
16	7	-5.485568	1.825249	0.202069
17	1	-5.638219	2.809405	0.365305
18	1	-6.188916	1.135977	0.452264
19	1	-3.032073	-0.239164	-0.172090
20	8	0.862084	-1.227044	-0.456327
21	6	4.120066	0.392385	-0.702118
22	1	3.775149	1.427698	-0.570754
23	1	4.537932	0.312463	-1.714847
24	7	3.043979	-0.583904	-0.620658
25	6	5.252185	0.099295	0.318179
26	6	4.699174	0.184721	1.752249
27	1	4.257897	1.169789	1.949988
28	1	3.927614	-0.573355	1.927368
29	1	5.500601	0.024157	2.482860
30	6	6.339428	1.171724	0.118612
31	1	7.170468	1.007480	0.814314
32	1	6.744256	1.143788	-0.900486
33	1	5.945833	2.179541	0.299415
34	6	5.849412	-1.296660	0.066009
35	1	6.270234	-1.368974	-0.944690
36	1	6.655436	-1.502556	0.780192
37	1	5.090453	-2.077749	0.172921

**Thermodynamic data for the second NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.301554
Thermal correction to energy, Hartree	0.322968
Thermal correction to enthalpy, Hartree	0.323912
Thermal correction to Gibbs free energy, Hartree	0.247506
Sum of electronic and zero-point energies, Hartree	-949.686256
Sum of electronic and thermal energies, Hartree	-949.664842
Sum of electronic and thermal enthalpies, Hartree	-949.663898
Sum of electronic and thermal Gibbs free energies, Hartree	-949.740304

**Coordinates for the third NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.706337	2.784960	-0.237015
2	6	0.665339	3.618590	-0.091002
3	1	2.756265	3.039530	-0.278913
4	1	0.662131	4.694576	0.015380
5	6	-0.568059	2.810983	-0.087812
6	8	-1.727796	3.142832	0.031212
7	6	1.191273	1.409068	-0.347296
8	7	-2.577548	-0.775005	-0.047270
9	6	-3.827845	-0.258354	0.297653
10	6	-2.242849	-2.110604	-0.342280
11	8	-1.104389	-2.376226	-0.726998
12	8	-4.837951	-0.964032	0.419735
13	7	-3.218427	-3.027930	-0.143653
14	1	-4.162333	-2.700361	0.042546
15	1	-3.047299	-3.959606	-0.491974
16	7	-3.843660	1.079738	0.517124
17	1	-4.753153	1.492582	0.666191
18	1	-3.077038	1.707036	0.282352
19	1	-1.790672	-0.141756	-0.153608
20	8	-0.212600	1.490260	-0.246933
21	6	3.135595	0.081751	-0.617358
22	1	3.707882	0.980507	-0.346703
23	1	3.347851	-0.137492	-1.672733
24	7	1.697064	0.269136	-0.511596
25	6	3.621651	-1.116391	0.239705
26	6	3.305212	-0.857841	1.723913
27	1	3.776064	0.069276	2.074745
28	1	2.225556	-0.773757	1.890649
29	1	3.679494	-1.679513	2.345658
30	6	5.145013	-1.233380	0.047918
31	1	5.539438	-2.076755	0.626496
32	1	5.402604	-1.399708	-1.005325
33	1	5.661890	-0.326039	0.384060
34	6	2.938399	-2.414194	-0.228541
35	1	3.187095	-2.632855	-1.274879
36	1	3.274415	-3.263059	0.378856
37	1	1.849297	-2.344384	-0.148478

**Thermodynamic data for the third NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.301479
Thermal correction to energy, Hartree	0.322736
Thermal correction to enthalpy, Hartree	0.323680
Thermal correction to Gibbs free energy, Hartree	0.248455
Sum of electronic and zero-point energies, Hartree	-949.684637
Sum of electronic and thermal energies, Hartree	-949.663381
Sum of electronic and thermal enthalpies, Hartree	-949.662436
Sum of electronic and thermal Gibbs free energies, Hartree	-949.737662

**Coordinates for transition state of the first NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.788290	0.113572	0.646449
2	6	-1.821228	-1.211275	1.114653
3	1	-2.384493	0.913841	1.059915
4	1	-2.469568	-1.595714	1.887550
5	6	-0.501428	-1.795011	0.897804
6	8	-0.026187	-2.872728	1.190576
7	6	-0.410169	0.364768	0.175831
8	7	3.249900	-1.244931	-0.294389
9	6	3.886624	-2.310525	0.354969
10	6	3.828092	-0.353509	-1.208903
11	8	4.978521	-0.431293	-1.625810
12	8	5.081767	-2.567806	0.263741
13	7	2.941460	0.600646	-1.637285
14	1	2.095157	0.844924	-1.117701
15	1	3.355071	1.341279	-2.186576
16	7	3.033873	-3.019501	1.160950
17	1	3.416825	-3.878640	1.529856
18	1	2.021181	-2.983613	1.061606
19	1	2.263094	-1.110276	-0.094647
20	8	0.272648	-0.861320	0.208926
21	6	-0.367687	2.685101	-0.286481
22	1	-1.418028	2.671768	0.034704
23	1	-0.353537	2.991848	-1.340857
24	7	0.253007	1.366784	-0.217821
25	6	0.394049	3.751612	0.545483
26	6	0.385017	3.362156	2.034806
27	1	-0.640172	3.264298	2.413974
28	1	0.900120	2.409667	2.201344
29	1	0.891346	4.127363	2.634910
30	6	-0.344015	5.090729	0.357815
31	1	0.149933	5.883943	0.930985
32	1	-0.354090	5.395483	-0.695984
33	1	-1.383680	5.027282	0.701708
34	6	1.844220	3.892528	0.049145
35	1	1.873768	4.168245	-1.012493
36	1	2.365841	4.675196	0.612754
37	1	2.402926	2.959534	0.172241
38	6	-4.080924	-0.412422	-0.966334
39	6	-4.110931	-1.768024	-0.531117
40	6	-2.931916	-2.493320	-0.453363
41	6	-2.867283	0.184346	-1.296131
42	1	-2.100635	-2.296747	-1.119165
43	1	-2.059921	-0.394593	-1.728727

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-2.849126	1.239195	-1.555113
45	1	-2.931841	-3.484148	-0.008172
46	6	-5.376956	-2.337898	0.068565
47	1	-5.230242	-3.371882	0.390952
48	1	-5.717828	-1.755418	0.934259
49	1	-6.196090	-2.326517	-0.660726
50	6	-5.319488	0.443709	-0.837994
51	1	-6.142617	0.032977	-1.435557
52	1	-5.678094	0.491034	0.198656
53	1	-5.133086	1.464639	-1.180520

**Thermodynamic data for transition state of the first NI complex with biuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.446118
Thermal correction to energy, Hartree	0.474728
Thermal correction to enthalpy, Hartree	0.475672
Thermal correction to Gibbs free energy, Hartree	0.385036
Sum of electronic and zero-point energies, Hartree	-1184.134352
Sum of electronic and thermal energies, Hartree	-1184.105742
Sum of electronic and thermal enthalpies, Hartree	-1184.104797
Sum of electronic and thermal Gibbs free energies, Hartree	-1184.195433

**Coordinates for transition state of the second NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.344728	0.452011	-0.980117
2	6	-0.051983	0.350833	-1.096534
3	1	1.965413	1.045814	-1.635634
4	6	-0.435667	-0.969840	-0.605694
5	8	-1.528675	-1.512015	-0.550402
6	6	1.820427	-0.856838	-0.481778
7	7	-4.335702	-0.846619	-0.122707
8	6	-4.984969	0.395541	-0.110464
9	6	-4.828488	-2.082324	0.293608
10	8	-5.986111	-2.257597	0.692984
11	8	-4.346918	1.413924	-0.392312
12	7	-3.921583	-3.091340	0.186065
13	1	-2.936417	-2.891666	0.047857
14	1	-4.172107	-3.967446	0.621254
15	7	-6.305923	0.379010	0.183792
16	1	-6.750116	1.269246	0.354049
17	1	-6.711557	-0.483946	0.535937
18	1	-3.358320	-0.798855	-0.408297
19	8	0.681989	-1.617873	-0.137310
20	6	4.164929	-0.709189	-0.695745
21	1	4.046365	0.383674	-0.658734
22	1	4.407157	-0.968840	-1.736675
23	7	2.940915	-1.417451	-0.340232
24	6	5.358412	-1.122117	0.200411
25	6	5.050442	-0.783963	1.670045
26	1	4.880195	0.292202	1.802693
27	1	4.155386	-1.312799	2.015651
28	1	5.886778	-1.071228	2.318491
29	6	6.593310	-0.329661	-0.266597
30	1	7.470802	-0.591834	0.336189
31	1	6.831531	-0.545597	-1.315639
32	1	6.434032	0.751792	-0.172308
33	6	5.628824	-2.630678	0.055593
34	1	5.879219	-2.887704	-0.981558
35	1	6.471214	-2.934325	0.688684
36	1	4.752053	-3.217372	0.346812
37	1	-0.674000	0.877461	-1.804615
38	6	-1.020800	1.555287	0.609673
39	6	-0.398586	2.776088	0.392669
40	1	-2.083499	1.446788	0.407474
41	6	1.017402	2.879452	0.487973
42	6	-1.205463	3.924329	-0.172887
43	6	1.777952	1.748590	0.773803

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	6	1.709267	4.146740	0.041178
45	1	-2.262341	3.657113	-0.251661
46	1	-1.128257	4.811787	0.467793
47	1	-0.852747	4.224241	-1.168204
48	1	1.388595	0.957936	1.403839
49	1	2.860997	1.829673	0.777936
50	1	1.491491	4.382759	-1.008976
51	1	1.371260	5.007276	0.631476
52	1	2.793735	4.067795	0.153053
53	1	-0.601528	0.823765	1.290183

**Thermodynamic data for transition state of the second NI complex with biuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.445943
Thermal correction to energy, Hartree	0.474708
Thermal correction to enthalpy, Hartree	0.475652
Thermal correction to Gibbs free energy, Hartree	0.383293
Sum of electronic and zero-point energies, Hartree	-1184.140172
Sum of electronic and thermal energies, Hartree	-1184.111407
Sum of electronic and thermal enthalpies, Hartree	-1184.110463
Sum of electronic and thermal Gibbs free energies, Hartree	-1184.202822

**Coordinates for transition state of the third NI complex with biuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.918812	0.014831	0.733910
2	6	-1.824685	-1.323813	1.148547
3	1	-2.605154	0.732235	1.161241
4	1	-2.455253	-1.814772	1.874293
5	6	-0.445229	-1.753639	0.950680
6	8	0.118183	-2.800338	1.212609
7	6	-0.558439	0.433437	0.327931
8	7	3.377054	-1.131400	-0.274472
9	6	3.939959	-2.243134	0.354157
10	6	4.002515	-0.218603	-1.144231
11	8	3.329757	0.661128	-1.681928
12	8	5.133040	-2.553397	0.235161
13	7	5.338687	-0.365575	-1.304051
14	1	5.787302	-1.193249	-0.921413
15	1	5.776576	0.180776	-2.030801
16	7	3.078530	-2.941119	1.137293
17	1	3.432582	-3.815298	1.499405
18	1	2.064785	-2.834531	1.092762
19	1	2.389315	-0.933085	-0.138306
20	8	0.254721	-0.721039	0.343072
21	6	-0.759925	2.758524	-0.046504
22	1	-1.687175	2.714816	0.544454
23	1	-1.051231	2.931279	-1.092648
24	7	-0.003558	1.515059	0.000670
25	6	0.087723	3.964503	0.430230
26	6	0.528511	3.746185	1.888874
27	1	-0.339043	3.623206	2.549952
28	1	1.154101	2.851807	1.982541
29	1	1.107027	4.604335	2.251213
30	6	-0.793940	5.223455	0.339635
31	1	-0.235933	6.109531	0.664533
32	1	-1.132231	5.399648	-0.689085
33	1	-1.682610	5.135688	0.977127
34	6	1.322278	4.130508	-0.474772
35	1	1.023990	4.342366	-1.509648
36	1	1.944889	4.964788	-0.129404
37	1	1.934051	3.223138	-0.481020
38	6	-4.086046	-0.654172	-0.975011
39	6	-4.004980	-2.028765	-0.611653
40	6	-2.767885	-2.646334	-0.523618
41	6	-2.921098	0.068781	-1.221339
42	1	-1.932563	-2.335629	-1.138545
43	1	-2.051378	-0.410704	-1.654934

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-2.995124	1.132042	-1.430977
45	1	-2.689257	-3.653945	-0.125472
46	6	-5.234855	-2.745534	-0.099754
47	1	-5.000934	-3.773642	0.188360
48	1	-5.674324	-2.239070	0.769237
49	1	-6.015218	-2.783008	-0.869797
50	6	-5.402499	0.077269	-0.853702
51	1	-6.163901	-0.376102	-1.500252
52	1	-5.798473	0.039717	0.169883
53	1	-5.300969	1.127077	-1.140368

**Thermodynamic data for transition state of the third NI complex with biuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.445537
Thermal correction to energy, Hartree	0.474291
Thermal correction to enthalpy, Hartree	0.475235
Thermal correction to Gibbs free energy, Hartree	0.383477
Sum of electronic and zero-point energies, Hartree	-1184.139200
Sum of electronic and thermal energies, Hartree	-1184.110446
Sum of electronic and thermal enthalpies, Hartree	-1184.109501
Sum of electronic and thermal Gibbs free energies, Hartree	-1184.201260

**Coordinates for the first NI complex with dithiobiuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	2.391816	2.510794	-0.606775
2	6	1.544286	3.549317	-0.533153
3	1	3.463257	2.543378	-0.745755
4	1	1.758600	4.607144	-0.595633
5	6	0.182195	3.020483	-0.338008
6	8	-0.886547	3.571683	-0.213470
7	6	1.615799	1.266053	-0.470166
8	7	-2.116782	-0.183139	-0.095393
9	6	-3.162745	0.336470	0.658860
10	6	-1.965080	-1.392374	-0.765045
11	7	-0.677653	-1.676386	-1.021176
12	1	0.119637	-1.111399	-0.712249
13	1	-0.483248	-2.475404	-1.608334
14	7	-3.093329	1.673255	0.775117
15	1	-3.739142	2.126039	1.406430
16	1	-2.397612	2.257342	0.310646
17	1	-1.310250	0.435804	-0.170191
18	8	0.275373	1.639220	-0.305017
19	6	3.232027	-0.461555	-0.644578
20	1	3.958538	0.352031	-0.766294
21	1	3.238000	-1.051351	-1.569844
22	7	1.869342	0.029899	-0.479523
23	6	3.682664	-1.376156	0.527066
24	6	3.664627	-0.587912	1.849055
25	1	4.299696	0.304849	1.789572
26	1	2.650263	-0.266361	2.110219
27	1	4.039313	-1.210706	2.669451
28	6	5.121651	-1.828865	0.214207
29	1	5.495893	-2.483430	1.009519
30	1	5.168596	-2.386002	-0.729348
31	1	5.802597	-0.972548	0.136656
32	6	2.767073	-2.608767	0.634903
33	1	2.765480	-3.183754	-0.299415
34	1	3.115881	-3.271518	1.435406
35	1	1.733899	-2.326180	0.861351
36	16	-4.359951	-0.548420	1.454477
37	16	-3.209233	-2.391924	-1.316705

**Thermodynamic data for the first NI complex with dithiobiuret optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.297838
Thermal correction to energy, Hartree	0.319363
Thermal correction to enthalpy, Hartree	0.320307
Thermal correction to Gibbs free energy, Hartree	0.245078
Sum of electronic and zero-point energies, Hartree	-1595.587226
Sum of electronic and thermal energies, Hartree	-1595.565701
Sum of electronic and thermal enthalpies, Hartree	-1595.564757
Sum of electronic and thermal Gibbs free energies, Hartree	-1595.639986

**Coordinates for the second NI complex with dithiobiuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.922955	1.335889	-0.422125
2	6	0.589252	1.258932	-0.296439
3	1	2.531536	2.227794	-0.474577
4	6	0.225610	-0.168152	-0.270925
5	8	-0.868302	-0.692251	-0.168886
6	6	2.461179	-0.035155	-0.484216
7	7	-3.713180	-0.032609	0.045743
8	6	-4.295138	1.225317	0.117837
9	6	-4.244276	-1.311914	0.050008
10	7	-3.309653	-2.266569	-0.043944
11	1	-2.316642	-2.056160	-0.107945
12	1	-3.605130	-3.232304	-0.048382
13	7	-5.615822	1.322372	0.220413
14	1	-6.028423	2.243401	0.270580
15	1	-6.200441	0.483648	0.244704
16	1	-2.693622	0.016952	-0.026211
17	8	1.362912	-0.913102	-0.384666
18	6	4.793804	0.281452	-0.716228
19	1	4.587606	1.351634	-0.574474
20	1	5.168879	0.152221	-1.740434
21	7	3.604307	-0.549207	-0.605207
22	6	5.906504	-0.159734	0.271606
23	6	5.409004	-0.008951	1.720638
24	1	5.104266	1.024152	1.930422
25	1	4.551315	-0.661886	1.917448
26	1	6.202951	-0.274130	2.428553
27	6	7.116983	0.763983	0.041210
28	1	7.937416	0.493687	0.715965
29	1	7.488700	0.684457	-0.987772
30	1	6.861416	1.814055	0.228820
31	6	6.311303	-1.620086	0.001869
32	1	6.688335	-1.742336	-1.021220
33	1	7.105743	-1.929714	0.691164
34	1	5.462118	-2.297852	0.132853
35	1	-0.147707	2.047585	-0.221510
36	16	-3.269509	2.582137	0.070522
37	16	-5.892855	-1.718998	0.158977

**Thermodynamic data for the second NI complex with dithiobiuret optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.297109
Thermal correction to energy, Hartree	0.318970
Thermal correction to enthalpy, Hartree	0.319914
Thermal correction to Gibbs free energy, Hartree	0.240816
Sum of electronic and zero-point energies, Hartree	-1595.596937
Sum of electronic and thermal energies, Hartree	-1595.575076
Sum of electronic and thermal enthalpies, Hartree	-1595.574132
Sum of electronic and thermal Gibbs free energies, Hartree	-1595.653230

**Coordinates for the third NI complex with dithiobiuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	2.259332	2.448386	-0.846652
2	6	1.294673	3.380758	-0.824299
3	1	3.299271	2.581234	-1.110347
4	1	1.357409	4.434181	-1.059409
5	6	0.045052	2.728295	-0.398416
6	8	-1.067589	3.185012	-0.233160
7	6	1.673606	1.158801	-0.439700
8	7	-2.572366	-0.333850	-0.127165
9	6	-3.473443	0.276493	0.733349
10	6	-2.592931	-1.551039	-0.801678
11	7	-3.615543	-2.375413	-0.606365
12	1	-4.359716	-2.137661	0.053670
13	1	-3.625669	-3.254817	-1.104043
14	7	-3.141789	1.534342	1.041098
15	1	-3.747630	2.039480	1.672896
16	1	-2.385243	2.055488	0.588519
17	1	-1.724023	0.190340	-0.331258
18	8	0.307040	1.396349	-0.182601
19	6	3.498613	-0.342900	-0.528158
20	1	4.117305	0.539401	-0.744194
21	1	3.515525	-0.982420	-1.420807
22	7	2.101955	-0.014394	-0.284245
23	6	4.127204	-1.131315	0.651656
24	6	4.102804	-0.270930	1.927921
25	1	4.638089	0.675387	1.779426
26	1	3.076238	-0.035655	2.230229
27	1	4.584232	-0.801658	2.757545
28	6	5.584963	-1.445462	0.266976
29	1	6.077940	-2.009638	1.067090
30	1	5.634788	-2.047992	-0.648315
31	1	6.162229	-0.527788	0.099730
32	6	3.358788	-2.444027	0.885779
33	1	3.384271	-3.081116	-0.007054
34	1	3.808173	-3.006953	1.712363
35	1	2.310560	-2.251070	1.133695
36	16	-4.867622	-0.443037	1.393268
37	16	-1.302198	-1.903638	-1.847491

**Thermodynamic data for the third NI complex with dithiobiuret optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.297115
Thermal correction to energy, Hartree	0.318864
Thermal correction to enthalpy, Hartree	0.319808
Thermal correction to Gibbs free energy, Hartree	0.242080
Sum of electronic and zero-point energies, Hartree	-1595.594787
Sum of electronic and thermal energies, Hartree	-1595.573038
Sum of electronic and thermal enthalpies, Hartree	-1595.572094
Sum of electronic and thermal Gibbs free energies, Hartree	-1595.649823

Coordinates for transition state of the first NI complex with dithiobiuret
optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	2.225243	-0.027242	-0.660326
2	6	2.122891	-1.353068	-1.118084
3	1	2.908242	0.699532	-1.075751
4	1	2.748378	-1.820377	-1.863294
5	6	0.750219	-1.793047	-0.918239
6	8	0.161919	-2.816584	-1.203847
7	6	0.870894	0.376772	-0.226184
8	7	-2.893816	-0.813682	0.170292
9	6	-3.608983	-1.651496	-0.675338
10	6	-3.291611	0.003713	1.223310
11	7	-2.385374	0.954667	1.497438
12	1	-1.529822	1.124620	0.951803
13	1	-2.536340	1.518497	2.322340
14	7	-2.824765	-2.556707	-1.282926
15	1	-3.239770	-3.124412	-2.008255
16	1	-1.821053	-2.659692	-1.115289
17	1	-1.888825	-0.795376	-0.007626
18	8	0.064507	-0.770211	-0.255817
19	6	1.067759	2.694931	0.209233
20	1	2.110199	2.565127	-0.110569
21	1	1.085961	3.001288	1.263553
22	7	0.309730	1.449151	0.140485
23	6	0.428589	3.837421	-0.623970
24	6	0.363589	3.436078	-2.108563
25	1	1.360656	3.199258	-2.500847
26	1	-0.276429	2.559294	-2.256476
27	1	-0.046105	4.256304	-2.709671
28	6	1.330517	5.076086	-0.463133
29	1	0.924023	5.921740	-1.029866
30	1	1.405453	5.381717	0.587713
31	1	2.345074	4.882231	-0.832550
32	6	-0.983868	4.162556	-0.105492
33	1	-0.960305	4.449407	0.953296
34	1	-1.413402	4.999267	-0.669091
35	1	-1.659196	3.307473	-0.210218
36	6	4.404238	-0.751333	1.007853
37	6	4.320478	-2.114244	0.601233
38	6	3.084307	-2.732750	0.513001
39	6	3.241255	-0.038192	1.290631
40	1	2.255371	-2.439543	1.144935
41	1	2.376943	-0.533179	1.717731
42	1	3.316343	1.017637	1.534702
43	1	3.001571	-3.727264	0.084211

Center Number	Atomic Number	Atomic Type	Coordinates, Å		
			X	Y	Z
44	6	0	5.544482	-2.810947	0.050042
45	1	0	5.309892	-3.831061	-0.264280
46	1	0	5.967236	-2.276696	-0.810405
47	1	0	6.336740	-2.866804	0.806486
48	6	0	5.718453	-0.015338	0.897157
49	1	0	6.485788	-0.489796	1.521052
50	1	0	6.103635	-0.020265	-0.131076
51	1	0	5.619544	1.024422	1.218747
52	16	0	-5.257933	-1.545914	-1.029295
53	16	0	-4.684090	-0.182985	2.162433

**Thermodynamic data for transition state of the first NI complex with dithiobiuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.441483
Thermal correction to energy, Hartree	0.470625
Thermal correction to enthalpy, Hartree	0.471570
Thermal correction to Gibbs free energy, Hartree	0.379231
Sum of electronic and zero-point energies, Hartree	-1830.044411
Sum of electronic and thermal energies, Hartree	-1830.015269
Sum of electronic and thermal enthalpies, Hartree	-1830.014325
Sum of electronic and thermal Gibbs free energies, Hartree	-1830.106663

Coordinates for transition state of the second NI complex with dithiobiuret
optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.852399	0.619600	-0.924104
2	6	0.454337	0.712318	-1.034952
3	1	2.544034	1.188937	-1.528570
4	6	-0.098458	-0.584086	-0.666965
5	8	-1.255427	-0.982225	-0.648087
6	6	2.151246	-0.786660	-0.568886
7	7	-4.114955	-0.678244	-0.147772
8	6	-4.929969	0.426275	-0.350638
9	6	-4.363188	-1.945254	0.357962
10	7	-3.269563	-2.714892	0.394305
11	1	-2.357190	-2.377008	0.084999
12	1	-3.354711	-3.656839	0.748488
13	7	-6.216546	0.349658	-0.029214
14	1	-6.799923	1.160456	-0.181885
15	1	-6.606864	-0.511961	0.359812
16	1	-3.147507	-0.501503	-0.429287
17	8	0.920449	-1.418143	-0.280561
18	6	4.494602	-0.943320	-0.811030
19	1	4.523057	0.151082	-0.705697
20	1	4.706533	-1.168199	-1.866398
21	7	3.184738	-1.504335	-0.503173
22	6	5.617047	-1.567933	0.054657
23	6	5.357145	-1.274123	1.543115
24	1	5.340537	-0.194090	1.738096
25	1	4.396803	-1.691863	1.865133
26	1	6.144301	-1.712883	2.167840
27	6	6.950362	-0.928714	-0.375081
28	1	7.781029	-1.337969	0.211764
29	1	7.161430	-1.122463	-1.434245
30	1	6.939813	0.158283	-0.226683
31	6	5.676805	-3.088980	-0.174635
32	1	5.881455	-3.320989	-1.227531
33	1	6.474551	-3.538383	0.428886
34	1	4.730393	-3.565309	0.098998
35	1	-0.097013	1.393113	-1.665504
36	6	-0.341737	1.868603	0.824250
37	6	0.449023	3.001986	0.721883
38	1	-1.410083	1.929020	0.634703
39	6	1.866317	2.886371	0.793373
40	6	-0.179516	4.313115	0.304439
41	6	2.454786	1.631563	0.936671
42	6	2.734015	4.079640	0.467542
43	1	-1.267963	4.228816	0.250573

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	0.059986	5.108232	1.021170
45	1	0.185279	4.651063	-0.674206
46	1	1.960259	0.844530	1.493623
47	1	3.538188	1.556931	0.928865
48	1	2.541343	4.460629	-0.544206
49	1	2.535212	4.909124	1.157219
50	1	3.795616	3.829870	0.539617
51	1	-0.029771	1.010654	1.406917
52	16	-4.224005	1.828211	-1.007504
53	16	-5.866369	-2.538588	0.894508

**Thermodynamic data for transition state of the first NI complex with dithiobiuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.440902
Thermal correction to energy, Hartree	0.470337
Thermal correction to enthalpy, Hartree	0.471281
Thermal correction to Gibbs free energy, Hartree	0.375292
Sum of electronic and zero-point energies, Hartree	-1830.051534
Sum of electronic and thermal energies, Hartree	-1830.022100
Sum of electronic and thermal enthalpies, Hartree	-1830.021155
Sum of electronic and thermal Gibbs free energies, Hartree	-1830.117144

Coordinates for transition state of the third NI complex with dithiobiuret
optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	2.176766	-0.236137	-0.801282
2	6	1.778844	-1.451841	-1.383387
3	1	3.067176	0.301923	-1.094716
4	1	2.341927	-2.040286	-2.091511
5	6	0.327730	-1.506918	-1.350262
6	8	-0.465214	-2.330209	-1.776024
7	6	0.934181	0.504884	-0.473822
8	7	-3.172422	-0.583046	0.274238
9	6	-3.960091	-0.995765	-0.791469
10	6	-3.486983	-0.150850	1.557901
11	7	-4.764384	-0.022778	1.899067
12	1	-5.507356	-0.200404	1.219060
13	1	-4.981925	0.284296	2.836845
14	7	-3.255634	-1.516681	-1.800474
15	1	-3.767113	-1.827609	-2.614941
16	1	-2.257250	-1.751965	-1.747649
17	1	-2.165287	-0.593830	0.114578
18	8	-0.143829	-0.381988	-0.687717
19	6	1.703609	2.642718	0.167811
20	1	2.685556	2.319808	-0.208640
21	1	1.794103	2.747691	1.258182
22	7	0.650419	1.667967	-0.083795
23	6	1.368107	4.033335	-0.430037
24	6	1.229029	3.924001	-1.959151
25	1	2.153932	3.549122	-2.415773
26	1	0.415832	3.243207	-2.233755
27	1	1.012205	4.904933	-2.398631
28	6	2.530679	4.981550	-0.082605
29	1	2.340533	5.985342	-0.480239
30	1	2.661187	5.070605	1.003114
31	1	3.477345	4.626784	-0.508833
32	6	0.061591	4.572906	0.178763
33	1	0.148656	4.679815	1.267393
34	1	-0.177293	5.559069	-0.237044
35	1	-0.776975	3.901208	-0.028554
36	6	3.877243	-1.601139	0.992180
37	6	3.491507	-2.876936	0.487969
38	6	2.157811	-3.145027	0.236572
39	6	2.913087	-0.615565	1.202025
40	1	1.362196	-2.663462	0.790621
41	1	1.910225	-0.881867	1.515259
42	1	3.233438	0.368604	1.532228
43	1	1.871101	-4.062013	-0.270167

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	6	4.549684	-3.849788	0.015734
45	1	4.097062	-4.760838	-0.384090
46	1	5.187401	-3.415039	-0.764438
47	1	5.212650	-4.139209	0.840230
48	6	5.340544	-1.233955	1.062714
49	1	5.882770	-1.913652	1.731679
50	1	5.828751	-1.306229	0.081641
51	1	5.476520	-0.215697	1.435650
52	16	-5.655125	-0.859318	-0.892469
53	16	-2.208681	0.180331	2.627547

**Thermodynamic data for transition state of the third NI complex with dithiobiuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.440959
Thermal correction to energy, Hartree	0.470270
Thermal correction to enthalpy, Hartree	0.471214
Thermal correction to Gibbs free energy, Hartree	0.377123
Sum of electronic and zero-point energies, Hartree	-1830.050241
Sum of electronic and thermal energies, Hartree	-1830.020930
Sum of electronic and thermal enthalpies, Hartree	-1830.019986
Sum of electronic and thermal Gibbs free energies, Hartree	-1830.114077

**Coordinates for the first NI complex with Shreiner's thiourea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	2.513457	-4.243635	-1.312258
2	6	1.335414	-3.860996	-1.829575
3	1	3.050253	-5.162672	-1.501793
4	6	1.013476	-2.533556	-1.279799
5	8	0.061695	-1.805301	-1.495478
6	6	2.987420	-3.185963	-0.402472
7	7	-2.130350	-0.042288	-0.391515
8	6	-1.412251	1.053709	0.011104
9	7	-0.106461	0.960302	-0.386706
10	1	0.169203	0.060649	-0.785756
11	1	-1.588108	-0.804411	-0.793721
12	8	2.014050	-2.165047	-0.424683
13	6	5.046313	-4.013185	0.415111
14	1	4.957173	-4.789805	-0.357394
15	1	4.940385	-4.506708	1.390782
16	7	3.990315	-3.014347	0.338233
17	6	6.458078	-3.374811	0.339391
18	6	6.616638	-2.603300	-0.983627
19	1	6.416020	-3.248882	-1.848117
20	1	5.934512	-1.747596	-1.029380
21	1	7.639644	-2.221214	-1.082184
22	6	7.481129	-4.524492	0.396453
23	1	8.502623	-4.128511	0.361809
24	1	7.377674	-5.104639	1.321731
25	1	7.359854	-5.212085	-0.449628
26	6	6.679619	-2.424644	1.529818
27	1	6.585262	-2.958668	2.483738
28	1	7.686228	-1.991522	1.487855
29	1	5.957275	-1.603428	1.525048
30	1	0.695465	-4.379554	-2.529857
31	16	-2.047022	2.324155	0.927823
32	6	0.964317	1.855240	-0.178345
33	6	2.225642	1.301430	0.067251
34	6	0.833067	3.245852	-0.294237
35	6	3.340287	2.130813	0.202151
36	1	2.335348	0.224637	0.150197
37	6	1.954259	4.058408	-0.136396
38	1	-0.129536	3.682343	-0.518500
39	6	3.216922	3.514633	0.111527
40	1	4.082986	4.155308	0.220005
41	6	1.792403	5.554204	-0.200614
42	6	4.681688	1.486881	0.426807
43	9	4.648509	0.624161	1.472031

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	9	5.072254	0.765055	-0.653256
45	9	5.653314	2.386096	0.677579
46	9	2.905733	6.162296	-0.667033
47	9	0.766610	5.919702	-1.000691
48	9	1.542290	6.082860	1.021583
49	6	-3.487588	-0.357650	-0.166311
50	6	-4.518725	0.580835	-0.285918
51	6	-3.800637	-1.696148	0.103589
52	6	-5.842013	0.176381	-0.104400
53	1	-4.290800	1.607964	-0.532736
54	6	-5.128797	-2.085776	0.264752
55	1	-3.005663	-2.429847	0.183306
56	6	-6.161702	-1.152642	0.171446
57	1	-7.193831	-1.458344	0.293491
58	6	-6.935992	1.208774	-0.179428
59	6	-5.452506	-3.516415	0.604760
60	9	-4.487147	-4.367344	0.194369
61	9	-5.590635	-3.693355	1.940631
62	9	-6.613168	-3.915358	0.038620
63	9	-7.122355	1.825539	1.012262
64	9	-6.653971	2.178287	-1.078159
65	9	-8.122502	0.665832	-0.528773

**Thermodynamic data for the first NI complex with Schreiner's thiourea optimized
at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.452395
Thermal correction to energy, Hartree	0.494819
Thermal correction to enthalpy, Hartree	0.495763
Thermal correction to Gibbs free energy, Hartree	0.366414
Sum of electronic and zero-point energies, Hartree	-2914.014129
Sum of electronic and thermal energies, Hartree	-2913.971705
Sum of electronic and thermal enthalpies, Hartree	-2913.970761
Sum of electronic and thermal Gibbs free energies, Hartree	-2914.100110

**Coordinates for the second NI complex with Shreiner's thiourea optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.862626	-3.991396	2.129966
2	6	0.633881	-3.818043	2.642376
3	1	2.589681	-4.744249	2.400687
4	1	0.131872	-4.382667	3.415699
5	6	0.015064	-2.669152	1.960976
6	8	-1.071074	-2.146976	2.102437
7	6	2.085689	-2.971314	1.090852
8	7	0.381233	0.795410	0.297968
9	6	-0.899913	1.094316	-0.096504
10	7	-1.798839	0.181762	0.377372
11	1	-1.432959	-0.587393	0.946120
12	1	0.553719	-0.160226	0.603223
13	8	0.914762	-2.187694	1.036145
14	6	4.270954	-3.412734	0.288432
15	1	4.335852	-4.156646	1.094306
16	1	5.058417	-2.668846	0.456252
17	7	3.017598	-2.672735	0.298687
18	6	4.539926	-4.113187	-1.073067
19	6	3.485662	-5.206809	-1.320762
20	1	3.487223	-5.951307	-0.514789
21	1	2.477138	-4.784091	-1.392421
22	1	3.693670	-5.731749	-2.260379
23	6	5.936780	-4.755955	-0.978416
24	1	6.179685	-5.277944	-1.911045
25	1	6.711971	-3.999926	-0.804340
26	1	5.986778	-5.487364	-0.162502
27	6	4.517003	-3.090760	-2.223164
28	1	5.235567	-2.281531	-2.052571
29	1	4.775640	-3.580643	-3.169417
30	1	3.526147	-2.639166	-2.335293
31	16	-1.291728	2.401537	-1.095517
32	6	-3.179316	0.053816	0.100480
33	6	-3.685922	-1.246435	-0.029509
34	6	-4.054646	1.143737	0.032660
35	6	-5.047781	-1.448747	-0.246727
36	1	-3.011980	-2.093582	0.036482
37	6	-5.412474	0.922700	-0.203142
38	1	-3.680329	2.147908	0.170499
39	6	-5.922188	-0.366805	-0.347656
40	1	-6.977844	-0.525670	-0.528561
41	6	-5.582895	-2.853728	-0.322813
42	6	-6.326676	2.111897	-0.336199
43	9	-5.869588	-3.345885	0.906597

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	9	-4.693115	-3.703074	-0.883042
45	9	-6.721076	-2.922768	-1.046991
46	9	-6.006431	3.091077	0.539719
47	9	-6.256816	2.660630	-1.572793
48	9	-7.619921	1.785709	-0.123762
49	6	1.552311	1.572387	0.166784
50	6	1.562754	2.957430	0.384352
51	6	2.754523	0.906548	-0.096011
52	6	2.762844	3.659234	0.304394
53	1	0.645471	3.474679	0.627808
54	6	3.951153	1.626314	-0.151421
55	1	2.759490	-0.170338	-0.245915
56	6	3.967973	3.005395	0.036109
57	1	4.897726	3.557869	-0.011101
58	6	5.225941	0.875010	-0.426480
59	6	2.752692	5.154851	0.477992
60	9	2.558674	5.794091	-0.700860
61	9	1.766865	5.561925	1.308086
62	9	3.920402	5.612691	0.981286
63	9	6.311508	1.674130	-0.413880
64	9	5.193085	0.262847	-1.635218
65	9	5.436356	-0.101021	0.491712

**Thermodynamic data for the second NI complex with Schreiner's thiourea
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.452346
Thermal correction to energy, Hartree	0.494728
Thermal correction to enthalpy, Hartree	0.495672
Thermal correction to Gibbs free energy, Hartree	0.366685
Sum of electronic and zero-point energies, Hartree	-2914.014034
Sum of electronic and thermal energies, Hartree	-2913.971652
Sum of electronic and thermal enthalpies, Hartree	-2913.970707
Sum of electronic and thermal Gibbs free energies, Hartree	-2914.099700

**Coordinates for transition state of the first NI complex with Schreiner's thiourea
optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-2.27253	-3.45404	-0.30243
2	6	-1.03215	-3.67527	-0.92828
3	1	-2.86276	-4.24092	0.14586
4	1	-0.57887	-4.63224	-1.13641
5	6	-0.22239	-2.48303	-0.75253
6	8	0.91825	-2.20756	-1.08604
7	6	-2.18356	-2.12791	0.35470
8	7	0.07834	1.31665	-0.17733
9	6	1.41922	1.48513	0.06449
10	7	2.12158	0.33962	-0.18282
11	1	1.58798	-0.47760	-0.50121
12	1	-0.26451	0.35716	-0.20474
13	8	-0.98297	-1.53174	-0.08421
14	6	-4.14818	-1.97576	1.66513
15	1	-4.39499	-2.96924	1.26426
16	1	-4.92353	-1.27910	1.32230
17	7	-2.88164	-1.46039	1.16361
18	6	-4.19498	-2.03560	3.21553
19	6	-3.16824	-3.05931	3.73273
20	1	-3.37126	-4.06208	3.33588
21	1	-2.14845	-2.78046	3.44444
22	1	-3.20227	-3.11976	4.82707
23	6	-5.61440	-2.48158	3.61346
24	1	-5.70106	-2.55962	4.70351
25	1	-6.36794	-1.76343	3.26743
26	1	-5.85999	-3.46207	3.18698
27	6	-3.90009	-0.65039	3.81802
28	1	-4.59075	0.10814	3.43245
29	1	-4.00324	-0.68053	4.90946
30	1	-2.88228	-0.32485	3.58141
31	6	-3.64216	-4.09759	-2.68472
32	6	-2.42965	-4.30538	-3.40419
33	6	-1.38357	-3.41091	-3.26530
34	6	-3.75844	-3.01188	-1.81662
35	1	-1.54969	-2.36789	-3.02820
36	1	-3.25558	-2.07641	-2.03329
37	1	-4.67053	-2.90041	-1.23705
38	1	-0.41384	-3.63152	-3.70198
39	6	-2.20373	-5.61014	-4.13574
40	1	-1.21197	-5.63800	-4.59429
41	1	-2.29567	-6.47584	-3.46755
42	1	-2.94519	-5.74629	-4.93250
43	6	-4.69768	-5.17739	-2.66766

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-5.06325	-5.38337	-3.68117
45	1	-4.30454	-6.12599	-2.27844
46	1	-5.55343	-4.88630	-2.05351
47	16	2.08816	2.92422	0.65328
48	6	3.48145	0.04121	0.05475
49	6	3.78269	-1.27685	0.42872
50	6	4.52507	0.95492	-0.13627
51	6	5.10545	-1.66388	0.63058
52	1	2.98004	-1.99390	0.55742
53	6	5.84308	0.55275	0.08695
54	1	4.31057	1.96207	-0.46130
55	6	6.14889	-0.75108	0.47411
56	1	7.17599	-1.05164	0.64283
57	6	5.41754	-3.09690	0.96945
58	6	6.94884	1.56554	-0.05126
59	9	5.68497	-3.82526	-0.14150
60	9	4.38819	-3.70680	1.59713
61	9	6.50048	-3.20014	1.77155
62	9	6.66626	2.50021	-0.98567
63	9	7.16654	2.22898	1.11005
64	9	8.12180	0.99004	-0.39674
65	6	-0.94680	2.28629	-0.20090
66	6	-0.77399	3.55021	-0.78240
67	6	-2.20517	1.91748	0.28914
68	6	-1.84740	4.43587	-0.83851
69	1	0.18392	3.82900	-1.19837
70	6	-3.27394	2.81364	0.20523
71	1	-2.35225	0.93168	0.72488
72	6	-3.10603	4.08041	-0.34774
73	1	-3.93812	4.77009	-0.41184
74	6	-4.61165	2.39734	0.75617
75	6	-1.63932	5.81264	-1.41096
76	9	-1.28473	6.70423	-0.45402
77	9	-0.66179	5.83307	-2.34367
78	9	-2.76189	6.29225	-1.99162
79	9	-5.60184	3.23759	0.39032
80	9	-4.60611	2.35943	2.11211
81	9	-4.96195	1.15701	0.33862

**Thermodynamic data for transition state of the first NI complex with dithiobiuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.595980
Thermal correction to energy, Hartree	0.646122
Thermal correction to enthalpy, Hartree	0.647067
Thermal correction to Gibbs free energy, Hartree	0.499739
Sum of electronic and zero-point energies, Hartree	-3148.470269
Sum of electronic and thermal energies, Hartree	-3148.420126
Sum of electronic and thermal enthalpies, Hartree	-3148.419182
Sum of electronic and thermal Gibbs free energies, Hartree	-3148.566510

**Coordinates for transition state of the second NI complex with Schreiner's
thiourea optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-2.79721	-3.27327	-0.02341
2	6	-1.53252	-3.25386	0.59315
3	1	-3.19195	-4.12830	-0.55427
4	6	-1.04446	-1.88547	0.55299
5	8	0.00092	-1.38866	0.95361
6	6	-3.02684	-1.90569	-0.54716
7	7	2.44760	0.08650	0.20872
8	6	1.96135	1.35298	0.01328
9	7	0.65520	1.44669	0.40945
10	1	0.20505	0.55998	0.65394
11	1	1.75653	-0.61734	0.46750
12	8	-2.00302	-1.08493	-0.02568
13	6	-4.93346	-2.13087	-1.92186
14	1	-5.20872	-3.00533	-1.31422
15	1	-4.57221	-2.51450	-2.88699
16	7	-3.85129	-1.35732	-1.32461
17	6	-6.19457	-1.26992	-2.17786
18	6	-6.71276	-0.68333	-0.85201
19	1	-6.94971	-1.47619	-0.13066
20	1	-5.97126	-0.01765	-0.39805
21	1	-7.62843	-0.10351	-1.02045
22	6	-7.26695	-2.18750	-2.79367
23	1	-8.18274	-1.62263	-3.00351
24	1	-6.92131	-2.62721	-3.73767
25	1	-7.52868	-3.00888	-2.11493
26	6	-5.86673	-0.12838	-3.15742
27	1	-5.49748	-0.52237	-4.11286
28	1	-6.76412	0.46684	-3.36576
29	1	-5.10470	0.53987	-2.74621
30	1	-0.85520	-4.08719	0.70033
31	6	-1.88371	-3.34284	2.92917
32	6	-2.69017	-4.46721	2.96335
33	1	-0.87829	-3.37900	3.33848
34	6	-3.93512	-4.46800	2.27155
35	6	-2.14811	-5.75718	3.53839
36	6	-4.31871	-3.35133	1.52882
37	6	-4.71777	-5.75250	2.13577
38	1	-1.16603	-5.60406	3.99314
39	1	-2.81727	-6.15351	4.31183
40	1	-2.05229	-6.53825	2.77337
41	1	-4.03481	-2.35335	1.84155
42	1	-5.24915	-3.39225	0.97003
43	1	-4.12744	-6.54105	1.65047

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-5.00772	-6.14057	3.12001
45	1	-5.62890	-5.60156	1.55157
46	1	-2.29563	-2.34743	2.82205
47	16	2.84564	2.61648	-0.68177
48	6	-0.21903	2.55347	0.34945
49	6	-1.55135	2.30476	0.00114
50	6	0.16966	3.85263	0.70395
51	6	-2.47912	3.34781	-0.00509
52	1	-1.86125	1.29700	-0.25633
53	6	-0.76729	4.88418	0.67396
54	1	1.18684	4.04813	1.01185
55	6	-2.09736	4.64674	0.31960
56	1	-2.81979	5.45303	0.31135
57	6	-0.32563	6.28694	0.99675
58	6	-3.89863	3.03591	-0.39587
59	9	-3.98362	2.64895	-1.69316
60	9	-4.40431	2.01739	0.34209
61	9	-4.72217	4.09177	-0.24113
62	9	-1.33081	7.02604	1.51640
63	9	0.69197	6.30625	1.88588
64	9	0.10917	6.94090	-0.10758
65	6	3.72518	-0.43704	-0.07979
66	6	4.91282	0.25725	0.18567
67	6	3.78859	-1.74550	-0.57349
68	6	6.13914	-0.35219	-0.07498
69	1	4.87595	1.25295	0.60336
70	6	5.02499	-2.34513	-0.81472
71	1	2.87139	-2.29325	-0.76503
72	6	6.21073	-1.65267	-0.57734
73	1	7.16944	-2.12132	-0.76266
74	6	7.41126	0.41938	0.15814
75	6	5.06695	-3.73262	-1.39757
76	9	4.06897	-4.50951	-0.91957
77	9	4.93134	-3.71235	-2.74534
78	9	6.23271	-4.35972	-1.13030
79	9	7.81178	1.07033	-0.96061
80	9	7.27052	1.35364	1.12377
81	9	8.43076	-0.38975	0.52303

**Thermodynamic data for transition state of the second NI complex with Shreiner's
thiourea optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.596260
Thermal correction to energy, Hartree	0.646223
Thermal correction to enthalpy, Hartree	0.647168
Thermal correction to Gibbs free energy, Hartree	0.501646
Sum of electronic and zero-point energies, Hartree	-3148.469329
Sum of electronic and thermal energies, Hartree	-3148.419366
Sum of electronic and thermal enthalpies, Hartree	-3148.418422
Sum of electronic and thermal Gibbs free energies, Hartree	-3148.563943

**Coordinates for the first NI complex with Shreiner's dithiobiuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-0.876678	3.619137	2.085274
2	6	0.272484	3.311293	2.708314
3	1	-1.544297	4.440930	2.303205
4	1	0.751675	3.813115	3.537343
5	6	0.836019	2.111572	2.066158
6	8	1.844704	1.477252	2.282726
7	6	-1.107305	2.634147	1.014193
8	7	0.457136	-0.885846	-0.267946
9	6	1.761551	-1.191834	-0.672097
10	6	-0.714791	-1.627266	-0.365874
11	7	-1.799993	-0.801707	-0.278127
12	1	-1.645484	0.200906	-0.403411
13	7	2.662332	-0.589253	0.155284
14	1	2.281833	-0.040068	0.929724
15	1	0.345910	0.017955	0.190618
16	8	-0.026370	1.738489	1.053273
17	6	-3.149751	3.304822	0.016119
18	1	-3.220514	4.021863	0.844198
19	1	-4.035630	2.661481	0.063096
20	7	-1.992758	2.423860	0.140385
21	6	-3.178563	4.086575	-1.329785
22	6	-1.988156	5.059247	-1.400958
23	1	-1.994866	5.761386	-0.558138
24	1	-1.030461	4.526602	-1.394111
25	1	-2.033265	5.647944	-2.324401
26	6	-4.500688	4.877962	-1.351285
27	1	-4.586314	5.450328	-2.281992
28	1	-5.364033	4.204868	-1.287310
29	1	-4.557637	5.586119	-0.515754
30	6	-3.138639	3.125146	-2.531726
31	1	-4.015588	2.467513	-2.547286
32	1	-3.141924	3.694326	-3.468599
33	1	-2.237964	2.502609	-2.520754
34	16	2.125282	-2.067733	-2.049664
35	16	-0.791469	-3.294507	-0.501856
36	6	-3.162611	-1.131995	-0.099421
37	6	-4.097174	-0.319664	-0.746944
38	6	-3.606485	-2.150338	0.753285
39	6	-5.462465	-0.506223	-0.530377
40	1	-3.751102	0.460075	-1.415284
41	6	-4.975306	-2.344531	0.932839
42	1	-2.894566	-2.771716	1.277967
43	6	-5.915907	-1.525215	0.303362

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-6.975875	-1.675317	0.466478
45	6	4.067174	-0.471772	0.031587
46	6	4.649029	0.713865	0.500530
47	6	4.884579	-1.496158	-0.460516
48	6	6.032219	0.876718	0.457424
49	1	4.019441	1.502811	0.896922
50	6	6.266355	-1.308112	-0.508316
51	1	4.449368	-2.427736	-0.789806
52	6	6.853191	-0.126996	-0.056105
53	1	7.927469	0.006176	-0.095912
54	6	-6.428328	0.456392	-1.166893
55	6	-5.448613	-3.483670	1.797751
56	6	6.648150	2.128561	1.023802
57	6	7.135757	-2.386510	-1.100127
58	9	-5.624650	-4.616184	1.076340
59	9	-6.632189	-3.208841	2.388794
60	9	-4.565221	-3.777257	2.776666
61	9	-7.692833	-0.005615	-1.167756
62	9	-6.440644	1.648320	-0.510758
63	9	-6.091550	0.733371	-2.448241
64	9	6.897213	2.005132	2.349479
65	9	5.839193	3.201027	0.877472
66	9	7.825230	2.423322	0.430717
67	9	6.595581	-3.614876	-0.945466
68	9	7.320965	-2.204189	-2.429520
69	9	8.363221	-2.408938	-0.535383

**Thermodynamic data for the first NI complex with Shreiner's dithiobiuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.477533
Thermal correction to energy, Hartree	0.522980
Thermal correction to enthalpy, Hartree	0.523924
Thermal correction to Gibbs free energy, Hartree	0.388896
Sum of electronic and zero-point energies, Hartree	-3405.641589
Sum of electronic and thermal energies, Hartree	-3405.596142
Sum of electronic and thermal enthalpies, Hartree	-3405.595197
Sum of electronic and thermal Gibbs free energies, Hartree	-3405.730226

**Coordinates for the second NI complex with Shreiner's dithiobiuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	3.838919	-4.383389	-0.925042
2	6	2.726906	-4.116909	-1.628464
3	1	4.438065	-5.282785	-0.952713
4	6	2.272316	-2.767801	-1.254154
5	8	1.325296	-2.117410	-1.660357
6	6	4.134083	-3.224480	-0.064566
7	7	-1.096908	-0.493676	-0.776620
8	6	-2.411221	-0.953153	-0.663776
9	6	-0.458421	0.694643	-0.450753
10	7	0.861618	0.631784	-0.760022
11	1	1.212679	-0.281942	-1.063129
12	7	-3.307699	-0.097279	-0.145544
13	1	-2.908280	0.793297	0.190415
14	1	-0.498675	-1.222307	-1.164922
15	8	3.128201	-2.267261	-0.314608
16	6	6.090790	-3.855910	1.104709
17	1	6.155043	-4.695586	0.398577
18	1	5.860887	-4.275457	2.093591
19	7	5.013192	-2.930462	0.786388
20	6	7.466160	-3.142914	1.182184
21	6	7.789525	-2.475086	-0.166836
22	1	7.761861	-3.202185	-0.988370
23	1	7.077770	-1.674104	-0.393638
24	1	8.793413	-2.034847	-0.143904
25	6	8.521430	-4.219904	1.495761
26	1	9.516451	-3.766971	1.574695
27	1	8.306655	-4.724684	2.445785
28	1	8.562139	-4.982660	0.708490
29	6	7.456990	-2.086165	2.301496
30	1	7.239533	-2.544219	3.274685
31	1	8.437193	-1.599597	2.373341
32	1	6.707769	-1.311809	2.113799
33	1	2.213292	-4.731808	-2.354315
34	16	-2.702823	-2.538858	-1.170557
35	16	-1.196996	2.039259	0.263720
36	6	-4.692433	-0.274662	0.080430
37	6	-5.225711	0.312712	1.234436
38	6	-5.537831	-0.928937	-0.821085
39	6	-6.593000	0.229805	1.489174
40	1	-4.571474	0.827568	1.929401
41	6	-6.903182	-1.009905	-0.544714
42	1	-5.136155	-1.365823	-1.724424
43	6	-7.442814	-0.437145	0.606404

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-8.504772	-0.506067	0.809986
45	6	1.863391	1.616264	-0.570597
46	6	3.095861	1.190020	-0.067474
47	6	1.686127	2.953891	-0.941545
48	6	4.141830	2.103260	0.073206
49	1	3.235021	0.150425	0.210315
50	6	2.736550	3.855500	-0.775852
51	1	0.748082	3.282093	-1.367529
52	6	3.970474	3.442261	-0.269384
53	1	4.782219	4.149201	-0.152947
54	6	-7.817546	-1.663154	-1.548121
55	6	-7.154764	0.806113	2.762142
56	6	2.517682	5.306951	-1.114734
57	6	5.468929	1.600388	0.575783
58	9	-7.264753	-0.135593	3.729083
59	9	-6.377351	1.791540	3.259510
60	9	-8.391451	1.318096	2.575294
61	9	-8.920071	-2.179677	-0.962917
62	9	-7.203044	-2.665428	-2.213194
63	9	-8.246304	-0.779561	-2.481114
64	9	5.318105	0.820522	1.673340
65	9	6.095959	0.839123	-0.354671
66	9	6.309318	2.601460	0.902840
67	9	3.669677	5.925861	-1.452267
68	9	1.657356	5.459431	-2.145454
69	9	1.997309	5.989213	-0.067036

**Thermodynamic data for the second NI complex with Shreiner's dithiobiuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.476787
Thermal correction to energy, Hartree	0.522461
Thermal correction to enthalpy, Hartree	0.523405
Thermal correction to Gibbs free energy, Hartree	0.384554
Sum of electronic and zero-point energies, Hartree	-3405.652885
Sum of electronic and thermal energies, Hartree	-3405.607211
Sum of electronic and thermal enthalpies, Hartree	-3405.606267
Sum of electronic and thermal Gibbs free energies, Hartree	-3405.745118

**Coordinates for the third NI complex with Shreiner's dithiobiuret optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.549421	5.493174	1.456566
2	6	2.607849	4.716143	1.734007
3	1	1.470082	6.565271	1.570015
4	1	3.578534	4.995265	2.119722
5	6	2.239330	3.325867	1.417618
6	8	2.885435	2.300116	1.520182
7	6	0.461334	4.635628	0.953529
8	7	0.053925	-0.066962	0.777002
9	6	1.065372	-0.872366	0.272985
10	6	-1.341759	-0.173505	0.829693
11	7	-1.887646	-1.222707	0.192815
12	1	-1.202881	-1.887928	-0.201705
13	7	2.287913	-0.336435	0.507339
14	1	2.341334	0.619300	0.881279
15	1	0.352457	0.780848	1.252544
16	8	0.952778	3.313814	0.951267
17	6	-1.306531	6.149970	0.533516
18	1	-0.591970	6.941573	0.799180
19	1	-2.099641	6.154939	1.293127
20	7	-0.720657	4.818217	0.560749
21	6	-1.944786	6.479779	-0.842496
22	6	-0.863235	6.468274	-1.937785
23	1	-0.062467	7.184530	-1.714177
24	1	-0.410611	5.475719	-2.041409
25	1	-1.296292	6.742280	-2.906901
26	6	-2.558530	7.888289	-0.735399
27	1	-3.023263	8.175819	-1.685555
28	1	-3.331546	7.927347	0.041876
29	1	-1.797094	8.640150	-0.494120
30	6	-3.046490	5.459050	-1.178316
31	1	-3.837629	5.469151	-0.418346
32	1	-3.506264	5.697051	-2.144740
33	1	-2.642691	4.443476	-1.232905
34	16	0.825484	-2.331802	-0.552808
35	16	-2.156819	1.014696	1.708632
36	6	-3.245616	-1.596568	0.072581
37	6	-3.525144	-2.968487	0.065930
38	6	-4.282364	-0.675933	-0.115733
39	6	-4.834383	-3.412598	-0.112639
40	1	-2.722571	-3.683836	0.209701
41	6	-5.587871	-1.138590	-0.279717
42	1	-4.071654	0.383418	-0.142993
43	6	-5.878159	-2.503148	-0.278549

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-6.895935	-2.850595	-0.409039
45	6	3.553103	-0.879602	0.163895
46	6	4.489425	-0.022887	-0.423117
47	6	3.906816	-2.197425	0.468658
48	6	5.768652	-0.492653	-0.720309
49	1	4.216331	1.002128	-0.646502
50	6	5.184952	-2.655625	0.149855
51	1	3.198953	-2.851635	0.959330
52	6	6.123498	-1.813001	-0.446468
53	1	7.114997	-2.177296	-0.686679
54	6	-5.110217	-4.891641	-0.183007
55	6	-6.710219	-0.142843	-0.415601
56	6	6.791103	0.451578	-1.295821
57	6	5.536619	-4.095176	0.420516
58	9	-7.246143	0.171055	0.788030
59	9	-7.717500	-0.622157	-1.177890
60	9	-6.294743	1.015310	-0.973008
61	9	-6.360190	-5.191902	0.230438
62	9	-4.992041	-5.359249	-1.448590
63	9	-4.248321	-5.601846	0.577410
64	9	7.498431	1.073518	-0.322653
65	9	6.218312	1.420599	-2.042799
66	9	7.684370	-0.191335	-2.078652
67	9	4.917198	-4.564389	1.525927
68	9	5.167991	-4.899434	-0.604679
69	9	6.864600	-4.266140	0.595558

**Thermodynamic data for the third NI complex with Shreiner's dithiobiuret
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.476464
Thermal correction to energy, Hartree	0.522235
Thermal correction to enthalpy, Hartree	0.523180
Thermal correction to Gibbs free energy, Hartree	0.383310
Sum of electronic and zero-point energies, Hartree	-3405.648030
Sum of electronic and thermal energies, Hartree	-3405.602258
Sum of electronic and thermal enthalpies, Hartree	-3405.601314
Sum of electronic and thermal Gibbs free energies, Hartree	-3405.741184

**Coordinates for transition state of the first NI complex with Schreiner's
dithiobiuret optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Atomic Type	Coordinates, Å		
			X	Y	Z
1	6	0	0.911773	3.516341	-0.083099
2	6	0	-0.325256	3.575559	-0.752358
3	1	0	1.330922	4.344288	0.469903
4	1	0	-0.946360	4.450289	-0.869580
5	6	0	-0.905100	2.243804	-0.742784
6	8	0	-1.963759	1.797018	-1.144503
7	6	0	1.056518	2.131592	0.417773
8	7	0	-0.664414	-1.474691	0.113743
9	6	0	-1.992760	-1.845558	0.332749
10	6	0	0.481809	-2.247875	-0.043585
11	7	0	1.589607	-1.503378	0.242473
12	1	0	1.461203	-0.616006	0.740972
13	7	0	-2.835834	-0.893904	-0.159995
14	1	0	-2.412106	-0.067357	-0.594819
15	1	0	-0.500141	-0.470367	0.031392
16	8	0	0.013962	1.379580	-0.148218
17	6	0	2.959736	2.207196	1.819768
18	1	0	3.082193	3.228340	1.434900
19	1	0	3.870419	1.653923	1.560614
20	7	0	1.842968	1.508235	1.187001
21	6	0	2.848826	2.277802	3.368999
22	6	0	1.613286	3.101916	3.772997
23	1	0	1.653888	4.114168	3.351619
24	1	0	0.685696	2.628266	3.432374
25	1	0	1.557337	3.197496	4.863613
26	6	0	4.127422	2.972798	3.875950
27	1	0	4.115607	3.047592	4.969456
28	1	0	5.022845	2.409332	3.585996
29	1	0	4.219410	3.988278	3.471599
30	6	0	2.758237	0.870196	3.985638
31	1	0	3.664140	0.286472	3.782813
32	1	0	2.654221	0.940085	5.074879
33	1	0	1.894598	0.317643	3.601226
34	6	0	2.201293	4.675218	-2.325376
35	6	0	0.983475	4.726687	-3.062911
36	6	0	0.128241	3.637638	-3.058871
37	6	0	2.514943	3.540138	-1.579617
38	1	0	0.493854	2.625568	-2.938809
39	1	0	2.202475	2.556335	-1.909473
40	1	0	3.418582	3.541054	-0.976923
41	1	0	-0.857053	3.716338	-3.509101
42	6	0	0.518907	6.037245	-3.657843
43	1	0	-0.452312	5.925873	-4.146462

Center Number	Atomic Number	Atomic Type	Coordinates, Å		
			X	Y	Z
44	1	0	0.431436	6.824047	-2.897846
45	1	0	1.232163	6.400881	-4.407573
46	6	0	3.026645	5.928096	-2.153939
47	1	0	3.358465	6.313414	-3.125797
48	1	0	2.450719	6.732945	-1.678320
49	1	0	3.914286	5.739020	-1.545256
50	16	0	-2.457302	-3.206711	1.191584
51	16	0	0.511037	-3.836183	-0.576572
52	6	0	2.949526	-1.801906	-0.001397
53	6	0	3.869072	-1.370722	0.957689
54	6	0	3.410616	-2.407180	-1.177502
55	6	0	5.238703	-1.520686	0.738685
56	1	0	3.506605	-0.914813	1.871071
57	6	0	4.780873	-2.577773	-1.367072
58	1	0	2.710655	-2.726980	-1.936277
59	6	0	5.708046	-2.132516	-0.420483
60	1	0	6.770903	-2.255385	-0.588678
61	6	0	-4.238633	-0.780222	-0.009218
62	6	0	-4.761789	0.507663	0.164704
63	6	0	-5.107470	-1.873830	-0.103214
64	6	0	-6.139844	0.692259	0.267315
65	1	0	-4.090157	1.357418	0.215975
66	6	0	-6.482636	-1.670438	0.014336
67	1	0	-4.715647	-2.865040	-0.277768
68	6	0	-7.011729	-0.394038	0.203947
69	1	0	-8.081280	-0.247486	0.292204
70	6	0	6.194210	-0.953116	1.753389
71	6	0	5.275617	-3.286535	-2.600729
72	6	0	-6.691460	2.087532	0.393246
73	6	0	-7.408361	-2.857764	-0.024675
74	9	0	5.460878	-4.608978	-2.374152
75	9	0	6.462785	-2.794219	-3.019735
76	9	0	4.407948	-3.182706	-3.630377
77	9	0	7.443975	-1.433788	1.610200
78	9	0	6.274049	0.400639	1.653198
79	9	0	5.796963	-1.216145	3.020710
80	9	0	-6.871606	2.664177	-0.819370
81	9	0	-5.862991	2.897124	1.089422
82	9	0	-7.890451	2.101816	1.014899
83	9	0	-6.914090	-3.859890	-0.783882
84	9	0	-7.617666	-3.369906	1.211966
85	9	0	-8.622199	-2.532910	-0.522211

**Thermodynamic data for transition state of the first NI complex with Schreiner's
dithiobiuret optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.621456
Thermal correction to energy, Hartree	0.674517
Thermal correction to enthalpy, Hartree	0.675461
Thermal correction to Gibbs free energy, Hartree	0.522117
Sum of electronic and zero-point energies, Hartree	-3640.098922
Sum of electronic and thermal energies, Hartree	-3640.045861
Sum of electronic and thermal enthalpies, Hartree	-3640.044917
Sum of electronic and thermal Gibbs free energies, Hartree	-3640.198262

**Coordinates for transition state of the second NI complex with Schreiner's
dithiobiuret optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Atomic Type	Coordinates, Å		
			X	Y	Z
1	6	0	3.846150	-3.304458	0.547831
2	6	0	2.646287	-3.390129	-0.182439
3	1	0	4.215841	-4.093456	1.187684
4	6	0	2.108274	-2.046177	-0.303425
5	8	0	1.085729	-1.632188	-0.837803
6	6	0	3.981523	-1.887865	0.963165
7	7	0	-1.511050	-0.238135	-0.404893
8	6	0	-2.758255	-0.834080	-0.213118
9	6	0	-1.057332	1.074195	-0.388910
10	7	0	0.267829	1.128178	-0.673762
11	1	0	0.751177	0.223980	-0.747077
12	7	0	-3.789975	-0.012247	0.043411
13	1	0	-3.532043	0.980506	0.161383
14	1	0	-0.797035	-0.946865	-0.579607
15	8	0	2.978675	-1.159267	0.283854
16	6	0	5.764691	-1.899392	2.513598
17	1	0	6.122031	-2.817463	2.024722
18	1	0	5.334031	-2.199205	3.479912
19	7	0	4.712689	-1.235785	1.753354
20	6	0	6.967478	-0.962218	2.782996
21	6	0	7.580460	-0.493847	1.450634
22	1	0	7.905177	-1.345830	0.839511
23	1	0	6.859612	0.089795	0.868395
24	1	0	8.458225	0.138197	1.632366
25	6	0	8.011512	-1.763174	3.582828
26	1	0	8.885992	-1.141026	3.806654
27	1	0	7.598618	-2.115660	4.536342
28	1	0	8.359530	-2.639323	3.021530
29	6	0	6.514003	0.259692	3.602571
30	1	0	6.073170	-0.048135	4.559350
31	1	0	7.368406	0.911212	3.822978
32	1	0	5.769997	0.847601	3.057359
33	1	0	2.011283	-4.257380	-0.279335
34	6	0	3.218011	-3.629301	-2.455427
35	6	0	4.046514	-4.731706	-2.334496
36	1	0	2.256425	-3.720747	-2.952177
37	6	0	5.220740	-4.651205	-1.532380
38	6	0	3.584210	-6.072906	-2.860095
39	6	0	5.515181	-3.473041	-0.846591
40	6	0	6.007387	-5.904120	-1.228751
41	1	0	2.650019	-5.976129	-3.419131
42	1	0	4.332700	-6.510688	-3.531718
43	1	0	3.424354	-6.796907	-2.050843

Center Number	Atomic Number	Atomic Type	Coordinates, Å		
			X	Y	Z
44	1	0	5.248069	-2.508622	-1.262286
45	1	0	6.386723	-3.449905	-0.199150
46	1	0	5.389727	-6.662588	-0.729573
47	1	0	6.381675	-6.364019	-2.151542
48	1	0	6.866123	-5.689390	-0.587749
49	1	0	3.598810	-2.618174	-2.385556
50	16	0	-2.815128	-2.521641	-0.302299
51	16	0	-2.003729	2.431857	-0.028833
52	6	0	-5.153484	-0.327501	0.249498
53	6	0	-5.839029	0.409930	1.221237
54	6	0	-5.841659	-1.269455	-0.522650
55	6	0	-7.200715	0.192084	1.428508
56	1	0	-5.307927	1.147524	1.813187
57	6	0	-7.201417	-1.480049	-0.295980
58	1	0	-5.322785	-1.826361	-1.290237
59	6	0	-7.892071	-0.758086	0.678058
60	1	0	-8.948545	-0.929847	0.845407
61	6	0	1.115888	2.261847	-0.732664
62	6	0	2.384608	2.144744	-0.158755
63	6	0	0.761826	3.437345	-1.406450
64	6	0	3.288843	3.204851	-0.248437
65	1	0	2.666212	1.226117	0.345181
66	6	0	1.671406	4.491185	-1.470134
67	1	0	-0.202802	3.520749	-1.887044
68	6	0	2.940195	4.387671	-0.894030
69	1	0	3.643857	5.208237	-0.958353
70	6	0	-7.952140	-2.449294	-1.171483
71	6	0	-7.913295	0.942727	2.522555
72	6	0	1.266461	5.779066	-2.138140
73	6	0	4.650184	3.029122	0.370099
74	9	0	-7.848994	0.283098	3.703574
75	9	0	-7.375844	2.164797	2.727953
76	9	0	-9.223306	1.116251	2.242515
77	9	0	-8.995841	-3.009663	-0.521749
78	9	0	-7.160556	-3.451893	-1.609928
79	9	0	-8.457501	-1.839716	-2.270620
80	9	0	4.558256	2.736264	1.690168
81	9	0	5.325199	2.003774	-0.205060
82	9	0	5.418055	4.130105	0.254782
83	9	0	2.317467	6.392580	-2.725405
84	9	0	0.327235	5.584159	-3.089044
85	9	0	0.747916	6.659042	-1.248631

**Thermodynamic data for transition state of the second NI complex with
Schreiner's dithiobiuret optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.620733
Thermal correction to energy, Hartree	0.673923
Thermal correction to enthalpy, Hartree	0.674867
Thermal correction to Gibbs free energy, Hartree	0.520932
Sum of electronic and zero-point energies, Hartree	-3640.108102
Sum of electronic and thermal energies, Hartree	-3640.054913
Sum of electronic and thermal enthalpies, Hartree	-3640.053969
Sum of electronic and thermal Gibbs free energies, Hartree	-3640.207903

**Coordinates for transition state of the third NI complex with Schreiner's
dithiobiuret optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-2.863532	4.046933	-0.396583
2	6	-3.584655	3.020873	-1.032372
3	1	-3.327447	4.920840	0.039101
4	1	-4.638201	3.022336	-1.266028
5	6	-2.861337	1.779845	-0.828604
6	8	-3.111992	0.628812	-1.155565
7	6	-1.715386	3.397872	0.282832
8	7	0.393234	-0.416755	-0.245189
9	6	-0.237027	-1.610416	0.084824
10	6	1.733456	-0.041815	-0.383098
11	7	2.656656	-0.951690	-0.031077
12	1	2.276917	-1.862183	0.273987
13	7	-1.569527	-1.549403	-0.141656
14	1	-1.979485	-0.671777	-0.495827
15	1	-0.217889	0.365229	-0.477192
16	8	-1.688236	2.052235	-0.147724
17	6	-0.785321	5.123189	1.599504
18	1	-1.713060	5.679790	1.400517
19	1	0.023296	5.638454	1.062016
20	7	-0.830837	3.753286	1.104818
21	6	-0.478352	5.183555	3.117235
22	6	-1.582879	4.453586	3.902577
23	1	-2.566544	4.902141	3.713526
24	1	-1.633701	3.395996	3.621339
25	1	-1.391284	4.508552	4.980793
26	6	-0.446185	6.667403	3.527906
27	1	-0.225586	6.765957	4.597315
28	1	0.325654	7.217129	2.974889
29	1	-1.409967	7.156486	3.339027
30	6	0.888215	4.537809	3.408547
31	1	1.693060	5.062945	2.878688
32	1	1.111852	4.577266	4.481309
33	1	0.904495	3.489835	3.093838
34	6	-2.812256	5.546529	-2.785804
35	6	-3.492314	4.531877	-3.519766
36	6	-3.130492	3.206230	-3.361285
37	6	-1.802027	5.198599	-1.889131
38	1	-2.123848	2.915113	-3.089754
39	1	-1.158571	4.348594	-2.085436
40	1	-1.333241	5.982138	-1.300483
41	1	-3.728586	2.418829	-3.810896
42	6	-4.746411	4.875241	-4.293151
43	1	-5.178454	3.985318	-4.757962

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	-5.511708	5.331668	-3.652698
45	1	-4.530019	5.597336	-5.089945
46	6	-3.346024	6.959299	-2.789482
47	1	-3.363332	7.368963	-3.806837
48	1	-4.377780	7.006792	-2.416079
49	1	-2.730460	7.617740	-2.171546
50	16	0.541807	-2.971557	0.729728
51	16	2.038441	1.498168	-1.007387
52	6	4.067325	-0.851174	-0.099237
53	6	4.769255	-1.970035	-0.559596
54	6	4.766209	0.275858	0.345267
55	6	6.163717	-1.952742	-0.588321
56	1	4.226199	-2.842972	-0.904839
57	6	6.159952	0.280915	0.297497
58	1	4.228948	1.130683	0.731398
59	6	6.869966	-0.826492	-0.168261
60	1	7.952909	-0.813070	-0.198637
61	6	-2.546680	-2.543241	0.131104
62	6	-3.723558	-2.131069	0.763347
63	6	-2.405807	-3.870961	-0.284843
64	6	-4.747576	-3.050308	0.993321
65	1	-3.833627	-1.098116	1.073440
66	6	-3.432802	-4.780501	-0.033269
67	1	-1.513814	-4.185666	-0.808758
68	6	-4.607676	-4.381832	0.605812
69	1	-5.401465	-5.095043	0.791810
70	6	6.912153	-3.182537	-1.030291
71	6	6.907725	1.520553	0.713724
72	6	-6.033493	-2.579802	1.620097
73	6	-3.249855	-6.224555	-0.420667
74	9	7.117700	2.351582	-0.335066
75	9	8.122058	1.226988	1.228204
76	9	6.232395	2.228764	1.644805
77	9	8.096956	-2.873030	-1.600191
78	9	7.181554	-4.003658	0.012616
79	9	6.206673	-3.907079	-1.926037
80	9	-6.888103	-2.086253	0.692575
81	9	-5.822692	-1.593161	2.519161
82	9	-6.680020	-3.579375	2.257170
83	9	-2.473131	-6.358274	-1.518014
84	9	-2.655704	-6.933610	0.568509
85	9	-4.429024	-6.829742	-0.681338

**Thermodynamic data for transition state of the third NI complex with Schreiner's
dithiobiuret optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.620419
Thermal correction to energy, Hartree	0.673719
Thermal correction to enthalpy, Hartree	0.674663
Thermal correction to Gibbs free energy, Hartree	0.518531
Sum of electronic and zero-point energies, Hartree	-3640.103467
Sum of electronic and thermal energies, Hartree	-3640.050167
Sum of electronic and thermal enthalpies, Hartree	-3640.049223
Sum of electronic and thermal Gibbs free energies, Hartree	-3640.205355

**Coordinates for the NI complex with dithiobiuret and Zn^{2+} optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-2.933351	-0.074165	0.834315
2	6	-2.803162	-1.352796	1.223765
3	1	-3.844361	0.501854	0.752280
4	1	-3.569492	-2.051849	1.528088
5	6	-1.374491	-1.706209	1.173633
6	8	-0.783490	-2.731681	1.424589
7	6	-1.596858	0.451402	0.513013
8	7	2.246001	-0.610177	0.059785
9	6	2.922080	-1.705248	0.569536
10	6	2.525784	0.343652	-0.896948
11	7	1.591876	1.263478	-1.048168
12	1	0.688723	1.309533	-0.538222
13	1	1.748607	1.984248	-1.743418
14	7	2.142425	-2.583916	1.178956
15	1	2.575001	-3.366488	1.656072
16	1	1.115066	-2.555486	1.190917
17	1	1.288789	-0.539746	0.416237
18	8	-0.682920	-0.585305	0.747285
19	6	-1.959191	2.696320	-0.196296
20	1	-3.027494	2.465414	-0.103060
21	1	-1.766196	2.963417	-1.242257
22	7	-1.118448	1.538694	0.087978
23	6	-1.616445	3.919868	0.699621
24	6	-1.931523	3.600157	2.171977
25	1	-2.983970	3.318938	2.301308
26	1	-1.310508	2.779410	2.548536
27	1	-1.740292	4.476989	2.800959
28	6	-2.504194	5.084526	0.220645
29	1	-2.319638	5.976457	0.829848
30	1	-2.294002	5.341876	-0.824455
31	1	-3.569296	4.837071	0.302576
32	6	-0.134246	4.306199	0.548734
33	1	0.119101	4.510838	-0.498841
34	1	0.080458	5.211530	1.127991
35	1	0.528475	3.513803	0.912066
36	16	4.611117	-2.033133	0.592735
37	16	3.863968	0.399394	-1.993572
38	30	5.559426	-0.263810	-0.569179

**Thermodynamic data for the NI complex with dithiobiuret and Zn²⁺ optimized at
B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.300722
Thermal correction to energy, Hartree	0.323260
Thermal correction to enthalpy, Hartree	0.324205
Thermal correction to Gibbs free energy, Hartree	0.246962
Sum of electronic and zero-point energies, Hartree	-3374.452281
Sum of electronic and thermal energies, Hartree	-3374.429742
Sum of electronic and thermal enthalpies, Hartree	-3374.428798
Sum of electronic and thermal Gibbs free energies, Hartree	-3374.506041

Coordinates for transition state of the NI complex with dithiobiuret and Zn^{2+}
optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-3.018461	-0.116956	0.607010
2	6	-2.843651	-1.421913	1.106234
3	1	-3.774034	0.564234	0.971423
4	1	-3.486584	-1.932557	1.806217
5	6	-1.441510	-1.764390	0.995291
6	8	-0.792472	-2.739165	1.326110
7	6	-1.670385	0.381923	0.261721
8	7	2.157477	-0.558566	0.027007
9	6	2.831291	-1.518910	0.757879
10	6	2.500813	0.423299	-0.886145
11	7	1.537803	1.287927	-1.136279
12	1	0.596585	1.312907	-0.680338
13	1	1.714072	2.001807	-1.834319
14	7	2.049249	-2.432799	1.304206
15	1	2.474324	-3.130556	1.903865
16	1	1.022502	-2.484562	1.202913
17	1	1.143640	-0.589536	0.187849
18	8	-0.784541	-0.698942	0.363319
19	6	-1.988650	2.683430	-0.232115
20	1	-3.050004	2.472099	-0.051263
21	1	-1.891388	3.006875	-1.276254
22	7	-1.161834	1.487567	-0.083519
23	6	-1.546138	3.850706	0.690735
24	6	-1.695654	3.444044	2.167706
25	1	-2.731071	3.166336	2.400687
26	1	-1.051545	2.593049	2.415821
27	1	-1.417771	4.276841	2.824062
28	6	-2.474851	5.041674	0.385207
29	1	-2.215013	5.899416	1.015918
30	1	-2.388028	5.356456	-0.661933
31	1	-3.524959	4.790365	0.577357
32	6	-0.088498	4.252540	0.402513
33	1	0.051047	4.513877	-0.653907
34	1	0.189988	5.126689	1.002495
35	1	0.608874	3.445384	0.649662
36	6	-5.019452	-1.013225	-1.166465
37	6	-4.880493	-2.367718	-0.744433
38	6	-3.620082	-2.915205	-0.585248
39	6	-3.884956	-0.231512	-1.384835
40	1	-2.768821	-2.570355	-1.158463
41	1	-2.971197	-0.677477	-1.760671
42	1	-4.013644	0.812599	-1.655176
43	1	-3.502950	-3.897298	-0.136557

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	6	-6.093002	-3.131975	-0.261767
45	1	-5.820389	-4.138192	0.065964
46	1	-6.591446	-2.623346	0.573239
47	1	-6.836809	-3.229406	-1.061665
48	6	-6.378151	-0.356610	-1.139754
49	1	-7.078558	-0.882463	-1.800004
50	1	-6.819845	-0.377775	-0.134692
51	1	-6.323245	0.684619	-1.466443
52	16	4.508520	-1.618313	1.170831
53	16	3.935525	0.564255	-1.852322
54	30	5.458659	-0.301479	-0.416616

Thermodynamic data for transition state of the NI complex with dithiobiuret and Zn²⁺ optimized at B3LYP/6-31G(d) level

Zero-point correction, Hartree	0.444676
Thermal correction to energy, Hartree	0.474634
Thermal correction to enthalpy, Hartree	0.475578
Thermal correction to Gibbs free energy, Hartree	0.382618
Sum of electronic and zero-point energies, Hartree	-3608.911043
Sum of electronic and thermal energies, Hartree	-3608.881085
Sum of electronic and thermal enthalpies, Hartree	-3608.880141
Sum of electronic and thermal Gibbs free energies, Hartree	-3608.973101

**Coordinates for the NI complex with 2,6-diaminopyridinium ion optimized at
B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	1.909563	2.586067	-0.501771
2	6	0.994425	3.543742	-0.282804
3	1	2.961216	2.716505	-0.714570
4	1	1.122803	4.617153	-0.275707
5	6	-0.304809	2.893719	-0.035583
6	8	-1.400512	3.344931	0.202980
7	6	1.245412	1.274667	-0.406605
8	7	-2.319747	-0.414013	0.006062
9	6	-2.028622	-1.711358	-0.332699
10	7	-0.747193	-2.002009	-0.616812
11	1	0.009653	-1.315095	-0.580134
12	1	-0.506064	-2.946236	-0.879779
13	7	-3.693739	1.342801	0.651779
14	1	-4.621096	1.724995	0.769462
15	1	-2.940331	2.012007	0.503567
16	1	-1.549952	0.256067	0.018685
17	8	-0.103356	1.525186	-0.118675
18	6	2.976461	-0.293378	-0.816641
19	1	3.611267	0.586276	-0.982034
20	1	2.953795	-0.866150	-1.751878
21	7	1.593525	0.067057	-0.523857
22	6	3.613734	-1.179564	0.290041
23	6	3.661841	-0.409761	1.621963
24	1	4.217473	0.530653	1.519182
25	1	2.655791	-0.172704	1.985735
26	1	4.161319	-1.009965	2.391050
27	6	5.047259	-1.506201	-0.170770
28	1	5.551065	-2.133988	0.572970
29	1	5.046311	-2.049464	-1.123532
30	1	5.644315	-0.595404	-0.300173
31	6	2.820592	-2.486800	0.465743
32	1	2.758495	-3.043825	-0.477384
33	1	3.312885	-3.131772	1.202785
34	1	1.801567	-2.296912	0.817734
35	6	-3.080053	-2.636276	-0.360032
36	1	-2.877439	-3.667127	-0.622393
37	6	-3.575653	0.042683	0.315347
38	6	-4.361846	-2.194709	-0.047396
39	1	-5.180599	-2.907663	-0.069587
40	6	-4.634246	-0.871025	0.289992
41	1	-5.635800	-0.535976	0.528652

**Thermodynamic data for the NI complex with 2,6-diaminopyridinium ion
optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.346775
Thermal correction to energy, Hartree	0.367942
Thermal correction to enthalpy, Hartree	0.368887
Thermal correction to Gibbs free energy, Hartree	0.294777
Sum of electronic and zero-point energies, Hartree	-915.134048
Sum of electronic and thermal energies, Hartree	-915.112881
Sum of electronic and thermal enthalpies, Hartree	-915.111937
Sum of electronic and thermal Gibbs free energies, Hartree	-915.186047

**Coordinates for transition state of the NI complex with 2,6-diaminopyridinium ion
optimized at B3LYP/6-31G(d) level**

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-1.957268	0.030008	0.608406
2	6	-1.873266	-1.260189	1.162903
3	1	-2.641165	0.788110	0.961546
4	1	-2.520449	-1.672392	1.921784
5	6	-0.504392	-1.727198	1.016881
6	8	0.067046	-2.737843	1.373739
7	6	-0.589013	0.396874	0.182323
8	7	3.085132	-0.963511	-0.158897
9	6	3.672489	0.065902	-0.850160
10	7	2.876580	1.082785	-1.229659
11	1	1.915476	1.196259	-0.886790
12	1	3.303231	1.884450	-1.671196
13	7	3.036811	-2.995705	0.959642
14	1	3.487671	-3.852182	1.245966
15	1	2.027137	-2.926198	1.090135
16	1	2.082612	-0.895153	0.029406
17	8	0.203608	-0.754093	0.301264
18	6	-0.755186	2.686251	-0.396522
19	1	-1.826212	2.558920	-0.191233
20	1	-0.657352	2.975206	-1.450930
21	7	-0.008198	1.441959	-0.230269
22	6	-0.215589	3.847709	0.481839
23	6	-0.359182	3.496380	1.973598
24	1	-1.405236	3.294077	2.235823
25	1	0.234150	2.613333	2.235886
26	1	-0.013907	4.328697	2.597951
27	6	-1.068779	5.089877	0.159936
28	1	-0.734616	5.947736	0.754698
29	1	-0.988729	5.364412	-0.899079
30	1	-2.128190	4.917624	0.385807
31	6	1.258825	4.141895	0.152869
32	1	1.389251	4.372221	-0.911959
33	1	1.611547	5.006513	0.727397
34	1	1.903880	3.292422	0.399056
35	6	-4.106643	-0.788996	-1.045116
36	6	-4.049709	-2.123074	-0.547420
37	6	-2.825278	-2.750875	-0.395145
38	6	-2.928194	-0.109960	-1.349748
39	1	-1.978499	-2.509027	-1.024968
40	1	-2.063035	-0.643079	-1.726336
41	1	-2.986552	0.926281	-1.670266
42	1	-2.763777	-3.714287	0.102646
43	6	5.040833	-0.024937	-1.131718

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	1	5.528944	0.775606	-1.673413
45	6	3.750015	-2.080495	0.279411
46	6	5.734995	-1.151442	-0.698894
47	1	6.796691	-1.226610	-0.914467
48	6	5.118871	-2.183860	0.002474
49	1	5.667157	-3.055610	0.337000
50	6	-5.412338	-0.030930	-1.010675
51	1	-5.820723	0.031976	0.006563
52	1	-5.291355	0.985758	-1.392718
53	1	-6.171787	-0.533214	-1.622344
54	6	-5.293943	-2.765892	0.023664

**Thermodynamic data for transition state of the NI complex with
2,6-diaminopyridinium ion optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.490792
Thermal correction to energy, Hartree	0.519428
Thermal correction to enthalpy, Hartree	0.520372
Thermal correction to Gibbs free energy, Hartree	0.429841
Sum of electronic and zero-point energies, Hartree	-1149.591172
Sum of electronic and thermal energies, Hartree	-1149.562536
Sum of electronic and thermal enthalpies, Hartree	-1149.561592
Sum of electronic and thermal Gibbs free energies, Hartree	-1149.652123

Coordinates for the NI complex with N,N'-diacetyl-2,6-diaminopyridinium ion
optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Atomic Type	Coordinates, Å		
			X	Y	Z
1	6	0	-1.818425	-2.962060	-1.121865
2	6	0	-0.672065	-3.629891	-1.329767
3	1	0	-2.825736	-3.344265	-1.207308
4	1	0	-0.529460	-4.662534	-1.615940
5	6	0	0.448123	-2.707895	-1.082765
6	8	0	1.647551	-2.864033	-1.104187
7	6	0	-1.491921	-1.576683	-0.742514
8	7	0	1.577266	0.839035	-0.080493
9	6	0	1.000120	2.077967	-0.122508
10	7	0	-0.316517	2.108439	-0.536302
11	1	0	-0.851880	1.233279	-0.521204
12	7	0	3.276583	-0.711951	0.226159
13	1	0	2.659314	-1.382849	-0.239052
14	1	0	0.999484	0.038267	-0.350625
15	8	0	-0.093016	-1.474757	-0.759237
16	6	0	-3.595805	-0.579077	-0.325634
17	1	0	-4.017598	-1.478359	-0.791170
18	1	0	-3.970717	0.285882	-0.883324
19	7	0	-2.138816	-0.540558	-0.423888
20	6	0	-4.106704	-0.483582	1.143040
21	6	0	-3.615458	-1.692255	1.959522
22	1	0	-3.931817	-2.639177	1.504702
23	1	0	-2.523712	-1.704242	2.051871
24	1	0	-4.031560	-1.656793	2.972810
25	6	0	-5.646059	-0.498496	1.076118
26	1	0	-6.069957	-0.426444	2.084084
27	1	0	-6.027420	0.346334	0.490188
28	1	0	-6.018079	-1.423964	0.620519
29	6	0	-3.632406	0.822188	1.804988
30	1	0	-4.010836	1.699482	1.266334
31	1	0	-4.005172	0.881438	2.834017
32	1	0	-2.539955	0.885076	1.838696
33	6	0	1.769843	3.178198	0.247225
34	1	0	1.334587	4.163511	0.219377
35	6	0	2.872085	0.602689	0.291212
36	6	0	3.086993	2.958236	0.644657
37	1	0	3.691424	3.809480	0.941010
38	6	0	3.657571	1.689197	0.675573
39	1	0	4.678209	1.521215	0.978229
40	6	0	-0.989380	3.242912	-1.009489
41	6	0	4.493276	-1.232938	0.687424
42	8	0	-0.469956	4.345125	-1.056601
43	8	0	5.334380	-0.551662	1.248708

Center Number	Atomic Number	Atomic Type	Coordinates, Å		
			X	Y	Z
44	6	0	4.657099	-2.709907	0.409015
45	1	0	3.781509	-3.279539	0.734523
46	1	0	4.779125	-2.876956	-0.667377
47	1	0	5.546070	-3.066262	0.929767
48	6	0	-2.409981	2.973447	-1.448937
49	1	0	-2.477459	2.083002	-2.080930
50	1	0	-3.047129	2.817273	-0.571446
51	1	0	-2.773951	3.842699	-1.997335

Thermodynamic data for the NI complex with N,N'-diacetyl-2,6-diaminopyridinium ion optimized at B3LYP/6-31G(d) level

Zero-point correction, Hartree	0.423626
Thermal correction to energy, Hartree	0.451152
Thermal correction to enthalpy, Hartree	0.452096
Thermal correction to Gibbs free energy, Hartree	0.363322
Sum of electronic and zero-point energies, Hartree	-1220.366678
Sum of electronic and thermal energies, Hartree	-1220.339143
Sum of electronic and thermal enthalpies, Hartree	-1220.338198
Sum of electronic and thermal Gibbs free energies, Hartree	-1220.426972

Coordinates for transition state of the NI complex with N,N'-diacetyl-2,6-diaminopyridinium ion optimized at B3LYP/6-31G(d) level

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
1	6	-2.489629	-0.406070	0.584262
2	6	-2.177708	-1.777888	0.640371
3	1	-3.224747	0.061089	1.223670
4	1	-2.692760	-2.529148	1.218759
5	6	-0.786226	-1.939615	0.277992
6	8	-0.033528	-2.895040	0.258138
7	6	-1.228592	0.297209	0.258072
8	7	2.564314	-0.224444	-0.339217
9	6	2.939932	0.994473	-0.831405
10	7	1.902958	1.850371	-1.144139
11	1	0.986084	1.687909	-0.699289
12	7	2.858336	-2.378714	0.472500
13	1	1.845235	-2.490736	0.351025
14	1	1.557384	-0.409681	-0.263767
15	8	-0.293465	-0.681733	-0.105170
16	6	-1.721907	2.575037	0.657122
17	1	-2.756073	2.227429	0.775518
18	1	-1.720302	3.320296	-0.146872
19	7	-0.824866	1.496083	0.244333
20	6	-1.277418	3.268683	1.975861
21	6	-1.273528	2.256624	3.135853
22	1	-2.260988	1.796901	3.268397
23	1	-0.544259	1.455856	2.970379
24	1	-1.011001	2.756266	4.075544
25	6	-2.304219	4.380234	2.266304
26	1	-2.039048	4.914571	3.185810
27	1	-2.338447	5.112563	1.450614
28	1	-3.312749	3.969410	2.396335
29	6	0.121338	3.892280	1.823132
30	1	0.133777	4.646969	1.026939
31	1	0.419607	4.388647	2.753981
32	1	0.877604	3.136086	1.589167
33	6	-4.651239	-0.908906	-1.150889
34	6	-4.389755	-2.310214	-1.186723
35	6	-3.094359	-2.767877	-1.342332
36	6	-3.596367	0.000217	-1.234886
37	1	-2.340211	-2.191082	-1.862289
38	1	-2.716694	-0.228298	-1.825881
39	1	-3.813715	1.061690	-1.155651
40	1	-2.871540	-3.825613	-1.236969
41	6	4.299190	1.262674	-0.969773
42	1	4.615518	2.216155	-1.360295
43	6	3.437020	-1.209118	0.032243

Center Number	Atomic Number	Coordinates, Å		
		X	Y	Z
44	6	5.207328	0.277280	-0.587456
45	1	6.269261	0.480002	-0.682983
46	6	4.804504	-0.956432	-0.084653
47	1	5.508238	-1.718181	0.208752
48	6	-6.028036	-0.413981	-0.780368
49	1	-6.339267	-0.778231	0.207614
50	1	-6.068727	0.677823	-0.769678
51	1	-6.777186	-0.773988	-1.496091
52	6	-5.490472	-3.288522	-0.841528
53	1	-5.908836	-3.099425	0.155090
54	1	-6.321064	-3.209033	-1.553312
55	1	-5.124765	-4.317987	-0.867805
56	6	1.991340	2.923971	-2.035714
57	6	3.524081	-3.471148	1.040881
58	8	3.029198	3.231357	-2.599620
59	8	4.727001	-3.482859	1.244674
60	6	2.613390	-4.637015	1.353923
61	1	1.654797	-4.312597	1.766874
62	1	2.407043	-5.194388	0.432241
63	1	3.121929	-5.298186	2.056480
64	6	0.691050	3.670828	-2.231062
65	1	-0.173535	3.001834	-2.239869
66	1	0.557286	4.390452	-1.415121
67	1	0.745007	4.221392	-3.171197

**Thermodynamic data for transition state of the NI complex with N,N'-diacetyl-
2,6-diaminopyridinium ion optimized at B3LYP/6-31G(d) level**

Zero-point correction, Hartree	0.566984
Thermal correction to energy, Hartree	0.602300
Thermal correction to enthalpy, Hartree	0.603244
Thermal correction to Gibbs free energy, Hartree	0.496070
Sum of electronic and zero-point energies, Hartree	-1454.826072
Sum of electronic and thermal energies, Hartree	-1454.790756
Sum of electronic and thermal enthalpies, Hartree	-1454.789812
Sum of electronic and thermal Gibbs free energies, Hartree	-1454.896986

Maģistra darbs „Vairāku izmeklētu organisko reakciju pētījumi ar molekulārās modelēšanas metodēm” izstrādāts LU Ķīmijas fakultātē un Eötvös Loránd University, ķīmijas nodaļā.

Ar savu parakstu apliecinu, ka pētījums veikts patstāvīgi, izmantoti tikai tajā norādītie informācijas avoti un iesniegtā darba elektroniskā kopija atbilst izdrukai.

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