

# A DFT Study of the Reactivity Indexes of Ionic [4 + 2<sup>+</sup>] Diels-Alder Cycloaddition to Nitrilium and Immonium Ions

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**Abstract:** The global electrophilicity index, defined within the conceptual density functional theory (DFT), was used to classify the dienes and dienophiles currently used in Diels-Alder reactions on a unique scale of electrophilicity. The index, obtained within the Kohn-Sham scheme, is based on the HOMO and LUMO energies. A systematic study of the global reactivity indexes of the reagents involved in formal [4 + 2<sup>+</sup>] Diels-Alder cycloaddition reactions of nitrilium and immonium ions with isoprene is presented.

**Keywords:** Diels-Alder, reactivity indexes, nitrilium, immonium, electrophilicity, nucleophilicity.

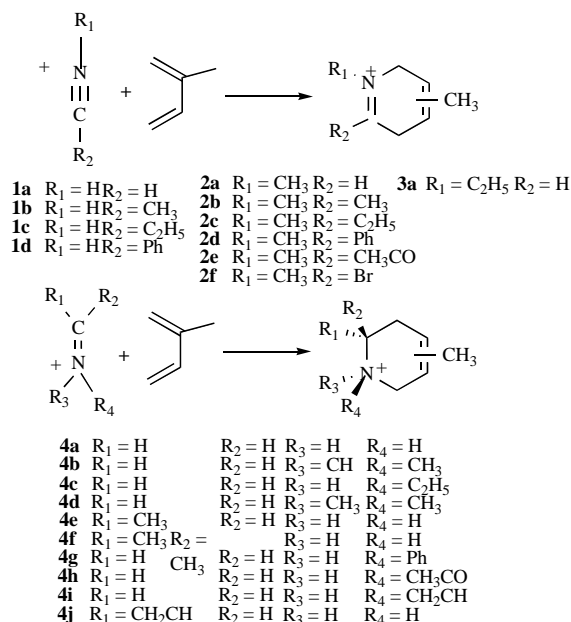
## INTRODUCTION

The conceptual density functional theory (DFT) developed by Parr and Yang [1, 3] is a powerful framework to understand chemical reactivity. It is based on electronic structure descriptors of the isolated reactants from the dawn of theoretical chemistry. However, this formulation as many ordering principles and concepts employed in Chemistry can be traced to early quantum molecular models, such as the Hückel molecular orbital (HMO) theory [4], the valence bond (VB) approximation [5-7], as well the frontier orbital theory (HOMO-LUMO gap) of Fukui [8] can be considered as simple conceptual tools to deal chemical reactivity.

Instead the aforementioned formulation is governed by the analysis of the static descriptors [9] of electronic properties of reactants, the derived quantities provide important clues to board the course of chemical reactions. In a formal framework it has allowed introducing in a many empirical chemical concepts like electronegativity [10], hardness [11], so-called reaction force [12], Fukui function [13], electrophilicity [14], electrofugality and nucleofugality [1, 2, 9, 15-18], nucleophilicity and solution phase ionization potentials, homofugality [19, 20], nucleophilicity [21], among others. In particular, the introduction of concepts like electrophilicity and nucleophilicity to define electron deficient (electrophile) and electron rich (nucleophile) species has gained a continuous interest to construct empirical scales classifying atoms, molecules and charged species [22-29]. The availability of empirical scales of electrophilicity and nucleophilicity, usually based on kinetic parameters, has been very useful to rationalize the chemical reactivity, in terms of selectivity, reaction mechanisms, solvent, substituent effects, etc. [30]. Most of them were early defined by Parr and co-workers and are well described [2]. New developments were recently reviewed [1, 31].

The use of the global electrophilicity index [32], defined within the DFT [2, 11] was reported [29, 33] to classify the

dienes and dienophiles currently used in Diels-Alder (DA) reactions on a unique scale of electrophilicity. A good correlation between the difference in electrophilicity for the diene and dienophile pair,  $\Delta\omega$ , and the feasibility of the cycloaddition was found [29, 33]. Nitrilium ions ( $R-C\equiv N^+-R$ ) and immonium ions ( $RR_1C=N^+R_2R_3$ ) are important and common ionic species that they might undergo gas-phase Diels-Alder cycloadditions with dienes. In addition, many nitrilium ions occur in the stratosphere and the lower atmosphere [34]. This article therefore describes a systematic study of the reactivity indexes of the formal [4 + 2<sup>+</sup>] cycloaddition reactions of nitrilium and immonium ions with isoprene (Scheme 1). These reactions have been studied by means of multiple stage mass spectrometric experiments, performed using a pentaquadrupole instrument. These experiments were complemented by frontier orbital theory using the semiempirical AM1 method [35].



**Scheme 1.** [4 + 2<sup>+</sup>] cycloaddition reactions of nitrilium and immonium ions with isoprene.

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## COMPUTATIONAL DETAILS

The reactivity indexes were estimated according to the equations proposed by Parr *et al.* [2, 11, 32]. The electronic chemical potential ( $\mu$ ) and chemical hardness ( $\eta$ ) were evaluated in terms of the one electron energies of frontier molecular orbital HOMO and LUMO using the following equations:

$$\mu \approx \frac{E_{HOMO} + E_{LUMO}}{2}$$

$$\eta \approx E_{LUMO} - E_{HOMO}$$

The global electrophilicity index ( $\omega$ ) which measures the stabilization in energy when the system acquires an additional electronic charge  $\Delta N$  from the environment is given by:

$$\omega = \frac{\mu^2}{2\eta}$$

in terms of the electronic chemical potential and the chemical hardness. Moreover, Domingo *et al.* [29, 36] introduced an empirical (relative) nucleophilicity index,  $N$ , based on the HOMO energies obtained within the Kohn-Sham scheme [37] and defined as:

$$N = E_{HOMO(Nu)} - E_{HOMO(ref)}$$

The reference value for this nucleophilicity scale is taken by tetracyanoethylene to obtain a scale with only positive values.

Full geometry optimizations were carried out with the Gaussian 03 suite of programs [38]. The calculations were performed within the density functional theory (DFT) [2, 39] using the B3LYP/6-31G\* level of theory [40-42]. The geometry optimizations were carried with the Bery analytical gradient optimization method [43-44].

## RESULTS AND DISCUSSION

The electronic chemical potential ( $\mu$ ), the chemical hardness ( $\eta$ ), the global electrophilicity ( $\omega$ ), and the global nucleophilicity ( $N$ ) for isoprene and different nitrilium and immonium ions are shown in Table 1.

The chemical potential of isoprene ( $\mu = -0.1362$  au) is higher than all the nitrilium and immonium ions, which ranges from  $-0.3266$  au to  $-0.5058$  au, and the model predicts that the net charge transfer for these ionic DA reactions is expected to occur from the isoprene to the electron-deficient ions. Isoprene presents a low electrophilicity value ( $\omega = 1.24$  eV) and could be classified as a moderate electrophile within the electrophilicity scale [33] and the nitrilium and immonium ions are located as strong electrophiles with

**Table 1. Electronic Chemical Potential,  $\mu$ , Chemical Hardness,  $\eta$ , Global Electrophilicity,  $\omega$ , and Global Nucleophilicity,  $N$ , for Isoprene and the Nitrilium and Immonium Ions**

	$\mu$ (a.u.)	$\eta$ (a.u.)	$\omega$ (eV)	$N$ (eV)
<b>Isoprene</b>	-0,1362	0,2032	<b>1,24</b>	<b>2,65</b>
<b>1a</b>	-0,5058	0,4010	<b>8,68</b>	<b>-10,10</b>
<b>1b</b>	-0,4401	0,3680	<b>7,16</b>	<b>-7,86</b>
<b>1c</b>	-0,4023	0,3122	<b>7,05</b>	<b>-6,07</b>
<b>1d</b>	-0,3428	0,1797	<b>8,90</b>	<b>-2,65</b>
<b>2a</b>	-0,4380	0,3478	<b>7,50</b>	<b>-7,53</b>
<b>2b</b>	-0,3960	0,3430	<b>6,22</b>	<b>-6,32</b>
<b>2c</b>	-0,3776	0,3206	<b>6,05</b>	<b>-5,52</b>
<b>2d</b>	-0,3266	0,1856	<b>7,82</b>	<b>-2,29</b>
<b>2e</b>	-0,3909	0,2060	<b>10,09</b>	<b>-4,32</b>
<b>2f</b>	-0,3864	0,2928	<b>6,94</b>	<b>-5,38</b>
<b>3a</b>	-0,4028	0,2986	<b>7,39</b>	<b>-5,90</b>
<b>4a</b>	-0,4863	0,3337	<b>9,64</b>	<b>-8,65</b>
<b>4b</b>	-0,4366	0,2826	<b>9,18</b>	<b>-6,61</b>
<b>4c</b>	-0,4114	0,2578	<b>8,93</b>	<b>-5,58</b>
<b>4d</b>	-0,4096	0,2713	<b>8,41</b>	<b>-5,72</b>
<b>4e</b>	-0,4374	0,2976	<b>8,74</b>	<b>-6,83</b>
<b>4f</b>	-0,4113	0,2899	<b>7,94</b>	<b>-6,01</b>
<b>4g</b>	-0,3465	0,1464	<b>11,16</b>	<b>-2,30</b>
<b>4h</b>	-0,3465	0,1463	<b>11,16</b>	<b>-2,30</b>
<b>4i</b>	-0,3851	0,1834	<b>11,00</b>	<b>-3,85</b>
<b>4j</b>	-0,3910	0,2003	<b>10,39</b>	<b>-4,24</b>

values bigger than 6.22 eV. Therefore, isoprene acts as a nucleophile in these ionic DA reactions and the nitrilium and immonium ions as electrophiles. Thus the corresponding DA reaction should have an ionic character and, as a result, the nucleophilic addition of isoprene should have an insignificant activation barrier. This behavior is in agreement with the high nucleophilicity of isoprene ( $N = 2.65$  eV) and the negative values for the rest of the ions.

### Nitrilium Ions 1

The group of  $R-C\equiv N^+-H$  nitrilium ions has electrophilicity values ranging from 7.05 eV for **1c** to 8.90 eV for the ion **1d**. The  $\Delta\omega$  for the reaction between the  $H-C\equiv N^+-H$  nitrilium ion and isoprene has a high value of 7.44 eV. Large difference in electrophilicity within the pairs of substrates studied suggests the ionic character of their reaction and, consequently, low activation energy [33]. Experimentally, all the nitrilium ions display reactivity with isoprene and yield product spectra that are dominated by the proton transfer products [35]. When substitution electron-withdrawing groups are increased in the dienophile an increase in the electrophilicity power of the compound is observed. For instance, when a phenyl group is added on the nitrilium ion, ion **1d**, the value of  $\Delta\omega$  is increased to 7.66 eV, and decreased to 5.92 and 5.82 eV when the substituent is a methyl or ethyl group respectively.

### Nitrilium Ions 2

The methyl-substituted nitrilium ion (**2a**),  $H-C\equiv N^+-CH_3$ , has an electrophilicity value of 7.50 eV and a  $\Delta\omega = 6.26$  eV, when the DA reaction takes place with isoprene. According to this model, chemical substitution in the diene with electron-releasing groups make it less electrophilic in global terms. For instance, substitution of the terminal hydrogen atom in ion nitrilium **2a** by a methyl or ethyl group brings the electrophilicity power from 7.50 eV in ion **2a** to 6.22 and 6.05 eV in compounds **2b** and **2c**. However, if the substituent is a phenyl group the electrophilicity value increases until 7.82 eV, ion **2d**, and 10.09 eV when it is substituted by the electron-withdrawing  $-COCH_3$  group in compound **2e**. Replacement of the terminal hydrogen by a halogen, bromine in ion **2f**, produces a slight decrease in the electrophilic power of 0.56 eV. In striking contrast to the behavior of ions **1b**, its isomers **2a** react readily with isoprene to give the Diels-Alder cycloadduct [35]. Eberlin *et al.* found that a dramatic change in reactivity was observed when the methyne hydrogen in **2a** was replaced by a methyl (**2b**), ethyl (**2c**), or phenyl (**2d**) group, respectively. These nitrilium ions display a very low overall reactivity and the proton transfer products are therefore dominated [35]. Comparing this result with the electrophilicity power, we can observe that ions **2b** and **2c** have a value lower than **2a**, however the compound **2d** is slightly higher.

### Nitrilium Ion 3

Experimentally, the ion **3a** ( $H-C\equiv N^+-C_2H_5$ ) reacts with isoprene to form the corresponding adduct, although the extent to which this reaction occurs and also the overall reactivity of the ion are both smaller than for ion **2a** [35]. In

Table 1 we can compare the reactivity indexes of these ions. The electrophilicity value is 7.50 eV for ion **2a** and 7.39 eV for **2b**, and a value of nucleophilicity of -7.53 eV and -5.90 eV, respectively.

### Immonium Ions 4

A systematic series of several immonium ions (**4a-j**) was investigated for their ability to undergo gas-phase  $[4+2^+]$  cycloaddition reactions with isoprene by Eberlin *et al.* [35]. The ion **4a** reacts extremely with isoprene to form an abundant DA adduct. Alkyl substitution dramatically decreases the extent to which both the cycloaddition and proton transfer reactions occur. The N-phenyl-substituted (**4g**) and N-acetyl substituted (**4h**) ions favor cycloaddition as the two immonium ions that correspond to the protonated forms of the 2-aza (**4i**) and 1-aza-butadiene (**4j**). The vinyl-substituted ion **4j**, however, is much less reactive with isoprene than ion **4i** [35]. According to the electrophilicity values obtained in Table 1, the  $\Delta\omega$  for the DA reaction between ion **4a** and isoprene has the very high value of 8.40 eV and is expected to have an ionic character. Inclusion of an alkyl group on the ion  $CH_2 = NH_2^+$  decreases the  $\Delta\omega$  between 7.94 eV for ion **4b** and 6.70 for ion **4f**. When a hydrogen atom of ion **4a** is substituted by an electron-withdrawing group as phenyl (ion **4g**), brings the  $\Delta\omega$  to 9.92 eV, the same value when the substituent is the  $-COCH_3$  group (ion **4h**). The two last ions, **4i** and **4j**, are isomers but they have different reactivity indexes, the first ion is more electrophile ( $\omega = 11.00$  eV) than the second ( $\omega = 10.39$  eV) and, as a result, the DA reaction of ion **4i** with isoprene is much more reactive than ion **4j**. This prediction is in clear agreement with the experimental results [35].

## CONCLUSIONS

The global electrophilicity index, defined within the DFT becomes a useful quantity to classify the dienes and dienophiles currently used in Diels-Alder reactions on a unique scale of electrophilicity. Reactivity indexes were used to test the electrophilicity trend of ionic  $[4+2^+]$  Diels-Alder cycloaddition to nitrilium and immonium ions in the gas phase. The electrophilicity order obtained with the reactivity indexes shows good correlations with the experimental results. Substituted ions with electron-withdrawing groups markedly increase the electrophilic reactivity of the compound.

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## REFERENCES

- [1] Geerlings, P.; De Proft, F.; Langenaeker, W.; Conceptual density functional theory. *Chem. Rev.*, **2003**, 103, 1793.

- [2] Parr, R. G.; Weitao, Y. Density-Functional Theory of Atoms and Molecules, Oxford University Press, New York, **1989**.
- [3] Yang, W.; Mortier, W. J.; The use of Global and Local Molecular-Parameters for the Analysis of the Gas-Phase Basicity of Amines. *J. Am. Chem. Soc.*, **1986**, 108, 5708.
- [4] Hückel, E.; Quantum Theoretical Contributions to the benzene problem. I. The electron configuration of benzene and related compounds. *Z. Physik*, **1931**, 71, 204.
- [5] Heisenberg, W.; Multi-body problem and resonance in the quantum mechanics. *Z. Physik*, **1926**, 38, 411.
- [6] Heitler, W.; London, F.; Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik *Z. Physik*, **1927**, 41, 455.
- [7] Hurley, A. C.; Lennardjones, J.; Pople, J. A.; The molecular orbital theory of chemical valency. 16. A theory of paired-electrons in polyatomic molecules. *Proc. R. Soc. Lond.*, **1953**, 220, 446.
- [8] Fukui, K.; Role of Frontier Orbitals in Chemical Reactions. Science, **1982**, 218, 747.
- [9] Chermette, H.; Chemical reactivity indexed in density functional theory. *J. Comput. Chem.*, **1999**, 20, 129.
- [10] Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E.; Electronegativity - Density functional viewpoint. *J. Chem. Phys.*, **1978**, 68, 3801.
- [11] Parr, R. G.; Pearson, R. G.; Absolute Hardness - Companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* **1983**, 105, 7512.
- [12] Toro-Labbe, A.; Characterization of chemical reactoins from the profiles of energy, chemical potential and hardness. *J. Phys. Chem. A*, **1999**, 103, 4398.
- [13] Parr, R. G.; Yang, W. T.; Density Functional - Approach to the Frontier-Electron Theory of Chemical Reactivity. *J. Am. Chem. Soc.*, **1984**, 106, 4049.
- [14] Parr, R. G.; Von Szentpaly, L.; Liu, S. B.; Electrophilicity index. *J. Am. Chem. Soc.*, **1999**, 121, 1922.
- [15] Campodónico, R.; Andrés, J.; Aizman, A.; Contreras, R.; Nucleofugality index in  $\alpha$ -elimination reactions. *Chem. Phys. Lett.*, **2007**, 439, 177.
- [16] Ayers, P. W.; Anderson, J. S. W.; Rodriguez, J. I.; Jawed, Z.; Indices for predicting the quality of leaving groups. *Phys. Chem. Chem. Phys.*, **2005**, 7, 1918.
- [17] Ayers, P. W.; Anderson, J. S. W.; Bartolotti, L. J.; Perturbative perspectives on the chemical reaction prediction problem. *Int. J. Quantum Chem.*, **2005**, 101, 520.
- [18] Geerlings, P.; De Proft, F.; Conceptual DFT: the chemical relevance of higher response functions. *Phys. Chem. Chem. Phys.*, **2008**, 10, 3028.
- [19] Contreras, R.; Andrés, J.; Safont, V. S.; Campodónico, R.; Santos, J. G.; A Theoretical Study of the Relationship between Nucleophilicity and Ionization Potentials in Solution Phase. *J. Phys. Chem. A*, **2003**, 107, 5588.
- [20] Guerra, D.; Castillo, R.; Andrés, J.; Fuentealba, A.; Aizman, A.; Contreras, R.; Homofugality: A new reactivity index describing the leaving group ability in homolytic substitution reactions. *Chem. Phys. Lett.*, **2006**, 424, 437.
- [21] Cedillo, A.; Contreras, R.; Galván, M.; Aizman, A.; Andrés, J.; Safont, V. S.; *J. Phys. Chem. A*, Nucleophilicity Index from Perturbed Electrostatic Potentials. **2007**, 111, 2442.
- [22] Swain, C. G.; Scott, C. B.; Quantitative Correlation of Relative Rates. Comparison of Hydroxide Ion with Other Nucleophilic Reagents toward Alkyl Halides, Esters, Epoxides and Acyl Halides. *J. Am. Chem. Soc.*, **1953**, 75, 141.
- [23] Richie, D. D.; Cation-anion combination reactions. 26. A review. *Can. J. Chem.*, **1986**, 64, 2239.
- [24] Legon, A. C.; Millen, D. J.; Hydrogen bonding as a probe of electron densities: limiting gas-phase nucleophilicities and electrophilicities of B and HX. *J. Am. Chem. Soc.*, **1987**, 109, 356.
- [25] Mayr, H.; Patz, M.; Scale of Nucleophilicity and Electrophilicity: A System for Ordering Polar Organic and Organometallic Reactions. *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 938.
- [26] Pérez, P.; Toro-Labbe, A.; Aizman, A.; Contreras, R.; Comparison between Experimental and Theoretical Scales of Electrophilicity in Benzhydryl Cations. *J. Org. Chem.*, **2002**, 67, 4747.
- [27] Jaramillo, P.; Domingo, L. R.; Pérez, P.; Towards an intrinsic nucleofugality scale: The leaving group (LG) ability in CH3LG model system. *Chem. Phys. Lett.*, **2006**, 420, 95.
- [28] Campodónico, R.; Santos, J. G.; Andrés, J.; Contreras, R.; Mechanisms of the substitution reactions of phosphoramidites and their congeners. *J. Phys. Org. Chem.*, **2004**, 17, 1.
- [29] Domingo, L. R.; Sáez, J. A.; Understanding the mechanism of polar Diels-Alder reactions. *Org. Biomol. Chem.*, **2009**, 7, 3576.
- [30] Campodónico, R.; Santos, J. G.; Andrés, J.; Contreras, R.; Mayr, H.; Patz, M.; Scales of Nucleophilicity and Electrophilicity: A System for Ordering Polar Organic and Organometallic Reactions. *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 938.
- [31] Chattaraj, P. K.; Sarkar U.; Roy, D. R.; Electrophilicity index. *Chem. Rev.*, **2006**, 106, 2065.
- [32] Parr, R. G.; Von Szentpaly, L.; Liu, S. B.; Electrophilicity Index. *J. Am. Chem. Soc.*, **1999**, 121, 1922.
- [33] Domingo, L. R.; Aurell, M. J.; Pérez, P.; Contreras, R.; Quantitative characterization of the global electrophilicity power of common diene/dienophile pairs in Diels-Alder reactions. *Tetrahedron*, **2002**, 58, 4417.
- [34] Wincel, H.; Fokkens, R. H.; Nibbering, N. M. M.; On the structure and isomerization/dissociation reactions of C3H6N+ generated by methylation of acetonitrile in the gas phase. *Int. J. Mass Spectrom. Ion Processes*, **1989**, 91, 339.
- [35] Eberlin, M. N.; Morgon, N. H.; Yang, S. S.; Shay, B. J.; Cooks, R. G.; Polar [4+2+] Diels-Alder Cycloaddition to Nitrilium and Immonium Ions in the Gas Phase: Applications of Multiple Stage Mass Spectrometry in a Pentaquadrupole Instrument. *Am. Soc. Mass Spectrom.*, **1995**, 6, 1.
- [36] Domingo, L. R.; Chamorro, E.; Pérez, P.; Understanding the Reactivity of Captodative Ethylenes in Polar Cycloaddition Reactions. A Theoretical Study. *J. Org. Chem.*, **2008**, 73, 4615.
- [37] Kohn W.; Sham, L. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.*, **1965**, 140, 1133.
- [38] Frisch, G. W. T. M. J.; Schlegel, H. B.; Scuseria, G. E.; Robb, J. R. C. M. A.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, J. C. B. K. N.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, B. M. V.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, H. N. G. A.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, J. H. R.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, M. K. H.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, J. J. C.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, R. C. A. J.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, G. A. V. K.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, S. D. V. G.; Daniels, A. D.; Strain, M. C.; Farkas, D. K. M. O.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. V. O. J. B.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, B. B. S. J.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, R. L. M. I.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, A. N. C. Y.; Challacombe, M.; Gill, P. M. W.; Johnson, W. C. B. Wong, M. W.; Gonzalez, C.; Pople, J. A. in Gaussian03, Inc., Pittsburgh PA, **2003**.
- [39] Ziegler, T.; Approximate density functional theory as a practical tool in molecular energetics and dynamics. *Chem. Rev.*, **1991**, 91, 651.
- [40] Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, **1993**, 98, 5648.
- [41] Lee, C.; Yang, W. Parr, R. G.; Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **1988**, 37, 785.
- [42] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab initio Molecular Orbital Theory, New York, **1986**.
- [43] Schlegel, H. B.; Optimization of equilibrium geometries and transition structures. *J. Comput. Chem.*, **1982**, 3, 214.
- [44] Schlegel H. B. in Geometry Optimization on Potential Energy Surface, (Ed. D. R. E. Yarkony), World Scientific Publishing, Singapore, **1994**.