# Inter*net* Electronic Journal of
# Molecular Design

# Aromatization Energy of Cyclopropenyl Cation

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**Citation of the article:**
C. H. Suresh and N. Koga, Aromatization Energy of Cyclopropenyl Cation, *Internet Electron. J. Mol. Des.* **2002**, *1*, 603–609, http://www.biochempress.com.

# Aromatization Energy of Cyclopropenyl Cation[#]

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**Abstract**

**Motivation.** A radical based homodesmotic reaction (HDR) is designed for the accurate calculation of the aromatic stabilization energy of cyclopropenyl cation. The energy of the HDR ($\Delta E$) accounts for the energy released when the cyclic $2\pi$ electron cationic conjugation is changed to a linear $2\pi$ electron cationic conjugation. In other words, $\Delta E$ corresponds to the aromatic stabilization energy of cyclopropenyl cation. The value of the aromatic stabilization at G2 level is found to be 127.0 kJ/mol. This stabilization energy is much smaller as compared to the value of 247.3 kJ/mol calculated by Glukhovtsev *et al.* in 1996 using a reaction falsely described as a homodesmotic reaction. In fact, their value accounted mainly the total $\pi$ electron conjugation energy of $(C_3H_3)^+$ and not to its aromatic stabilization.

**Method.** B3LYP/6–31G(d,p) and G2 level calculations on homodesmotic reaction were used in this study.

**Results.** The aromatic stabilization energy of cyclopropenyl cation at B3LYP/6–31G(d,p) and G2 levels are, respectively, 115.4 and 127.0 kJ/mol.

**Conclusions.** A new homodesmotic reaction is designed for the accurate estimation of the aromatic stabilization energy of cyclopropenyl cation.

**Keywords.** Aromaticity; cyclopropenyl cation; DFT calculations; G2 calculations; homodesmotic reaction; isodesmic reaction.

| Abbreviations and notations | |
| --- | --- |
| HDR, homodesmotic reaction | ZPVE, zero–point vibrational energy |
| IDR, isodesmic reaction | |

# 1 INTRODUCTION

Aromaticity is a fundamental concept in chemistry [1-6]. Among aromatic hydrocarbons, the cyclopropenyl cation is the simplest one. This cation plays a central role in many important processes in physical and organic chemistry. The spectroscopic techniques have established a cyclic planar $D_{3h}$ structure for this cation [7-10]. This was also confirmed by several *ab initio* quantum chemical calculations [11-13]. Isodesmic and homodesmotic reactions are frequently used for the

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study of aromaticity from the energetic point of view [14–16]. In isodesmic reactions (IDR), there is a matching of the bonds in reactants and products species according to their formal type (single, double, or triple). George *et al.* [16–17] used a subclass of IDR known as homodesmotic reaction (HDR) to evaluate the stabilization energies for cyclic conjugated hydrocarbons. In both sides of HDR reactions there are equal numbers of each type of carbon–carbon bonds ($C_{sp3}$–$C_{sp3}$, $C_{sp2}$–$C_{sp3}$, $C_{sp2}$–$C_{sp2}$, $C_{sp2}$=$C_{sp2}$, *etc.*) as well as equal number of each type of carbon atom ($C_{sp3}$, $C_{sp2}$, *etc.*) with zero, one, two, and three hydrogen atoms.

In 1976 Radom *et al.* [11] have calculated the resonance energy of $(C_3H_3)^+$ using the reaction given in Eq. (1). They found a value of 290.51 kcal/mol for this at the HF/6-31G*//HF/STO-3G level. In 1996 Glukhovtsev *et al.* [13] calculated the energetics of the same reaction at the G2 level. However, they describe the reaction as a HDR incorrectly, and also consider the energy of the reaction as the aromatic stabilization energy of $(C_3H_3)^+$ to obtain a value of 247.3 kJ/mol. In true sense it is not an HDR because at the reactant and product sides of the reaction, the formal type of the C–C bonds are not balanced. For example, at the reactant side there are three $C_{sp2}$–$C_{sp2}$ bonds and three $C_{sp3}$–$C_{sp3}$ bonds. On the other hand, the product side has one $C_{sp2}$–$C_{sp2}$, one $C_{sp3}$–$C_{sp3}$ and four $C_{sp3}$–$C_{sp2}$ bonds. Because of this imbalance in the C–C bonding, the aromaticity value obtained by them could be erroneous. One may also note that the reactant side has no hydrogen atoms that can participate in hyperconjugative interaction with the ring carbon atoms. But the product side has six such hydrogen atoms. Another point to be noted in this reaction is that as compared to the reactant side, the charge and the π bond are separated in the product side, meaning that there is no π conjugation in the product side. Therefore, the energy of the reaction is actually a good approximation to the total π electron conjugation energy of $(C_3H_3)^+$ and not to its aromatic stabilization. Aromatic stabilization of a molecule corresponds to the extra stabilization achieved by that molecule due to π electron cyclic delocalization as compared to a matching π electron acyclic delocalization. Therefore, in order to get the aromatic stabilization of $(C_3H_3)^+$ it is necessary to subtract the linear π conjugation energy of the allyl cation from the energy of the reaction in Eq. (1).



$$(1)$$
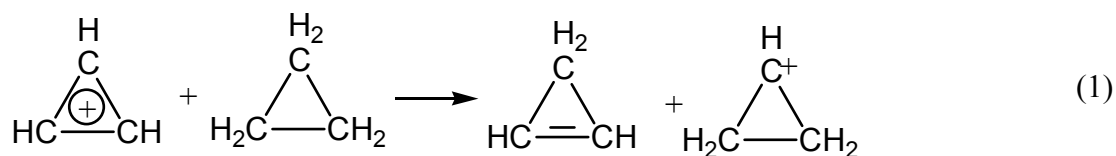
Very recently, we have proposed radical based homodesmotic reactions [18] for the accurate calculation of the aromaticity of benzene and antiaromaticity of cyclobutadiene, cf. Eqs. (2) and (3). In these reactions, the hybridization type as well as the bonding nature of the C–C and C–H bonds are conserved in both sides of the reactions. Further, the strain effects are almost balanced at both sides of the reaction because of the use of cyclic radical systems. The energy of these reactions therefore represents the energy released when an *n* electron cyclic conjugation changed to an *n* electron linear conjugation. At the MP4(SDQ)/6–31G(d,p) level, the reaction in Eq. (2) predicted an

aromatic stability of 121.76 kJ/mol for benzene and the reaction in Eq. (3) predicted an antiaromatic destabilization of 171.76 kJ/mol for cyclobutadiene.



$$(2)$$



$$(3)$$
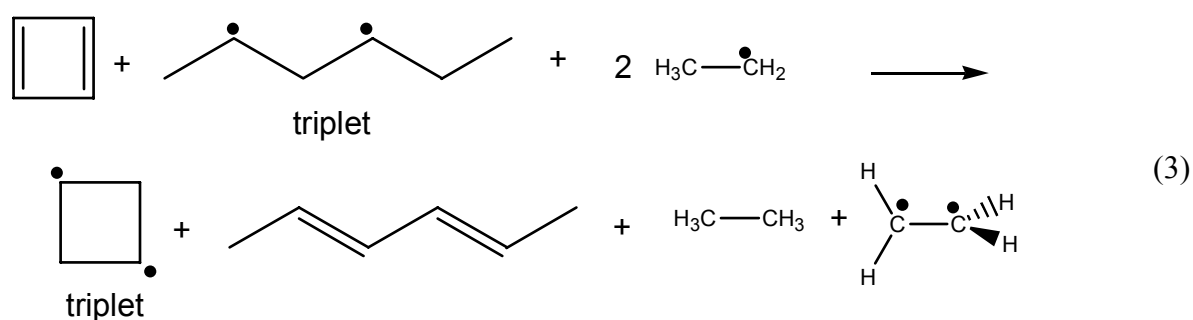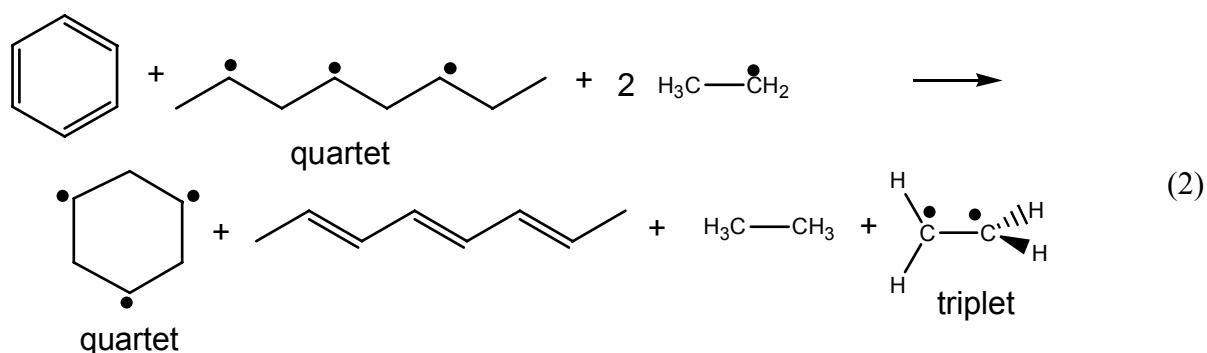
It is expected that a radical based homodesmotic reaction similar to that given in Eqs. (2) or (3) could give a more accurate quantitative value for the aromaticity of cyclopropenyl cation. In this work such a reaction is studied.

## 2 MATERIALS AND METHODS

All calculations were performed with the Gaussian 98 suite of programs [19] at the B3LYP/6-31G(d,p) level [20,21] density functional theory and *ab initio* G2 level methods [22] as implemented in the package. At first all the molecules studied herein were optimized at the B3LYP/6-31G(d,p) level. The optimized geometries were confirmed as minima by frequency calculations at the same level of theory. These geometries were further optimized at the MP2(full)/6-31G(d) level for the G2 level calculations. G2 level energy calculations have been done using the MP2 level geometries (default procedure). At the G2 level, the total energy of a molecule approximately corresponds to the total energy at QCISD(T)/6-311+G(3df,2p) level for MP2(full)/6-31G(d) optimized geometry, with the incorporation of scaled HF/6-31G(d) zero-point vibrational energies (ZPVEs) and a so-called higher level correction. To obtain theoretical enthalpies at 298 K, vibrational contributions to temperature corrections were calculated with the use of harmonic frequencies computed at the HF/6-31G(d) level and scaled by 0.8929 according to the G2 scheme.

## 3 RESULTS AND DISCUSSION

The IDR reaction given in Eq. (4) represents the change of the cyclic $2\pi$ electron cationic conjugation to a linear $2\pi$ electron cationic conjugation. Eq. (4) can be made homodesmotic by adding Eq. (5) to it, which gives Eq. (6). Eq. (5) represents the change of one $C_{sp3}$–$C_{sp2}$ and one $C_{sp2}$–H bonds to one $C_{sp2}$–$C_{sp2}$ (formal single bond) and one $C_{sp3}$–H bonds. The reaction in Eq. (6) is a good example of a HDR because in this reaction, not only the number and types of CC and CH bonds are conserved, but also the number of hyperconjugated hydrogen atoms are equal at the reactant and product sides. Moreover, the use of the cyclic system **P2** at the product side is expected to cancel out a major portion of the strain energy of cyclopropenyl cation in the reactant side. For the biradical systems the highest spin state, the triplet state is used in the calculation. Therefore, the $C_{sp2}$–$C_{sp2}$ bond of **P3** in the product side can be considered as a formal $C_{sp2}$–$C_{sp2}$ single bond. It means that the number of formal $C_{sp2}$–$C_{sp2}$ single bonds are also conserved in the reaction, two each at the reactant and product sides of Eq. (6).



$$\text{(4)}$$



$$\text{(5)}$$



$$\text{(6)}$$
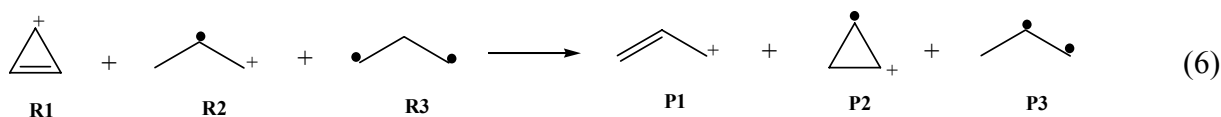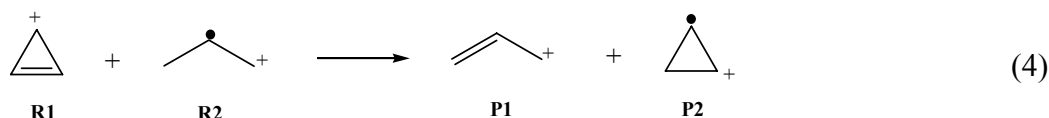
The optimized geometries of the systems in Eq. (6) at the MP2(full)/6–31G(d) levels are depicted in Figure 1 along with their B3LYP/6–31G(d,p) C–C bond length parameters. In general, all these systems show nearly the same geometrical parameters at both B3LYP/6–31G(d,p) and MP2(full)/6–31G(d) levels of theories. The cyclopropenyl cation **R1** has a planar $D_{3h}$ structure with C–C bond length equal to 1.366 Å. The mass spectrometric and spectroscopic experimental data as well as previous *ab intio* calculations support this structure as the most stable isomer of the $(C_3H_3)^+$ molecular cation [8–14]. The charge of this cation is equally distributed on the carbon atoms. As compared to $(C_3H_3)^+$, the linear $\pi$ conjugated allyl cation (**P1**) has longer C–C bond length (1.382 Å) and the charge is largely concentrated on the terminal carbon atoms (Figure 1). In the case of the acyclic radical cation **R2** and the corresponding cyclic radical cation **P2**, the charge and spin density are mainly shared by the $C_{sp2}$ carbon atoms. The spin density values of the biradical triplet systems **R3** and **P3** suggest that the unpaired electrons lie exclusively on the $C_{sp2}$ carbon atoms. There is only a small increase in the over all C–C bond lengths on going from the reactant side to the product side. For instance, at MP2 level, the sum of C–C bond lengths for the reactant and product sides are 9.954 and 9.979 Å respectively (corresponding B3LYP values are 9.952 and 9.993 Å,

respectively). What is the major change when **R1** + **R2** + **R3** gives **P1** + **P2** + **P3**? It is undoubtedly the change of the cyclic $2\pi$ electron delocalization in **R1** to the linear $2\pi$ electron delocalization in **P1**. In other words it corresponds to the transformation of an aromatic system to a nonaromatic system. All other electronic effects including the strain effects are nearly conserved in both sides of the reaction. It means that the energy released $\Delta E$ in the process **R1** + **R2** + **R3** → **P1** + **P2** + **P3** is a very good approximation to the extra stabilization of cyclopropenyl cation due to the cyclic $\pi$ electron conjugation as compared to the matching linear $\pi$ conjugation in the allyl cation. It implies that $\Delta E$ is in fact a very good approximation to the classical aromatization energy of $(C_3H_3)^+$. At the B3LYP/6–31G(d,p) level, $\Delta E$ is 115.39 kJ/mol. On the other hand, the G2 level value of $\Delta E$ at 0 K and 298 K are respectively 127.63 and 127.03 kJ/mol. These values are much smaller as compared to the value of 247.3 kJ/mol calculated by Glukhovtsev *et al*. [13] using the reaction given in Eq. (1). In fact, their value accounted mainly the total $\pi$ electron conjugation energy of $(C_3H_3)^+$ and not its aromatic stabilization.
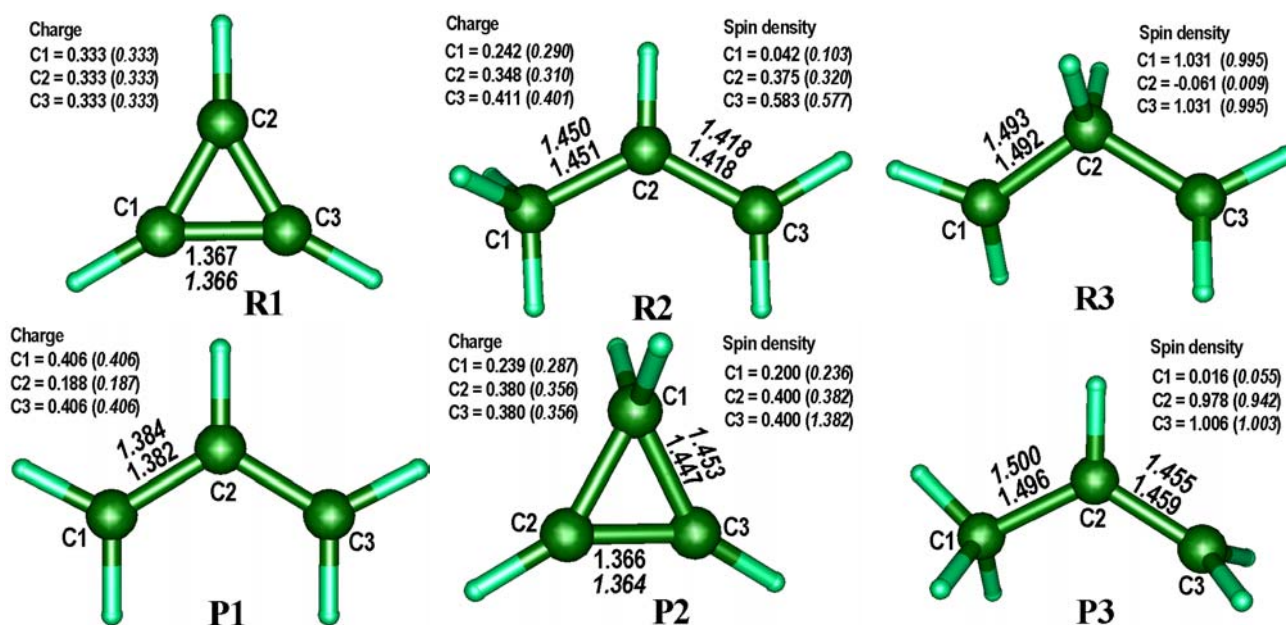


**Figure 1.** Optimized geometries at the MP2(full)/6–31G(d) level. Mulliken atomic charges and spin densities with hydrogens summed into carbon atoms are also given. MP2 values are given in regular font. All the values in italics are at the B3LYP/6–31G(d,p) level.

Note that since **P3** has radical centers on adjacent carbon atoms, the radical–radical interaction in it could be slightly higher than that in **R3**. Yet another point is that the strain energy of **R1** at the reactant side is accounted by the strain energy of **P2** at the product side. However, since **P2** has a larger triangular structure than **R1**, the ring strain of the former could be slightly smaller than the latter. In other words, the radical effects are slightly over–estimated and the ring strain effects are slightly under–estimated at the product side of the reaction in Eq. (6) leading to a partial cancellation of both effects when $\Delta E$ is calculated.

# 4 CONCLUSIONS

A radical based homodesmotic reaction, Eq. (6), is designed for a very good estimate of the aromatic stabilization of $(C_3H_3)^+$. In this reaction the number of each type of carbon–carbon bonds ($C_{sp3}$–$C_{sp3}$, $C_{sp2}$–$C_{sp3}$, $C_{sp2}$–$C_{sp2}$, $C_{sp2}$=$C_{sp2}$), number of each type of carbon–hydrogen bonds ($C_{sp3}$–H, $C_{sp2}$–H) and the number of each type of carbon atoms ($C_{sp3}$, $C_{sp2}$) with zero, one, two, and three hydrogen atoms are conserved. Further, the strain effects are nearly balanced at both sides of the reaction. The $\Delta E$ of the reaction provides a very good estimate of the extra stabilization of the cyclic $2\pi$ electron cationic cyclic conjugation as compared to a matching $2\pi$ electron cationic acyclic conjugation. The aromatic stabilization energy of $(C_3H_3)^+$ ($\Delta E$) at the B3LYP/6–31G(d,p) level is 115.39 kJ/mol and its G2 level value at 0 K and 298 K are, respectively, 127.63 and 127.03 kJ/mol.

**Acknowledgment**

**Supplementary Material**

Optimized geometries and energies at the B3LYP/6–31G(d,p) and MP2(full)/6–31G(d) levels and G2 level energetics for the systems **R1**, **R2**, **R3**, **P1**, **P2**, and **P3**.

# 5 REFERENCES

[1]  P. J. Garrat, Aromaticity, Wiley, New York, 1986.

[2]  Special issue of *Chem. Rev*. on Aromaticity, **2001**, *101*, 1115-1566, guest editor P. v. R. Schleyer.

[3]  T. M. Krygowski, M. K. Cyranski, Z. Czarnocki, G. Häfelinger, and A. R. Katritzky, Aromaticity: A Theoretical Concept of Immense Practical Importance*, Tetrahedron* **2000**, *56*, 1783-1796.

[4]  P. v. R. Schleyer and H. Jiao, What is Aromaticity, *Pure Appl. Chem*. **1996**, *68*, 209-218.

[5]  V. I. Minkin, M. N. Glukhovtsev, and B. Y. Simkin, Aromaticity and Antiaromaticity. Electronic and Structural Aspects, J. Wiley, New York, 1994.

[6]  M. K. Cyranski, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, To What Extent Can Aromaticity Be Defined Uniquely? *J. Org. Chem*., **2002**, *67*, 1333-1338.

[7]  R. Breslow and J. T. Groves, Cyclopropenyl cation. Synthesis and characterization, *J. Am. Chem. Soc.* **1970**, *92*, 984–987.

[8]  P. J. Ausloos and S. G. Lias, Discrimination of $C_3H_3^+$ Structures on the Basis of Chemical Reactivity*, J. Am. Chem. Soc.* **1981**, *103*, 6505–6507.

[9]  D. W. Minsek and P. Chen, Photoelectron Spectrum of the Propargyl Radical in a Supersonic Beam*, J. Phys. Chem*. **1990**, *94*, 8399–8401.

[10]  G. B. I. Scott, D. A. Fairley, C. G. Freeman, M. J. McEvan, and V. G. Anicich, $C_mH_n^+$ Reactions with Atomic and Molecular Nitrogen: An Experimental Study, *J. Phys. Chem. A* **1999**, *103*, 1073–1077.

[11]  L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXII. Structures and Stabilities of $C_3H_3^+$ and $C_3H^+$ Cations*, J. Am. Chem. Soc*. **1976**, *98*, 10–14.

[12]  K. Raghavachari, R. A. Whiteside, J. A. Pople, and P. v. R. Schleyer, Molecular Orbital Theory of the Electronic Structure of Organic Molecules. 40. Structures and Energies of C1-C3 Carbocations Including Effects of Electron Correlation, *J. Am. Chem. Soc.* **1981**, 103, 5649–5657.

[13]  M. N. Glukhovtsev, S. Laiter, and A. Pross, Thermochemical Assessment of the Aromatic and Antiaromatic Characters of the Cyclopropenyl Cation, Cyclopropenyl Anion, and Cyclopropenyl Radical: A High-Level Computational Study, *J. Phys. Chem*. **1996**, *100*, 17801–17806.

[14]  W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, Molecular Orbital Theory of the Electronic Structure of Organic Compounds. V. Molecular theory of Bond Separation*, J. Am. Chem. Soc*. **1970**, *92*, 4796–4801.

[15] L. Radom, W. J. Hehre, and J. A. Pople, Molecular Orbital Theory of the Electronic Structure of Organic Compounds. VII. Systematic Study of Energies, Conformations, and Bond Interactions, *J. Am. Chem. Soc.* **1971**, *93*, 289–300.

[16] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, An Alternate Approach to the Problem of Assessing Stabilization Energies in Cyclic Conjugated Hydrocarbons, *Theor. Chim. Acta* **1975**, *38*, 121–129.

[17] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, An Alternative Approach to the Problem of Assessing Destabilization Energies (Strain Energies) in Cyclic Hydrocarbons*, Tetrahedron*, **1976**, *32*, 317–323.

[18] C. H. Suresh and N. Koga, Accurate Calculation of Aromaticity of Benzene and Antiaromaticity of Cyclobutadiene: New Homodesmotic Reactions, *J. Org. Chem.* **2002**, 67, 1965–1968.

[19] *Gaussian 98*, *Revision A.9*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al–Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head–Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[20] C. Lee, W. Yang, and R. G. Parr, Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density*, Phys. Rev. B* **1988**, *3*7, 785–789.

[21] A. D. Becke, Density-Functional Thermochemistry. III. The Role of Exact Exchange*, J. Chem. Phys.* **1993**, *98*, 5648–5652.

[22] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, Gaussian-2 theory for molecular energies of first- and second-row compounds*, J.Chem. Phys.* **1991**, *94*, 7221–7230.