ORGANIC LETTERS

2013
Vol. 15, No. 10
2442–2445

Evaluation of Triplet Aromaticity by the Isomerization Stabilization Energy

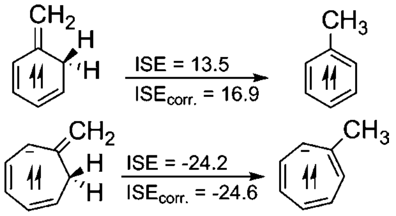
Jun Zhu,[*,†,§] Ke An,[†] and Paul von Ragué Schleyer[‡]

State Key Laboratory of Physical Chemistry of Solid Surfaces, Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China, Department of Chemistry, University of Georgia, Athens, Georgia 30602-2525, United States, and Laboratory of Chemical Genomics, Shenzhen Graduate School of Peking University, Shenzhen 518055, China

jun.zhu@xmu.edu.cn

Received April 3, 2013

ABSTRACT



The many manifestations of aromaticity have long fascinated both experimentalists and theoreticians. Due to their degenerate half-filled MOs, triplet [*n*]annulenes with $4n$ π-electrons are also aromatic, but the degree of their stabilization has been difficult to quantify. The isomerization stabilization energy (ISE) method has been applied to evaluate the triplet aromaticity. The reliability of this approach is indicated by the strong correlation of the ISE results with NICS(1)$_{zz}$, a magnetic indicator of triplet state aromaticity.

Aromaticity, a key organic chemistry concept, has attracted the long and continuing interest of both experimental and theoretical chemists[1] since Kekulé's structural proposals for benzene in 1865.[2] However, aromaticity is not directly observable and its quantitative evaluation depends on the method employed. Nevertheless, various criteria based on geometric,[3] energetic,[4] magnetic,[5] and electronic properties have been used to describe aromatic and antiaromatic systems. Among these approaches, the isomerization stabilization energy (ISE) method proposed by Schleyer and Pühlhofer[4b,6] is an efficient and convenient way to evaluate aromaticity by the energy difference between a methyl derivative of the aromatic system and its nonaromatic exocyclic methylene isomer.

The aromaticity in triplet states is largely unexplored[7] since evaluations are more difficult than those of the singlet ground state (S_0). Among the limited studies available,[8] Gogonea, Schleyer, and Schreiner[8a] noted that several criteria demonstrate the triplet aromaticity of $4n$ π-electron annulenes: planarization, bond-length equalization, aromatic stabilization energies, negative nucleus-independent chemical shifts (NICS),[9] downfield ^{1}H NMR shifts, and significantly elevated diamagnetic susceptibilities.[8a] Fowler et al. identified the aromatic character of the open-shell

---

[†] Xiamen University.

[‡] University of Georgia.

[§] Shenzhen Graduate School of Peking University.

(1) (a) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley: New York, 1994. (b) Thematic Issues of Chemical Reviews, Schleyer, P. v. R., Guest Editor; *Chem. Rev.* 2001, *101*, 1115. (c) Schleyer, P. v. R., Guest Editor; *Chem. Rev.* 2005, *105*, 3433. (d) *Chem. Commun.*, **2012**, themed online issue (www.rsc.org/cc/aroma). (e) Yang, Y.-F.; Cheng, G.-J.; Zhu, J.; Zhang, X.; Inoue, S.; Wu, Y.-D. *Chem.—Eur. J.* **2012**, *18*, 7516.

(2) Kekulé, A. *Bull. Soc. Chim. Fr. (Paris)* **1865**, *3*, 98.

(3) Krygowski, T. M.; Cyranski, M. K. *Chem. Rev.* **2001**, *101*, 1385.

(4) (a) Slayden, S. W.; Liebman, J. F. *Chem. Rev.* **2001**, *101*, 1541. (b) Cyranski, M. K. *Chem. Rev.* **2005**, *105*, 3773.

(5) (a) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842. (b) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301. (c) Gomes, J. A.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349.

(6) Schleyer, P. v. R.; Puhlhofer, F. *Org. Lett.* **2002**, *4*, 2873.

(7) Ottosson, H. *Nat. Chem.* **2012**, *4*, 969.

(8) (a) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1945. (b) Fowler, P. W.; Steiner, E.; Jenneskens, L. W. *Chem. Phys. Lett.* **2003**, *371*, 719. (c) Villaume, S.; Fogarty, H. A.; Ottosson, H. *ChemPhysChem.* **2008**, *9*, 257. (d) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 7303. (e) Feixas, F.; Vandenbusche, J.; Bultink, P.; Matito, E.; Solà, M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20690.

10.1021/ol400908z

states of $4n$ π-electron monocycles on the basis of the ring current.[8b] Ottosson's group examined triplet-state aromatic $4n$ π-electron annulenes in comparison with singlet-state $4n + 2$ π-electron annulenes by computing the bifurcation values of the π-basins of the electron localization function.[8c] Karadakov assessed the ground- and excited-state aromaticity and antiaromaticity in benzene and cyclobutadiene by various magnetic criteria including NICS, ^{1}H NMR shielding, and magnetic susceptibilities calculated using complete-active-space self-consistent field wave functions constructed from gauge-including atomic orbitals.[8d] Feixas et al. analyzed the electron delocalization and aromaticity of a series of low-lying excited states of cyclobutadiene, benzene, and cyclooctatetraene with different multiplicities by means of electron delocalization measures.[8e] As almost all these analyses are based on the magnetic and electronic properties, developing a generally applicable energetic method is important. Can the efficient and convenient ISE method used to evaluate the aromaticity in the S_0 state[6] be applied to the aromaticity in the lowest triplet state (T_1) as well? We report here an extensive study of the aromaticity of the representative set of monocyclic species **1**–**9** in the T_1 state shown in Figure 1.[10]

We first examined a $4n + 2$ π-electron example, with the ISE of the T_1 state of benzene at the B3LYP/6-311++G(d,p) level;[11] this is based on toluene **1b** and its nonaromatic methylenecyclohexadiene isomer **1a** (Scheme 1). According to Baird's rule,[12] the lowest $\pi\pi^*$ triplet state of planar monocyclic conjugated rings with $4n$ π-electrons are aromatic, but the T_1 state of benzene with $4n + 2$ π-electrons should be antiaromatic. Indeed, the computed positive ISE value (13.5 kcal/mol, eq 1) indicates the antiaromaticity of the T_1 state of benzene.

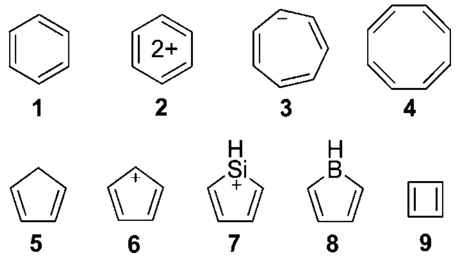
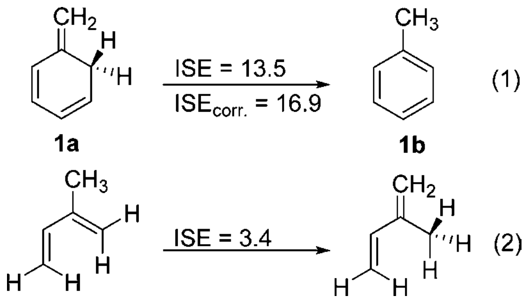


Figure 1. Monocyclic species in this study.

Scheme 1. ISE (kcal/mol) of Benzene in the T_1 State



Since eq 1 has an *anti–syn* diene conformation mismatch,[6] we corrected it by adding the energy of eq 2 in which the fragment geometries were fixed exactly to those in **1a** and **1b** and terminated with hydrogen atoms. The corrected ISE value (16.9 kcal/mol, eq 1) results. Notably, when the T_1 state is used in eq 2, the *anti* conformation is *less stable* than the *syn* form by 3.4 kcal/mol. Optimizing *anti* and *syn* butadiene in both S_0 and T_1 states confirmed this result (Figure 2). In sharp contrast with the butadiene S_0 state where the *anti* conformation is 3.5 kcal/mol *lower* in energy than the *syn* form, the electronic energy of the T_1 state of *anti* butadiene is 2.2 kcal/mol *higher* than that of the *syn* form (Figure 2). The geometrical differences reflect the opposite stabilities of the *anti*- and *syn*-butadiene conformers in the S_0 and T_1 states. The higher stability of the *anti* form in the S_0 state could be due to the better conjugation as indicated by its shorter central C–C bond length (Figure 2). In contrast, the *syn* form of the T_1 state has a planar and more delocalized structure; it has the smallest bond length alternation (BLA).

We investigated the aromaticity of **2**–**9** similarly (Schemes 2 and 3). The corrections applied in Scheme 2 to the benzene dication, the cycloheptatrienyl anion, and cyclooctatetraene were also computed by the same strategy. The corrected ISE of the benzene dication **2** (−14.5 kcal/mol) suggests the aromaticity of its T_1 state, which supports Baird's rule[12a] and contrasts sharply with the antiaromaticity of the T_1 state of benzene indicated by the positive ISE value in eq 1. Interestingly, the corrected ISE of the cycloheptatrienyl anion is almost same as that of cyclooctatetraene, suggesting a comparable magnitude of aromaticity in the T_1 state.

However, when the size of a ring becomes smaller, our correction method employing hydrogen atom termination becomes unreliable due to the significant repulsion between the newly introduced terminal hydrogen atoms. Therefore, the energies for the monocyclic species **5**–**9** with five membered rings or smaller (Scheme 3) are uncorrected. According to Baird's rule,[12a] nonaromatic molecules in the S_0 state should also be nonaromatic in the T_1 state. Indeed, the 0.6 kcal/mol ISE of triplet

---

(9) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075. (c) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863.

(10) The T_1 states of other 6π heterocyclic species, such as pyridine, furan, thiophene, and pyrrole, were also examined. However, the triplet states of all these compounds have significantly pyramidalized geometries at the heteroatoms (such nonplanar structures reduce the antiaromaticity). Morover, the nonplanarity in $(CH)_9^+$ is not neglectable as the largest dihedral angle containing four carbon atoms is 35.3° at the B3LYP/6-311++G(d,p) level. Therefore, these species are not included here and will be discussed elsewhere.

(11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(12) (a) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941. (b) Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317.

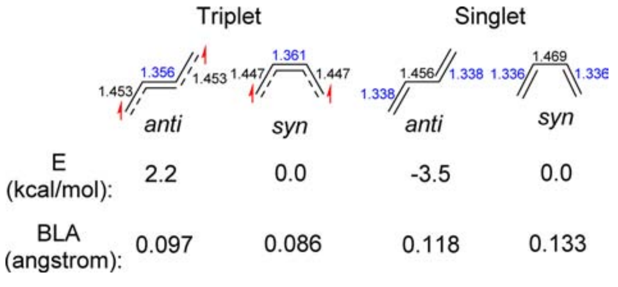
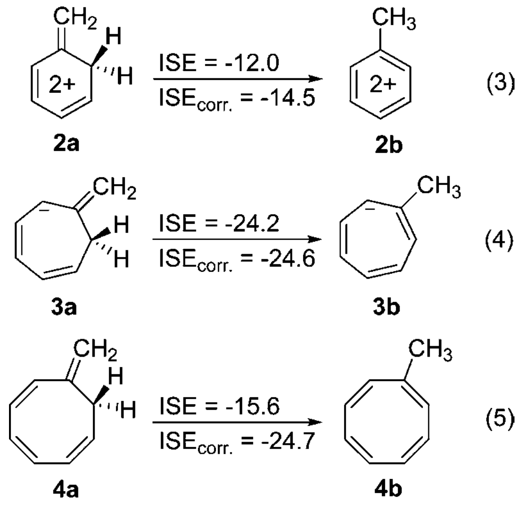


Figure 2. Structures and energies of *anti*- and *syn*-butadiene conformations in their S_0 and T_1 states.

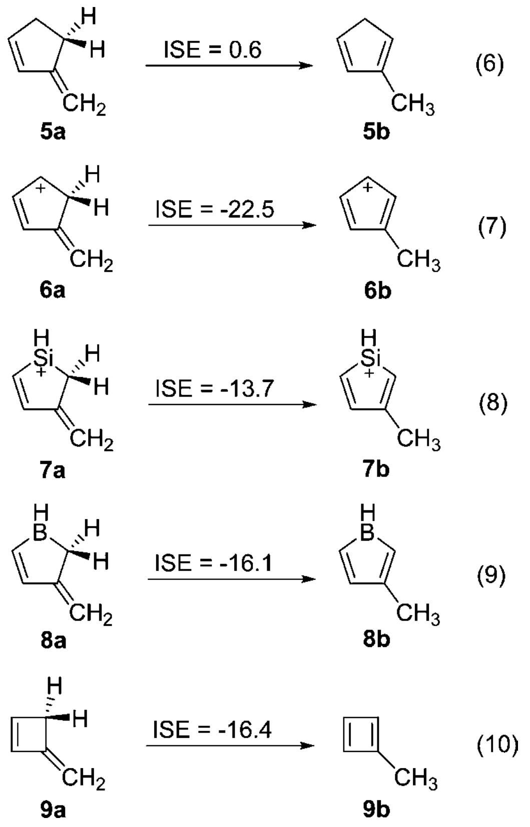
Scheme 2. ISEs (kcal/mol) of Annulenes **2**−**4** in the T_1 State



cyclopentadiene (C_5H_6) (eq 6) suggests its nonaromaticity. All the ISE values of the remaining $4n$ π-species, **6**−**9**, are negative, indicating the aromaticity in the T_1 state. The ISE of **7** is significantly less than that of **6** ($C_5H_5^+$),[13] in line with the weak conjugation indicated by the C−C bond BLAs (0 vs 0.034 Å). The negative values in eqs 8 and 9 suggest that the ISE method is also applicable to planar heterocycles in the T_1 state.[14] The negative value of eq 10 indicates the aromaticity of cyclobutadiene in the T_1 state, in sharp contrast to its antiaromaticity in the S_0 state.[15]

The reliability of this ISE method for these species was examined by comparisons with their readily computed NICS$(1)_{zz}$ values. This version of NICS is the negative of the out-of-plane tensor component of the magnetic shielding at a position 1.0 Å above the ring center.[9c] The NICS$(1)_{zz}$ index performs well and is recommended as a substitute for NICS$(0)_{\pi zz}$, the most advanced and precise NICS version.[9c] Remarkably, the NICS$(1)_{zz}$ values of the cycloheptatrienyl anion **3** (−32.7 ppm) and cyclooctatetraene

Scheme 3. ISEs (kcal/mol) of **5**−**9** in the T_1 State



4 (−32.4 ppm) are very close to each other, in line with their almost identical corrected ISE values (eqs 4 and 5). Moreover, the correlation shown in Figure 3 between the NICS$(1)_{zz}$ values in the T_1 state (NICS$(T_1;1)_{zz}$) and ISE indicates the reliability of both methods.

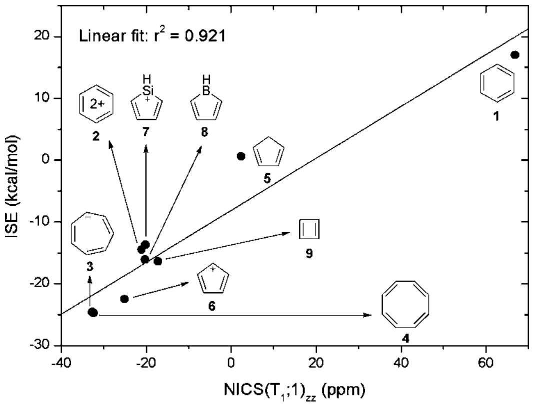


Figure 3. Plot of ISE vs NICS$(T_1;1)_{zz}$ for a series of planar monocyclic species (**1**−**9**) with $4n$ and $4n + 2$ π electrons in the T_1 state.

These methods can also be applied to a bicyclic system. The computed negative ISE value of the T_1 state of pentalene (−12.5 kcal/mol, Scheme 4), as well as the −30.0 ppm NICS$(1)_{zz}$, indicates its aromaticity. These values are in

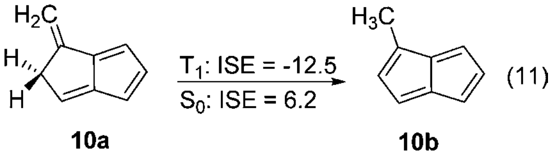
---

[13] (a) Wörner, H. J.; Merkt, F. *J. Chem. Phys.* **2007**, *127*, 034303. (b) Wörner, H. J.; Merkt, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 293.

[14] Nyulaszi, L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872.

[15] Wu, J. I.; Mo, Y.; Evangelista, F. A.; Schleyer, P. v. R. *Chem. Commun.* **2012**, *48*, 8437.

Scheme 4. ISE (kcal/mol) of Pentalene in the S_0 and T_1 States



sharp contrast to the positive (antiaromatic) ISE (6.2 kcal/mol) and NICS(1)$_{zz}$ (56.5 ppm) values in the S_0 state.

In conclusion, the ISE method[6] can be extended to confirm the aromaticity of the T_1 state of $4n$ π-cyclic species.[12] Most annulenes with $4n + 2$ π-electrons in the T_1 state have a strong tendency to reduce their antiaromaticity by nonplanar deformations.

Acknowledgment. This work was supported by the National Science Foundation of China (Nos. 21103142, 21172184, and 21133007), the National Basic Research Program of China (Nos. 2011CB808504), the Program for Changjiang Scholars and Innovative Research Team in University, the Fundamental Research Funds for the Central Universities (2012121021), and, in the USA, NSF Grant CHE-105-7466.

Supporting Information Available. Computational details, selective bond lengths, spatial plots of the π-molecular orbitals for some cyclic species in the T_1 state, and the Cartesian coordinates for all the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.