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Recommendations for the Evaluation of Aromatic Stabilization Energies

Paul von Ragué Schleyer*,[†,‡] and Frank Pühlhofer[†,‡]

Computational Chemistry Annex, Department of Chemistry, University of Georgia, Athens, Georgia 30602-2525, and Institute of Organic Chemistry, University of Erlangen-Nuremberg, Henkestr. 42, D-91054 Erlangen, Germany

schleyer@chem.uga.edu

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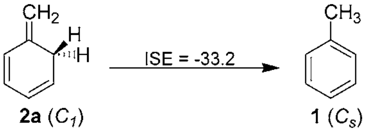
ABSTRACT

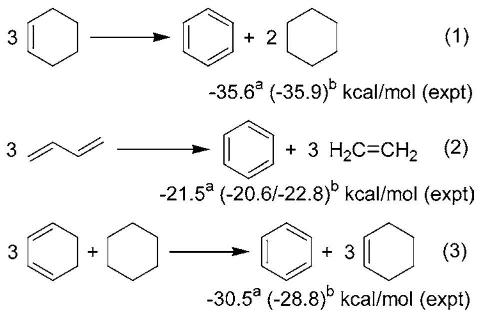


Perturbing influences, such as strain and the presence of heteroatoms, complicate the evaluation of aromatic stabilization energies (ASE). These complications are overcome easily by employing the "isomerization method". This is based on the differences (ISE) between total energies computed for only two species: a methyl derivative of the aromatic system and its nonaromatic exocyclic methylene isomer. The ISEs of benzene, pyridine, and naphthalene as well as the strained [5]paracyclophane, methano[10]annulene, and octadehydro[14]annulene are evaluated.

In 1955, Wheland reviewed authoritatively the various estimates of the resonance energy (RE) of aromatic hydrocarbons based on experimental data.[1] RE values near 36 kcal/mol (eq 1) were representative for benzene.[2]

Such REs purport to measure the total stabilization relative to a hypothetical system lacking resonance, but strain, hyperconjugation, and differences in the types of bonds and the hybridization are not taken into account. Likewise, the normal stabilization present in conjugated, but not aromatic, systems is not considered. Hence, Dewar and Schmeising[3] argued that eq 1 greatly overestimates the "decrease in total π energy" and proposed eq 2 as a measure of the "aromatic stabilization energy" (ASE).

However, this equation has a "fatal flaw." It employs the appreciably lower energy (3.5 kcal/mol at B3LYP/6-311+G** + ZPE) of the *anti* conformation of butadiene, rather than the energy of the *syn* form, which is present in benzene. Consequently, we have proposed the homodesmotic and strain-balanced eq 3, based on 1,3-cyclohexadiene, to evaluate SEs. (Arguably, 1,3-cyclohexadiene, as a cyclic conjugated diene, and cyclohexene are far more appropriate reference standards for SE estimation of cyclic benzenoid hydrocarbons than the often-employed *anti*-butadiene and ethylene).[4] Equation 3 gives ca. 10 kcal/mol higher ASEs than eq 2, roughly three times the *anti*-*syn* butadiene difference.



[a] Calc from $\Delta_f H$ (see ref 2a). [b] Calc from $\Delta_f H$ (see ref 2b).

Given the present availability of accurate energies obtainable from quantum chemical computations, eq 3 can be

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[†] University of Georgia.
[‡] University of Erlangen-Nuremberg.

[1] Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955.

[2] (a) Pedley J. B.; Naylor R. D.; Kirby S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986; p 87ff. (b) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*, NIST Standard Reference Database No. 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD; July 2001 (http://webbook.nist.gov).

[3] Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166.

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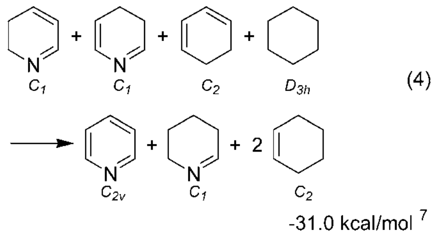
adapted widely, e.g., to obtain reliable SE estimates for acenes[4] and for five-[5] and six-membered heterocycles.[6] Equation 4 for pyridine is illustrative.[7]

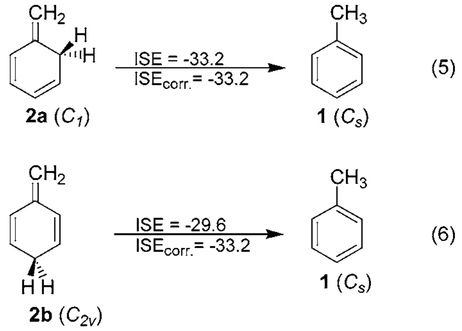


Equations 3 and 4 have the drawback of requiring the computation of several reference molecules. We now espouse, discuss, and evaluate an alternative method requiring the computation of only a single reference molecule, a nonaromatic isomer of the methyl derivative of the aromatic system. This “isomerization stabilization energy“ (ISE) method can be applied to evaluate highly strained systems; three examples are given here.

The underlying idea behind ISE is not new, but due to experimental limitations, there have been few applications. The best-known earlier example is based on the comparison of the enolization energies of cyclohexanone to that of 2,4-cyclohexadienone (the latter gives phenol). This gives an SE estimate of 34 kcal/mol,[8] in close agreement with that derived from eqs 1 and 3. Recent collaborations have reported our computed ISEs for benzene, naphthalene, and their monosila counterparts, as well as for pyrene and its cyclapenta derivatives.[9] We have tested this ISE method extensively and have explored several different variants. Our recommended method is described in detail here and applied to several strained systems, whose ASEs would be difficult to evaluate reliably otherwise.

The value for the benzene ISE can be derived from toluene **1** (which has an ASE practically identical to benzene) and two nonaromatic methylenecyclohexadiene isomers **2a** and **2b** (Scheme 1).[7]

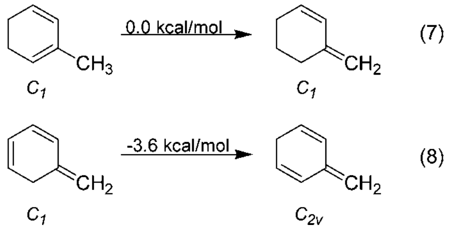
Scheme 1[a]



[a] ISE values in kcal/mol.

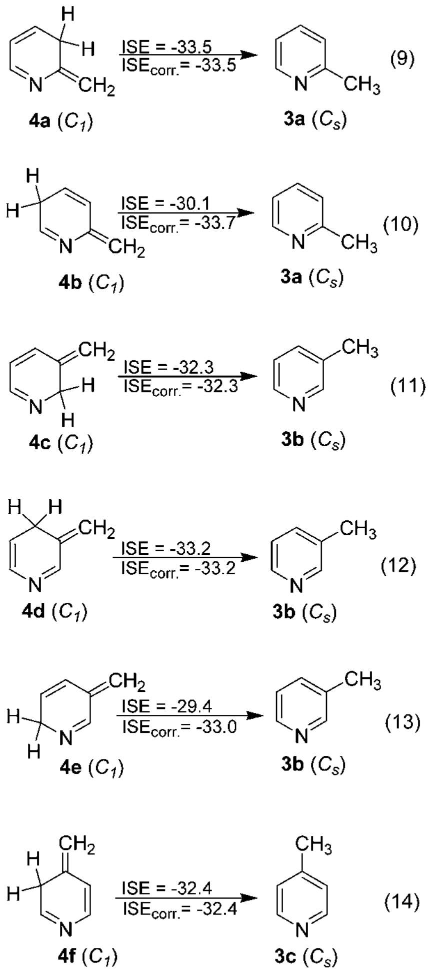
Since eqs 5 and 6 have *anti-syn* diene mismatches, the former is corrected by addition of eq 7 and the latter by addition of eqs 7 and 8 (Scheme 2).[7] The results are in good agreement with experimental values based on eq 3. Note that the 3.6 kcal/mol difference between the ISEs of eqs 7 and 8 corresponds to the *anti-syn* butadiene energy difference.

Scheme 2



The position of the methyl group, e.g., in heterocycles, is seldom critical. The three picolines **3** are related to six nonaromatic methylene isomers **4**; Scheme 3 gives the

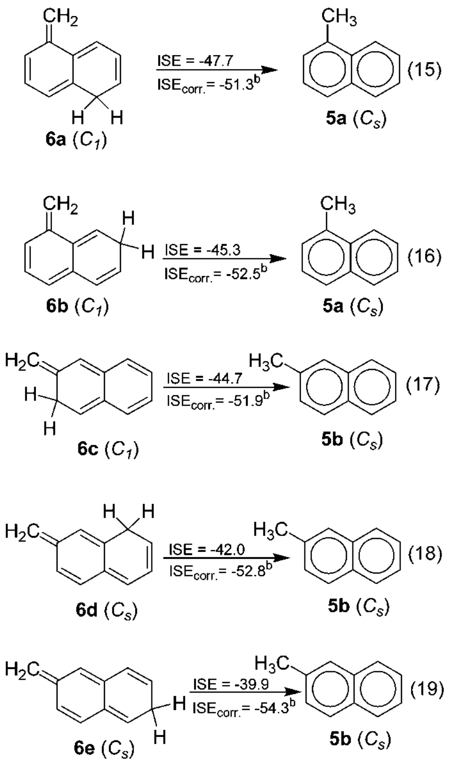
Scheme 3



uncorrected and the corrected ISEs (using the values from Scheme 2 for simplicity). All the corrected values lie within a 1.4 kcal/mol range and are not far from the pyridine ASE, −31.0 kcal/mol, given by eq 4.[7]

The ISE method can be applied to polycyclic aromatic compounds,[4] but the corrections become more critical. The two methylnaphthalenes **5** are related to five methylene isomers **6** in eqs 15−19 (Scheme 4). The corrections needed depend on the number of *anti* diene units in the methylene derivatives **6**. The corrections from Scheme 2, again applied for simplicity, work well. The corrections are based on the total number of *anti* diene units in the exocyclic methylene reference molecule (see footnote b, Scheme 4 for details).

Scheme 4[a]



[a] Most stable geometries; energies in kcal/mol at B3LYP/6-311+G** + ZPE (B3LYP/6-13G*; unscaled. [b]Corrections depend on the number of *anti* diene units in the products, 2 for **6a**, 3 for **6b** and **6c**, 4 for **6d**, and 5 for **6e**. The first correction, based on eq 7, is 0.0. The subsequent corrections, based on eq 8, are −3.6 kcal/mol each.

The corrected ISE values agree with the experimental ASEs for naphthalene calculated by an extension of eq 3 (using *trans*-decalin) and heats of formation for the component molecules, −53.4 ± 2.8 (Pedley et al.)[2a] and −50.5 ± 2.8 kcal/mol (NIST).[2b] The disturbingly large discrepancy between these two experimental values (arising from the accumulation of small differences in the Δ_fH's listed in the two standard compilations), along with the experimental uncertainties, exceed the variations in the ISEs (3 kcal/mol, Scheme 4). Schemes 3 and 4 show that the ISE method is almost independent of the choice of isomer provided the corrections are applied.

The ISE method is especially effective in evaluating the ASEs of the most difficult cases: highly strained systems. There have been no really good ways to disentangle the effects of destabilizing distortions from the stabilization conferred by cyclic electron delocalization.

One of the first and best known nonplanar aromatic, the Vogel−Roth 1,6-methano[10]annulene **7**, is a bridged naphthalene with 10 π electrons.[10] Its ISE (−25.4 kcal/mol) is based on the **7a**−**7b** energy difference (Figure 1). While appreciable, this value is only half the naphthalene ISE (Scheme 4).

The highly distorted benzene, [5]paracyclophane **8**, is an even more extreme case. Schaefer *et al.*'s theoretical investigation analyzed six different criteria, but they could not decide whether **8** was aromatic or not.[11] The energy difference between **8a** and **8b**, with very similar skeletal geometries, gives ISE = −19.5 kcal/mol. Thus, the distortion in **8** reduces the ASE of the benzene moiety by 12 kcal/mol (compare eq 3 and Scheme 1).[12]

Our third example, octadehydro[14]annulene **9**, has inward and outward bowed acetylenes.[13] The ISE, −16.3 kcal/mol based on **9a** and **9b**, is similar to that of other 14 π electron species we have evaluated.[14]

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(4) (a) Schleyer, P. v. R.; Manoharan, M.; Jiao H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643. (b) See Suresh, C. H.; Koga, N. *J. Org. Chem.* **2002**, *67*, 1965, for another approach giving SE = 29 kcal/mol for benzene.

(5) Cyrañski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1338.

(6) Sauers, R. R. et al. Manuscript in preparation.

(7) All energies refer to minima optimized in their most stable geometries at B3LYP/6-311+G** using Gaussian 98 (Frisch, M. J. et al., Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998). Zero-point energies computed at B3LYP/6-31G* were applied.

(8) Minkin, V. J.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley: New York, 1994; p 80.

(9) (a) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nageses, S.l Scheyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336. (b) Havenith, R. W. A.; Jiao, H.; Jenneskens, W.; van Lenthe, J. H.; Sarobe, M.; Schleyer, P. v. R.; Kataoka, M.; Necula, A.; Scott, L. T. *J. Am. Chem. Soc.* **2002**, **124**, 2363. The ISE corrections recommended in the present paper were not applied in these publications or in ref 4a.

(10) (a) Vogel, E.; Roth, H. D. *Angew. Chem.* **1964**, *76*, 145; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 228. (b) Jiao, H.; Hommes, N. J. R. v. E.; Schleyer, P. v. R. *Org. Lett.*, submitted.

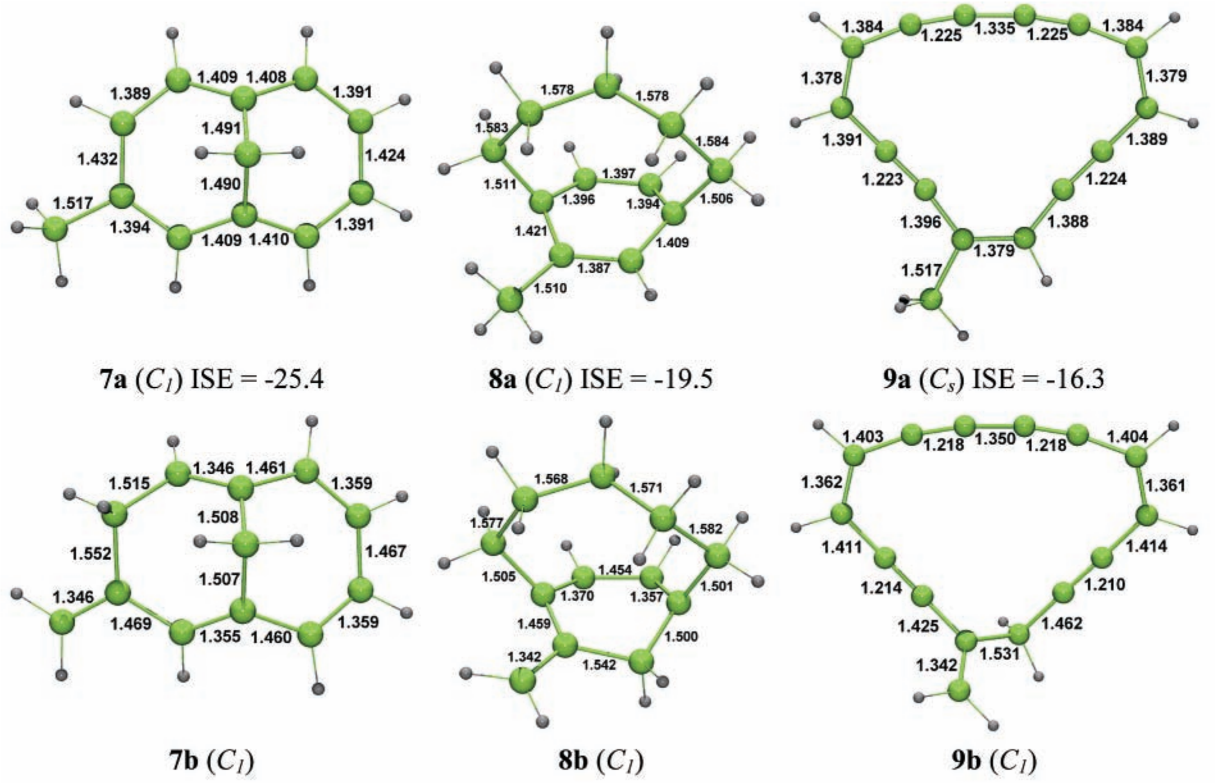
(11) Rice, J. E.; Lee, T. J.; Remington, R. B.; Allen, W. D.; Clabo, D. A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 2902.

(12) The NICS(1) values at B3LYP/6-31+G*//B3LYP/6-311+G** are as follows: benzene (−10.6),[4] toluene (−10.0), pyridine (−10.0), naphthalene (−10.8; each ring),[4] **7** (−15.5/−19.2; 6/10-membered ring),[10] **8** (−13.5/−7.5; into/out of cage), and **9** (−12.2).

(13) Boydston, A. J.; Haley, M. M. *Org. Lett.* **2001**, *3*, 3599.

(14) Schleyer, P. v. R. et al. Unpublished data.

(15) Lower levels of theory give similar results, but the corrections (Scheme 2) should be reevaluated. Where possible, higher symmetry isomers (e.g., **2b**) may be chosen to save computer time. The preferred methyl group conformation generally aligns an H in the plane of the shorter adjacent CC bond. A methyl CH is perpendicular when the adjacent CC bond lengths are equal. As most ISE species lack symmetry (C_1 point group), preoptimization at semiempirical or other lower levels is recommended. As was done here, vibrational frequencies and the derived ZPEs also can be from lower levels.



7a (C_1) ISE = -25.4 **8a** (C_1) ISE = -19.5 **9a** (C_s) ISE = -16.3

7b (C_1) **8b** (C_1) **9b** (C_1)

Figure 1. Structures and ISE values in kcal/mol (C−C bond lengths in Å).

We conclude that the ISE method, with application of the *syn*-*anti* corrections, is easily applied and very effective for evaluating ASEs, particularly of strained systems.[15]

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Supporting Information Available: Detailed computational information for all compounds in Schemes 1−4, Figure 1, and some examples at lower levels of theory are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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