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The Acenes: Is There a Relationship between Aromatic Stabilization and Reactivity?

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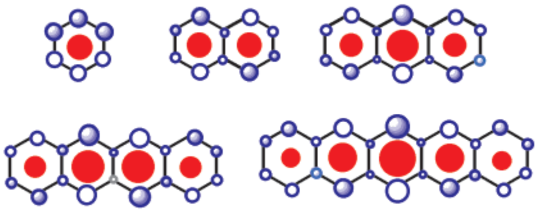
ABSTRACT



Despite the increasing reactivity from benzene to heptacene, the acene resonance energies per π electron are nearly constant. The reactivities (computed activation energies) of the individual acene rings correlate with the reaction energies and depend on the product stabilities. Nucleus-independent chemical shifts (NICS; note the sizes of the red dots, above) indicate that the more reactive inner rings actually are more aromatic than the less reactive outer rings and even more aromatic than benzene itself.

The behavior of a homologous series of polycyclic aromatic hydrocarbons, the “linear acenes”, poses many unsolved problems.[1] These acenes become less persistent (less “stable”) and more reactive[1−6] with an increase in the number of rings, so that the higher members cannot be characterized experimentally. Anthracene is protonated,[6] adds bromine, and undergoes Diels−Alder reactions[5] at the central ring, while tetracene and pentacene participate in even more remarkable 1,4-cycloadditions.[3,4] The successive reduction in the band gap[7] (reflected in the UV spectra) and reduction of the ionization potential,[8a] as well as the increasing proton[6] and electron affinities,[8b] also are examples of monotonic behavior in the acene series. Such progressions in acene properties appear to coincide with the sequential loss of benzenoid character (aromaticity) predicted by several early MO

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(1) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964; Vols. 1, 2. (b) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972. (c) Bjorseth, A., Ed. *Handbook of Polycyclic Aromatic Hydrocarbons*; Dekker: New York, 1983. (d) Cooke, M., Dennis, A. J., Eds. *Polynuclear Aromatic Hydrocarbons: A Decade of Progress*; Battelle Press: Columbus, 1988. (e) Biermann, D.; Schmidt, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 8163, 3173 and references cited. (f) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997.

(2) (a) Aihara, J.-I. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3193. (b) Aihara, J.-I. *J. Phys. Chem. A* **1999**, *103*, 7487. (c) Aihara, J.-I. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2185. (d) Aihara, J.-I. *J. Am. Chem. Soc.* **1977**, *99*, 2048.

(3) (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *18*, 779. (b) Fleming, I. *Frontier Orbital and Organic Chemical Reactions*; Wiley: Chichester, 1976.

(4) (a) Bachmann, W. E.; Scott, L. B. *J. Am. Chem. Soc.* **1948**, *70*, 1458. (b) Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Philip, D.; Stoddart, J. F. *Pure Appl. Chem.* **1993**, *65*, 119. (c) Murata, Y.; Kato, N.; Fujiwara, K.; Komatsu, K. *J. Org. Chem.* **1999**, *64*, 3483.

(5) (a) Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631. (b) Herndon, W. C. *J. Chem. Soc., Chem. Commun.* **1977**, 817.

(6) Wang, D. Z.; Streitwieser, A. *Theor. Chem. Acc.* **1999**, *102*, 78.

(7) (a) Tyutyulkov, N. N.; Polansky, O. E. *Z. Naturwiss. A* **1975**, *30*, 1308. (b) Lee, S. L.; Yang, K. C.; Sheu, J. H.; Lu, Y. J. *Int. J. Quantum Chem.* **1995**, suppl. *29*, 509. (c) Nijegorodov, N.; Ramachandran, V.; Winkoun, D. P. *Spectrochim. Acta A* **1997**, *53*, 1813. (d) For the most recent theoretical study, see: Houk, K. N.; Lee, P. S.; Nendel, M. *J. Org. Chem.* **2001**, *66*, 5107.

(8) (a) Chen, E. S.; Chen, E. C. M.; Sane, N.; Talley, L.; Kozanecki, N.; Shulze, S. *J. Chem. Phys.* **1999**, *110*, 9319. (b) Rienstra-Kiracofe, J. C.; Barden, C. J.; Brown, S. T.; Schaefer, H. F. *J. Phys. Chem. A* **2001**, *105*, 524.

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Table 1. Computed Resonance Energies (kcal/mol), Total (RE) and Per π Electron; Global HOMA Values, and the ΣNICS of All the Individual Rings

acene	$\mathrm{RE}_{\mathrm{DFT}}$[a] /$\pi$ e	$\mathrm{RE}_{\mathrm{expt}}$[b] /$\pi$ e	$\mathrm{RE}_{\mathrm{Wheland}}$[c] /$\pi$ e	$\mathrm{RE}_{\mathrm{Wiber}}$[d] /$\pi$ e	$\mathrm{RE}_{\mathrm{SN}}$[e] **/$\pi$ e**	$\mathrm{RE}_{\mathrm{CSK-mod}}$[f] /$\pi$ e	HOMA[g] global	ΣNICS(X)[h] $X = 0/X = 1$
benzene	32.8	29.7	36.4	36	31.8	20.9	0.991	−8.8/−10.6
	5.47	**4.95**	**6.06**	**6.0**	**5.30**	**3.49**		
naphthalene	59.8	51.7	61.2	60	53.5	41.5	0.881	−17.8/−21.6
	5.98	**5.17**	**6.12**	**6.0**	**5.35**	**4.15**		
anthracene	83.7	70.7	83.7	80	72.1	62.0	0.718	−26.7/−32.9
	5.98	**5.05**	**5.98**	**5.7**	**5.15**	**4.43**		
tetracene	104.8	94.2	110.0	99	95.5	82.5	0.668	−36.0/−44.4
	5.82	**5.23**	**6.11**	**5.5**	**5.30**	**4.58**		
pentacene	127.6	117.3		117		103.0	0.628	−45.2/−56.1
	5.80	**5.33**		**5.3**		**4.68**		
hexacene	153.9	139.5				123.5	0.629	−54.8/−67.6
	5.91	**5.37**				**4.75**		
heptacene	175.5					144.0	0.624	−64.9/−79.7
	5.85					**4.80**		

[a] Computed by eq 1 using B3LYP/6-311+G** + ZPE energies. [b] Calculated from experimental heats of formation (Pedley et al., ref 15a, and NIST data, ref 17) using eq 1 (Benson increments, C−(C)$_2$(H$_2$) −5.00 kcal/mol and C−(C)$_3$(H) −2.40 kcal/mol, ref 15b, gave the saturated acene energies). [c] Values from experimental heats of formation and Franklin increments (ref 10b). [d] Based on B3LYP/6-311G* energies and assumed RE's of benzene and naphthalene (ref 13). [e] Calculated in ref 12a from earlier Benson increments for olefins, C$_d$−(C)(H) 8.59 and C$_d$−(C)$_2$ 10.34 kcal/mol. [f] Values based on increments for conjugated olefins, C$_d$−(C$_d$)(H) 6.78 and C$_d$−(C$_d$)$_2$ 12.3 kcal/mol (see refs 15b and 17, Supporting Information, and text). [g] Values based on B3LYP/6-311G* geometries (ref 11b). [h] NICS at IGLO/TZ2P//B3LYP/6-311+G**.

treatments and by Clar's qualitative sextet concept.[1a,b,9] Since only one ring in each acene can be assigned three double bonds without duplication, the number of nonsextet rings increases along the acene series. We now confirm the contrary view that there is no significant decrease in the relative aromatic stabilization along the acene series: the differences in reactivity depend on the change of aromaticity during reaction.[5] Our results extend Herndon's investigations[5] and support, for example, a common textbook explanation for the greater reactivity of the central ring of anthracene.[10a]

Stabilization Energies. The collected data in Table 1 establish that the stabilization (resonance) energies (SE) of linear acenes increase uniformly from benzene to heptacene and that the SE per π electron remains essentially constant along the series. These evaluations used different methods and various energy determinations.[10−13] The results using our recommended SE method, based on eq 1 and DFT[14] as well as experimental[15] energies, are given in columns 2 and 3. (Cyclohexene and 1,3-cyclohexadiene, as a cyclic conjugated diene, are far more appropriate reference standards for SE estimation of cyclic benzenoid hydrocarbons than the often employed s-*trans*-butadiene and ethylene.)

$$n\ \text{1,3-cyclohexadiene} + \textit{trans}\text{-perhydroacene} = \text{acene} + n\ \text{cyclohexene}\ (n = 3, 5, 7...) \quad (1)$$

Earlier acene evaluations of Wheland,[10b] Wiberg,[13] and Schleyer[12a] (columns 4−6) also showed that the SE's per π electron do NOT decrease significantly along the acene series. In contrast, Cyrañski, Stepien, and Kyrgowski (CSK)[11b] (also see ref 16) claimed recently that the SE/π electron decreases rapidly down the acene series as does the global HOMA (Harmonic Oscillator Model of Aromaticity) geometry-based measure of the total aromaticity (Table 1, column 8).

The CSK SE evaluation was based on the 1993 Cohen−Benson enthalpy increments.[15b] These were used to generate both the acene heats of formation and the hypothetical conjugated (but not aromatic) comparison data. Unfortunately, the value for the critical C$_d$−(C$_d$)$_2$ increment tabulated in 1993 was based only on a single, inappropriate compound (azulene) and is much too low.[15c] The data in Table 1, column 7 were recalculated using the CSK procedure and our newly evaluated 12.3 kcal/mol value for the C$_d$−(C$_d$)$_2$ increment (based on NIST data for nine reference compounds).[17] This actually results in an *increase* in SE/π e along the acene

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(9) Suresh, C. H.; Gadre, S. R. *J. Org. Chem*. **1999**, *64*, 2505.

(10) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955. (a) p 517 (b) Table 3.7, p 98

(11) (a) Cyrañski, M. K.; Krygowski, T. M. *Tetrahedron* **1998**, *54*, 14919. (b) Cyrañski, M. K.; Stepieñ, B. T.; Krygowski, T. M. *Tetrahedron* **2000**, *56*, 9663. (c) Giambiagi, M.; de Giambiagi, M. S.; Silva, C. D. s. S.; de Figueiredo, A. P. *Phys. Chem. Chem. Phys*. **2000**, *2*, 3381. (d) Krygowski, T. M.; Cyrañski, M. K. *Chem. Rev*. **2001**, *101*, 1385.

(12) (a) Schleyer, P. v. R.; Najafian, K. In *The Borane, Carborane and Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York 1998; p 169. (b) Notario, R.; Abboud, J.-L. *J. Phys. Chem. A* **1998**, *102*, 5290.

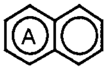
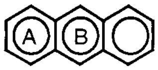
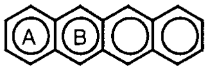
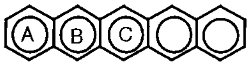
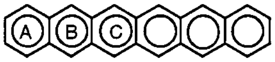
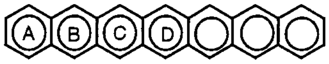
(13) Wiberg, K. B. *J. Org. Chem*. **1997**, *62*, 5720.

(14) The acene and other related geometries (see Tables 1 and 2) were optimized at B3LYP//6-311+G** using Gaussian 98 (Frisch, M. J. et al., Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998). The stationary points in the reactions (Table 3) were computed at B3LYP/6-31G*. NICS employed the Perdew-Wang-91 functional, the IGLO-III TZ2P basis set and the Pipek-Mezey σ, π localization (Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916) available in the deMon NMR program (Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898. Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298).

(15) (a) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall, London, 1986. (b) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419. (c) Benson, S. W., private communication 2001, based on dimethylfulvene.

(16) Slayden, S. W.; Liebman, J. F. *Chem. Rev.* **2001**, *101*, 1541 (The Slayden−Liebman SE/π electron values decrease somewhat along the acene series but, in our view, are based on inappropriate equations. These are not homodesmotic, as claimed, for naphthalene and the higher acenes.)

Table 2. Total NICS and Dissected π-Contributions (Total and Remote)[a] Calculated at the Ring Centers and 1 Å Above of Acenes). The Weighted Average NICS and HOMA Values for Each Acene Are Shown in Bold Font

acene	ring	NICS(0)	NICS(1)	NICS(0)π total[a]/remote	NICS(1)π total[a]/remote	HOMA/ ring[b]
	A	−8.8	−10.6	−20.7/0.0	−9.6/0.0	0.991
		−8.8	**−10.6**	**−20.7**	**−9.6**	**0.991**
	A	−8.9	−10.8	−20.3/0.0	−10.1/0.0	0.787
		−8.9	**−10.8**	**−20.3**	**−10.1**	**0.787**
	A	−7.6	−9.9	−19.8/−1.1	−10.1/−0.5	0.632
	B	−11.5	−13.1	−22.9/−0.6	−11.3/−0.2	0.732
		−8.9	**−11.0**	**−20.8**	**−10.5**	**0.665**
	A	−6.6	−9.1	−19.6/−2.0	−9.3/−0.7	0.539
	B	−11.4	−13.1	−22.7/−1.2	−13.3/−0.7	0.632
		−9.0	**−11.1**	**−21.2**	**−11.1**	**0.586**
	A	−5.8	−8.5	−19.1/−1.9	−8.8/−0.5	0.453
	B	−10.7	−12.6	−22.7/−2.0	−12.2/−1.1	0.574
	C	−12.2	−13.9	−23.6/−1.7	−13.5/−1.4	0.608
		−9.0	**−11.2**	**−21.4**	**−11.1**	**0.532**
	A	−5.1	−7.9	−18.5/−1.8	−8.4/−0.5	0.460
	B	−10.1	−12.0	−22.4/−2.5	−12.2/−1.5	0.528
	C	−12.2	−13.9	−23.9/−2.1	−13.5/−1.4	0.543
		−9.1	**−11.3**	**−21.5**	**−11.2**	**0.510**
	A	−4.7	−7.6	−18.0/−1.7	−7.9/−0.2	0.444
	B	−9.5	−11.5	−21.8/−2.5	−11.5/−1.2	0.505
	C	−11.9	−13.6	−23.9/−2.6	−13.6/−1.7	0.517
	D	−12.7	−14.3	−24.3/−2.1	−14.0/−1.4	0.513
		−9.3	**−11.4**	**−21.7**	**−11.4**	**0.492**

[a] The “total π” entries include the contributions from the three C═C double bonds of the local ring, as well as those from the remote rings (given after the slash). [b] The HOMA values of the individual rings (from ref 11b).

series. The considerable falloff of the global HOMA values,[11b] not supported by the other SE data in Table 1 either, raises doubts concerning the reliability of evaluations using this geometry-based index.

NICS Values. Many details are revealed by magnetic property analysis of the acenes, on the basis of the nucleus-independent chemical shifts (NICS).[18] The individual rings in the acenes are characterized in Table 2 by the NICS total values and by the π contributions at the same points. The NICS(0) data, illustrated visually in Figure 2 and in the Abstract, indicate (like the other NICS values) not only that the inner rings exhibit greater diatropic ring currents than the outer rings but that the inner rings in this sense are more aromatic than benzene itself. This conclusion does not agree with the HOMA values for the individual rings listed in Table 2, even though NICS and HOMA correlate well.[11] The π-density current circulations of the respective rings[19] also are in accord with the steady increase in NICS in going from the end to the middle rings. The regular progressions along the acene series are noteworthy as is the fact that the NICS(1) and NICS(1)π values are quite similar.[18b,c]

The NICS π values are due to the local π contributions of the three localized C═C double bonds in the same rings as well as the π contributions of the more remote C═C's. The latter contributions are small (10% or less). Hence, each benzenoid ring in the acenes behaves as a rather separate or localized entity in this respect.

The rather localized origins of NICS of the individual acene rings suggest that the easily computed sum of all the NICS values might serve as a global aromaticity index for such polycyclic systems. Although some “double counting” is involved, Figure 1 shows excellent correlations between both ΣNICS(0) and the ΣNICS(1) vs the SE values from Table 1, column 2. Since the SE/πe's (Table 1) are nearly

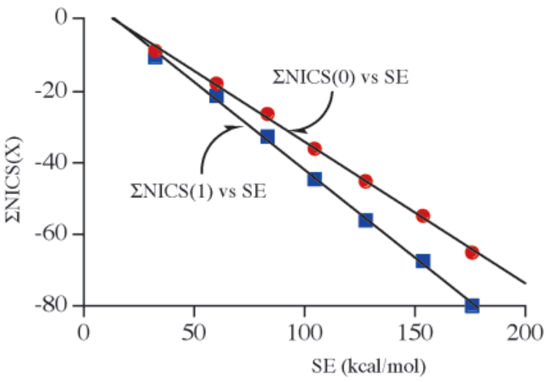


Figure 1. Correlations (R^2 = 0.998) of SE (Table 1, column 2) of acenes versus the total NICS(0) and NICS(1) sums.

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(17) (a) http://webbook.nist.gov/chemistry, see Supporting Information. Data from: (b) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499.

constant, the NICS(0) and NICS(1) weighted averages (i.e., average NICS behavior per ring) also are strikingly similar (Table 2, bold values).

Reactivities. While the aromaticity increases from the end to the center acene rings, as shown by NICS(total) and NICS(π) as well as by HOMA (Table 2), the magnitudes of the HOMO coefficients also increase similarly (Figure 2).

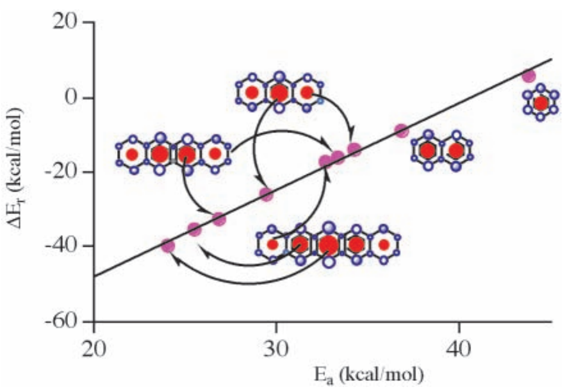
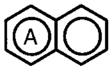
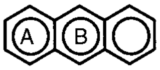
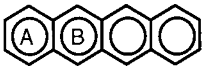
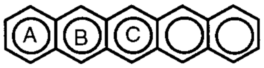


Figure 2. Correlation (R^2 = 0.997) of the activation (E_a) versus the reaction (ΔE) energies (B3LYP/6-31G* + ZPE data) of acetylene addition to acene rings. The red dots are based on total NICS(0) values in Table 2. The HOMO coefficients are indicated in blue (also see the Abstract and Synopsis).

Table 3. Barriers (E_a) and Reaction Energies (ΔH_r, kcal/mol) of Diels−Alder Additions of Acetylene to the Various Acene Rings

acene	E_a [a]	ΔH_r [a]
	43.8 (A)	6.1 (A)
	36.8 (A)	–8.7 (A)
	34.3 (A) 29.4 (B)	–13.9 (A) –26.2 (B)
	33.3 (A) 26.8 (B)	–16.1 (A) –32.6 (B)
	32.7 (A) 25.5 (B) 24.0 (C)	–17.3 (A) –35.4 (B) –39.5 (C)

[a] Computed at the B3LYP/6-31G* + ZPE (HF/6-31G*) level.

These coefficients are consistent with the regioselectivity of Diels−Alder reactions that prefer the middle rings (despite their greater aromaticity) to an increasing extent[5] (note E_a and ΔH_f in Table 3). Nevertheless, the reactivity differences of the individual rings in each acene cannot be a ground state phenomenon, since the ground states and their energies are exactly the same. Instead, the energies of the products are decisive; these correlate with the activation energies (Figure 2): the smaller aromaticity loss during reactions of the central rings (larger reaction exothermicities) is reflected quantitatively in the reduced activation energies. The change in band gaps,[1] IP's,[8a] and EA's[8b] also influence the reactivities.

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Supporting Information Available: New evaluation of the $C_d-(C_d)_2$ increment for olefins. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (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) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (c) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.

(19) (a) Steiner, E.; Fowler, P. W. *Int. J. Quantum Chem.* **1996**, *60*, 609. (b) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349. (c) Haigh, C. W.; Mallion, R. B. *J. Chem. Phys.* **1982**, *76*, 4063. (d) Steiner, E.; Fowler, P. W. *J. Phys. Chem. A* **2001**, *105*, 9553.