Delocalization Energy of π Electrons as an Index for Aromaticity of Polycyclic Hydrocarbons

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SINDO1 calculations of an improved π electron delocalization energy with geometry optimization were performed for a large number of mono- and polycyclic hydrocarbon rings and compared with ab initio results. The suitability of the delocalization energy as aromaticity index is demonstrated. For a comparison of the aromaticity of molecules with different size and different number of rings, a normalized delocalization energy per broken π bond in the reference state was introduced. With this criterion the aromaticity of polycyclic conjugated hydrocarbons with four- and six-membered rings was examined and an energetic aromaticity scale established.

1. Introduction

Since the introduction of Hückel theory the importance of the delocalization of the π electrons for the description of aromaticity was intensively discussed.[1–10] Most of the authors have now agreed that the geometry of molecules with conjugated double bonds is determined by the fact that the energy of the σ electrons forms a minimum at a geometry with equal bond lengths, whereas the π electrons tend to a geometry with alternating bond lengths.[3,5–8,10] Nevertheless it is obvious that the properties attributed to aromaticity depend on the delocalization of the π electrons although this delocalization is enforced by the σ electrons.[8] So aromaticity may be considered as consisting of two components, the equalization of bond lengths caused by the σ electrons and the typical aromatic properties like the chemical behavior caused by the delocalization of the π electrons.

This may be the reason why a statistical analysis shows that aromaticity is at least a two-dimensional phenomenon.[11,12] There is an orthogonality between two classes of aromaticity criteria, namely the magnetic and the energetic[11] or the geometric and the energetic criteria.[12] The energetic criteria describe the delocalization of the π electrons. The information of these criteria is related to the chemical aspect of aromaticity. This concerns the reactivity properties of addition and electrophilic substitution reactions. A frequently used energetic criterion is the resonance energy RE. This is the energy difference between the real molecule with delocalized π electrons E_{del} and a fictitious reference molecule with localized π electrons E_{loc}.[2,3,8,11]

$$\mathrm{RE} = E_{\mathrm{loc}} - E_{\mathrm{del}} \tag{1.1}$$

This concept was introduced first by Pauling.[13]

The resonance energy is usually estimated using the heats of formation, the hydrogenation energies, or the heats of combustion of the delocalized system and the reference system with localized π MOs. The values for the reference system are approached by adding bond increments of systems without conjugated π bonds. Because there are different possibilities to choose the bond increments, the resonance energies are not unique. For benzene the values vary between 36 kcal/mol and 64 kcal/mol.[14] Dewar et al. determine the resonance energy RE by taking conjugated polyenes to get the bond increments.[2] Their values for the resonance energy are smaller than those of the other authors. For benzene they obtain a value of 28.3 kcal/mol.[15] To compare the Dewar resonance energy RE_n with the other resonance energies, it is necessary to standardize the other resonance energies RE with respect to butadiene by using the equation

$$\mathrm{RE}_n = \mathrm{RE} - n\mathrm{RE(butadiene)} \tag{1.2}$$

in which n is the number of single bonds between the nonconjugated localized π electron bonds in the reference molecule. Very similar to Dewar's method is the estimation of the resonance energy by determining the heat of the homodesmotic reactions, e.g. the reaction

$$\text{benzene} + 3\ \text{ethylene} \rightarrow 3\ \text{butadiene} \tag{1.3}$$

The heat of this reaction is 21.1 kcal/mol.[16]

Hess and Schaad[17] determine the resonance energy by an alternative procedure. They have chosen more sophisticated bond increments. Their newest value for the resonance energy of benzene is 23.4 kcal/mol with a 6-31G* basis set.[18]

Kollmar proposed a method to calculate the delocalization energy.[19] In this method the π MOs are localized

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(1) Hückel, E. *Z. Elektrochem.* **1937,** *43,* 752, 827.

(2) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.

(3) Epiotis, N. D. *Lecture Notes in Chemistry 34*; Springer: Berlin-Heidelberg-New York-Tokyo, 1983; p 358 ff.

(4) Baird, N. C. *J. Org. Chem.* **1986,** *51,* 3907.

(5) Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987,** *109,* 363.

(6) Stanger, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1988,** *53,* 4879.

(7) Heilbronner, E. *J. Chem. Educ.* **1989,** *66,* 471.

(8) Jug, K.; Köster, A. M. *J. Am. Chem. Soc.* **1990,** *112,* 6772.

(9) Aihara, J. *Bull. Chem. Soc. Jpn.* **1990,** *63,* 1956.

(10) Janoschek, R. *J. Mol. Struct.* (*Theochem*) **1991,** *75,* 197.

(11) Katritzky, A. R.; Barczynski, P.; Musumarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989,** *111,* 7.

(12) Jug, K.; Köster, A. M. *J. Phys. Org. Chem.* **1991,** *4,* 163.

(13) Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed.; Cornell University Press: Ithaca, New York, 1960.

(14) Lewis, D.; Peters, D. *Facts and Theories of Aromaticity*; The Macmillan Press Ltd.: London, Basingstroke, 1975; p 19.

(15) Dewar, M. J. S.; Holder, A. J. *Heterocycles* **1989,** *28*(2), 1135.

(16) (a) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976,** *11,* 1222. (b) George, P.; Trachtman, M.; Brett, A. M.; Brock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977,** *8,* 1036.

(17) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971,** *93,* 305.

(18) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983,** *105,* 7500.

(19) Kollmar, H. *J. Am. Chem. Soc.* **1971,** *101,* 4832.

0022-3263/94/1959-2546$04.50/0

and the energy difference between the systems with localized π MOs and with delocalized π MOs is calculated. To localize the π MOs, the author replaces the delocalized π MOs by an appropriate number of π MOs of ethylene. The delocalization energies RE of this method are much larger than those of the previous methods, but the normalized resonance energies RE_n are comparable.

We describe an improvement of the method of Kollmar. Our localization is carried out within the SCF procedure. Also Kollmar used standard single and double bond lengths for the so-called adiabatic localized structures, whereas we optimize the reference structure. A relaxation of the σ MOs and the π MOs is possible. The method is applicable not only to hydrocarbons, but also to molecules with heteroatoms. It is implemented in the semiempirical method SINDO1.[20] This method was originally designed for geometries and energies of molecules with first-row atoms. The reliability was extensively tested.[21] The delocalization energy is calculated and compared for different systems with conjugated double bonds.

2. Calculation of Delocalization Energy

Kollmar used three different methods for the localization of π MOs.[19] The delocalized π MOs were replaced by an appropriate number of π MOs of ethylene, or the square roots of the corresponding diagonal elements of the bond order matrix were chosen as basis function coefficients, or the localization procedure of Boys[22] was used and the resulting localized π orbitals were truncated.

Our method of localizing the π MOs is somewhat different because we use π MOs which are localized within the Fock method. In planar molecules, the Fock matrix can be separated in a σ block and a π block. We localize the π block by setting the off-diagonal elements of nonresonating atoms in the reference molecule equal to zero. The π part of the Fock matrix is separated in several blocks, one for each localized part of the molecule. The localized blocks of π electrons are separated by fictitious walls, which they cannot penetrate. The method of deleting specific elements of the Fock matrix[23] is used by Kitaura and Morokuma[24a] for the analysis of intermolecular forces and by Faust et al.[24b] for a neutral bond orbital procedure.

Then the σ block and each π block of the Fock matrix is diagonalized to obtain the σ MOs and the localized π MOs. Separate diagonalization of each π block is necessary for symmetry reasons. This method can be used (a) in one step after the end of the standard SCF procedure for delocalized σ and π MOs, or (b) in each SCF step.

For method b, relaxation of the σ MOs and the localized π MOs occurs. The importance of the relaxation must be tested. In both methods the diagonalization leads to a reference state with localized π MOs. The delocalization energy DE_v is then calculated as the energy difference between the energies E^v_{loc} of the fictitious reference state with localized π MOs and E_{del} of the ground state of the molecule with delocalized π MOs at geometry G_{del}. We have chosen the expression delocalization energy to avoid confusion with the different definitions of resonance energy.

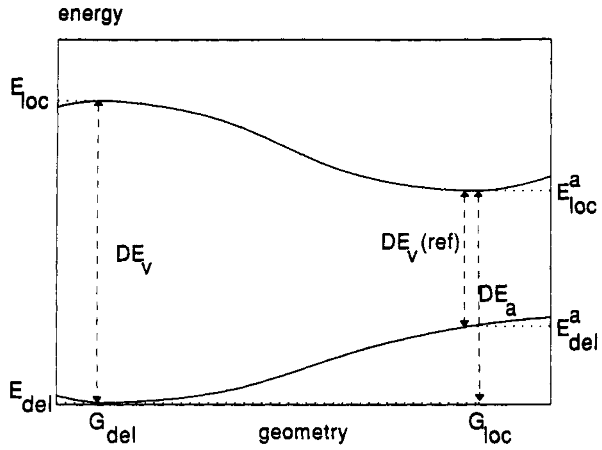

Figure 1. Delocalization energy scheme for delocalized and localized π electron system of benzene.

$$\mathrm{DE}_v = E^v_{\mathrm{loc}} - E_{\mathrm{del}} \tag{2.1}$$

DE is always greater than or equal to zero. We perform a geometry optimization of the reference state. At its optimized geometry G_{loc}, the reference state has the energy E^a_{loc} (Figure 1). The energy difference E^a_{loc} minus E_{del} is the adiabatic delocalization energy DE_a.

$$\mathrm{DE}_a = E^a_{\mathrm{loc}} - E_{\mathrm{del}} \tag{2.2}$$

DE_a shows directly the difference between the energy of the real molecule and the molecule as it would be without delocalization of π electrons. DE_v(ref) is the vertical delocalization energy at the geometry G_{loc}.

To compare the delocalization energies of systems of different size, we divide the total DE by the number of walls described above, so that a normalized delocalization energy (DE_n) is defined.

$$\mathrm{DE}_n = \mathrm{DE}/\text{number of walls} \tag{2.3}$$

For example, in systems with a different number of six-membered rings, like benzene, and naphthalene, and anthracene, DE_n is 1/3 DE per ring. For monocyclic molecules of different ring size, DE_n equals 2 DE per π electron. With this method we combine the well-known methods of calculating resonance energy per ring and resonance energy per π electron. It is taken into account that in polycyclic systems the delocalization of π electrons takes place not only in the outer perimeter, but also along the bridges.

For all calculations the semiempirical method SINDO1[20] is used. Equilibrium geometries are fully optimized. The geometry of the localized structure is optimized with fixed dihedral angles.

3. Results and Discussion

First we examine benzene, butadiene, and cyclobutadiene, the standard aromatic, nonaromatic, and antiaromatic systems. The results for DE are shown in Table 1. The vertical delocalization energy DE_v describes the

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(20) Nanda, D. N.; Jug, K. *Theor. Chim. Acta* **1980**, *57*, 95.

(21) Jug, K.; Nanda, D. N. *Theor. Chim. Acta* **1980**, *57*, 107, 131.

(22) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.

(23) (a) Foster, J. P.; Weinhold, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 7211; (b) Reed, A. E.; Curtis, L. A.; Weinhold, F. J. *Chem. Rev.* **1988**, *88*, 899. (c) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. J. *QCPE Bull.* **1990**, *10*, 58.

(24) (a) Kitaura, K.; Morokuma, K. *Int. Quant. Chem.* **1976**, *10*, 325. (b) Faust, R.; Glendening, E. D.; Streitwieser, A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 8263.

Table 1. Delocalization and Resonance Energies of Benzene, Butadiene, and Cyclobutadiene (kcal/mol)

molecule	DE_v	DE_a	DE_v(ref)	RE_v^a	RE_a^a	RE_v^a(ref)	RE^b
benzene (1a)	111.6	64.6	48.4	96.4	56.0	52.7	23.4
butadiene (14)	14.4	13.0	11.9	10.0	9.7		
cyclobutadiene (22)	0.0	0.0	0.0	0.0	0.0		−54.7

[a] Reference 19. [b] Reference 17.

delocalization of π electrons at the optimized ground state of the molecule. The adiabatic delocalization energy DE_a is the energy difference between the ground state energy for the molecule and the energy of the optimized reference state.

Kollmar's resonance energies are comparable to our DEs. His values are somewhat smaller, possibly as a consequence of the use of different geometries and wave functions. For a comparison with theoretical and experimental incremental resonance energies,[17,18,25] the adiabatic delocalization energy must be used, because the systems used for the increments have alternating bond lengths which is also the case for the optimized reference state. Here the changes in single and double bond lengths are most pronounced in aromatic systems (benzene: 0.141 Å, −0.071 Å), less in nonaromatic systems (butadiene: 0.051 Å, −0.006 Å), and vanishing in antiaromatic systems (cyclobutadiene: 0.0 Å, 0.0 Å).

Compared to the Hess–Schaad resonance energy, our delocalization energy of benzene is much larger. The reason is a different position of the zero point. Cyclobutadiene has a resonance energy RE of −54.7 kcal/mol and a delocalization energy DE of 0.0 kcal/mol. The differences DE_a(benzene) − DE_a(cyclobutadiene) and RE(benzene) − RE(cyclobutadiene) are 64.6 and 78.1 kcal/mol, respectively. There is no direct relation between the DE and Hess–Schaad resonance energy, because the increments are not chosen directly from the considered molecule. The bond lengths of the molecules included by Hess and Schaad[17] in their calculation of bond increments are between the bond lengths of benzene with delocalized π MOs and optimized benzene with localized π MOs. Therefore it seems reasonable that the difference RE(benzene) − RE(cyclobutadiene) is between DE_v(benzene) and DE_a(benzene). In Figure 2 we compare DE_a with resonance energies from experimental heats of combustion.[25,26] We observe an approximate linear dependence between these properties.

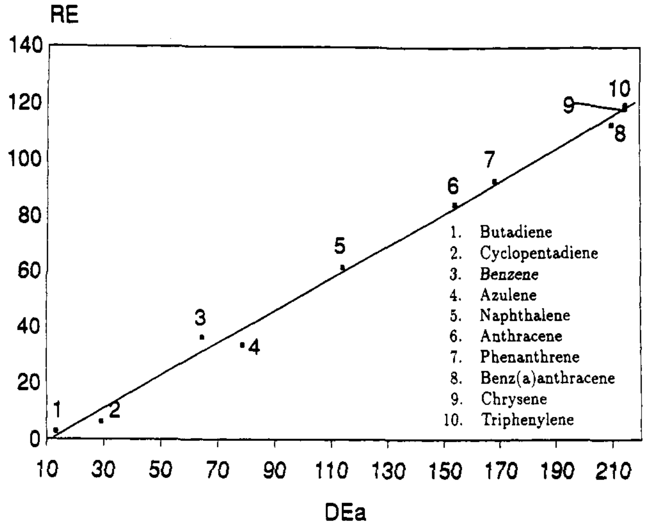

Figure 2. Comparison of adiabatic delocalization energy DE_a (kcal/mol) and resonance energy RE (kcal/mol) from heats of combustion.

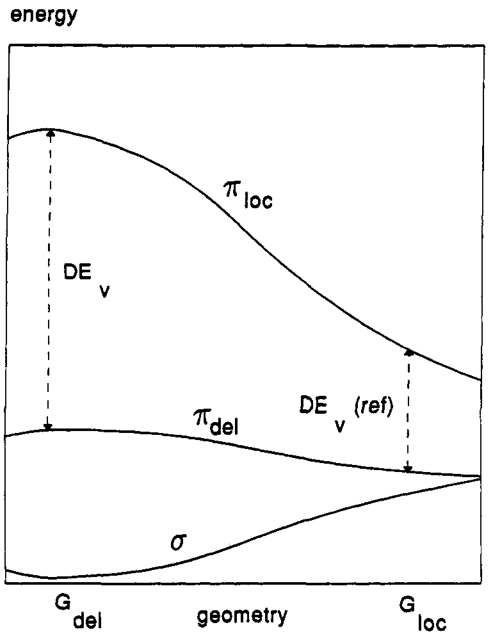

Figure 3. Partitioning scheme for σ and π electron energies of benzene.

At the minimum of the π localized reference state of benzene we calculated the vertical delocalization energy DE_v(ref) (Figure 1). The value of 48.4 kcal/mol is rather large compared to butadiene. A substantial degree of π electron delocalization of the ground state even at the optimized geometry G_{loc} of the reference state is responsible for this large DE_v(ref). This is in line with observations of Kollmar[19] and Faust et al.[24b] But it is now important to understand that there is no contradiction to the result of Jug and Köster[8] that the π electrons prefer a geometry with alternating bond lengths. Due to this tendency we find that the energy of the delocalized π electrons at the π localized minimum geometry G_{loc} of form cyclohexatriene is 15.5 kcal/mol below the π electron energy of benzene at its minimum geometry G_{del}. The π electrons prefer the cyclohexatriene geometry rather than the geometry of benzene in D_{6h} symmetry. In D_{6h} symmetry there is a maximum of the π electron energy curve π_{loc} (Figure 3). Compared to the localized situation of the π electrons, this maximum is flattened by the delocalization of the π electrons as seen in the curve for π_{del}, but it remains a maximum. The D_{6h} structure is finally determined by the σ electrons, because of the more flattened curve for π_{del}.

In the following we shall concentrate on the normalized adiabatic delocalization energy. A large value of DE_{na} shows that the maximum of the π electron energy at equal bond lengths is substantially flattened by the delocalization of π electrons. As the influence of the σ electrons on the geometry grows, the bond lengths approach the σ minimum.

In molecules with more complicated structures like naphthalene there is more than one possibility to localize

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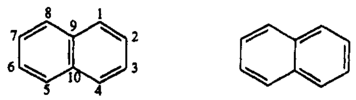
(25) Wheland, G. *Resonance in Organic Chemistry*; Wiley: New York, 1955; p 98.

(26) Allinger, N. L.; Cava, M. P.; de Jong, D. C.; Johnson, C. R.; Lebel, N. A.; Stevens, C. L. Organische Chemie, Walter de Gruyter: Berlin, New York, 1980; p 397.



L_1 L_2

Figure 4. Kekulé structures of naphthalene.

Table 2. Bond Lengths (Å) and Bond Orders of Naphthalene (with labels from Figure 4)

	r_{19}	r_{12}	r_{23}	r_{910}
bond length	1.486	1.386	1.464	1.465
bond order	1.52	1.92	1.55	1.69

Table 3. Delocalization Energy DE_a (kcal/mol) without (a) and with (b) Relaxation of MOs with Localized π Electron System

molecule	a	b
butadiene (14)	13.2	13.2
benzene (1a)	64.6	64.6
fluorobenzene (1b)	64.0	63.9
benzocyclobutene (12)	69.5	69.3

the π system. The two structures L_1 and L_2 for naphthalene are presented in Figure 4.

At the ground state equilibrium geometry of naphthalene L_2 is 11.6 kcal/mol higher in energy than L_1. It has been suggested[27] to use the most stable Kekulé structure, because such a structure would be realized if the π electrons could not delocalize. Therefore we choose L_1 to calculate the delocalization energy. This means that we use the smallest DE_a. If we compare geometry and bond orders[28] of L_1 and L_2 with that of the fully optimized structure with the delocalized π system (Table 2), we see that L_1 is closer to this minimum than L_2. For other systems the situation is very similar. For this reason we always choose the corresponding Kekulé structure as reference state, a procedure which was already adopted by Nakajima and Kataoka.[29] But even if we used a weighting procedure for the π localized Kekulé structures, there would be no substantial changes in Figure 2. This is trivial for benzene. For naphthalene, anthracene, and other polycyclic hydrocarbons we have found very similar energies for the optimized π localiced Kekulé structures, differing by less than 2 kcal/mol. This is in agreement with an observation by Hess and Schaad.[17]

In Table 3 we compare delocalization energies DE_a without (method a) and with (method b) relaxation of the σ and localized π MOs. We find no significant differences for these two methods in hydrocarbons and have therefore chosen method a for such systems.

In the following we use the normalized delocalization energy DE_{na} as an aromaticity scale and present values for a large number of hydrocarbon ring systems in Figure 5. Benzene and substituted benzenes have DE_{na} values from 21.5 to 20.6 kcal/mol. Naphthalene is more aromatic than anthracene, as expected from addition reaction experiments.[30] DE_{na} of phenanthrene is larger than DE_{na} of anthracene. This result is also obtained by resonance energy measurements.[31]

The DE_{na} of polyenes like butadiene should separate aromatic and antiaromatic molecules. All the molecules considered as antiaromatic, like fulvene or pentalene, have lower DE_{na} than butadiene, while the DE_{na} value of aromatic molecules is higher than that of butadiene. Combinations of six- and four-membered rings are of interest, because of the combination of aromatic and antiaromatic rings.[23,32,33] Of special interest is the influence of the π electrons in these molecules. We have calculated some selected examples (Figure 3) and have listed important bond lengths of the ground state minimum in Table 4 in order to see the relative similarities. It is noteworthy that the geometry of the four-membered rings is closer to the geometry of tetramethylenecyclobutane (**16**) than to cyclobutadiene (**22**). This reduces the antiaromaticity of the four-membered rings, but also the aromaticity of the annelated six-membered rings by localizing the π electrons in the benzene rings. In the linearly annelated systems **9** and **19** a bond localization of the central benzene ring is not possible because of symmetry reasons. Therefore the four-membered rings are more cyclobutadiene-like than they are in the other molecules. The bond lengths in the central rings are nearly equal. As we shall see below this causes a decrease of DE_{na} in these two molecules. The combinations of four- and six-membered rings have higher DE_{na} than butadiene if the number of walls in all six-membered rings is larger than in all four-membered rings. Examples are benzocyclobutene **12**, biphenylene (**7**), [3]phenylene **9**,**10**, and [4]phenylene **11**. Biphenylene (**7**) is the most aromatic of these systems with a DE_{na} value of 16.3 kcal/mol. In **7** there are six walls in the six-membered rings and two walls in the four-membered ring. DE_{na} of linear [3]phenylene **9** is very close to DE_{na} of angular [3]phenylene **10** (15.7 and 15.5 kcal/mol, respectively), and [4]phenylene **11** has DE_{na} 15.1 kcal/mol. The high reactivity of **9**[33a] may be caused by the cyclobutadiene-like four-membered rings. The higher value of DE_{na} for **9** compared to **10** may result from the delocalization of π electrons in the central ring.

If the number of walls in all four-membered rings is larger than in all six-membered rings the molecules are antiaromatic. Examples are **15**, **17**, and **19**. Like Faust et al., we found **19** to be of D_{2h} symmetry. In contrast to the phenylene-fused benzenes **9** and **10**, the linear isomer **19** of the cyclobutadiene-fused benzenes is 13.3 kcal/mol higher in energy than the angular **15**. DE_{na} of **15** indeed is higher than DE_{na} of **19** (11.7 and 10.5 kcal/mol, respectively). In general we can say that linear annelation of a benzene ring by benzene rings leads to a decrease of DE_{na} for every annelated benzene ring. DE_{na} of naphthalene **2**, anthracene **5**, and tetracene **8** is 19.0 kcal/mol, 17.1 kcal/mol, and 16.1 kcal/mol, respectively. The influence of an angular annelation is nearly negligible. DE_{na} of phenanthrene **4** and triphenylene **3** is 18.7 and 18.8 kcal/mol, respectively, nearly the same as naphthalene. Also if the benzene ring is annelated by two cyclobutadienes, a linear annelation leads to a stronger decrease of DE_{na} than does an angular annelation (Figure 5). In

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[27] Wheland, G. *Resonance in Organic Chemistry*; Wiley: New York, 1955; p 75.

[28] Jug, K. *Theor. Chim. Acta* **1979**, *51*, 331.

[29] Nakajima, T.; Kataoka, M. *Theor. Chim. Acta* **1993**, *85*, 27.

[30] Garratt, P. J. *Aromaticity*; John Wiley and Sons: New York, Chichester, Brisbane, Toronto, Singapore, 1986; p 233.

[31] Streitwieser, A.; Heathcock, C. H. *Organische Chemie*; Verlag Chemie: Weinheim, Deerfield Beach, FL, Basel, 1980; p 1236.

[32] Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.

[33] (a) Berris, G. C.; Hovakeemian, G. H.; Lai, Y.-H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670. (b) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150. (c) Stanger, A. *J. Am. Chem. Soc.* 1991, *113*, 8277. (d) Barton, J. W.; Rowe, D. J. *Tetrahedron* **1985**, *41*, 1323.

[34] Maksić, Z. B.; Eckert-Maksić, M.; Kovaček, D.; Margetić, D. *J. Mol. Struct.* (*Theochem*) **1992**, *260*, 241.

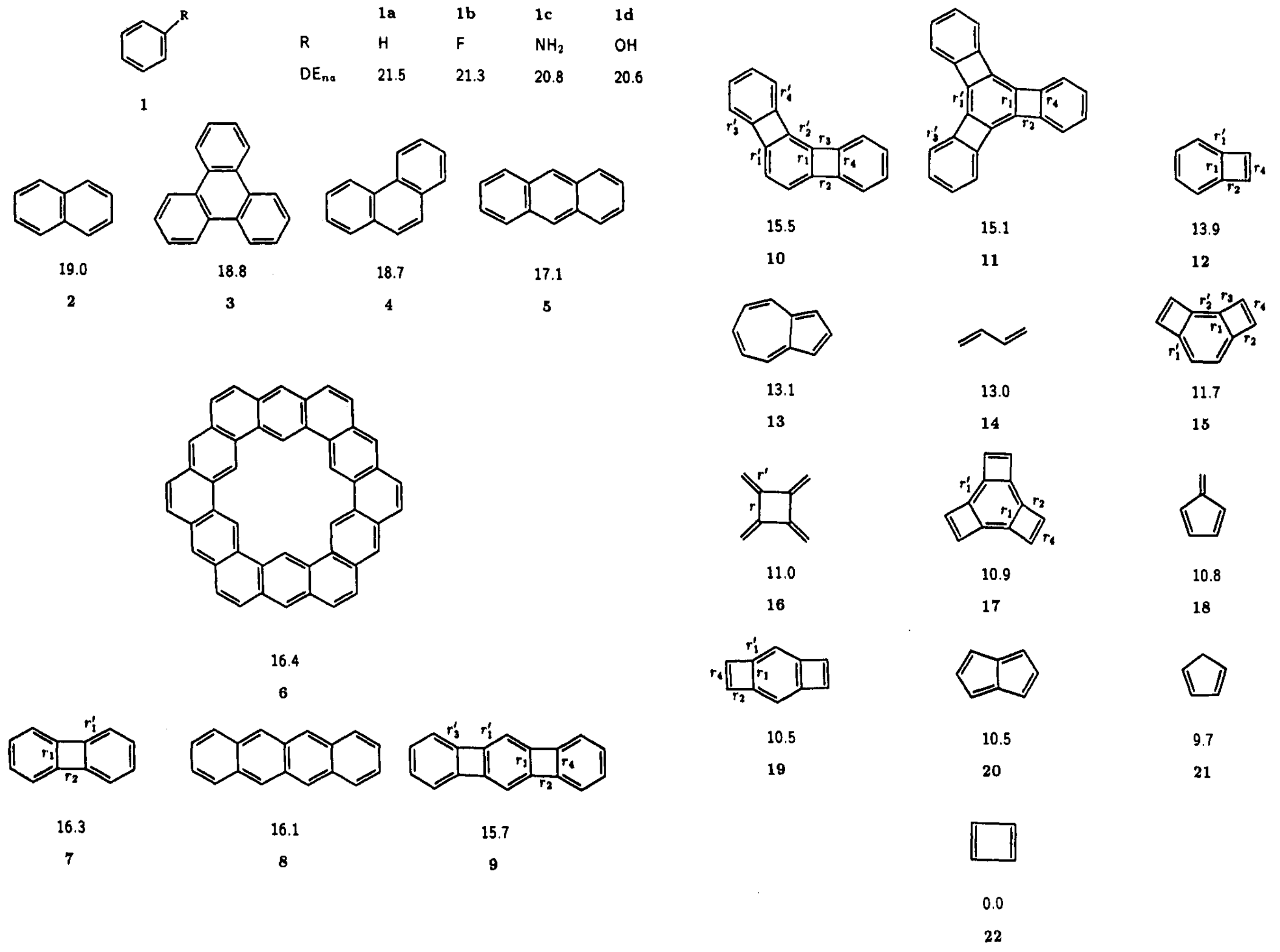

Figure 5. Delocalization energies DE_{na} (kcal/mol).

Table 4. Bond Lengths (Å) of Selected Molecules with ab Initio Results in Parentheses and Labels from Figure 5

molecule	r_1	r_2	r_3	r_4
16	1.55	1.55	1.55	1.55
7	1.51	1.54	1.54	1.51
10	1.52	1.54	1.54	1.52
11	1.55	1.53	1.53	1.51
9	1.46	1.55	1.55	1.50
15	1.54 (1.49^a) (1.48^b)	1.54 (1.52^b)	1.53 (1.52^a) (1.52^b)	1.36 (1.36^a) (1.34^b)
17	1.57 (1.52^a) (1.52^b)	1.53 (1.49^a) (1.50^b)	1.53	1.36 (1.36^a) (1.34^b)
12	1.48 (1.44^a) (1.43^b)	1.55 (1.53^a) (1.54^b)	1.55	1.35 (1.35^a) (1.34^b)
19	1.45 (1.39^b)	1.57 (1.57^b)	1.57	1.34 (1.33^b)
22	1.33	1.58	1.58	1.33

molecule	r'_1	r'_2	r'_3	r'_4
16	1.34	1.34	1.34	1.34
7	1.39	1.39	1.39	1.39
10	1.38	1.38	1.39	1.39
11	1.37	1.37	1.40	1.40
9	1.43	1.43	1.39	1.39
15	1.37 (1.38^a) (1.33^b)	1.37 (1.37^a) (1.31^b)		
17	1.36 (1.33^a) (1.31^b)	1.36		
12	1.39 (1.36^a) (1.34^b)	1.39		
19	1.42 (1.38^b)	1.42		

[a] 3-21G.[34] [b] 3-21G.[24b]

contrast to the benzene-annelated benzenes angular annelation of a cyclobutadiene ring decreases DE_{na} clearly.

The situation is somewhat different if a benzene ring is annelated by benzocyclobutene. Linear and angular [3]-phenylene have nearly the same DE_{na}. The reason for the decrease of DE_{na} is different in **9** and **10**. In **10** the central benzene ring with its alternating bond lengths is responsible for the decrease of DE_{na}. In **9** the cyclobutadiene-like four-membered rings are responsible for the decrease of DE_{na}. DE_{na} of kekulene is 16.4 kcal/mol. The aromaticity of this molecule is lower than in anthracene.

4. Conclusions

We have used the delocalization energy as an index for aromaticity. An advantage of this method is that only the molecule of interest must be considered. No reference molecules with geometries different from the considered molecule have to be introduced. We deal only with stationary points on the hypersurface of the molecule considered and its reference state. The geometry of the reference state is subsequently optimized. To compare molecules of different size and of different numbers of rings, we have defined a normalized delocalization energy DE_n. From the large number of aromatic, antiaromatic and nonaromatic molecules studied benzene is the molecule with highest DE_{na} and cyclobutadiene is the zero point. Aromatic and antiaromatic systems are clearly separated. The results show that DE_{na} is a useful aromaticity index. For polycyclic compounds with fourand six-membered rings it could be shown that the aromaticity of a molecule with a benzene ring fused to other rings depends on the type of fusion (linear or angular) of the benzene ring and on the kind of substituent (antiaromatic or aromatic). Since the method is very general, it can be implemented also for ab initio wave functions. We are presently engaged in such work, in order to see where improvements in the numbers can be made.

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