J. Am. Chem. Soc. 1991, 113, 787-793

Prediction of Carbon–Hydrogen Bond Dissociation Energies for Polycyclic Aromatic Hydrocarbons of Arbitrary Size

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Received December 14, 1989

Abstract: A method has been developed for estimating C–H bond dissociation energies at the edges of polycyclic aromatic hydrocarbons of arbitrary size. A series of reference molecules having well-established bond dissociation enthalpies are used to represent several types of dissociations. For each type, Huckel molecular orbital theory is used to calculate the π-electron energy difference between reactant and product. This difference is then used to calculate relative bond dissociation enthalpies. Predictions are also made of C–H bond dissociation enthalpies at the perimeters of infinite graphite layers having several different edge structures. Energies depend principally on chemical structures near the bond of interest and little on overall molecular size. Along with available ionization energies, these results also allow estimation of proton affinities at the edges of a layer of graphite. These proton affinities depend on both the chemical structures at the site of protonation and the overall molecular size.

Introduction

It is generally assumed that graphite and other carbonaceous materials are composed largely of polycyclic aromatic molecules of varying shape, size, and edge structure. While there is no reason to believe that reactions of these substances cannot be described in conventional chemical terms, the diversity of possible structures vastly complicates detailed chemical discussion. As a result, a more realistic view of the chemistry of these molecules requires some means of simplifying the problem and providing semiquantitative structure–reactivity relations.

Fortunately, the chemistry of small polycyclic aromatic molecules has been thoroughly studied both experimentally and theoretically and is generally well understood. The electronic properties of these molecules are quite sensitive to the topology of their networks of mobile π-electrons. Semiempirical theories have been developed and applied successfully to a variety of π-electron molecules.[1-6] If such theories extrapolate to proper graphite limits, then they should also be applicable to the large π-electron molecules present in many forms of solid carbon.

We have previously examined the convergence behavior of five methods of calculation: structure–resonance theory (SRT), perturbation molecular orbital (PMO) theory, self-consistent field (SCF) molecular orbital theory, group additivity (GA) theory, and Huckel molecular orbital (HMO) theory.[7-11] Only the GA and HMO theories coverge to correct graphite limits. Group additivity has been used to predict available heats of formation of molecules.[12] However, it is easy to find cases in which it fails to predict known differences in isomer stabilities, and it cannot provide resonance energies of radicals. This is not surprising since GA accounts only for nearest-neighbor effects; π-electron properties are longer range phenomena. Huckel theory, on the other hand, takes into account the delocalized nature of the π-electrons. For many years, it has been used successfully to predict a variety of properties of small polycyclic aromatic molecules. It is computationally simple and, as mentioned above, converges to the correct graphite limits. It is reasonable to believe that it should be equally applicable to the large polycyclic aromatic molecules that make up graphitic substances.

Much of the chemistry of graphitic substances is likely to involve reactions of delocalized free radicals. The major factor determining the relative reactivities of these radicals is their resonance stabilization energy (RSE). This is a measure of the decrease in energy resulting from odd-electron delocalization. RSE is often defined as the difference between the bond dissociation enthalpy (BDE) of a molecule yielding a stabilized radical and the BDE of a paraffinic analogue. Thus, a BDE of 88 kcal/mol in toluene implies a RSE of 10 kcal/mol relative to the C–H bond in ethane (assuming BDE = 98 kcal/mol).

In the present work, we use HMO theory to predict RSE and, hence, obtain carbon–hydrogen bond dissociation energies and hydrogen atom affinities of polycyclic aromatic molecules of arbitrary size. With estimates of ionization potentials of free radicals, these values yield proton affinities as well.

Our approach is to estimate BDEs relative to a series of reference molecules whose BDEs are reasonably well-established. This is done in an effort to avoid the calculation of small differences in σ-bonding energies, values that we cannot reliably estimate. For an arbitrary bond dissociation reaction, the π-electron energy difference, calculated by Huckel theory, is compared with the π-energy difference for a reference dissociation of the same type. From these energy differences we estimate the BDE for the reaction for a number of compounds and compare them with the available experimental data. We also predict limits for BDEs for hydrogens attached to the edges of infinite graphite layers having several different edge structures.

Method and Discussion

All the dissociation reactions considered here transform an sp^3 into an sp^2 carbon atom and convert a localized σ-electron into a delocalized π-electron. Three factors influence the reaction thermochemistry: (1) π-electron delocalization, (2) distortion of the σ-bonding framework, and (3) changes in steric interactions between adjacent bound hydrogens.

Increased π-electron delocalization in the product will reduce its heat of formation relative to that of the reactant molecule. The change will be proportional to the Huckel energy difference between reactant and product. Specifically, this contribution to the BDE will be expressed as $p_h \Delta E = p_h(E_p - E_r)$, where p_h is the proportionality factor and E_p and E_r are the Huckel π-bonding

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(1) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: New York, 1966.

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

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(10) Stein, S. E.; Brown, R. L. In *Molecular Structures and Energetics*; Liebman, J., Greenberg, A., Eds.; VCH Publishers: New York, 1987; Chapter 2.

(11) Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 3721.

(12) Stein, S. E.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977**, *81*, 314.

energies of the product and reactant molecules, respectively. (Huckel energy units are β, the Huckel resonance integral.)

Increased stability for π-bonds results in σ-bond compression. Schaad and Hess[13] have shown that the σ-compression energy is in practice proportional to the π-electron energy. Thus, it need not be explicitly considered since it is implicitly contained in the parameter p_h. Another effect of changes in σ-bonds is a change in ring-strain energy resulting from changes in bond angles. It is hoped that these will be accounted for by dealing only with differences in BDEs for structurally related bonds, so that strain effects will cancel.

We have considered several examples of hydrogen detachment from methyl groups attached to aromatic ring systems. Because the two remaining hydrogens are now in the plane of the ring system, one or both may experience steric interactions with adjacent hydrogens on the ring system. This is the same as the close H,H interaction of the type observed in phenanthrene. This contribution to the BDE will be expressed as $p_s\Delta S = p_s(S_p - S_r)$, where S_p and S_r are the numbers of H,H type interactions in the product and reactant, respectively, and p_s is the proportionality factor.

The two parameters p_h and p_s will suffice to relate the BDE for the bond of interest to the BDE of a structurally related reference bond. We use for our correlation

$$\mathrm{BDE} = \mathrm{BDE}_{\mathrm{ref}} - p_h(\Delta E - \Delta E_{\mathrm{ref}}) + p_s(\Delta S - \Delta S_{\mathrm{ref}}) \quad (1)$$

Here, $\mathrm{BDE}_{\mathrm{ref}}$ is the BDE for the particular reference bond, ΔE_{ref} is the associated Huckel energy difference, and ΔS_{ref} is the difference in the number of H,H interactions. All the reference reactions considered in the present work have $\Delta S_{\mathrm{ref}} = 0$. BDE, E, and ΔS are the corresponding quantities for the reaction of interest.

To determine a value for p_h, we use experimental values for the enthalpies of H atom addition to benzene and to the 9-position in anthracene. These values are -21 ± 2 kcal/mol[14] and -44.9 ± 2 kcal/mol,[15] respectively. Let BDE in eq 1 be the bond dissociation enthalpy for H detachment (21 kcal/mol) from benzene. The Huckel energy for benzene (the product) is 8β; with one H atom added (the reactant) it is 5.4641β, giving $\Delta E = 2.5359\beta$. Let $\mathrm{BDE}_{\mathrm{ref}}$ in eq 1 be the bond dissociation enthalpy for H detachment (44.9 kcal/mol) from the 9-position in anthracene. The Huckel energy for anthracene is 19.3137β; with one H atom added to the 9-position it is 17.3005β, giving $\Delta E_{\mathrm{ref}} = 2.01323\beta$. Substituting these values into eq 1 (no H,H interactions are involved), we get $p_h = 45.7 \pm 3$ kcal/mol. The uncertainty here is that derived from the uncertainties in the two experimental BDE values.

For the second parameter p_s we use a value of 2 kcal/mol. It was obtained in previous work[11] from a fit of experimental heats of formation of a number of small aromatic hydrocarbons.

To cover most of the edge structures of interest, we have picked five reference reactions. These include hydrogen detachment from primary sp^3 carbons and detachment from four different varieties of secondary sp^3 carbons. Note that, on the basis of resonance stabilization energy alone, relative bond strengths for the reference reactions are not well predicted. For instance, the experimental benzylic C–H bond strength in fluorene is somewhat stronger than for 9,10-dihydroanthracene, while relative computed RSE values suggest that it should be weaker. We presume that these differences are due to differences in σ-bonding (strain) energies and attempt to compensate for these with our chosen reference reactions.

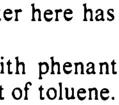
Methyl C–H Bond Dissociation Enthalpies. For H detachment from a primary carbon, we use the experimental value of 88 kcal/mol for the BDE of toluene[16] as the reference. Table I lists several BDEs derived from this reference BDE and eq 1. There are some experimental BDEs available for several small compounds, and these are shown in parentheses. Agreement is good, although differences from the reference BDE are not large.

By extrapolation, we have calculated the BDEs for H detachment from a methyl group attached to several types of infinitely extended structures. The parent molecules with anthracene-like edges are inherently unstable. Benzylic radical formation adds another π-electron center at an edge, and this normally increases their stability. Thus, BDEs for such hydrogens are considerably smaller than that for toluene. Examples shown in Table I are methyls attached to an infinitely long anthracene-like chain and an infinite graphite sheet having an anthracene-type edge. An exception occurs for methyls on the *corner* of an infinitely large hexagonally symmetric molecule with the anthracene-type edge. Carbons at these corners are not strongly bound by resonance to the rest of the molecule. The corner ring resembles the central ring in phenanthrene, a relatively stable aromatic ring. Addition of another π-electron center here has relatively little influence on its stability.

Analogous examples with phenanthrene-type edges exhibit BDEs much closer the that of toluene. These molecules already possess a large amount of resonance energy and gain relatively little stability by forming radicals.

Unstrained Diaryl Methyl C–H Bond Dissociation Enthalpies. The first type of secondary C–H bond we consider is that of a carbon atom attached to two sp^2 carbons in a six-membered ring. For the prototype we use the BDE observed for H detachment from 9,10-dihydroanthracene. This value is 76.3 kcal/mol.[17] Some representative BDEs calculated from this reference BDE and eq 1 are shown in Table II. Diphenylmethane is included in this list, although it is a special case. To match the prototype, the two phenyl groups in this compound should be nearly coplanar. In diphenylmethane they are inclined 40° to one another[18a] because of the steric hindrance of ring H atoms. MNDO calculations indicate that in the diphenylmethyl radical this angle is approximately 10° smaller.[18b] Huckel theory accommodates a twist in a π-bond by weighting the Coulomb integral, β, by the cosine of the twist angle.[4] Exact agreement with experiment[17,19] for the radical (possibly fortuitous) ensues from this modification of the simple theory.

Phenalenylic radicals are one class of compounds for which our application of structure-resonance theory was unsuccessful.[20]



Direct observation by ESR[21] of phenalenyl radicals at room temperature implies that their resonance stabilization energy is greater than 28 kcal/mol. One version of SRT predicts 22 kcal/mol for the RSE, while another yields 47 kcal/mol, a value that seems much too large. The present HMO method, on the other hand, predicts a BDE for phenalene of 58 kcal/mol, which in turn implies a RSE for the phenalenyl radical of 37 kcal/mol. (This is the amount by which the BDE is lower than the 95 kcal/mol observed for aliphatic secondary carbons.) This more reasonable value represents a success for the HMO method. Further examples of phenalenylic radicals in Table II show the

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[13] Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1971**, *94*, 3068.

[14] Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152.

[15] This value of 44.9 kcal/mol for the BDE of an H atom attached to the 9-position in anthracene was derived from the experimental BDE for H detachment from dihydroanthracene and the experimental heat of hydrogenation of anthracene as discussed in the Appendix.

[16] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[17] Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031.

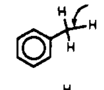
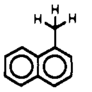
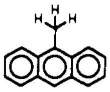
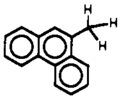
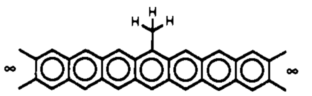
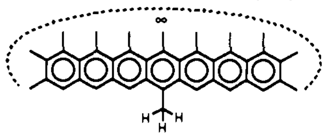
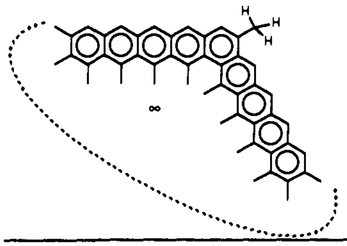
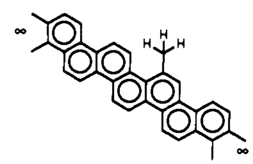
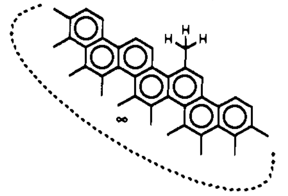
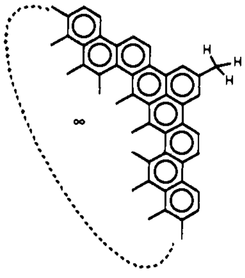
[18] (a) Dougherty, D. A.; Mislow, K.; Blount, J. F.; Wooten, J. B.; Jacobus, J. *J. Am. Chem. Soc.* **1977**, *99*, 6149. (b) Kafafi, S. A. Personal communication.

[19] (a) Robaugh, D. A. Ph.D. Thesis, West Virginia University, Morgantown, WV, 1983. (b) Stein, S. E. *ACS Symp. Ser.* **1981**, *No. 169*, 97.

[20] Stein, S. E. In *Chemistry of Coal Conversion*; Schlosberg, R., Ed.; Plenum: New York, 1985.

[21] Sogo, P. B.; Nakazaki, M. J.; Calvin, M. J. *J. Chem. Phys.* **1957**, *26*, 1343.

Table I. Bond Dissociation Enthalpies for H Detachment from Primary Carbons

bond[a]	ΔE (β)	ΔS	BDE (kcal/mol)
	0.7206	0	88.0[b]
	0.8121	1	86.1 (85.1)[c]
	0.9511	2	82.0 (81.8)[c] (81.4)[d]
	0.8133	1	86.0 (85.1)[c]
	1.2300[e]	2	69.2
	1.3616[f]	2	63.2
	0.8810[g]	1	82.9
	0.8158[h]		83.7[i]
	0.8446[j]		82.3
	0.7421[k]		87.0

[a] Dotted lines and infinity symbol denote an arbitrarily large, two-dimensional benzenoid layer. [b] This is the reference reaction for this set. See ref 16. [c] Reference 28. [d] Reference 23. [e] This is the limiting Huckel π-energy change for benzylic C–H dissociation from an infinite-length anthracene-like acene chain. [f] Limiting Huckel π-energy change for benzylic C–H dissociation from an infinite graphite sheet having an anthracene-type edge. [g] Limiting Huckel π-energy change for benzylic C–H dissociation from the corner position on hexagonally symmetric molecules having anthracene-type edges (series 1 molecules in ref 11). [h] Limiting Huckel π-energy change for benzylic C–H dissociation from an infinite-length phenanthrene-like acene chain. [i] These BDEs do not include steric effects of close H,H interactions. The hinderence is different from the S_1 type considered above and presumably larger. Both parent molecule and radical are affected. [j] Limiting Huckel π-energy change for benzylic C–H dissociation from an infinite graphite sheet having a phenanthracene-type edge. [k] Limiting Huckel π-energy change for benzylic C–H dissociation from the corner position on hexagonally symmetric molecules having phenanthracene-type edges (series 3 molecules in ref 11).

effect of symmetrically appending infinite acene chains.

C–H Bond Dissociation Enthalpies for Hydroaromatic Structures. For the second type of secondary C–H bond we consider carbon atoms attached to one sp^2 and one aliphatic carbon. As a reference we use H detachment from 9,10-dihydrophenanthrene. We derived a value of 84.6 kcal/mol for the BDE of this reaction from the experimental heats of hydrogenation of phenanthrene and anthracene and from the experimental BDE for H detachment from 9,10-dihydroanthracene. The calculation is discussed in the Appendix. Several BDEs corresponding to this prototype are shown in Table III. The agreement between theory and the single available experimental value (that for 1,3-cyclohexadiene) is gratifying.

C–H Bond Dissociation Enthalpies for Fluorene-Like Methylene Groups. The third type of secondary C–H bond considered involves a carbon in a five-membered ring attached to two sp^2 carbons. As reference we use fluorene with an experimental BDE of 80.1 kcal/mol.[22] A recent determination by Bordwell's group is in excellent agreement with this value.[23] Examples of BDEs based on this prototype are shown in Table IV. For indene, a BDE can be determined from several experimental differences in RSEs[24] and the observed BDE for diphenylmethane,[17,19] which again is in good accord with Bordwell's measurement.[23] The value obtained, 77.5 kcal/mol, is 2.5 kcal/mol higher than our HMO prediction. The experimental values for 1,3-cyclopentadiene average 3 kcal/mol higher than our value. Perhaps the most noteworthy facet of these bond strengths is the relatively small range in BDE. The range of estimated BDEs for all species in Table IV is only 8 kcal/mol. It appears that radicals centered on five-membered rings gain little additional stability by conjugation with extended aromatic networks, in accord with the conclusions of Bordwell based on experimental values.

H Atom Affinities. As a final series, we consider radicals produced by attaching H atoms to different positions on various polycyclic aromatic hydrocarbons. These measure, in effect, bond dissociation energies for radicals. Table V shows a number of such BDEs expressed as enthalpies of H atom addition to the positions indicated. The reference was the BDE for H atom detachment from 9-hydroanthryl radicals to form anthracene. For this we used the value 44.9 kcal/mol, derived from the experimental BDE for H detachment from 9,10-dihydroanthracene and the experimental heat of hydrogenation of anthracene. Details of the calculation are given in the Appendix. Note that the experimental enthalpy of H attachment to benzene was also used here implicitly. This happens because this value was used in determining the parameter p_h.

In addition to BDE predictions for some small compounds, we have also determined limiting BDEs for H atoms attached to the

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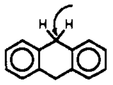
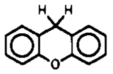
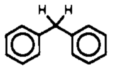
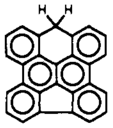
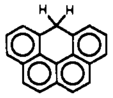
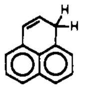
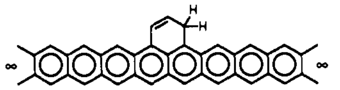
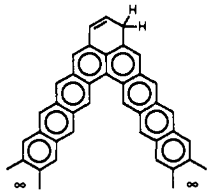
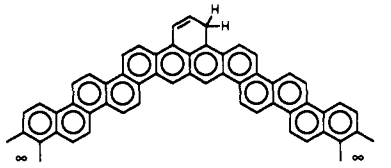
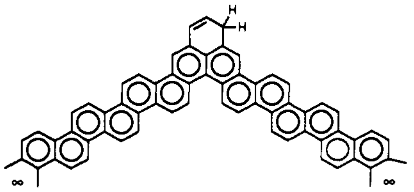
(22) Manka, M.; Brown, R. L.; Stein, S. E. *Int. J. Chem. Kinet.* **1987**, *19*, 943.

(23) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1229.

(24) Robaugh, D. A.; Stein, S. E. *J. Am. Chem. Soc.* **1986**, *108*, 3224.

Table II. Bond Dissociation Enthalpies for H Detachment from Secondary Carbons Attached to Two sp^2 Carbons in a Six-Membered Ring

bond	ΔE (β)	BDE (kcal/mol)
	1.3006	76.3[a]
	1.3464	74.2
	1.2027[b]	80.6 (80.9)[c] (81.8)[d]
	1.5125	66.6
	1.5089	66.8
	1.6978	58.1
	2.3	31
	1.7	58
	1.9	49
	1.7	58

[a] This is the reference reaction for this set. See ref 17. [b] Phenyl groups in radical twisted 35° relative to one another. [c] References 17 and 19. [d] Reference 18.

edge of a coronene-shaped hole in a graphite sheet, an infinite anthracene-like acene chain, a graphite sheet with an anthracene-type edge, an infinite phenanthrene-like chain, and a graphite sheet with a phenanthrene-type edge. Our results for these limits are similar to those shown in Table I for the benzylic radicals. Structures with anthracene-like ("zigzag") edges gain appreciable stability by attaching H atoms and thereby disrupting inherently unstable aromatic networks while the highly stable phenanthrene-type structures are already quite stable.

Free valence[4,25] is an index that has been used to correlate reactivities at different sites in π-electron molecules. It is based on the assumption that atoms in reactive positions have weak π-bonds with their neighbors. One would expect free valence to correlate with the H atom attachment energies calculated above. A reactive position with a large free valence should also have a large H atom affinity. A plot of free valence versus these attachment enthalpies is shown in Figure 1 for a sampling of the compounds appearing in Table V and edge positions on a very

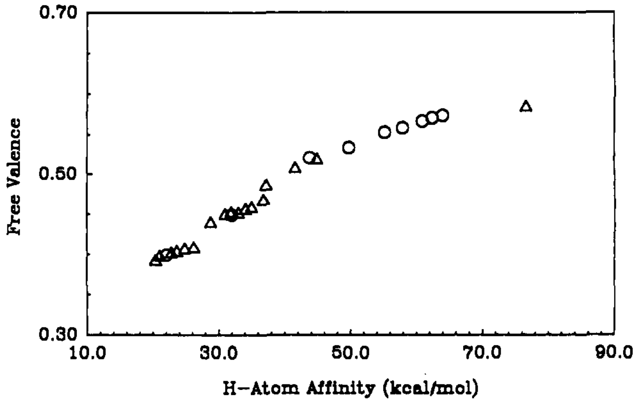


Figure 1. HMO energies for H atom addition versus HMO free valence. Triangles are for selected sites shown in Table V (benzene, naphthalene, phenanthrene, anthracene, pyrene, and kekulene and anthracene-edge extrapolation). Circles are for edges of anthracene-edge hexagonal molecule having 13 rings along each of its six edges.

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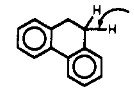
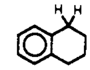
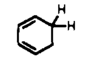
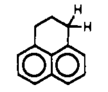
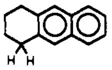
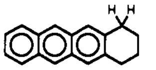
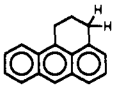
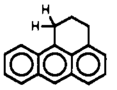
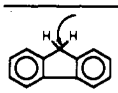
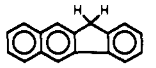
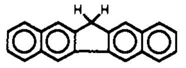
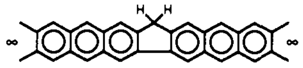
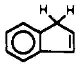
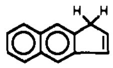
(25) Coulson, C. A. *Discuss. Faraday Soc.* **1947**, *2*, 9.

Table III. Bond Dissociation Enthalpies for H Detachment from Secondary Carbons Attached to One sp^2 and One sp^3 Carbon

bond	ΔE (β)	BDE (kcal/mol)
	0.7671	84.6[a]
	0.7206	86.7
	0.9920	74.3 (73)[b]
	0.8121	82.5
	0.7437	85.7
	0.7697	84.5
	0.8481	80.9
	0.9511	76.2

[a] This is the reference reaction for this set. BDE was derived from the experimental heats of hydrogenation of phenanthrene and anthracene and from the experimental BDE for H detachment from dihydroanthracene and from the experimental enthalpy for H attachment to benzene. See Appendix for details of the calculation. [b] Reference 16.

Table IV. Bond Dissociation Enthalpies for H Atom Detachment from Secondary Carbons Attached to Two sp^2 Carbons in a Five-Membered Ring

bond	ΔE (β)	BDE (kcal/mol)
	1.3414	80.1[a] (79.5)[b]
	1.3702	78.8
	1.3796	78.4
	1.52	72
	1.4514	75.0 (77.5)[c] (78.8)[b]
	1.5220	72.1
	1.3820	78.8 (78.8)[b] (81.2)[d]

[a] This is the reference reaction for this set. BDE value from ref 22. [b] Reference 23. [c] Experimental BDE determine from several empirical RSE differences (see ref 24) and the observed BDE for diphenylmethane (see ref 17 and 19). [d] Furugama, S.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *3*, 237.

large "zigzag" molecule. The correlation is generally good, although clearly the two calculated properties are not equivalent. Because of its closer connection to real properties (reaction thermodynamics), we feel that H attachment energies are more useful reactivity parameters than free valence.

Proton Affinities

As illustrated in the thermodynamic cycle below, the proton affinity of a specific site is equal to the sum of neutral H atom affinity at this site and the difference in ionization potentials of the product H adduct radical and a free H atom.

$$\begin{tikzcd}
H^+ + C{=}C \arrow[r, "PA"] \arrow[d, "-IP(H^\bullet)"'] & {}^+C{-}C{-}H \\
H^\bullet + C{=}C \arrow[r, "\text{H atom affinity}"] & {}^\bullet C{-}C{-}H \arrow[u, "IP({}^\bullet C{-}C{-}H)"']
\end{tikzcd}$$

$$PA = IP(\text{radical}) - IP(\text{H atom}) + \text{H atom affinity} \qquad (2)$$

Viewed in this way, protonation is the sum of two separate electron-transfer processes. In the first step, the incoming H atom removes one of two π-electrons in a filled orbital, forming a C–H bond and leaving behind an unpaired electron. In the second step, the unpaired electron is removed (ionized).

As discussed above, energies of H atom addition in the first step are sensitive to the chemical structures near the site of reaction and for the stable structures examined depend little on overall molecular size. H atom addition energies measure, in effect, the stability of π-bonding at the site of attack.

The IP of a delocalized radical, which determines the energy of the second step, can depend on the overall size of the conjugated π-system. Regardless of detailed chemical structure, for extended two-dimensional π-networks, the IP should converge with increasing molecular size to the single-layer graphite limit.

The IP of an arbitrarily large two-dimensional sheet of graphite is presumed to be approximately equal to the work function of graphite, 4.7 eV.[26] Thus, the IP of graphite is approximately 4 eV (100 kcal) less than the ionization energy of typical delocalized π-radicals (8 eV for the cyclohexadienyl radical and 7.8 eV for the 9-hydroanthryl radical, see Table VI). Hence, large, highly condensed PAH radicals will have substantially lower IPs than conventional π-radicals. Since neutral H atom affinities do not depend directly on size, they will have similar H atom affinities for large and small systems. Consequently, according to eq 2, PAs will be much greater for the large PAH networks than for conventional PAH-derived radicals.

To gain a more quantitative picture, in Table VI are listed a number of H atom affinities and radical IPs. The range of variation of experimental radical IPs is far less than the predicted maximum range of 100 kcal. Even coronene is still far from the graphite limit. Apparently, benzenoid clusters of this nature must become very large before their PAs increase appreciably.

The considerably greater ease of ionizing graphite compared to a small radical presumably results from a higher degree of electron–electron repulsion associated with the least stable occupied orbital in graphite.

A possible flaw in this argument is our assignment of the IP of an extended polycyclic layer to the IP of graphite. However, for our qualitative conclusions to be changed, the IP of this layer would have to be more than 3 eV higher than the accepted work function of graphite. We have found no evidence in the literature for such a large difference.

The practical result of the above discussion is that proton affinities are sensitive to both the site of protonation and the overall size and shape of the molecule. Hence, it appears that large, more highly condensed PAH clusters, as may be found in carbonized materials, will tend to have far higher PAs than conventional PAHs. On the other hand, even for very large PAH clusters with IPs all near the limiting infinite plane limit, differences in the PA of different sites are predicted to closely parallel differences in neutral H atom affinities.

Summary

Huckel theory provides a unique, reliable means of estimating H atom and proton affinities for very large benzenoid polycyclic

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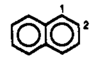
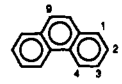
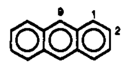
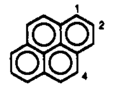
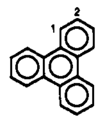
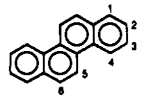
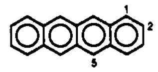
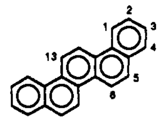
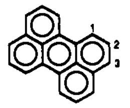
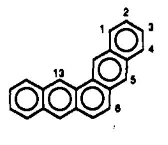
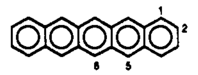
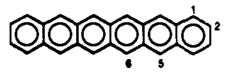
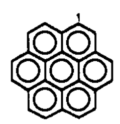
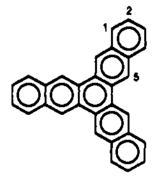
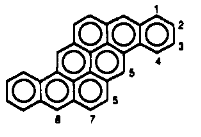
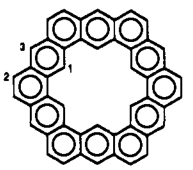
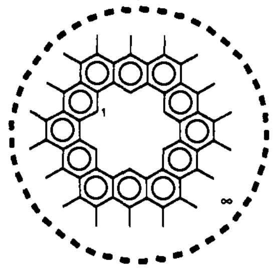
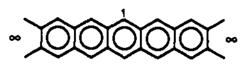
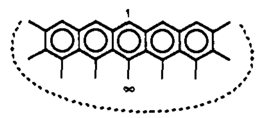
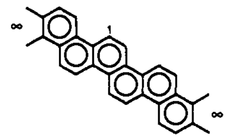
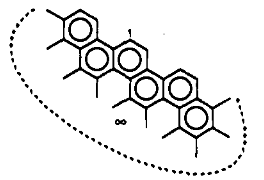
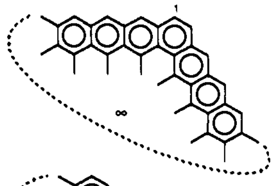
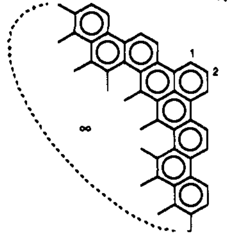
[26] Braun, A.; Bush, G. *Helv. Phys. Acta.* **1947**, *20*, 133.

Table V. Bond Dissociation Enthalpies for Radicals Produced by Attaching H Atoms to the Edges of Aromatic Hydrocarbons

compd[a]	posn	$-\Delta H_{298}$ (kcal/mol) for H atom addn
	1	21[b]
	1	32
	2	24
	1	31
	2	23
	3	25
	4	31[c]
	9	32
	1	35
	2	26
	9	44.9[d]
	1	37
	2	20
	4	33
	1	30[c]
	2	24
	1	32
	2	23
	3	25
	4	32[c]
	5	32[c]
	6	34
	1	36
	2	28
	5	49
	1	32[c]
	2	25
	3	23
	4	32
	5	34
	6	32[c]
	13	33[c]
	1	38[c]
	2	22
	3	39
	1	34
	2	26
	3	25
	4	34
	5	43
	6	35
	13	43[c]
	1	32
	2	29
	5	50
	6	53
	1	38
	2	30
	5	51
	6	54
	1	32
	1	33
	2	25
	5	42[c]
	1	36
	2	23
	3	30
	4	31[c]
	5	47[c]
	6	35[c]
	7	37
	8	51
	1	42[c]
	2	34
	3	42
	1	48[c] (graphite lim)
	1	61 (infinite-chain lim)
	1	78 (graphite lim)
	1	34[c] (infinite-chain lim)
	1	36[c] (graphite lim)
	1[e]	38 (graphite lim)
	1[f]	40[c]
	2[f]	23 (graphite lim)

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[a] Dotted lines and infinity symbol denote an arbitrarily large, two-dimensional benzenoid layer. [b] This is the experimental enthalpy for H attachment to benzene.[14] Since it was used to derive a value for the parameter p_h, the theory must give the same value. [c] The small effects of the phenanthrene-type H,H steric interactions are included in these values. [d] This is explicit reference experimental BDE. Details of its derivation are discussed in the Appendix. [e] Limiting BDE for corner position on hexagonally symmetric molecules having anthracene-type edges (series 1 molecules in ref 11). [f] Limiting BDEs for corner positions on hexagonally symmetric molecules having phenanthrene-type edges (series 2 molecules in ref 11).

Table VI. Proton Affinites and Related Properties of PAHs and Single-Layer Graphite[a]

radical	ΔPA[b]	ΔH atom affinity[c]	ΔIP[d]
benzene	(0)	(0)	(0)
naphthalene	11.5	11	1
phenanthrene	14.9	11	4
chrysene	18.5	13	6
anthracene	24.6	24	1
tetracene	33.9	28	6
pyrene	23.7	12	12
perylene	28.2	18	10
coronene	22.2	11	11
single-layer graphite	(60–100)[e]	15[f]–55[g]	45[h]

[a] All units are kilocalories per mole. [b] Except where noted, from: Mautner, M. *J. Phys. Chem.* **1980**, *84*, 2716. [c] From present work. [d] =ΔPA−Δ(H atom affinity), except where noted. Addition to the most reactive site is assumed in all cases. [e] =Δ(H atom affinity) + Δ(radical IP). Assumes ionization of the most stable radical in all cases. [f] Limiting "armchair" (phenanthrene-like) edge value. [g] Limiting "zigzag" (anthracene-like) edge value. [h] From work function of graphite (4.7 eV[26]).

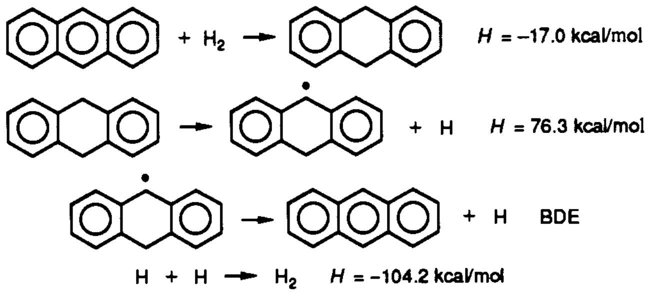
aromatic structures. Except for the highly unstable "zigzag" (linear acene-like) edges, H atom addition energies are determined almost entirely by the chemical structures within several atoms of the reaction site and have values similar to those in conventional polycyclic aromatic hydrocarbons. We have used several reference reactions to estimate H atom addition energies for large PAHs. With these, one is able to estimate the energetics of reactions of PAH structures too large to isolate for experimental study.

It is argued that proton affinities, which depend on ionization potentials as well as the H atom affinities, are sensitive to molecular size because of the pronounced size dependence of the former property. Available data suggest, however, that the large increases predicted in infinite layer limit are not observable for conventional PAHs (up to 24 carbon atoms).

Acknowledgment. This work was supported by a grant from the Gas Research Institute.

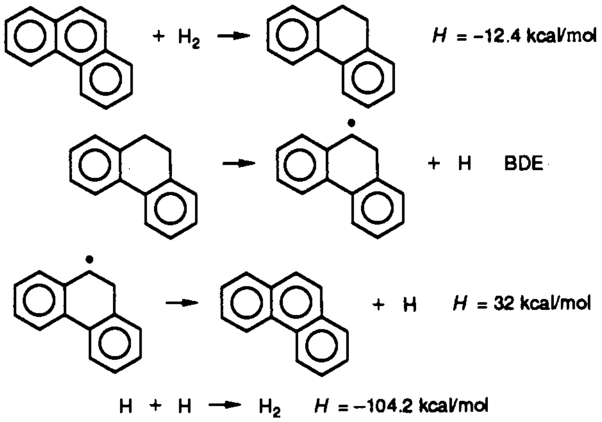
Appendix

Determination of Bond Dissociation Enthalpies for 9-Hydroanthryl Radicals and 9,10-Dihydrophenanthrene. The BDE for H atom detachment from 9-hydroanthryl radicals to form anthracene was determined from the experimental BDE for H detachment from 9,10-dihydroanthracene[16,27,28] and the heat of hydrogenation of anthracene.[29] Addition of the following reactions provides an equation that can be solved for the desired BDE:



From this, we get BDE equal to 44.9 kcal/mol.

In an analogous manner, we calculated the BDE for 9,10-dihydrophenanthrene from the experimental heat of hydrogenation of phenanthrene[30] and the heat of H atom attachment to the 9-position of phenanthrene. This latter quantity was calculated from our HMO method from the observed heats of H atom attachment to benzene and anthracene (these quantities fix the value of p_h). This is the value of 32 kcal/mol that appears for phenanthrene in Table V. Addition of the following reactions gives the required BDE:



This gives a value for BDE of 84.6 kcal/mol.

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(27) Manka, M. J.; Stein, S. E. *J. Phys. Chem.* **1984**, *88*, 5914.

(28) McMillen, D. F.; Trevor, P. L.; Golden, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 7400.

(29) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(30) Lee Bechtold, S. H. *J. Chem. Thermodyn.* **1979**, *11*, 464.