J. Am. Chem. Soc. 1989, 111, 5675-5680

Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 11. The Benzenoid Aromatics

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Abstract: Ab initio calculations have been performed at the SCF level in the STO-3G, 3-21G, and 6-31G* basis sets on a variety of benzenoid and nonbenzenoid aromatic hydrocarbons, ranging from benzene to coronene. It is shown that (1) the enthalpy changes for homodesmic reactions involving only benzenoid aromatics can be computed accurately in all three bases and (2) there exist group equivalents for each basis set that enable conversion of ab initio total SCF energies to accurate heats of formation. Several examples demonstrate the extension of the method to substituted benzenes. The implications of these results concerning the correlation energies of aromatic hydrocarbons and the relationship of finite planar aromatics to the infinite graphitic sheet are discussed.

The determination of standard heats of formation by ab initio calculation is usually based upon one of two schemes: (1) calculation of the enthalpy change of a homodesmic reaction in which the subject molecule participates[2] (a homodesmic reaction balances the numbers of bonds of each type (single, double, triple) formed between atoms of the same chemical group and hybridization[3]); (2) use of group equivalents[4] or atom equivalents[5] for fragments of the molecule in conjunction with its ab initio total SCF energy. The first of these provides heats of formation for nonaromatic hydrocarbons accurate to a few kcal/mol at the 6-31G* SCF[6a] level except when highly strained molecules are involved, in which case second-order correlation energies (RMP2) must be included.[7] The second scheme, at the 6-31G* SCF level, is comparable in accuracy to the first. (A group-equivalent scheme can be thought of as a homodesmic reaction in which the groups themselves serve as the reactants and the subject molecule as the product.)

Both of these schemes are unreliable for aromatic hydrocarbons. For example, the heat of formation of benzene derived from the homodesmic reaction

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

is in error by 3.7 and 7.9 kcal/mol at the 6-31G* SCF and RMP2 levels, respectively, and these defects are not reduced by substantial enlargement of the basis set.[8] The atom-equivalent scheme furnishes a heat of formation of benzene too low by 7.7 kcal/mol.[5]

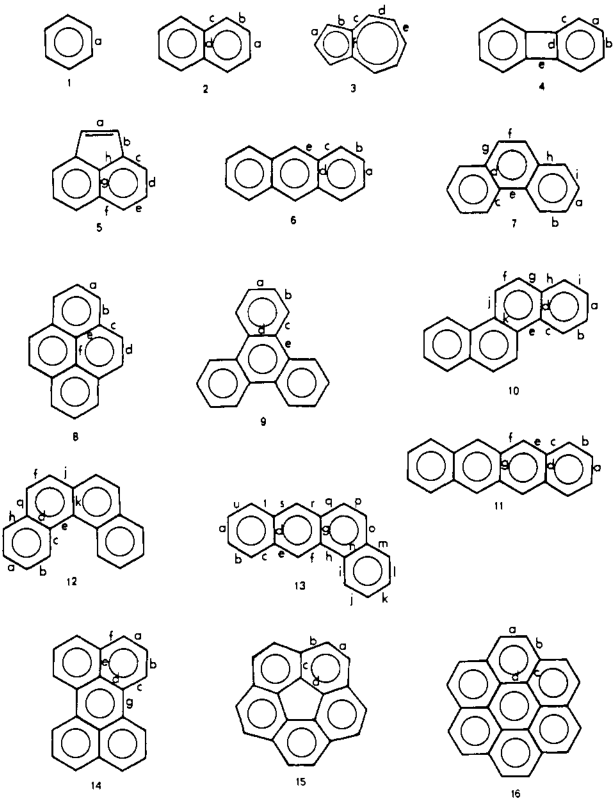
For naphthalene, the homodesmic reaction

$$\text{naphthalene} + 5\ \text{ethylene} + 4\ \text{propene} \rightarrow 6\ \text{butadiene} + 2\ \text{isobutene}$$

furnishes a heat of reaction in error by 6.6 and 14.3 kcal/mol at the 6-31G* SCF and RMP2 levels, respectively. The heat of formation derived from atom equivalents in the same basis is too low by 8.9 kcal/mol.

It is not unreasonable that difficulty should be encountered when an aromatic molecule is associated with (nonaromatic) olefins in a homodesmic scheme or with group equivalents derived from such olefins at the SCF level: electron delocalization may not be amenable to distribution among localized moieties; even if it were, these might not be the same as those of unconjugated or linearly conjugated olefins. Moreover, the CC bond lengths and thus the σ systems of aromatic molecules can differ appreciably from those of (localized) olefins.

Chart I



In approaching the ab initio thermochemistry of the aromatics, we deal first with the following two questions: (1) Can accurate enthalpy changes of homodesmic reactions containing *only* aromatic species be derived from their ab initio SCF energies? If so, (2) can group equivalents be obtained that serve to convert ab initio SCF energies of aromatics to accurate heats of formation? We show here that the answers to both of these questions are in the affirmative, even for small basis sets, when the aromatics are restricted to the class of condensed benzenoid hydrocarbons. (The implication of these results concerning the role of electron correlation is discussed below.) Moreover, it also appears that a mixed group-equivalent scheme at the 6-31G* SCF level is applicable to species having both aromatic and nonaromatic moieties; several examples are provided. The significance of this result is that the

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(1) For part 10 of the series see: Schulman, J. M.; Miller, M. A.; Disch, R. L. *Pure Appl. Chem.* in press.

(2) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 1202.

(3) (a) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222. (c) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036.

(4) (a) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 197. (b) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.

(5) Ibrahim, M. A.; Schleyer, P. v. R. *J. Comput. Chem.* **1985**, *6*, 157.

(6) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217. (b) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (c) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(7) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

(8) Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* **1988**, *152*, 402.

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Table I. STO-3G and Experimental Bond Lengths (angstroms)

molecule	bond	calcd	exptl[a]	exptl − calcd
benzene	a	1.387	1.399	0.012
naphthalene	a	1.425	1.412	−0.013
	b	1.353	1.371	0.018
	c	1.432	1.422	−0.010
	d	1.405	1.420	0.015
azulene	a	1.391	1.399	0.009
	b	1.396	1.418	0.022
	c	1.392	1.383	−0.008
	d	1.389	1.406	0.017
	e	1.391	1.403	0.011
	f	1.502	1.501	−0.001
biphenylene	a	1.426	1.419	−0.007
	b	1.367	1.385	0.018
	c	1.353	1.372	0.019
	d	1.426	1.426	0.000
	e	1.516	1.514	−0.002
acenaphthylene[b]	a	1.331	1.395	0.064
	b	1.495	1.466	−0.029
	c	1.357	1.381	0.024
	d	1.435	1.424	−0.011
	e	1.360	1.382	0.022
	d	1.436	1.433	−0.003
	g	1.377	1.386	0.009
	h	1.421	1.441	0.020
anthracene	a	1.444	1.418	−0.026
	b	1.341	1.375	0.034
	c	1.451	1.444	−0.007
	d	1.425	1.433	0.008
	e	1.393	1.405	0.012
phenanthrene	a	1.409	1.394	−0.015
	b	1.364	1.384	0.020
	c	1.418	1.409	−0.009
	d	1.402	1.420	0.018
	e	1.473	1.465	−0.008
	f	1.334	1.350	0.016
	g	1.454	1.453	−0.001
	h	1.417	1.423	0.006
	i	1.363	1.386	0.023
pyrene	a	1.385	1.395	0.010
	b	1.395	1.406	0.011
	c	1.462	1.438	−0.024
	d	1.333	1.367	0.034
	e	1.413	1.425	0.012
	f	1.446	1.430	−0.016
triphenylene	a	1.398	1.397	−0.001
	b	1.369	1.381	0.012
	c	1.411	1.410	−0.001
	d	1.402	1.413	0.011
	e	1.485	1.458	−0.027
chrysene	a	1.414	1.394	−0.020
	b	1.360	1.381	0.021
	c	1.425	1.409	−0.016
	d	1.402	1.407	0.005
	e	1.464	1.468	0.004
	f	1.340	1.369	0.029
	g	1.442	1.421	−0.021
	h	1.422	1.428	0.006
	i	1.358	1.363	0.005
	j	1.446	1.428	−0.018
	k	1.390	1.401	0.011
tetracene	a	1.454	1.459	0.005
	b	1.336	1.381	0.045
	c	1.460	1.420	−0.040
	d	1.442	1.420	−0.022
	e	1.371	1.390	0.019
	f	1.416	1.404	−0.012
	g	1.427	1.460	0.033
3,4-benzophenanthrene	a	1.414	1.409	−0.005
	b	1.360	1.378	0.018
	c	1.427	1.433	0.006
	d	1.407	1.431	0.024
	e	1.470	1.446	−0.024
	f	1.338	1.342	0.004
	g	1.444	1.443	−0.001
	h	1.423	1.391	−0.032
	i	1.359	1.374	0.015
	j	1.445	1.430	−0.015
	k	1.389	1.412	0.023
1,2-benzanthracene[c]	a	1.438	1.405	−0.033
	b	1.346	1.358	0.012
	c	1.444	1.417	−0.027
	d	1.414	1.422	0.008
	e	1.406	1.408	0.002
	f	1.380	1.385	0.005
	g	1.430	1.426	−0.004
	h	1.479	1.466	−0.013
	i	1.409	1.400	−0.009
	j	1.369	1.358	−0.011
	k	1.401	1.387	−0.014
	l	1.369	1.359	−0.010
	m	1.404	1.405	0.001
	n	1.401	1.407	0.006
	o	1.465	1.437	−0.028
	p	1.329	1.338	0.009
	q	1.463	1.439	−0.024
	r	1.382	1.390	0.008
	s	1.408	1.394	−0.014
	t	1.445	1.423	−0.022
	u	1.346	1.354	0.008
perylene	a	1.353	1.370	0.017
	b	1.417	1.418	0.001
	c	1.367	1.397	0.030
	d	1.440	1.425	−0.015
	e	1.410	1.424	0.014
	f	1.427	1.400	−0.027
	g	1.499	1.471	−0.028
corannulene	a	1.363	1.402	0.039
	b	1.462	1.440	−0.022
	c	1.361	1.391	0.030
	d	1.423	1.413	−0.010
coronene[d]	a	1.349	1.362 (1.385)	0.013
	b	1.437	1.444 (1.415)	0.007
	c	1.396	1.381 (1.430)	−0.015
	d	1.438	1.438 (1.430)	−0.000

[a] The experimental values are given by: Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975 (except for acenaphthylene and coronene). [b] Reference 13. [c] The experimental values are averages derived from five methyl-substituted benzanthracenes. Briant, C. E.; Jones, D. W.; Shaw, J. D. *J. Mol. Struct.* **1985**, *130*, 167. [d] The X-ray values are those of ref 19a. The electron-diffraction values, given in parentheses, are those of ref 19b.

thermochemistry of a very large number of molecules, heretofore excluded, is brought within the province of ab initio molecular orbital theory.

Methods

The geometries of the molecules shown in Chart I were optimized at the STO-3G SCF level[6b] assuming the following symmetries: D_{6h}, benzene (**1**), coronene (**16**); D_{3h}, triphenylene (**9**); D_{2h}, naphthalene (**2**), biphenylene (**4**), anthracene (**6**), pyrene (**8**), tetracene (**11**), perylene (**14**); C_{2v}, azulene (**3**), phenanthrene (**7**), acenaphthylene (**5**); C_{2h}, chrysene (**10**); C_2, 3,4-benzophenanthrene (benzo[*c*]phenanthrene) (**12**); C_s, 1,2-benzanthracene (benz[*a*]anthracene) (**13**); D_{5h} and C_{5v}, corannulene (**15**). The molecular energies at these geometries were also calculated at the 3-21G[6c] and 6-31G*[6a] SCF levels. Group equivalents were obtained in each basis set from the SCF energies, using a training set containing all molecules except azulene, biphenylene, acenaphthylene, tetracene, corannulene, and coronene.

The perspective drawing of 3,4-benzophenanthrene was obtained with Chem-X, designed and distributed by Chemical Design, Ltd., Oxford, England.

Geometries

The calculated bond lengths, given in Table I, range from 1.329 to 1.516 Å, the average for 114 bonds being 1.408 Å. The corresponding experimental range and average are 1.338–1,514 and 1.409 Å; the rms deviation between calculation and experiment is 0.021 Å. Good agreement with experimental geometries has also been obtained with the MOMM[9] and MMP2[10] molecular

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(9) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 3817, and private communication.

Table II. Total Energies of Aromatic Hydrocarbons (au)[a]

molecule	STO-3G	3-21G	6-31G*
benzene (C_6H_6)	−227.8914	−229.4190	−230.7029
naphthalene ($C_{10}H_8$)	−378.6868	−381.2146	−383.3543
azulene ($C_{10}H_8$)	−378.5925	−381.1366	−383.2819
biphenylene ($C_{12}H_8$)	−453.4176	−456.4368	−459.0138
acenaphthylene ($C_{12}H_8$)	−453.4829	−456.5020	−459.0728
anthracene ($C_{14}H_{10}$)	−529.4725	−533.0017	−535.9975
phenanthrene ($C_{14}H_{10}$)	−529.4874	−533.0142	−536.0088
pyrene ($C_{16}H_{10}$)	−604.3253	−608.3439	−611.7667
triphenylene ($C_{18}H_{12}$)	−680.2860	−684.8106	−688.6593
chrysene ($C_{18}H_{12}$)	−680.2838	−684.8096	−688.6595
tetracene ($C_{18}H_{12}$)	−680.2535	−684.7848	−688.6375
3,4-benzophenanthrene ($C_{18}H_{12}$)	−680.2702	−684.7983	−688.6480
1,2-benzanthracene ($C_{18}H_{12}$)	−680.2770	−684.8045	−688.6558
perylene ($C_{20}H_{12}$)	−755.1125	−760.1275	−764.4049
corannulene ($C_{20}H_{10}$)[b]	−753.9035	−758.9051	−763.1871
coronene ($C_{24}H_{12}$)	−904.8227	−910.8177	−915.9503

[a] The 3-21G and 6-31G* SCF energies were calculated at the STO-3G geometries. [b] Total corresponding energies for planar corannulene are −753.8893, −758.8887 and −763.1730 au.

mechanics methods, which include a molecular orbital calculation for the conjugated π system.

Several of the geometries merit comment. The STO-3G geometry and energy of naphthalene agree with those reported previously by Haddon and Raghavachari.[11a] These same authors have shown that for azulene (**3**) a C_s structure is more stable in the STO-3G basis, by 3.7 kcal/mol, than the C_{2v} form, whereas the latter form is the more stable in the 6-31G[11b] basis and is the form observed experimentally. The energies of azulene employed here were obtained at the STO-3G (C_{2v}) geometry. The 6-31G* SCF value of its dipole moment is 1.51 D, with the positive end toward the seven-membered ring. This value is probably an overestimate: in passing from 6-31G SCF to 6-31G RMP2, the dipole moment is reduced by 0.50 D.[11b] Application of this correction to the 6-31G* SCF value, 1.51 D, gives a dipole moment of about 1.0 D, in good agreement with the experimental values of 0.80[12a] and 1.08 D.[12b]

Another nonalternant hydrocarbon for which the calculated geometries are in some disagreement with experiment is acenaphthylene (**5**), whose STO-3G C_1C_2 bond length is 1.331 Å vs 1.395 ± 0.011 Å found by neutron diffraction.[13] On the other hand, the neutron diffraction C_1H_1 bond length, 1.052 ± 0.013 Å, is much smaller than the STO-3G value, 1.081 Å; the other three experimental CH bond lengths, 1.090, 1.094, and 1.077 Å, are normal. In an effort to resolve these discrepancies, the geometry of acenaphthylene was optimized at the 6-31G* SCF level. This produced a C_1C_2 bond length of 1.340 Å, in better agreement with the STO-3G value than with experiment, and provided a normal C_1H_1 bond length, 1.073 Å. The 6-31G//6-31G* (in the usual notation) energy of acenaphthylene, −459.0738 au, is only 0.6 kcal/mol lower than the 6-31G*//STO-3G value given in Table II. The AM1 method[14] gives a C_1C_2 bond length of 1.371 Å but provides no evidence for a short C_1H_1 bond.

Triphenylene (**9**) was assumed to have D_{3h} symmetry, although its X-ray structure indicates slight out-of-plane distortions. Molecular mechanics calculations suggest that these distortions reduce the energy of the planar form by only 0.1 kcal/mol,[9] so the assumption of planarity probably introduces only a very small error. In contrast, for 3,4-benzophenanthrene ([4]helicene, **12**), the out-of-plane distortions cannot be ignored; even in the optimized C_2 structure, Figure 1, the inner hydrogens are still only 1.96 Å apart, approximately the same distance found for the corresponding hydrogens of phenanthrene. The agreement of the calculated CCCC dihedral angles with experiment[15] is good, although several large deviations from experimental values are found: 2.4°, 4–4a–5–6; −2.6°, 4–4a–12c–12b; −2.2°, 4–4a–12c–1; 2.2°, 12b–12c–1–2. The deviations from experiment for these angles found with the AM1 method, 0.6°, 0.0°, −0.7°, and −0.5°, are smaller. Vogler, using a molecular mechanics method,[16] has reported good agreement with experiment for the averaged out-of-plane distortions of 3,4-benzophenanthrene.

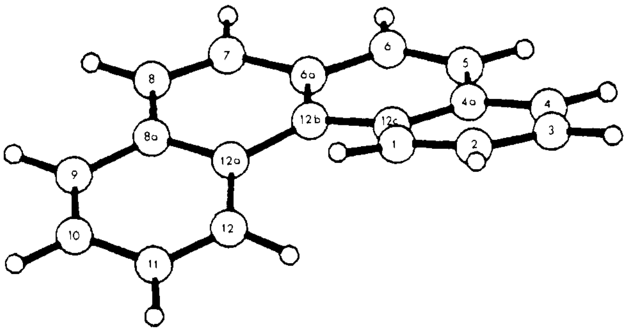


Figure 1. Perspective drawing of 3,4-benzophenanthrene optimized in the STO-3G basis.

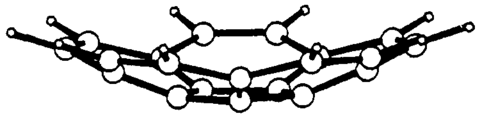
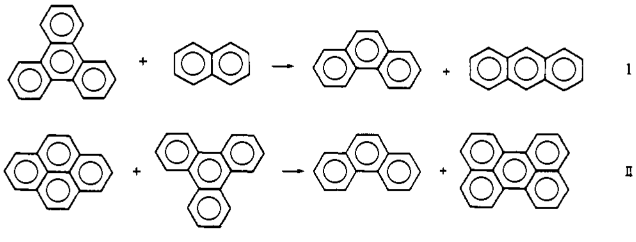


Figure 2. Perspective drawing of corannulene optimized in the STO-3G basis.

Chart II



The geometry of corannulene (**15**) was optimized in both D_{5h} and C_{5v} symmetries. The C_{5v} form, Figure 2, is lower in energy by 8.8, 10.3, and 8.8 kcal/mol in the STO-3G, 3-21G, and 6-31G* basis sets, respectively; the MOMM energy difference is 5.7 kcal/mol.[9] The STO-3G CC bond lengths of corannulene are in fair agreement with the X-ray values.[17] Bonds c and d are analogues of the short and long bonds of the icosahedral C_{60} molecule, whose STO-3G values are 1.376 and 1.465 Å;[18a] the lengths of bonds c and d in corannulene are 1.361 and 1.423 Å.

There have been two experimental studies of the structure of coronene (**16**). We find somewhat better agreement with the X-ray results[19a] than with the electron diffraction values.[19b]

The 6-31G* energy of benzene calculated at its own geometry is lower than that at the STO-3G geometry by only 0.1 kcal/mol. Similarly, the 6-31G*//6-31G* SCF energy of azulene, −383.2826 au, is 0.4 kcal/mol lower than the 6-31G*//STO-3G value, and the energy lowering in acenaphthylene is only 0.6 kcal/mol. However, the STO-3G, 3-21G, and 6-31G* energies of phenanthrene calculated at a geometry in which the CC bond lengths are fixed at 1.404 Å are 11.1, 8.1, and 8.1 kcal/mol higher than

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(10) Sprague, J. T.; Tai, J. C.; Yuh, Y.; Allinger, N. A. *J. Comput. Chem.* **1987**, *8*, 581.

(11) (a) Haddon, R. C.; Raghavachari, K. *J. Chem. Phys.* **1983**, *79*, 1093. (b) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1981**, *104*, 3516.

(12) (a) Tobler, H. J.; Bander, H. H. *J. Mol. Spectrosc.* **1965**, *18*, 239. (b) McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman: San Francisco, 1963.

(13) Wood, R. A.; Welberry, T. R.; Rae, A. D. *J. Chem. Soc., Perkin Trans 2* **1985**, 451.

(14) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(15) Hirshfeld, F. L.; Sandler, S.; Schmidt, G. M. J. *J. Chem. Soc.* **1963**, 2108.

(16) Vogler, H. *J. Mol. Struct.* (*THEOCHEM*) **1985**, *125*, 333.

(17) Hanson, J. C.; Nordman, C. E. *Acta. Crystallogr., Sect. B* **1976**, *32*, 1147.

(18) (a) Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* **1986**, *125*, 465. (b) Schulman, J. M.; Disch, R. L.; Miller, M. A.; Peck, R. C. *Chem. Phys. Lett.* **1987**, *141*, 45.

(19) (a) Robertson, J. M.; White, J. G. *J. Chem. Soc.* **1945**, 607. (b) Bastiansen, O.; Skancke, P. N. *Adv. Chem. Phys.* **1961**, *3*, 323.

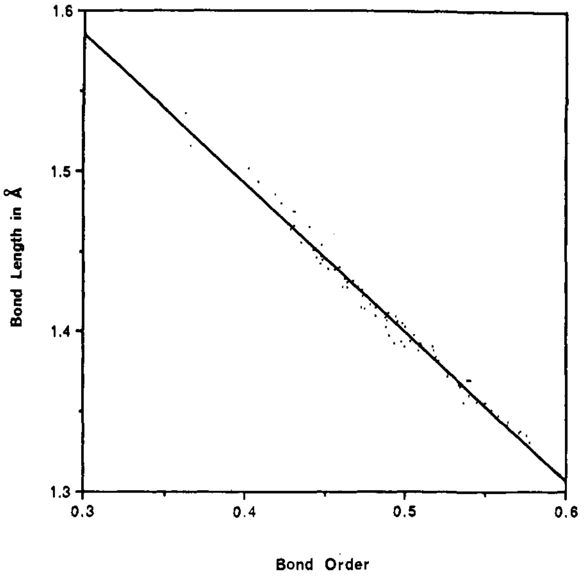

Figure 3. Least-squares fit of the STO-3G CC bond lengths to the Mulliken total overlap populations of the bonded carbons. The figure includes the CC bond of ethane, whose length and bond order are 1.538 Å and 0.363, respectively.

the corresponding values at the STO-3G geometry. This suggests that standard geometries are not sufficient for the calculation of total energies of condensed benzenoid hydrocarbons. They are probably useful, however, for comparing the effects of substituents on the same benzenoid skeleton.[20]

The length of bond C_iC_j correlates well with the product of STO-3G p–π atomic orbital coefficients and with the Mulliken total bond order, n_{ij}[21] (Figure 3).

Thermochemistry

Homodesmic Reactions. The STO-3G, 3-21G, and 6-31G* energies of the 16 aromatic hydrocarbons (Chart I), calculated at their STO-3G geometries, are given in Table II. These energies furnish accurate heats of reaction for the model homodesmic reactions I and II (Chart II). The largest reactant in reaction I is triphenylene (**9**), and the calculated ΔH of reaction, 8.1, 5.8, and 4.6 kcal/mol in the STO-3G, 3-21G, and 6-31G* basis sets are in good agreement with experiment, 5.6 kcal/mol. For reaction II, the largest reactant is perylene, and the calculated values in these same basis sets are 7.2, 8.0, and 7.7 kcal/mol, which compare well with the experimental value, 8.23 kcal/mol. No correction was made for the small zero-point and thermal effects, since the experimental error for each reaction, ca. 4 kcal/mol, is much larger. In the few instances where optimizations were carried out in the 3-21G and 6-31G* basis sets, the molecular energies obtained were lower than those of Table II by less than 1 kcal/mol. The internal consistency of the theoretical ΔH values is remarkable in view of the large ab initio energies being combined: the total energy of reactants (or products) is of the order of -10^5 kcal/mol. More important, the agreement with experiment, even for the STO-3G basis set, is remarkably good.

Several sets of isomers are among the compounds considered: naphthalene and azulene; biphenylene and acenaphthylene; anthracene and phenanthrene; the five $C_{18}H_{12}$ isomers triphenylene, chrysene, tetracene, 3,4-benzophenanthrene, and 1,2-benzanthracene. For the reaction

phenanthrene → anthracene

which involves two benzenoid aromatics, the calculated isomerization energies are 9.3, 7.8, and 7.1 kcal/mol in the STO-3G, 3-21G, and 6-31G* basis sets, in reasonable agreement with experiment, 5.9 kcal/mol.

Table III. Group Equivalents for Benzenoid Aromatics (au)

	group equivalent (GE)		
group	STO-3G	3-21G	6-31G*
$=C_bH-$	-37.987 22	-38.241 98	-38.456 00
$=C_b<$	-37.422 80	-37.667 73	-37.881 38

The energy differences of the five $C_{18}H_{12}$ isomers are in good agreement with experiment (and with the number of Kekulé structures) except for tetracene, whose experimental heat of formation, 69.8 kcal/mol, is virtually the same as that of 3,4-benzophenanthrene, 69.6 kcal/mol. We tentatively conclude, as have Kao,[9] Sprague et al.,[10] and Dewar,[22] that the experimental heat of formation of tetracene is in error.

A simple homodesmic isomerization for which good agreement with experiment is not found at the SCF level is

naphthalene → azulene

Here the product is not a benzenoid aromatic. The calculated isomerization energies are 59.2, 48.9, and 45.4 kcal/mol at the STO-3G, 3-21G, and 6-31G* SCF levels, while the experimental value is 37.65 ± 1.15 kcal/mol, based upon 73.5 kcal/mol for the heat of formation of azulene. Inclusion of electron correlation to second order in the 6-31G* basis lowers the isomerization energy from 45.4 to 34.8 kcal/mol, which is in error by only 2.8 kcal/mol. Haddon and Raghavachari[11a] have reported similar improvement at the RMP2 level in the 6-31G basis.

For the reaction

acenaphthylene → biphenylene

in which neither molecule is completely benzenoid, the agreement with the experimental enthalpy change, 42.8 ± 2.7 kcal/mol is fair, the calculated values being 41.0, 40.9, and 37.0 kcal/mol. The better agreement in the smaller basis sets almost certainly arises from a cancellation of errors.

Group Equivalents for Benzenoid Aromatics. Since ab initio energies provide accurate enthalpy changes for homodesmic reactions involving only benzenoid hydrocarbons, it is not surprising that suitable group equivalents (GEs) for the benzenoids can be found. For the hydrocarbon C_nH_m, which can be described as $(CH)_mC_{n-m}$, we employ m CH groups, denoted $=C_bH-$, and $(n - m)$ groups, denoted $=C_b<$, for carbons devoid of hydrogens such as C_9 and C_{10} of naphthalene. Following Wiberg,[4] we obtain the group equivalents for each basis by fitting the experimental heats of formation to differences between the ab initio energies E_{SCF} and the sums of the m and $(n - m)$ group equivalents according to the equation

$$\Delta H_f = E_{SCF} - m\mathrm{GE}[=C_bH-] - (n - m)\mathrm{GE}[=C_b<] \quad (1)$$

The training set consists of ten molecules: those studied save for the nonbenzenoids azulene, biphenylene, and acenaphthylene; tetracene, whose experimental heat of formation is in question; and corannulene and coronene, whose heats of formation are unknown. The group equivalents for each basis are given in Table III. The aromatic $=C_b<$ group equivalents in the 3-21G and 6-31G* basis sets can be compared with the Ibrahim–Schleyer olefinic carbon atom equivalents,[5] which these authors denote $C_d-(C_d)(C)_2$. The aromatic group (or atom) equivalents are algebraically larger by 0.002 25 and 0.002 33 au. The aromatic $=C_bH-$ group equivalents can be compared with the corresponding olefinic $=CH-$ group equivalents derived from the Ibrahim–Schleyer values.[5] In this case the aromatic values are algebraically smaller by 0.002 44 and 0.002 27 au. (A slight error is introduced by comparing group equivalents obtained using optimized 6-31G* geometries with values derived from STO-3G geometries.) Calculated heats of formation of molecules having equal numbers of $=CH-$ and $=C<$ groups, such as corannulene and coronene, are nearly identical with those obtained from olefinic

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[20] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 360–369.

[21] Mulliken, R. S. *J. Chem. Phys.* **1983**, *79*, 1093.

[22] Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; p 172.

Table IV. Heats of Formation of Aromatic Hydrocarbons (kcal/mol)

molecule	from group equivalents[a] STO-3G	3-21G	6-31G*	exptl[b]
benzene (**1**)	20.0	20.6	20.8	19.81
naphthalene (**2**)	35.5	35.6	35.4	35.85
azulene (**3**)	94.7	84.5	80.9	69.06, 73.5
biphenylene (**4**)	107.5	106.6	100.2	104.43, 115.2
acenaphthylene (**5**)	66.6	65.7	63.2	62.04, 61.6
anthracene (**6**)	57.0	55.8	55.2	55.44, 55.2
phenanthrene (**7**)	47.7	48.0	48.2	49.52, 49.5
pyrene (**8**)	52.5	51.6	51.2	51.59
triphenylene (**9**)	61.1	62.5	63.4	63.4
chrysene (**10**)	62.5	63.1	63.3	62.8
tetracene (**11**)	81.5	78.7	77.0	69.8
3,4-benzophenanthrene (**12**)	71.1	70.2	70.5	69.6
1,2-benzanthracene (**13**)	66.8	66.3	65.6	69.63, 65.97
perylene (**14**)	73.1	74.1	74.2	73.7
corannulene (**15**)	123.4	120.5	117.2	
coronene (**16**)	61.2	62.0	61.7	

[a] The group equivalents are given in Table **III**; 1 au = 627.5 kcal/mol. [b] Experimental values are cited by Kao.[9]

GEs, owing to offsetting differences between the two types of equivalent.

The calculated heats of formation of all 16 molecules are given in Table IV; the respective rms deviations for the training set are 1.2, 0.7, and 0.7 kcal/mol in the STO-3G, 3-21G, and 6-31G* bases. (In computing the rms deviations, experimental values closest to the calculated values were selected.)

The heats of formation of tetracene in the 3-21G and 6-31G* basis sets are 78.7 and 77.0 kcal/mol, respectively, whereas the experimental value is 69.8 kcal/mol. The calculated values are similar to the MOMM[9] and MM2[10] molecular mechanics values of 77.58 and 76.19 kcal/mol. The ab initio results are consistent with earlier suggestions that the experimental heat of formation of tetracene is in error.[9,10,22] If the ab initio and molecular mechanics results are correct, tetracene is the least stable of the $C_{18}H_{12}$ isomers; even 3,4-benzophenanthrene, which is distorted to a significant extent, is more stable by 6–10 kcal/mol.

The 6-31G* heat of formation of corannulene is 117.2 kcal/mol, which is close to the MOMM value, 115.2 kcal/mol;[9] there is no experimental value. The combination of σ strain and decreased resonance stabilization, due to its nonbenzenoid and tub-shaped structure, combine to make the heat of formation of corannulene 66 kcal/mol more than five-sixths that of coronene (both molecules have $m/n = {}^1/_2$). The small difference in energy between the tub and planar forms of corannulene shows that the increase in resonance stabilization of the planar form nearly compensates for the increase in angle strain.

A case of disagreement between the ab initio and the MMP2 method is perylene, for which the 3-21G and 6-31G* heats of formation are 74.1 and 74.2 kcal/mol, while the MMP2 value is 79.0 kcal/mol. However, the experimental value of 73.7 kcal/mol and the MOMM value, 72.88 kcal/mol, are similar to the ab initio result.

For the nonbenzenoid aromatics, the largest error in a calculated heat of formation, ca. 7 kcal/mol, is found for azulene; somewhat better results are obtained for biphenylene and acenaphthylene.

Extension of the Group-Equivalent Scheme to Substituted Aromatics

It is of interest to determine whether the group-equivalent scheme can be applied to benzenoid hydrocarbons that have saturated or coupled linkages or nonhydrocarbon substituents. The following examples offer encouragement.

The 6-31G* SCF energy of toluene (C_s) at the STO-3G geometry is −269.7402 au. Its heat of formation can be calculated by using −39.598 36 au for the methyl group equivalent,[5] five $=C_bH-$ group equivalents, and one $=C_b<$ group equivalent (Table III). The result is 12.3 kcal/mol, in good agreement with experiment, 11.99 ± 0.10 kcal/mol.[23]

A similar calculation can be made for the heat of formation of fluorobenzene, whose 6-31G*//STO-3G energy is −329.5530 au. Its heat of formation, obtained with the aromatic group equivalents and the fluorine atom equivalent,[5] is −26.2 kcal/mol, compared with the experimental value of −27.76 ± 0.29 kcal/mol.[23]

The 6-31G*//STO-3G energy of aniline is −285.7280 au. Use of the aromatic group equivalents and an amino equivalent[5] gives 21.8 kcal/mol for the heat of formation of aniline, in good agreement with the experimental value, 20.81 ± 0.18 kcal/mol.[23]

A recent study has obtained −454.648 48 au for the energy of biphenyl in the STO-3G basis.[24] The STO-3G group equivalents of Table III lead to a heat of formation of 43.5 kcal/mol, in agreement with the experimental value, 43.5 ± 0.60 kcal/mol.[23]

We have previously obtained −2244.2193 au for the STO-3G energy of C_{60} (−37.40366/C).[18b] Use of eq 1 with $m = 0$ gives a $\Delta H_f/C$ of 12.0 kcal/mol. This value is an overestimate since the STO-3G basis cannot adequately represent the strain effects in C_{60}. An extrapolation, based upon calculations on C_{24}, gives a $\Delta H_f/C$ of 9.7 kcal/mol;[18b] a similar value, 8.83 kcal/mol, was obtained by Almlöf and Lüthi, who extrapolated ab initio SCF energies of a variety of carbon clusters and hydrocarbons.[25]

Discussion

The present work shows that ab initio SCF energies can furnish accurate molecular geometries and heats of formation of condensed benzenoid aromatic hydrocarbons. This fact implies the almost complete cancellation of the correlation energies of products and reactants in homodesmic reactions involving benzenoid aromatics exclusively. Such cancellation for many nonaromatics is well documented and explicable in terms of the local nature of C—C, C=C, C—H bonds, etc.

The following analysis shows that there is an even stronger regularity in the correlation energies. The choice of $=C_bH-$ and $=C_b<$ as the moieties upon which to base a group-equivalent scheme is not unique. Alternative choices that give equally good fits to the experimental data are (1) CC and CH bonds and (2) carbon and hydrogen atoms. In the first case, since the number of CC linkages in an unsubstituted C_nH_m aromatic is ${}^1/_2\,(3n - m)$, we may write

$$\Delta H_f = E_{SCF} - m\mathrm{GE[CH]} - \tfrac{1}{2}(3n - m)\mathrm{GE[CC]} \tag{2}$$

where $\mathrm{GE[CC]} = {}^2/_3\mathrm{GE}[=C_b<]$ and $\mathrm{GE[CH]} = \mathrm{GE}[=C_bH-] - \mathrm{GE[CC]}$. In the second case, the GEs are atom equivalents:

$$\Delta H_f = E_{SCF} - n\mathrm{GE[C]} - m\mathrm{GE[H]} \tag{3}$$

where $\mathrm{GE[C]} = \mathrm{GE}[=C_b<]$ and $\mathrm{GE[H]} = \mathrm{GE}[=C_bH-] - \mathrm{GE}[=C_b<]$.

A plot of the 6-31G* SCF energies per carbon atom of benzene, naphthalene, phenanthrene, triphenylene, pyrene, perylene, and coronene against m/n is linear with a standard deviation of 0.0006 au. The intercept, −37.8773 au, can be taken as the 6-31G* energy of a carbon atom in a hypothetical gaseous graphitic sheet. Use of this value in eq 3 with $m = 0$ furnishes $\Delta H_f/n = 2.5$ kcal/mol, the standard heat of formation per mole of carbon of the graphitic sheet. This is identical with the standard heat of sublimation per mole of carbon of graphite to graphitic sheets and may be compared with the known heats of sublimation per mole of carbon of benzenoid aromatics, which range from 1.41 (pyrene) to 1.74 kcal/mol (naphthalene).[23] The agreement of these values with 2.5 kcal/mol is reasonable. It suggests that eq 3 holds for substantially larger benzenoid aromatics than have been treated here.

Equation 3 can be taken a step further if we assume that it continues to hold (a) as the restricted Hartree–Fock (RHF) limit is approached and (b) in the limit of 0 K (albeit with GEs which differ slightly from those at 298 K). Combining eq 4, the complete

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[23] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

[24] Hafelinger, G.; Regelmann, C. *J. Comput. Chem.* **1987**, *8*, 1057.

[25] Almlöf, J.; Lüthi, H. P. *Supercomputer Research in Chemistry and Chemical Engineering*; ACS Symposium Series 353; American Chemical Society: Washington, D.C., 1987.

$$\Delta H_f = E_{\mathrm{RHF}}(\mathrm{C}_n\mathrm{H}_m) + E_{\mathrm{corr}}(\mathrm{C}_n\mathrm{H}_m) + E_{\mathrm{zpt}}(\mathrm{C}_n\mathrm{H}_m) - nH(\mathrm{C,graphite}) - (m/2)H(\mathrm{H}_2\mathrm{,gas}) \quad (4)$$

expression for the ideal gas-phase heat of formation at 0 K, with eq 3 furnishes

$$E_{\mathrm{corr}}(\mathrm{C}_n\mathrm{H}_m) = n\{H(\mathrm{C,graphite}) - \mathrm{GE}_{\mathrm{RHF}}[\mathrm{C}]\} + m\{\tfrac{1}{2}H(\mathrm{H}_2\mathrm{,gas}) - \mathrm{GE}_{\mathrm{RHF}}[\mathrm{H}]\} - E_{\mathrm{zpt}}(\mathrm{C}_n\mathrm{H}_m) \quad (5)$$

It has been shown that the zero-point energies (E_{zpt}) of hydrocarbons are linear functions of n and m.[26] Therefore

$$E_{\mathrm{corr}}(\mathrm{C}_n\mathrm{H}_m) = nA + mB + C$$

where A, B, and C are constants: aromatic hydrocarbons whose heats of formation are adequately described by eq 3 have correlation energies that are linear functions of the numbers of carbon and hydrogen atoms. This result is consistent with the ability of SCF energy differences (even in finite basis sets) to provide accurate enthalpy changes for homodesmic reactions involving only benzenoid aromatics. It is also consistent with the inability of ab initio SCF energies to provide good heats of reaction and formation for the nonbenzenoids azulene, acenaphthylene, and biphenylene, when either homodesmic reactions or group-equivalent schemes are employed: "nonregular" effects of electron correlation are present that cannot be accounted for in either scheme. This conclusion is consistent with the observed improvement of the naphthalene → azulene isomerization energy when electron correlation to second order is included.

This work demonstrates that aromatics of even moderate size are amenable to accurate ab initio study. Future application of the ab initio methods may be to molecules with deformed benzene rings, such as the cyclophanes and paracyclophanes, or to benzenoids that are either difficult to prepare or reactive. Ab initio calculation will frequently not be the method of choice, since more economical molecular mechanics methods can be quite successful. But we note that, except for benzene itself, the semiempirical AM1 method does not furnish good heats of formation for the aromatics; positive deviations from experiment of 10 kcal/mol or more are not unusual, e.g., 13.4 kcal/mol for chrysene. The AM1 geometries, however, are generally superior to the ab initio values and are comparable to those obtained by molecular mechanics. Heats of formation for many aromatics, obtained with the AM1 predecessor MNDO, have been reported by Hites and Simonsick;[27] MNDO values show positive deviations similar to those found with AM1, e.g., 11.9 kcal/mol for chrysene.

Acknowledgment. This research was supported, in part, by Grants 666356, 667253, and 668248 of the PSC-CUNY Research Award Program of the City University of New York and a grant of computing time from the City University Committee on Research Computing. Part of this work was conducted, with vector programs developed by us (The Queens College Quantum Chemistry Package), using the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State, and the IBM Corporation and members of the Corporate Research Institute.

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(26) Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.

(27) Hites, R. A.; Simonsick, W. J., Jr. *Calculated Properties of Polycyclic Aromatic Hydrocarbons*; Physical Sciences Data 29; Elsevier: Amsterdam, 1987.

Hydration Effects on $\mathrm{S_N2}$ Reactions: An Integral Equation Study of Free Energy Surfaces and Corrections to Transition-State Theory

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Abstract: New ab initio quantum chemical calculations and the extended RISM integral equation method are used to examine the aqueous phase $\mathrm{S_N2}$ reaction of chloride with methyl chloride. Behavior in the region around the transition state is emphasized. By application, it is shown that the integral equation approach is particularly effective for examining the shape of the free energy surface, the variation of results with solvent model, and the relative contributions of energy and entropy to the net free energy. Further, it is shown that in the limiting case of fast reaction dynamics and rapid charge transfer near the transition state, the correction to the transition-state theory rate constant can be estimated within the integral equation framework; results obtained agree reasonably with those derived from extensive dynamical simulation.

I. Introduction

Bimolecular nucleophilic substitution reactions of the type $\mathrm{X^-} + \mathrm{CH_3Y} \Leftrightarrow \mathrm{CH_3X} + \mathrm{Y^-}$ are among the most widely studied chemical reactions.[1,2] Investigations of such reactions have played an important role in the development of fundamental ideas in physical organic chemistry. In particular, these charge-transfer reactions provide a dramatic example of the influence of the solvent on chemical reaction rates.[3] The gas-phase and aqueous solution reaction rate constants for such reactions typically differ by 20 orders of magnitude.[4]

Recently, theoretical efforts have begun to address the description of such reactions in solution at a fully molecular level, with emphasis on the prototype case $\mathrm{X} = \mathrm{Y} = \mathrm{Cl^-}$. In particular, both the free energy surface for the adiabatic motion of reactants to products in water[1] and the solvent dynamical contributions to

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(1) Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 154.

(2) Shaik, S. S. *J. Am. Chem. Soc.* **1984**, *106*, 1227.

(3) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

(4) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

0002-7863/89/1511-5680$01.50/0