J. Am. Chem. Soc. **1992**, *114*, 41-47

interactions in the carbon-protonated species. (4) Our results are consistent with recent experimental findings for ynamines in aqueous solution.

Acknowledgment. We thank Professor Jerry Kresge for a preprint of ref 1 and gratefully acknowledge a generous allocation of computer time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

Registry No. 1, 52900-33-1; **2**, 56359-27-4; **3**, 20729-41-3; **4**, 593-67-9; **5**, 78507-80-9; **6**, 56359-27-4; **7**, 64709-59-7; **8**, 17619-22-6; **9**, 52324-04-6; **10**, 64066-03-1; $HC\equiv COH$, 32038-79-2.

Empirical Model Calculations for Thermodynamic and Structural Properties of Condensed Polycyclic Aromatic Hydrocarbons

William C. Herndon,* Paul C. Nowak, Dallas A. Connor, and Peiping Lin

Contribution from the Department of Chemistry, University of Texas at El Paso,
El Paso, Texas 79968. Received May 6, 1991

Abstract: The majority of condensed polycyclic benzenoid aromatic hydrocarbons exist as highly nonplanar molecular structures. Group additivity methods, AM1 calculations, and molecular mechanics are compared as general tools for estimating relative and absolute stabilities in nonplanar members of this class of compounds and for correlating the sparse experimental ΔH_f° data. The AM1 computations give large, variable (positive) errors compared to the experimental ΔH_f°'s, whereas molecular mechanics and group additivity precisely model the same data. Molecular mechanics calculations for 153 polybenzenoid compounds with up to seven benzenoid rings indicate that 72 are highly nonplanar. The ability of group additivity methods to represent structural strain and the energetic consequences of nonplanarity in the polycyclic benzenoids is demonstrated by a precise partition of the calculated molecular mechanics ΔH_f° as a sum of CC and CH bond energy terms, steric interference parameters, and resonance energies.

1. Introduction

We are engaged in systematic studies of various classes of condensed polycyclic benzenoid aromatic hydrocarbons (PBAHs),[1,2] with an emphasis on understanding the effects of topological variations in structure on planarity, nonplanarity, and molecular stabilities. As part of this work, we have recently used a computerized coding system[3] and graph-theoretical algorithms to demonstrate that the majority of PBAHs capable of actual existence must possess highly nonplanar chiral and nonchiral molecular geometries.[4] Thus, for example, 6693 distinct polyhex graphs with ten rings can be drawn that correspond to catacondensed[5] PBAH constitutional isomers with the formula $C_{42}H_{24}$. However, easily perceived steric factors ensure that the $C_{42}H_{24}$ polybenzenoid system will actually consist of 12 882 nonplanar pairs of enantiomers, 47 achiral nonplanar species, and only 600 planar or near-planar compounds.[3]

Other than the graph-theory approach, the main tools for our studies have been AM1[6] and molecular mechanics[7] (MM) calculations. The reliance on computation is due primarily to the sparse amount of available experimental ΔH_f° data, which is limited to values for only nine catacondensed and two pericondensed compounds.[8,9] Therefore, in part, the work which is reported here was carried out to evaluate the general reliability and convenience of alternate and readily available theoretical protocols for obtaining the structural and thermodynamic properties of polybenzenoid systems.

The collected experimental information on thermodynamic stabilities is compared with the results of MM, AM1, and group additivity procedures in the following section of this paper. Then results of MM calculations for PBAHs with as many as seven rings are tabulated and discussed. Simple group additivity (GA) analyses are shown to provide acceptable replications of both the experimental and the theoretical thermodynamic data. The GA formalism also allows a delineation of the substructures which induce both small and large degrees of nonplanarity in PBAH molecular frameworks.

Table I. Experimental and Calculated ΔH_f° (kcal/mol) for PBAHs

compd	exptl[a]	PCM[b]	MM3[c]	AM1[d]	GA1[e]	GARE[f]
benzene	20.0 (0.2)[g]	19.3	20.3	22.0	18.4	20.3
naphthalene	36.0 (0.3)	34.9	36.0	40.6	35.8	35.2
anthracene	55.2 (0.6)	55.6	55.2	62.9	53.3	53.8
phenanthrene	49.7 (0.6)	49.2	50.7	57.4	52.2	50.6
tetracene	72.3 (1.3)	78.2	76.2	86.9	70.8	74.1
benz[*a*]-anthracene	70.3 (0.9)	68.1	68.6	78.3	69.7	67.6
chrysene	66.0 (1.1)	65.9	67.0	76.2	68.5	67.1
triphenylene	66.5 (1.0)	66.9	67.5	75.5	67.3	67.1
benzo[*c*]-phenanthrene	69.6 (1.1)	69.3	71.8	81.2	69.6	69.6
pyrene	54.0 (0.3)	57.4	58.2	67.4	58.6[g]	55.3[h]
perylene	78.4 (0.6)	79.3		89.3	73.8[g]	77.2[h]
av error (exptl vs calc)		1.4	1.5	9.1	1.9	1.1

[a] Reference 14. [b] Reference 10. [c] Reference 11. [d] Reference 6. [e] Based on a five parameter group additivity equation. See Table II. [f] Group additivity models with a resonance energy parameter (GA2-(RE) and GA3(RE)) give essentially identical predicted ΔH_f°. See text and Table II. [g] Estimated absolute value of experimental error. See ref 14. [h] Experimental and estimated ΔH_f°'s modified by energy/enthalpy correction term. See text.

---

* Author to whom correspondence should be addressed.

(1) Herndon, W. C. In *Polynuclear Aromatic Compounds*; ACS Advances in Chemistry Series No. 217; Ebert, L., Ed.; American Chemical Society: Washington, DC, 1988.

(2) Herndon, W. C.; Connor, D. A.; Lin, P. *Pure Appl. Chem.* **1990**, *62*, 435.

(3) Herndon, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 4546.

(4) The concept and numerous examples of highly nonplanar polycyclic aromatic compounds were reviewed as early as 1954: Harnik, E.; Herbstein, F. H.; Schmidt, G. M. J.; Hirshfeld, A. L. *J. Chem. Soc.* **1954**, 3288. Also, see: Ferguson, G.; Robertson, J. M. *Adv. Phys. Org. Chem.* **1963**, *1*, 203. Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964; Vol. 1, Chapter 16.

0002-7863/92/1514-41$03.00/0 © 1992 American Chemical Society

Table II. Group Additivity $\Delta H_f°$ Models for PBAHs

GA1[a]		GA2(RE)[a]		GA3(RE)[a]	
C_H	3.06 (0.44)	C_H	6.77 (1.09)	CH	2.36 (0.60)
$C_{CH.CH.C}$	5.69 (1.07)	$C_{CH.CH.C}$	6.70 (0.70)	CC	4.46 (0.42)
$C_{CH.C.C}$	5.10 (0.94)	$C_{CH.C.C}$	8.41 (1.10)		
C_{int}	2.54 (1.31)	C_{int}	6.61 (1.40)	S3	3.49 (1.00)
C_{per}	5.63 (3.55)	C_{per}	12.55 (2.89)	S4	9.45 (2.58)
		LN(SC)	−29.39 (8.42)	LN(SC)	−29.75 (5.88)
(multiple R)^2	0.979		0.994		0.994
standard error	3.279		1.938		1.770
av error	1.890		1.104		1.101
F ratio	69.6		161.8		242.4

[a] Parameter list, followed by parameter value and standard deviations. All values in kcal.

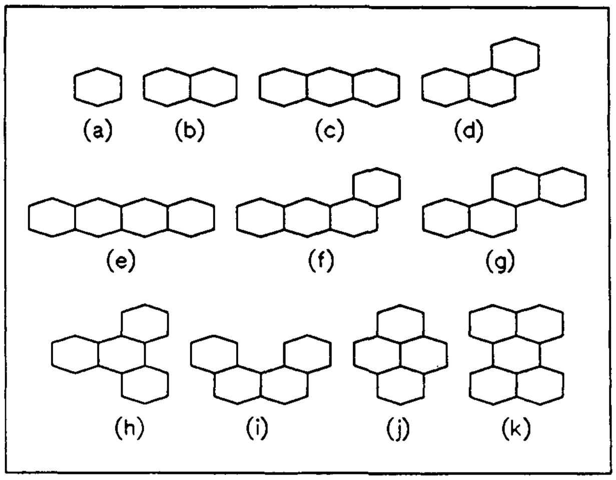

Figure 1. Polyhex drawings for compounds with known experimental $\Delta H_f°$: (a) benzene, (b) naphthalene, (c) anthracene, (d) phenanthrene, (e) tetracene, (f) benz[*a*]anthracene, (g) chrysene, (h) triphenylene, (i) benzo[*c*]phenanthrene, (j) pyrene, and (k) perylene.

2. Heats of Formation for PBAHs

The results of PCM-MM methods, AM1 calculations, and GA procedures are compared with the experimental $\Delta H_f°$ data for PBAHs in Table I. PCM refers to the PCMODEL molecular mechanics (personal computer) software package from Serena Software.[10] The MM3 values are taken from the recently published paper by Allinger et al.[11] Polyhex drawings of the compounds listed in Table I are given in Figure 1.

Points to note in connection with Table I are as follows:

(a) For both MM and AM1, the calculated $\Delta H_f°$ are straightforward utilizations of the available computer programs.[6,10] The calculations that duplicate previously published work[12,13] give identical calculated values of $\Delta H_f°$.

(b) The experimental values are taken from the most recent compilation of recommended $\Delta H_f°$ for the PBAHs[9] or they have been derived from additional or more up-to-date thermodynamic data.[14] The actual primary sources of data have been checked in each case.

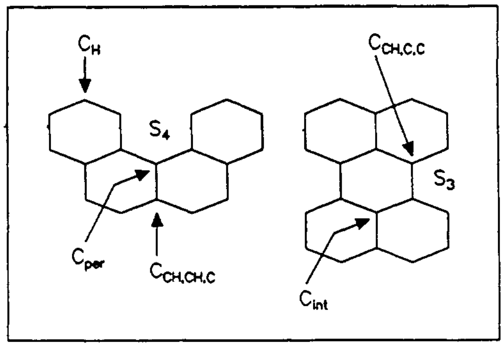

Figure 2. Atom-types and steric parameters for group additivity $\Delta H_f°$ equations.

(c) AM1 calculations are unreliable to precisely model the experimental $\Delta H_f°$.

(d) The discrepancies of MM calculated and experimental values for tetracene are greater than four times the average error. Therefore, in agreement with previous speculation,[13,15,16] we have a reservation concerning the accuracy of the reported experimental $\Delta H_f°$. However, in the absence of additional experimental information, the tetracene $\Delta H_f°$ is included in the model studies described below.

(e) The MM and AM1 values for benzo[*c*]phenanthrene are for optimized, highly nonplanar structures. The MM interplanar four-ring dihedral angle of 30.5° is in good agreement with the 29.6° value established by the X-ray crystallographic coordinates.[17] Planar geometries are 8.6 (PCM-MM) and 12.3 (AM1) kcal higher in energy.

(f) The PCM-MM calculations also reproduce the small degree of nonplanarity and assymmetrical sense of twisting found for the experimental crystal structure of triphenylene.[18,19] However, a slightly twisted geometry is calculated for perylene, not in good agreement with the crystal structure, which is slightly folded around the long molecular axis.[20,21] This unusual molecular

---

(5) Balaban, A. T.; Harary, F. *Tetrahedron* **1968**, *24*, 2505.

(6) Dewar, M. J. S.; Stewart, J. J. P.; Egger, M. Program No. 527, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47401.

(7) For a review, see: Burkett, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

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

(9) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(10) PCMODEL, Version 3, Serena Software, Box 3076, Bloomington, IN 47402. For a review, see: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Adv. Molecular Modeling* **1990**, *2*, 65.

(11) Allinger, N.; Li, F.; Yan, L.; Tai, J. C. *J. Comput. Chem.* **1990**, *11*, 868.

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

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

(14) The principal source of $\Delta H_f°$ data is Pedley et al.[9] Exceptions or differences from single recommended values[9] are based on various sources as follows (all values in kcal): $\Delta H_f°$(benzene) = 20.0, uses $\Delta H°$(vapor) = 8.30 (Chickos, J., Department of Chemistry, University of Missouri at St. Louis, private communication and confirmed in our laboratory); $\Delta H_f°$(anthracene) = 55.2, average of three recommended[9] values; $\Delta H_f°$(phenanthrene) = 49.7, uses average of recommended[9] $\Delta H°$(sublimation) = 23.95 and $\Delta H°$(sublimation) = 24.15 (Malaspina, L.; Bardi, G.; Gigli, R. *J. Chem. Thermodynamics* **1974**, *6*, 1053); $\Delta H_f°$(perylene) = 78.4 uses recommended[9] $\Delta H_f°$(solid) = 43.7 and $\Delta H°$(sublimation) = 34.7 (Gigli, R.; Malaspina, L.; Bardi, G. *Ann. Chim. (Rome)* **1973**, *63*, 627).

(15) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 3817.

(16) Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Amer. Chem. Soc.* **1989**, *111*, 5675.

(17) (a) Herbstein, F. H.; Schmidt, G. M. J. *J. Chem. Soc.* **1954**, 3302. (b) Hirshfeld, A. L.; Sandler, S.; Schmidt, G. M. J. *J. Chem. Soc.* **1963**, 2108. (c) Hirshfeld, A. L. *J. Chem. Soc.* **1963**, 2126.

(18) Ahmed, F. R.; Trotter, J. *Acta Crystallogr.* **1963**, *16*, 503.

(19) Ferraris, G.; Jones, D. W.; Yerkess, J. *Zeit. Kristallogr.* **1973**, *138*, 113.

(20) Tanaka, J. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1237.

(21) Camerman, A.; Trotter, J. *Proc. Roy. Soc.* **1964**, *A279*, 129.

geometry was attributed to intermolecular crystal packing forces.[21]

(g) By themselves, resonance energies are only approximate guides to relative stabilities. For example, the most stable catacondensed isomer with four rings is chrysene, both experimentally and from the MM calculations, rather than the compound with the highest resonance energy, which is triphenylene.[22] Also, benzo[*c*]phenanthrene is destabilized relative to chrysene, due to steric interference of hydrogen atoms at the 1 and 12 positions (see below), although their resonance energies are virtually equivalent in all theoretical treatments.[22]

3. Group Additivity Procedures

Stein, Golden, and Benson[23] originally defined and derived thermochemical values for atom-type additivity constants for PBAHs. A modification of their four-parameter scheme is illustrated in Figure 2, obtained by designation of an interior carbon atom parameter (interior $C_{C,C,C} = C_{int}$), combined with division of the perimeter carbon atoms into four independent types (C_H, $C_{CH,CH,C}$, $C_{CH,C,C}$ and perimeter $C_{C,C,C} = C_{per}$). The values of these five parameters have been calculated to correlate the updated $\Delta H_f°$ data given in Table I, and the results of the correlation are listed under the GA1 heading. The optimized values of the atom-type terms and the statistical information which indicates the precision of the fit of the GA1 model to the $\Delta H_f°$ data are listed in Table II.

In the cases of pericondensed pyrene and perylene, the experimental $\Delta H_f°$ values have been modified prior to regression analysis by subtracting the correction term derived by Somayajulu and Zwolinski,[24] which is based on arguments summarized by Nelander and Sunner.[25] This correction, which amounts to $(1 + n/6 - m/3)RT$ for PBAHs with the formula C_nH_m, is due to the fact that GA parameters refer to internal molecular energy terms rather than to enthalpy values. The energy/enthalpy adjustment is only 0.2 kcal for either pyrene or perylene and has been neglected, justifiably, in most previous considerations of this data. However, the correction is applied for data in Table I because we wish to derive theoretically valid, predictive measures of strain energies, and because we will examine pericondensed PBAHs with very large numbers of rings in subsequent work, where corrections of this type will be larger. Thus, the GA calculated $\Delta H_f°$'s in Table I are obtained by summing contributions for the parameters listed in Table II and adding the term $(1 + n/6 - m/3)RT$.

In the Stein et al. procedure,[23] the interior carbon parameter C_{int} was estimated by assuming that the ΔH of sublimation per carbon atom for large PBAHs (1.45 kcal/mol) was equal to the $\Delta H_f°$ for this group, and the C_H parameter was chosen as 1/6 of the $\Delta H_f°$ for benzene. In the present analysis, the completely optimized value for C_H is the only parameter found close to a former value (3.05 and 3.30, respectively). Also, as shown and discussed below, all parameters take on substantially different magnitudes in GA models if an additional term to represent resonance energy (RE) is included in the model calculation.

The perimeter carbon C_{per} term in GA1 is a unique parameter found only in benzo[*c*]phenanthrene for this set of data. As a consequence, C_{per} corrects the calculated $\Delta H_f°$ of benzo[*c*]phenanthrene to the exact experimental value. It follows that the C_{per} parameter cannot be differentiated from a steric interaction term which would represent the interference of the two carbon–hydrogen bonds separated by four C–C bonds (S_4) which is present in this molecule. For our purposes, it seems more reasonable to attribute the high degree of nonplanarity found in benzo[*c*]phenanthrene as being due to the existence of this steric factor rather than to the existence of C_{per}.

Regardless of how one views this aspect of the molecular structure, the destabilizing term has a larger positive value when a stabilizing RE term is included in the GA model. The RE estimate used for the GA2(RE) model is the natural logarithm of the Kekule structure count (SC), an algorithm which has been found to give calculated REs tantamount to results obtained from LCAO-MO-SCF procedures.[26] The GA atom parameters combined with the LN(SC) estimates of RE lead to a critical improvement in the correlation of the $\Delta H_f°$ data, e.g., the standard error of the correlation decreases by almost a factor of 2 (Table II), with a concomitant increase in the F-ratio statistic. In previous work[2] we fitted results of PCM $\Delta H_f°$ calculations for all 58 catacondensed PBAHs with six or fewer rings to GA-type equations, both without and with the stabilizing RE term. The same order of improvement in the conformity of the model was observed.

A much earlier analysis of this type,[27] carried out to correlate the older PBAH $\Delta H_f°$ data, used five preselected parameters, i.e., CC and CH bond terms, theoretical estimates of resonance energies, and steric terms (S_3 and S_4 in Figure 2). However, in the present work, all atom, bond, and steric descriptors were initially considered as candidate parameters for combination with the RE LN(SC) terms to obtain a $\Delta H_f°$ regression equation. Every parameter was entered into the potential model correlation equation, and the individual terms were screened for inclusion in the final equation using a standard stepwise multivariate linear regression analysis. The forward entry method was used, coupled with the backward elimination procedure. The values of the statistical options controlling the criteria for inclusion of independent variables were those recommended on the basis of Monte Carlo studies of linear regression models.[28]

The stepwise regression analysis only allows the same five independent variables as previously selected (CH, CC, RE, S_3, and S_4), and their optimized values are listed in the last column of Table II. The statistical parameters in Table II show that this GA3(RE) model is an excellent rectification of the updated experimental $\Delta H_f°$ data. One can also see that the unique S_4 term is permitted; indeed, it is required by statistical criteria for inclusion of a regression parameter. However, even though a specific term to account for the probable small experimental nonplanarities of triphenenylene and perylene in the gas phase was included in the list of possible parameters, it was not admissible as an independent variable according to the statistical regression criteria. This may be due to the paucity and experimental accuracy of the dependent variable $\Delta H_f°$ data combined with the expected small size of such a parameter, i.e., 1.25 kcal, according to MM calculations summarized in the next section.

Notice that the GA2(RE) and GA3(RE) models give practically identical results, albeit with one additional parameter for the GA2(RE) scheme. For this set of data, the equivalence between the two resonance energy models is readily established as being due to the following algebraic relationships:

$$\mathrm{CH} = C_H$$

$$\mathrm{CC} = C_H + 1.5(C_{CH,CH,C} + C_{CH,C,C} + C_{int} + C_{per})$$

$$S_3 = 0.5(C_{CH,C,C}) - C_{per}$$

$$S_4 = C_{per}$$

A consequence of this algebraic equivalence is that choosing between the GA2(RE) and GA3(RE) group additivity models to correlate the experimental $\Delta H_f°$ data becomes a matter of preference, although one might argue for the latter model which has the smaller number of parameters. In any case, structural interpretations of the magnitudes of the regression coefficients for the parameters must remain questionable if based solely on the experimental data.

4. Group Additivity and Molecular Mechanics

We have carried out PCM-MM calculations for all catacondensed PBAHs with six and fewer rings (58 compounds) and reported these results earlier.[2] We have now added PCM-MM calculations for an additional four catacondensed structures with hexahelicene substructures and for all 91 pericondensed PBAHs with seven and fewer rings for a total of 153 compounds. The IUPAC names for these systems and the calculated $\Delta H_f°$(MM) are given in Table III. Drawings of the polyhex structures are available upon request. According to the calculations, 72 of the 153 compounds are highly nonplanar, while 39 show small deviations from planarity. Highly nonplanar MM structures are designated with superscript "*a*" and slightly nonplanar compounds are denoted with "*b*". In general, X-ray crystallographic structures are in good agreement with the calculated MM geometries, including structures for highly nonplanar compounds **9**,[17] **21**,[30] **54**,[31] **55**,[32] and **106**,[33] and also including slightly nonplanar **8**[17] (triphenylene) and **16**[34] (picene). The results in

---

[22] HMO, Hess and Schaad, Dewar, and VB resonance energies are, respectively, as follows: triphenylene 7.27β, 1.01β, 2.65 eV, 2.65 eV; chrysene, 7.19β, 0.95β, 2.48 eV, 2.52 eV; benzo[*c*]phenanthrene, 7.19β, 0.95β, 2.48 eV, 2.52 eV. For references, see: Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631.

[23] Stein, S. E.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977**, *81*, 314.

[24] Somayajulu, G. R.; Zwolinski, B. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, 1928.

[25] Nelander, B.; Sunner, S. *J. Chem. Phys.* **1966**, *44*, 2476.

[26] Swinbourne-Sheldrake, R.; Herndon, W. C.; Gutman, I. *Tetrahedron Lett.* **1975**, 755. See: Herndon, W. C. *Israel J. Chem.* **1980**, *20*, 270 for additional references.

[27] Herndon, W. C. *Thermochim. Acta* **1974**, *8*, 225.

[28] Bendel, R. B.; Afifi, A. A. *J. Am. Stat. Assoc.* **1977**, *72*, 46.

[29] See: Herndon, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 7605 for references to the X-ray structures of planar condensed PBAHs, reported before 1974.

[30] McIntosh, A. O.; Robertson, J. M.; Vand, V. *J. Chem. Soc.* **1954**, 1661.

[31] De Rango, C.; Tsoucaris, G.; Declerq, J. P.; Germain, G.; Putzeys, J. P. *Cryst. Struct. Comm.* **1973**, *2*, 189.

[32] Herbstein, F. H. *Acta Crystallogr.* **1979**, *B35*, 1661.

[33] Roberts, P. J.; Ferguson, G. *Acta Crystallogr.* **1977**, *B33*, 1244.

Table III. Structure Parameters and Calculated MM and GA $\Delta H_{\mathrm{f}}^{\circ}$ (kcal/mol) for PBAHs

compd no.	IUPAC name (exptl $\Delta H_{\mathrm{f}}^{\circ}$)	MM	GA	CC	CH	SC	S_3	S_4	S_5	S_6	T
1	benzene (20.0)	19.30	18.89	6	6	2	0	0	0	0	0
2	naphthalene (36.0)	34.90	35.08	11	8	3	0	0	0	0	0
3	anthracene (35.2)	55.60	54.90	16	10	4	0	0	0	0	0
4	phenanthrene (49.7)	49.20	50.04	16	10	5	1	0	0	0	0
5	naphthacene (72.3)	78.20	76.70	21	12	5	0	0	0	0	0
6	benz[*a*]anthracene (70.3)	68.10	68.35	21	12	7	1	0	0	0	0
7	chrysene (66.0)	65.90	66.24	21	12	8	2	0	0	0	0
8	triphenylene[b] (66.5)	67.00	68.37	21	12	9	3	0	0	0	3
9	benzo[*c*]phenanthrene[a] (69.6)	69.30	69.86	21	12	8	0	1	0	0	0
10	pentacene	101.90	99.76	26	14	6	0	0	0	0	0
11	benzo[*a*]naphthacene	89.80	89.29	26	14	9	1	0	0	0	0
12	dibenz[*a,j*]anthracene	81.10	82.43	26	14	12	2	0	0	0	0
13	dibenz[*a,h*]anthracene	81.10	82.43	26	14	12	2	0	0	0	0
14	benzo[*b*]chrysene	85.70	85.11	26	14	11	2	0	0	0	0
15	pentaphene	86.20	86.04	26	14	10	1	0	0	0	0
16	picene	81.80	81.97	26	14	13	3	0	0	0	0
17	benzo[*b*]triphenylene[b]	85.00	85.72	26	14	13	3	0	0	0	3
18	dibenzo[*b,g*]phenanthrene[a]	88.70	88.73	26	14	11	0	1	0	0	0
19	benzo[*c*]chrysene[a]	84.50	85.59	26	14	13	1	1	0	0	0
20	benzo[*g*]chrysene[a]	86.30	86.56	26	14	14	2	1	0	0	1
21	dibenzo[*c,g*]phenanthrene[a]	86.10	86.18	26	14	13	0	0	1	0	0
22	Hexacene	126.20	123.69	31	16	7	0	0	0	0	0
23	benzo[*a*]pentacene	113.00	111.78	31	16	11	1	0	0	0	0
24	naphtho[2,1-*a*]naphthacene	107.70	106.36	31	16	14	2	0	0	0	0
25	dibenzo[*b,k*]chrysene	105.60	104.24	31	16	15	2	0	0	0	0
26	dibenzo[*a,l*]naphthacene	101.70	102.25	31	16	16	2	0	0	0	0
27	naphtho[2,1-*b*]chrysene[b]	98.40	98.96	31	16	19	3	0	0	0	0
28	hexaphene	107.30	106.64	31	16	13	1	0	0	0	0
29	benzo[*c*]pentaphene	99.40	100.38	31	16	17	2	0	0	0	0
30	benzo[*a*]pentaphene	99.80	100.38	31	16	17	2	0	0	0	0
31	dibenzo[*a,j*]naphthacene	101.70	102.25	31	16	16	2	0	0	0	0
32	benzo[*b*]picene[b]	100.80	100.63	31	16	18	3	0	0	0	0
33	naphtho[1,2-*b*]chrysene[b]	97.80	98.96	31	16	19	3	0	0	0	0
34	benzo[*c*]picene[b]	97.80	97.88	31	16	21	4	0	0	0	0
35	benzo[*h*]pentaphene[b]	102.60	102.71	31	16	19	3	0	0	0	3
36	naphtho[1,2-*b*]triphenylene[b]	98.40	100.20	31	16	22	4	0	0	0	3
37	dibenzo[*a,c*]naphthacene[b]	106.40	106.13	31	16	17	3	0	0	0	3
38	dibenzo[*b,l*]chrysene[a]	104.00	104.24	31	16	18	1	1	0	0	0
39	benzo[*a*]picene[a]	100.80	101.50	31	16	21	2	1	0	0	0
40	benzo[*a*]naphth[2,1-*j*]anthracene[a]	101.20	102.58	31	16	19	1	1	0	0	0
41	naphtho[1,2-*a*]naphthacene[a]	110.90	109.98	31	16	14	0	1	0	0	0
42	benzo[*a*]naphth[2,1-*j*]anthracene[a]	101.30	102.58	31	16	19	1	1	0	0	0
43	naphtho[1,2-*c*]chrysene[a]	100.50	101.50	31	16	21	2	1	0	0	0
44	naphtho[2,3-*c*]chrysene[a]	103.60	104.24	31	16	18	1	1	0	0	0
45	anthra[1,2-*a*]anthracene[a]	108.40	107.85	31	16	15	0	1	0	0	0
46	benzo[*f*]picene[a]	101.20	101.95	31	16	23	3	1	0	0	1
47	dibenzo[*b,g*]chrysene[a]	106.20	105.83	31	16	19	2	1	0	0	1
48	dibenzo[*b,p*]chrysene[a]	104.60	104.25	31	16	20	2	1	0	0	1
49	naphtho[2,3-*g*]chrysene[a]	104.50	104.25	31	16	20	2	1	0	0	1
50	dibenzo[*c,g*]chrysene[a]	102.40	102.54	31	16	23	2	0	1	0	1
51	naphtho[2,1-*c*]chrysene[a]	101.60	102.09	31	16	21	1	0	1	0	0
52	phenanth[4,3-*a*]anthracene[a]	104.90	104.83	31	16	18	0	0	1	0	0
53	naphtho[1,2-*g*]chrysene[a]	104.10	103.91	31	16	22	2	0	1	0	1
54	phenanthro[4,3-*c*]phenanthrene[a]	103.80	104.07	31	16	21	0	0	0	1	0
55	dibenzo[*g,p*]chrysene[a,c]	105.20	105.01	31	16	24	2	2	0	0	0
56	dibenzo[*c,l*]chrysene[a,c]	103.00	105.12	31	16	21	0	2	0	0	0
57	dibenzo[*c,p*]chrysene[a,c]	105.60	105.69	31	16	22	1	2	0	0	0
58	benzo[*s*]picene[a,c]	106.30	105.69	31	16	22	1	2	0	0	0
59	pyrene (54.0)	57.29	57.88	19	10	6	0	0	0	0	0
60	benzo[*def*]chrysene	75.79	76.08	24	12	9	1	0	0	0	0
61	benzo[*e*]pyrene[b]	72.78	73.15	24	12	11	2	0	0	0	1
62	perylene[b] (78.4)	79.26	79.33	24	12	9	2	0	0	0	1
63	dibenzo[*def,mno*]chrysene	85.80	86.29	27	12	10	0	0	0	0	0
64	dibenzo[*c,mno*]chrysene[a]	94.16	94.64	29	14	15	0	1	0	0	0
65	naphtho[2,1,8-*aqr*]naphthacene	96.11	95.89	29	14	12	1	0	0	0	0
66	benzo[*pqr*]picene	90.80	91.03	29	14	15	2	0	0	0	0
67	naphtho[4,3,2,1-*def*]chrysene[b]	91.14	90.42	29	14	17	3	0	0	0	1
68	dibenzo[*b,def*]chrysene	96.48	95.43	29	14	13	2	0	0	0	0
69	benzo[*rst*]pentaphene	92.48	93.15	29	14	14	2	0	0	0	0
70	dibenzo[*def,p*]chrysene[a]	95.75	94.66	29	14	16	1	1	0	0	0
71	naphtho[1,8,7-*ghi*]chrysene[a]	93.02	92.79	29	14	17	1	1	0	0	0
72	dibenzo[*de,qr*]naphthacene[b]	90.55	90.29	29	14	16	2	0	0	0	1
73	dibenzo[*fg,op*]naphthacene[b]	90.19	88.67	29	14	20	4	0	0	0	2
74	benzo[*b*]perylene[b]	94.30	94.28	29	14	15	3	0	0	0	1
75	benzo[*a*]perylene[a]	104.05	103.51	29	14	12	1	1	0	0	0
76	benzo[*ghi*]perylene	77.01	77.94	27	12	14	1	0	0	0	0
77	dibenzo[*de,mn*]naphthacene	107.55	106.75	29	14	9	2	0	0	0	0

Table III (Continued)

compd no.	IUPAC name (exptl $\Delta H_f°$)	MM	GA	CC	CH	SC	S_3	S_4	S_5	S_6	T
78	benzo[*mno*]naphtho[2,1-*c*]chrysene[a]	111.38	111.44	34	16	24	0	0	1	0	0
79	naphtho[2,1,8-*auv*]pentaphene[a]	112.65	112.96	34	16	21	0	1	0	0	0
80	tribenzo[*a,c,mno*]chrysene[a]	110.26	110.48	34	16	27	2	1	0	0	1
81	benzo[*c*]naphtho[4,3,2,1-*mno*]chrysene[a]	109.04	109.36	34	16	28	2	1	0	0	1
82	tribenzo[*c,k,mno*]chrysene[a]	113.55	113.53	34	16	22	1	1	0	0	0
83	dibenzo[*a,rst*]pentaphene[a]	111.22	112.16	34	16	23	1	1	0	0	0
84	tribenzo[*c,g,mno*]chrysene[a]	110.66	109.81	34	16	27	1	0	1	0	0
85	benzo[*mno*]naphtho[4,3-*c*]chrysene[a]	110.30	110.85	34	16	24	1	1	0	0	0
86	benzo[*l*]naphtho[2,1,8-*aqr*]naphthacene	108.63	109.34	34	16	21	2	0	0	0	0
87	naphtho[2,1,8-*aqr*]pentacene	118.43	117.69	34	16	15	1	0	0	0	0
88	benzo[*a*]naphtho[2,1,8-*hij*]naphthacene	108.30	109.34	34	16	21	2	0	0	0	0
89	benzo[*c*]naphtho[2,1,8-*aqr*]naphthacene[b]	111.13	109.79	34	16	23	3	0	0	0	1
90	anthra[2,1,9-*aqr*]naphthacene	116.69	115.84	34	16	17	2	0	0	0	0
91	benzo[*vwx*]hexaphene	112.23	112.42	34	16	19	2	0	0	0	0
92	phenanthro[9,10,1-*aqr*]naphthacene[a]	116.64	114.96	34	16	21	1	1	0	0	0
93	dibenzo[*c,pqr*]picene[b]	107.07	107.23	34	16	24	3	0	0	0	0
94	naphtho[1,8,7-*cde*]pentaphene	109.75	109.34	34	16	21	2	0	0	0	0
95	dibenzo[*a,pqr*]picene[a]	110.15	110.85	34	16	24	1	1	0	0	0
96	benzo[*l*]naphtho[1,8,7-*ghi*]chrysene[b]	106.42	105.74	34	16	28	4	0	0	0	1
97	dibenzo[*n,pqr*]picene[b]	110.25	109.91	34	16	22	3	0	0	0	0
98	dibenzo[*m,pqr*]picene[b]	107.94	108.54	34	16	23	3	0	0	0	0
99	dibenzo[*j,pqr*]picene[a]	109.49	109.23	34	16	27	2	1	0	0	0
100	phenanthro[1,2,3,4-*def*]chrysene[a]	110.86	110.39	34	16	26	2	1	0	0	0
101	naphtho[2,1,8-*fgh*]pentaphene[b]	108.52	107.23	34	16	25	3	0	0	0	1
102	benzo[*b*]naphtho[1,8,7-*pqr*]chrysene[a]	111.14	110.39	34	16	26	2	1	0	0	0
103	tribenzo[*b,def,p*]chrysene[a]	115.50	112.85	34	16	24	2	1	0	0	0
104	dibenzo[*h,rst*]pentaphene[b]	108.17	106.86	34	16	27	4	0	0	0	1
105	benzo[*fg*]naphtho[3,2,1-*op*]naphthacene[a]	110.86	109.23	34	16	30	3	1	0	0	1
106	naphtho[4,3,2,1-*rst*]pentaphene[a,c]	117.54	116.47	34	16	24	0	2	0	0	0
107	benzo[*l*]naphtho[1,8,7-*ghi*]chrysene[a,c]	115.68	115.21	34	16	25	0	2	0	0	0
108	benzo[*de*]naphtho[4,3,2-*qr*]naphthacene[a]	114.13	112.16	34	16	23	1	1	0	0	0
109	benzo[*def*]naphtho[4,3-*p*]chrysene[a]	113.87	112.18	34	16	25	1	0	1	0	0
110	naphtho[2,1,8,7-*pqrst*]pentaphene	101.85	102.50	32	14	16	1	0	0	0	0
111	anthra[2,1,9,8-*aopqr*]naphthacene	106.68	106.61	32	14	14	1	0	0	0	0
112	benzo[*def*]naphtho[4,3,2,1-*mno*]chrysene[b]	100.71	100.46	32	14	19	2	0	0	0	1
113	benzo[*c*]naphtho[1,8,7-*ghi*]chrysene[a]	108.67	108.70	34	16	28	1	0	1	0	0
114	dibenzo[*de,uv*]pentaphene[a]	112.82	112.16	34	16	23	1	1	0	0	0
115	naphtho[2,1,8-*def*]picene[a]	107.66	108.11	34	16	28	2	1	0	0	0
116	benzo[*g*]naphtho[1,8,7-*pqr*]chrysene[a,c]	112.10	112.65	34	16	29	1	2	0	0	0
117	tribenzo[*a,fg,op*]naphthacene[a]	108.84	108.23	34	16	31	3	1	0	0	1
118	tribenzo[*a,hi,mn*]naphthacene[b]	103.95	104.86	34	16	27	3	0	0	0	1
119	dibenzo[*de,uv*]pentaphene[b]	111.71	110.59	34	16	21	2	0	0	0	1
120	dibenzo[*fg,st*]pentacene[b]	106.93	105.91	34	16	29	4	0	0	0	2
121	naphtho[2,1-*b*]perylene[a]	113.74	114.10	34	16	24	2	1	0	0	1
122	dibenzo[*de,st*]pentacene[b]	113.22	112.59	34	16	21	3	0	0	0	1
123	naphtho[4,3-*b*]perylene[b]	110.91	110.48	34	16	24	4	0	0	0	1
124	dibenzo[*fg,ij*]pentaphene[b]	109.32	109.23	34	16	25	4	0	0	0	1
125	dibenzo[*fg,qr*]pentacene[b]	109.83	109.23	34	16	25	4	0	0	0	1
126	dibenzo[*b,e*]perylene[a]	115.41	114.10	34	16	24	2	1	0	0	1
127	naphtho[2,1-*a*]perylene[a]	116.83	118.21	34	16	21	2	1	0	0	1
128	dibenzo[*fg,uv*]pentaphene[a]	126.39	125.31	34	16	15	1	1	0	0	0
129	naphtho[4,3-*a*]perylene[a]	117.24	117.55	34	16	21	1	0	1	0	0
130	dibenzo[*a,o*]perylene[a]	127.49	125.92	34	16	16	1	0	1	0	0
131	dibenzo[*a,n*]perylene[a]	118.66	118.46	34	16	20	2	1	0	0	0
132	dibenzo[*a,k*]perylene[a]	118.91	118.46	34	16	20	2	1	0	0	0
133	dibenzo[*a,j*]perylene[a,c]	128.31	128.95	34	16	16	0	2	0	0	0
134	dibenzo[*a,f*]perylene[a,c]	130.53	130.93	34	16	15	0	2	0	0	0
135	dibenzo[*a,e*]perylene[a]	117.42	116.96	34	16	21	2	1	0	0	0
136	coronene	78.13	80.42	30	12	20	0	0	0	0	0
137	dibenzo[*f,pqr*]perylene[a]	101.16	101.25	32	14	20	0	1	0	0	0
138	dibenzo[*b,ghi*]perylene	94.00	94.70	32	14	22	2	0	0	0	0
139	dibenzo[*b,pqr*]perylene[b]	93.91	94.02	32	14	25	3	0	0	0	1
140	naphtho[4,3,2,1-*ghi*]perylene[b]	96.50	96.58	32	14	23	3	0	0	0	1
141	dibenzo[*cd,Im*]perylene[b]	100.84	102.12	32	14	18	2	0	0	0	1
142	naphtho[1,8,7-*bcd*]perylene[b]	100.84	102.12	32	14	18	2	0	0	0	1
143	dibenzo[*de,kl*]pentaphene[b]	134.89	137.42	34	16	9	3	0	0	0	0
144	dibenzo[*de,op*]pentacene	134.18	135.42	34	16	9	2	0	0	0	0
145	dibenzo[*de,ij*]pentaphene[b]	120.76	121.70	34	16	15	3	0	0	0	0
146	dibenzo[*pq,uv*]pentaphene[a]	138.35	141.62	34	16	9	0	0	1	0	0
147	dibenzo[*de,qr*]pentacene[b]	120.88	121.70	34	16	15	3	0	0	0	0
148	benzo[*de*]naphtho[3,2,1-*mn*]naphthacene[a]	130.35	132.18	34	16	12	1	1	0	0	0
149	tribenzo[*a,de,mn*]naphthacene[b]	128.32	128.56	34	16	12	3	0	0	0	0
150	benzo[*b*]phenanthro[4,3-*g*]phenanthrene[a]	123.53	122.81	36	18	29	0	0	0	1	0
151	phenanthro[3,4-*c*]chrysene[a]	119.31	119.92	36	18	34	1	0	0	1	0
152	benzo[*g*]naphtho[2,1-*c*]chrysene[a]	120.44	120.56	36	18	37	2	0	0	1	1
153	phenanthro[4,3-*g*]chrysene[a]	121.69	121.41	36	18	36	2	0	0	1	1

[a] Highly nonplanar. [b] Slightly nonplanar. [c] Diastereomeric systems.

Table IV. Group Additivity Equation for Molecular Mechanics $\Delta H_f°$ Values

parameter	parameter coeff	standard deviation	
CC	5.087	0.048	$N = 153$
CH	1.617	0.082	squared multiple $R = 0.997$
S_3	2.001	0.117	standard error = 0.976
S_4	7.619	0.185	av error = 0.736
S_5	10.208	0.354	F ratio = 7156.4
S_6	14.193	0.516	
T	1.249	0.147	
LNSC	−30.773	0.390	
$(1 + n/6 - m/3)RT^a$			

[a] Energy/enthalpy correction for molecules with formula C_nH_m. See text.

Table III are for the most stable form in nine cases (designated with superscript *c*) where two or more diastereoisomeric forms are calculated to exist.

The same procedure that was used to establish the GA3(RE) model (Tables I and II) was then applied to the MM $\Delta H_f°$ data listed in Table III, including adjustment by the energy/enthalpy factor discussed previously. The GA modeled heats of formation of the 153 PBAHs are also listed in Table III, along with the structural terms which are found to determine the optimum model GA equation as given by multidimensional least-squares analysis. The coefficients for the optimum additivity equation for the MM data and the statistical parameters for the equation are summarized in Table IV.

The best GA equation for the MM data turns out to be composed of exactly the same molecular parameters that fit the experimental $\Delta H_f°$ results, augmented by three new steric terms, S_5, S_6, and T. The presence of S_4 or any one of these new destabilizing substructure features leads to a calculated nonplanar equilibrium geometry for the global lowest heat of formation. All of these parameters represent easily identified, self-evident steric interference effects in PBAHs, defined by the following descriptions:

1. S_4, the benzo[*c*]phenanthrene fjord-region substructure parameter, a 1,5-hydrogen–hydrogen interaction term, identified in the earlier work.[2,27]
2. S_5, a dibenzo[*c*,*g*]phenanthrene (pentahelicene) 1,6-hydrogen–hydrogen interaction term.
3. S_6, a parameter for the phenanthro[3,4-*c*]phenanthrene (hexahelicene) substructure involving overlap of hydrogen/carbon atoms of an initial ring with carbon/hydrogen atoms of the sixth ring in the helicene structure.
4. T, a parameter characterized by condensation of phenanthroid fragments sharing a common central ring in which the fusion generates pairs of S_3 bay region hydrogen atoms that are interlocked in a restricted molecular environment. This locked molecular substructure is responsible for the calculated slightly nonplanar structures of triphenylene and perylene (see Discussion in the next section). This T parameter is not in a one-to-one correspondence with the triphenylene substructure as proposed in the Herndon, Connor, and Lin study[2] on catacondensed PBAHs. Instead, statistical analysis shows that each restricted environment S_3–S_3 pair must be counted as a separate structural feature. Therefore, as illustrated in Figure 3, triphenylene contains three S_3 structural terms and also three T interactions, each of which arises from the interactions of distinct S_3–S_3 pairs. However, perylene and benzo[*e*]pyrene each contain two S_3 interactions but only one T substructure feature.

The presence of one or more of the first three of these structural terms always gives a molecular structure that deviates substantially from planarity, whereas the T substructure, by itself, only leads to a slightly nonplanar arrangement of the atoms. It should be noted that the PCM-MM $\Delta H_f°$ given in the Herndon et al. study[2] for those catacondensed systems containing the newly defined T interaction have all been recalculated (compounds **8**, **16**, **17**, **27**, **32**, **33**, **34**, **35**, **36**, and **37**). In every case, the formerly obtained planar geometry is now identified as a local minimum, and a slightly nonplanar geometry at a slightly lower energy (of the order of one kcal or less) is determined to be the global MM minimum.

No single structural factor has been statistically delimited that will account for the MM calculated slight nonplanarities of an additional 13 compounds (**16**, **27**, **32–34**, **93**, **96–98**, **143**, **145**, **147**, and **149** in Table III). However, as mentioned before, MM and X-ray[34] structures are in agreement for **16** (picene), the only compound in this group so studied. There are three or more S_3's in each of these PBAHs, but they are arranged in a variety of ways, and the structural types vary from zigzag-type catacondensed systems to compounds containing pyrene pericondensed substructures. One can infer that the energy factor leading to the small nonplanarities in these structures must be somewhat less than the 0.98 kcal value of the standard deviation of the estimated $\Delta H_f°$ in the overall analysis.

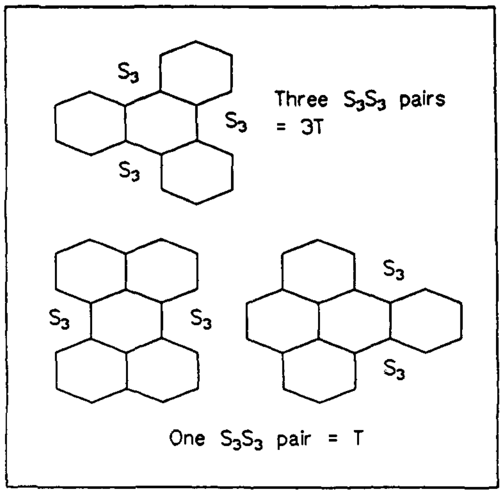

Figure 3. The relationship of S_3 and T group additivity steric parameters.

5. Evaluation and Discussion

Substructures in PBAHs resulting in high degrees of nonplanarity are S_4 and S_5 fragments, as found in benzo[*c*]phenanthrene and dibenzo[*c*,*g*]phenanthrene, and the overlapping rings present in hexahelicene (S_6) and higher helicenes[35] (S_7, etc.). All steric parameters turn out to have positive (destabilizing) values. Therefore, nonplanarity can be rationalized as a partial compensation for destabilizing repulsive interactions between nonbonded atoms that would exist in planar structures. The GA3(RE) model for the experimental data (last columns, Table I and II) and the GA(MM) analysis (Table IV) are group additivity procedures which seek to partition the $\Delta H_f°$ in such a way as to delineate the energy effects of these kinds of steric features. The increasing magnitude of the steric factors that cause nonplanarity, in the order $T < S_4 < S_5 < S_6$, is an expected result since the molecular environment is obviously more crowded in this same order.

Slight degrees of nonplanarity (associated with the T parameter or other arrangements of three and more S_3's) result from an accumulation of bay regions which are arranged in such a way that pairs of hydrogen atoms cannot lengthen their interatomic distances to relieve repulsive interactions without increasing repulsion in adjacent, closely coupled interactions. The destabilizing T factor should manifest itself in the experimental data for triphenylene and perylene. However, the MM correlations show that the augmented effect is small in terms of energy (1.25 kcal), and it cannot be discerned statistically (using the experimental $\Delta H_f°$ data) in the presence of five larger stabilizing and destabilizing factors. The calculated discrepancy with the actual experimental nonplanarity of perylene cannot be resolved. The folded X-ray geometry for perylene[20,21] may be one of those rare cases where intermolecular packing forces actually do induce a molecular deformation.

The correlations of the $\Delta H_f°$ data in terms of a GA model are precise. However, these models give high-quality rectifications of the data if, and only if, a resonance energy parameter is included as one term of the regression equation. This is true for either the experimental $\Delta H_f°$ data or the calculated MM values. Therefore, in our opinion, it is mandatory to include the effects of resonance stabilization energy in any type of GA approach to calculating

---

(34) De, A.; Ghosh, R.; Roychowdhury, S.; Roychowdhury, P. *Acta Crystallogr.* **1985**, *C41*, 907.

(35) See: Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63. Meurer, K. P.; Vogtle, F. *Top. Curr. Chem.* **1985**, *127*, 1 for references to the X-ray structures of helicenes.

thermodynamic properties of PBAHs or PBAH derivatives. Although RE terms were not included in the original Stein et al.[23] GA scheme, those authors were well-aware of isomeric systems with identical numbers of GA parameters but with large differences in stabilizing REs. Consequently, they acknowledged the general desirability of an RE parameter but preferred a shorter additive procedure leaving out resonance energy stabilization factors. The results summarized in the present work indicate that this is no longer justifiable. The increased precision of the GA model with a resonance energy parameter warrants the minor effort required for a SC or even more complex RE calculations.

Incidentally, one should note the value of the regression coefficient for the LN(SC) term (−30.8 kcal), which is remarkably close to the optimum value (−27.3 kcal) determined in several previous studies of π resonance energies for many different types of π species.[26] This correspondence lends support for the use of the SC algorithm for calculating resonance energies.[36] It also implies that the highly nonplanar PBAH compounds considered in this work are not affected by a loss of π resonance energy due to their nonplanarity. This result is not surprising if one considers the fact that the nonplanar deformations of the molecular structures are generally not abrupt but are gradually distributed over the entire molecular framework. Every ring is therefore locally near-planar, and every p-orbital is in near-parallel alignment with nearest-neighbor p-orbitals. Consequently, only slight diminutions in resonance energies would be expected, arguing from either resonance theory or molecular orbital points of view.

We wish to reemphasize, however, that resonance energies alone must be considered to be very approximate predictors of relative thermodynamic stabilities in PBAHs, especially the nonplanar systems. This is because the π delocalization energy contributes only a small fraction of the total energy contributions that determine the PBAH molecular structure, and because the topologies of PBAH carbon skeletons that engender destabilizing steric effects are precisely those topologies that are associated with larger stabilizing resonance terms. In other words, the SC for a PBAH generally increases as destabilizing kinks are introduced in the molecular framework. The utility of ongoing graph-theoretical studies that restrict discussions of PBAHs to the (putative) planar systems[37–40] is, therefore, doubtful, since most experimentally obtainable PBAH structures will be highly nonplanar molecules. In addition, the general applicability of recent treatments[41–45] of PBAH thermodynamic properties that dismiss stereochemical factors and/or the resonance factors discussed above should be evaluated before use.

We conclude that a thermodynamic group additivity/resonance energy model of PBAHs with a parameterization based on MM calculations can reasonably predict both planar and nonplanar PBAH relative stabilities and heats of formation. Bond enthalpy terms, steric parameters, and resonance energies reflect the critical stabilizing and destabilizing internal energy contributions. We postulate that the GA model may be applied to very large PBAHs to yield valid approximations to experimental heats of formation. We infer that the values of the parameters defined in this study are transferable and can therefore be retained in an ongoing study of more complex steric interactions that can exist in larger PBAH systems. An investigation of ring strain energies in nonalternant aromatic molecules, including three-dimensional polyhedral aromatic species, using this same approach, is also in progress.

Acknowledgment. The financial support of the Welch Foundation of Houston, Texas, and of the University of Texas at El Paso Materials Research Center of Excellence (a component of the Minority Research Centers of Excellence sponsored by the National Science Foundation) is gratefully acknowledged.

---

(36) The use of the ln (SC) algorithm for various properties of polycyclic aromatics has been questioned by Stein and Brown (Stein, S. E.; Brown, R. L. In *Molecular Structures and Energetics*; Greenberg, A., Liebman, J. F., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Vol. 2. Also, see: Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 3721.) and by Eilfield and Schmidt (Eilfield, P.; Schmidt, W. *J. Elect. Spectrosc. Relat. Phenom.* **1981**, *24*, 101.) based on empirical results. The correlations presented here do not negate the criticisms raised in these earlier papers. However, more recent papers on the foundations of resonance-theoretic models by Klein and coworkers clarify and support the use of the SC algorithm as an accurate approximation for resonance energy. See, e.g.: Klein, D. J.; Seitz, W. A. *J. Mol. Struct.* (*Theochem*) **1988**, *169*, 167. Garcia-Bach, M. A.; Valenti, R.; Klein, D. J. *J. Mol. Struct.* (*Theochem*) **1989**, *185*, 287. Klein, D. J.; Trinajstic, N. *Pure Appl. Chem.* **1989**, *61*, 2107. Klein, D. J. *Topics in Current Chem.* **1990**, *153*, 57.

(37) Dias, J. R. *Acc. Chem. Res.* **1985**, *18*, 241. Dias, J. R. *Theor. Chim. Acta* **1990**, *77*, 143.

(38) Knop, J. V.; Muller, W. R.; Syzmanski, K.; Trinajstic, N. *Computer Generation of Certain Classes of Molecules*; Assoc. of Chemists and Technologists: Zagreb, Yugoslavia, 1985; CRC Press: Boca Raton, FL, 1983; Vol. 1, Chapter 6 and Appendix.

(39) Balaban, A. T.; Brunvoll, J.; Ciolowski, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I.; He, W. C.; He, W. J.; Knop, J. V.; Muller, W. R.; Syzmanski, K.; Tosic, R.; Trinajstic, N. *Z. Naturforsch.* **1987**, *42a*, 863.

(40) Brunvoll, J.; Cyvin, S. J. *Z. Naturforsch.* **1990**, *45a*, 69. Cyvin, S. J.; Brunvoll, J. *Chem. Phys. Lett.* **1990**, *170*, 364.

(41) Stein, S. E.; Fahr, A. *J. Phys. Chem.* **1985**, *89*, 3714.

(42) Moiseeva, N. F.; Dorofeeva, O. V.; Jorish, V. S. *Thermochim. Acta* **1989**, *153*, 77.

(43) Alberty, R. A.; Reif, A. K. *J. Phys. Chem. Ref. Data* **1988**, *17*, 241.

(44) Alberty, R. A.; Chung, A. B.; Reif, A. K. *J. Phys. Chem. Ref. Data* **1989**, *18*, 77.

(45) Alberty, R. A.; Chung, A. B.; Reif, A. K. *J. Phys. Chem. Ref. Data* **1990**, *19*, 349.