

## Structure-enthalpy relationships in polycyclic cata-condensed aromatic hydrocarbons

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**Abstract** - A large fraction (30 of 62) of the cata-condensed polycyclic benzenoid aromatic hydrocarbons with one to six rings have nonplanar pi carbon atom frameworks, with the minimum angle of nonplanarity approximately 30°. In addition to 17 pairs of enantiomers, four of the nonplanar cata-condensed benzenoids with six rings are predicted to be capable of existing as pairs of twisted diastereoisomers. Many of the nonplanar benzenoids are thermodynamically more stable than isomeric planar compounds. The MMX molecular mechanics force field provides reasonable estimates of  $\Delta H_f^\circ(g)$  and geometric structures for cata-condensed benzenoids, in good agreement with the limited experimental data. AM1 calculations are not useful to determine the  $\Delta H_f^\circ(g)$  of these compounds. A group additivity method that incorporates C-C and C-H bond terms, a resonance energy term and steric parameters can be used to accurately model the MMX and the experimental  $\Delta H_f^\circ(g)$  data. Both MMX and the group additivity/resonance energy procedure can also be used for predictive purposes and to estimate resonance energies.

### 1 INTRODUCTION

Carbon atoms in the  $sp^2$  hybridization state are generally regarded to lead to molecular structures with planar geometrical constraints. This belief can engender the impression that the condensed polycyclic benzenoid aromatic hydrocarbons (PBAH's) are generally planar. However, this is countered by the numerous examples in the class of compounds called the helicenes (refs. 1, 2) and by the several published X-ray structures for other highly nonplanar condensed PBAH's (refs. 3-14). We have recently suggested that polycyclic benzenoids and their derivatives which possess these nonplanar pi structures should be considered as a separate general subclass of aromatic compounds, differentiated from the commonly accepted two-dimensional pi species (ref. 15).

The understanding that simple polycyclic aromatic benzenoids can be nonplanar is not an original concept. As examples, the famous book on aromatic compounds by Clar, published in 1964 contains a short chapter entitled "Non-planar, Overcrowded Aromatic Hydrocarbons" (ref. 16), and, in work dating from the same period, Newman and co-workers synthesized and studied the properties of many substituted benzenoids that were optically active due to a nonplanar pi framework (refs. 17, 18). Also, the authors of the X-ray studies referred to above were well aware of the nonplanarity of the molecules they were investigating, and the helicenes are, of course, condensed polycyclic aromatic hydrocarbons with high degrees of pi-system nonplanarity.

In part, the present work was stimulated by the realization that a *majority* of PBAH's capable of existence will possess highly nonplanar structures (ref. 15). A question by Trinajstić (ref. 19) regarding the best way to calculate resonance energies of PBAH's was also a primary stimulus because we infer that a knowledge of how to estimate heats of formation has to precede calculations of resonance energies. Thus, the main objective of this paper will be to understand the thermodynamic enthalpic properties and structural characteristics (including nonplanarity) of the cata-condensed subclass of PBAH's. The rationale for restricting the discussion to this subclass, and the precise definition of the term "cata-condensed" will be given in the next section.

We hope to ascertain the most reliable theoretical model that can be used to predict cata-condensed PBAH heats of formation. Our initial approach will be to calculate theoretical heats of formation using molecular mechanics, semi-empirical quantum mechanical calculations and group additivity methods. The results of these calculations will be examined for consistency, and evaluated by comparisons with the very limited experimental data. Then, an attempt will be made to correlate the experimental and theoretical enthalpy data with other simple structural models, in particular restricted models that only include bond terms, steric parameters and resonance energy terms. Finally, estimates of cata-condensed PBAH resonance energies will be presented based on these model calculations.

## 2 CLASSES OF POLYCYCLIC BENZENOID HYDROCARBONS

Polycyclic benzenoid aromatic hydrocarbons are commonly defined as hydrocarbons containing only fused benzene rings. The definitions (ref. 20) of cata-condensed and peri-condensed systems are based on the associated characteristic graphs which are formed by joining the centers of adjacent rings. The benzenoid is cata-condensed if the resulting characteristic graph is noncyclic. Otherwise, if the characteristic graph contains cycles, the benzenoid system is defined as peri-condensed. The PBAH systems that can be derived from benzene by fusion of other benzenoid rings are depicted in the structures in Fig. 1, in which the benzene ring is symbolized using a hexagon. Compounds represented by the first four drawings are classified as cata-condensed, and the remaining are peri-condensed. Note that the first three structures depicted in the second row describe the carbon skeletons of PBAH's without Kekule structures which are not expected to exist as stable benzenoids.

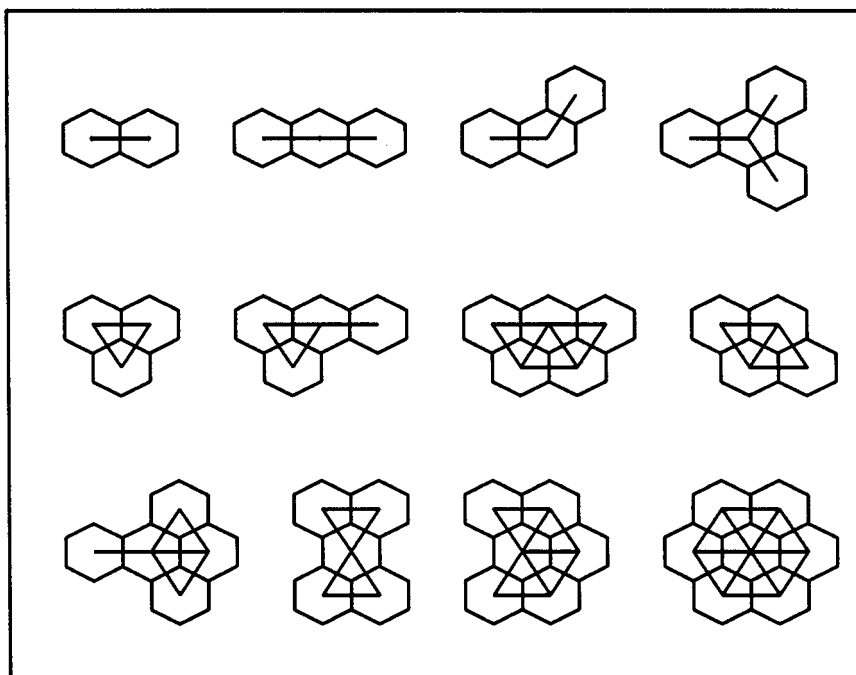


Fig. 1. Cata- and peri-condensed PBAH's derived from benzene and their characteristic graphs.

The characteristic graph of benzene consists of a single point. Therefore benzene falls in the subclass of cata-condensed systems, and it will be considered to be the prototype molecule in this class. All other cata-condensed PBAH's can be further classified into non-branched, e.g., the first three structures in Fig. 1, which have two endpoints for the characteristic graph, and branched, e.g., the fourth structure, whose characteristic graphs have three or more endpoints. The results of the present work show that this distinction is useful, since the compounds with branched characteristic graphs seem to incorporate destabilizing steric effects not found in the unbranched systems.

The structural drawings for the carbon skeletons of all benzenoid aromatic hydrocarbons to be considered in this work are given in Fig. 2. The systems investigated comprise 58 cata-condensed PBAH molecular graphs containing one through six rings. Figure 2 anticipates one of the major result of this work by identifying the drawings which represent compounds that would exist as nonplanar molecules. They are designated as enantiomeric or diastereoisomeric systems with an asterisk or two asterisks, respectively.

Peri-condensed systems were excluded from this study because experimental heat of formation data are available for only two peri-condensed molecules, i.e., pyrene and perylene (refs. 21, 22). The variety of structural types (Fig. 1) is also larger than we are presently prepared to examine. The restriction of the molecular size to six rings was imposed by our desire to examine complete subsets of isomeric molecular structures. This was feasible with six rings since there are only 37 such systems, but the number of calculations for the substantially larger number (123) of cata-condensed PBAH's systems with seven rings was impracticable.

The IUPAC (ref. 23) names and some common names (in parentheses) for the aromatic compounds corresponding to the structures in Fig. 2 are listed below the figure. We believe that this list corrects several misassignments present in a recent book (ref. 24).

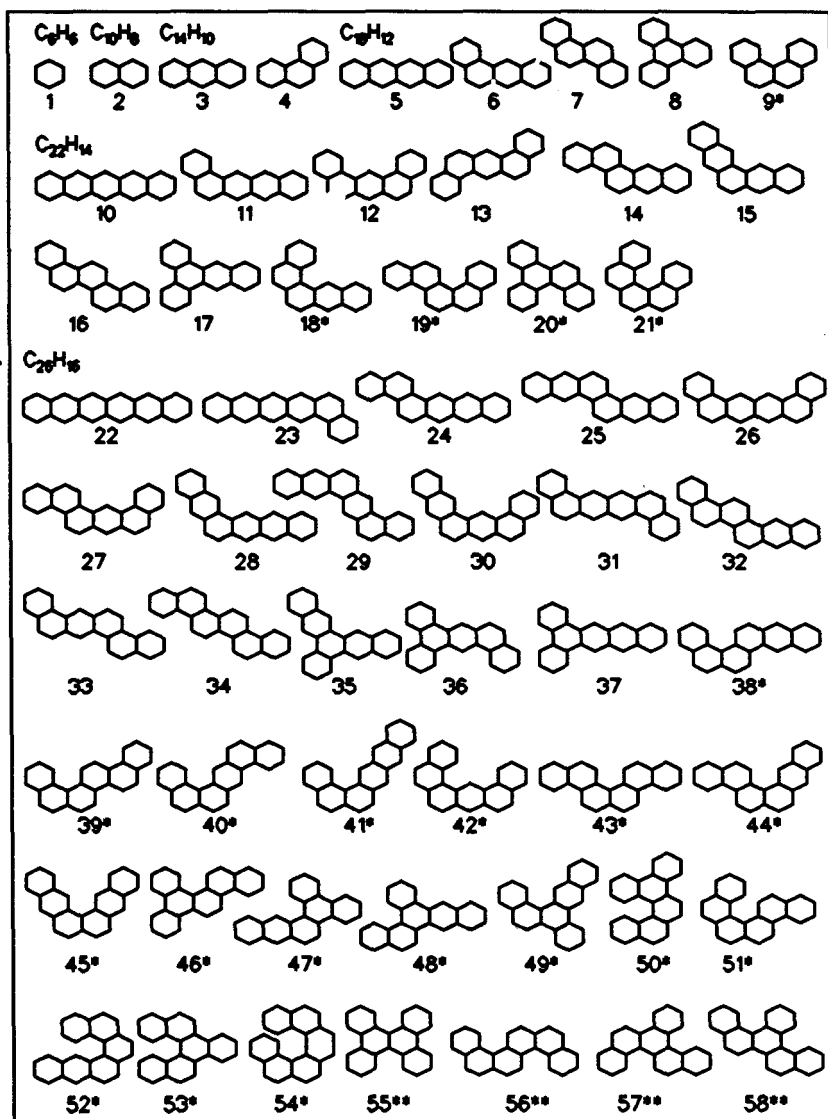


Fig. 2. Molecular graphs for cata-condensed PBAH's (one to six rings).  
Enantiomeric systems (\*). Diastereomeric systems (\*\*).

- 1 Benzene; 2 Naphthalene; 3 Anthracene; 4 Phenanthrene; 5 Naphthacene (tetracene);  
6 Benz[a]anthracene; 7 Chrysene; 8 Triphenylene; 9 Benzo[c]phenanthrene; 10 Pentacene;  
11 Benzo[a]naphthacene (benzo[a]tetracene); 12 Dibenz[a,j]anthracene; 13 Dibenz[a,h]anthracene;  
14 Benzo[b]chrysene; 15 Pentaphene; 16, Picene; 17 Benzo[b]triphenylene (dibenz[a,c]anthracene);  
18 Dibenzo[b,g]phenanthrene; 19 Benzo[c]chrysene; 20 Benzo[g]chrysene;  
21 Dibenzo[c,g]phenanthrene (pentahelicene or [5]helicene); 22 Hexacene; 23 Benzo[a]pentacene;  
24 Naphtho[2,1-a]naphthacene; 25 Dibenzo[b,k]chrysene; 26 Dibenzo[a,l]naphthacene;  
27 Naphtho[2,1-b]chrysene; 28 Hexaphene; 29 Benzo[c]pentaphene; 30 Benzo[a]pentaphene;  
31 Dibenzo[a,j]naphthacene; 32 Benzo[b]picene; 33 Naphtho[1,2-b]chrysene; 34 Benzo[c]picene;  
35 Benzo[h]pentaphene; 36 Naphtho[1,2-b]triphenylene; 37 Dibenzo[a,c]naphthacene;  
38 Dibenzo[b,l]chrysene; 39 Benzo[a]picene; 40 Benzo[a]naphth[1,2-h]anthracene;  
41 Naphtho[1,2-a]naphthacene; 42 Benzo[a]naphth[2,1-j]anthracene; 43 Naphtho[1,2-c]chrysene;  
44 Naphtho[2,3-c]chrysene; 45 Anthra[1,2-a]anthracene; 46, Benzo[f]picene;  
47 Dibenzo[b,g]chrysene; 48 Dibenzo[b,p]chrysene; 49 Naphtho[2,3-g]chrysene;  
50 Dibenzo[c,g]chrysene (benzo[f]pentahelicene); 51 Naphtho[2,1-c]chrysene (benzo[c]pentahelicene);  
52 Phenanthro[4,3-a]anthracene (benzo[b]pentahelicene); 53 Naphtho[1,2-g]chrysene  
(benzo[j]pentahelicene); 54 Phenanthro[3,4-c]phenanthrene (hexahelicene or [6]helicene);  
55 Dibenzo[g,p]chrysene (tetrabenzonaphthalene); 56 Dibenzo[c,l]chrysene; 57 Dibenzo[c,p]chrysene;  
58 Benzo[s]picene.

### 3 COMPUTATIONAL METHODS AND PROCEDURES

Heats of formation and other thermodynamic properties for benzenoid compounds are not generally available, and actual experimental values of heats of formation are only known for nine cata-condensed PBAH's (refs. 21, 22, 25-28), e.g., structures 1 through 9 in Fig. 2. The major portion of the present work will therefore make use of computational procedures to obtain  $\Delta H_f^\circ(g)$ . However, comparisons with the experimental values will be carried out whenever possible.

The molecular orbital computational program used in this work is the AM1 (ref. 29) (IBM 3090 version) package available from the Quantum Chemistry Program Exchange, Chemistry Department, Room 204, Indiana University, Bloomington, Indiana 47401. The program employs a general-purpose semiempirical all-valence-electron molecular orbital procedure. It is more accurate than the previous programs MINDO/3 and MNDO (refs. 30, 31), particularly in the treatment of crowded molecules or compounds with ring strain. A second source of computational data was the PCMODEL (MMX) package obtained from Serena Software, Box 3076, Bloomington, Indiana 47402-3076. This program provides an estimate of the equilibrium geometry and energy of organic compounds from a combined molecular mechanics and SCF pi electron calculation. The PCMODEL/MMX/PI force field incorporates the MM2(77) program of Allinger (refs. 32-34), primarily developed for hydrocarbons. The current version of PCMODEL is particularly convenient since it allows graphical structure input and global optimization within a single module running on a personal computer.

Both AM1 and MMX, of course, provide precise details of the calculated geometric structures of organic compounds. Again, for benzenoids, there is a paucity of experimental data, with X-ray crystallographic or neutron diffraction data available for only 14 of the condensed PBAH's whose structures are represented in Fig. 2, i.e., 1 - 10, 16, 21, 54, and 55 (refs. 3-8, 12, 35-37). A detailed comparison of experimental and calculated structures is underway, but will not be reported here. In the present work, calculated structures will generally only be used to identify structural features that contribute to an understanding of the calculated or experimental  $\Delta H_f^\circ(g)$ .

Group additivity methods to estimate  $\Delta H_f^\circ(g)$  of aromatic benzenoids have been suggested by Cox and Pilcher (ref. 21), and by Stein, Golden and Benson (ref. 38), based on work of Benson and Buss (ref. 40). A group in the Stein, Golden, Benson (SGB) scheme consists of a polyvalent atom with its covalently bonded neighbors. As an example, naphthalene is composed of eight CH groups and two C-(CH)<sub>2</sub>(C) groups, which we represent as A and B respectively, exemplified in Fig. 3. Additional groups, C-(CH)(C)<sub>2</sub> and C-(C)<sub>3</sub>, C and D, respectively, are necessary to complete the SGB analysis. A complete file of these groups and steric factors, to be discussed later, is available upon request.

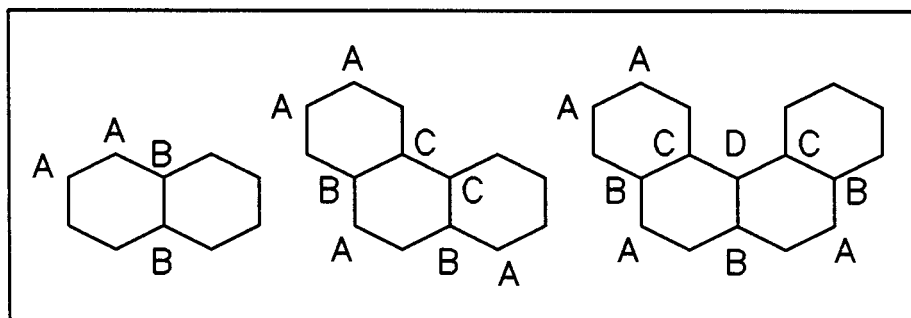


Fig. 3. SGB groups for naphthalene, phenanthrene and benzo[c]phenanthrene.

The SGB analysis makes no provision for estimating the resonance energy (RE) of the delocalized pi system, although one normally assumes that resonance energy is an important necessary aspect of thermodynamic properties in aromatic compounds. The inclusion of RE in the SGB model can be carried out by partitioning the heats of formation of PBAH's into resonance energy terms and group  $\Delta H_f^\circ$  terms, in which the aromatic carbon-group  $\Delta H_f^\circ$  terms would have numerical values different from those given by Stein, *et al.* (ref. 38). An equivalent  $\Delta H_f^\circ(g)$  scheme of this type for PBAH's has been proposed by Herndon (ref. 27) which incorporates a term for resonance energies, in addition to C-C and C-H bond parameters, and steric interference terms. In this approach, which will be further evaluated in the present work, the resonance energies (in units of a resonance exchange integral) are calculated using valence bond resonance theory (refs. 39-42), the unit value being given by the statistical fit to experimental data.

Herndon and co-workers have also shown empirically that resonance energies calculated by various SCF level molecular orbital methods are accurately related to the natural logarithm of the number of Kekule valence bond structures (ref. 43), and that the number of stable Kekule structures (structure count, SC) of PBAH's can be obtained by using several different simple paper-and-pencil procedures (refs. 44, 45). The  $\log(SC)$  algorithm will be used in section 6 to partition the  $\Delta H_f^\circ(g)$ (MMX) and the MMX pi energies into RE and constant group terms, and to compare group additivity methods for  $\Delta H_f^\circ(g)$  without resonance energy terms to the same types of analyses with resonance.

#### 4 PBAH HEATS OF FORMATION

The useful and significant computational results of this study are summarized in Table 1. This table lists the calculated ground state geometries and the AM1, MMX and SGB heats of formation for all of the cata-condensed PBAH's through six rings (identified in Fig. 2). The experimentally determined  $\Delta H_f^\circ(g)$  for the first nine compounds are also listed (refs. 21, 22, 25-28). The remaining entries comprise the results from the already mentioned group additivity/resonance energy analysis of the MMX heats of formation (column headed GA/RE in the table) and resonance energies derived from that analysis (RE1 and RE2), which will be discussed in section 6. Finally, the point group is designated for the nonplanar structures.

The calculated AM1 and MMX ground-state geometries agree in every case, and experimental geometries where known (refs. 3-8, 12, 35-37) are also completely consistent with the calculations. AM1 and MMX calculations both indicate that 26 of the 58 molecular graphs actually represent highly nonplanar molecular systems. The compounds with a  $C_2$  point group would exist as pairs of enantiomers, and four of the  $C_{26}H_{16}$  systems with six rings (55 - 58) should give rise to diastereoisomeric pairs (designated a and b in the table). Systems 55, 56, and 58 would be each comprised of a meso compound and an enantiomeric pair, and 57 would represent two pairs of enantiomers.

The SGB  $\Delta H_f^\circ(g)$  are calculated using the original parameterization (ref. 38). Missing SGB results are due to the fact that the SGB calculations cannot distinguish between the diastereoisomeric systems, and the  $\Delta H_f^\circ(g)$  values for helicenes structures (21, 50 - 54) cannot be determined because there are no experimental data to define the required parameters. Parameters for the missing helicene-type steric interactions will be derived from the MMX  $\Delta H_f^\circ(g)$  calculations in section 6 using the group analysis including resonance energy.

Alberty and Reif (ref. 46) have also recently used the SGB method to calculate the  $\Delta H_f^\circ(g)$  of the PBAH's with one to six rings. Tables of  $\Delta H_f^\circ(g)$ ,  $\Delta S_f^\circ(g)$ ,  $\Delta G_f^\circ(g)$  and  $C_p^\circ(g)$  are obtained for the individual compounds, and the results are used to allow the calculation of tables of average isomer group thermodynamic properties for the six isomer groups represented in Figs. 2-4. The Alberty and Reif work has serious inconsistencies in addition to the approximations inherent in the SGB additivity method. The most critical incorrect aspect of their work is an imposed restriction to supposedly planar molecular structures, on the grounds that the nonplanar compounds "would be expected to have significantly higher energies" and "they would not contribute very much to isomer group thermodynamic properties". As already mentioned, an important result of the calculations carried out for this work is that 19 compounds with a benzo[c]phenanthrene substructure (9, 18-21, 38-49), assumed to be planar by Alberty and Reif, would actually possess highly nonplanar ground-state structures, and that the excluded nonplanar helicene-type structures will be more stable than many of the more linear planar structures that were included in their analysis. Furthermore, they overlooked the possibility of diastereoisomeric compounds in systems 55-58. These observations indicate that one may question the utility of the Alberty and Reif tables of thermodynamic functions.

The misconception regarding planarity in the benzenoids will also contribute to difficulties in using the calculated MNDO data on benzenoids in a recent book entitled "Calculated Molecular Properties of Polycyclic Aromatic Hydrocarbons" by Hites and Simonsick (ref. 47). In their work, planarity is imposed on all structures except for benzo[c]phenanthrene and its simple monomethyl derivatives. AM1 and MNDO are, of course, highly related semi-empirical quantum mechanical treatments. Thus, in every case, calculated  $\Delta H_f^\circ(g)$  values for planar compounds listed in both Table 1 and the Hites-Simonsick compendium agree to within approx. two kcal. However, the MNDO heats of formation for 15 other cata-condensed PBAH's are more positive than the AM1 results by 12 to 60 kcal, due to the fact that the final MNDO geometry is not geometry-optimized. Studies of an additional 35 suspect peri-condensed and non-alternant benzenoids in the HS work are in progress.

#### 5 EVALUATION OF CALCULATED AND EXPERIMENTAL $\Delta H_f^\circ(g)$

The AM1, MMX, and SGB theoretical results for  $\Delta H_f^\circ(g)$  given in Table 1 are discordant when compared with each other, and the AM1 calculations are highly discordant when compared to the experimental results. In fact the residual errors are so large for the AM1 calculations, averaging 10.0 kcal, as to disqualify its use to correlate the experimental data, much less to use it as a predictive tool for  $\Delta H_f^\circ(g)$ . One might anticipate that relative values would be more reliable, and that it would be possible to use AM1 calculations to predict the relative stabilities of isomeric systems with some hope of success. However, the fact that AM1 fails to find triphenylene (8) less stable than chrysene (7) does not support this conjecture. Additional experimental data will be required to resolve this question.

One also finds that the MMX value for the heat of formation of compound 5 (naphthacene) is in serious disagreement with the experimental result. However, in order to be an acceptable figure, and in order to be consistent with the overall results, the experimental difference between compounds 5 and 6 should be much larger than the reported 2.7 kcal/mol. The completely linear compounds (3, 5, 10, 22) are always calculated to be much less stable than any of the other members of each isomer family, and the difference increases uniformly as the compounds become larger. Even the linear three-ring compound, anthracene, is less stable than the angular isomer, phenanthrene, by over five kcal, both experimentally and theoretically, and the naphthacene instability should substantially exceed this five kcal value. Therefore, the experimental  $\Delta H_f^\circ(g)$  for naphthacene should not be considered in an analysis of the experimental  $\Delta H_f^\circ(g)$  data.

Table 1. Calculated and experimental  $\Delta H_f^\circ(g)$  (Kcal), resonance energies (Kcal) and geometries.

Cpd.	AM1	MMX	SGB	Expt.	GA/RE	RE1	RE2	Geom.
1	22.0	19.3	19.8	20.0	19.1	-26.9	-26.2	planar
2	40.6	34.9	36.0	36.0	34.8	-42.6	-41.5	planar
3	62.9	55.6	52.2	54.9	55.1	-53.7	-52.4	planar
4	57.4	49.2	50.0	49.4	49.7	-62.4	-60.8	planar
5	86.9	78.2	68.4	68.6	77.8	-62.4	-60.8	planar
6	78.3	68.1	66.2	65.9	68.0	-75.5	-73.5	planar
7	76.2	65.9	64.0	63.1	66.2	-80.6	-78.5	planar
8	75.5	67.2	61.8	63.9	68.2	-85.2	-83.0	planar
9	81.2	69.3	67.0	69.6	69.3	-80.6	-78.5	C
10	111.9	101.9	84.6	----	102.1	-69.5	-67.9	planar
11	101.5	89.8	82.4	----	89.7	-85.2	-83.0	planar
12	94.4	81.1	80.2	----	81.8	-96.4	-93.9	planar
13	94.2	81.1	80.2	----	81.8	-96.4	-93.9	planar
14	97.7	85.7	80.2	----	85.2	-93.0	-90.6	planar
15	98.4	86.2	82.4	----	85.6	-89.3	-89.0	planar
16	94.3	81.9	78.0	----	82.0	-99.5	-96.9	planar
17	95.6	85.4	78.0	----	85.3	-99.5	-96.9	planar
18	102.5	88.7	83.2	----	88.3	-93.0	-90.6	C
19	99.2	84.5	81.0	----	85.1	-99.5	-96.9	C
20	99.5	86.3	78.8	----	85.2	-102.3	-99.7	C
21	103.5	86.1	----	----	86.1	-99.5	-96.9	C
22	137.3	126.2	95.0	----	127.6	-75.4	-73.5	planar
23	126.0	113.0	92.0	----	113.3	-93.0	-90.6	planar
24	121.3	107.7	96.4	----	107.3	-102.3	-99.7	planar
25	119.5	105.6	96.4	----	104.6	-105.0	-102.3	planar
26	116.4	101.7	94.2	----	102.1	-107.5	-104.7	planar
27	113.6	98.6	92.0	----	98.7	-114.2	-111.2	planar
28	121.3	107.3	95.9	----	106.8	-99.5	-96.9	planar
29	114.6	99.4	94.2	----	99.7	-109.9	-107.0	planar
30	114.8	99.8	92.8	----	99.7	-109.9	-107.0	planar
31	116.4	101.7	95.0	----	102.1	-107.5	-104.7	planar
32	115.6	101.3	99.4	----	100.8	-112.1	-109.2	planar
33	113.4	97.9	98.6	----	98.7	-114.2	-111.2	planar
34	112.7	97.8	96.4	----	98.1	-118.1	-115.0	planar
35	115.3	103.5	97.2	----	102.0	-114.2	-111.2	planar
36	112.0	98.6	94.2	----	99.6	-119.9	-116.8	planar
37	118.5	106.9	95.0	----	106.3	-109.9	-107.0	planar
38	120.4	104.0	96.4	----	103.9	-112.1	-109.2	C
39	117.5	100.8	96.4	----	101.2	-118.1	-115.0	C
40	118.2	101.2	94.2	----	101.8	-114.2	-111.2	C
41	125.9	110.9	95.9	----	110.4	-102.3	-99.7	C
42	118.4	101.3	93.7	----	101.8	-114.2	-111.2	C
43	117.5	100.5	98.1	----	101.2	-118.1	-115.0	C
44	120.2	103.6	97.2	----	103.9	-112.1	-109.2	C
45	124.1	108.4	95.0	----	107.7	-105.0	-102.3	C
46	117.1	101.2	97.2	----	101.0	-121.6	-118.4	C
47	121.2	106.2	94.2	----	105.1	-114.2	-111.2	C
48	119.8	104.6	99.4	----	103.1	-116.2	-113.2	C
49	119.7	104.5	97.2	----	103.1	-116.2	-113.2	C
50	121.1	102.4	----	----	102.0	-121.6	-118.4	C
51	121.6	101.6	----	----	102.2	-118.1	-115.0	C
52	124.6	104.9	----	----	104.9	-112.1	-109.2	C
53	122.9	104.1	----	----	103.7	-119.9	-116.8	C
54	127.9	103.8	----	----	103.8	-118.1	-115.0	C
55a	121.1	105.2	98.6	----	105.8	-123.2	-120.0	D
55b	125.5	110.7	----	----	----	----	----	D <sub>H</sub>
56a	124.3	103.0	100.8	----	104.3	-118.1	-115.0	S
56b	121.6	106.3	----	----	----	----	----	S
57a	124.1	105.6	96.4	----	105.8	-119.9	-116.8	S
57b	123.7	107.7	----	----	----	----	----	S
58a	125.5	106.3	95.0	----	105.8	-119.9	-116.8	S
58b	122.5	106.4	----	----	----	----	----	S

Excluding naphthalene, it is possible to derive first-order linear relationships with rather high precision which relate the calculated  $\Delta H_f^{\circ}(g)$ (MMX) and  $\Delta H_f^{\circ}(g)$ (SGB) values to the experimental values. The statistical parameters of these equations are summarized in Table 2.

Table 2. Linear Correlations Between Calculated and Experimental  $\Delta H_f^{\circ}(g)$ .

Equation	Num. Cpd.	Corr. Coeff.	Std. Error
EXPT = 2.664 + 0.935(MMX)	8	0.997	1.311
EXPT = -0.313 + 1.020(SGB)	8	0.996	1.569
MMX = -2.994 + 1.087(SGB)	8	0.996	1.862
MMX = -4.476 + 1.158(SGB)	52	0.968	5.219

Either linear relationship gives a reasonable correlation of the experimental data, including the  $\Delta H_f^{\circ}(g)$  value for the nonplanar benzo[*c*]phenanthrene. For predictive purposes, the possibility exists that the remaining MMX or SGB values in Table 1 could be adjusted to give more valid estimates of  $\Delta H_f^{\circ}(g)$  by using these linear equations. However, the poor correlation between MMX and SGB demonstrated by the fourth equation in Table 2 is not impressive, and this result indicates that the validity of predicting  $\Delta H_f^{\circ}(g)$  using at least one of these procedures must be questioned. The results obtained from the additivity structural models including resonance terms to be discussed in the next section strongly suggest that the experimentally unknown  $\Delta H_f^{\circ}(g)$  are calculated accurately by the MMX molecular mechanics method, and not by the original SGB procedure. The usefulness of a group additivity/resonance method that models the MMX calculations will also be demonstrated.

## 6 GROUP ADDITIVITY/RESONANCE MODELS FOR $\Delta H_f^{\circ}(g)$ OF PBAH'S

Two simple, realistic models that include resonance terms, steric interactions and bond or group parameters can be suggested to correlate experimental and theoretical heats of formation of cata-condensed PBAH's. The steric interactions in such models are represented by  $S_3$  to  $S_6$  and T (illustrated in Fig. 4), and the resonance energy (RE) of each system can be calculated by the  $\log(SC)$  algorithm described previously. The other parameters would be C-C and C-H bond terms in the first method, and the Stein, Golden, Benson terms (A, B, C and D in Fig. 3) for the group method. Not surprisingly, one can demonstrate that the two models are algebraically equivalent. As a consequence, the SGB model including resonance will not be considered further in this discussion.

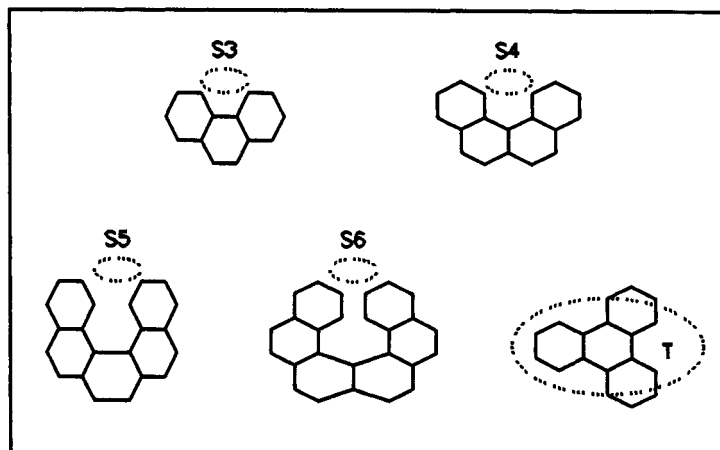


Fig. 4. Steric interactions in PBAH's

The parameters  $S_3$  through  $S_6$  characterize destabilizing steric interactions that arise in phenanthrene, benzo[*c*]phenanthrene, dibenzo[*c,g*]phenanthrene (common name - pentahelicene) and hexahelicene, respectively. The T parameter is due to triphenylene substructures, and it represents the coupling of three  $S_3$  terms in a planar structure that cannot be relieved by the normal molecular distortion associated with the  $S_3$  bay-region of phenanthrene. The inclusion of the T steric parameter was not part of our initial postulates, but was found to be a valid parameter through trial and error. Large improvements in the statistical rectification of both the experimental and the MMX theoretical data are manifest when this parameter is used (see below).

An analysis of the experimental  $\Delta H_f^\circ(g)$  data using the bond and steric parameters model with increasing number of terms is outlined in Table 3.

Table 3. Correlations of Additivity Models for  $\Delta H_f^\circ(g)$  with Experimental  $\Delta H_f^\circ(g)$ .

Parameters	Corr. Coeff.	Std. Error.	F-Ratio
C-C, C-H, $S_3$ , $S_4$	0.997	1.696	$2.1 \times 10^3$
C-C, C-H, $S_3$ , $S_4$ , RE	0.999	1.135	$3.8 \times 10^3$
C-C, C-H, $S_3$ , $S_4$ , T	1.000	0.977	$5.1 \times 10^3$
C-C, C-H, $S_3$ , $S_4$ , T, RE	1.000	0.538	$1.4 \times 10^4$

The first model with four parameters is equivalent to the group model which gave the SGB results in Table 1 and which led to the second equation in Table 2. The small differences in statistical parameters from those in Table 2 are due to the fact that the A, B and C parameters in the SGB method were determined by optimization, but the D parameter was chosen equal to the heat of sublimation of graphite per carbon atom rather than obtained from PBAH data. In addition, the Table 3 analysis does not include the suspected experimental naphthacene heat of formation.

The effects of adding the T steric term and the resonance energy estimate are clearly justified as indicated by the much improved statistics of the correlations. For example, there is a large increase in the F-ratio statistic even after the addition of both the T and RE parameters. The final regression expression is

$$\Delta H_f^\circ(g)(\text{empirical}) = 4.425(\text{CC}) + 1.786(\text{CH}) - 0.130(S_3) + 6.308(S_4) + 3.897(\text{T}) - 24.563(\log(\text{SC})) \quad (1)$$

This equation correlates the experimental results with an average deviation of less than 0.2 kcal. For a purely empirical approach, equation 1 can be used to calculate  $\Delta H_f^\circ(g)$  for cata-condensed PBAH's if no additional destabilizing steric features are present in the molecular structure. However, the presence of  $S_5$  or  $S_6$  substructures or a large increase in the size of the PBAH under consideration would be likely to obviate the utility of the equation.

An additivity analysis of all of the MMX  $\Delta H_f^\circ(g)$  data allows the determination of steric parameters  $S_5$  and  $S_6$ . For consistency, we redetermine all of the other parameters as well, rather than use the Equation 1 values based on the eight experimental heats of formation. Inclusion of the  $\log(\text{SC})$  term allows the regression analysis to also model the resonance energy of each system, and this will then permit estimation of resonance energies after regression coefficients are determined. In the case of the four diastereoisomeric systems, the molecules with the higher calculated  $\Delta H_f^\circ(g)(\text{MMX})$  of each pair are not included in the additivity/resonance model.

The model equation given by the group additivity/resonance (GA/RE) analysis is

$$\Delta H_f^\circ(g)(\text{A/R}) = 5.353(\text{CC}) + 2.316(\text{CH}) + 3.295(S_3) + 9.693(S_4) + 13.973(S_5) + 18.893(S_6) + 3.299(\text{T}) - 38.779(\log(\text{SC})) \quad (2)$$

which has correlation coefficient = 1.000, a standard error of 0.691 kcal and a statistical F-ratio of  $1.4 \times 10^5$ . An analysis without the  $\log(\text{SC})$  resonance energy term gives a standard deviation five times higher (3.7 kcal) and an F-ratio 25 times lower ( $5 \times 10^3$ ) than for equation 2. The complete results of this structural model analysis of the MMX  $\Delta H_f^\circ(g)$  data are listed in the GA/RE column of Table 1.

The coefficients of the steric interaction terms increase in a regular manner in going from  $S_3$  to  $S_6$  with the average increment being 5.1 kcal/mol. This increasing increment is reasonable since the destabilizing steric interactions must obviously worsen going from  $S_3$  to  $S_6$ . The assumption that the same order of increase applies to any successive steric interaction term allows extension of the predictive usefulness of the A/R model and equation 2 to larger systems with overlapping hepta, octa or nonahelicene-type rings. The values of the predicted steric terms  $S_7$ ,  $S_8$  and  $S_9$  are 24.2, 29.3 and 34.4 kcal, respectively. The actual values of these terms, defined using MMX calculations for the three molecules and the parameters in equation 2, are 23.64, 29.18 and 35.08 kcal, respectively, which demonstrates the essential correctness of the extrapolation. However, we cannot calculate  $S_{10}$  or larger steric terms using the PCMODEL molecular mechanics program because of the limitation of the number of pi carbon atoms to 40.

Table 1 also contains calculated values of resonance energies for each of the 58 cata-condensed PBAH's. The RE1 values are the results of fitting the MMX  $\Delta H_f^\circ(g)$  data to the additivity/resonance model, but the RE2 resonance energies are derived directly from the pi-SCF submodule of the MMX calculation in a completely independent manner as follows. PCMODEL gives a calculated total pi energy as one of the terms contributing to the heat of formation. The elements of the SCF density matrix are used to weight the



MMX natural bond distance terms, the force constants and the two-fold torsional barrier terms, but the pi calculation is otherwise separate from the molecular mechanics results. The later terms determine the major part of the force field energy, and also the major part of the heat of formation calculation. We reasoned that the pi energy would be a linear function of only the number of pi centers except for the resonance energy component, which would, of course, depend upon molecular cyclicly and topology.

The excellent linear correlation shown by equation 3 (std. error 1.260, F-ratio  $1.1 \times 10^6$ ), in which resonance energy is again modeled by  $\log(\text{SC})$ , supports this inference, and the regression coefficient for the  $\log(\text{SC})$  term determines the RE2 resonance energy in Table 1.

$$\text{SCF}(\text{PI}) = 15.60 - 51.664(\#C) - 37.771(\text{Log}(\text{SC})) \quad (3)$$

The very close correspondence of RE1 and RE2 in Table 1 is due to the near equivalence of the regression coefficients, 38.779 from Equation 2, and 37.771 from Equation 3, which weight the  $\log(\text{SC})$  term. These consistent results confirm the general use of the  $\log(\text{SC})$  algorithm to estimate relative resonance stabilization energies in benzenoids, and suggest that these calculated resonance energies can be used as valid approximations.

## 7 SUMMARY AND CONCLUSIONS

One of the surprising results of the calculations presented in this work is that a very large fraction (30 of 62) of the cata-condensed compounds turn out to have nonplanar structures with the minimum angle of nonplanarity approximately  $30^\circ$ . In related work, we have further demonstrated that the fraction of cata-condensed PBAH's incorporating the nonplanar benzo[c]phenanthrene ( $S_4$ ) or other helicene-type substructures increases with increasing size. For example, only 600 of the possible 6693 cata-condensed PBAH's with ten rings could actually exist as planar molecules. Therefore, nonplanarity in the cata-condensed benzenoids is evidently a widespread and important structural feature which must be included as part of any structural analysis. There is experimental evidence that shows that this conclusion holds for peri-condensed PBAH's as well. The X-ray crystal structures of several large peri-condensed PBAH's with  $S_4$  substructures have been determined and each one exhibits large deviations from planarity (refs. 9-14).

A second interesting result is that many of the nonplanar systems among these PBAH's are computed to be thermodynamically more stable than many of the planar molecules. From an examination of the data, one can attribute the source of this destabilization in the cata-condensed benzenoids to the presence of linear substructures in these systems. The planar molecules usually contain a linear anthracene substructure, whereas the nonplanar compounds always contain angular helicene substructures. The association of thermodynamic instability with a linear structure is, of course, in agreement with the analysis of the experimental data given in section 5 which led us to question the experimental  $\Delta H_f^\circ(\text{g})$  for naphthalene.

Two of the primary conclusions of this work are that the MMX molecular mechanics force field provides reliable estimates of  $\Delta H_f^\circ(\text{g})$  for cata-condensed PBAH's, in good agreement with experiment where comparisons can be made, and that the AM1 computations do not give reasonable results in this regard. We have further demonstrated that the MMX  $\Delta H_f^\circ(\text{g})$  can be accurately reproduced by a realistic chemical additivity model with bond enthalpy, steric, and resonance energy terms, and we have shown that the resonance energies are critical parameters in modelling the  $\Delta H_f^\circ(\text{g})$  (MMX). Two independent approaches to estimating the resonance energies give highly congruent values (Table 1), and we propose that these resonance energies can be taken as accurate approximations.

We believe that equation 2 (including  $S_7$ ,  $S_8$  and  $S_9$  terms) can be used to estimate values for  $\Delta H_f^\circ(\text{g})$  which are likely to be reasonably close to experimental values for cata-condensed PBAH's not present in the parameterization. The only exceptions might be compounds with complex steric interactions that have not been investigated in this work. Generally, it would be necessary for such compounds to contain more than ten rings, and also closely coupled trios or possibly quartets of steric interactions. However, overlapping rings, as in the nonplanar helicenes are well-accommodated by the model calculation.

The group additivity/resonance energy model (equation 2) is particularly easy to use since it does not require computer facilities. The only difficulties would lie in the prediction of  $\Delta H_f^\circ(\text{g})$  for compounds with very unusual structural features. Also, like other empirical models, it cannot distinguish between the diastereoisomeric systems. This disadvantage does not exist if one simply uses the MMX molecular mechanics force field to calculate  $\Delta H_f^\circ(\text{g})$ . However, we propose that both types of approaches are valid, and we anticipate that the  $\Delta H_f^\circ(\text{g})$  of planar and nonplanar peri-condensed PBAH's will be successfully analyzed using analogous procedures.

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## REFERENCES

1. W. H. Laarhoven and W. J. C. Prinsen, *Top. Curr. Chem.*, **125**, 63-130 (1984).
2. K. P. Meurer and F. Vogtle, *Top. Curr. Chem.*, **127**, 1-76 (1985).
3. A. O. McIntosh, J. M. Robertson and V. Vand, *J. Chem. Soc.*, 1661-1668 (1954).
4. E. Harnik, F. H. Herbstein, G. M. J. Schmidt and A. L. Hirshfeld, *J. Chem. Soc.*, 3288-3294 (1954).
5. F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3302-3313 (1954).
6. F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3314-3319 (1954).
7. J. M. Robertson and J. Trotter, *J. Chem. Soc.*, 2614-2623 (1959).
8. A. L. Hirshfeld, S. Sandler and G. M. J. Schmidt, *J. Chem. Soc.*, 2108-2124 (1964).
9. K. W. Muir and J. M. Robertson, *Acta Cryst.*, **B28**, 879-884 (1971).
10. Y. Kohno, M. Konno, Y. Saito and H. Inokuchi, *Acta Cryst.*, **B31**, 2076-2080 (1975).
11. I. Oonishi, S. Fujisawa, J. Aoki and T. Danno, *Bull. Chem. Soc. Jap.*, **51**, 2256-2260 (1977).
12. F. H. Herbstein, *Acta Cryst.*, **B35**, 1661-1670 (1979).
13. S. Fujisawa, I. Oonishi, J. Aoki, Y. Ohashi and Y. Sasada, *Bull. Chem. Soc. Jap.*, **55**, 3424-3428 (1982).
14. I. Oonishi, S. Fujisawa, J. Aoki and Y. Ohashi, *Bull. Chem. Soc. Jap.*, **59**, 2233-2236 (1986).
15. W. C. Herndon in *Polynuclear Aromatic Compounds*, ACS Advances in Chemistry Series No. 217, L. Ebert, Ed., chpt 1, Amer. Chem. Soc., Washington, D. C. (1988).
16. E. Clar, *Polycyclic Hydrocarbons*, Vol. 1, chpt. 16, Academic Press, New York (1964).
17. M. S. Newman and W. B. Wheatley, *J. Amer. Chem. Soc.*, **70**, 1913-1916 (1948);  
M. S. Newman and H. S. Whitehouse, *J. Amer. Chem. Soc.*, **71**, 3664-3667 (1949);  
M. S. Newman and R. M. Wise, *J. Amer. Chem. Soc.*, **78**, 450-454 (1956);  
M. S. Newman and D. K. Phillips, *J. Amer. Chem. Soc.*, **81**, 3667-3670 (1959);  
M. S. Newman, R. G. Mentzer and G. Slomp, *J. Amer. Chem. Soc.*, **85**, 4018-4020 (1963).
18. M. A. Frisch, C. Barker, J. L. Margrave and M. S. Newman, *J. Amer. Chem. Soc.*, **85**, 2356-2357 (1965); H. A. Karnes, B. D. Kybett, M. H. Wilson, J. L. Margrave and M. S. Newman, *J. Amer. Chem. Soc.*, **87**, 5554-5558 (1965); H. A. Karnes, M. L. Rose, J. W. Collat and M. S. Newman, *J. Amer. Chem. Soc.*, **90**, 458-461 (1968).
19. N. Trinajstić, Discussions at the Third International Conference on Mathematical Chemistry, Galveston, Texas, March 5-9, 1989.
20. A. T. Balaban and F. Harary, *Tetrahedron*, **24**, 2505-2516 (1968).
21. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York (1970).
22. J. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds*, Chapman and Hall, London (1986).
23. J. Rigaudy and S. P. Klesney, *Nomenclature of Organic Chemistry*, 1979 Edition, section A-21.
24. J. R. Dias, *Handbook of Polycyclic Hydrocarbons, Part A, Benzenoid Hydrocarbons*, Elsevier, Amsterdam (1987).
25. The recommended  $\Delta H_f^\circ(g)$  in ref. 21 make use of erroneous heats of sublimation for naphthalene, chrysene and triphenylene. The values of  $\Delta H_f^\circ(g)$  that we choose are based primarily on data obtained from the citations in refs. 21 and 26-28. The  $\Delta H_f^\circ(g)$  for benzene is based on a value of  $\Delta H_f^\circ(\text{sublimation})$  of 8.3 kcal per mole. (private communication, J. Chickos, Dept. of Chem., Univ. of Missouri at St. Louis, Nov. 25, 1986), which has been confirmed in our laboratories.
26. R. J. Irving, *J. Chem. Therm.*, **4**, 793-794 (1972).
27. W. C. Herndon, *Thermochim. Acta*, **8**, 225-237 (1974).
28. C. G. DeKruif, *J. Chem. Therm.*, **12**, 243-248 (1980).
29. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Amer. Chem. Soc.*, **107**, 3902-3909 (1985).
30. R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **97**, 1285-1294, 1302-1307 (1975).
31. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, **99**, 4899-4907 (1977).
32. N. L. Allinger, *J. Amer. Chem. Soc.*, **99**, 8127-8134 (1977).
33. For a review see U. Burkett and N. L. Allinger, *Molecular Mechanics*, ACS Monograph 177, Amer. Chem. Soc., Washington, D. C. (1982).
34. J. T. Sprague, J. C. Tai, Y. Yuh and N. L. Allinger, *J. Comput. Chem.*, **8**, 581-(1987).
35. See W. C. Herndon, *J. Amer. Chem. Soc.*, **96**, 7605-7614 (1974) for leading references to the structures of planar cata-condensed PBAH's.
36. A. De, R. Ghosh, S. Roychowdhury and P. Roychowdhury, *Acta Cryst.*, **C41**, 907-909 (1985).
37. I. Navaza, G. Tsoucaris, G. Le Bas, A. Navaza and C. de Rango, *Bull. Soc. Chim. Belg.*, **88**, 863-970 (1979).
38. S. E. Stein, D. M. Golden and S. W. Benson, *J. Phys. Chem.*, **81**, 314-317 (1977).
39. W. C. Herndon, *J. Amer. Chem. Soc.*, **95**, 2404-2406 (1973).
40. W. C. Herndon and M. L. Ellzey, Jr., *J. Amer. Chem. Soc.*, **96**, 6631-6642 (1974).
41. W. C. Herndon, *Israel J. Chem.*, **20**, 270-275 (1980).
42. I. Gutman and W. C. Herndon, *Chem. Phys. Letts.*, **34**, 387-391 (1975).
43. R. Swinbourne-Sheldrake, W. C. Herndon and I. Gutman, *Tetrahedron Letts.*, 755-758 (1975).
44. W. C. Herndon, *Tetrahedron*, **29**, 3-12 (1973).
45. W. C. Herndon, *J. Chem. Educ.*, **51**, 10-15 (1974).
46. R. A. Alberty and A. K. Reif, *J. Phys. Chem. Ref. Data*, **17**, 241-254 (1988).
47. R. A. Hites and W. J. Simonsick, Jr., *Calculated Molecular Properties of Polycyclic Aromatic Hydrocarbons*, Elsevier, Amsterdam (1987).