

Crystallization of Large Planar Polycyclic Aromatic Hydrocarbons: The Molecular and Crystal Structures of Hexabeno[bc,ef,hi,kl,no,qr]coronene and Benzo[1,2,3-bc:4,5,6-b'c']dicononene[†]

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Abstract: Single crystals of the two large planar condensed polycyclic aromatic hydrocarbons hexabeno[bc,ef,hi,kl,no,qr]coronene (HBC) and benzo[1,2,3-bc:4,5,6-b'c']dicononene (BDC) have been grown from molten pyrene using mesitylene as a flux, and their crystal structures have been determined by X-ray analysis. BDC (C₄₈H₂₀) is the largest pericondensed polycyclic aromatic hydrocarbon whose crystal structure has hitherto been determined. The structure of HBC (C₄₂H₁₈) agrees with that determined previously for a twinned crystal. Crystallographic details for HBC: monoclinic, space group *P2₁/a*, *a* = 18.431(3) Å, *b* = 5.119(1) Å, *c* = 12.929(2) Å, β = 112.57(1)°, *V* = 1126.4(3) Å³, *Z* = 2, *R* = 0.056. Crystallographic details for BDC: monoclinic, space group *P2₁/c*, *a* = 10.376(1) Å, *b* = 3.823(1) Å, *c* = 31.914(3) Å, β = 90.24(1)°, *V* = 1266.1(9) Å³, *Z* = 2, *R* = 0.052. HBC crystallizes in the γ motif, whereas BDC crystallizes in the β motif, although both are planar within experimental error. For BDC, the angle between the planes of the molecules in the crystal is 50°, and for HBC, 84°; otherwise the packing is the same. The angle difference can be attributed to the shape of the molecules. Pauling bond order (resonance VB theory), HMO, π -SCF, molecular mechanics (MM), MNDO, AMI, PM3 semiempirical SCF protocols, and *ab initio* HF calculations all reproduce the experimentally determined bond lengths, bond angles, and short contact distances between intramolecular nonbonded atoms for both compounds. The MM procedure does not reproduce the observed planar molecular geometries. Bond angles and short contact distances are well described by molecular mechanics, semiempirical approaches, and the STO-3G *ab initio* method. These procedures predict disparate thermochemical heats of formation.

Introduction

Planarity is often presumed to be the significant geometric characteristic of the molecular structures of polycyclic aromatic compounds.¹ However, it has recently become apparent that a majority of polycyclic aromatics are not planar but exist with highly nonplanar, even chiral, molecular frameworks.^{2,3} The structure features responsible for nonplanarity include steric interference of the benzenoid rings and substituents, and three-dimensional topological constraints. Helicenic benzenoid aro-

matic hydrocarbons⁴ and the polyhedral fullerenes⁵ are two examples of well-known classes of such compounds.

Still, the planar or near-planar condensed polycyclic benzenoid aromatic hydrocarbons (PAH's) comprise an important small subclass of polynuclear aromatics. One significant reason is the (geometric) separation of *p* and *s* electrons that occurs in the molecular structures of these compounds. As a consequence, the planar aromatics are of great theoretical interest and their structures serve as test systems for theoretical calculations ranging from simplified valence bond (VB) and Hückel molecular orbital procedures to intermediate levels of *ab initio* MO quantum theory.^{1,2d,e,6}

We became interested in the molecular and crystal structures of very large PAH's because compounds of this type have been found to yield highly anisotropic cokes by solid-state carboniza-

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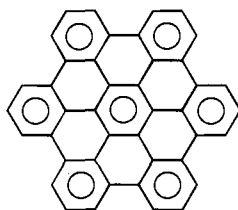
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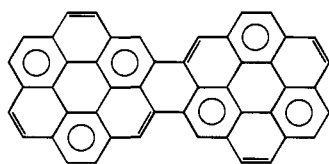
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tion. As they directly carbonize without formation of an intermediate mesophase state,⁷ the coke so obtained contains graphite layers which are oriented as in the original crystal. We surmised that a knowledge of the crystal packing would be useful in understanding this chemistry and also in predicting the type of coke obtained. Planar molecules are particularly interesting because they are expected to lead to regions of local graphitic structure. Here we describe the crystal structure determination of two large planar polycyclic aromatic compounds and show that their packing is a result of the shape of the molecules.

The two compounds we have investigated are hexabenzocoronene [*bc,ef,hi,kl,no,qr*]coronene (HBC) and benzo[1,2,3-*bc*:4,5,6-*b'c'*]diconene (BDC). The crystal structure of HBC was first



HBC



BDC

published by Robertson and Trotter⁸ using diffraction data collected from a twinned crystal. We chose to look at HBC because it was the largest known pericondensed⁹ PAH (13 benzene rings)¹⁰ whose crystal structure had been determined by X-ray analysis¹¹ at the time we started this work and because we had previously had some success in growing large single crystals of the second compound from molten pyrene using mesitylene as a flux. The structure of this second compound, BDC,¹² first described as Boente's "dicononylene", has been

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deduced by PE and UV spectroscopy,^{12b} but the authors reported that they were not able to interpret the X-ray data because of crystal disorder and twinning. We were interested in the crystal structure of BDC because of its large size (15 benzene rings) and its intermediate shape between that of a disk and that of a rectangle, similar to the shape of quaterrylene.¹³

We were also concerned with evaluating the ability of theoretical calculations to reproduce the molecular structures of large condensed PAH's.^{2b,d} A variety of semiempirical MO methods are readily available, and recent work by Schulman and co-workers has demonstrated the feasibility of using *ab initio* MO theory to elucidate properties of large PAH's.¹⁴ Also, in our work, we routinely obtain the results of molecular mechanics, π -SCF, HMO, and Pauling bond order calculations. Comparisons of the results of all of these types of theoretical procedures with the experimentally determined bond lengths, bond angles, and important short contact distances between nonbonded atoms will be given below. The predicted thermochemical stabilities of HBC and BDC, based on the molecular mechanics and the semiempirical MO calculations, will also be summarized and evaluated. However, the significance of the structural results for the solid-state carbonization of HBC and BDC will be reported elsewhere.^{7b}

Experimental Section

Syntheses and Sample Preparation. Hexabenzocoronene [*bc,ef,hi,kl,no,qr*]coronene (HBC)¹⁵ and benzo[1,2,3-*bc*:4,5,6-*b'c'*]diconene (BDC)¹² were synthesized as described in the literature. Suitable single crystals were obtained by slowly recrystallizing both compounds from molten pyrene followed by addition of mesitylene to prevent cocrystallization of pyrene as follows. HBC (24.4 g) was ground with 5.40 g of pyrene (99.3% pure), and the mixture was transferred into a glass ampule equipped with a three-way stopcock. After the ampule was evacuated and filled with argon, it was placed vertically into a tubular furnace heated to 350 °C. Most of the HBC dissolved in the molten pyrene within 30 min, forming a yellow solution. The temperature was slowly reduced from 350 to 271 °C at 0.2 °C/min and kept at 271 °C for 12 h. After further cooling to 180 °C at 0.2 °C/min, 5 mL of mesitylene was added in order to keep the pyrene in solution and to prevent its crystallization on further reduction of the temperature. The mesitylene solution was removed by a pipette from the crystals of HBC, and this washing procedure was repeated at 180 °C by using four additional portions of 5 mL each of mesitylene. The ampule was cooled to 100 °C, and the crystals were washed by five portions of 5 mL each of toluene in a similar manner. Finally, after they were cooled to room temperature, the crystals were washed with ether and dried in a stream of argon. Yellow needles and brown-yellow plates were obtained. An X-ray powder diffraction pattern from a mixture of both showed the sample to be uniform. Plates of HBC were used for the structure analysis.

Similarly, as described for HBC, 22.1 mg of BDC and 5.40 g of pyrene were heated to 400 °C. Within 30 min, the BDC dissolved to form an orange solution having a greenish fluorescence. Within 9 h the temperature was reduced to 281 °C at 0.2–0.4 °C/min and kept at this temperature for 12 h. After the solution was cooled from 281 to 175 °C within 2 h, the pyrene was removed as outlined above by washing with five portions of 5 mL each of mesitylene at this temperature and subsequently with five portions of 5 mL each of toluene

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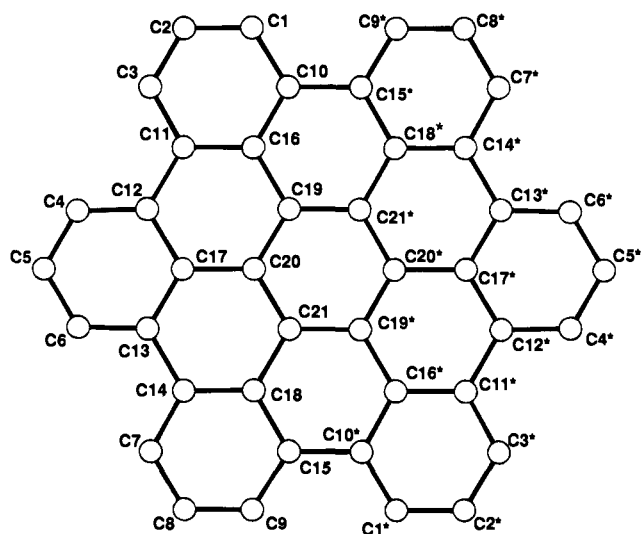
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Table 1. Details of the X-ray Crystal Structure Analyses of HBC and BDC (Data Collection and Structure Solution)

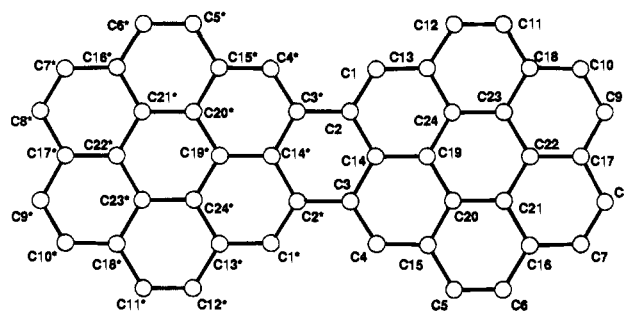
	HBC	BDC
formula	C ₄₂ H ₁₈	C ₄₈ H ₂₀
MW	522.6	596.7
cryst color	dark yellow	dark red
cryst syst	monoclinic	monoclinic
space group [no.]	<i>P</i> 2 ₁ / <i>a</i> [14]	<i>P</i> 2 ₁ / <i>c</i> [14]
<i>a</i> , Å	18.431(3)	10.376(1)
<i>b</i> , Å	5.119(1)	3.832(1)
<i>c</i> , Å	12.929(2)	31.914(3)
β , deg	112.57(1)	90.24(1)
<i>V</i> , Å ³	1126.4	1266.1
<i>Z</i>	2	2
<i>d</i> _{calcd} , g cm ⁻³	1.54	1.57
μ , cm ⁻¹	6.30	6.40
Cu K α radiation (λ), Å	1.54178	1.54178
<i>F</i> (000), e	540	616
diffractometer	Enraf-Nonius CAD4	
scan mode	$\omega-2\theta$	$\omega-2\theta$
[(<i>sin</i> θ)/ λ] _{max} , Å ⁻¹	0.63	0.63
<i>T</i> , °C	20	20
abs corr	none	none
no. of measd rflns	9540 [$\pm h, \pm k, \pm l$]	8981 [$\pm h, \pm k, \pm l$]
no. of indep rflns	2320	2608
no. of obsd rflns [<i>I</i> > 2 σ (<i>I</i>)]	2044	2187
<i>R</i> _{av}	0.05	0.03
no. of refined params	226	257
<i>R</i>	0.056	0.052
<i>R</i> _w (<i>w</i> = 1/ σ^2 (<i>F</i> _o))	0.058	0.057
resid electron dens, e Å ⁻³	0.28	0.27
struct soln	direct methods	direct methods

**Figure 1.** Molecular structure of hexabenzobenzene (HBC).

at 100 °C. After they were cooled to room temperature, the dark-red, almost black needles were washed additionally with ether and dried in streaming argon.

Crystal Structure Determinations. The crystals chosen for X-ray analysis (HBC, 0.14 × 0.28 × 0.67 mm; BDC, 0.11 × 0.18 × 0.60 mm) were mounted under argon in glass capillaries. Intensity data were collected on an Enraf Nonius CAD4 diffractometer using a scan speed of 1–10° depending on an initial prescan. Details of the crystal structure determinations of HBC and BDC are given in Table 1. The molecular structures are shown in Figures 1 (HBC) and 2 (BDC) together with their atomic numbering schemes. Atomic positional parameters and equivalent isotropic thermal parameters are given in Tables 2 (HBC) and 3 (BDC). Programs used and sources of scattering factor data are given in ref 16.

Computational Methods. Pauling bond order and HMO calculations were carried out using in-house programs running on personal computers. The molecular mechanics software was MMX, incorporated

**Figure 2.** Molecular structure of benzo[1,2,3-*bc*:4,5,6-*b'c'*]diconene (BDC).**Table 2.** Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) of HBC

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
C(1)	0.2081(1)	0.7167(2)	0.1498(1)	0.046(1)
C(2)	0.2297(1)	0.7188(3)	0.2643(1)	0.050(1)
C(3)	0.1969(1)	0.5453(3)	0.3148(1)	0.049(1)
C(4)	0.1287(1)	0.1713(3)	0.4211(1)	0.054(1)
C(5)	0.0964(1)	-0.0050(3)	0.4712(1)	0.063(1)
C(6)	0.0395(1)	-0.1776(3)	0.4071(1)	0.055(1)
C(7)	-0.0829(1)	-0.5340(3)	0.2711(1)	0.048(1)
C(8)	-0.1392(1)	-0.7077(3)	0.2063(1)	0.050(1)
C(9)	-0.1614(1)	-0.7107(3)	0.0921(1)	0.045(1)
C(10)	0.1520(1)	0.5388(2)	0.0826(1)	0.037(1)
C(11)	0.1407(1)	0.3628(2)	0.2518(1)	0.039(1)
C(12)	0.1057(1)	0.1784(2)	0.3048(1)	0.041(1)
C(13)	0.0136(1)	-0.1777(2)	0.2905(1)	0.041(1)
C(14)	-0.0472(1)	-0.3585(2)	0.2224(1)	0.039(1)
C(15)	-0.1285(1)	-0.5374(2)	0.0388(1)	0.037(1)
C(16)	0.1174(1)	0.3605(2)	0.1337(1)	0.035(1)
C(17)	0.0474(1)	0.0006(2)	0.2383(1)	0.036(1)
C(18)	-0.0705(1)	-0.3578(2)	0.1043(1)	0.035(1)
C(19)	0.0581(1)	0.1780(2)	0.0662(1)	0.033(1)
C(20)	0.0233(1)	0.0013(2)	0.1178(1)	0.033(1)
C(21)	-0.0349(1)	-0.1771(2)	0.0519(1)	0.033(1)
H(1)	0.2319(9)	0.842(3)	0.115(1)	0.063(4)
H(2)	0.2679(9)	0.847(3)	0.311(1)	0.065(4)
H(3)	0.2124(9)	0.551(3)	0.399(1)	0.071(4)
H(4)	0.170(1)	0.297(3)	0.467(1)	0.070(4)
H(5)	0.1138(9)	-0.006(3)	0.557(2)	0.082(5)
H(6)	0.017(1)	-0.296(4)	0.445(1)	0.085(5)
H(7)	-0.0679(9)	-0.531(3)	0.356(1)	0.064(4)
H(8)	-0.163(1)	-0.821(3)	0.244(1)	0.078(5)
H(9)	-0.2002(9)	-0.839(3)	0.046(1)	0.067(4)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$$

in the PCMODEL molecular modeling software package (Serena Software, Inc.).¹⁷ The π -SCF bond orders constitute part of the extended output from a PCMODEL calculation. MINDO and AMI results were obtained using AMPAC 2.10,¹⁸ implemented on the CRAY Y-MP8/864 computer at the University of Texas at Austin. The Austin CRAY was also employed for the *ab initio* calculations, which were

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Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (\AA^2) of BDC

atom	x	y	z	U_{eq}^a
C(1)	-0.1305(1)	0.3200(4)	0.0675(1)	0.028(1)
C(2)	-0.0680(1)	0.1646(3)	0.0344(1)	0.024(1)
C(3)	0.1359(1)	-0.0793(3)	0.0051(1)	0.024(1)
C(4)	0.2652(1)	-0.1515(4)	0.0106(1)	0.027(1)
C(5)	0.4661(1)	-0.1464(4)	0.0532(1)	0.031(1)
C(6)	0.5288(1)	-0.0658(4)	0.0897(1)	0.032(1)
C(7)	0.5263(1)	0.1772(4)	0.1621(1)	0.034(1)
C(8)	0.4613(1)	0.3309(4)	0.1942(1)	0.034(1)
C(9)	0.2570(1)	0.5658(4)	0.2236(1)	0.034(1)
C(10)	0.1287(1)	0.6373(4)	0.2195(1)	0.033(1)
C(11)	-0.0725(1)	0.6298(4)	0.1766(1)	0.032(1)
C(12)	-0.1345(1)	0.5544(4)	0.1400(1)	0.031(1)
C(13)	-0.0684(1)	0.3998(4)	0.1057(1)	0.026(1)
C(14)	0.0661(1)	0.0824(3)	0.0385(1)	0.023(1)
C(15)	0.3325(1)	-0.0719(4)	0.0481(1)	0.026(1)
C(16)	0.4636(1)	0.0910(4)	0.1237(1)	0.029(1)
C(17)	0.0611(1)	0.5580(4)	0.1819(1)	0.029(1)
C(19)	0.1313(1)	0.1627(3)	0.0765(1)	0.024(1)
C(20)	0.2648(1)	0.0861(3)	0.0813(1)	0.025(1)
C(21)	0.3307(1)	0.1678(4)	0.1194(1)	0.026(1)
C(22)	0.2628(1)	0.3263(4)	0.1529(1)	0.027(1)
C(23)	0.1290(1)	0.4022(3)	0.1485(1)	0.026(1)
C(24)	0.064(1)	0.3214(4)	0.1101(1)	0.025(1)
H(1)	-0.225(1)	0.382(4)	0.0651(4)	0.037(4)
H(4)	0.317(1)	-0.264(4)	-0.0121(4)	0.039(4)
H(5)	0.514(1)	-0.251(5)	0.0291(4)	0.040(4)
H(6)	0.625(1)	-0.114(4)	0.0926(4)	0.046(4)
H(7)	0.621(1)	0.122(4)	0.1642(4)	0.050(5)
H(8)	0.507(1)	0.390(4)	0.2223(5)	0.057(5)
H(9)	0.304(1)	0.615(4)	0.2508(5)	0.054(5)
H(10)	0.080(1)	0.746(4)	0.2429(4)	0.042(4)
H(11)	-0.118(1)	0.740(4)	0.2003(4)	0.040(4)
H(12)	-0.230(1)	0.605(4)	0.1368(4)	0.044(4)

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$$

carried out at the HF/STO-3G level using Gaussian 92, revision B.¹⁹ The HyperChem software package (Release 2, Autodesk, Inc.) was used to obtain the PM3 results.²⁰

Results and Discussion

In this section, the experimental structural findings will be cited and discussed, accompanied by historical perspective and by presentations of the theoretical results where appropriate. The reader may consult two recent review articles for a general background, detailed delineations of PAH structural types and characteristics, and listings of extant X-ray structures of PAH's.^{2e,21}

Crystal Packing. The first attempt to classify the crystal structures of aromatic hydrocarbons was made in 1951 by Robertson, who described two broad but fairly distinct types.²² The first type comprised disklike molecules with an area that was large compared with their thickness, and Robertson noted that such molecules tend to stack in columns, with the planes of the molecules in adjacent columns lying almost perpendicular to one another and about 45° to the symmetry plane of the crystal. The second type arose from flat and disklike (ellipsoid) molecules but of smaller area. In this case, he found that the molecules tended to be more steeply inclined to the symmetry plane of the crystal and the repeat distance (corresponding to the shortest unit cell length) was on the order of 6 Å. In the intervening years, the crystal structures of many aromatic hydrocarbons have been determined, and in 1989, Desiraju and

Gavezzotti modified Robertson's classification and defined four basic structural types for aromatic hydrocarbons: herringbone, sandwich, γ , and β .²¹

Desiraju and Gavezzotti defined the γ structure type for aromatic hydrocarbons as that in which the main C··C interactions are between parallel translated molecules, a sort of flattened-out herringbone.^{21a} The term γ originates from Schmidt,²³ who used it to designate crystal structures of *trans*-cinnamic acids with a distance between the C–C double bonds of 4.9 ± 0.2 Å. The γ structures have an axial range of 4.6–5.4 Å. Desiraju and Gavezzotti reported that, while the γ packing corresponds to Robertson's first category, both sandwich and herringbone structures occur in his second group, and they also noted that the β structures are not explicitly mentioned in his scheme. Desiraju and Gavezzotti characterized β structures as those made up of "graphitic" planes with strong C··C interactions without much contribution from C··H contacts and defined them as those in which the shortest unit cell axis is shorter than 4 Å.²¹ In this group they found nonplanar PAH's containing E-type (C_5) bay regions.

According to the unit cell criteria, HBC crystallizes in the γ motif whereas BDC crystallizes in the β motif. As we shall see below, the difference has less to do with the strength of the C··C interactions, the number of E-type atoms in the structures, and the planarity of the molecules but rather is caused by the different shapes of the molecules since HBC and BDC are both planar. The packing diagrams are shown side by side for the two compounds in Figure 3 (HBC, left). It is immediately apparent that, apart from the angle between the planes of the molecules, the packing is very similar in the two compounds. As can be clearly seen in Figure 3b,d, the unit cells can be viewed from a direction along which all molecules are orientated side-on. In addition, all molecules in the cells are found to make a fixed angle with the basal plane (010). The angles are 48.0° for HBC and 25.2° for BDC.

In order to understand the difference in the angles of the molecules to the basal plane of the unit cells, it is instructive to scrutinize the crystal structures of large polycyclic aromatic compounds found in the literature. Including the structure of BDC, there are now in all six reports of structures of planar PAH's containing 10 or more benzene rings. Important details of the packing of these compounds in the crystal are given in Table 4 together with that of the large disklike molecule [18]-annulene for comparison. The PAH's are arranged in order of increasing number of benzene rings. One of the important features of all the structures is that, although they have different shapes, they all crystallize in one of two space groups $P2_1/a$ (or c) or $C2/c$. Kitaigorodsky²⁴ has shown that the possible space groups that allow close-packing for molecules with a center of symmetry are restricted to $P1$, $P2_1/c$ (or a), $C2/c$, or $Pbca$. We may, therefore, safely conclude that the coordination number 6 in a layer can be provided with any mutual orientation

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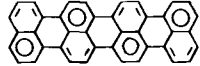
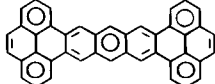
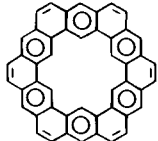

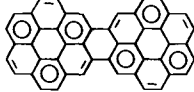

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Table 4. Packing Details for Large Planar Polycyclic Aromatic Hydrocarbons (10 Benzene Rings or More)

compd ^a	no. of benzene rings	space group	packing type ^b	packing coeff ^c	coord no. ^d	<i>b</i> cell axis length (Å) ^e	ring plane–basal plane angle (deg) ^f	interplanar angle (deg) ^g	interplanar distance (Å)	center-to-center offset (Å)
 ovalene ^h (OVALEN01 C ₃₂ H ₁₄)	10	<i>P</i> 2 ₁ / <i>a</i>	γ	0.7962	14	4.70 ± 1	42.8	85.6	3.45	3.20
 quaterrylene ⁱ (QUARTER10, C ₄₀ H ₂₀)		<i>P</i> 2 ₁ / <i>a</i>	sandwich	0.8198	14	10.630(3)	55.6	68.8	3.41	2.09
 tetrabenzoseptacene ^j (TBZHCE, C ₄₂ H ₂₂)	11	<i>P</i> 2 ₁ / <i>n</i>	β	0.7897	14	3.860(2)	22.6	45.2 16.2 ^m	3.56	1.48
 kekulene ^k (KEKULN10, C ₄₈ H ₂₄)	12	<i>C</i> 2/ <i>c</i>	γ	0.8026	14	4.579(1)	42.8	85.6	3.36	3.11
 HBC (C ₄₂ H ₁₈)	13	<i>P</i> 2 ₁ / <i>a</i>	γ	0.8226	14	5.119(1)	48.0	84.0	3.42	3.80
 BDC (C ₄₈ H ₂₀)	15	<i>P</i> 2 ₁ / <i>c</i>	β	0.8361	14	3.823(1)	25.2	50.4	3.46	1.63
 [18]annulene ^l (ANULEN, C ₁₈ H ₁₈)		<i>P</i> 2 ₁ / <i>a</i>	γ	0.7536	14	4.800 ± 2	48.8	82.4	3.16	3.61

^a Trivial name (Cambridge Crystallographic Database REFCODE,¹¹ formula). ^b According to refs 21 and 23. ^c Defined by Kitaigorodsky,²⁴ calculated with the program PACK.²⁵ ^d Number of nearest neighbors. ^e This is equivalent to the repeat stack distance in all γ structures. ^f Basal plane defined as (010). ^g Angle between planes in adjacent stacks. ^h Reference 26. ⁱ Reference 13. ^j Reference 27. ^k Reference 10. ^l Reference 28. ^m Independent molecules.

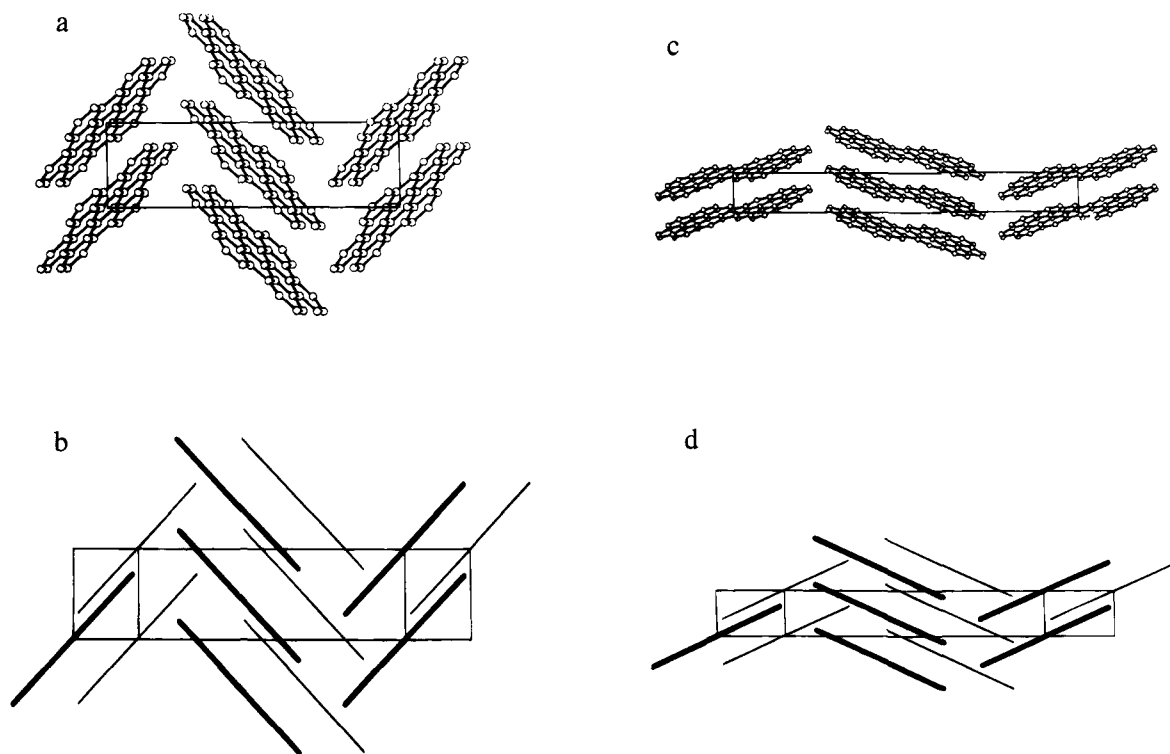


Figure 3. Crystal packings of HBC (a,b) and BDC (c,d): Views along the a axis (a,c) and perpendicular to the mean planes through the molecules (b,d) (solid lines, front). The (010) plane is horizontal (basal plane). The ring plane–basal plane angles are 48.0° (HBC) and 25.2° (BDC).

of the molecules. Indeed, all the molecules have large packing coefficients (>0.75), also consistent with close-packed structures. However, whereas the usual coordination number (number of nearest neighbors) for close-packing of spheres is 12, all of the planar compounds listed in Table 4 have coordination numbers of 14.

Selected geometrical details of the packing of these molecules are given on the right-hand side of Table 4. Apart from quaterrylene, which crystallizes in the sandwich motif, the crystal structures of the planar PAH's can be broadly divided into two groups, in agreement with Desiraju and Gavezzotti's γ and β classifications. Tetrabenzocoronene and BDC have short b cell axis lengths (<4 Å) and correspondingly small angles between the molecular plane and the basal plane (010) ($\approx 25^\circ$), whereas ovalene, kekulene, and HBC (and indeed, annulene) have larger b cell axis lengths together with ring plane–basal plane angles of around 45° . Interestingly, there is a clear relationship between the tilting angle of the molecules within the stacks and the shape of the molecules, with the long molecules, tetrabenzocoronene and BDC, exhibiting significantly smaller tilting angles. As all the molecules except for quaterrylene pack as stacks, there are simple relationships between the shortest unit cell length (b), the ring plane–basal plane angle (θ), the interplanar angle (2θ), the interplanar distance ($b \cos(\theta)$) and the center-to-center offset ($b \sin(\theta)$). Thus, as can be seen in Table 4, the center-to-center offset varies quite considerably in going down the series but the interplanar distance remains relatively constant [$3.44(7)$ Å]. Again the two long molecules with the smaller interplanar angles, tetrabenzocoronene and BDC, have small offsets, whereas the disklike molecules have interplanar angles close to 90° and center-to-center offsets of 3.11 – 3.80 Å, corresponding approximately to the interplanar distance.

The unit cell b axis for BDC is $3.823(1)$ Å, and the analogous distance for tetrabenzocoronene is $3.860(2)$ Å, placing them both clearly in the β group. In fact, unit cell repeat distances less than 4 Å have previously been overwhelmingly observed

for β -type aromatic hydrocarbons, which are always highly nonplanar molecules and, with one exception, also chiral. These β -type PAH's crystallize in layered (graphitic) structures perpendicular to parallel adjacent stacks and, according to Desiraju and Gavezzotti, are characterized mainly by strong stacking tendencies due to $C \cdots C$ intermolecular interactions. Being essentially planar, BDC and tetrabenzocoronene constitute exceptions to a strict interpretation of these general rules.²¹ An increased flattening of the herringbone pattern (γ) is observed, and this flattening necessarily results in a smaller b axis distance. How could this flattening out come about?

Clearly intermolecular π interactions are not involved: although the arrangements of the stacks relative to one another are different in the two compounds, the interplanar distances are very similar (HBC $3.424(8)$ and BDC $3.459(10)$ Å), in spite of the translational differences of one molecule to another, and only slightly larger than the interplanar distance in graphite (3.35 Å). Figures 4 and 5 give the normal projection of two parallel molecules of HBC and BDC. The projection for BDC is reminiscent of that for graphite. The center-to-center offsets are 3.8 Å for HBC and only 1.63 Å for BDC. Hunter and Sanders²⁹ have described the observed offsets in annulene and kekulene in terms of π – π interactions, but neither the almost identical offsets in phthalocyanine³⁰ and nickel phthalocyanine³¹ nor the very different offsets in HBC and BDC can be explained in these terms.

Figure 6 shows the 14 nearest neighbors of HBC (left) and BDC (right) in the form of four independent close-packed layers. Each layer shares the central molecule (colored yellow) and two others with one of the other layers. Essentially the packing is characterized by columns or stacks (center of each figure), which are themselves close-packed by dove-tailing of the individual molecules in the stacks. Inspection of Figure 6 shows that, apart

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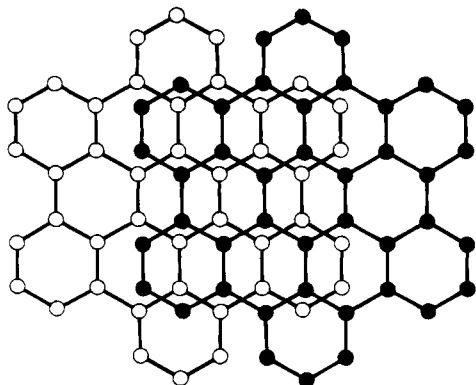


Figure 4. View of two neighboring molecules of HBC projected onto the molecular planes showing the displacement of the molecules in the stacks.

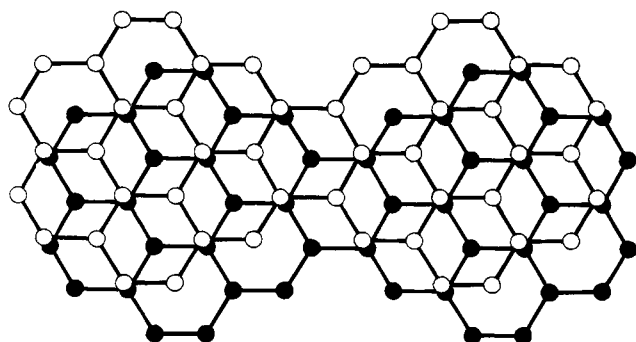


Figure 5. View of the two neighboring molecules of BDC projected onto the molecular planes showing the displacement of the molecules in the stacks.

from the angle that the individual molecules make to the column direction, there is no difference in the packing of the two molecules.³² The angle adopted is determined by the ability of the columns to close-pack. Simply, columns with a circular cross section pack less efficiently (more empty space) than columns with elliptical cross sections. Thus HBC overcomes the disadvantage of its disklike shape by tilting further than BDC, which in addition to its elliptical shape has bay regions which promote interstack packing (similar to that for tetrabenzoheptacene). As can be seen in Figure 6 (right), large center-to-center offsets for BDC are also prevented by the interstack packing in the bay regions, which in turn results in smaller tilt angles.

The change in the unit cell *b* distance is, therefore, a consequence of close-packing of the PAH's rather than any particular interaction between the molecules. Thus, the question as to whether BDC belongs to the γ or β motif depends on whether one considers the short axis length or the condition of nonplanarity as the prerequisite for the definition of the β type. If the short axis length is the chosen criterion, then it is not sufficient to distinguish it from the γ motif. In any case, the crystal structure of BDC does not belong to the sandwich motif, as predicted by Desiraju and Gavezzotti.^{21a}

In summary, both HBC and BDC form close-packed structures. The difference in the packing of the two compounds lies in the angle that the molecules are tilted within the columns. For BDC, close-packing of the columns is achieved with a smaller tilt angle than for HBC on account of its shape.

(32) Indeed, topologically, the packing is the same; we calculated the contents of the unit cell for a hypothetical structure using the fractional coordinates of HBC and the unit cell parameters ($a = 31.914 \text{ \AA}$, $b = 3.832 \text{ \AA}$, $c = 10.376 \text{ \AA}$, $\beta = 90.24^\circ$ (i.e., those of BDC)) and observed a packing almost identical to that observed for BDC (tilt angle 29° ; BDC 25°). The hypothetical molecule was lengthened by 150%.

Table 5. Libration Corrected Bond Distances (\AA) and Correction Factor (10^3 \AA)

HBC				
C(1)–C(2)	1.379(2)	–2	C(1)–C(10)	1.402(2) 0
C(2)–C(3)	1.371(2)	–1	C(3)–C(11)	1.403(2) –1
C(4)–C(5)	1.374(2)	–1	C(4)–C(12)	1.399(2) –1
C(5)–C(6)	1.380(2)	–1	C(6)–C(13)	1.398(2) –1
C(7)–C(8)	1.381(2)	–1	C(7)–C(14)	1.399(2) –1
C(8)–C(9)	1.375(2)	–2	C(9)–C(15)	1.398(2) –1
C(10)–C(16)	1.415(1)	–1	C(10)–C(15)*	1.461(2) –1
C(11)–C(12)	1.456(2)	–1	C(11)–C(16)	1.420(2) –1
C(12)–C(17)	1.420(2)	–1	C(13)–C(14)	1.461(2) –1
C(13)–C(17)	1.416(2)	–1	C(14)–C(18)	1.420(2) –1
C(15)–C(18)	1.420(2)	–1	C(16)–C(19)	1.449(2) –1
C(17)–C(20)	1.449(2)	–2	C(18)–C(21)	1.447(1) –2
C(19)–C(20)	1.417(1)	–2	C(19)–C(21)*	1.420(2) –1
C(20)–C(21)	1.419(1)	–1		
BDC				
C(1)–C(2)	1.377(2)	0	C(1)–C(13)	1.412(2) 0
C(2)–C(14)	1.433(2)	–1	C(2)–C(3)*	1.478(2) +1
C(3)–C(4)	1.381(2)	0	C(3)–C(14)	1.431(2) 0
C(4)–C(15)	1.415(2)	0	C(5)–C(6)	1.367(2) 0
C(5)–C(15)	1.425(2)	0	C(6)–C(16)	1.415(2) 0
C(7)–C(8)	1.363(2)	–1	C(7)–C(16)	1.424(2) 0
C(8)–C(17)	1.419(2)	0	C(9)–C(10)	1.366(2) +1
C(9)–C(17)	1.416(2)	0	C(10)–C(18)	1.422(2) 0
C(11)–C(12)	1.362(0)	0	C(11)–C(18)	1.424(2) –1
C(12)–C(13)	1.424(2)	0	C(13)–C(24)	1.414(2) 0
C(14)–C(19)	1.421(2)	0	C(15)–C(20)	1.411(2) 0
C(16)–C(21)	1.417(2)	0	C(17)–C(22)	1.420(2) 0
C(18)–C(23)	1.413(2)	0	C(19)–C(20)	1.424(2) 0
C(19)–C(24)	1.420(2)	–1	C(20)–C(21)	1.428(2) 0
C(21)–C(22)	1.419(2)	0	C(22)–C(23)	1.424(2) 0
C(23)–C(24)	1.428(2)	0		

Molecular Planarity. Both HBC and BDC are found to possess essentially planar molecular frameworks. The average deviation of carbon atoms from the mean plane is 0.02 \AA for HBC and 0.01 \AA for BDC. In both cases, the deviation is insignificant within the accuracy of the experiment. The C–C–C torsion angles in the bay regions for both HBC and BDC are also zero within experimental error. A comparison with other PAH structures^{2c} indicates that one expects neither the strictly pericondensed HBC nor the mixed cata-pericondensed BDC system to be rigorously planar. Each molecule has two or more bay regions in close proximity, a circumstance which uniformly leads to slight but discernible degrees of nonplanarity in all previous examples.^{2e} PAH molecules of this type, with twist or dihedral angles at bay regions less than 5° , were previously classified in a “near-planar” category.^{2e} Near-planar and planar PAH's were then categorized as a single group, distinguished from the more numerous highly nonplanar aromatic systems. In general, planarity, near-planarity, and high degrees of nonplanarity were modeled correctly by MMX calculations.^{2d,e}

As expected, based on these previous investigations, planar MMX structures for both HBC and BDC turn out to be local minima. The global minimum for BDC, located in an extremely flat region of the MMX energy surface, has a dihedral C–C–C twist angle at the central bay region of 15.5° , and the minimized nonplanar structure is 0.97 kcal more stable than the planar form. The global minimized S_6 structure for HBC has twist angles of 14.8° at each of the six bay regions, with a calculated $\Delta\Delta H_f^\circ$ of -3.47 kcal . The $\Delta\Delta H_f^\circ$ estimates are in rough agreement with the molecular mechanics increment in ΔH_f° per bay region/bay region interaction which was previously estimated to be somewhat less than 0.7 kcal . Other available molecular mechanics force fields give similar results.³³ However, all of the semiempirical procedures and the *ab initio*

(33) Unpublished results.

Table 6. Experimental and Calculated Bond Distances^a and Bond Orders

bond	<i>d</i> (X-ray)	<i>p</i> ^P	<i>p</i> ^{HMO}	<i>p</i> ^{SCF}	<i>d</i> (MMX)	<i>d</i> (MNDO)	<i>d</i> (AM1)	<i>d</i> (PM3)	<i>d</i> (STO-3G)
Hexabenzocoronene									
1-2	1.3758 (12/7)	0.5	0.667	0.667	1.393	1.398	1.389	1.387	1.386
3-11	1.3990 (12/5)	0.5	0.613	0.636	1.410	1.417	1.402	1.398	1.391
11-22	1.4583 (6/5)	0.1	0.413	0.329	1.467	1.472	1.451	1.455	1.480
10-16	1.4175 (12/5)	0.4	0.547	0.589	1.422	1.435	1.418	1.411	1.400
16-19	1.4467 (6/2)	0.2	0.488	0.395	1.456	1.466	1.444	1.443	1.476
19-20	1.4173 (6/4)	0.4	0.542	0.583	1.422	1.431	1.415	1.410	1.412
Benzodibenzocoronene									
2-3	1.4790 (2/0)	0.0	0.411	0.287	1.481	1.483	1.460	1.464	1.498
1-2	1.3790 (4/4)	0.7	0.664	0.755	1.391	1.392	1.381	1.377	1.365
2-15	1.4315 (4/1)	0.3	0.512	0.476	1.442	1.455	1.435	1.432	1.446
1-13	1.4135 (4/3)	0.3	0.561	0.507	1.428	1.435	1.419	1.419	1.427
12-13	1.4245 (4/1)	0.3	0.530	0.474	1.436	1.443	1.427	1.427	1.437
13-24	1.4125 (4/3)	0.4	0.529	0.611	1.407	1.418	1.407	1.402	1.391
5-6	1.3645 (4/5)	0.7	0.478	0.806	1.375	1.376	1.368	1.365	1.348
6-16	1.4190 (4/8)	0.3	0.535	0.479	1.434	1.441	1.426	1.425	1.437
7-16	1.4235 (4/1)	0.3	0.540	0.488	1.433	1.441	1.425	1.425	1.437
16-21	1.4150 (4/4)	0.4	0.535	0.617	1.410	1.423	1.409	1.402	1.394
7-8	1.3635 (4/4)	0.7	0.743	0.800	1.377	1.377	1.369	1.365	1.349
8-17	1.4175 (4/4)	0.3	0.538	0.485	1.434	1.441	1.425	1.425	1.435
17-22	1.4200 (2/0)	0.4	0.538	0.615	1.410	1.423	1.409	1.401	1.394
21-22	1.4215 (4/5)	0.3	0.521	0.482	1.432	1.448	1.428	1.427	1.436
20-21	1.4280 (4/0)	0.3	0.526	0.479	1.435	1.450	1.429	1.428	1.437
19-20	1.4215 (4/5)	0.3	0.519	0.481	1.434	1.449	1.429	1.429	1.433
14-19	1.4210 (2/2)	0.4	0.547	0.619	1.416	1.426	1.411	1.404	1.400

^a Distances (*d*) in angstroms.

calculations minimize to strictly planar structures, even using the nonplanar MMX geometries as starting seed geometries.

Bond Lengths. The experimental bond distances for HBC and BDC are listed in Table 5 together with their corrections for thermal motion. Librational corrections using the method of Schomaker and Trueblood³⁴ differ from the uncorrected distances by less than one standard deviation. Bond distances agree with the local molecular symmetry and reflect closely distances expected from Clar's sextet rule.³⁵ In HBC, the range of C-C distances is smaller than for BDC [HBC: min C2-C3 1.373(2) Å, max C10-C15 1.460(2) Å, Δ = 0.087 Å; BDC: min C11-C12 1.362(2) Å, max C2-C3* 1.479(2) Å, Δ = 0.117 Å]. Table 6 contains experimental and calculated bond distances, and the figures given in the table are averages over all independent values assuming *D*_{6h} and *D*_{2h} point group symmetries, respectively. The first value given in parentheses corresponds to the number of symmetry related bonds whose bond lengths have been averaged; the second figure represents the full spread (10⁻³ Å) of the experimental X-ray results over the symmetrized bonds. The bond length standard deviations for the independent bonds are all 0.002 Å or less.

Table 6 also lists Pauling, HMO, and π-SCF bond orders and predicted bond lengths obtained using the MMX, MNDO, AM1, PM3, and *ab initio* STO-3G procedures. Figures 7 and 8 compare the results of these calculations with those obtained from experiment. The statistical parameters for the plots in the figures are summarized in Table 7. A depiction of the correlations between all the theoretical bond parameters is given in Figure 9. As expected, there is a general congruence between calculated bond parameters, especially for the three semiempirical procedures. There does seem to be a consistent and significant difference between HMO and all of the other theoretical methods at bond orders in the vicinity of 0.3, which corresponds to bonds with *d* = 1.42 Å.

The solid line in each plot in Figures 7 and 8 represents the least-squares fit of the plotted data. A perfect correspondence

of theoretical and experimental bond lengths would give rise to corner-to-corner lines in both figures. A deviation from the diagonal line indicates systematic incongruity of theory and experiment. The predicted bond lengths in the Figure 8 bond order plots are the values obtained from the precise bond order correlation equations³⁶ of the experimental bond distances for ethylene (1.337 Å), benzene (1.399 Å), and graphite (1.421 Å). These are given in eqs 1 and 2 for Pauling bond orders (*p*^P)

$$d = 1.462 - 0.126(p^P) \quad (1)$$

$$d = 1.519 - 0.182(p^{HMO/SCF}) \quad (2)$$

and MO bond orders (*p*^{MO}), respectively. The HMO and π-SCF bond orders are equal for this standard set of π systems. Both linear equations have correlation coefficients of unity (five significant figures) and standard errors of estimate less than 0.001 Å.

The best regression of the bond length data is given by the Hückel MO procedure (*R* = 0.972), followed closely by the results using the semiempirical AM1 (0.967) and MNDO (0.964) procedures. Nevertheless, the results in Table 7 confirm the impression engendered by the plots in Figures 7 and 8; in practical terms, all of the theoretical methods correlate with the X-ray data for HBC and BDC within acceptable error limits. However, all of the correlation coefficients are significantly higher than values reported earlier^{2e} for bond order and MMX calculations applied to all previous X-ray data (ca. 0.900). This may be due, in part, to the poor quality of some of the older X-ray data, in contrast to the higher precision in the present data set.

Predictive capabilities and the ability to correlate are, of course, two different measures of the efficacy of theories. The quantum mechanical and molecular mechanics procedures should predict bond lengths directly; an absence of systematic errors in the predictions would be a desirable attribute. In addition, it could be argued that any correlation of bond orders with experimental bond lengths in PAH's should also account

(34) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1968**, *B24*, 63-76.

(35) Clar, E. *Polycyclic Hydrocarbons*; Academic: New York, 1964; Vols. I and II. Clar, E. *The Aromatic Sextet*, J. Wiley: London, 1972.

(36) See ref 2e for discussion.

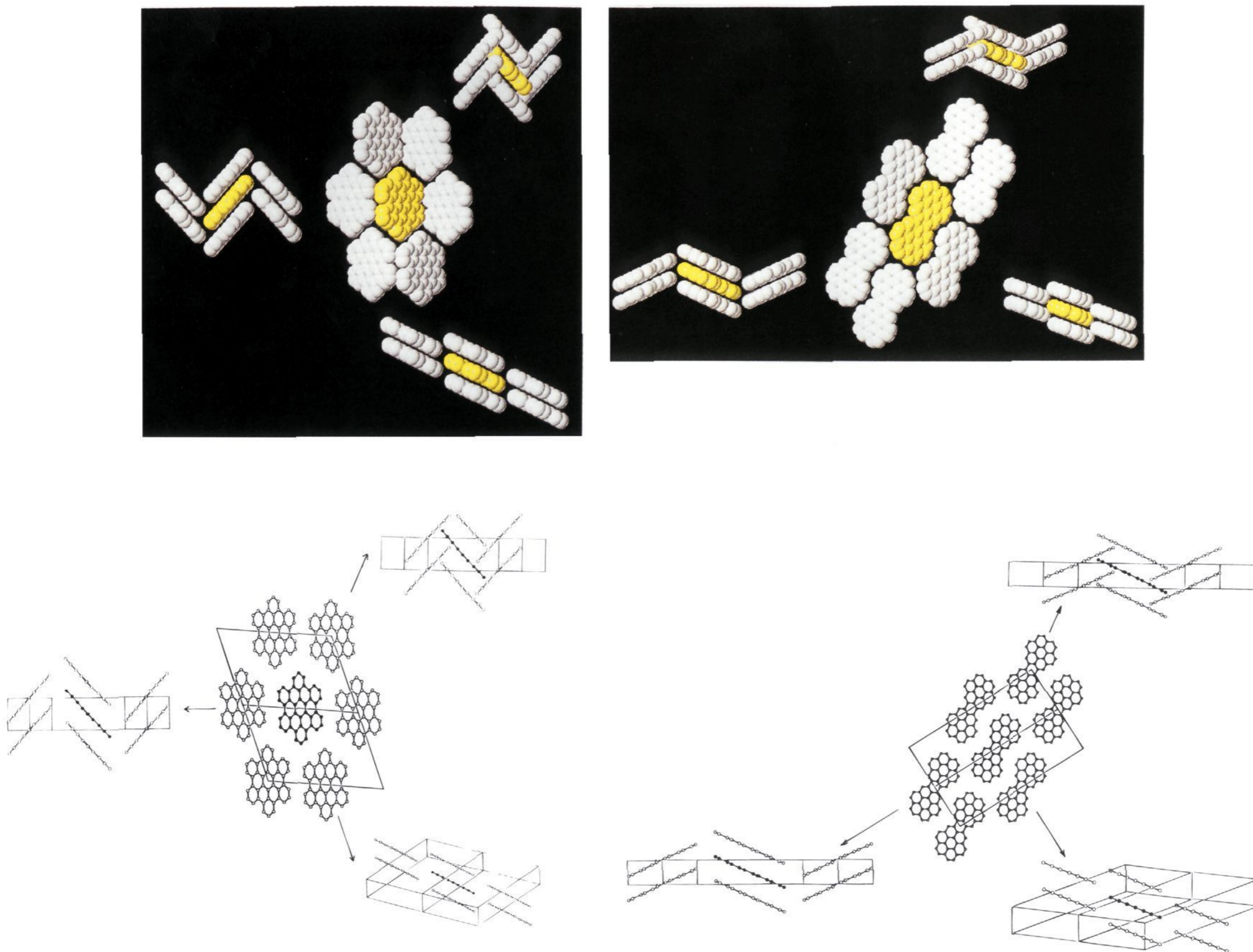


Figure 6. Illustration of the close-packing around one molecule of HBC (left) and BDC (right). In the center of each picture is a view perpendicular to the stacks direction. Each projection shares the central molecule (colored yellow) and two others, giving a total number of nearest neighbors of 14. The arrows denote the directions of the cross sections.

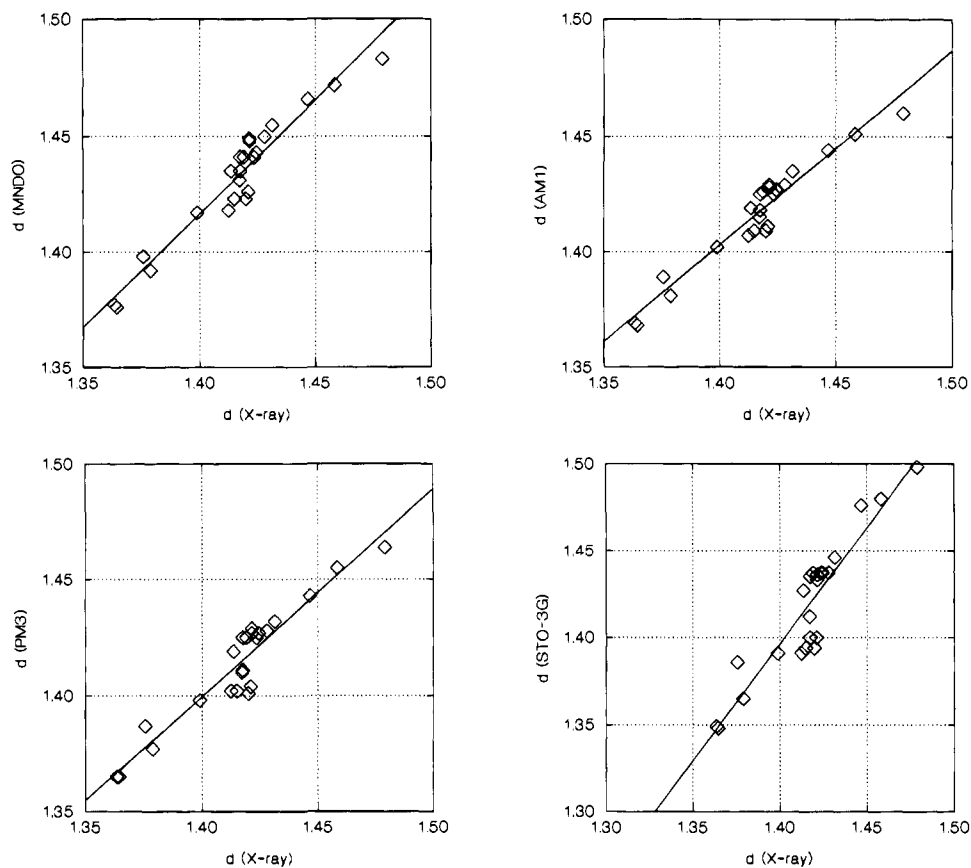


Figure 7. Comparison of agreement between experimental and calculated bond lengths (semiempirical and STO-3G methods).

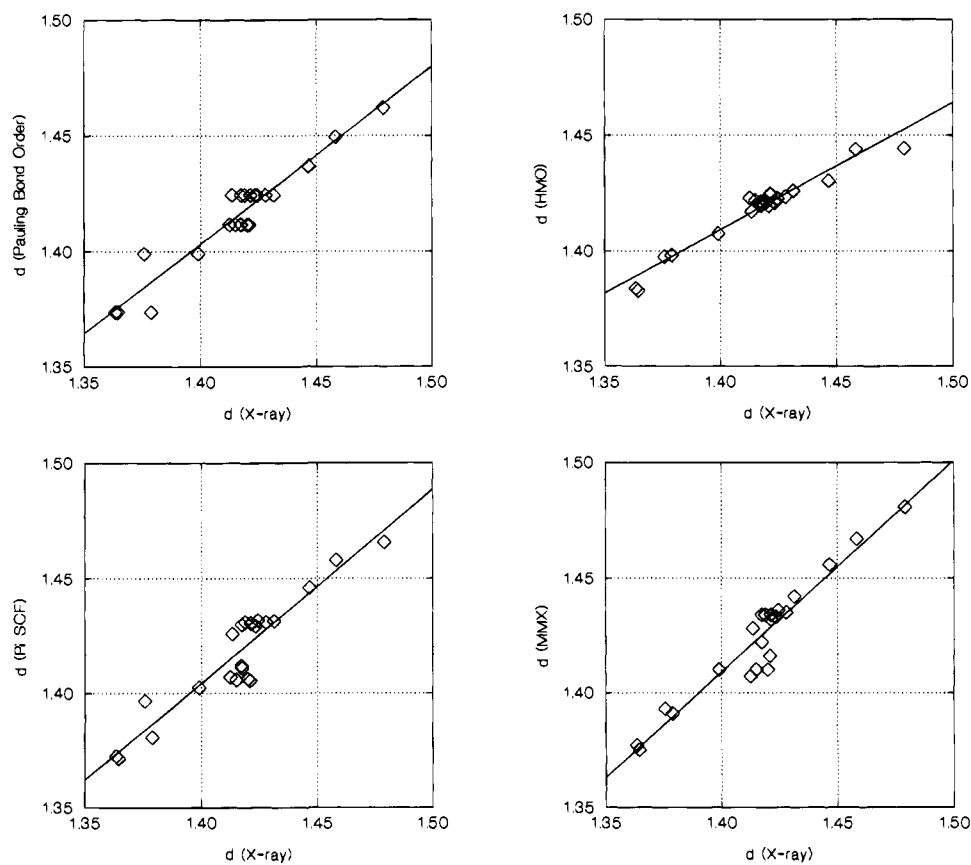


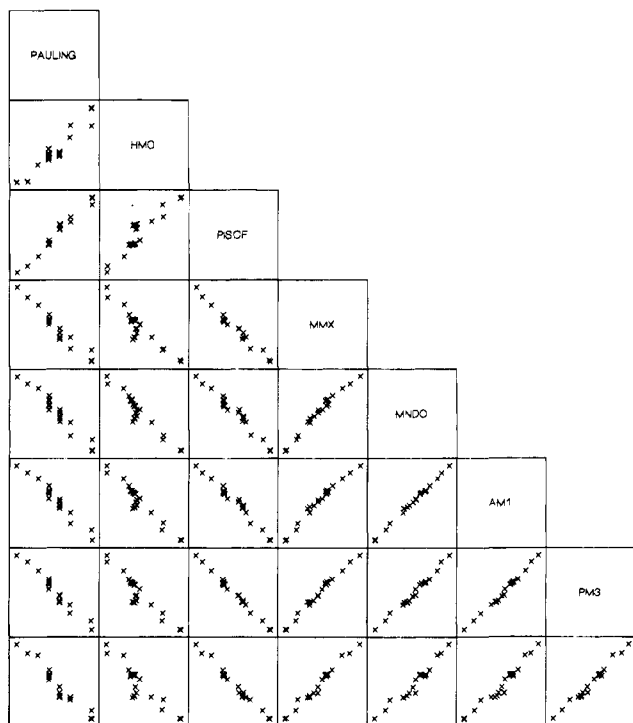
Figure 8. Comparison of agreement between experimental and calculated bond lengths (bond order and MMX methods).

for the observed bond distances in ethylene, benzene, and graphite, where the relationships between bond orders and

distances are unequivocal and known with high accuracy. Using these criteria, the MNDO procedure fails because it systemati-

Table 7. Linear Correlations of Calculated Bond Parameters with Experimental Bond Distances (Å)

bond parameter	intercept	slope	corr coeff	std error
p^P	1.472	-0.151	0.958	0.008
p^{HMO}	1.590	-0.313	0.972	0.007
p^{SCF}	1.520	-0.189	0.936	0.010
$d(\text{MMX})$	-0.007	1.000	0.960	0.008
$d(\text{MNDO})$	0.062	0.946	0.964	0.007
$d(\text{AM1})$	-0.064	1.116	0.967	0.007
$d(\text{PM3})$	-0.012	1.010	0.951	0.009
$d(\text{STO-3G})$	0.508	0.640	0.926	0.010

**Figure 9.** Quantitative depiction of the correlations between all of the theoretical bond parameters: last row, STO-3G.

cally predicts bond lengths for HBC and BDC that are too long by ca. 0.02 Å and the predictive power of the HMO method is unsatisfactory if one requires the inclusion of ethylene and graphite in the data set. The other theoretical procedures are more or less acceptable in their predictive capabilities, with average deviations from experiment ranging between 0.005 and 0.008 Å (Table 7). The PM3 and MMX methods exhibit the least amounts of systematic error.

Heats of Formation. The results of MMX calculations on 153 catacondensed and pericondensed PAH's have been used to parameterize a group additivity (GA) method for $\Delta H_f^\circ(\text{g})$. A precise GA procedure was found^{2d} that partitioned the MMX energy into CH and CC bond terms, destabilizing steric interference parameters, and an algorithmic estimate of stabilizing resonance energy.³⁷ Likewise, experimental $\Delta H_f^\circ(\text{g})$ values are known for nine catacondensed and two pericondensed PAH's, and these $\Delta H_f^\circ(\text{g})$ values have been analyzed to yield a similar GA method, in this case based on experiment.^{2d} Finally, the molecular mechanics procedure and the three semiempirical MO methods all also lead to an empirical predicted $\Delta H_f^\circ(\text{g})$ value.

$\Delta H_f^\circ(\text{g})$ values (in kcal) calculated using the methods listed above, for the molecules under discussion, are as follows: for

HBC, 141.2 (GA_{expl}), 164.6 (MNDO), 177.3 (AM1), 148.5 (PM3), 157.0 (MMX), and 154.6 (GA_{MMX}), and for BDC, 153.8 (GA_{expl}), 175.1 (MNDO), 201.1 (AM1), 175.4 (PM3), 170.0 (MMX), and 170.0 (GA_{MMX}). The MMX values are for the planar local minima geometries, and both of the GA results have been corrected by the term $1 + n/6 - m/3$ (for PAH's with formula C_nH_m) as explained in previous work.^{2d}

The GA_{expl} estimate is the lowest (highest stability) in each case, and the AM1 prediction is consistently the highest. Note the agreement of PM3 with MNDO in the case of BDC and the large disagreement in the two calculations for HBC, which illustrates the inconsistencies in the semiempirical estimates. Although we tentatively reject the AM1 $\Delta H_f^\circ(\text{g})$ estimates (see below), we are reluctant to accept the GA_{expl} values because of the large discrepancies with the results of the molecular mechanics procedure, which, of course, is also highly parameterized with experimental data. The GA_{expl} parameterization is also uncertain due to the restricted number (11) and relatively small sizes of the compounds in the data base used to establish five parameters. We infer that it is not yet possible to predict an experimental $\Delta H_f^\circ(\text{g})$ for a large PAH to better than approximately ± 20 kcal. However, the range of possible $\Delta H_f^\circ(\text{g})$ values is substantially lowered if one discounts the AM1 results. This can be justified since previous work^{2d} has shown that the AM1 method consistently gives large, unpredictable, positive zero errors compared to the known PAH experimental $\Delta H_f^\circ(\text{g})$ values.

Conclusions

In two cases, it has been found that the addition of mesitylene can be useful for the preparation of single crystals of large polycyclic aromatic compounds from pyrene. The added mesitylene prevents cocrystallization of pyrene by reducing its melting point. As a result it has been possible to obtain single crystals of two large planar PAH's (13 and 15 benzene rings) and determine their crystal structures. Both compounds are found to be planar within experimental error even though they contain C_4 bay areas. This would appear to confirm the view that as the PAH's become larger the tendency for bay areas to deviate from planarity becomes less. Interatomic C-C bond distances within HBC and BDC vary significantly, but they are consistent with Clar's sextet rule,³⁵ and indeed, the planarity of bay regions can be attributed to the long C-C distances observed at the central C-C-C-C bond.

A comparison of the packing details of HBC and BDC with those of several other large planar PAH's confirms that the packing of these molecules is largely determined by van der Waals attractive forces, resulting in close-packed structures with individual molecules attaining a coordination number of 14, a condition for close-packing in all three dimensions. An important consequence of this, particularly for these large planar molecules, is that they pack in stacks, which are in turn close-packed. The necessary high coordination numbers for close-packing are attained by the molecules tilting together within the stacks. For rectangular or plank-shaped molecules, the angle of tilt is smaller than for disk-shaped molecules which tilt by around 45°. For disk-shaped molecules such as ovalene, kekulene, HBC, and annulene, this results in a center-to-center offset that is approximately equal to the interplanar distance, ca. 3.4 Å. Of all the large planar PAH's whose crystal structures have been determined, thus far only quaterylene exhibits a sandwich structure.

The X-ray structural data for HBC and BDC comprise the main results of this paper. However, this precise data afforded the opportunity to evaluate several theoretical approaches that

(37) Resonance energies modeled by the log(Kekule structure count) algorithm described in the following: Swinbourne-Sheldrake, R.; Herndon, W. C.; Gutman, I. *Tetrahedron Lett.* **1975**, 755-758. For additional references, see: Herndon, W. C. *Isr. J. Chem.* **1980**, 20, 270-275.

could be used to correlate and analyze the experimental results. We now see that it is certainly feasible to study geometric parameters and other properties of large PAH compounds by a variety of theoretical procedures. However, the work which we have presented demonstrates that no theoretical procedure is consistently better or more useful than the others, at least for the PAH systems considered in this work. Actually, in terms of correlating the experimental bond lengths that are reported here, there seems to have been little change since 1960, the year in which Cruickshank and Sparks³⁸ pointed out that simple resonance theory, i.e., Pauling bond orders, accounted well for the relative and absolute bond lengths in the structures of PAH compounds. The present results support the argument that the Pauling bond order is still a viable, quantitative structural concept.

The results of the $\Delta H_f^\circ(g)$ calculations are somewhat disappointing. We had anticipated finding consistent predicted $\Delta H_f^\circ(g)$ values, which would then support using several of these methods as general tools for calculating thermodynamic properties of PAH's and other aromatic compounds, for example, fullerenes and their derivatives. This is especially important because of the paucity of experimental thermodynamic data for aromatics of any type. However, it is apparent that the $\Delta H_f^\circ(g)$

(38) Cruickshank, D. W. J.; Sparks, R. A. *Proc. R. Soc.* **1960**, A258, 270–285. Also see: Cruickshank, D. W. J. *Tetrahedron* **1962**, 17, 155–161.

(g) results are highly disparate and that additional development and testing are required. Parameters are available to estimate $\Delta H_f^\circ(g)$ values of PAH's by combining *ab initio* STO-3G and 6-31G* total energies with group equivalents, and useful additions to the sparse set of experimental values of ΔH_f° have been obtained.¹⁴ The use of this type of approach to predict $\Delta H_f^\circ(g)$ for HBC and BDC, and for other large PAH's, is under investigation.

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Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, and bond distances and angles for HBC and BDC (11 pages); tables of observed and calculated structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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