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Thermal and Magnetic Properties of Coronene and Related Molecules

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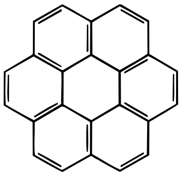
Ab initio calculations of coronene and other benzenoid aromatic hydrocarbons at the SCF, MP2, and density-functional levels are used to estimate the gas-phase $\Delta H_f°$ of coronene. The results obtained show that the best improvement over the SCF $\Delta H_f°$ is obtained using the correlation-corrected B3LYP density-functional method, while the MP2 results appear to make agreement with the experimental value worse. The B3LYP/6-311G** $\Delta H_f°$ of coronene and benzo[*ghi*]perylene are 71.8 and 73.2 kcal/mol. The computed proton and ^{13}C NMR chemical shifts of coronene are in good agreement with experiment. The calculated nucleus-independent chemical shifts (NICS) suggest that the central ring of coronene has diminished aromatic character, but the peripheral rings are fully aromatic. For benzo[*ghi*]perylene, the NICS values reveal that only three of the five peripheral rings are fully aromatic. The magnetic susceptibility of coronene shows a large exhaltation, Λ, relative to a nonaromatic model system. Thermal and magnetic properties show a small additional aromatic character in coronene over and above model systems.

Coronene (**1**), an important polycyclic aromatic hydrocarbon with regard to combustion, materials science, and toxicity, is one of the simplest polycyclic benzenoid hydrocarbons that are representative of a graphitic fragment. Coronene has also been implicated as a source of infrared emission from interstellar matter.[1] A recent gram-scale synthesis of coronene and the related benzo[*ghi*]perylene (**2**) has recently been reported, providing a potential entry into coronene derivatives.[2]



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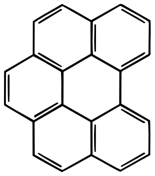

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This paper reports new estimates of the heats of formation of coronene and benzo[*ghi*]perylene based upon ab initio molecular orbital calculations. It also considers their magnetic shieldings and susceptibilities to determine, in part, whether any extra aromatic character, magnetic or thermal, attends the "ring of rings".

Computational Methods

For the thermochemistry, this paper extends our earlier study at the SCF level[3] by use of MP2 and density-functional calculations. MP2 calculations were performed on an IBM 3090 computer using programs written by us. Density-functional calculations were performed with GAUSSIAN 94[4] on DEC Alpha AXP 2100 servers. Vibrational frequencies were computed at the HF 6-31G* level.[5] We use the notation TZpp to identify the TZp polarized triple-ζ basis set of Ahlrichs[6] augmented by a set of p-orbitals on H as a single primitive of exponent 0.8. For C and H the TZp basis is (10s6p1d/5s) contracted to [6s3p1d/3s]. TZpp energies are somewhat lower than those of 6-311G**.

Chemical shifts were calculated by the gauge-invariant atomic orbital (GIAO) method[7,8] at the HF 6-31G* level. Magnetic susceptibilities were computed using the continuous set of gage transformations (CSGT).[9,10]

TABLE 1: SCF Energies (hartrees)

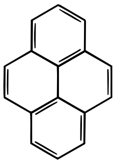
molecule	HF/6-31G*	HF/TZpp	HF/6-311G**
benzene	−230.703 14	−230.772 01	−230.754 10
pyrene	−611.767 96	−611.931 61	−611.886 34
triphenylene	−688.660 25	−688.846 37	−688.795 11
coronene	−915.952 55	−916.187 86	−916.120 73

Heats of Formation

Coronene. In a previous study,[3] we used the ab initio ΔH of the homodesmic reaction (reaction 1) and the experimental

$$3 \text{ pyrene} \rightarrow \text{coronene} + \text{triphenylene} + \text{benzene} \qquad (1)$$

heats of formation of pyrene (**3**), triphenylene (**4**), and benzene (**6**) to obtain the $\Delta H_f°$ of coronene at 298 K. We obtained approximately 70 kcal/mol and suggested that 76.5 kcal/mol is an upper limit to $\Delta H_f°$ of coronene.



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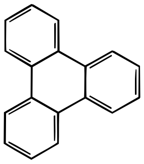

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In the present study we include the effect upon the calculated $\Delta H_f°$ of electron correlation, expansion of the atomic orbital basis set, and inclusion of zero-point energies and thermal contributions to the enthalpy. The correlation energy is assessed by MP2 and density-functional (DFT) calculations. As will be seen, coronene provides a useful test of these methods.

$\Delta H_f°$ of coronene is obtained from the calculated ΔH_r for reaction 1 and the experimental $\Delta H_f°$ of pyrene, triphenylene, and benzene:

$$\Delta H_{f,}{}^{\circ}{}_{\mathbf{1}} = \Delta H_r + 3\Delta H_{f,}{}^{\circ}{}_{\mathbf{3}} - \Delta H_{f,}{}^{\circ}{}_{\mathbf{4}} - \Delta H_{f,}{}^{\circ}{}_{\mathbf{6}} \qquad (2)$$

Ab initio energies of the molecules participating in reaction 1 are given in Tables 1 and 2. The heats of formation of **3**, **4**,

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TABLE 2: MP2 and DFT Energies (hartrees)

molecule	MP2/6-31G*//6-31G*	B3LYP/6-31G*	B3LYP/6-311G**
benzene	−231.456 50	−232.248 65	−232.308 55
pyrene	−613.782 93	−615.773 13	−615.910 48
triphenylene	−690.930 82	−693.181 02	−693.338 03
coronene	−918.979 73	−921.897 91	−922.093 16

TABLE 3: Ab Initio Heats of Reaction 1 and Derived $\Delta H_{\mathrm{f}}{}^{\circ}$ of Coronene (kcal/mol)

method	ΔH_{r} (1)[a]	$\Delta H_{\mathrm{f},}{}^{\circ}{}_{\mathbf{1}}$
HF/6-31G*	−7.1	69.4
HF/TZpp	−6.7	69.8
HF/6-311G**	−6.4	70.1
B3LYP/6-31G*	−4.6	71.9
B3LYP/6-311G**	−4.7	71.8
MP2/6-31G*	−11.0	65.5

[a] Zero-point and thermal corrections of 0.5 kcal/mol are included in ΔH_{r}.

and **6** in the compilation of Pedley et al.[11] are 53.9 ± 0.3, 65.5 ± 1.0, and 19.7 ± 0.2 kcal/mol, respectively. Values of $\Delta H_{\mathrm{f}}{}^{\circ}$ of gaseous coronene at 298 K calculated from eq 2 at the various levels, including zero-point energy and thermal corrections, are displayed in Table 3.

The vibrational frequencies at the HF/6-31G* level, scaled by 0.9153 as recommended by Scott and Radom,[12] were used to obtain zero-point energies. These values (kcal/mol) are: 61.9 (benzene), 127.7 (pyrene), 148.8 (triphenylene), and 172.5 (coronene); they are almost identical to those obtained from an empirical formula[13] for a C_mH_n hydrocarbon. The scaled HF 6-31G* frequencies are also in good agreement with scaled B3LYP cc-pVDZ values reported recently by Martin.[14] The lowest vibrational mode of coronene has a scaled frequency of 88.3 cm^{-1} (e_{2u}) vs the B3LYP value of 88.9 cm^{-1}. For triphenylene, the lowest mode (e″) has a frequency of 50.8 cm^{-1}. Thus, we find no evidence of distortions from D_{3h} symmetry such as those found in the X-ray structures.[15,16] The zero-point energy contribution to the ΔH of reaction 1 is 0.1 kcal/mol. The near cancellation of zero-point energies is expected since the molecularity of reaction 1 is zero.[13]

A thermal correction, $\Delta\Delta H$, of 0.4 kcal/mol from 0 to 298 K is obtained from the vibrational frequencies without scaling, the effect of which is small. Together, the zero-point and thermal corrections to ΔH_{r} of reaction 1 amount to 0.5 kcal/mol. Values of ΔH_{r}, including these corrections, are given in Table 3.

The B3LYP values of ΔH_{r} are algebraically larger by 2.5 and 1.7 kcal/mol than the corresponding SCF values, reflected in the greater calculated $\Delta H_{\mathrm{f}}{}^{\circ}$ of coronene. At the B3LYP/6-311G** level, the $\Delta H_{\mathrm{f}}{}^{\circ}$ of coronene is 71.8 kcal/mol.

In contrast to B3LYP, the MP2/6-31G*//HF/6-31G* value of ΔH_{r}, −11.0 kcal/mol, is algebraically smaller than its SCF counterpart by 3.9 kcal/mol, predicting $\Delta H_{\mathrm{f},}{}^{\circ}{}_{\mathbf{1}}$ to be smaller than the B3LYP values by more than 6 kcal/mol. This appears to indicate a failure of the MP2 method for the ΔH_{r} of reaction 1, reminiscent of its failure for the reaction

$$\text{benzene} + 3\ \text{ethylene} \rightarrow 3\ \text{butadiene} \qquad (3)$$

reported previously.[17] The ΔH_{r} of this reaction, 21.5 kcal/mol, is correctly obtained at the B3LYP/6-31G** level (21.9 kcal/mol).

The present results indicate that $\Delta H_{\mathrm{f}}{}^{\circ}$ of coronene is ca. 71.8 kcal/mol. A slightly higher estimated $\Delta H_{\mathrm{f}}{}^{\circ}$ of coronene, 74.8 kcal/mol, is obtained by the group-equivalent method of Herndon.[18]

TABLE 4: Chemical Shifts in ppm from TMS

nucleus	GIAO/HF/6-31G*	expt[c]
	Coronene	
C_1	122.7	122.5
C_{12a}	127.3	128.65
C_{12b}	124.7	126.08
H	9.2	8.9
NICS(0)[a]	+0.8	
NICS(1)[a]	−4.0	
NICS(0)[b]	−11.3	
	Benzo[*ghi*]perylene	
H_1	9.5	8.8
H_2	8.5	7.9
H_3	8.5	8.0
H_4	8.3	8.0
H_5	8.4	8.0
H_6	8.2	8.7
NICS(0,A)[d]	−12.4	
NICS(1,A)	−14.0	
NICS(0,B)	−6.0	
NICS(1,B)	−8.9	
NICS(0,C)	−13.1	
NICS(1,C)	−14.7	
NICS(0,D)	+2.4	
NICS(1,D)	−2.4	

[a] Central ring. [b] Outer ring. [c] Reference 20 for coronene and 22 for benzo[*ghi*]perylene. [d] The letter following 0 or 1 denotes the ring identified in the text.

An experimental heat of formation of crystalline coronene has recently been published, 152.5 ± 6.9 kJ/mol (36.4 ± 1.6 kcal/mol).[19] For comparison with our results, an accurate value of the standard heat of sublimation of **1** at 298 K is also required. Several measurements of ΔH_{sub} of coronene at a variety of temperatures well above 298 K have been reported, ranging from 128.4 to 151.0 kJ/mol, comparable in magnitude to the heat of formation of the crystal. Their correction to 298 K, requiring knowledge of the molar heat capacity C_{p} of crystalline coronene, remains to be made.

Benzo[*ghi*]perylene. The $\Delta H_{\mathrm{f}}{}^{\circ}$ of benzo[*ghi*]perylene can be estimated by means of the homodesmic reaction

$$\mathbf{2} + \text{pyrene} \rightarrow \text{coronene} + \text{phenanthrene} \qquad (4)$$

The B3LYP/6-311G** ΔH_{r} of this reaction is −5.7 kcal/mol. In conjunction with the calculated $\Delta H_{\mathrm{f},}{}^{\circ}{}_{\mathbf{1}} = 71.8$ kcal/mol and the experimental $\Delta H_{\mathrm{f}}{}^{\circ}$ of pyrene and phenanthrene (49.6 kcal/mol), the $\Delta H_{\mathrm{f}}{}^{\circ}$ of **2** is calculated to be 73.2 kcal/mol. The finding that $\Delta H_{\mathrm{f}}{}^{\circ}$ of **2** exceeds that of coronene by ca. 1 kcal/mol is consistent with our previous SCF study.[3]

NMR Chemical Shifts

Coronene. The ^{13}C and ^{1}H GIAO/HF/6-31G* chemical shifts of coronene, relative to tetramethylsilane (TMS), are given in Table 4, where the outer (hydrogen-bearing), middle, and inner carbons are respectively numbered C_1, C_{12a}, and C_{12b}. The calculated shift for the outer carbon, 122.7 ppm, is in good agreement with the experimental value ($CHCl_3$), 122.5 ppm.[20] The calculated shifts for the middle and inner carbons, 127.3 and 124.7 ppm, respectively, are in reasonable agreement with the experimental values of 128.65 and 126.08 ppm and provide a tentative assignment for these resonances. The calculated proton shielding is 9.2 ppm downfield from TMS, in reasonable agreement with the measured value ($CDCl_3$) of 8.9 ppm.[20]

Schleyer et al.[21] have employed calculated nucleus-independent chemical shifts (NICS) to assess the (magnetically-defined) aromatic character of monocyclic and polycyclic ring systems.

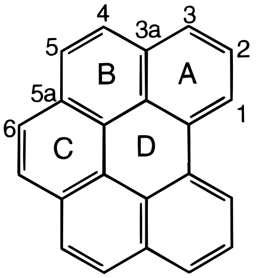
TABLE 5: Calculated Molecular Susceptibilities (ppm cgs)[a]

molecule	χ_{ip}	$\chi_{\perp}$	χ_{iso}	χ_{aniso}
ethylene	−13.2	−22.4	−16.3	5.2
butadiene[b]	−23.8	−40.6	−29.5	9.3
benzene	−30.9	−97.1	−53.0 (−54.8)[c]	33.1
naphthalene	−47.4	−176.0	−90.3 (−91.9)	65.8
phenanthrene	−64.0	−245.1	−124.4 (−127.9)	91.9
pyrene	−70.7	−313.2	−151.5 (−155)	122.7
triphenylene	−80.9	−301.6	−154.5 (−157)	110.4
benzpyrene	−87.4	−369.7	−181.5	141.3
benzo[*ghi*]perylene	−93.9	−423.5	−203.8	165.0
coronene	−100.7	−570.2	−257.2 (−243)	234.7

[a] CSGT values at the B3LYP/6-311G** level. [b] Calculated as the average of *s-cis*-butadiene and *s-trans*-butadiene. [c] Experimental values in parentheses are cited by Dauben et al., refs 23−25.

Aromatic and antiaromatic rings have negative and positive NICS values, respectively. For coronene, we find NICS(0) = +0.8 for the central ring and −11.3 for the outer rings. The outer-ring value is similar to that found for other aromatic rings, e.g. −11.5 for benzene, −11.4 for naphthalene, and −10.8 for the outer rings of triphenylene.[21] The positive NICS(0) value for the central ring of coronene (0.8) is unusual for a benzene ring (cf. −3.0 at the center of triphenylene[21]). The NICS(1) value is −4.0 (test point 1 Å above the center) vs −12.9 for benzene. Thus, the central ring of coronene has substantially diminished aromatic character.

Benzo[*ghi*]perylene. The experimental proton chemical shifts of **2** (CS_2) have been measured by Clar et al. and by Matthews et al.[22] These and the calculated values are given in Table 4. Apart from H_1, all proton shifts are slightly upfield from the coronene proton at δ 8.9. The calculated ^{13}C shifts of **2** range from 119.9 to 130.7 ppm, where the smallest corresponds to C_1 and the largest to C_{3a}. These are in good agreement with the experimental shifts of 6-methylbenzo[*ghi*]perylene,[2] whose ring carbons resonate from 120.4 to 132.2 ppm downfield from TMS ($CDCl_3$).



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Magnetic Susceptibilities

The diamagnetic susceptibilities of coronene and other relevant compounds, calculated with the CSGT method at the B3LYP/6-311G** level, are given in Table 5. Also given are the experimental mean susceptibilities χ_{iso} (often denoted simply as χ) reported by Dauben and co-workers.[23−25] Here, with the molecule in the *xy*-plane, $\chi_{iso} = {}^1/_3\,(\chi_{xx} + \chi_{yy} + \chi_{zz})$, $\chi_{ip} = {}^1/_2(\chi_{xx} + \chi_{yy})$, $\chi_{\perp} = \chi_{zz}$, and $\chi_{aniso} = -{}^1/_2(\chi_{\perp} + \chi_2 - 2\chi_1)$, where χ_1 is numerically the smallest principal element (either χ_{xx} or χ_{yy}) and χ_2 is intermediate in magnitude between $\chi_{\perp}$ and χ_1. In the molecules considered here, χ_1 and χ_2 differ by little, so it is approximately true (exactly so for symmetric tops) that $\chi_{aniso} = -{}^1/_2(\chi_{\perp} - \chi_{ip})$, one-half the difference between the perpendicular and mean in-plane susceptibilities.

TABLE 6: Susceptibility Increments For Forming Benzene Rings, in ppm cgs

sequence	$\Delta\chi_{ip}$	$\Delta\chi_{\perp}$
butadiene → benzene	−7.1	−56.5
phenanthrene → pyrene	−6.7	−68.1
triphenylene → benzpyrene	−6.5	−68.1
benzpyrene → benzo[*ghi*]perylene	−6.5	−53.8
benzo[*ghi*]perylene → coronene	−6.8	−146.7

The magnetic susceptibility exhaltation, Λ, is the difference between χ for the molecule and χ' for a model nonaromatic system.[26] This quantity, more easily obtained experimentally than the individual tensor components, is a useful indicator of aromatic (or antiaromatic) character.[23−25,27]

Λ of coronene can be estimated as the change in the isotropic susceptibility, $\Delta\chi_{iso}$, of reaction 5. For butadiene we use the

$$18\ \text{butadiene} \rightarrow \text{coronene} + 24\ \text{ethylene} \qquad (5)$$

average of the *s-cis* and *s-trans* isomers.[28] The values in Table 5 give $\Delta\chi_{iso} = -117$ ppm cgs, which is similar to Λ estimated by Dauben et al., −103 ppm.[23,24] An appreciable negative value is expected for a large aromatic system. The major part, −126 ppm, arises from the elements $\chi_{\perp}$.

On the Superaromatic Character of Coronene

The present magnetic and thermochemical data allow comment on the question of enhanced aromatic character in coronene.

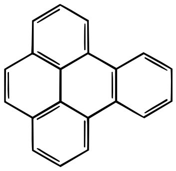
We consider first the magnetic data. As pointed out long ago by Clar,[29] the chemical shift of the protons of coronene, δ 8.9, is downfield from those of polycyclic aromatic hydrogens (PAHs) such as **2**, devoid of extra cyclic character. Ring−current effects in coronene have been described by Clar as the "rotation of electronic sextets". The NICS(0) values of 0.8 and 2.4 show the central rings of coronene and benzo[*ghi*]perylene (ring D) to be slightly aromatic, at most. Thus, any extra magnetic effects must be sought in its cycle of rings, relative to suitable "acyclic" models.

The NICS(0) values at the centroids of the peripheral rings of coronene are −11.3, indicating full aromatic character. In benzo[*ghi*]perylene rings, A and C are fully aromatic, −12.4 and −13.1, but ring B (−6.0) is less so. The NICS values in the periphery of **2** are similar to those of phenanthrene.[21]

The magnetic susceptibilities, χ, given in Table 5, are also revealing. For sequences of PAHs differing by one C_2 fragment, addition of each new benzene ring leads to a nearly constant change in the in-plane components, χ_{ip}, from −7 to −8 ppm, Table 6. The change in the perpendicular component $\Delta\chi_{\perp}$ ranges from −54 to −68, except for **2** → **1**, where the change is −147.

These effects can also be examined by means of homodesmic reactions involving the exchange of C_2 fragments. Reaction 6

$$2\ \text{benzo}[ghi]\text{perylene} \rightarrow \text{coronene} + \text{benzpyrene}\ (\mathbf{5}) \qquad (6)$$



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has $\Delta\chi_{ip} = -0.3$ ppm cgs and $\Delta\chi_{\perp} = -92.9$ ppm. $\Delta\chi_{iso} = -31.1$ ppm. Similar results are found for reaction 4 where $\Delta\chi_{iso} = -26.3$ ppm.

With regard to thermochemistry, we note that ΔH_r of homodesmic reactions among aromatic species producing coronene as a product are generally small but negative. For example, the B3LYP/6-311G** ΔH_r of reactions 1, 6, and 7 are −4.7,

$$6 \text{ phenanthrene} \rightarrow \mathbf{1} + 6 \text{ naphthalene} \qquad (7)$$

−4.0, and −14.7 kcal/mol, respectively. Thus, coronene has an additional thermal stability.

By both magnetic and thermochemical criteria, coronene has a discernible enhancement of aromatic character.

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