Bowl Stacking in Curved Polynuclear Aromatic Hydrocarbons: Crystal and Molecular Structure of Cyclopentacorannulene

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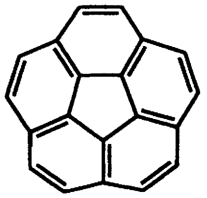
Cyclopentacorannulene (dibenzo[*ghi,mno*]cyclopenta[*cd*]fluoranthene) exhibits long-range concave–convex bowl stacking in the crystal; its molecular structure is satisfactorily described by *ab initio* calculations at both HF/3-21G and HF/6-31G* levels.

The discovery of the fullerenes[1] has prompted a general interest in bowl-shaped aromatic hydrocarbons whose carbon frameworks are represented on the buckminsterfullerene surface. The first known and simplest example is corannulene[2] ($C_{20}H_{10}$, **1**) whose carbon framework represents the polar cap of buckminsterfullerene. Of course an exciting feature of curved hydrocarbons is their bowl shape, and this leads to the interesting question about their potential for complexation in a convex/concave relationship. This latter type of stacking might be expected for the minimum energy arrangement of two bowl-shaped molecules since it maximizes attractive van der Waals interactions. Moreover, in addition to the interaction of two bowl-shaped compounds, such a relationship could also occur between bowl-shaped hydrocarbons and spherical molecules of roughly the same curvature: *e.g.* buckminsterfullerene or other fullerenes.

Bowl-shaped corannulene undergoes rapid bowl-to-bowl inversion in solution,[3] and X-ray analysis shows[4] several different relative orientations of two molecules of **1** with very little bowl stacking.† Thus, even though such concave–convex interactions have been observed in the gas phase between corannulene and the corannulene radical cation **2**, and between corannulene and buckminsterfullerene radical cation **3**,[5] there has been no evidence to suggest the importance of such relationships in either solution or in the solid state.

In contrast to corannulene itself, cyclopentacorannulenes **4** and **5** are presumed to be 'locked' into the bowl shape, at least on the NMR timescale, since the *endo* and *exo* benzylic protons of **4** remain distinct, even at elevated temperatures.[6] We now provide molecular and crystal structure data for cyclopentacorannulene **5** showing that the additional five-membered ring not only generates considerably more curvature, but also leads to 'bowl stacking' in the crystal, an arrangement absent in corannulene itself.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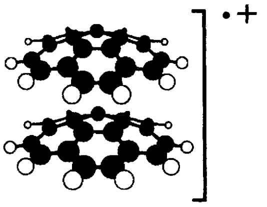
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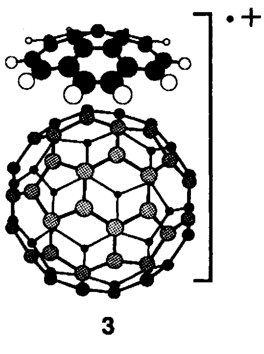
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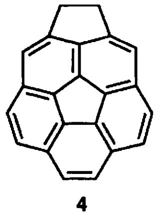
Slow crystallization of **5** from diethyl ether solution provided orange platelets which were subjected to X-ray crystallographic analysis‡ revealing a remarkable crystal packing pattern (Fig. 1) in which the bowl-shaped molecules are positioned to a high degree in a concave to convex orientation exhibiting long-range stacking. The X-ray data show 24 intermolecular C···C distances shorter than 3.8 Å, approximately the sum of the van der Waals radii, for every two stacked molecules in the crystal. In accord with predictions based on semiempirical calculations,[6] the region of the surface in **5** that is in closest proximity to the extra bridge is slightly more curved than in corannulene itself. The average distances of the rim carbon atoms from the best plane defined by the five hub carbon atoms C(10b)–C(10f) are 1.18, 1.19, 1.03, 0.97 and 0.90 Å for C(9a), C(10), C(1), C(2) and C(3), respectively, while the analogous distance in **1** is found to be 0.89 Å.[4]

Since **5** represents only the second curved polynuclear aromatic known for which crystal structure data exists, it was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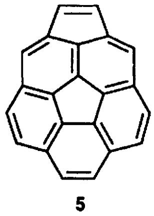
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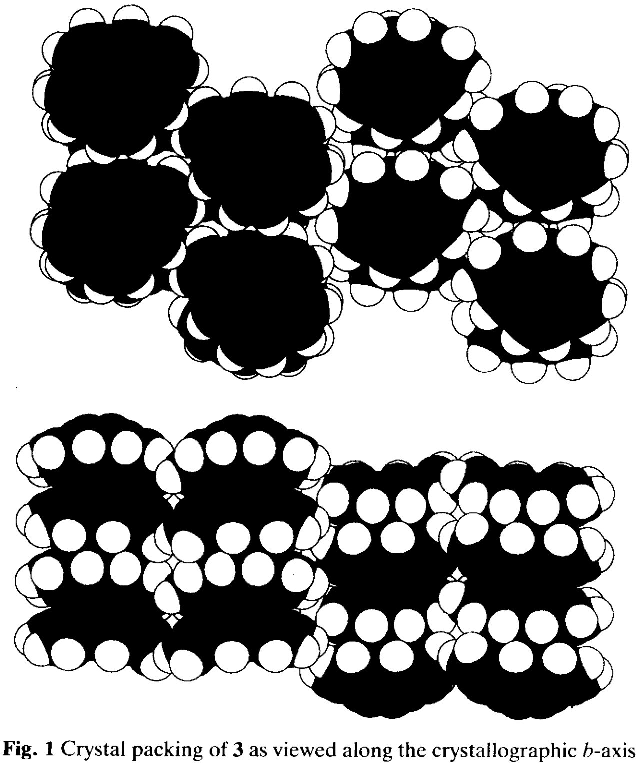
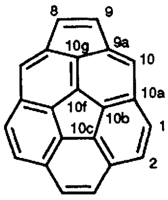


Fig. 1 Crystal packing of **3** as viewed along the crystallographic *b*-axis (upper) and *a*-axis (lower)

Table 1 Comparison of experimental bond lengths (Å)[a] with *ab initio* results



	X-Ray	3-21G	6-31G*
C(1)–C(2)	1.372	1.367	1.369
C(1)–C(10a)	1.436	1.448	1.448
C(2)–C(2a)	1.431	1.446	1.447
C(2a)–C(3)	1.451	1.451	1.452
C(2a)–C(10c)	1.370	1.361	1.363
C(3)–C(4)	1.368	1.362	1.364
C(6a)–C(7)	1.451	1.464	1.464
C(6a)–C(10e)	1.383	1.371	1.373
C(7)–C(7a)	1.374	1.367	1.371
C(7a)–C(8)	1.467	1.503	1.493
C(7a)–C(10g)	1.419	1.425	1.423
C(8)–C(9)	1.388	1.344	1.344
C(10b)–C(10c)	1.417	1.423	1.420
C(10b)–C(10f)	1.412	1.416	1.410
C(10c)–C(10d)	1.432	1.430	1.427
C(10f)–C(10g)	1.344	1.335	1.337

[a] An arithmetic mean value given for bonds that are equivalent under assumed C_s molecular symmetry. The experimental standard deviations for individual distances are 0.004–0.005 Å.

of interest to see how well theoretical methods handle these compounds in what is expected to be an important new series. Table 1 presents C–C bond lengths in the crystal together with *ab initio* values calculated at the HF/3-21G and HF/6-31G* levels.[7] Agreement between experiment and theory is generally good with rms deviations of 0.017 and 0.015 Å for 3-21G and 6-31G*, respectively. The only notable differences are found for the C(7a)–C(8) and C(8)–C(9) bonds in the external five-membered ring: the former is calculated as too long and the latter as too short by *ca.* 0.03 and 0.04 Å, respectively. This discrepancy is presumably not due to a deficiency of the basis set used since improvement from 3-21G to 6-31G* shortens the C(7a)–C(8) bond only slightly with the C(8)–C(9) bond unchanged. Similarly, post-HF electron correlation effects on the semiempirical PM3 level[8] geometry showed virtually no bond length dependence despite the order of CI used. However, the crystal structure determination of **1** showed that differences in bond lengths, which are identical by symmetry in the isolated molecule, can reach as much as 0.05 Å due to experimental error and/or crystal packing effects.[4] With this in mind, it appears that the performance of the *ab initio* method is indeed satisfactory.

The depth of the bowl of **5** is also well described by theory. The calculated distances of the rim carbon atoms C(9), C(9a), C(10), C(1), C(2) and C(3) from the plane of the central five-membered ring are 2.08, 1.24, 1.24, 1.04, 0.96 and 0.89 Å at the 3-21G level, and 2.00, 1.19, 1.19, 1.00, 0.93, 0.85 at the 6-31G* level, respectively, in excellent agreement with the crystal data.§

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Footnotes

† One of these orientations somewhat resembles concave–convex stacking, but it contains only eight intermolecular C···C distances shorter than 3.8 Å. Moreover, this stacking is limited to an interaction within a given pair of molecules; *i.e.* no long-range stacking is observed.

‡ *Crystal data*: $C_{22}H_{10}$, $M = 274.32$, orthorhombic, space group *Pbca*, $a = 9.441(2)$, $b = 7.593(2)$, $c = 36.081(5)$ Å, $V = 2587(2)$ Å^3, $Z = 8$; $D_c = 1.409$ g cm^{-3}, $F(000) = 1136$, $T = 296$ K, $R = 0.055$, $R^1 = 0.068$ for 1807 observed data having $2 < \theta < 75°$ and $I > 3\sigma(I)$. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Cu-Kα radiation ($\lambda = 1.54184$ Å) and a graphite monochromator. Hydrogen atoms were placed in calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ It should be noted that an interesting class of cup-shaped compounds known as tribenzotriquinacenes also show stacking, although in this case hydrogen or alkyl groups at the vertex of three fused, five-membered rings prevent close packing of the aromatic rings.[9]

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