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1,2,5,6-Tetraketopyracene: Synthesis, and Structure by Ab Initio Calculation and X-Ray Analysis

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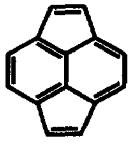
Abstract: *The title compound is conveniently synthesized from the known 1,2-diketopyracene via NBS bromination followed by reaction with silver nitrate in acetonitrile, and treatment with sodium acetate trihydrate in DMSO. Its structure determined by semiempirical PM3 and ab initio calculations is in excellent agreement with the x-ray analysis, and suggests that the bond alternation observed in pyracylene and related compounds is probably not due to antiaromaticity.*

Although there was an interest in the electronic properties of pyracylene (**1**),[1] its synthesis remained elusive until reported by Trost and Bright in 1967.[2] A year earlier, Trost had reported the synthesis of pyracyloquinone (**2**),[3] and remarked that naphthalene derivatives in which both sets of peri positions are bridged by sp^2 carbons were generally unknown. Indeed, such compounds have been difficult to synthesize, and have also proved difficult to handle due to enhanced reactivity at the unsaturated, bridging positions. More recently, pyracylene has received attention as an important unit of the buckminsterfullerene structure that explains some of the chemistry of C_{60}.[4]



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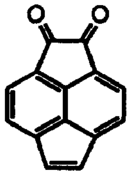

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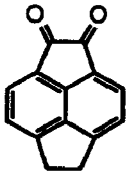

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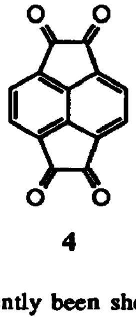

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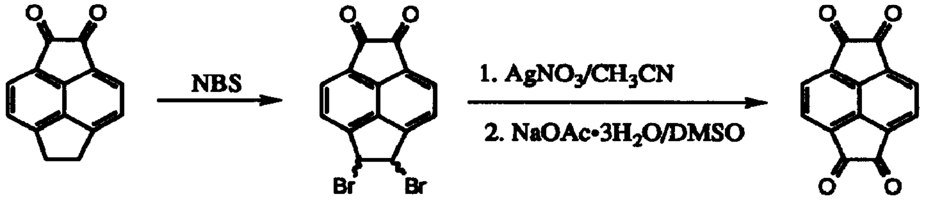
Compounds containing the acenaphthenequinone moiety have recently been shown to be important synthetic intermediates since they can be converted to 7,10-bis(dihalovinyl)fluoranthenes which undergo flash vacuum pyrolysis to produce corannulenes.[5] Corannulene itself, whose carbon framework represents the polar cap of buckminsterfullerene, has been prepared from acenaphthenequinone in this way.[5] Although it is considerably curved, corannulene undergoes rapid bowl-to-bowl inversion; however, ethanocorannulene–prepared in an analogous manner, but beginning with **3**–is "locked" into a bowl conformation, at least on the NMR time scale.[6] Hence our general interest in the structure of pyracylene related compounds, coupled with their potential as intermediates in the synthesis of polynuclear aromatics whose carbon frameworks are represented on the C_{60} surface, led us to undertake the synthesis of 1,2,5,6-tetraketopyracene (4).

All of our initial attempts to prepare 4 failed. Oxidation of 3 with dichromate cleaves the diketo function resulting in the formation of an anhydride. Similarly, the reaction of 2 with typical double bond reagents like epoxidation, halohydrin formation followed by oxidation, chromyl chloride oxidation and osmium dihydroxylation were all unsuccessful. However, we finally learned that the dibromo derivative 5 could be converted to 4, generally in yields of 55-70%, by treatment with silver nitrate and sodium acetate. The typical procedure is as follows: A solution of silver nitrate (1.3 g, 8.8 mmol) in 25 mL of acetonitrile was added to a solution of 5[3,7] (1.1 g, 3 mmol) in 70 mL of acetonitrile, containing a drop of water, at reflux. Stirring at reflux was continued for 1 hr followed by filtration and evaporation of the solvent under reduced pressure to afford the crude nitrate ester in 72-85% yield.[8] The ester (0.7 g, 2.2 mol) was then dissolved in 20 mL of DMSO, sodium acetate trihydrate (60 mg, 0.4 mmol) was added, and the mixture was stirred for 1 hr at room temperature. It was then poured into 200 mL of brine; the precipitate was separated, washed thoroughly with water, and dried in vacuo (420 mg, 80%).[9]



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The ultimate structure proof for 4 came from the x-ray diffraction study. Orange crystals were obtained by recrystallization of the product from DMF. It turned out, however, that solvent molecules are incorporated into

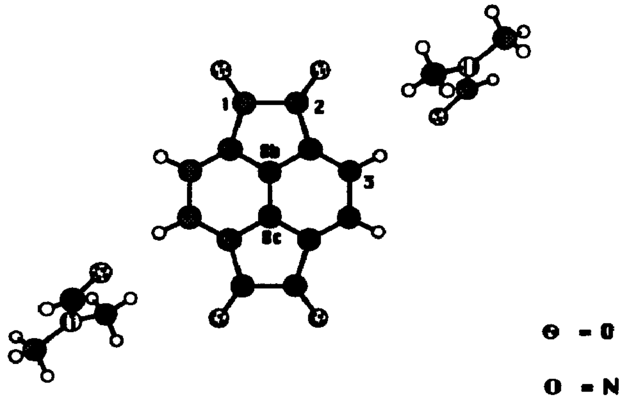

Figure 1: X-ray Crystal Structure of 4·2DMF.

the crystal, and being only weakly bound, they desorb slowly at room temperature, destroying the crystal. The decomposition does not take place at low temperature, however, and so an orange plate (0.88 x 0.62 x 0.01 mm) was subjected to x-ray diffraction analysis at 115 K.[10] It revealed two DMF molecules associated with each molecule of 4. There is some disorder in the crystal–two different orientations of the solvent molecules were found with populations of 85 and 15%. The molecule of 4 lies on the crystallographic inversion center; it is slightly distorted from the highest possible D_{2h} symmetry to C_i. The distortion results in slight nonplanarity of the molecular skeleton, with the largest deviations from the least-square plane of 0.057 Å for the carbonyl oxygen atoms at C(1) and C(5) and -0.059 Å for the oxygen atoms at C(2) and C(6). The deviations of the carbon atoms do not exceed 0.04 Å. This slight distortion from planarity may safely be attributed to crystal packing forces, especially if one considers the presence of the solvent molecules in the crystal. The theoretical calculations performed at semiempirical PM3[11] and ab initio 3-21G levels[12] both predict the D_{2h} structure to represent the minimum energy conformation of isolated 4.[13]

Despite the effects of the crystal field, the agreement between the bond lengths and angles determined for 4 in the crystal and the calculated parameters by both theoretical methods is very good (Table 1), with rms deviations of 0.005 (PM3) or 0.006 Å (ab initio) for bond lengths and 0.6 (PM3) or 0.4° (ab initio) for the bond angles. These deviations are actually within the range of the standard error of the x-ray experiment.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) in 4 as Found in the Crystal, and as Calculated by PM3 and ab initio Methods.

bond	x-ray[a]	PM3	ab initio	bond angle	x-ray[a]	PM3	ab initio
C(1) - C(2)	1.579	1.581	1.580	C(1)-C(2)-C(2a)	106.0	106.4	105.8
C(2) - C(2a)	1.501	1.497	1.492	C(1)-C(8a)-C(8b)	104.4	104.9	105.4
C(2a) - C(3)	1.376	1.373	1.365	C(2a)-C(3)-C4)	119.8	120.7	120.0
C(2a) - C(8b)	1.395	1.418	1.397	C(2a)-C(8b)-C(8a)	119.2	117.4	117.7
C(3) - C(4)	1.433	1.438	1.434	C(2a)-C(8b)-C(8c)	120.5	121.3	121.2
C(8b) - C(8c)	1.385	1.367	1.353	C(3)-C(2a)-C(8b)	120.1	118.0	118.8
C(1) - O(1)	1.206	1.203	1.201	O(1)-C(1)-C(2)	124.0	125.9	124.3

[a] The molecular parameters given in this table were obtained as arithmetic means of experimental values which are equivalent under assumed D_{2h} molecular symmetry. The differences in the parameters averaged with the above assumption do not exceed 0.007 Å and 1.3° for bond lengths and angles, respectively, with the experimental standard deviations of 0.004 - 0.005 Å and 0.3°.

Comparison of the crystal structure of 4 with acenaphthenequinone (6)[14] reveals significant similarity. The only visible effect of the additional strain introduced by the additional five-membered ring in 4 is the elongation of the C(1)–C(2) bond (1.579 Å) as compared to 1.53 Å in 6. Otherwise, the bond lengths in 6 differ from the analogous bonds in 4 by less than 0.02 Å.

Like 1 and 2, 4 may be considered as an example of a system with a slightly perturbed antiaromatic periphery.[1] The results of early work by Trost and coworkers suggested a significant degree of antiaromaticity in both 1 and 2.[1,7a,15] It was believed that the central aromatic double bond perturbs the periphery only very slightly, and that steric constraints reduce the ability of the molecule to relieve unfavorable electronic interactions by bond alternation.[1] However, a recent x-ray structure determination of 1 found a quite pronounced bond length alternation in the periphery,[16] and we observe a very similar pattern of bond alternation in 4. In fact, the bond lengths in the periphery of 4 differ by less than 0.01 Å from the analogous bonds in 1, with the obvious exception of the C(1)–C(2) bond. As mentioned above, a similar pattern is found for the periphery of 6 which does not contain a 12-electron peripheral system. Thus it seems safe to conclude that the bond alternation patterns in pyracylene and related systems are not necessarily related to any antiaromaticity that exists in the periphery. Instead, the geometry of the periphery seems to be governed by the properties of the naphthalenic unit perturbed by the strain introduced by the bridging of the peri positions.

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8. These are typical yields; we have carried out the reaction numerous times with occasional problems in reproducibility that we do not yet fully understand.
9. (a) ^{1}H NMR (400.13 MHz, DMSO-d_6) 8.29 (s, 4H); ^{13}C NMR (100.61 MHz, DMSO-d_6) 122.8, 131.7, 141.8, 185.4; The residual DMSO bands were used as reference (2.49 and 39.5 ppm for ^{1}H and ^{13}C NMR, respectively). (b) The tetraketone gradually decomposes in a sealed capillary, but does not melt below 375 °C. (c) High resolution mass spec. Calcd for $C_{14}H_4O_4$: 236.0110. Found: 236.0102.
10. Empirical formula $C_{20}H_{18}N_2O_6$ (4·2DMF); monoclinic, space group C2/c, a = 19.963(9) Å, b = 6.139(2) Å, c = 14.316 (7) Å, $\beta = 94.85(4)^\circ$, V = 1763(9) Å^3, Z = 4, $D_c = 1.426$ g cm^{-3}, Mo K_α radiation, T = 115 K, R = 0.055, Rw = 0.057 for 1045 observed data having $1 < \Theta < 25^\circ$ and $I > 3\sigma(I)$. Detailed X-ray crystallographic data are available from Cambridge Crystallographic Data Centre.
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