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The Structure of 9,10-Dihydro-9,10-bis(hydroxymethyl)-9,10-ethanoanthracene-11,12-anhydride

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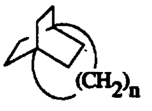
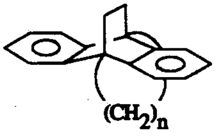
Abstract: The title compound, prepared as an intermediate in the synthesis of dibenzo[2.2.2.n]paddlanes, exhibits rapid conformational interconversion on the NMR timescale. The X-ray structure is reported and compared to molecular mechanics calculations. The results imply significant steric crowding in the title compound.

Since the publication twenty years ago of work[1,2,3] drawing attention to the unusual structural properties of paddlanes, these compounds, particularly the [2.2.2.n]paddlanes (1), have provided challenging synthetic targets. The [2.2.2.n]paddlanes, where n is small (6-12), are of special interest because of the distortion of the bridgehead carbon atoms toward pyramidal and square-planar geometries.[4,5,6]



1



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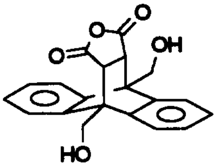
In pursuing the synthesis of dibenzo analogues of the [2.2.2.n]paddlanes (2), we have prepared 9,10-dihydro-9,10-bis(hydroxymethyl)-9,10-ethanoanthracene-11,12-anhydride (3) as a synthetic intermediate.[7] The variety of possible conformations for 3 involving rotation about the two bridgehead carbon to hydroxymethyl carbon bonds, the possibility of intramolecular hydrogen bonding in some of these conformations and the potential for restricted rotation, motivated us to examine the structure of 3. Of course, rotational barriers for 3 that are purely steric in origin would be expected to be significantly lower than the observed 15 kcal mol^{-1} barrier for 4.[8]



3

4

Molecular mechanics calculations[9] on the six staggered conformations (excluding enantiomeric conformations) of **3** gave the results listed in Table 1. There are three staggered positions possible for the OH of each hydroxymethyl group, these being (1) between the two phenyl rings; (2) between phenyl and hydrogen; and (3) between phenyl and anhydride. In position 3, the possibility of hydrogen bond formation between the hydroxyl groups and the anhydride carbonyls must also be considered. The heats of formation of the conformers ranged from -151.24 to -159.05 kcal mol^{-1}, a range of approximately 7.8 kcal mol^{-1}, with the ordering of the conformers (low energy to high energy) being: 2,2 < 1,2 < 1,1 < 2,3 < 1,3 < 3,3. When the OH of one of the hydroxymethyl substituents was fixed in an eclipsed position relative to one of the phenyl rings, the minimized heat of formation rose to -145.69 kcal mol^{-1}, an average increase of 12.6 kcal mol^{-1} depending on the starting conformation, which we take as a first approximation for the rotational barrier of the hydroxymethyl group in this molecule. The X-ray coordinates (*vide infra*) were also minimized, giving results identical to those obtained for the 1,2 conformer.

Table 1. Molecular Mechanics Data for the Conformers of **3**.

Conformer	Heat of Formation (kcal mol^{-1})	Strain Energy	Dipole Moment	Steric Energy (kcal mol^{-1})
1,1	-157.37	1.79	1.84	38.67
2,2	-159.05	1.63	2.98	36.99
3,3	-151.24	2.12	5.56	44.80
1,2	-158.43	1.67	1.51	37.60
1,3	-154.74	1.94	3.20	41.31
2,3	-155.70	1.85	3.82	40.37
Eclipsed	-145.69	2.61	1.51	50.24

The room-temperature ^{1}H NMR for **3** (100 MHz, d_6-DMSO) is relatively simple and is consistent with rapid interconversion of conformers. The aromatic protons appear as two multiplets (7.65 ppm, 2H and 7.27 ppm, 6H), the OH protons as a broad singlet at 5.49 ppm (identified by D_2O exchange), the anhydride ring protons as a singlet at 3.81 ppm, and the methylene protons as a broadened singlet (an unresolved AB quartet) at 4.86 ppm. At -85°C (300 MHz, d_6-acetone) the separation of the doublets of the AB quartet is increased by ca. 0.15 ppm and selective broadening is observable.

X-ray crystallographic analysis of **3** afforded the structure shown in Figure 1.[10] A comparison of the crystal structure data and molecular modeling results is presented in Table 2, but we will note here that an intermolecular distance of 1.83Å between carbonyl oxygen and hydroxyl hydrogen was also found and is suggestive of an intermolecular hydrogen bond. Trotter and Wireko[11] recently obtained the structure of 9,10-dihydro-9,10-ethenoanthracene (dibenzobarrelene, **5**) while earlier Oliver, Fallon, and Smith[12] reported the structure of 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarbonitrile (**6**) and the structure of 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**7**) was reported by Czugler, Weber, and Ahrendt.[13] Selected comparisons of **3** and all of these compounds appear in Table 3.

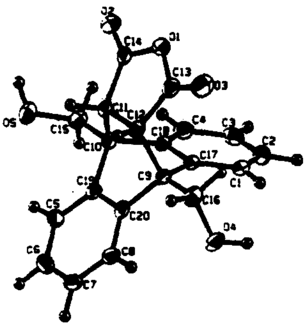


Figure 1. ORTEP drawing of the crystal structure for compound 3.

In conclusion, the title compound exhibits rapid conformational interconversion on the NMR timescale at room temperature, a result that is consistent with the rotational barrier estimated from molecular mechanics calculations. Those calculations also suggest that the conformers for which intramolecular hydrogen bonding is possible are the least important and that the three lowest energy conformers occur within a range of ΔH_f of less than 1.5 kcal mol^{-1}. NMR chemical shift changes observed at low temperature are consistent with a temperature-dependent distribution of molecules amongst two or more conformational states. The X-ray crystal structure does not correspond to either conformer capable of intramolecular hydrogen bonding, nor to the global minimum conformer located by molecular mechanics procedures. The propensity of this compound to form intermolecular hydrogen bonds in the solid state may explain this latter result. Finally, a general lengthening of bridgehead bonds in 3 compared to 7, along with the beginnings of selective broadening in the low temperature NMR spectra, does reflect significant steric crowding for 3.

Table 2. Comparison of X-ray data and molecular modeling results for selected bonds in 3.

Bond Angles (degrees)		
Atoms	Calculated	Measured
C9 - C12 - C11	111.21	110.7(3)
C9 - C12 - C13	115.36	113.7(3)
C11 - C12 - C13	103.77	104.3(3)
C12 - C9 - C17	104.71	105.3(3)
C12 - C9 - C20	103.93	103.5(3)
C16 - C9 - C17	114.75	116.0(3)
C16 - C9 - C20	114.08	115.4(3)
C11 - C10 - C18	105.98	106.6(3)
C11 - C10 - C19	104.94	103.9(3)
C15 - C10 - C18	114.33	113.8(3)

Dihedral (Torsional) Angles (degrees)		
Atoms	Calculated	Measured
O4-C16-C9-C12	177.74	175.6(3)
O4-C16-C9-C20	59.58	59.9(4)
O4-C16-C9-C17	-62.60	-66.1(4)
O5-C15-C10-C11	-53.17	-54.1(4)
O5-C15-C10-C19	66.60	63.5(4)
O5-C15-C10-C18	-174.10	-174.9(3)

Bond Distances (Å)		
Atoms	Calculated	Measured
C9 - C12	1.548	1.581(5)
C10 - C11	1.553	1.565(5)

Table 3. Selected comparisons between the X-ray structure of compound **3** and similar structures reported by other workers.

Atoms	Cmpd 3	Cmpd 5	Cmpd 6	Atoms	Cmpd 3	Cmpd 7
		(degrees)			(Å)	(mean bond lengths, Å)
C12 - C9 - C17	105.3	105.6	104.9	C9 - C12	1.581	1.559(8)
C12 - C9 - C20	103.5	105.9	104.9	C10 - C11	1.565	1.559(8)
C11 - C10 - C18	106.6	106.1	104.3	C9 - C20	1.516	1.506(2)
C11 - C10 - C19	103.9	106.0	105.3	C9 - C17	1.529	1.506(2)

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7. Compound **3** was prepared from 9,10-bis(chloromethyl)anthracene using first the two-step procedure of Miller, Roger, and Tawney (*J. Am. Chem. Soc.*, **1955**, *77*, **2845**) to generate 9,10-anthracenedimethanol, followed by a Diels-Alder reaction with maleic anhydride following the general procedure of Bachman and Kloetzel (*J. Am. Chem. Soc.* **1938**, *60*, 481).
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9. Molecular mechanics calculations were performed using the computer program PCMODEL386 version 4.0, available from Serena Software, P.O. Box 3076, Bloomington, IN 47402.
10. Clear yellow prism crystals of **3** suitable for X-ray diffraction were obtained on recrystallization from acetone/water. Crystal data for **3**: $C_{20}H_{16}0_5$; triclinic, space group P$\bar{1}$ (#2), a = 9.094(1)Å, b = 10.473(2), c = 8.522(1), α = 104.28(1)°, β = 104.78(1), γ = 100.62(1); 2753 independent reflections of which 2574 where considered observed. The structure was solved by direct methods (SHELXS-86), R = 0.057. Full details of the crystal structure analysis including tables of atomic coordinates and thermal parameters may be obtained from the Cambridge Crystallographic Data Centre.
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