# BREDT'S RULE-V†

## A BRIDGEHEAD BENZENE RING

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Abstract—<sup>1</sup>H and <sup>13</sup>C NMR have been used to determine the conformation of Treibs' hemiacetal (1), to study the strain in the bridgehead benzene ring and to evaluate Ar-O orbital overlap in this distorted molecule.

Treibs' hemiacetal (1)<sup>1</sup> is a unique "anti-Bredt" molecule in which an aromatic ring straddles the bridgehead. It is apparent, from molecular models, that it is strained and that the aromatic ring is bent almost 20° out of planarity<sup>2</sup> about an axis through  $C_1$  and  $C_5$ . Models also show that the 7-membered ring can adopt two conformations and that neither of these allows efficient overlap between the aromatic  $\pi$ -orbital and the non-bonding p-orbitals on the ether-oxygen.

The molcule therefore presents a number of interesting features: a conformational question and a bent benzene ring in which *both* contributing Kekulé structures infringe Bredt's rule. Moreover, it is likely that these formal double bond "isomers" will differ in energy,<sup>3</sup> so reducing the aromaticity of the ring. This paper invesitgates these questions.

### Conformation

From molecular models the hemiacetal is able to adopt only two stable conformations 1a and 1b, in each of which, one of the protons in the 7-membered ring is forced under the edge of the aromatic ring. It is one of the striking features of the <sup>1</sup>H NMR spectrum (Experimental) that this *endo*-proton appears as a multiplet at  $\delta$ 0.84 ppm. Moreover, the chemical shift and shape of this signal remains unaltered, apart from broadening, between -80 and +100°, so the possibility of an 1a=1b



Table 1. <sup>1</sup>H NMR couplings (1a)

Coupling	Angle	J (obs) Hz		
наснр	110°	15		
HaCCHC	173*	13		
Haccha	77•	2.7		

Part IV; G. L. Buchanan, Org. Magnetic Res. 11, 45 (1978).

equilibrium can be discounted; the hemiacetal is locked in one conformation. At 360 MHz the shielded signal is resolved into an octet with observed couplings of 2.7, 13 and 15 Hz. This octet is assigned to H<sub>a</sub> in conformer 1a rather than 1b and the couplings are consistent with the bond angles as measured on a model (Table 1). Irradiation at  $\delta$  2.1 cleanly removes the 13 Hz coupling but the remaining couplings involve two components of the overlapping 3H multiplet centred at  $ca \ \delta$  1.6 and only partial decouplings could be achieved. Conversely, irradiation at  $\delta$  0.84 simplified the signal at  $\delta$  2.1 and induced deep seated changes in the  $\delta$  1.6 multiplet. That the benzylic signals at  $\delta$  3.4 and 3.13 were unaltered is also consistent with the conclusion that conformer 1a is preferred to 1b.

## Aromatic ring

The UV spectrum of 1 ( $\lambda_{max}^{EiOH}$  265.5 nm; log  $\epsilon$  2.34) shows the low intensity absorption expected of an aromatic either with reduced p- $\pi$  overlap.<sup>4</sup> It is also devoid of fine structure and this is characteristic of a non-planar benzene ring.<sup>5</sup>

In the <sup>1</sup>H NMR spectrum the aromatic protons give rise to a tight 3H multiplet at  $\delta$  7-6.9. In chemical shift they are therefore not significantly different from those observed in [7] *m*-cyclophane<sup>6</sup> or indeed in 2.6dimethylanisole. Even at 360 MHz the spectrum was not first order, and no coupling constants were obtained.

It was expected that any changes in bond angles or in hybridisation, associated with ring distortion, would be reflected in aberrant <sup>13</sup>C NMR chemical shifts or <sup>1</sup>J<sub>CH</sub> values. In the cycloalkabenzene series (2) such effects have been observed<sup>7</sup> in the smallest member, cyclopropabenzene, at or adjacent to the bridgehead positions. However, the <sup>13</sup>C NMR spectrum of Treib's hemiacetal (Table 2) reflects only the reduced delocalisation of the non-bonded electrons on the ether O. Indeed mole-



Cpd		C(1)	C(2)	C(3)	C(4)	C (5)	C(6)	e (calc)	Ref
3	5	113.8	128.9	120.1	128.9	113.8	159.2	0°	8
	$J_{CH}^{(Hz)}$	156	<u>158</u>	162	<u>158</u>	<u>156</u>	-		9
4	6	129.3	127.6	122.6	127.6	129.3	156.2	44°	8
5	6	141.4	123.9	123.3	123.9	141.4	154.7	52°	8
1	6	136.1	(124.1)	124.9	(126.1)	136.1	155.1	74°	
	<sup>1</sup> J <sub>CH</sub> (Hz)	-	( <u>158.9</u> )	158.8	( <u>159.0</u> )	-	-		

Table 2. <sup>13</sup>C NMR aromatic signals

Table 3.	чС	NMR	assignments	(la)
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155.14(s)	136.14(2C,s)	126.14	(d) 124.9	9 (đ)	124.09(d)	102.83(s)
<sup>C</sup> 6	C <sub>1</sub> and C <sub>5</sub>	C <sub>2</sub> /C	C	3	C <sub>4</sub> /C <sub>2</sub>	C <sub>9</sub>
39.42(t) $C_3/C_{12}$	38.715(t) C <sub>12</sub> /C <sub>7</sub>	27.20(t) C <sub>8</sub> /C <sub>11</sub>	25.0(t) C <sub>11</sub> /C <sub>8</sub>	19.	47(t) <sup>2</sup> 9	

cule fits comfortably into the series of nonplanar aryl ethers 3-5 and the Ar-O-C torsion angle (ca 73) as measured <sup>2</sup> from a model of 1a, is startlingly close to that calculated from the empirical relationship,<sup>8</sup> cos<sup>2</sup>  $\theta$  = (125.3- $\delta$ )/5.2, in which  $\delta$  is the chemical shift of C(3), the p-C atom. The chemical shifts of the bridgehead atoms lie close to the values calculated from standard relationships.<sup>10</sup> Likewise, the <sup>1</sup>J<sub>CH</sub> couplings are normal. For further details of the <sup>13</sup>C NMR spectrum see the Experimental.

#### EXPERIMENTAL

Treibs' hemiacetal (1). Inability to duplicate Treibs' apparatus<sup>1</sup> and isolation method forced us to devise an alternative method, as follows.

Tetrahydroacenapthene (40 g) was oxygenated at room temp through a sinter for 100 hr in all-glass apparatus. The resulting oil, in light petroleum (125 ml) was extracted with 90% MeOH-water (2×25 ml). The extract was concentrated on a rotary evaporator after which extraction into ether and base wash yielded on an oily residue. This residue was triturated with n-pentane and after 24 hr at 0°, the solvent was decanted off, leaving a thick gum of crude hyperoxide (1.8 g). Partial crystallisation of this gum gave material which was identified as Treib's symmetrical peroxide m.p. (n-pentane) 193-194° (lit. m.p. 187°); m/e 346. The residual crude hydroperoxide from two runs (680 mg), in dry pyridine (2 ml), was added to a suspension of p-nitrobenzoyl chloride (680 mg) in dry pyridine (2 ml) at 5° with stirring. The mixture was allowed to stir for 1 hr at room temp. Ice cold dil HSO4 was then added till the pH was ca 4 and a gummy solid was precipitated. Extraction into ether and base wash yielded the crude p-nitrobenzoate which could not be purified by the lit procedure. Purification was however possible using either of two methods:

(a) Preparative tlc of a portion of the crude product (400 mg) on five plates using 50% CHCl<sub>3</sub>-EtOAc as eluant gave a band with  $R_f$  0.6 which fluoresced green in UV light and afforded the *p*-nitrobenzoate as crystals m.p. 105°. Recrystallisation from light petroleum yielded pure ester (140 mg) m.p. 108-109° (lit. m.p. 108-109°) m/e 339.

(b) The crude product (0.8 g) in 50% CHCl<sub>3</sub>-light petroleum was poured on to a column of dry silica (15 g) and eluted with the same solvent mixture. The first 60 ml of eluant afforded the *p*-nitrobenzoate (240 mg) m.p. 103°. Recrystallisation from

light petroleum yielded the pure ester (225 mg) m.p. 108-109°.

Hydrolysis of the *p*-nitrobenzoate as described,<sup>1</sup> afforded the hemiacetal (1) m.p. 75–76° from n-pentane (lit. m.p. 76.5–77.5°) *m/e* 190, 162, 135, 115 and 92;  $\nu_{max}^{CCL_4}$  3600, 3560–3200 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.84 (1H), *ca* 1.6 (3H), 2.1 (1H), 2.25–2.5 (3H), 3.0 (1H exch. in D<sub>2</sub>O), 3.1 (1H), 3.4 (1H), 6.9–7.0 (3H), all multiplets. <sup>13</sup>C NMR. see Tables 2 and 3. Assignments were made using off resonance and gated decoupled spectra, C<sub>3</sub> being identified on the assumption that <sup>2</sup>J<sub>c</sub>H will be very small, as the only clean doublet. C<sub>2</sub> and C<sub>4</sub> showed additional subsplittings assigned to <sup>3</sup>J<sub>Cb</sub> coupling.

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