

Proton Nuclear Magnetic Resonance Spectra and Conformation in 1,4-Dihydrobenzenes and 9,10-Dihydroanthracenes

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Analysis of the 220 MHz ^1H n.m.r. spectra of 2,6-dimethoxy- and 2,6-bis(trideuteriomethyl)-1,4-dihydrobenzoic acids leads to the conclusion that the equilibrium geometry of the dihydrobenzene rings in these molecules is essentially planar. Although the equilibrium conformation of the ring in most 1,4-dihydrobenzenes is probably planar, Laane and Lord's far-i.r. data on dihydrobenzene itself suggest that the time-averaged geometry of the thermally populated vibrational states at 300 K is significantly boat-shaped. This allows earlier results, from which a boat conformation had been inferred, to be reconciled with more recent conclusions.

The pseudoaxial–pseudoaxial *cis* homoallylic coupling constant of dihydroanthracene has been estimated to be 4.8 Hz. The values of homoallylic coupling constants in 9,10-dihydroanthracenes are in fair agreement with estimates based on a recent INDO analysis of the angular dependence of homoallylic coupling.

THE geometry of the cyclohexadiene ring in 1,4-dihydrobenzenes ‡ and 9,10-dihydroanthracenes has been the subject of many experiments and much debate. However it now seems to be generally accepted that the boat geometry found for dihydroanthracene in the crystal¹

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‡ For purposes of clarity in the discussion of substituted analogues, the name dihydrobenzene is preferred to cyclohexadiene.

¹ W. G. Ferrier and J. Iball, *Chem. and Ind.*, 1954, 1296.

² P. W. Rabideau and J. W. Paschal, *J. Amer. Chem. Soc.*, 1972, **94**, 5801, and references therein.

is retained in solution,² except that a boat \rightleftharpoons boat inversion takes place which is rapid on the n.m.r. time scale.

The lowest energy conformation of 1,4-dihydrobenzene, on the other hand, is now believed to be planar.^{3–6} This

³ N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, 1972, **94**, 5734; for a conflicting conclusion see V. G. Dashevskii, V. A. Naumov, and N. M. Zaripov, *J. Struct. Chem.*, 1970, **11**, 687.

⁴ O. Ermer and S. Lifson, *J. Amer. Chem. Soc.*, 1973, **95**, 4121.

⁵ J. Laane and R. C. Lord, *J. Mol. Spectroscopy*, 1971, **39**, 340.

⁶ J. W. Paschal and P. W. Rabideau, *J. Amer. Chem. Soc.*, 1974, **96**, 272.

is most clearly demonstrated by the analysis by Laane and Lord⁵ of the far-i.r. spectrum where the boat \rightleftharpoons boat inversion is directly observable. Some seven vibrational levels are populated at room temperature, and from the transition frequencies a shallow, symmetrical potential well with a single (planar) minimum was deduced. This experimental result is entirely consistent with the results of recent force-field calculations,^{3,4} and it is clear that the preference for eclipsed conformations about the four sp^3 - sp^2 C-C bonds⁷ just outweighs the bond-angle strain necessary to achieve a planar structure.

Despite these general conclusions, no adequate discussion of the pertinent literature seems to have been presented. For example, in a somewhat cursory survey,³ one group cites n.m.r. data⁸ for dihydrobenzene itself as supporting a planar structure. In fact the experimental work in question is now considered best interpreted in terms of a shallow boat geometry.^{9,10} Indeed, when cognizance is taken of subsequent INDO calculations of the dihedral dependence of homoallylic coupling,¹¹ then this particular n.m.r. result⁸ leads to a geometry very similar to that deduced from an electron diffraction study.¹² In the latter work,¹² the degree of ring puckering, defined by the dihedral angle α in Figure 1, was measured apparently with high precision ($\alpha = 159.3 \pm 0.7^\circ$).

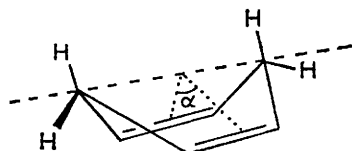


FIGURE 1

Our own interest in these problems stems from our original observations of very large homoallylic couplings in the n.m.r. spectra of 1,4-dihydrobenzenes,¹³ and our anticipation,⁹ on empirical grounds, of the INDO result that for a planar dihydrobenzene the *trans* homoallylic coupling would be somewhat greater than the *cis* (Figure 2), whereas earlier calculations of Karplus¹⁴ had predicted that these would be equal.



$$J_{1,4} = J_{1',4'} = J_{cis}$$

$$J_{1,4'} = J_{1',4} = J_{trans}$$

FIGURE 2

Because much of the early experimental evidence concerning 1,4-dihydrobenzene¹⁵ had not seemed to

⁷ See, for example, G. J. Karabatsos, and D. J. Fenoglio *Topics Stereochem.*, 1970, **5**, 167.

⁸ E. W. Garbisch and M. J. Griffith, *J. Amer. Chem. Soc.*, 1968, **90**, 3590.

⁹ D. J. Atkinson and M. J. Perkins, *Tetrahedron Letters*, 1969, 2335.

¹⁰ E. W. Garbisch and M. J. Griffith, *J. Amer. Chem. Soc.*, 1970, **92**, 1107.

¹¹ M. Barfield and S. Sternhell, *J. Amer. Chem. Soc.*, 1972, **94**, 1905.

carry the conviction which we now feel must be accorded to Laane and Lord's result,⁵ we decided to investigate long-range coupling in the n.m.r. spectra of 1,2,6-trisubstituted 1,4-dihydrobenzenes. The homoallylic splitting pattern in 1-substituted 1,4-dihydrobenzenes

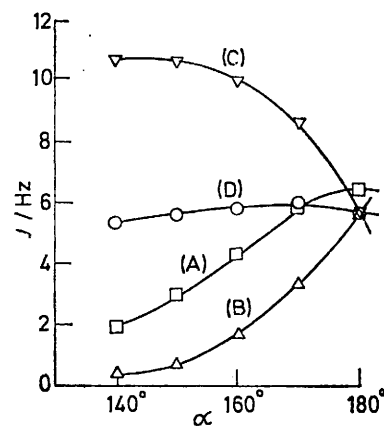


FIGURE 3 Calculated conformational dependence of homoallylic coupling in 1,4-dihydrobenzene: (A) J_{trans} (pseudo equatorial-pseudo axial); (B) J_{cis} (pseudo equatorial-pseudo equatorial); (C) J_{cis} (pseudo axial-pseudo axial); (D) J_{cis} (mean value for equally populated equilibrating structures)

normally approximates to that of an AX_2 or AB_2 system;^{13,16} however it has not generally been clear whether this is due to a true equality of the *cis* and *trans* couplings, or instead represents a case of deceptive simplicity consequent upon the isochronous nature of the strongly coupled protons on C-4. Unfortunately, 1,4-disubstituted 1,4-dihydrobenzenes with which this could be tested are relatively inaccessible.

Figure 3 shows the calculated dependence of the *cis* and *trans* couplings as a function of α . The plots have been obtained from the dihedral dependence of homoallylic splitting computed by Barfield and Sternhell using the INDO procedure¹¹ ($\times 2$ to allow for the dual path coupling), together with the approximate relationship (i) between α and the dihedral angle θ between

$$\alpha = 180^\circ - |\theta - 60^\circ| \quad (i)$$

C(1)-H and C(2)-H (C_{2v} symmetry is assumed for the six-carbon framework). Also plotted in Figure 5 is the dependence on α of the mean *cis* coupling, assuming boat \rightleftharpoons boat inversion between two *equivalent* conformations which are *equally populated*. The calculated inequality of the *cis* and *trans* couplings of the planar structure is at once evident. It is also evident that for a 1-substituted 1,4-dihydrobenzene the *cis* and *trans* homoallylic couplings will be approximately equal for

¹² H. Obershammer and S. H. Bauer, *J. Amer. Chem. Soc.*, 1969, **91**, 10.

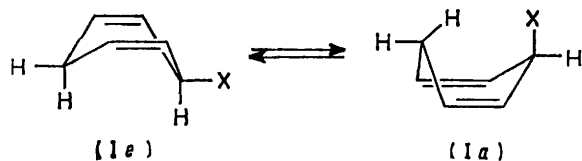
¹³ L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Comm.*, 1965, 456.

¹⁴ M. Karplus, *J. Chem. Phys.*, 1960, **33**, 1842; *J. Amer. Chem. Soc.*, 1960, **82**, 4431.

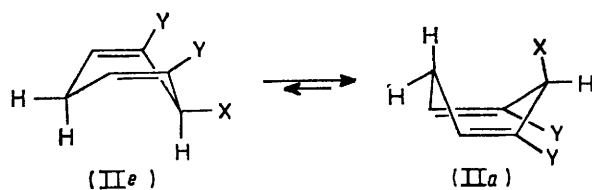
¹⁵ See, for example, H. Gerding and F. A. Haak, *Rec. Trav. chim.*, 1949, **68**, 293; B. J. Monostori and A. Weber, *J. Mol. Spectroscopy*, 1964, **12**, 129; H. D. Stidham, *Spectrochim. Acta*, 1965, **21**, 23, and the discussion in ref. 12.

¹⁶ J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, 1970, **35**, 2038.

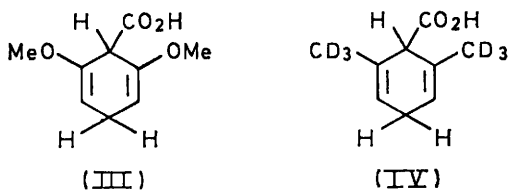
structures close to planar, unless boat geometry is preferred and one conformation is strongly favoured over the other (*Ie*) \rightleftharpoons (*Ia*).



Although it had been suggested that a group such as CO₂H might favour (*Ie*) over (*Ia*),¹⁶ inspection of space-filling models led us to conclude that only very large groups, e.g. Bu^t or Ph₃C,⁹ would significantly influence conformation. On the other hand, in 1,2,6-trisubstituted 1,4-dihydrobenzenes the situation should approximate to that in 9-substituted dihydroanthracenes,² in which quite small substituents preferentially adopt a pseudoaxial orientation. In this event, any significant deviation from coplanarity should be revealed in a reduction in the observed homoallylic splitting, since in the preferred boat (*IIa*) both the *cis* and the *trans* coupling will be reduced relative to their values in a planar conformation (Figure 3).



To investigate this, we have synthesised the trisubstituted compounds (III) and (IV). Deuteriation of the methyl groups was essential in (IV) to avoid additional unresolvable long-range splittings. Interpretation

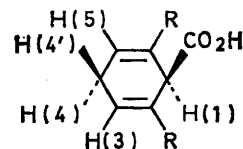


of the spectra was greatly facilitated by the discovery that in neither compound were the C-4 protons isochronous, and computer simulation of the 220 MHz spectrum allowed all the couplings to be determined with reasonable precision. The results are presented in the Table. Two features are of especial note. First, in each case the vicinal couplings of both C-4 protons are very similar. This can only be explained in terms of an approximately planar time-averaged geometry. This conclusion is identical with that of Paschal and Rabideau⁶ who, with the aid of paramagnetic shift reagents,* were able to measure the coupling constants

* The possibility that association with shift reagent may affect conformation cannot be excluded here; see e.g. J. F. Caputo and A. R. Martin, *Tetrahedron Letters*, 1971, 4547.

of 1,4-dihydrobenzyl alcohol and its 3-fluoro-derivative; in both compounds the vicinal proton couplings to the protons on C-4 were identical, being 3.0 and 3.5 Hz for the two compounds. In our examples the mean value of ca. 3.6 Hz is close to this, as is the mean of 3.5 Hz

Frequencies and coupling constants for the ring protons in the 2,6-disubstituted 1,4-dihydrobenzoic acids (III) and (IV), as obtained by computer simulation of their 220 MHz ¹H n.m.r. spectra (CDCl₃ solution)



Numbering as indicated. The frequencies are relative to an arbitrary reference point; the assignments of H(4) and H(4') may have to be reversed

¹ H Spectral parameter	(III)	(IV)
Chemical shift frequencies (Hz)		
ν_1	295	241
ν_2, ν_5	523	727
$\nu_{4'}$	94.3	116.0
ν_4	66.3	89.1
Coupling constants		
$J_{1,3}$	-0.8	-0.8
$J_{1,4'}$	6.8	6.25
$J_{1,4}$	6.3	6.0
$J_{3,4'}$	3.3	3.25
$J_{3,4}$	4.0	4.0
$J_{3,5}$	0	0
$J_{4,4'}$	-21.8	-22.2
Line-width used for simulation	1.2 Hz	2.0 Hz

found by Marshall *et al.*^{17,18} for the vicinal couplings to the two protons on C-4 in 1,4-dihydro-1-naphthoic acid. In that case the individual values were 4.60 and 2.44 Hz,¹⁷ but an approximately planar geometry was still preferred.¹⁸ This is reasonable, since if we assume a \cos^2 dependence of the vicinal coupling on dihedral angle, these values indicate that for the dihydronaphthoic acid $\alpha > 170^\circ$ (probably ca. 175°). For (III) and (IV) a much smaller mean deviation from planarity is indicated. It should, however, be emphasised that even for identical vicinal couplings the only conclusion can be that the time averaged geometry is planar. It is not inconsistent with rapid interconversion of two equally populated boat conformations. Models suggest that, in this event, if α were $>150^\circ$ then a substituent as small as CH₂·OH might have so small a conformational preference that near equal populations of two conformations might be possible. We feel, however, that this explanation is most unlikely with (III) and (IV) where, particularly with (IV), interaction between the substituents becomes pronounced for quite small puckering of the ring if the CO₂H group is pseudoequatorially oriented. We shall return to this point in a brief discussion of dihydronaphthalenes. It was precisely

¹⁷ J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, 1971, **36**, 2011.

¹⁸ J. L. Marshall, A. M. Ibrag, and P. N. Jenkins, *J. Org. Chem.*, 1972, **37**, 1863.

this consideration which led Paschal and Rabideau⁶ to study the fluorinated dihydrobenzyl alcohol. They argued that for interconversion of two substantially puckered boat conformers the time-averaged H-4,F vicinal couplings should be quite large. In the event they were less than 2 Hz, and an essentially planar structure was inferred, although this magnitude of coupling seems low even for a planar structure, according to calculations¹⁹ of the angular dependence of such interaction.

The second feature of interest in our results is the diminished magnitude of the *cis* and *trans* homoallylic couplings compared with those in dihydrobenzoic acid,¹³ separately determined to be 8.3 and 8.9 Hz,¹⁶ but without stereochemical assignment. A part of this difference may be attributed to a substituent effect, since whilst $J_{1,4}$ (mean) in dihydrobenzene is 8.8 Hz,⁸ $J_{2,5}$ in 2,5-dihydro-*m*-xylene is only 8.0 Hz.* However the difference here is less than half of that found for the corresponding acids. That the diminished homoallylic coupling is not due to ring puckering, as proposed at the inception of this investigation, may be inferred from the near equality of the *cis* and *trans* coupling constants. This is not consistent with a significantly puckered geometry where the two possible conformations are not equally populated (Figure 3). It is noteworthy that with the exception of (III) and (IV), all 1,4-dihydrobenzenes examined have been found to have homoallylic coupling constants significantly larger than predicted by the Barfield and Sternhell analysis.

In view of the inference from the vicinal coupling constants that the mean geometry of the dihydrobenzene ring is flat in all those instances where these constants have been measured, and the agreement between this, Laane and Lord's results, and the most recent conformation energy calculations, it is necessary to re-examine the homoallylic couplings determined for 1,4-dihydrobenzene itself, which equally clearly indicate a shallow boat conformation. Paradoxically the two sets of results *are* self-consistent, for the vicinal couplings indicate the mean geometry of the ring, whilst the homoallylic splittings of dihydrobenzene indicate the mean deviation from planarity (*i.e.* in either direction).

1,4-Dihydrobenzene is oscillating about a planar energy minimum, with vibrational amplitudes sufficiently large at room temperature⁵ that a Boltzmann calculation based on Laane and Lord's results gives $\alpha = 167^\circ$ for the time-averaged deviation from planarity (assuming sinusoidal oscillation). The ratio of the *cis* to the *trans* homoallylic couplings of 1.2 for this compound (data of Figure 3) gives a mean deviation of $\alpha = ca. 164^\circ$.

* We thank Dr. R. P. Corbally for this result.

† For example, detailed calculations suggest that equation (i) may be in error by as much as 3° at points in the range $180^\circ > \alpha > 140^\circ$.

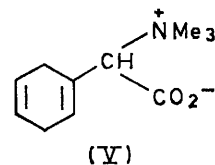
‡ The calculations of ref. 19 suggest that oscillation between boat structures of $\alpha > 160^\circ$ would not be readily detected by the experiment with fluorinated dihydrobenzyl alcohol.⁶

§ This may be a gross oversimplification; for example it completely neglects coupling through the σ framework which is included in the INDO calculation.

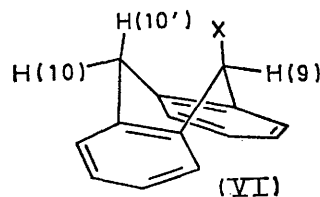
When the assumptions and approximations of the theory[†] are taken into consideration, this agreement seems very good.‡

Probably the electron diffraction result¹² can be explained in essentially the same fashion,³ although the deviation from planarity indicated is somewhat greater despite relating to a lower temperature. An independent electron diffraction study has in fact led to assignment of a planar structure.²⁰ However, there seems little doubt that the pronounced out-of-plane bending of the molecule must influence the reliability of any such measurements. Finally, since the vibration frequency in question is probably of the same order as, or rather less than, the reciprocal of the dielectric relaxation time for 1,4-dihydrobenzene, this could also account for the residual dipole moment found for this molecule.²¹

Two X-ray crystallographic studies on derivatives of 1,4-dihydrobenzene have found the ring to be planar.^{22,23} As pointed out in the report of one of these,²² packing forces in the crystal may be sufficiently great to perturb the ring from its equilibrium geometry. This seems particularly relevant to the case of the amino-acid derivative (V).²³



The homoallylic couplings of dihydroanthracenes have invariably been found to be much smaller than those for dihydrobenzenes. However the values measured are for 9-substituted derivatives and almost always relate to essentially one conformation of a highly puckered ring² in which the C(9)-H bond is nearly orthogonal to the π -system [structure (VI)]. Using the geometry ($\alpha = 145^\circ$) found in the crystal,¹ and reducing the coupling constants of Figure 3 by a factor of 0.67 to allow for the reduced π -bonding of the benzene double bonds,[§] one can predict that $J_{9,10} =$



$ca. 1.3$ and $J_{9,10} = ca. 0.23$ Hz, in remarkably close agreement with the experimentally determined values of $ca. 1.1$ and 0.4 Hz, respectively.² The coupling

¹⁹ K. Hirao, N. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, 1973, **95**, 31.

²⁰ G. Dallinga and L. H. Tomenan, *J. Mol. Struct.*, 1967-68, **1**, 117.

²¹ W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Amer. Chem. Soc.*, 1964, **86**, 3126.

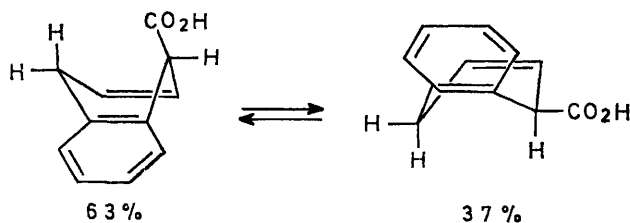
²² M. J. Bennett, J. T. Purdham, S. Takada, and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 4063.

²³ R. J. Jandacek and S. H. Simonsen, *J. Amer. Chem. Soc.*, 1969, **91**, 6663.

between the two pseudoaxial (ψ_a) protons in a boat conformation of dihydroanthracene should be much larger, since hyperconjugative overlap with the π -system is close to a maximum. The calculated value is 7.0 Hz ($= 10.4 \times 0.67$). It has now proved possible to obtain an experimental estimate for this by measuring the mean homoallylic splitting in dihydroanthracene itself by observing the ^{13}C satellite spectrum of the protons on C-9 and C-10. With aromatic protons decoupled, this appeared as two 1:2:1 triplets with a line spacing of 1.85 Hz. The assumption that this is a mean of one ψ_a, ψ_a splitting, one ψ_e, ψ_e splitting (*ca.* 0.4 Hz), and two ψ_e, ψ_a splittings (*ca.* 1.1 Hz), allows us to estimate 4.8 Hz for ψ_a, ψ_a , in modest agreement with the calculated value.

The preferred geometry of 1,4-dihydronaphthalenes may be similar to that of dihydrobenzenes, as already mentioned. On the other hand, the experimental results^{17,18} do not rule out a geometry intermediate between those of dihydrobenzenes and dihydroanthracenes. For example, the vicinal couplings to the protons on C-4 of dihydronaphthoic acid are consistent with a mean value of α of *ca.* 175°. However this *could* arise from an equilibration of two opposite boat conformers each with α 160°, but with unequal populations (63 and 37%). For this degree of distortion from planarity the steric interaction between one benzene ring and CO_2H may be quite small.

It may be no more than coincidence, but for this situation, with assumptions similar to those employed already, the data of Figure 3 give $J_{cis} = 4.1$ and $J_{trans} = 3.6$ Hz for the homoallylic coupling constants, in close accord with the experimental values of 4.36 and 3.84 Hz. In the published report the larger value was actually assigned to J_{trans} ,¹⁸ but it is not clear how this assignment was made.



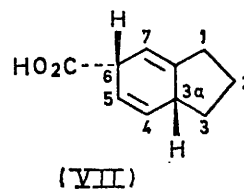
Perhaps the most reasonable interpretation is that there is oscillation about an approximately planar geometry which may represent an energy minimum, or may be raised slightly above two minima. The potential well should have an even shallower base than is the case with dihydrobenzene, so that the amplitude of the vibrations at room temperature will be greater; finally, the well will be unsymmetrical because of steric interactions with the carboxylate substituent.

Other n.m.r. parameters can be brought to bear on

Note added in proof: Other examples of 1,4-dihydrobenzene derivatives for which one boat conformation is preferred have been described recently (J. L. Marshall and B.-H. Song, *J. Org. Chem.*, 1975, **40**, 1942; P. W. Rabideau, J. W. Paschal, and L. E. Patterson, Abstracts, 170th A.C.S. National Meeting, Chicago, August, 1975, Orgn 116).

these problems. For example it has been pointed out by Marshall *et al.*¹⁸ that the geminal coupling between the protons on C-4 is unusually large, which would be consistent with a flattened structure and distortion of the tetrahedral bond angles. However there is evidence that the geminal coupling between protons on an allylic carbon atom is relatively large irrespective of any angular distortion.²⁴ Furthermore, the magnitude of the $^{13}\text{C}, \text{H}$ coupling at C-1 in 1,4-dihydrobenzene⁸ is normal for a tetrahedral carbon atom.

There have been some interesting theoretical studies on the splitting of the π -electron energy levels in 1,4-dihydrobenzene.²⁵ In an attempt to interpret the photoelectron spectrum of this molecule these calculations had assumed a planar geometry. However, a more recent analysis^{26a} finds that the experimental results accord better with a slightly puckered structure. (Comparison was made with an electron diffraction α -value of 163°, but this appears to be a parameter defining the non-planarity of 1,2-dihydrobenzene^{26b} rather than the 1,4-isomer.) We are currently attempting to synthesise cyclohexadienes with α *ca.* 150–160° by fusing small rings to C-1 and C-2. In the latter structures strain is minimised by pseudo-equatorial fusion at C-1. Thus the dihydroindanecarboxylic acid (VII) apparently has a puckered dihydrobenzene ring, since $J_{3a,6} = 12$ Hz.²⁷



EXPERIMENTAL

Materials.—2-Bromo-*m*-xylene was deuteriated in the methyl groups (>98% deuterium incorporation by n.m.r.) by repeated exposure to potassium *t*-butoxide in [$^2\text{H}_6$]dimethyl sulphoxide. The deuteriated material was converted into the corresponding Grignard reagent and carboxylated. The resulting 2,6-bis(trideuteriomethyl)-benzoic acid was reduced without purification to the 1,4-dihydro-derivative with sodium in liquid ammonia by a procedure described for the preparation of dihydrobenzoic acid,²⁸ except that a large excess of sodium was necessary. This did not cause over-reduction as it does with benzoic acid itself. The [$^2\text{H}_6$]dimethylbenzoic acid had m.p. 69.5° (from benzene–light petroleum–ethanol), τ (60 MHz; CDCl_3) –0.6br (1 H, s), 4.4br (2 H, t, J 4 Hz), 6.6br (1 H, t, J 6 Hz), and 7.25 (2 H, m); m/e 158 (M^+) and 113 ($M^+ - \text{CO}_2\text{H}$, base peak).

²⁴ S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

²⁵ P. Bischof, J. A. Hashnall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, 1969, **52**, 1745; *Tetrahedron Letters*, 1970, 1033; R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, 1970, **92**, 706.

²⁶ (a) E. Heilbronner, *Israel J. Chem.*, 1972, **10**, 143; (b) G. Dallinga and L. H. Toneman, *J. Mol. Structure*, 1967–1968, **1**, 11.

²⁷ G. H. Whitham and S. G. Davies, unpublished observations; we are grateful to Dr. Whitham for permission to cite this result.

²⁸ M. E. Kuehne and B. F. Lambert, *Org. Synth.*, Coll. Vol. V, p. 400.

The undeuteriated acid was also synthesised,²⁹ and had an additional proton resonance at τ 8.3br (6 H, s).

1,4-Dihydro-2,6-dimethoxybenzoic acid, prepared by sodium-liquid ammonia reduction of 2,6-dimethoxybenzoic acid, again with an excess of sodium, had m.p. 129.5° (decomp.) (from benzene-light petroleum-ethanol), τ (60 MHz; CDCl₃) 0.3br (1 H, s), 5.1br (2 H, t, J 4 Hz), 6.1 (1 H, t, J 6 Hz), 6.4 (6 H, s), and 7.05 (2 H, m) (Found: C, 59.5; H, 6.5. C₉H₁₂O₄ requires C, 59.8; H, 6.5%).

¹H N.m.r. Spectra.—The 220 MHz spectra were recorded by PCMU, Harwell. Double-resonance experiments with dihydrobenzene and dihydroanthracene were recorded at 90 MHz on a Perkin-Elmer R32 instrument (CDCl₃). The

spectral simulation was carried out using the program NMRCAL supplied with a Nicolet 1080 system attached to a Bruker HFX 90 spectrometer.

We thank the S.R.C. for a studentship (to M. C. G.), P.C.M.U., and R. Redmond (Chelsea College) for the 220 and 90 MHz spectra, respectively, and A. W. Ellis for helpful comments.

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²⁹ H. Van Bekkum, C. B. Van den Bosch, G. Van Minnen-Pathuis, J. C. De Mos, and A. M. Van Wijk, *Rec. Trav. chim.*, 1971, **90**, 137.