

## Long-range Coupling in the Proton Magnetic Resonance Spectra of 1,4-Dihydrobenzenes

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BERSON and WILCOTT have recently hinted<sup>1</sup> at the possibility of an unexpected long-range coupling in the n.m.r. spectrum of a 1,4-dihydrobenzene derivative. This prompts us to record some of our observations in this area.

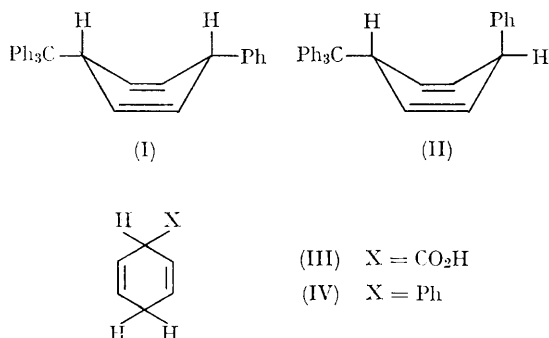
We have found coupling constants from 7.4 c./sec. to 11 c./sec. (depending on stereochemistry) between the 1- and 4-protons of unsymmetrical 1,4-dihydrobenzenes.

The compounds initially examined<sup>2</sup> were the stereoisomeric 1,4-dihydro-4-tritylbiphenyls (I) and (II).<sup>3</sup> For each isomer the methine hydrogen signals appear as broad doublets (see Figure) in which the major splitting corresponds to mutual spin interaction, as was shown by decoupling experiments. As 1,4-dihydrobenzene is considered to exist in a boat form<sup>4</sup> (models suggest a very

small energy barrier to boat-boat inversion), the preferred conformations of the two isomers are probably those shown in structures (I) and (II). Assignment of configuration to the two compounds was originally based on three self-consistent, but equivocal, criteria.<sup>3b</sup> That designated "cis" has  $J_{1-4} \approx 11$  c./sec., while for the "trans"-isomer  $J_{1-4} \approx 7.5$  c./sec. The larger coupling might be anticipated for the cis-structure (I), with the two hydrogens in a pseudo-axial configuration;<sup>5</sup> however, two of the twenty aromatic protons of this compound were unusually shielded ( $\tau$  ca. 3.8), which is not readily reconciled with structure (I). On the other hand, the *ortho*-protons of the pseudo-axial phenyl group in structure (II) might be expected to be appreciably shielded by the double bonds of the dihydrobenzene. The stereochemistry of these compounds therefore remains in doubt.

We have also observed long-range coupling in the 2-chloro-derivative<sup>6</sup> of one of the above compounds, as well as in the simpler 1,4-dihydrobenzoic acid (III) and 1,4-dihydrobiphenyl (IV). In each of the latter two examples, the methylene protons (broadened doublet) couple strongly with the methine proton (triplet). For both compounds  $J_{1-4} \approx 9$  c./sec. Surprisingly the methylene protons showed no chemical-shift separation, and appear to couple equally with the methine proton. This may be associated with boat-to-boat inversion of the cyclohexadiene ring.

Homoallylic<sup>7</sup> long-range coupling across a double bond is mainly transmitted through



<sup>1</sup> J. A. Berson and M. R. Willcott, *J. Amer. Chem. Soc.*, 1965, **87**, 2752, footnote 5.

<sup>2</sup> Spectra were recorded on Varian A60 or HR100 spectrometers, using solutions in carbon tetrachloride with Me<sub>4</sub>Si as internal standard.

<sup>3</sup> D. H. Hey, M. J. Perkins, and G. H. Williams, (a) *Tetrahedron Letters*, 1963, 445; (b) *J. Chem. Soc.*, 1965, 110.

<sup>4</sup> E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, London, Sydney, 1965, p. 125. W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Amer. Chem. Soc.*, 1964, **86**, 3126.

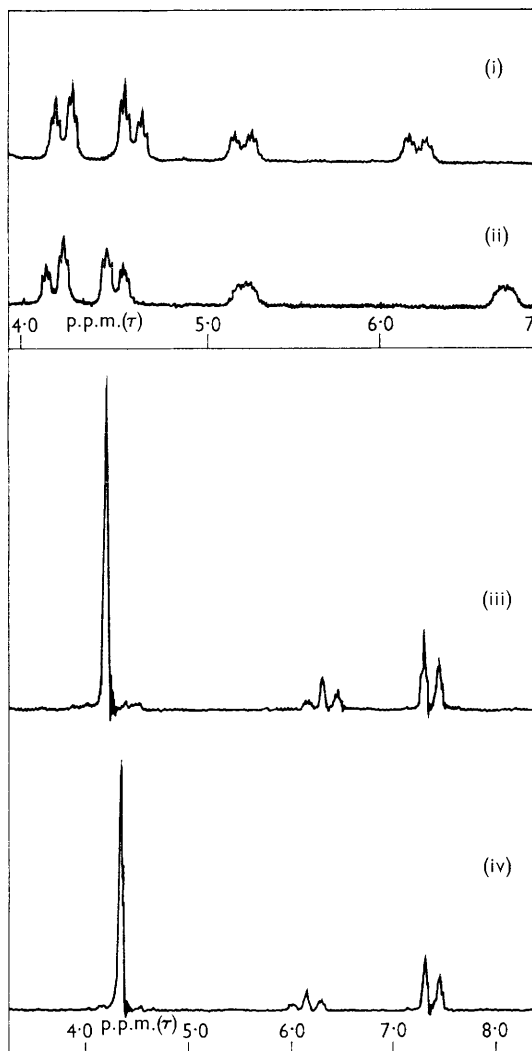
<sup>5</sup> D. W. Cameron, D. G. I. Kingston, N. Sheppard, and Lord Todd, *J. Chem. Soc.*, 1964, 98.

<sup>6</sup> This compound is obtained as a major product of the decomposition of phenylazotriphenylmethane in chlorobenzene (unpublished results of M.J.P.).

<sup>7</sup> Proton spin-spin coupling across three carbon-carbon bonds, the centre of which is double, is referred to as "homoallylic coupling." Long-range coupling in general is the subject of a recent review by S. Sternhell, *Rev. Pure Appl. Chem.*, 1964, **14**, 15.

$\pi$ -electrons. Therefore it is not so surprising that the dihydrobenzenes with two double bonds "in parallel," should exhibit appreciably stronger

coupling of this type than has previously been reported.<sup>8</sup>



Parts of the n.m.r. spectra of the "cis" (i) and "trans" (ii) isomers of 1,4-dihydro-4-tritylbiphenyl at 100 Mc.sec.; and of compounds (III) (iii) and (IV) (iv) at 60 Mc.sec. In each case only the signals due to the protons on the dihydrobenzene ring are shown.

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<sup>8</sup> The largest reported homoallylic coupling of which we are aware is 5 c./sec., H. H. Appel, R. P. M. Bond, and K. H. Overton, *Tetrahedron*, 1963, **19**, 635. More usual values range from ca. 1 to 3 c./sec. (see ref. 7).