Long-Range Splitting in the Nuclear Magnetic Resonance Spectrum of 1,4-Dihydrobenzoic Acid

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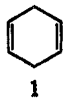
Previous examples of homoallylic proton–proton coupling[1] (with a symmetrically disposed π bond) indicate that this long-range coupling is generally very small[1-5]—such coupling constants usually do not exceed 3 Hz.[6] However, the 1,4-cyclohexadiene system has been reported to give an unusually large homoallylic coupling constant: 1,4-cyclohexadiene (1) has *cis* and *trans* coupling constants of 9.63 and 8.04 Hz, respectively,[7] and the isomeric 1-phenyl-4-trityl-1,4-cyclohexadienes (2) have *cis* and *trans* coupling constants of 11 and 7.5 Hz, respectively.[8]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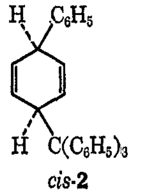
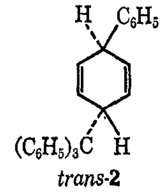
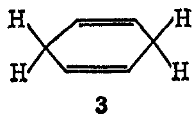

cis-**2**


trans-**2**

The large homoallylic coupling in 1,4-cyclohexadienes has allowed some workers to attach special significance to J_{cis}/J_{trans} ratios thus obtained. The small J_{cis}/J_{trans} ratio for 1 (*viz.*, 1.2) prompted Garbisch[7] to postulate a planar, or nearly so, conformation for 1,4-cyclohexadiene (3) rather than a highly puckered, or boat, conformation (4). Implicit in his discussion was the assumption that for the planar conformation (3), $J_{cis} = J_{trans}$.[9]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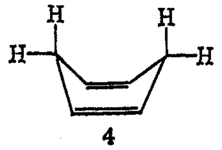
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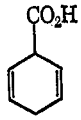
Atkinson and Perkins, who investigated the nmr of 2, believed that for the planar conformation (3) J_{cis} should be less than J_{trans}, that $J_{cis} = J_{trans}$ only when the ring is somewhat puckered, and that 1,4-cyclohexadiene is therefore *not* planar. For 2, they argued, the bulky substituents exaggerated the puckering to such an extent that now J_{cis} was considerably greater than J_{trans} ($J_{cis}/J_{trans} = 1.47$).

We report here our nmr studies of 1,4-dihydrobenzoic acid (**5**), a compound whose sterical requirements are somewhat different from those of 1 or 2. Models indicate that in planar **5** steric interaction occurs between the carboxylate group and the olefinic π bonds (see **5a**), and that a puckered conformation (**5b**) would be preferred with the carboxylate group in a pseudoequatorial position. The puckering in **5**, however, should not be as severe as in 2. Thus, **5** should represent a case between 1 and 2, unless 1 is highly puckered also.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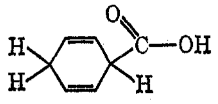
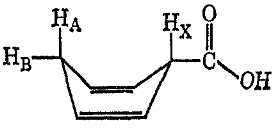
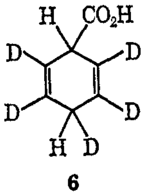
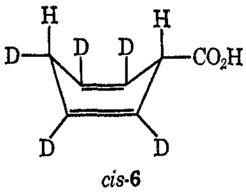

5a

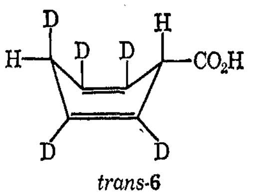

5b

The 60-MHz nmr spectrum of **5** exhibited a singlet at δ 11.71 (acid proton), a singlet at δ 5.80 (olefinic), a triplet at δ 3.71 with $J = 8.6$ Hz (methine), and a doublet at δ 2.53 with $J = 8.6$ (allylic). A first-order analysis of the spectrum, therefore, indicated that homoallylic coupling between the methine and the methylene protons existed to give a simple AX_2 system. The latter three signals, however, included perturbations which could arise from olefinic–aliphatic coupling and/or an actual ABX system.[10] The 100-MHz spectrum, with proton–proton decoupling,[11] indicated that most of the perturbations were due to olefinic–aliphatic coupling: the uncoupled olefinic signal appeared as a triplet (with a separation of 2 Hz) but simplified when either the methine or the methylene signals were irradiated, and irradiation of the olefinic signal simplified the methine and the methylene signals.

The nmr spectrum of **5** would also be consistent with a deceptively simple ABX system where both $\nu_0\delta_{AB}$ and $^1/_2(J_{AX} - J_{BX})$ are small compared with J_{AB}, and with the apparent coupling constant J_{app} being an average of J_{AX} and J_{BX}[12] (see **5b** where J_{AX} is J_{cis} and J_{BX} is J_{trans}). To explore the possibility of such a system, a sample of 2,3,4,5,6-pentadeuterio-1,4-dihydrobenzoic acid (**6**) was prepared (see Experimental Section). The sample of **6** was undoubtedly a mixture of *cis*- and


6


cis-**6**


trans-**6**

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(1) J. T. Pinhey and S. Sternhell, *Tetrahedron Lett.*, 275 (1963).

(2) J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961).

(3) W. F. Beach and J. H. Richards, *ibid.*, **26**, 3011 (1961).

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(5) S. Gronowitz, B. Gestblom, and R. A. Hoffman, *Acta Chem. Scand.*, **15**, 1201 (1961).

(6) For an excellent review, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(7) E. W. Garbisch, Jr. and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1968).

(8) D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969).

(9) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(10) In 9,10-dihydroanthracene systems, the two allylic protons can have a chemical shift up to 0.3 ppm and can have a coupling constant of 18 Hz: D. Nicholls and M. Szwarc, *J. Amer. Chem. Soc.*, **88**, 5757 (1966); R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969).

(11) We wish to thank D. H. Gibson and A. Shultz, University of Colorado, Boulder, Colo., for recording the 100-MHz spectra and for the irradiation experiments.

(12) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, New York, N. Y., 1965, p 363; R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961). Since J_{AB} should be about 18 Hz,[10] $\nu_0\delta_{AB}$ and $^1/_2(J_{AX} - J_{BX})$ could be a few hertz or less.

trans-dihydro compound[7,13–15] (*cis*-**6** and *trans*-**6**). If J_{cis} were significantly different from J_{trans}, then in the nmr spectrum of **6** each isomer should have two doublets distinguishable from those of the other isomer. However, the nmr spectrum of **6** exhibited (along with an acid proton at δ 12.05) only two sharp doublets centered at δ 3.73 and 2.58 with $J = 8.3$ Hz.[16] Thus, J_{cis} and J_{trans} were not significantly different.

The coupling constants for **5** and for **6** were slightly different (0.3 Hz). This observation has the following implications. In our sample of **6**, one isomer (either *cis* or *trans*) predominated whose coupling constant was 8.3 Hz. The other isomer, in order to average out J_{app} in **5** to be 8.6 Hz in an ABX system, must have $J = 8.9$ Hz. Thus, the J_{cis}/J_{trans} ratio (either 8.3/8.9 = 0.93 or 8.9/8.3 = 1.07) would be very close to unity.

If the puckering in **5** were intermediate between that in **1** and **2**, one would expect the J_{cis}/J_{trans} ratio for **5** to be between that of **1** and **2**. However, the ratio for **5** lies outside this range and is less than that for **1**. It is difficult to believe that **5** is *less* puckered than **1**. Instead, it is to be concluded that the J_{cis}/J_{trans} ratio is only a rough approximation of the degree of puckering, and that **1** and **5** are puckered to about the same extent. Since **5** would be expected to be puckered (*vide supra*), it would seem that 1,4-cyclohexadiene (**1**) is definitely in a boat conformation and that a single moderately sized substituent can be fitted into this conformation comfortably in the pseudo-equatorial position.

Experimental Section

Melting points were determined by a Thomas-Hoover melting point apparatus. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer and a Varian HA-100 spectrometer, using tetramethylsilane as the internal standard. Ultraviolet spectra were recorded on a Beckman DB spectrophotometer.

1,4-Dihydrobenzoic Acid (5).—This compound was prepared from benzoic acid by the procedure of Kuehne and Lambert[13] and was transparent in the region of 240–270 mμ, indicating the absence of the 1,3-cyclohexadiene chromophore.

Benzoic Acid-d_5.—Reaction of bromobenzene-d_5 (Stohler Isotope Chemicals, Azusa, Calif.) with magnesium and subsequent carbonation with Dry Ice[17] gave benzoic acid-d_5 in a 50% yield, mp (H_2O) 119–121°. An nmr spectrum of the product exhibited no signals in the aromatic region.

2,3,4,5,6-Pentadeuterio-1,4-dihydrobenzoic Acid (6).—Birch reduction of benzoic acid-d_5 in the usual manner[13] gave an 82% yield of **6**, bp 77–79° (0.4 mm).

Registry No.—**5**, 4794-04-1.

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(13) M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963).

(14) G. W. Brown and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7116 (1967).

(15) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969).

(16) Owing to the small extent of aliphatic-olefinic coupling in **5**, D–H coupling in **6** was negligible and deuterium decoupling was not necessary.

(17) H. Gilman, N. B. St. John, and F. Schulze, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 425. Our procedure is different from that of Gilman in that the Grignard reaction mixture was poured over Dry Ice instead of bubbling in gaseous carbon dioxide.

Electronic and Nuclear Magnetic Resonance Spectra of Dithizone

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Several metal complexes of dithizone (1,5-diphenylthiocarbazone) are photochromic when irradiated with visible light.[1] During a study of this photochromic system,[2] we became interested in the electronic spectra and photochromism of dithizone itself.

When dissolved in methylene chloride, dithizone forms an intense green solution having the spectrum shown by the solid line in Figure 1. Intense irradiation of the green solution with visible light, in *dry*, nonpolar solvents, produces a red, metastable form (dashed line in Figure 1) which returns very rapidly to the original green.[3] The orange, nonphotochromic dithizonate anion produced in alkaline solution is shown by the dotted line in Figure 1.

It is unusual for a neutral molecule of this size to possess the intense, low-energy absorption (molar absorptivity ≅ 37,000 at 6100 Å) shown by the long-wavelength band of the green form. No comparable band exists for the oxygen analog of dithizone (diphenylcarbazone) which is orange in neutral solution because of a weak $n \rightarrow \pi^*$ transition appearing as a shoulder on intense ultraviolet $\pi \rightarrow \pi^*$ transitions.

The relative intensities and $\lambda_{\max}$ values for the two visible bands in the dithizone spectrum depend upon the solvent, and some workers[4] have interpreted these changes to indicate that the two bands originate from a thiol–thione tautomeric system. Although we have observed such solvent effects, we have been unable to interpret them rigorously, since they appear to be complicated by acid–base equilibria, trace metal effects, and even oxidative decomposition of the dithizone.

We could not obtain the nmr spectrum of dithizone itself because of poor solubility, but we have obtained the spectrum of an alkylated derivative [1,5-di(*o*-ethylphenyl)thiocarbazone] in $CDCl_3$. The chemical shifts (τ values referred to TMS, Varian A-60) were −2.03 (1.6 protons), 1.9 and 2.67 (8 aromatic), 7.0 (4 methylene), and 8.6 (6 methyl). The signal at τ −2.03 showed no evidence of splitting over the temperature range +50 to −45° in $CHCl_3$ solution (in fact, the peak became somewhat narrower at lower temperatures) and disappeared upon addition of CH_3OD.

We feel that these nmr results favor a single (equivalent proton) structure instead of rapid exchange between a form containing S–H and a form containing N–H. For the latter case we would expect splitting

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(1) L. S. Meriwether, E. C. Breitner, and C. L. Sloan, *J. Amer. Chem. Soc.*, **87**, 4441 (1965).

(2) R. A. Coleman, W. H. Foster, Jr., J. Kazan, and M. Mason, Final report, "Synthesis of Chromotropic Colorants," Feb 1966, U. S. Army Natick Laboratories, Natick, Mass., Contract No. DA19-129-AMC-269(N), issued as Technical Report 66-0-CM, Series TS-138, AD630908.

(3) The photochromism of dithizone was previously reported by Meriwether, *et al.*[1]

(4) P. S. Pel'kis and R. G. Dubenko, *Zh. Obshch. Khim.*, **29**, 194 (1959).