pared to arylsilylcarbinols.[9,11] As might have been expected, on the basis that germylcarbinols do not rearrange to the corresponding germyl ether, when benzoyltriphenylgermane was treated with diazomethane phenacyltriphenylgermane was the only rearrangement product observed.

Further results, including the stereochemistry of the reaction at silicon, will be reported shortly.

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(11) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Am. Chem. Soc.*, **81**, 981 (1959).

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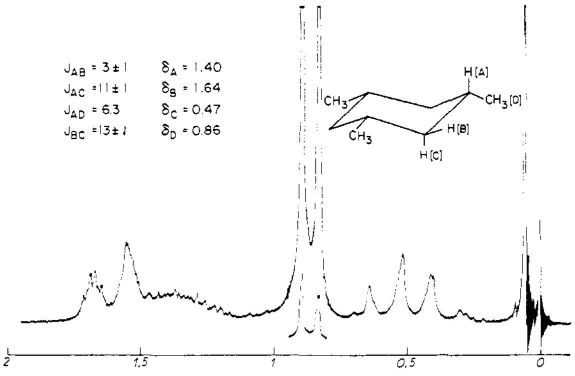
"Anomalous" Chemical Shifts in the Nuclear Magnetic Resonance Spectra of the 1,3,5-Trimethylcyclohexanes

Sir:

The nmr spectra of saturated cyclic organic molecules have been of considerable interest since the early work of Lemieux, *et al.*,[1] and Musher and Richards,[2] which showed the ability of nmr to distinguish among configurational isomers. Much of the work on the chemical shifts of carbocyclic molecules—as distinguished from saturated heterocycles, such as dioxane—has been, almost of necessity, restricted to observations on the carbinol protons of cyclohexanols.[1,3–5] The present empirical understanding of the effect of neighbor interactions on these chemical shifts is due to Eliel and co-workers[4] and to the recent work of Booth,[5] while attempts at the corresponding theoretical interpretation must be deemed relatively unsatisfactory,[3,6] particularly for nearest neighbor interactions.



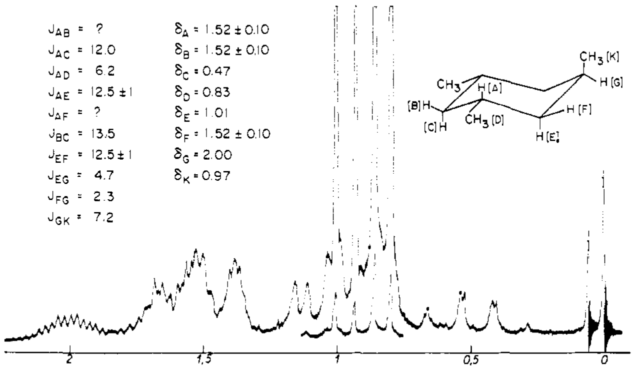


Figure 1 (top). The nmr spectrum of *cis,cis*-1,3,5-trimethylcyclohexane.

Figure 2 (bottom). The nmr spectrum of *cis-trans*-1,3,5-trimethylcyclohexane.

Owing to the large numbers of protons involved, there have been very few carbocyclic molecules whose spectra were found to be sufficiently simple to provide even approximate complete analyses.[7] Thus, despite advances in the use of massive deuteration and variable temperature probes, the chemical shifts of the various protons in some simple cyclic hydrocarbons are not known. Muller and Tosch[8] have discussed some "anomalous" features of the 60-MHz spectra of some of these hydrocarbons, which have been recently interpreted by Booth,[5] and this, along with our own similar unpublished work,[3] has prompted the present study of the two isomers of 1,3,5-trimethylcyclohexane at 100 MHz.

The nmr spectra of *cis,cis*-1,3,5- (I) and *cis,trans*-1,3,5-trimethylcyclohexane (II) taken at 100 MHz in dilute solution in CCl_4 and referred to internal TMS[9] are given in Figures 1 and 2, respectively. Also given in the figures are the coupling constants in hertz (absolute values) and chemical shifts in parts per million which could be obtained from straightforward first-order analyses aided and checked by double irradiation methods. For example, the doublet to low field of the methyl peaks in II was shown to be the low-field part of a triplet in which proton E is coupled to protons A and F by irradiating G. Also, although the conservative numbers in the figure give the same chemical shift for the protons A, B, and F of II, they were shown to be strongly coupled since irradiation at δ 1.62 ± 0.03 caused both the quartet of C and the methyl doublet of D to collapse, which thus favors somewhat centering A and B at δ ~1.62 with F at δ ~1.45. Since the total number of spins in each molecule is 18, complete analyses were not possible and, unless otherwise indicated, the errors in the δ's and in the J's for the ring protons are 0.02 ppm and 0.2 Hz, respectively, being for the most part due to the first-

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(1) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957); **80**, 6098 (1958).

(2) J. I. Musher and R. E. Richards, *Proc. Chem. Soc.*, 230 (1958). See also footnote 10 of J. I. Musher, *J. Am. Chem. Soc.*, **83**, 1146 (1961), for a discussion of the significance of the relatively sharp signal of *cis*-decalin and the dimethylcyclohexanes.

(3) J. I. Musher, Ph.D. Thesis, Harvard Univerity, 1962 (unpublished). Some of the data in this thesis are reported in J. I. Musher, *J. Chem. Phys.*, **35**, 1159 (1961). See also J. I. Musher, *ibid.*, **37**, 192 (1962), and *Mol. Phys.*, **6**, 93 (1963), for some critical remarks on the theoretical interpretation.

(4) E. L. Eliel, M. H. Gianni, T. H. Williams, and J. B. Stothers, *Tetrahedron Letters*, 741 (1962).

(5) H. Booth, *Tetrahedron*, **22**, 615 (1966).

(6) See A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1966), for a review of the more recent literature.

(7) See, *e.g.*, (a) J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961); (b) A. Segre, *Tetrahedron Letters*, **17**, 1001 (1964).

(8) N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962). The recent study of R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965), shows that the introduction of a methyl group at the angular position in adamantane shifts the adjacent methylene protons 0.30 ppm upfield.

(9) The peak at 7-Hz low field from TMS is due to hexamethyldisiloxane.

order analyses. The errors for both δ's and J's for the methyl protons are 0.1 Hz (0.001 ppm), and a rough upper limit on the various possible ^4J's which were not explicitly observed is 1.0 Hz.

The first striking observation is that the axial protons both at δ 0.47 in molecules I and II are probably the highest field noncyclopropanic methylenic protons which have been analyzed in the literature. These axial protons, which are sandwiched between two equatorial methyl groups, are what give rise to the "anomalous" high-field peaks in the 60-MHz spectra of *cis*-1,3-dimethylcyclohexane,[3,8] *cis*-1,1,3,5-trimethylcyclohexane,[8] and *cis*-3-methylcyclohexanol[3] reported previously, along with those of a number of 1,3-disubstituted cyclohexanes studied in our laboratories and interpreted by Booth.[5] They are shielded by 0.73 ppm from the axial protons in cyclohexane (δ 1.20),[10] in quite good agreement with the empirical prediction[5] based on the cyclohexanols[4] of 0.93 ppm.[11] The other axial methylenic protons of II are only shielded by 0.19 ppm relative to cyclohexane, which also compares relatively well with the prediction[4] of 0.27 ppm, and illustrates the important effect of the axial methyl group on the *trans* β-proton.[4]

The next striking observation is that the equatorial protons in I at δ 1.64 are shielded only by 0.04 ppm from the equatorial proton in cyclohexane (δ 1.68).[10] This is in severe disagreement with the predictions of 0.56 and 0.80 ppm based on the cyclohexanols[4] and on the cyclohexylamines,[5] respectively. What is more disturbing is that, if relatively undistorted geometry is assumed, then the equatorial methyl group is in precisely the same orientation with respect to both the adjacent methylene protons. Thus a shift of one proton without a comparable shift of the other cannot be rationalized by any theory whatsoever which does not go into the detailed electronic structure of the many-electron system. Unless there is significant molecular distortion, this result must be interpreted to mean, in simple language, that the substitution of an equatorial methyl group for a hydrogen atom affects the neighboring methylenic CH bonds differently because they were different (due to their neighboring geometry) to begin with.[14] Notice, *a propos*, that in the absence of geometric distortions all the equatorial methylenic protons in the two molecules are in identical immediate environments, and experiment shows all these chemical shifts to differ by 0.2 ppm at most.

The methine and methyl proton resonances also possess some features of interest. The axial methine proton at δ 1.40 (I) and δ ~1.52 (II) are close to the δ 1.4 estimated by Anet[13] for methylcyclohexane, and also to the δ 1.20 of the axial protons in cyclohexane itself, which corroborates Anet's strong coupling argument. The possible difference of 0.12 ± 0.10 between the values for these two protons can be compared with the ~0.2 ppm found in similar systems.[5] In II there are both axial and equatorial methine protons which differ by ~0.5 ppm, as in cyclohexane itself.

The axial methyl protons in II are *deshielded* relative to the equatorial methyl protons (which differ little from those in I) by 0.14 ppm. This is in the opposite direction from the axial–equatorial differences normally observed in the methylene protons, although it is in the same direction as observed for acetoxy groups.[7a] The low-temperature spectra[8] of *trans*-1,3- and *cis*-1,4-dimethylcyclohexanes exhibit the same behavior if the methyl groups are distinguished[12] by their different splittings (apparent coupling constants). While it is tempting to attribute this shift to the van der Waals deshielding due to the 1,3-diaxial interaction, it seems premature to do so. Clearly such effects depend on neighbor interactions, but examples such as *cis*-1,2-dimethylcyclohexane,[8] for which the methyl groups seem to have the same chemical shift, preclude such a simple picture. The apparent coupling constants of the methyl protons to the methine protons are 6.3 (5.2) Hz for the equatorial methyl of I and 6.2 (5.9) and 7.2 (7.2) Hz for the equatorial and axial methyls of II, respectively, in spectra taken at 100 (60)[3] MHz. The relatively small field dependence and the sharpness of the splitting of the equatorial methyl in II imply that the true J is close to the measured 6.2 Hz, and therefore we observe that axial methyl protons have a somewhat larger coupling constant with their methine proton than equatorial methyl protons have. Notice also that the strong coupling in I, as exhibited by the field dependence of the methyl splitting, takes place as much *via* the equatorial protons as through the axial protons as the respective (J/ν)'s are about equal.[15]

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(10) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964); F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *ibid.*, 146 (1964). The $\Delta\delta = 0.48$ ppm of these authors, neglecting isotope shifts, has been related to the known δ 1.436 of dilute cyclohexane in CCl_4 solution, to give the values used for the equatorial and axial protons. These differ by 0.03 ppm from those of Booth[5] based on ref 8.

(11) Booth[5] has also used such a prediction to explain the relatively sharp low-temperature spectrum of *cis*-1,2-dimethylcyclohexane (see also ref 2) and the sharp methyl peak of *trans*-1,2-dimethylcyclohexane. The present data can interpret the related fact that the methyl groups in *cis*-1,3-dimethylcyclohexane[12] and in *cis*-3-methylcyclohexanol[3] show apparent coupling constants of 3.7 and 4.9 Hz, respectively, as compared with the virtually unsplit methyl signals of the *trans*-1,2 and *trans*-1,4 derivatives (all at 40 MHz). The argument of Anet,[13] which explains the broad equatorial methyl peaks as distinguished from the sharp axial methyl doublets in terms of strong (or virtual) coupling among axial protons, predicts this observed approach to first-order spectra as the chemical shift differences of the axial protons is increased (which also occurs when the magnetic field strength is increased).[3,8]

(12) J. I. Musher, *Spectrochim. Acta*, 16, 835 (1960).

(13) F. A. L. Anet, *Can. J. Chem.* **39**, 2262 (1961). The first published spectrum of methylcyclohexane is in L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(14) For comparison purposes, the chemical shifts of the axial and equatorial protons in the analogous *cis,cis*-1,3,5-tri(4-pyridyl)cyclohexane[7b] are δ 1.80 and ~2.25, respectively. Apparently the pyridyl groups *deshield* the methylene protons equally (0.6 ppm) with respect to cyclohexane.

(15) Note Added in Proof. We have been informed that N. Muller and O. R. Hughes had previously analyzed the 100-MHz spectrum of compound I [M.Sc. thesis of O. R. Hughes, Purdue University, 1964]. They noted explicitly the "anomalous" behavior of the interaction of the neighbor methyl groups with the geminal protons and based on this they observed that "it seems hard to escape the conclusion that any *simple* theory of the origin of chemical shifts must be wrong."