^{1}H Nuclear Magnetic Resonance at Unnatural Abundance. First-order Spectra from Alicyclic and Aliphatic Hydrocarbons

By J. J. KATZ,* G. N. MCDONALD, and A. L. HARKNESS
(*Chemistry Division, Argonne National Laboratory, Argonne, Illinois* 60439)

Summary First-order ^{1}H n.m.r. spectra can easily be obtained from deuteriated alicyclic and aliphatic hydrocarbons containing a small amount of randomly distributed ^{1}H.

DEUTERIUM compounds in which ^{1}H is randomly distributed at a low, unnatural abundance permit the same kind of spectral simplification for ^{1}H magnetic resonance as is observed in ^{13}C spectra recorded at natural abundance. The potential value of such a procedure in eliminating spin–spin couplings from ^{1}H-spectra was clearly recognized by Garnett *et al.*[1] some years ago, but the recent development of pulse techniques for n.m.r. spectroscopy, with the attendant increase in the rate of data acquisition, now makes the use of ^{1}H at a low unnatural abundance a practical proposition. Under ^{2}H-decoupling, the spectra are then inevitably first-order. As it is possible to synthe size ^{2}H-compounds containing a small amount of statistically distributed ^{1}H by quite general procedures,[2] and to obtain compounds of biological importance (proteins, lipids, plant pigments, carbohydrates, *etc.*) of suitable isotopic composition by biosynthesis,[3] this procedure for simplifying ^{1}H n.m.r. spectra may find many uses.[4]

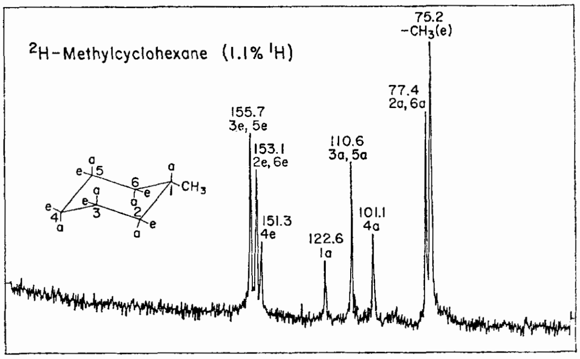

FIGURE. *First-order ^{1}H n.m.r. spectrum of methylcyclohexane recorded at* 100 *MHz by pulsed Fourier-transform spectroscopy. Chemical shifts are in Hz downfield from hexamethyldisiloxane. Concentration:* 1·9M *in* CCl_4*; sampling time,* 1000 *μs; pulse interval,* 4·3 *s;* 100 *pulses; total collection time,* 7·2 *min.*

The Figure shows a first-order fully assigned ^1H n.m.r. spectrum of methylcyclohexane, recorded on commercial [^2H]methylcyclohexane containing 1·1% ^1H. All the expected proton resonances are clearly visible. Assignments were made to be compatible with the partial assignments of Lambert and Takeuchi[5] from the spectra of [1,2,3,3,5,5-$^2H_6$]methylcyclohexane, and those of Garbisch *et al.*[6] for [3,3,4,4,5,5,6,6-$^2H_8$]methylcyclohexane. All three of the expected resonances of the CH_2 protons of n-octane can be obtained for ^2H-n-octane (*ca.* 3% ^1H) and four of the expected five CH_2 proton resonances are resolved in ^2H-n-dodecane (0·5% ^1H).[7] The CH_2 resonances for both hydrocarbons fall within a range of 3·7 Hz (at 100 MHz) and differences in chemical shifts of 0·6 Hz have been successfully resolved.

Some problems should be noted. ^1H n.m.r. spectroscopy at unnatural abundance demands very pure samples. Adventitious impurities, such as residual solvent, contain ^1H, and may therefore easily contribute as much to the spectra as the small amount of ^1H in the compound of interest. Further, it must be remembered that the compounds contain mainly ^2H, and thus, the ^1H chemical shifts are subject to deuterium isotope effects, which although small, are not necessarily negligible. Finally, spin–spin coupling information is lost, but it may be possible to choose a concentration of ^1H large enough to show spin–spin interactions without unduly complicating the spectrum.

(*Received*, 31*st January* 1972; *Com.* 145.)

---

[1] J. L. Garnett, L. J. Henderson, W. A. Sollich, and G. Van Dyke Tiers, *Tetrahedron Letters*, 1961, 576.

[2] J. L. Garnett and W. A. Sollich, *Austral. J. Chem.*, 1962, **15**, 56; Nguyen-Dinh-Nguyen and E. A. Stenhagen, Fr. P., 1,406,088 (Cl. C 07C), 1967; (*Chem. Abs.*, 1967, **67**, 63814).

[3] J. J. Katz and H. L. Crespi, in C. J. Collins and N. S. Bowman, 'Isotope Effects in Chemical Reactions,' A.C.S. Monograph 167, Van Nostrand Reinhold Co., New York, 1970, ch. 5, pp. 286—353.

[4] J. J. Katz and H. L. Crespi, *Pure Appl. Chem.*, 1972, in the press.

[5] J. B. Lambert and Y. Takeuchi, *Org. Magnetic Resonance*, 1969, **1**, 345.

[6] E. W. Garbisch, jun., B. L. Hawkins, and K. D. McKay, in C. Chindoglu, 'Conformational Analysis,' Academic Press, New York, 1971, pp. 93—109.

[7] J. G. Atkinson, M. O. Luke, and R. S. Stuart, *Canad. J. Chem.*, 1967, **45**, 1571.