in the relative intensity of this band. In compounds such as $C_8H_8PtI_2$, the reduction in intensity is very slight while the intensity of the band is decreased by a factor of 10 to 100 in the binuclear compounds.

The conformation of the cycloöctatetraene in this series of compounds currently is being investigated by X-ray diffraction techniques on single crystals of I.[5] Preliminary results indicate that the crystals are monoclinic with four molecules in a unit cell of a parameters a = 10.95 Å., b = 11.19 Å., c = 10.78 Å. and β = 111.2°. From characteristic absent reflections the crystals were assigned tentatively to space group C2/c or Cc. The shortest Pt–Pt distance was 4.03 Å. as determined from the two-dimensional Patterson function and a least squares refinement on the platinum contribution to the structure factor.

In $(OC)_3FeC_8H_8Fe(CO)_3$ Dickens and Lipscomb reported an eight membered "chair" configuration for cycloöctatetraene. In compound I the observed Pt–Pt bond distance is in close agreement with the distance one might expect if the cyclooctatetraene retained a "tub" configuration.

Further details on the preparative studies and structure determination will be reported shortly.

We wish to thank the Research Corporation for support.

(5) We wish to acknowledge the support of the Office of Ordnance Research in carrying out the structural studies.

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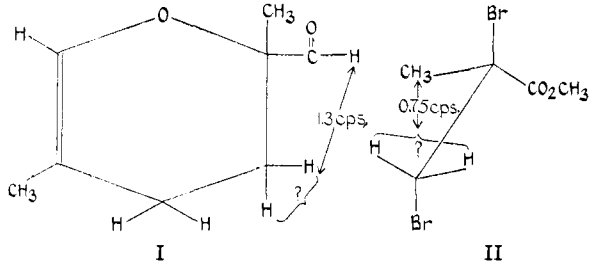
RECEIVED APRIL 26, 1961

LONG-RANGE SPIN–SPIN COUPLINGS IN THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF BICYCLO[2.1.1]HEXANES[1]

Sir:

The usual assumption that proton spin–spin couplings are negligibly small over more than three bonds in saturated systems[2] recently has been shown to be unfounded by the discovery of several counter-examples.[3] Thus, the aldehydic proton of



Long-range spin–spin couplings

methacrolein dimer (I) has been found to be split into a doublet (J = 1.3 cps.) by *one* of the two β-hydrogens, four single bonds away. Similarly, one of the non-equivalent methylene protons of methyl α,β-dibromoisobutyrate (II) couples with the α-methyl group (J = 0.75 cps.). We wish to report the first example of long-range spin–spin couplings of this type in rigid molecules, where the coupled protons occupy readily definable positions in space.[4]

The n.m.r. spectrum[5] of *exo*-5-chlorobicyclo-[2.1.1]hexane-*exo*-6-*t*-butylcarboxamide (III)[6] (see Fig. 1A) shows this long-range coupling with startling clarity. Peaks at 327 (broad), 173, 109 and 82 cps. of relative intensity 1:2:4:9 correspond to NH, bridgehead, methylene and *t*-butyl protons, respectively. The two doublets at 229 and 150 cps. form a typical AB pattern ($J \cong 7$ cps.), and must arise from the two protons on the one carbon bridges. From the values of the chemical shifts for these peaks,[7] the former may be assigned to the *endo* proton on the chlorine-bearing carbon (C_5) and the latter to the *endo* proton α to the amide group (C_6). It appears, then, that these two distant protons, at opposite corners of a folded cyclobutane ring, are responsible for this clear AB pattern. The extreme simplicity of this analysis is made possible by the apparent equivalence of the two methylene protons *cis* to the chlorinated bridge and those *cis* to the amide bridge, and by the fact that all the remaining 1,2-coupling constants (between the bridgehead protons and those on C_2, C_3, and the *endo* C_5 and C_6 positions) are either zero or else very small.[8]

In order to strengthen these arguments, the α-deuterioamide IV has been prepared and its n.m.r. spectrum examined (see Fig. 1B). The results are in accord with expectations. Thus, the proton at C_5 is now unsplit, the C_6 proton has vanished (indicating essentially complete deuteration), and the remainder of the spectrum is unchanged.

We also have examined the epimeric amides V and VI, in which the C_6 proton or deuteron occupies an *exo* position, with the results shown in Fig. 1C and 1D. Not unexpectedly, the upper and lower pairs of methylene protons in these compounds are no longer equivalent, so that they now give rise to a complex A_2B_2 pattern. Significantly, the 7 cps. long-range coupling no longer appears, demonstrating its rather special geometrical requirement. In the case of V, the bridgehead hydrogens are split into a doublet ($J \cong 2$ cps.) by the single *exo* C_6 proton. Interestingly, the C_6 proton itself, in its new configuration, is shifted downfield to a position about the same as that of the C_5 proton. Once

(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the 139th National Meeting in St. Louis, March 21–30, 1961 (abstract page 39-O).

(2) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chapt. 3; L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapt. 6; M. Karplus, *J. Am. Chem. Soc.*, **82**, 4431 (1960).

(3) D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

(4) For calculations of the shapes of bridged molecules of the type used in this study, see C. F. Wilcox, Jr., *ibid.*, **82**, 414 (1960).

(5) All spectra were taken at 60 Mc. in $CDCl_3$ with tetramethylsilane (0 cps., τ = 10) as an internal standard.

(6) The syntheses of all compounds discussed in this paper, as well as evidence for their configurations, will be described in detail in a forthcoming publication.

(7) L. M. Jackman, ref. 2, Chapt. 4; Figs. 1A and C give peak positions in both cps. and τ values, while Figs. 1B and 1D show τ values only.

(8) These fortunate but unexpected observations emphasize the limitation of the correlation of coupling constants with dihedral angles, as treated by M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

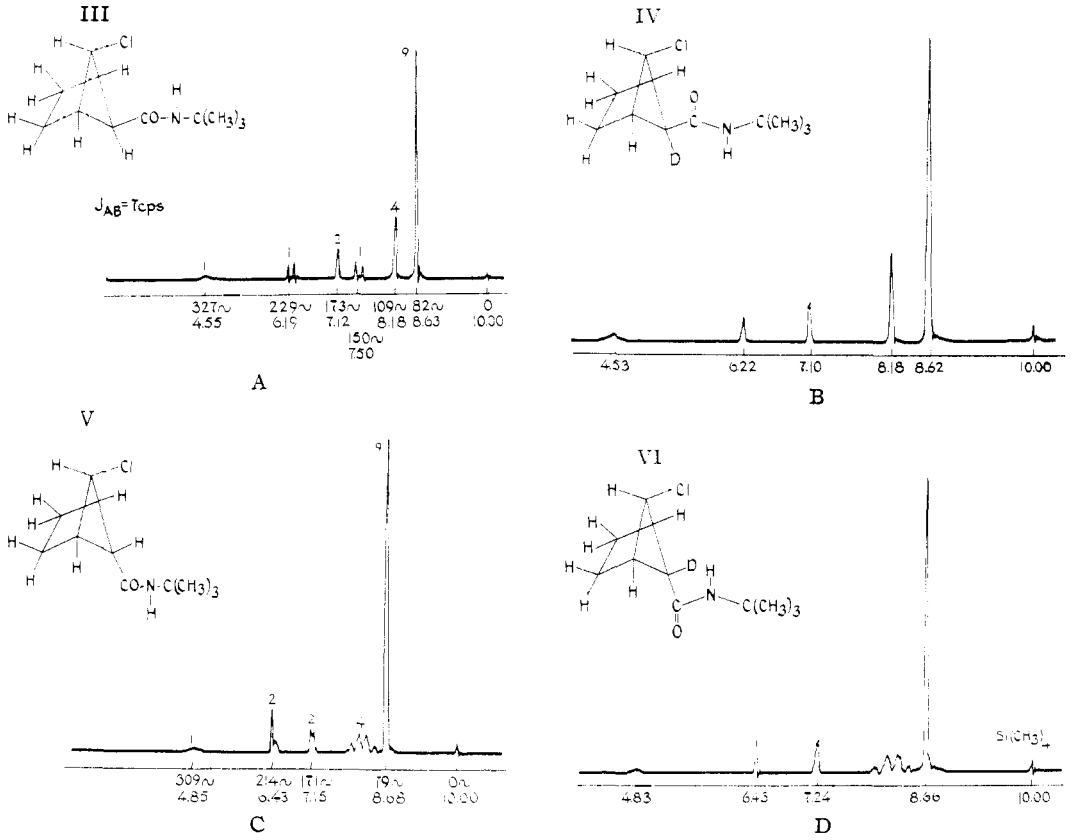


Fig. 1.—Nuclear magnetic resonance spectra: Curve A, 5-*exo*-chloro-6-*exo*-amide (III); curve B, 5-*exo*-chloro 6-*endo*-deuterio-6-*exo*-amide (IV); Curve C, 5-*exo*-chloro-6-*endo*-amide (V); Curve D, 5-*exo*-chloro-6-*exo*-deuterio-6-*endo*-amide (VI).

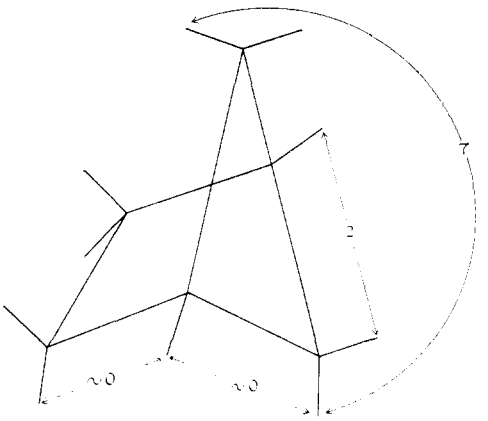


Fig. 2.—Some approximate proton spin–spin coupling constants for bicyclo[2.1.1]hexanes.

more, the deuterated analog (VI) shows remarkable simplicity.

These results, summarized in Fig. 2, suggest rather extensive interactions between a specific pair of protons separated by four single bonds, and smaller interactions between several pairs of adjacent protons. The long-range interaction may be rationalized by assuming fairly extensive overlap between the small lobes of the orbitals directed 180° away from the directions of the *endo* C_5 and C_6 to proton bonds (and consequently pointed *toward* each other). This explanation appears reasonable when a scale model[4] of the bicyclo[2.1.1]hexane nucleus is examined.

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(3) John Simon Guggenheim Foundation Fellow, 1960–1961. This author is most thankful to the Department of Chemistry of Stanford University for its cordial hospitality during the Winter and Spring 1961 Quarters.

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RECEIVED APRIL 15, 1961

THE STEREOCHEMISTRY OF THE ETHYLENEDIAMINETETRAACETATOAQUOFERRATE (III) ION[1]

Sir:

A persuasive *a priori* case for a fully chelated (*i.e.*, sexadentate) and *seven*-coördinate formulation, $Fe(OH_2)Y^-$, of the common ethylenediaminetetraacetato (EDTA; Y^{4-}) complex of ferric iron

(1) Part of a program supported by the National Science Foundation. We thank also the U. S. Army Research Office (Durham) and the Advanced Research Projects Agency for support of the work reported here.