A Novel Type of Long-range Spin Coupling across Five Single Bonds[1]

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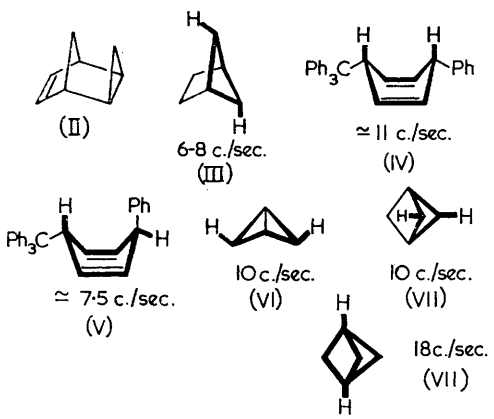
IN recent years, a number of types of long-range spin coupling have been reported and discussed.[2] In the course of n.m.r. studies of bridged ring compounds, we have found a novel type of long-range spin coupling across five single bonds in the 100 Mc./sec. spectrum of *endo*-tricyclo[3,2,1,$0^{2,4}$]-oct-6-ene (I),[3] which was taken with a Varian HA-100 spectrometer in the frequency-swept and external Me_4Si-locked mode as shown in Figure 1(a). To confirm the assignment of the signals, we made n.m.d.r. and n.m.t.r. experiments using two Hewlett–Packard HP-200ABR audio-oscillators and an HP-5212A electronic counter. On double irradiation at the frequency of the signal of H-6 (H-7), the downfield half of an AB-type quartet (τ 8·24 and 8·33), further split into multiplets, became somewhat sharper as shown in Figure 1(b). This fact results from the disappearance of the long-range spin couplings of H-8a to H-6 and H-7.[2a] Thus the signals at τ 8·24 and 8·33 were assigned to those of H-8a and H-8s, respectively. Double irradiation on H-1 and H-5 (τ 7·27) changes the signals of H-8a, H-8s, and H-2 (H-4) into those shown in Figure 1(c). It is quite certain from the coupling constants of protons on a cyclopropane ring that the multiplet at τ 9·46 and the doublet of triplets at τ 9·66 arise from H-3x and H-3n, respectively. Since it became highly possible that there is a long-range spin coupling between H-3x and H-8s in view of the spectra shown in Figures 1(a) and 1(c), we further made spin-decoupling experiments to confirm this finding. Double irradiation on H-8s and H-2 (H-4) gave the spectra shown in Figures 1(d) and 1(e), respectively. On triple irradiation at



the frequencies of H-1 (H-5) and H-3x, the signals of H-8a and H-8s collapse to an clear AB-type quartet as shown in Figure 1(f). Therefore, the existence of the long-range spin coupling of 2·3 c./sec. between H-3x and H-8s has been confirmed. On the other hand, all attempts to find out a similar coupling between the bridge-methylene protons and the methylene protons on

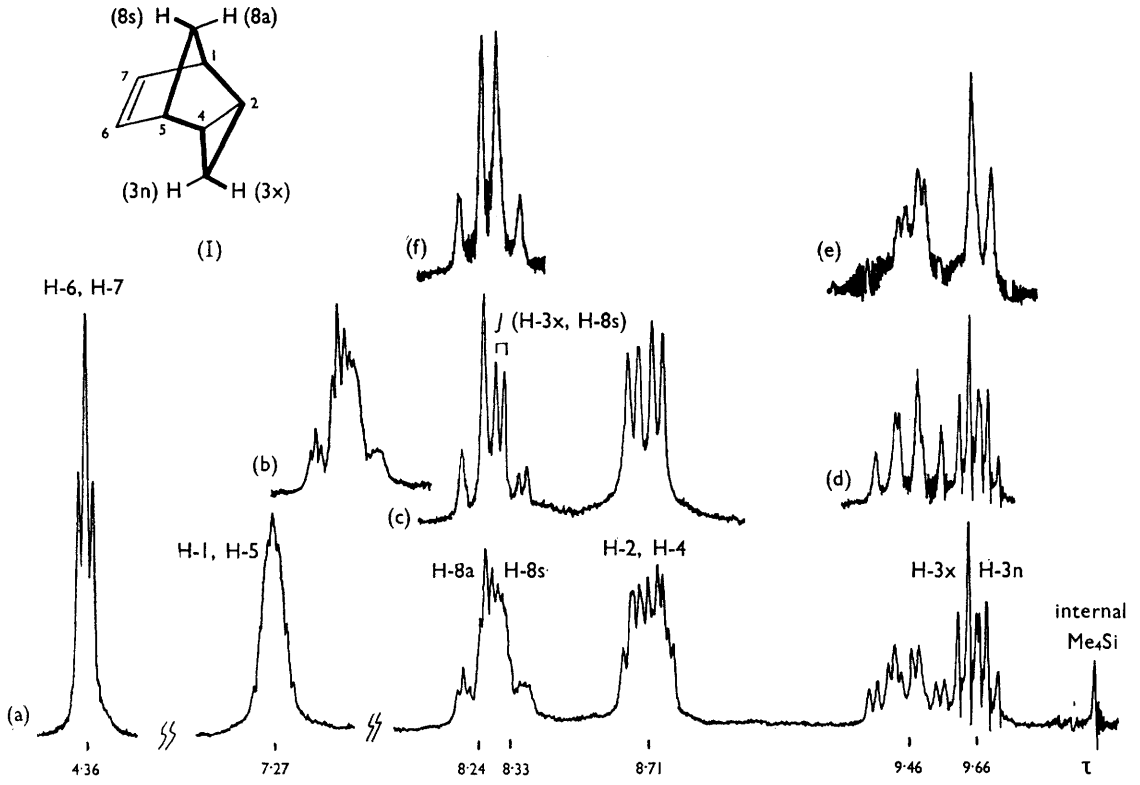


FIGURE 1

(a) N.m.r. spectrum of endo-*tricyclo*[3,2,1,$0^{2,4}$]-*oct*-6-*ene in carbon tetrachloride* (5%) *at* 100 *Mc./sec. (b) N.m.d.r. spectrum irradiated on H–6 and H–7. (c) N.m.d.r. spectrum irradiated on H–1 and H–5. (d) N.m.d.r. spectrum irradiated on H–8s. (e) N.m.d.r spectrum irradiated on H–2 and H–4. (f) N.m.t.r. spectrum irradiated on H–3x, and H–1 and H–5.*

the cyclopropane ring in tricyclo[3,2,1,$0^{2,4}$]-*exo*-oct-6-ene (II)[4] were unsuccessful.

This surprisingly large value of the long-range coupling across five single bonds in (I) can result from the transmission through the double "zig-zag" paths of σ-bonds between the two protons. Probably, the intervening cyclopropane ring also plays a significant role. Similarly, unexpectedly large values of long-range couplings have been observed in the spectra of several bicyclo[2,1,1]-hexane derivatives (III),[5] cyclohexa-1,4-dienes (IV and V),[6] and bicyclo-[1,1,0]butane and -[1,1,1]pentane derivatives[7] (VI and VII). These large values can also be ascribed to the double or triple path mechanism.[2b,6,8]

(*Received, October 25th,* 1966; *Com.* 822.)

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[8] We are indebted to Dr. J. M. Lehn of Université de Strasbourg, who gave us valuable information.

The following papers were originally published in Chem. Comm. 1966, 810, 812. *Unfortunately a block was accidentally omitted, which renders both papers unintelligible. We are therefore reproducing the two papers with all three blocks of formulae.*