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LONG-RANGE "VIRTUAL" COUPLING IN
exo,*exo*-3,6-DIBROMOBICYCLO[2.2.1]HEPTAN-2,5-DIONE

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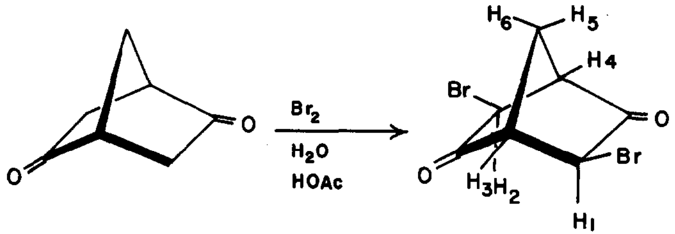
Long-range proton coupling over three intervening carbon atoms in the bicyclo[2.2.1] skeletal system is usually only observed when a particular geometrical arrangement, the "W" pattern, is present (3,4,5,6). The nuclear magnetic resonance (nmr) spectrum of *exo*,*exo*-3,6-dibromobicyclo[2.2.1]heptan-2,5-dione (II) was of interest, therefore, since it allowed the clear observation of the three different kinds of protons in this skeletal system.

Compound II (7) was prepared in a 35% yield by the bromination of bicyclo[2.2.1]heptan-2,5-dione (I) (8,9) with two moles of bromine under acidic conditions. The nmr spectrum (10) of II consisted of a triplet at 4.15 ppm (2 protons), a triplet at 3.30 ppm (2 protons), and a quintet at 2.26 ppm (2 protons) (Fig. 1).



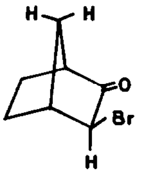
I

II

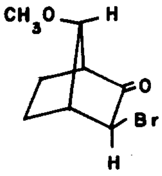
When H_5,H_6 was decoupled, the triplets of H_3,H_4 and H_1,H_2 both collapsed to singlets. Therefore, $J_{13} = J_{24} = 0$, which establishes the *exo*-configuration of the bromine atoms. It has been demonstrated that bridgehead protons in the bicyclo[2.2.1]heptanes couple to the adjacent *exo*-protons (J = 3-4 cps), but not to the adjacent *endo*-protons (5,6,11). When H_3,H_4 was decoupled, the triplet of H_1,H_2 was unaffected and when H_1,H_2 was decoupled, the triplet of H_3,H_4 was unaffected, confirming that $J_{13} = J_{24} = 0$.

When H_1,H_2 was decoupled, the quintet of H_5,H_6 collapsed to a triplet with a coupling constant of 1.3 cps. The magnitude of this coupling is consistant with the coupling of bridgehead protons to methylene bridge protons reported for similar compounds (J = 1-2 cps) (5,6).

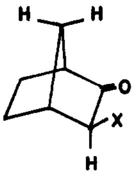
The unexpected observation was the triplet observed for H_1,H_2 and the quintet observed for H_5,H_6, which can be explained in terms of "virtual" coupling. Ordinarily, only the methylene bridge proton *anti* to the *endo*-proton produces splitting. For example, the *endo*-3-proton of *exo*-3-bromobicyclo[2.2.1]heptan-2-one (*III*) is a doublet (J = 3-4 cps), but the *endo*-3-proton of *exo*-3-bromo-*anti*-7-methoxybicyclo[2.2.1]heptan-2-one (*IV*) is a singlet. Similar results are observed for the *exo*-3-substituted norcamphors (*V*) and the *exo*-3-substituted camphors (*VI*), respectively (2).



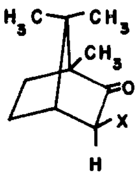
III



IV



V



VI

The observed triplet of the H_1,H_2 signal could result from equal coupling constants between the *endo*-protons and both of the methylene bridge protons,

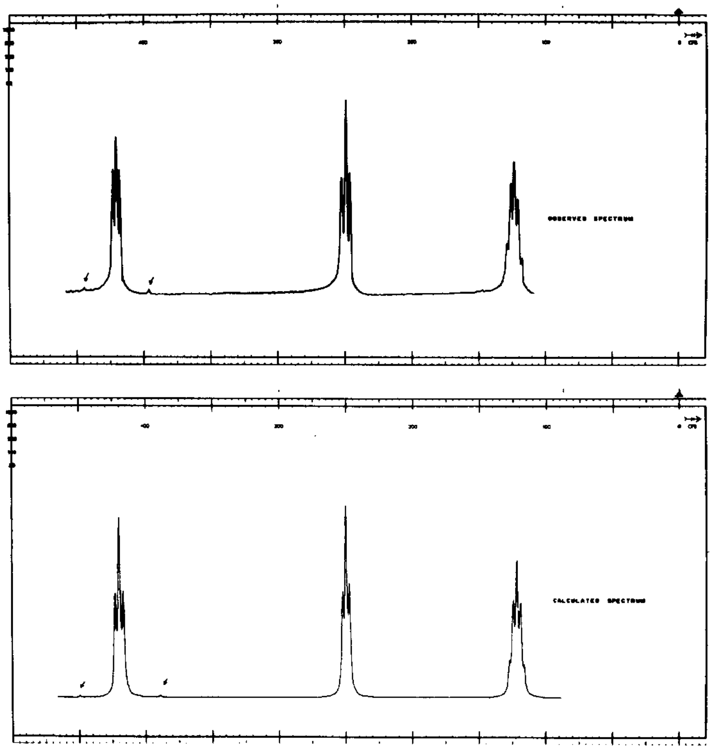


FIG. 1

Observed and Calculated nmr Spectra of

exo,*exo*-3,6-Dibromobicyclo[2.2.1]heptan-2,5-dione

that is, $J_{16} = J_{15} = J_{26} = J_{25}$. This, however, is unlikely, since it is well demonstrated that an *endo*-proton will only couple with the methylene bridge proton *anti* to it.

The alternate explanation, that of "virtual" coupling between H_1,H_2 and H_5,H_6, requires that the difference in chemical shift between H_5 and H_6 ($\Delta\delta$) be small compared to the geminal coupling between H_5 and H_6. When these conditions are met, only one coupling constant, J', will be observed for H_1,H_2 and H_5,H_6. The magnitude of J' is given by: $J' = \frac{1}{2}(J_{16} + J_{15}) = \frac{1}{2}(J_{25} + J_{26})$

(12).

The $\Delta\delta$ for H_5,H_6 is 0 cps and it is not unreasonable to assume a geminal coupling constant, J_{56}, of 12-15 cps, thus fulfilling the conditions for "virtual" coupling. Assuming that $J_{16} = J_{25} = 3.0$ cps and $J_{26} = J_{15} = 0$ cps, the calculated "virtual" coupling constant, J', is 1.5 cps. The experimentally observed J' is 1.3 cps. The relative intensity of the H_1,H_2 triplet is predicted to be 1:2:1, the observed relative intensity is 1:2.1:1.

The quintet of H_5,H_6 results from "virtual" coupling with H_1,H_2 to produce a triplet, J' = 1.3 cps, and further splitting into a triplet of triplets by the H_3,H_4 protons. Fortuitously, the coupling constant of H_3,H_4 and H_5,H_6 is also 1.3 cps, and the triplets overlap to produce a quintet of predicted relative intensity 1:4:6:4:1. The observed relative intensity is 1:3.7:5.9:3.7:1.

To demonstrate that this spectrum could result from "virtual" coupling, the spectrum was calculated by computer employing the LAOCOON I program (13). The best fit of the calculated spectrum to the observed spectrum was obtained with the coupling constants given in Table 1. The line width in Hz is 0.5 cps. A comparison of the calculated and observed spectra appears in Fig. 1. It is interesting to note that the two "satellite" peaks of the 4.15 ppm signal appear in the calculated spectrum as well and, therefore, represent actual weak transitions, not spinning side bands or C^{13} satellites.

	J_{1i}	J_{2i}	J_{3i}	J_{4i}	J_{5i}	J_{6i}
i = 1	-	0	0	0	0	3.0
i = 2	0	-	0	0	3.0	0
i = 3	0	0	-	0	1.3	1.3
i = 4	0	0	0	-	1.3	1.3
i = 5	0	3.0	1.3	1.3	-	15.0
i = 6	3.0	0	1.3	1.3	15.0	-

TABLE 1

Coupling Constants (cps) of *exo*,*exo*-3,6-Bicyclo[2.2.1]heptan-2,5-dione

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