THE BRIDGEHEAD PROTON SPIN COUPLING IN endo-cis-5,6-DIBROMONORBORNENE

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Abstract

The signals due to the vinyl and bromomethine protons in the 60-MHz p.m.r. spectrum of *endo-cis-5*,6-dibromonorbornene have been analysed in detail by means of the computer program LAOCN3. All non-zero coupling constants in the system are obtained. The value for the bridgehead-bridgehead coupling constant $J_{1,4}$ corrects a reported value obtained by an incorrect analysis procedure.

The value of the long-range coupling constant $(J_{1,4})$ between the bridgehead protons in *endo-cis*-5,6-dibromonorbornene (1) has been reported¹ to be approximately $1 \cdot 0$ Hz. In the calculation of this value, it was assumed that the spacing between the outer strong peaks in the multiplet due to the bridgehead protons is given by the sum of the couplings: $J_{1,2}+J_{1,3}+J_{1,4}+J_{1,6}+J_{1,7s}+J_{1,7a}$. In fact, since the bridgehead protons (H1 and H4) form the AA' part of an AA'XX' system both with the vinyl protons (H2 and H3) and with the bromomethine protons (H5 and H6), and the X_2 part of an ABX₂ spectrum with the bridging protons (H7s and H7a) this spacing does not depend upon the value of $J_{1,4}$ in a direct way.²

In order to obtain this coupling constant we have carried out a rigorous analysis of the 60-MHz spectrum of *endo-cis*-5,6-dibromonorbornene (1), parts of which are reproduced below. The signals due to the bromomethine protons (see Fig. 1(*a*)) appear as an approximately 1:1:1:1 quartet with two very low intensity bands on each side. These protons form an AA'XX' system with the bridgehead protons, H1 and H4. Analysis of this spectrum using the procedure recommended by Garbisch,² gave values for $J_{1,4}, J_{1,5}, J_{1,6}$, and $J_{5,6}$ which were further refined using the computer program LAOCN3 in the usual way.³ The signals due to the vinyl protons (see Fig. 1(*b*)) appear as a fairly similar multiplet but with each line split by 0.6 Hz due to long-range coupling with H_{7a} . Analysis of this spectrum in a similar way gave values for $J_{1,2}, J_{1,3}, J_{1,4}$, and $J_{2,3}$. The values of $J_{1,4}$ obtained from each analysis

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¹ Subramanian, P. M., Emerson, M. T., and LeBel, N. A., J. org. Chem., 1965, 30, 2624.

² Garbisch, E. W., J. chem. Educ., 1968, 45, 480.

³ Bothner-By, A. A., and Castellano, S. M., in "Computer Programs for Chemistry," (Ed. D. F. DeTar) Vol. 1 (Benjamin: New York 1968).

were in good agreement $(1 \cdot 32 \text{ and } 1 \cdot 34 \text{ Hz})$. The remaining couplings were measured using the multiplet rules. Values of the coupling constants obtained are shown in Table 1.



Fig. 1.—Signals due to (a) the bromomethine protons H5 and H6; (b) the vinyl protons H2 and H3.

TABLE 1

Br

(1)

COUPLING CONSTANTS (Hz) IN (1) Chemical shifts are reported elsewhere.¹ From measurement of the widths of spectral lines, values of unquoted coupling constants were found to be less than 0.1 Hz

Coupling constant	This work ^a	Ref. 1
1,2 = 3,4	3.0	· ·.
1,3 = 2,4	0.6	·
1,4	1.35	approx. 1.0
1,6 = 4,5	3.3	_
1,7s = 4,7s	2.05	approx. 2.1
1,7a = 4,7a	1.5	approx. 1.5
2,3	5.7	
2,7a = 3,7a	0.6	approx. 0.8
5,6	7.65	
7a,7s	9.7	9.6

* Values reproducible to within ± 0.1 Hz.

Experimental

H3

H2

endo-cis-5,6-Dibromonorbornene (1) was prepared and purified according to published procedures.⁴ Spectra were measured as 1_{M} solutions in CCl₄ with a Varian A-60A spectrometer. The

⁴ LeBel, N. A., Beirne, P. D., Karger, E. R., Powers, J. C., and Subramanian, P. M., J. Am. chem. Soc., 1963, 85, 3199, and references therein.

sweep width was calibrated by the usual sideband technique. Low-intensity signals were recorded by increasing amplitude and r.f. field settings. Calculations were carried out using an ICL 1902A computer. Due to limited core space it was necessary to reduce the capability of the program, LAOCN 3, to six spins and 200 transitions.

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