Signs of Fluorine–Fluorine Coupling Constants in Cyclobutenes

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THE use of proton–proton and proton–fluorine coupling constants as a function of dihedral angle to study the conformations of rigid compounds is very common, but little is known about even the qualitative dependence of fluorine–fluorine coupling constants on dihedral angle. Recently several fluorine–fluorine couplings in rigid compounds have been published.[1] We report here the analysis of the vicinal couplings in two fluorocyclobutenes. We have found that the two vicinal couplings in these molecules are quite large and of opposite sign. Evans has shown that *trans-* and *cis*-fluorine–fluorine couplings in substituted ethylenes are of opposite sign,[2] but we believe ours is the first direct determination of a positive vicinal coupling across a saturated bond. We report these results to emphasize the need for determining the sign of fluorine–fluorine couplings in rigid systems before attempting any correlations of these couplings with molecular parameters.

The AA′BB′ fluorine n.m.r. spectrum of 2-chloro-1-ethoxytetrafluorocyclobutene is reproduced in the Figure. The AA′ peaks are split into triplets by coupling to the methylene protons of the ethoxy-group, $J_{HF} = 0{\cdot}2$ Hz. The spectrum was analyzed by spin tickling following the procedure of Lustig *et al.*[3] Peaks 1, 2, 9, 10, 1′, 2′, 9′, and 10′ comprise the transitions between the "B" energy levels, giving $|L| = J_{AB} - J_{AB'} = 41{\cdot}8$ and $|M| = J_{AA'} - J_{BB'} = 9{\cdot}2$ Hz. $N = J_{AB} + J_{AB'} = 8{\cdot}5$ Hz is equal to the difference in energy of the 3 and 8 transitions. Spectra were then calculated for several values of $K = J_{AA'} + J_{BB'}$.[4] The difference between the calculated and observed transitions in the BB′ region is less than 0·1 Hz for $K = 390 \pm 10$ Hz (see Table). Tickling experiments confirm that N and K must have the same sign. The signs of M and L are not determined in an AA′BB′ spectrum; therefore the assignment of J_{AB} and $J_{AB'}$ or $J_{AA'}$ and $J_{BB'}$ is not known. If we

Calculated and observed BB′ transitions of 2-*chloro*-1-*ethoxytetrafluorocyclobutene. The spectrum was calculated by use of the n.m.r. program*[4] *with* $J_{AA'} = 200{\cdot}21$, $J_{AB} = J_{A'B'} = 25{\cdot}15$, $J_{AB'} = J_{A'B} = -16{\cdot}68$, $J_{BB'} = 191{\cdot}00$, $\nu_A = \nu_{A'} = -79{\cdot}05$ and $\nu_B = \nu_{B'} = 79{\cdot}05$ Hz.

Observed frequency	Calculated frequency	Calculated intensity
107·51	107·65	0·56
98·65	98·74	0·94
83·40	83·40	1·89
81·29	81·32	1·92
80·28	80·28	1·96
78·03	78·05	2·02
75·55	75·58	2·09
74·93	74·93	2·11
64·72	64·81	1·44
55·68	55·91	1·06

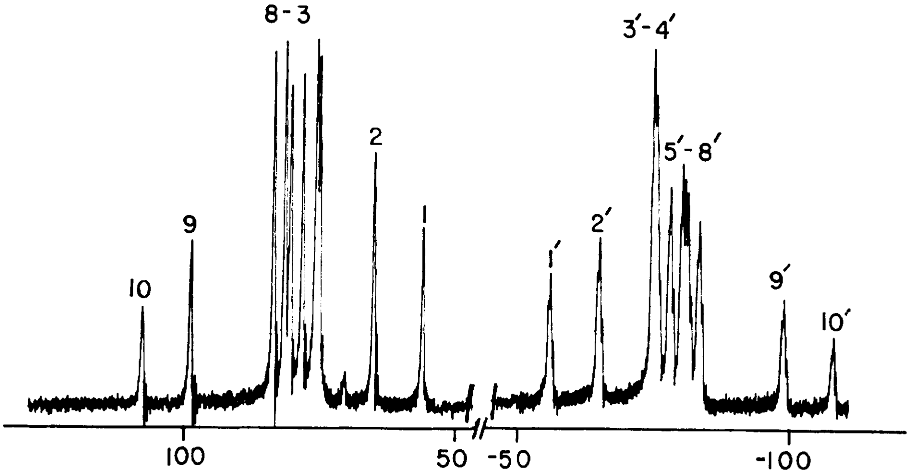

FIGURE. *Frequency-sweep fluorine n.m.r. spectrum of* 2-*chloro*-1-*ethoxytetrafluorocyclobutene at* 94·1 *MHz. The primed peaks are split into triplets by coupling to the methylene protons.*

assume the geminal couplings are positive,[1b] then the vicinal couplings, J_{AB} and $J_{AB'}$, are +25·2 and −16·7 ± 0·3 Hz. The chemical shifts are 116·95 and 118·63 p.p.m. upfield from the $CFCl_3$ solvent.

We have checked the signs of several other available cyclic compounds. Spin-tickling experiments[5] on the nearly first-order spectrum of 1,4-dichloro-3,3,4-trifluorocyclobutene proved that the two vicinal couplings are +26 and −12 Hz relative to the geminal coupling of +188 Hz.[6] Preliminary experiments on 1,1,2-trichloro-2,3,3-trifluorocyclobutane also give opposite signs for the vicinal couplings, ±9 and ±2 Hz.[6] We are in the process of assigning the chemical shifts of the fluorines in these compounds in order to determine which vicinal coupling is positive.

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[1] Examples include (a) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, 1966, **31**, 1859; (b) K. L. Williamson and B. A. Braman, *J. Amer. Chem. Soc.*, 1967, **89**, 6183; (c) S. F. Campbell, A. G. Hudson, E. F. Mooney, A. E. Pedler, R. Stephens, and K. N. Wood, *Spectrochim. Acta*, 1967, **23**, 2119; (d) K. W. Jolley, L. H. Stucliffe, and S. M. Walker, *Trans. Faraday Soc.*, 1968, **64**, 269; (e) R. E. Banks, M. G. Barlow, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.* (*C*), 1966, 981; (f) R. E. Banks, R. N. Haseldine, and V. Matthews, *J. Chem. Soc.* (*C*), 1967, 2263.

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[6] R. A. Newmark, G. R. Apai, and R. O. Michael, unpublished results.