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# Nuclear Magnetic Resonance Spectroscopy. Temperature Dependence of the Spectrum of Fluorocyclooctatetraene

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## Nuclear Magnetic Resonance Spectroscopy. Temperature Dependence of the Spectrum of Fluorocyclooctatetraene<sup>1</sup>

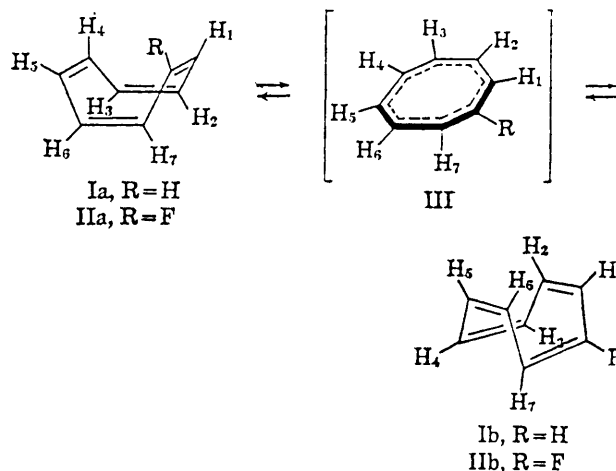
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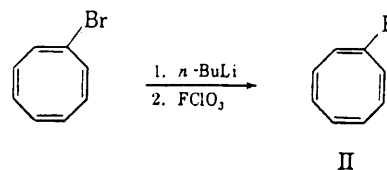
The fluorine n.m.r. spectrum of fluorocyclooctatetraene has been shown to be temperature dependent between 30 and  $-65^{\circ}$ . This is attributed to changes in the rate of an inversion-bond-shift process which is slow on the n.m.r. time scale at low temperatures. The free energy of activation for inversion is approximately 12 kcal./mole at  $-33^{\circ}$ .

Cyclooctatetraene and some of its derivatives appear to undergo inversion with or without accompanying bond shifts (most likely through considerably strained planar intermediates or transition states). The activation energy required for this kind of dynamic process is of considerable theoretical interest.<sup>2</sup> Anet and co-workers<sup>2a,b</sup> and Whitesides<sup>3</sup> have shown that the rate of establishment of the equilibrium represented by Ia  $\rightleftharpoons$  Ib can be studied by n.m.r. spectroscopy. In a further investigation of this phenomenon, we have investigated the temperature dependence of the fluorine n.m.r. spectrum of fluorocyclooctatetraene (II).

Fluorocyclooctatetraene was prepared for this study in 10% yield by reaction of perchloryl fluoride with an ethereal solution of cyclooctatetraenyllithium at  $-75^{\circ}$ . The product was purified by preparative gas chromatog-



raphy and the structure was confirmed by spectroscopic evidence. The proton n.m.r. spectrum of II showed a main signal at 345 with much weaker peaks at 320



and 322 c.p.s. This spectrum is compatible with a structure possessing only olefinic hydrogens. The ultraviolet spectrum of II with strong end absorption at 220  $m\mu$  and a broad  $\lambda_{max}$  at 285.5  $m\mu$  ( $\epsilon$  225) very

(1) Supported in part by the Office of Naval Research.

(2) (a) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962); (b) F. A. L. Anet, A. J. R. Brown, and Y. S. Lin, *ibid.*, **86**, 3576 (1964); (c) K. Mislow and H. D. Perlmutter, *ibid.*, **84**, 3591 (1962); (d) N. L. Allinger, *J. Org. Chem.*, **27**, 443 (1962).

(3) G. M. Whitesides and J. D. Roberts, unpublished results, California Institute of Technology; cf. J. D. Roberts, *J. Vsesnoe Chem. (USSR)*, **7**, 367 (1962).

closely resembles the spectra of cyclooctatetraene and its bromo and chloro derivatives.<sup>4</sup>

The temperature dependence of the fluorine n.m.r. spectrum of fluorocyclooctatetraene is shown in Figure 1. The complex fluorine signal which is observed at 29° is seen to broaden as the temperature is lowered and then coalesce at about -33°. As the temperature is lowered further, a doublet with considerable second-order splitting appears and remains unchanged below -65°. Surprisingly, the proton signal of II showed essentially no change over the same temperature range other than what could be attributed to viscous broadening at the low temperatures.

Rapid equilibration of IIa and IIb at room temperature should result in the averaging of these two forms such that the n.m.r. picture of fluorocyclooctatetraene at 29° will have the symmetry of the planar structure III but not (except accidentally) have the coupling constants or chemical shifts expected for III. The protons H<sub>1</sub> and H<sub>7</sub> will be equivalent with respect to their spin-spin coupling interactions with the fluorine atom, and the magnitude of this interaction,  $J_{H_{1,7}F}$ , will be the average of  $J_{H_1F} + J_{H_7F}$  for either IIa or IIb. The same kind of thing will be true for the proton pairs H<sub>2</sub>-H<sub>6</sub> and H<sub>3</sub>-H<sub>5</sub>, each of which can enter into long-range coupling with the fluorine atom.<sup>5</sup> Furthermore, at least some long-range coupling between proton H<sub>1</sub> and the fluorine atom might be expected on the basis of reported<sup>5a,b</sup> six-bond H-F couplings. These interactions could well lead to a very complex fluorine resonance in accord with the observed room-temperature fluorine signal.<sup>6</sup>

The doublet in the fluorine spectrum at -65° where inversion is slow must arise from a primary coupling between the fluorine atom and proton H<sub>1</sub> (IIa) or H<sub>7</sub> (IIb) which is situated *cis* with respect to the fluorine atom on the double bond. The separation of the two centers of the doublet is about 20 c.p.s. which agrees well with the *cis* H-F coupling constant range (13-19 c.p.s.) predicted by Karplus<sup>7</sup> in a study of the angular dependence of spin-spin coupling constants. On the other hand, coupling between the fluorine and adjacent proton H<sub>7</sub> of IIa or H<sub>1</sub> of IIb should be small since the dihedral angle in this case is about 80-85°, a minimum on the Karplus<sup>7</sup> scale. Possibly a weak coupling between the fluorine and this proton is responsible in part for the additional small splittings of the doublet although more than likely this is the result of long-range H-F coupling involving the other protons of the ring.

The complexity of the spectra of II precluded determination of the activation parameters for the cyclooctatetraene inversion bond-shift process. At the point where the principal doublet coalesces, -33°, the

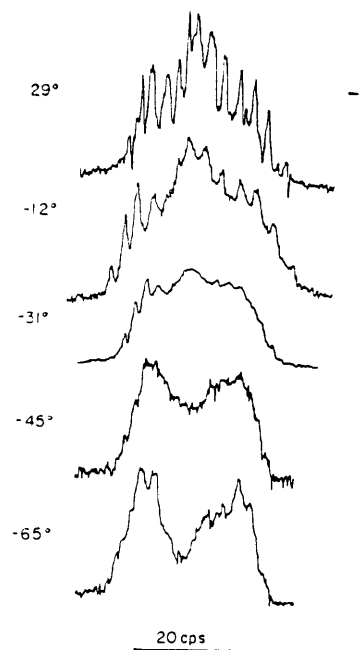


Figure 1. Temperature-dependent spectrum of fluorocyclooctatetraene in carbon disulfide solution. The field strength increases from left to right.

approximate reaction rate<sup>8</sup> is on the order of 44 sec., from which the free energy of activation can be calculated to be about 12 kcal./mole by the Eyring rate equation.

The present results parallel those obtained in studies of the temperature dependence of the <sup>13</sup>C satellites of cyclooctatetraene<sup>2a,3</sup> where the proton attached to the <sup>13</sup>C of the cyclooctatetraene ring serves as the X portion of the spectrum and experiences similar changes in spin-spin interactions of the other ring protons with changes in temperature as does the fluorine atom of fluorocyclooctatetraene. Thus, the <sup>13</sup>C satellite at room temperature is broad and complex and on cooling changes into a doublet with some second-order splitting. The free energy of activation for ring interconversion of cyclooctatetraene itself was found to be approximately 13.7 kcal./mole which is reasonably close to the value determined for fluorocyclooctatetraene.

## Experimental

**Fluorocyclooctatetraene.** An ethereal solution of cyclooctatetraenyllithium<sup>9</sup> was obtained from the reaction of 11.46 g. (0.0625 mole) of bromocyclooctatetraene with a *n*-butyllithium solution prepared from 11.0 g. (0.08 mole) of *n*-butyl bromide and 1.4 g. (0.20 mole) of lithium wire. Perchloryl fluoride (~2 g., 0.2 mole), was then bubbled into the cyclooctatetraenyllithium solution during 1 hr. while the temperature was maintained at -75°. The reaction was stirred for an additional hour at -75° and slowly allowed to warm. When the temperature reached -30°, the reaction mixture was poured into 400 ml. of water and extracted with ether. The dried ethereal extract was fractionally distilled at a bath temperature of 45°, and the desired fluorocyclooctatetraene was separated from the mixture of other products by pre-

(8) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

(9) A. C. Cope, M. Burg, and S. W. Fenton, *J. Am. Chem. Soc.*, **74**, 173 (1952).

(4) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 168 (1952).

(5) For examples of long-range H-F coupling see: (a) A. H. Lewin, *ibid.*, **86**, 2303 (1964); (b) A. D. Cross and P. W. Landis, *ibid.*, **84**, 1736 (1962); (c) A. D. Cross and P. W. Landis, *ibid.*, **84**, 3784 (1962); (d) M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962); (e) D. R. Davis, R. P. Lutz, and J. D. Roberts, *ibid.*, **83**, 246 (1961).

(6) Some confirmation of the suggested long-range H-F couplings were obtained from attempts to duplicate the room-temperature spectrum by computer procedures. A number of sample calculations indicated that the fluorine spectrum could not be reproduced even approximately by assuming that only two (or four) protons are in effect coupled to the fluorine.

(7) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

parative gas chromatography.<sup>10</sup> In this manner 0.520 g. (~10% based on recovered *n*-butyl bromide) of pale yellow fluorocyclooctatetraene was obtained.

*Anal.* Calcd. for C<sub>8</sub>H<sub>6</sub>F: C, 78.66; H, 5.78. Found: C, 78.89; H, 5.81.

The infrared spectrum showed absorption at 3000 (olefinic H), 1685, 1675 (sh.), and 1640 (C=C), and

(10) A Beckman Megachrome preparative gas chromatograph was employed with a column of 35% Carbowax 20M on firebrick.

1125 cm.<sup>-1</sup> (v.s.: C—F). The ultraviolet spectrum in 95% ethanol showed very strong end absorption at 220 mμ with a broad maximum at 285.5 mμ (ε 225). The proton n.m.r. spectrum showed a strong signal at 345 with much weaker peaks at 329 and 322 c.p.s.

The spectra shown in Figure 1 were obtained with a Varian high-resolution n.m.r. spectrometer Model V-5400 D having a 12-in. magnet equipped with Super Stabilizer operating at 56.4 Mc.