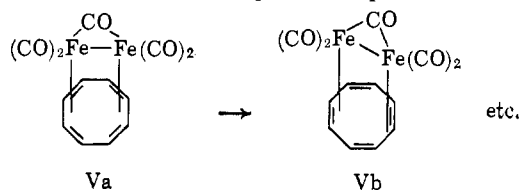


in solution. Thus, a rapid rotation of the Fe-Fe bond about 45° would render all protons equivalent.



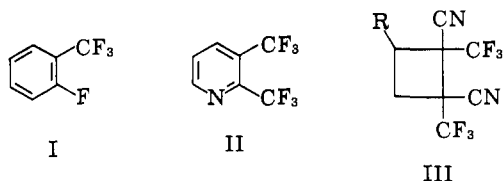
Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for financial assistance. We are also grateful to Badische Anilin und Soda Fabrik A.G. for a gift of cyclooctatetraene and to General Aniline and Film Corporation for a gift of $\text{Fe}(\text{CO})_5$.

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 Received January 7, 1965

The Stable Conformation of 1,1,4,4-Tetrafluorobutadiene

Sir:

The n.m.r. spectra of I,¹ II,² and *cis*- and *trans*-III² reveal that the long-range fluorine-fluorine spin-spin



coupling constant $J_{\text{FF}'}$ has a large value (20–30 c.p.s.) when the fluorine atoms are spatially close to each other. The large magnitude of $J_{\text{FF}'}$ in these cases has been attributed to a “through space” spin-spin interaction.^{2,3}

Servis and Roberts⁴ have studied the n.m.r. fluorine spectrum of $\text{F}_2\text{C}=\text{CH}-\text{CH}=\text{CF}_2$ in the liquid phase. $J_{\text{FF}'}$ is 36.6 c.p.s. in this case also. Based on the large value of $J_{\text{FF}'}$ and on the assumption of a “through space” contribution to the spin-spin coupling it would seem that $\text{CF}_2=\text{CH}-\text{CH}=\text{CF}_2$ exists in a *cisoid* form.

In theory at least this molecule can have two geometric configurations, *cis* and *trans* (see Figure 1).

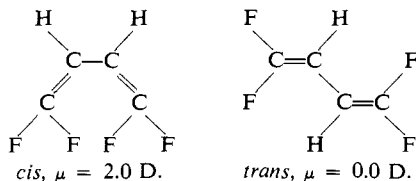


Figure 1. Geometrical isomers of 1,1,4,4-tetrafluorobutadiene.

Because of the partial conjugation of the single C-C bond, rotation about this bond will be hindered (probably about 10 kcal./mole). Lide has studied the rotational spectrum of isoprene⁵ and of fluoroprene.⁶

(1) H. S. Gutowsky and V. D. Mochel, *J. Chem. Phys.*, **39**, 1195 (1963).

(2) S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

(3) L. Petrakis and C. H. Sederholm, *ibid.*, **35**, 1243 (1961).

(4) K. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1339 (1965). The author is greatly indebted to Servis and Roberts for furnishing their n.m.r. results prior to publication.

(5) D. R. Lide, Jr., and M. Jen, *J. Chem. Phys.*, **40**, 252 (1964).

(6) D. R. Lide, Jr., *ibid.*, **37**, 2074 (1962).

In both cases Lide has been able to detect only the spectrum of the *trans* isomer and has estimated that the increase in free energy going from *trans* to *cis* must be at least 1 kcal./mole. He also was unable to find the microwave spectrum of butadiene and 2,3-dimethylbutadiene. The dipole moment of the *cis* form would be small ($\sim 0.4 \text{ D.}$), so that the intensity of absorption lines is low. In fact, there is no conclusive spectroscopic evidence for the existence of a *cis* isomer of any butadiene.

The stable geometric forms can best be determined by searching for the microwave spectrum. Because the intensities of pure rotational transitions are proportional to the square of the dipole moment, μ , and because the dipole moment of the *trans* species is zero by symmetry, a microwave spectrum is allowed only for the *cis* isomer. Here the latter would have a large dipole moment ($\sim 2 \text{ D.}$) and a dense and intense b-type spectrum. Hence a qualitative examination for the presence of a pure rotational spectrum will in itself confirm the presence or absence of large concentrations of the *cis* form. These results will be more sensitive than Lide's negative results with fluoroprene where the spectrum could be obscured by the spectra of the *trans* form, or with isoprene where the estimated dipole moment of the *cis* form, if present, is very small ($\sim 0.4 \text{ D.}$).

A 99% pure sample of $\text{CF}_2=\text{CHCH}=\text{CH}_2$ was generously offered by Servis and Roberts. The microwave region from 18 to 22 kMc. and from 24.5 to 25.0 kMc was thoroughly searched. The sample pressure was about 30μ , and the Stark voltage was kept between 500 and 1000 v. No pure rotational spectrum was found for this molecule; hence the molecule must exist primarily in the *trans* form. From intensity considerations, a concentration of 3% *cis* in the sample should easily have been detected. An equilibrium concentration of 3% corresponds to $\Delta F(\textit{cis-trans}) \approx 2.5 \text{ kcal.}$

Since in the *trans* isomer only the fluorine atoms on the same carbon are close to each other, at least in 1,1,4,4-tetrafluorobutadiene a “through space” interaction cannot account for the large long-range spin-spin coupling constant. These results render the “through space” explanation for large $J_{\text{FF}'}$ long-range coupling constants in other molecules doubtful. If the n.m.r. determination of the geometric forms of any other molecule is based on the magnitude of the long-range coupling constants, these results should best be confirmed by other means.

Acknowledgment.—The author expresses his sincere thanks to K. Servis and J. D. Roberts for bringing this problem to his attention and for furnishing the sample of $\text{CF}_2=\text{CH}-\text{CH}=\text{CF}_2$. A portion of this work was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract No. NAS7-100 sponsored by the National Aeronautics and Space Administration. The author is also indebted to the Public Health Service, under Grant GM 11979-01, and the Research Corporation for the support of this work.

(7) Consultant at the Jet Propulsion Laboratory.

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Received June 1, 1964