On the Molecular Structure of ("Cyclic") C_3F_6

By Walter F. Edgell

In line with our interest in fluorocarbons the Raman spectrum of "cyclic" C_3F_6 was determined early in 1946. The results were not published then because they were at variance with the reported "definite chemical evidence" for the cyclic structure which was later published.[1,2] Recently F. A. M. Buck and R. L. Livingston have made electron diffraction studies on this compound which also could not be interpreted with a ring model.[3] These two independent studies show clearly that this material does not have the cyclopropane structure—a conclusion also reached by other workers.[4]

Experimental Details

The Raman effect was determined in the liquid state using the spectrographic arrangement reported elsewhere.[5] The Raman tube was surrounded by an unsilvered Dewar which was maintained at low temperatures by dry air that had been passed through coils immersed in a Dry Ice–acetone slush and liquid air. The twenty Raman lines found are listed in Table I. The usual weak scattering power of fluorocarbons was observed and two of the lines listed were so weak that it would be better to consider them uncertain at present. This in no way influences the conclusions drawn.

TABLE I

THE RAMAN SPECTRUM OF C_3F_6

Description	Frequency (cm.$^{-1}$)
C=C stretching	1790 (S-)[a]
CF_3 symm. stretching	1386 (m)
CF_2 symm. stretching	1330 (m)
CF_3 assymm. stretching	1208 (m)
CF_3 assymm. stretching	1156 (m)
CF stretching	1020 (w)
CF_2 assymm. stretching	..
CF_3 symm. deformation	764 (S)
CF_3 assymm. deformation	714 (w)
CF_3 assymm. deformation	648 (S)
CF_2 rocking	607 (m)
CF_2 deformation	560 (S)
CF_2 wagging	511 (m)
CF_2 twisting	453 (vw)
C—C stretching	360 (S)
CF_3 bending	306 (vw)
CF bending	248 (w)
CF_3 bending	213 (w)
CF bending	173 (w)
C—C=C bending	140 (m)
CF_3 twisting	84 (w)

[a] S = strong, m = medium, w = weak.

TABLE II

FUNDAMENTAL VIBRATIONS OF C_3F_6 CYCLIC MODEL (D_{3h})

Description	Species	Activity[a]
CF_2 stretching	A_1'	R, p
Ring stretching	A_1'	R, p
CF_2 deformation	A_1'	R, p
CF_2 stretching	A_2''	I, ‖
CF_2 rocking	A_2''	I, ‖
CF_2 wagging	A_2'	Inactive
CF_2 twisting	A_1''	Inactive
CF_2 stretching	E'	R, dp; I, ⊥
Ring deformation	E'	R, dp; I, ⊥
CF_2 deformation	E'	R, dp; I, ⊥
CF_2 wagging	E'	R, dp; I, ⊥
CF_2 stretching	E''	R, dp
CF_2 rocking	E''	R, dp
CF_2 twisting	E''	R, dp

[a] R = Raman active; I = infrared active; p = polarized; dp = depolarized; ‖ = parallel; ⊥ = perpendicular.

The C_3F_6 was kindly supplied by the Jackson Laboratory of E. I. du Pont de Nemours and Co. The infrared spectrum from 2 to 15 μ was determined by Dr. J. R. Downing of the du Pont Experiment Station and appears in Table III, column 1.

TABLE III

THE INFRARED SPECTRUM OF C_3F_6 (1800 TO 750 CM^{-1})

"Cyclic" C_3F_6[a]	$CF_3CF{=}CF_2$[b]
1801 (S)	1798 (S)
1400 (S)	1398 (S)
1333 (S)	1336 (S)
1210 (S)	1210 (S)
1179 (S)	1178 (S)
1039 (S)	1035 (S)
767 (m)	767 (m)

S = strong; m = medium. [a] Origin: J. R. Downing (see text). [b] Origin: Donald G. Weiblen (see text).

Discussion of Results

The cyclic ring model, $\overline{\mathrm{C}F_2CF_2\mathrm{C}}F_2$, has the symmetry D_{3h} for which the selection rules and the approximate character of the vibrations, listed in Table II, may be obtained by group theoretical considerations. In contrast to the twenty Raman lines found, this model calls for but ten. To be sure this is about the number of stronger lines observed, but their frequencies do not correspond to the order of magnitude expected of a cyclic fluorocarbon.[5] Most important is the rather strong line at 1790 cm.$^{-1}$ for which no explanation seems possible in terms of this model; also five lines between 1000 and 1400 cm.$^{-1}$ are more than can be reasonably accounted for. A consideration of the C–F stretching vibrations is very significant. Experience has shown that they are found in the region *ca.* 1000 to *ca.* 1400 cm.$^{-1}$.[5-9] This model calls for three such Raman active fundamentals plus two that are infrared active—only one of which would

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(1) A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,394,581 (1946).

(2) J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, *Ind. Eng. Chem.*, **39**, 354 (1947); see also Lewis and Naylor, THIS JOURNAL, **69**, 1968 (1947).

(3) F. A. M. Buck and R. L. Livingston, THIS JOURNAL, **70**, 2817 (1948). The author wishes to thank Dr. R. L. Livingston for his kindness in making his results available in advance of publication.

(4) E. G. Young and W. S. Murray, *ibid.*, **70**, 2814 (1948).

(5) Walter F. Edgell, *ibid.*, **69**, 660 (1947).

(6) Geo. Glockler and W. F. Edgell, *J. Chem. Phys.*, **9**, 224 (1941).

(7) Geo. Glockler and G. Leader, *ibid.*, **8**, 699 (1940), and others.

(8) D. H. Rank and E. L. Pace, *ibid.*, **15**, 39 (1947).

(9) J. R. Nielsen, C. M. Richards and H. L. Murray, *ibid.*, **16**, 67 (1948).

appear in both spectra. This is in complete disagreement with the data; all five frequencies in this region appear in both the Raman and infrared spectra.

It is clear that "cyclic" C_3F_6 is not hexafluorocyclopropane.

The Raman spectrum indicates a molecule which has either no symmetry or at most one element of symmetry, in which case all 21 fundamental modes of vibration would appear individually in both the Raman and infrared spectra. Molecules containing a double bond have their stretching fundamental at *ca.* 1650 cm.$^{-1}$,[10] which is shifted in polyfluorinated ethylenes to *ca.* 1750 cm.$^{-1}$.[11,12] This corresponds to the Raman line found at 1790 cm.$^{-1}$ and the infrared band at 1798 cm.$^{-1}$. Thus the spectra indicate the structure $CF_3CF{=}CF_2$!

It is difficult to predict the character of the vibrations of this molecule because of the lack of symmetry restrictions and the complexity resulting from the large interactions between the fluorine atoms. An approximate description of them based upon the neglect of coupling between the groups is found in Table I. The correlation between the expected magnitudes[5-12] and the observations is good. No definite assignment of all the frequencies can be made yet. For example, it is not clear why only five lines are found in the region where the six C–F stretching vibrations are expected. Work now under way in this Laboratory on similar molecules should throw light on these matters, however. The correlation of Table I is given solely to show that the spectrum has the proper number of lines in the proper spectral region for such a model.

In order to conclusively demonstrate that "cyclic" C_3F_6 is in reality hexafluoropropylene, the infrared spectrum between 2 and 15μ of an authentic sample of $CF_3CF{=}CF_2$ is included in Table III, column 2. It is identical with that for "cyclic" C_3F_6. This spectrum was obtained and furnished by Mr. D. G. Weiblen of the Central Research Department, Minnesota Mining and Manufacturing Company, using material prepared by Lyle Hals of that laboratory.

It is now clear why the physical properties of $CF_3CF{=}CF_2$[13] are so close to those earlier reported for "cyclic" C_3F_6.

Acknowledgment.—The author is indebted to Dr. A. F. Benning who furnished the infrared spectrum and sample of C_3F_6. Thanks are also due to Mr. D. G. Weiblen for the infrared spectrum of hexafluoropropylene.

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

RECEIVED MAY 3, 1948

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[10] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, N. Y., 1945, p. 195.

[11] J. B. Hatcher and D. M. Yost, *J. Chem. Phys.*, **5**, 992 (1937).

[12] P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).

[13] Henne and Waalkes, THIS JOURNAL, **68**, 496 (1946).

The Identification of C_3F_6[1]

BY F. A. M. BUCK AND R. L. LIVINGSTON

The compound C_3F_6, obtained by pyrolysis of polytetrafluoroethylene and by pyrolysis of monochlorodifluoromethane has been reported to be hexafluorocyclopropane[2,3] although some doubt as to its identity has been expressed.[4] Interpretation of electron diffraction photographs of this compound has led us to the conclusion that the compound is not hexafluorocyclopropane but is hexafluoropropene. This conclusion has been reached independently by other workers.[5,6]

The electron diffraction photographs[7] were prepared using an apparatus built by Professor H. J. Yearian of the Purdue Physics Department. The sample of C_3F_6 was kindly supplied by Drs. Young and Benning of the Jackson Laboratory of E. I. du Pont de Nemours and Company. Diffraction maxima were observable on the photographs out to $s = 33$ ($s = 4\pi/\lambda \sin \theta/2$). A radial distribution curve (Fig. 1) was calculated using essentially a method previously described.[8] The five prominent peaks of this curve at 1.32, 2.16,

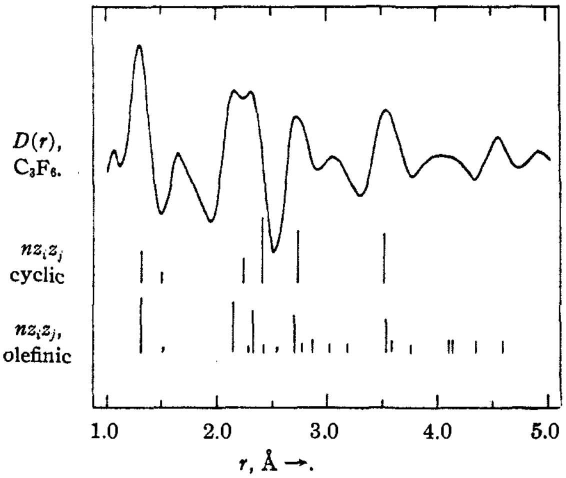

Fig. 1.—Radial distribution curve for C_3F_6. The lines under the curve correspond to bond distances in models of hexafluorocyclopropane and hexafluoropropene; the lengths of the lines indicate the relative weights, nz_iz_j, of the corresponding terms in the simplified intensity function.

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[1] From the Ph. D. thesis of F. A. M. Buck, duPont Fellow in Chemistry, Purdue University.

[2] A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,394,581 (February 12, 1946).

[3] J. D. Park, A. F. Benning, F. B. Downing, J. F. Laucius and R. C. McHarness, *Ind. Eng. Chem.*, **39**, 354 (1947).

[4] E. E. Lewis and M. A. Naylor, THIS JOURNAL, **69**, 1968 (1947).

[5] W. F. Edgell, *ibid.*, **70**, 2816 (1948). We appreciate the cooperation of Dr. Edgell in making his data available in advance of publication.

[6] E. G. Young and W. S. Murray, *ibid.*, **70**, 2814 (1948).

[7] For a general review of the method of electron diffraction, see L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

[8] R. Spitzer, W. J. Howell and V. Schomaker, THIS JOURNAL, **64**, 62 (1942).