

The Molecular Structure of Hexafluoropropene

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Electron diffraction photographs were prepared from a highly purified sample which was obtained from the Central Research Laboratories of the Minnesota Mining and Manufacturing Company. The photographs showed diffraction patterns extending to about $q=75$.

Models having a planar carbon ring (D_{3h} symmetry) gave rise to intensity curves which are in disagreement with the visual appearance of the diffraction patterns. Non-planar models were then constructed from planar models in the following way: One pair of diametrically opposite carbon atoms was raised above the plane while the other pair was lowered to the same extent keeping the CF_2 groups oriented so that a plane through the carbon atom of this group and the two adjacent carbon atoms bisected the FCF angle of the CF_2 group. These models have $D_{2d}(V_d)$ symmetry. Agreement with the diffraction data is obtained with models having this configuration and parameters within the following limits: C—F=1.31 to 1.34Å, C—C=1.57 to 1.62Å, $\angle FCF=107^\circ$ to 112° , α (angle between planes which bisect opposite CF_2 groups)= 157° to 163° . Further work is necessary in order to choose the best models and to estimate uncertainties but the final results should fall within the ranges indicated.

It is interesting to compare this compound with cyclobutane and hexafluoropropene. In the former, spectroscopic evidence¹ favors a planar carbon ring indicating that the non-planar ring in C_4F_8 may be attributed to repulsions between fluorine atoms attached to different carbon atoms. These repulsions may also be responsible for an increase in the C—C distance above the value of about 1.54Å which is observed in many hydrocarbons. In the case of hexafluoropropene, evidence has been obtained² for the fact that the closest approach of fluorine atoms attached to different carbon atoms is about 2.70Å, which is twice the van der Waals radius of fluorine. This same value appears in the acceptable models of C_4F_8 as the shortest distance between fluorine atoms attached to different carbon atoms. It thus appears likely that twice the van der Waals radius of fluorine does represent the closest distance of approach of fluorine atoms which are not attached to the same carbon atom. This is not the case with the other halogens.

Independent evidence for the non-planar carbon ring in C_4F_8 has been obtained from spectroscopic studies by Edgell and Weiblen.³

The authors wish to thank the Research Corporation for financial support of this work. They are grateful to Professor Edgell of the Chemistry Department who suggested the problem, and to Professor H. J. Yearian of the Physics Department for the use of his diffraction equipment and for many stimulating discussions.

* From the Ph.D. thesis of H. P. Lemaire, Research Corporation Fellow in Chemistry, Purdue University.

¹ T. P. Wilson, J. Chem. Phys. 11, 361 (1943).

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³ W. F. Edgell and D. G. Weiblen, J. Chem. Phys. 18, 571 (1950).

The Molecular Structure of Hexafluoropropene*

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December 8, 1949

THE preparation of electron diffraction photographs of C_3F_6 and their interpretation on the basis of a model of hexafluoropropene have been described in a previous article.¹ It is the purpose of this letter to indicate the nature of the acceptable models and those models which were rejected.

The models of hexafluoropropene were drawn graphically using the methods and techniques of descriptive geometry. This

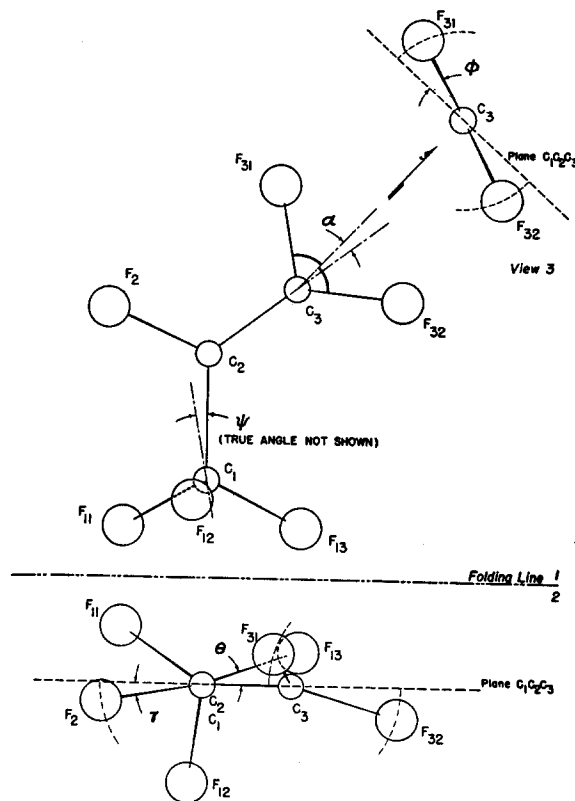


FIG. 1. Orthogonal projections of a molecular model of hexafluoropropene. The angle α is the angle between the line bisecting the $F_3C_1F_3$ angle and the extension of the C_2C_3 bond, ϕ is an angle describing a rotation of the $F_3C_1F_3$ group about the double bond, γ describes the rotation of F_2 about the direction C_1-C_2 as an axis and ψ is the angle between the trigonal axis of the CF_3 group and the direction C_1C_2 . The angle θ is the angle between two planes, one plane being determined by the three carbon atoms and the other by C_1 , C_2 and F_{11} .

afforded a convenient method of finding models consistent with the prominent peaks on the radial distribution curve.¹ During the investigation theoretical intensity curves were calculated for sixty-five models; many more models were rejected at the drawing board stage because they did not agree with the radial distribution curve.

The models considered may be conveniently classified as (1) "planar" models (having all atoms in one plane except the fluorine atoms in the CF_3 group) and (2) "strained" models (having some or all of the fluorine atoms of the $-CF=CF_2$ group not in the plane determined by the three carbon atoms). The values chosen for interatomic distances were those supported by spectroscopic and (unpublished) electron diffraction results on fluorocarbons and were always compatible with at least some of the major peaks on the radial distribution curve.

While in previous investigations it has been either assumed or demonstrated that atoms attached to double-bonded carbon atoms lie in the same plane, it was not possible in the case of hexafluoropropene to find a "planar" model which would give rise to an intensity curve agreeing with the visual appearance of the diffraction photographs. The "planar" models also fail to account for the radial distribution peak at 2.72Å unless the C—C or C—F distances are made unusually long, in which case disagreement with other peaks arises. The peak at 2.72Å is interpreted as corresponding to distances between fluorine atoms attached to different carbon atoms.

In order to construct models compatible with the radial distribution peaks at 1.32, 2.16, 2.32, 2.72 and 3.52Å, it was necessary to consider "strained" models. The strain parameters chosen are indicated in Fig. 1. Models in which these parameters are

given values of from 2° to 5° and with $\theta = 25^\circ$ give rise to acceptable intensity curves. A typical model has bonded C—F distances ranging from 1.31 to 1.35 Å, the bonded C—C distances about 0.02 Å less than the frequently observed values of 1.34 and 1.54 Å, the FCF angles nearly tetrahedral, $\angle C_1C_2C_3 = 126^\circ$ and $\angle C_1C_2F_2 = 114^\circ$.

Because of the large number of parameters it is not possible to eliminate all "planar" models but in view of the failure to find an acceptable "planar" model after many trials, the authors believe that the structure of this compound is best represented by a "strained" model in which none of the fluorine atoms is in the plane determined by the three carbon atoms. The strains are attributed to repulsions between fluorine atoms which are attached to different carbon atoms; these repulsions apparently twist the double bond to such an extent that the closest approach of fluorine atoms is almost exactly twice the van der Waals radius of fluorine, i.e., 2×1.35 Å. Additional and somewhat more conclusive evidence for the importance of such strains has been found in the halogenated benzenes² and in C_4F_8 .³

* From the Ph.D. thesis of F. A. M. Buck, du Pont Fellow in Chemistry, Purdue University, 1947–48.

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On the Molecular Configuration of Cyclic C_4F_8

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December 8, 1949

SEVERAL years ago one of us² studied the Raman spectrum of perfluorocyclobutane and concluded that it and the data then available on the infra-red spectrum "are in harmony with the planar ring model of symmetry D_{4h} ." The spectra have been investigated again with better equipment and new data obtained.

The sample used in this work was prepared by the pyrolysis of teflon.³ Experimental details will be presented later. The Raman spectrum was determined in the liquid state at about $-25^\circ C$ using a Lane-Wells spectrograph of camera aperture $F/3$. The results are found in Table I. Lines were also found shifted 301,

TABLE I. The Raman spectrum of cyclic C_4F_8 (to 1450 cm^{-1}).

ω (cm^{-1})	Density*	ω (cm^{-1})	Density*
190	m	783	vw
256	s	857	vw
272	s	971	w
346	m+	1008	s
361	vs	1052	w
440	vs	1216	s
573	vw	1278	m+
605	w+	1340	w
659	m	1398	vw
699	vs		
722	m	1431	m+

* s = strong, m = medium, w = weak, v = very.

382, 598, 643, 906, and 954 cm^{-1} from the Hg 4358 Å exciting line. These are believed to be the fundamentals 361, 440, 699, and 1008 cm^{-1} excited by Hg 4348 or Hg 4339 Å.

The infra-red spectrum was obtained with a Perkin-Elmer spectrometer, Model 12B, using NaCl and KBr optics. The results, through the region of the fundamentals, are found in Table II. Relative intensities are based on the scale: vs, 50 percent absorption at 2.5 mm pressure; s, 50 percent at 12.5 mm; m, 50 percent at 500 mm; w, 50–25 percent at 500 mm; vw, <25 percent at 500 mm, all in a 10-cm cell.

In general, the data obtained in another recent study of this molecule⁴ are in good agreement with those presented here. They have been interpreted in terms of the planar ring model.

TABLE II. The infra-red spectrum of cyclic C_4F_8 (400 to 1450 cm^{-1}).

ω (cm^{-1})	Intensity*	ω (cm^{-1})	Intensity*
425	vw	864†	w
444	m	890	w
467	w	899	w
502	vw	962	vs
531	vw	981	m
571	vs	1002	m
606	vw	1093	m
632	vw	1120	w
659	w	1153	s
684	w	1224†	vs
729†	w	1239†	vs
731†	w	1268	m
799	vw	1290	vs
845†	w	1229	vs
851†	w	1394	s
858†	w	1448	w

* s = strong, m = medium, w = weak, v = very.

† Peaks in a "single band" or region of absorption.

If cyclic C_4F_8 has a planar ring structure of symmetry D_{4h} , eleven fundamentals would be Raman active. Almost twice this number of lines are found in the spectrum range of the fundamentals, fifteen of which are of sufficient intensity to appear on all films of reasonable exposure. A molecule with this point group has a center of symmetry and transitions permitted in the Raman spectrum are forbidden in the infra-red spectrum and vice-versa. More than half of the Raman lines in the region of common observation correspond to infra-red bands with almost exact numerical coincidence or within the limits to be expected of spectra taken in different phases.

With the D_{4h} model, these features of the spectra must be attributed to the breakdown of selection rules either in the liquid state or at higher pressures, near coincidences in the frequencies of similar fundamental modes of vibration and the appearance of overtones or combinations in the Raman spectra. Because of the number of the "discrepancies" and the fact that allowed fundamentals of highly fluorinated molecules often appear weakly in Raman and infra-red spectra, it is believed that a question should be raised as to the correctness of the D_{4h} model. Independent evidence is required to prove this point.

An electron diffraction study of this molecule has been carried out by Lemaire and Livingston.⁵ They were unable to interpret their results in terms of the planar ring model of symmetry D_{4h} . Agreement between calculated and observed patterns were obtained for a model of symmetry V_d , the most likely non-planar ring structure.

One of us (W. F. E.) wishes to express his gratitude to the Research Corporation for a grant which made the purchase of the Lane-Wells spectrograph possible. Thanks are also due Mr. H. D. Mallory for preparing several Raman spectrograms and the Central Research Laboratories, Minnesota Mining and Manufacturing Company, for the samples.

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The Mechanism of the Decomposition of N_2O on ZnO as Catalyst

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February 3, 1950

UNDER this heading, Wagner¹ reports an attempt to correlate catalytic activity with conductive properties. Observing that the conductivity of $ZnO + 1$ percent Ga_2O_3 is 50 times greater than that of ZnO but that the rate of N_2O decomposition on these catalysts differs by a factor less than two, he concludes that the