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The Molecular Structures of Octafluorocyclobutane and of Methylcyclobutane<sup>1</sup>

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The structures of octafluorocyclobutane and of methylcyclobutane have been investigated by electron diffraction using both the radial distribution and visual correlation methods. The results indicate that C<sub>4</sub>F<sub>8</sub> has a non-planar carbon ring and the following parameters: C-F = 1.33 ± 0.02 Å., C-C = 1.60 ± 0.04 Å., <FCF = 109.5 ± 3°, α (the angle between planes which bisect opposite CF<sub>2</sub> groups) = 160 ± 4°; for such a model the C-C-C angle is about 89°. In methylcyclobutane, the C-C distance in the ring has been found to be 1.56 ± 0.03 Å. and the average C-C distance, 1.555 ± 0.02 Å. β, which is defined as the angle between the side chain bond direction and the bisector of the adjoining C-C-C angle in the ring, is assigned the value 130 ± 8°, corresponding to a C-C-CH<sub>3</sub> bond angle of approximately 118°.

## Introduction

The preliminary results of an electron diffraction investigation of the structure of octafluorocyclobutane have been described in a previous article.<sup>2</sup> It is the purpose of this paper to present the final results of this investigation and the results of the study of methylcyclobutane.

An electron diffraction investigation of hexafluoropropene<sup>3</sup> has led to the proposal of a strained configuration for this molecule; this apparently results from repulsions between fluorine atoms which are attached to different carbon atoms. It appeared possible that the fluorine atoms in C<sub>4</sub>F<sub>8</sub> would exhibit the same property and that the effect could be experimentally detectable. It is also significant that Edgell and Weiblen<sup>4</sup> have raised some doubt as to the correctness of the interpretation of spectroscopic data on the basis of a D<sub>4h</sub> configuration as given by Claassen.<sup>5</sup>

The conclusive evidence, obtained in this investigation, for a non-planar carbon ring and an unusually long C-C bond distance in the perfluoro derivative of cyclobutane led to the study of methylcyclobutane; it seemed possible that the carbon ring in the methyl derivative might also be non-planar. A theoretical intensity curve was calculated for a non-planar model of methylenecyclobutane in order to make a comparison with the published data on this compound.<sup>6,7</sup> The results showed that a non-planar structure is also compatible with experimental data, indicating that the exact structural nature of the ring in this compound is difficult to determine by electron diffraction. Calculations for methylcyclobutane showed that the intensity pattern was more sensitive to the folding parameter and its study was undertaken in the hope of obtaining information on the ring structure and the C-C distances.

## Experimental

The sample of octafluorocyclobutane (b.p. -6.1° to -6.0°) was obtained from Drs. Hals and Pearson of the Minnesota Mining and Manufacturing Company; the estimated purity was 99.5% on the basis of infrared spectroscopy.

(1) From the Ph.D. thesis of H. P. Lemaire, Research Corporation Fellow in Chemistry, Purdue University, 1949-1950.

(2) H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.*, **18**, 569 (1950).

(3) F. A. M. Buck and R. L. Livingston, *ibid.*, **18**, 570 (1950).

(4) W. F. Edgell and D. G. Weiblen, *ibid.*, **18**, 571 (1950).

(5) H. H. Claassen, *ibid.*, **18**, 543 (1950).

(6) S. H. Bauer and J. V. Beach, *This Journal*, **64**, 1142 (1942).

(7) W. Shaffer, V. Schomaker and I. R. Fischer, *ibid.*, **66**, 636 (1944).

The sample of methylcyclobutane was prepared in the NACA Cleveland Laboratories and made available by Dr. Greenlee of The Ohio State University. The constants given for the sample are: f.p. -161.51°, b.p. 36.98° (755 mm.) and 37.18° (760 mm.), *n*<sub>D</sub><sup>20</sup> 1.3878.

Electron diffraction photographs were prepared in the customary manner<sup>8</sup> using an apparatus built by Dr. H. J. Yecarian of the Purdue Physics Department. The camera distance was about 10.8 cm. and the electron wave length, as determined from photographs of zinc oxide, was about 0.055 Å. The recorded pattern for octafluorocyclobutane extended to a *q* value of about 75 and the pattern for methylcyclobutane to a *q* value of about 93.

**Octafluorocyclobutane.**—The radial distribution method<sup>9,10</sup> and the visual correlation method<sup>8,11</sup> were used in the interpretation of the recorded pattern. The radial distribution function was calculated from the equation

$$rD(r) = \sum_{q=1.2\dots}^{q_{\max}} I(q) \exp(-bq^2) \sin\left(\frac{\pi qr}{10}\right) \quad (1)$$

by the use of punched cards.<sup>9</sup> *I*(*q*) is the visual intensity curve (curve VIS, Fig. 4), which is drawn assuming no falling off of intensity with increasing *q*. The constant *b* was chosen so that exp(-*bq*<sup>2</sup>) = 0.10 at *q* = 100. The resulting curve (Fig. 3) shows major peaks at 1.34, 2.47 and 3.38 Å.

The theoretical intensity curves were calculated from the simplified expression

$$I(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \sin\left(\frac{\pi q r_{ij}}{10}\right) \quad (2)$$

Curves were calculated for planar models of type A, Fig. 1; in these models the FCF angle is bisected by the plane of the carbon ring and the symmetry is that of the D<sub>3h</sub> point group. The scale of all models was fixed by choosing C-F = 1.33 Å. while the C-C distance was varied from 1.48 to 1.64 Å. and the FCF angle was varied from 104.5 to 114.5° in increments of 2.5°.

Intensity curves for representative planar models are shown in Fig. 3; the parameters for these models are given in Fig. 2. Most of these curves are in such complete disagreement with the visual curve (curve VIS, Fig. 4) that a detailed correlation is impossible. Curves A<sub>180</sub>, C<sub>180</sub>, D<sub>180</sub> and F<sub>180</sub> fall into this category. Curves P<sub>180</sub> and R<sub>180</sub> show somewhat better agreement but retain certain obvious discrepancies, e.g., the occurrence of two maxima at *q* values of approximately 30 and 35 which does not correspond to the fourth maximum and its shelf-like formation.

Curves for planar models for which the FCF angle was extended to either 104.5 or 114.5° were in even worse agreement with the visual pattern.

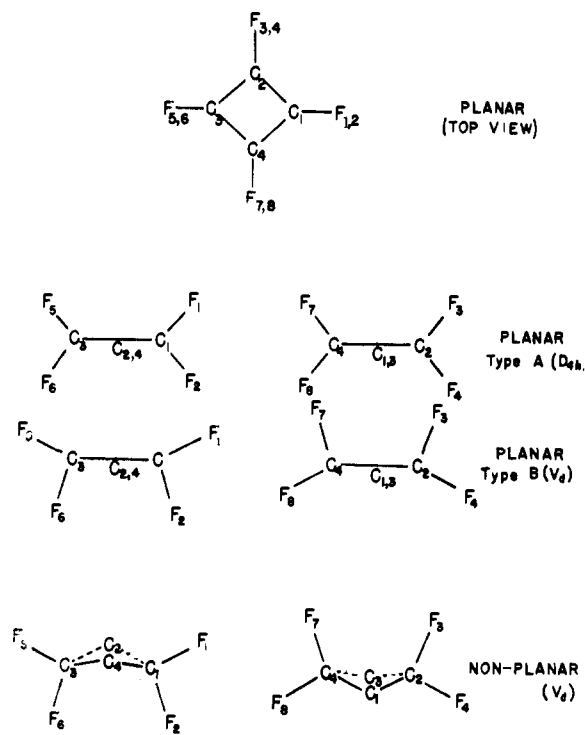
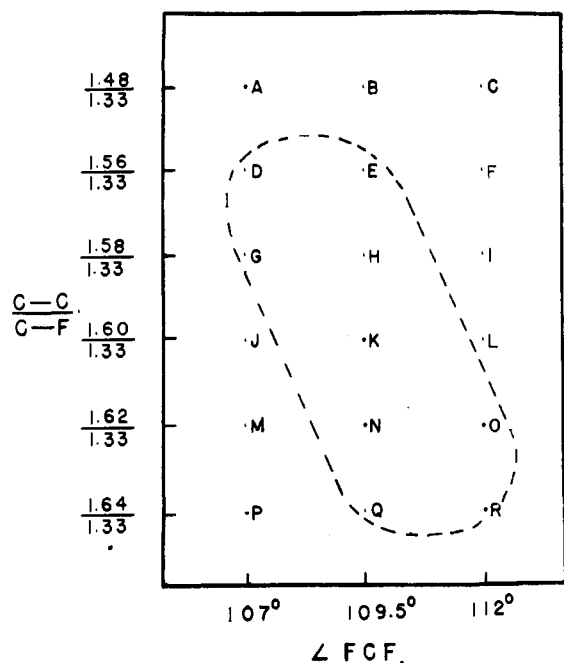
The disagreement between the radial distribution curve and the best planar model is indicated in Fig. 3 by lines drawn beneath the curve and labelled "planar." (The lengths of these lines are proportional to *nZ<sub>i</sub>Z<sub>j</sub>*.) The best planar model would give rise to a radial distribution which

(8) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(9) P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

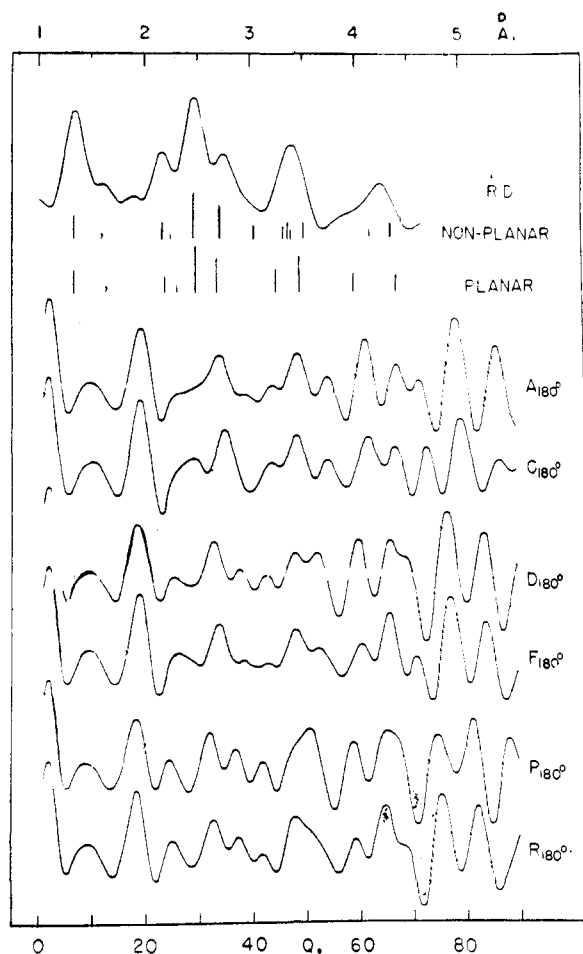
(10) L. Pauling and L. O. Brockway, *This Journal*, **57**, 2684 (1935).

(11) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).


 Fig. 1.—Types of  $C_4F_8$  models constructed.

 Fig. 2.—Parameter ranges studied for  $C_4F_8$ .

would have a much different appearance than the calculated curve in the region beyond 3 Å.

Non-planar models were 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 bisects the FCF angle of the  $CF_2$  group. These models have the symmetry  $V_4$  ( $D_{2d}$ ). The fourth parameter necessary to fix the structure of non-planar models was chosen as  $\alpha$ , the angle between planes which bisect opposite  $CF_2$  groups.


 Fig. 3.—Radial distribution function and theoretical intensity curves for planar models of  $C_4F_8$ .

This parameter was varied in  $5^\circ$  increments from  $180^\circ$  (planar model) to  $155^\circ$ . The C-C distance was varied in steps of  $0.02$  Å, from  $1.56$  to  $1.64$  Å, and the FCF angle varied from  $107$  to  $112^\circ$  as shown in the parameter chart (Fig. 2).

Intensity curves for models in which  $\alpha$  is  $160^\circ$  are shown in Fig. 4; these are labeled according to the parameter chart. Intensity curves for models in which angle  $\alpha$  is  $5^\circ$  or more removed from this value are in complete disagreement with the visual curve and are not shown.

Of the curves calculated, curve  $K_{160}$  was found to reproduce best the appearance of the observed pattern. The characteristic appearance of the fourth maximum, the relative depths of the fifth and sixth minima, and the asymmetry of the sixth maximum are all in close agreement with the visual interpretation. Intensity curves D, E, Q and R are not as accurate representations of the visual curve but do not show discrepancies sufficient to warrant their exclusion as acceptable models. In Q, R and E, the fifth and sixth minima are significantly different in depth but, keeping in mind the subjective errors in estimating the relative intensities, it appeared unjustifiable to exclude these models on this basis only.

Models J and P were rejected mainly on the basis of the appearance of the sixth maximum.

Models L and F are unacceptable because of the roundness of the fourth maximum; F shows further disagreement in the appearance of the pattern in the region of the sixth maximum.

The region of acceptable models is indicated in Fig. 2 by the dotted line.

Planar models of type B, Fig. 3, were also constructed. In these models the plane of the carbon ring does not bisect the FCF angle. Such models are not compatible with the radial distribution curve and were not considered in the exhaustive correlation procedure.

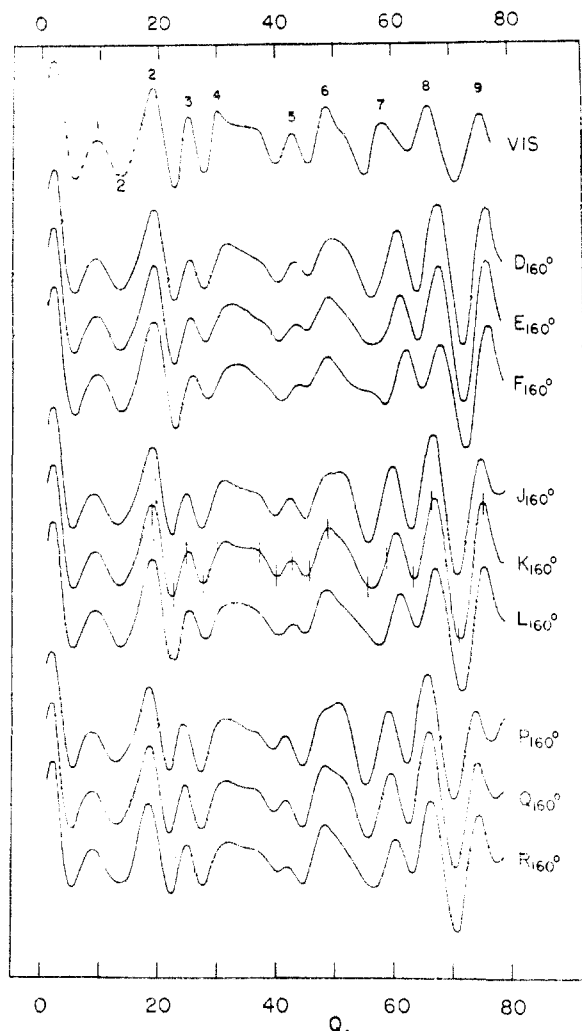


Fig. 4.—Visual curve and theoretical intensity curves for non-planar models of  $C_4F_8$ .

The effects of vibrations of the atoms were considered by calculation of a large number of curves for non-rigid models. A variety of different values were assumed for the damping factors and, in addition, planar models were tried in which special consideration was given to the mode of vibration which deforms the planar molecule into the non-planar molecule. The results of these calculations do not change in any way the conclusions which were reached on the basis of rigid models.

The results of the quantitative correlation for model  $K_{160}$  are summarized in Table I. Measurements on the second, fourth and seventh maxima and on the third minimum were not regarded as reliable and hence omitted in calculating the mean  $q(\text{calcd.})/q(\text{obsd.})$ .

The final bonded C-F distances obtained from acceptable models ranged from 1.32 to 1.34 Å.; the bonded C-C distances ranged from 1.58 to 1.63 Å., and the shortest distance between fluorine atoms attached to different carbon atoms varied from 2.70 to 2.73 Å. The best model is chosen as one with a non-planar carbon ring with C-F =  $1.33 \pm 0.02$  Å., C-C =  $1.60 \pm 0.04$  Å.,  $\angle FCF = 109.5 \pm 3^\circ$  and  $\alpha = 160 \pm 4^\circ$ . For this model the  $\angle CCC$  is nearly  $89^\circ$ . The agreement of this model with the radial distribution curve is indicated in Fig. 3 by the vertical lines labeled "non-planar."

**Methylcyclobutane.**—The radial distribution function was calculated from the visual curve (curve VIS, Fig. 7) by means of equation 1; the constant  $b$  was chosen so that the damping term ( $\exp(-bg^2)$ ) was 0.10 at  $q = 100$ . Major peaks in the curve (Fig. 6) occur at 1.55, 2.18 and 2.66 Å.

TABLE I  
ELECTRON DIFFRACTION DATA FOR OCTAFLUOROCYCLOBUTANE

Maximum	Minimum	$q_0$	$q/q_0$ ( $K_{160}^\circ$ )
2		19.07	(0.986)
	3	22.69	(0.983)
3		24.92	1.009
	4	27.69	1.002
4a		30.02	...
4b (shelf)		37.37	...
	5	40.04	1.005
5		42.87	0.997
	6	45.74	0.986
6		48.73	1.007
	7	55.51	1.018
7		59.43	1.020
	8	63.09	1.008
8		66.40	1.010
	9	71.08	1.002
9		75.37	0.998
	Mean		1.005
	Mean dev.		0.007

The peak at 1.55 Å. corresponds to the average bonded C-C distance and the one at 2.18 Å. to the cross-ring distance and the shortest non-bonded C-H distance; the peak at 2.66 Å. is identified with the shortest non-bonded distance between the carbon of the methyl group and the ring carbon atoms. A fourth peak at 1.12 Å. corresponds to the C-H distance but it is not as reliable as the others. The vertical lines drawn beneath the curve correspond to the interatomic distances in one of the best models ( $H_{160}$ ) as determined by the correlation method.

Theoretical intensity curves were obtained from the simplified scattering formula (2) in which the term  $e^{-b_{ij}/r^2}$  was included. The constant  $b_{ij}$  in the vibration factor was assigned the value 0.00018 for bonded C-H terms, 0.0003 for non-bonded C-H terms and zero for all C-C terms. Initial calculations showed that H-H terms, C-H distances which change with rotation of the methyl group, and C-H distances involving the side-chain carbon and the hydrogens on the ring make a negligible contribution to the intensity pattern; these were subsequently omitted from the intensity calculations. The exact values of the vibration factors assigned to the included C-H terms are not crucial since these terms have a relatively small effect on the intensity curve.

In order to limit the number of parameters the following assumptions were made about the structure: The H-C-H angle on the ring was assumed to be  $116^\circ$  and the plane of the H-C-H groups taken to be perpendicular to the plane of the ring and bisecting the ring angles. The C-C bond distances and angles in the ring were assumed equal and the C-H bond distances taken to be 1.09 Å.

There are four remaining parameters necessary to fix the structure. These were chosen as the bonded C-C distance, the side-chain C-C distance, the angle of folding of the ring  $\alpha$ , and angle  $\beta$  (see Fig. 5) which is the angle between the side-chain bond direction and the line bisecting the adjoining C-C-C angle in the ring. For non-planar models, a fifth parameter is necessary to fix the structure. This is illustrated in Fig. 5 in which are shown the two types of non-planar models which can be drawn. Only one important distance is affected by the type of folding and, as expected, intensity curves obtained from Type I and Type II models showed only minor differences. The comprehensive correlation method was subsequently restricted to Type I models since this type seems more plausible on the basis of expected steric factors.

Curves were calculated for planar models keeping the C-C side-chain distance fixed at 1.54 Å. and varying the two parameters C-C (ring) and  $\beta$  as shown in Fig. 5. Angle  $\alpha$  was then varied in  $10^\circ$  increments, from  $180$  to  $140^\circ$  for the listed values of  $\beta$  and with all C-C distances equal to 1.54 Å. Non-planar models were calculated for the other C-C ratios but it became apparent that these would not yield additional information.

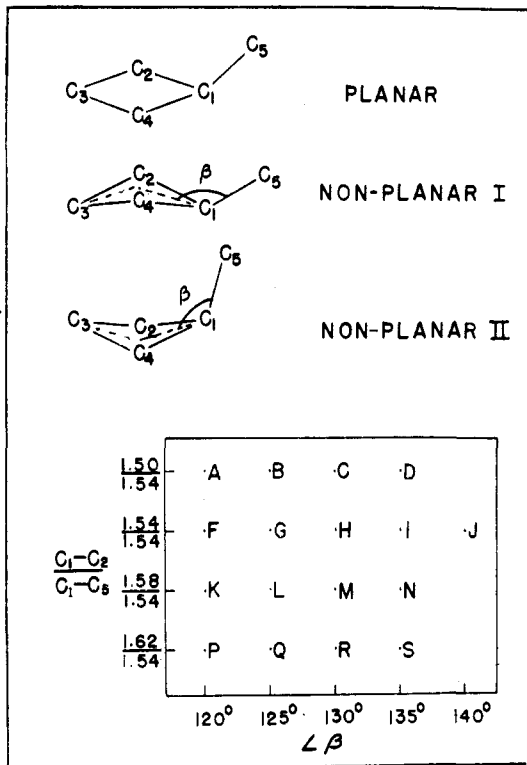


Fig. 5.—Types of models constructed and parameter ranges studied for methylcyclobutane.

Theoretical curves for a few representative planar models are shown in Fig. 6. Curves qualitatively compatible with the visual pattern were obtained for models B, G, M and R; of these, G and M give the best agreement. Curve B does not have a well-resolved fourth maximum and curve R shows a sixth maximum which is asymmetric; these discrepancies are not large enough, however, to validate the rejection of these models.

All other planar models can be rejected mainly on the basis of the fourth or the seventh maximum which are the structure sensitive features of the pattern. Curves from models with  $\beta = 120^\circ$  are all similar to  $F_{180}$  (Fig. 6) and show a fourth minimum which is too deep, a fourth maximum which is too weak and a seventh peak which is too sharp and narrow.

Curves C and H both show a well-defined doublet in place of the seventh maximum; it is possible, however, that this defect could be remedied by a different choice of damping factors.

Curves N and S illustrate the effect of increasing the angle  $\beta$  to  $135^\circ$ ; all such intensity curves show the seventh maximum as an unsymmetrical doublet with the inner member weaker than the outer; this feature is clearly incompatible with the visual pattern and it seems unlikely that it could be corrected by changing the values of the damping factors.

The effect on the intensity pattern of folding the carbon ring is illustrated in Fig. 7; the value of  $\alpha$  is indicated by a subscript. (Models are shown for only one C-C distance ratio since these illustrate adequately the general trend observed in curves calculated for other ratios.) Usually the most sensitive feature is the seventh maximum. The effect is seen from a comparison of the different H curves. Model  $H_{180}$  was rejected, as previously mentioned, because of the doublet appearance of the seventh maximum. Folding the ring decreases the intensity of the outer half of the doublet making curves  $H_{180}$  and  $H_{160}$  compatible with the visual curve. The other changes which occur as the ring is folded such as the changes in the relative intensities of the third and fifth maxima and the changes in the relative depths of the sixth, seventh and eighth minima are not large enough to justify a choice between these models. In  $H_{140}$ , the shape of the seventh maximum is incorrect, but this point is not significant enough to reject this model.

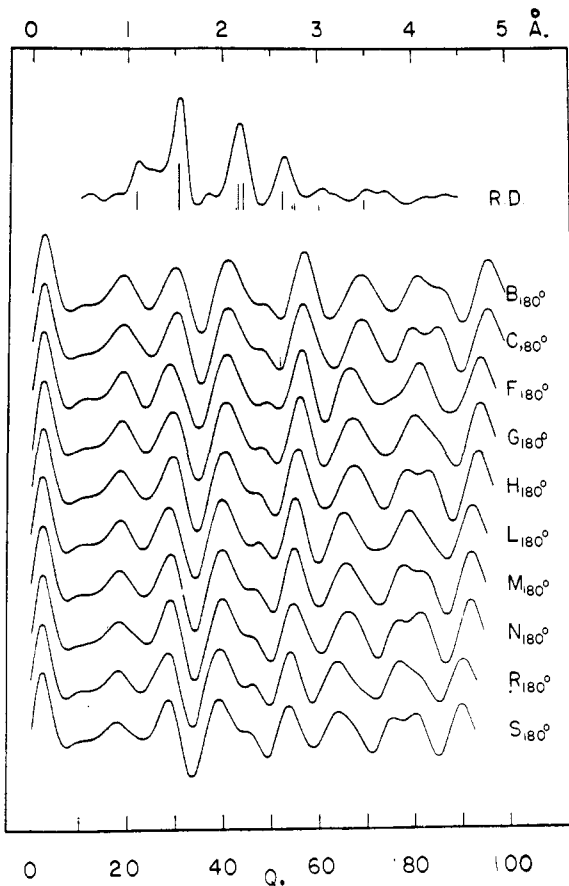


Fig. 6.—Radial distribution function and theoretical intensity curves for planar models of methylcyclobutane.

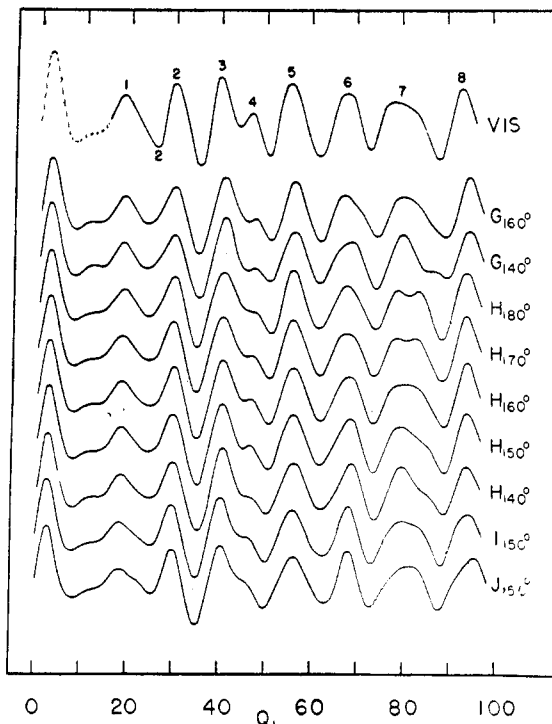


Fig. 7.—Visual curve and theoretical intensity curves for non-planar models of methylcyclobutane.

Curves  $G_{170}$ ,  $G_{160}$  and  $G_{150}$  are acceptable but  $G_{140}$  shows a discrepancy in the region of the seventh maximum.

Model  $I_{160}$  is the only model with  $\beta = 135^\circ$  and with all C-C distances equal to 1.54 Å, which was accepted. It is probable that other acceptable non-planar models with  $\beta = 135^\circ$  could be found for different values of the C-C (ring)/C-C (side-chain) ratio. Curves  $I_{170}$ ,  $I_{160}$  and  $I_{150}$  are not shown but can be safely rejected on the basis of the fourth and seventh maxima.

Curve J is typical of models having  $\beta = 140^\circ$  and can be rejected with certainty because of several obvious discrepancies.

Quantitative comparisons are given in Table II for one of the best planar models and also for one of the best non-planar models. Measurements on the first maximum and on the second minimum are unreliable because these features are somewhat diffuse and occur in a region of rapidly falling background; the seventh maximum is broad and asymmetric leading to large uncertainties in the estimation of its true position and in determining the corresponding  $q$ -value from the theoretical intensity curve.

TABLE II

ELECTRON DIFFRACTION DATA FOR METHYLCYCLOBUTANE

Maxi- mum	Mini- mum	$q_0$	$q/q_0$ ( $H_{100}^0$ )	$q/q_0$ ( $M_{100}^0$ )
1		18.56	(0.996)	(0.996)
	2	25.97	(.946)	(.900)
2		29.86	.998	.978
	3	35.46	.981	.964
3		39.85	1.016	1.004
	4	43.80	1.036	1.036
4		46.80	0.995	0.993
	5	50.70	0.996	.996
5		55.45	1.010	.992
	6	61.78	1.002	.974
6		67.67	1.006	.972
	7	72.95	1.007	.996
7		79.13	...	...
	8	87.91	1.011	.987
8		93.13	1.009	.989
	Mean		1.005	.990
	Mean dev.		0.009	.013

The quantitative comparison gives slight preference to non-planar models as the most acceptable ones since the quantitative agreement improves with increase in the extent of folding. The average deviation for planar models varies from 0.013 to 0.016 and for non-planar models from 0.008 to 0.013. The trend is seen by comparing models  $G_{180}$ ,  $G_{170}$ ,  $G_{160}$  and  $G_{150}$  for which the average deviations are 0.016, 0.013, 0.012 and 0.010, respectively.

It must be concluded that the planarity or non-planarity of the ring cannot be determined with certainty but it does appear possible that the ring is folded to an angle  $\alpha$  of about  $150$  or  $160^\circ$ . Consideration of all acceptable models leads to a C-C distance in the ring of  $1.56 \pm 0.03$  Å, and a side-chain distance  $1.54 \pm 0.06$  Å; the average C-C distance is  $1.555 \pm 0.02$  Å. The angle  $\beta$  cannot be fixed accurately; its average value is  $130^\circ$  with a maximum uncertainty of  $\pm 8^\circ$ .

## Discussion

The C-C bond distance found in methylcyclobutane is in good agreement with the results obtained in related compounds. The C-C distance in cyclobutane has been found to be  $1.565 \pm 0.02$  Å.<sup>12</sup> In methylenecyclobutane the values reported for the average C-C bond length are  $1.56 \pm 0.03$  Å,<sup>13</sup> and  $1.55 \pm 0.02$  Å;<sup>14</sup> in dimethylketene dimer the value given is  $1.56 \pm 0.05$  Å.<sup>15</sup>

It seems significant that in these compounds the bond length in the ring is only slightly higher than the value of 1.54 Å, which is observed in many hydrocarbons. This is in contrast to the C-C distance of 1.60 Å, found in  $C_4F_8$ . It appears plausible on the basis of the results obtained in  $C_3F_6$  that the fluorine atoms cause this significant lengthening of the C-C distance. It should be noted that in the case of  $C_3F_6$  it was found that the closest distance of approach of fluorine atoms attached to different carbon atoms is about 2.70 Å, which is twice the van der Waals radius of fluorine. As previously mentioned, essentially this same value (2.70 to 2.73 Å) occurs in all acceptable models of  $C_4F_8$ . It thus appears probable 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.

A recent X-ray study<sup>16</sup> of octachlorocyclobutane has shown that the ring in this compound is also folded to an angle of  $160^\circ$ . If the carbon ring in cyclobutane itself is planar, as is suggested by spectroscopic evidence,<sup>17</sup> then the non-planar ring in  $C_4F_8$  and  $C_4Cl_8$  must be attributed to repulsions between the halogen atoms. There remains the possibility, however, that the carbon ring is non-planar in cyclobutane and in derivatives such as methylcyclobutane.

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