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The Structure of C_8F_{12}, a Saturated Dimer of Hexafluorobutadiene

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The molecular formula and configuration of the saturated C_8F_{12} molecule has been elucidated. The carbon skeleton contains two bridge bonds which make four-membered and five-membered rings (tricyclo[3,3,0,0²,⁶]octane). The symmetry of the molecule is D_{2d}.

The material crystallizes in the triclinic system with one molecule in a unit cell having the dimensions $a = 6 \cdot 02$, $b = 6 \cdot 29$, $c = 7 \cdot 27$, $\alpha = 103 \cdot 6°$, $\beta = 107 \cdot 9°$, $\gamma = 106 \cdot 4°$. The statistical averages of normalized structure factors strongly indicate that the space group is $P\bar{1}$, and since the molecule does not have a center of symmetry, this implies that the crystal structure is disordered. Attempts to refine an ordered structure in $P1$ failed. Satisfactory refinement was obtained with a disordered structure (utilizing space group $P\bar{1}$) in which successive molecules may be subject to reversal of direction.

The structure was solved by obtaining the phases directly from the magnitudes of the structure factors by the application of the symbolic addition method for phase determination.

Introduction

Some years ago, the thermal reactions of hexafluoro-butadiene were investigated by Prober & Miller (1949). The first step resulted in a mixture of dimers which were dienes. Further heating of the dimers in a bomb yielded a large fraction of a material which boiled at 80 °C and melted at 40 °C. The material was found to have the molecular formula C_8F_{12} and was shown to be fully saturated. Prober & Miller (1949) suggested that the structural formula of C_8F_{12} may be

$$CF_2-CF-CF-CF_2$$
$$CF_2-CF-CF-CF_2 \quad \text{(I)}$$
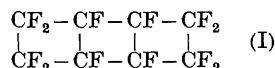
The structure has been elucidated by the application of the symbolic addition method of phase determination (Karle & Karle, 1963) to three-dimensional X-ray intensity data. The X-ray analysis shows that the compound is not in the form of three fused butane rings, but assumes the following configuration:

$$CF_2-CF-CF-CF_2$$
$$CF_2-CF-CF-CF_2 \quad \text{(II)}†$$
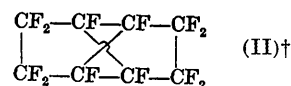
Experimental measurements

Single crystals of the compound were grown under vacuum by sublimation in thin-walled glass capillaries. The capillaries were 1 mm in diameter and had an average wall thickness of 0·01 mm. The crystals were mounted on the goniometer head so that the face of growth in the capillary was perpendicular to the rotation axis. Multiple-film, equi-inclination Weissenberg photographs were taken along the 100, 010 and $\bar{1}$10 directions with Cu $K\alpha$ radiation. Zero-layer NaCl reflections were superimposed on zero-layer photographs of C_8F_{12} for lattice constant measurements.

The diffraction results show a triclinic cell with the following parameters:

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† *Note added in proof*:—The configuration of a similar compound, C_8H_{12}, was inferred to be of type (II) on the basis of a nuclear magnetic resonance spectrum (Srinivasan, 1963).

$a = 6\cdot02 \pm 0\cdot01$ Å $\alpha = 103\cdot6 \pm 0\cdot4°$
$b = 6\cdot29 \pm 0\cdot01$ $\beta = 107\cdot9 \pm 0\cdot4$
$c = 7\cdot27 \pm 0\cdot01$ $\gamma = 106\cdot4 \pm 0\cdot4$

with $Z = 1$ and $\varrho_c = 2\cdot29$ g.cm^{-3}.

The relative intensities were determined by visual comparison of the reflections with an intensity strip. Lorentz, polarization, and Tunell factors, where applicable, were applied to the intensity data. By careful cross-calibration all data were reduced to the zero-layer a-axis photograph. There were 1048 reflections of which 753 were non-zero data.

The relative F^2 values were adjusted to an absolute scale by means of a K-curve and normalized structure factor magnitudes, $|E|$, were computed. For a triclinic space group,

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2 \Big/ \sum_{j=1}^{N} f_{j\mathbf{h}}^2 , \qquad (1)$$

where $F_{\mathbf{h}}^2$ is on an absolute scale and corrected for vibrational motion, N is the number of atoms in the unit cell and f_j is the atomic scattering factor for the jth atom. Statistical averages for the normalized structure factors and the distribution of $|E|$ magnitudes are listed in Table 1. The experimental values are compared with theoretical values computed for crystals with randomly distributed atoms. The statistical averages imply that the crystal is centrosymmetric and that its space group is therefore $P\bar{1}$.

Table 1. *Averages and distribution of normalized structure factors*

	Experimental	Centrosym.	Non-centrosym.
$\langle |E| \rangle$	0·753	0·798	0·886
$\langle |E^2-1| \rangle$	1·137	0·968	0·736

	Experimental	Theoretical
$|E| > 3\cdot0$	1·0%	0·3%
$|E| > 2\cdot0$	6·1%	5·0%
$|E| > 1\cdot0$	31·5%	32·0%

Phase determination

The phases were determined directly by the symbolic addition procedure (Karle & Karle, 1963). The origin was specified by assigning signs to three linearly independent reflections (Hauptman & Karle, 1953). The signs of four other reflections were specified with a letter symbol where each letter can mean either plus or minus. These seven assignments, which form the starting set for applying the Σ_2 formula, are shown in Table 2. The Σ_2 formula is

$$sE_{\mathbf{h}} \sim s \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h-k}} \qquad (2)$$

where s means 'sign of'.

The probability that the sign of $E_{\mathbf{h}}$ is plus is determined by the formula (Hauptman & Karle, 1953; Woolfson, 1954)

Table 2. *Assignment of three origin specifying reflections and four other reflections as a starting set for the application of Σ_2*

Sign	hkl	E
+	012	2·62
+	$71\bar{3}$	4·89
+	$\bar{5}2\bar{4}$	2·90
a	131	2·75
b	$51\bar{6}$	2·74
c	119	2·69
d	$50\bar{3}$	2·43

$$P_+(E_{\mathbf{h}}) = \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{\sigma_3 |E_{\mathbf{h}}| \sum\limits_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h-k}}}{\sigma_2^{3/2}} \qquad (3)$$

where

$$\sigma_n = \sum_{j=1}^{N} Z_j^n ,$$

Z_j being the atomic number of the jth atom in a cell containing N atoms. To obtain the highest probabilities that the sign indicated by Σ_2 was correct, the procedure was begun with those reflections which had the largest $|E|$ magnitudes.

In the initial stages of sign determination, only those reflections with $|E| > 1\cdot5$ were considered. In this initial set, there were many interactions between the reflections used to specify the origin and those assigned the symbols a or b. There were very few interactions with the reflections assigned the symbols c and d. As a result most of the phases determined for the initial set of reflections with $|E| > 1\cdot5$ were $+$, a, b, or ab and very few were functions of c or d. Accordingly, E-maps (three-dimensional Fourier maps with E values rather than F values for the coefficients) were computed for the combinations $--$, $+-$ and $-+$ for a and b, while c and d were disregarded.

None of these maps contained the correct number of peaks, nor were the peaks separated by meaningful distances. The combination $++$ for a and b was not considered at first because the overwhelming number of positive phases would result in a very large peak at the origin. However, the combination of $++$ for a and b, and $--$ for c and d did indeed prove to be the correct one. The phase determination was extended to reflections with $|E| > 1\cdot15$ and even then there was a preponderance of positive phases, although the E-map revealed all the atoms at this point. It was not until phases for all reflections with $|E|$ as small as 0·6 were determined, that the peak at the origin almost disappeared. There were 531 reflections with $|E| > 0\cdot6$. Phases for 450 were accepted as determined with the Σ_2 formula and phases for 81 were considered indeterminate, using the criterion that less than two-thirds of the contributors to Σ_2 for a particular reflection indicated the same sign. Of the 450 phases, fifteen were subsequently shown to be incorrect. All the incorrectly determined phases had low $|E|$ values ($|E| < 1\cdot1$) and relatively few contributors to the Σ_2 formula. The phase determination was facilitated by a high-speed computer,

although hand calculation is feasible. An E-map computed with 450 terms is illustrated in Fig. 1. Sections through maximum density are projected along the a axis.

Structure determination

On the assumption that the cell dimensions represent a real cell in space group $P\bar{1}$, the molecule of C_8F_{12} would be required to have a center of symmetry since there is only one molecule in the unit cell. Hence there would be only four carbon atoms and six fluorine atoms to place. An examination of the E-map illustrated in Fig. 1 revealed six heavy peaks (of weight seven or more on an arbitrary scale) which could represent the fluorine atoms. Four of these peaks, however, were not spherical in shape but ellipsoidal. Two of them, labelled F(4), F(9′) and F(3), F(10′), were elongated in the y direction, and the other two, F(5), F(11′) and F(2), F(8′), were elongated in the x direction. The carbon atoms were represented by four fairly spherical peaks of weight 2, approximately half-weight for carbon atoms as compared to fluorines, and by two ellipsoidal peaks of weight 4, each probably representing two carbon atoms. The appearance of the map suggested a disorder or, perhaps, a pseudocell.

It was necessary to fit the peaks of the E-map with two superimposed molecules. A centrosymmetric model based on formula (I) could not be made to fit, even if the molecules were highly twisted. Two superimposed molecules of a non-centrosymmetric model based on formula (II) fit all the peaks very readily. Attempts to refine a structure based upon
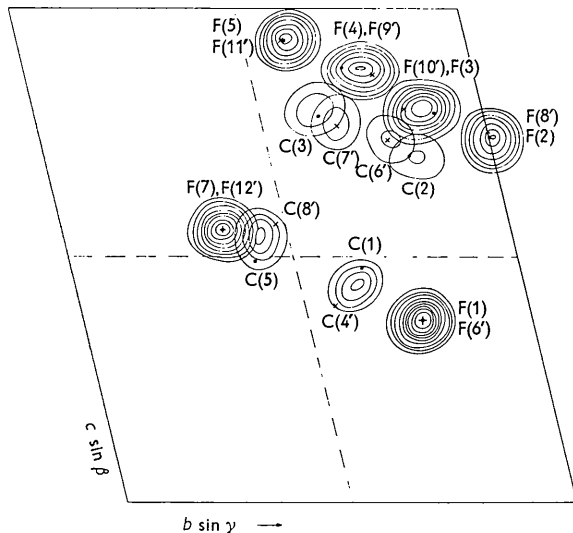

Fig. 1. A composite of a three-dimensional E map viewed along the a axis. The phases for all the 450 terms were determined by the symbolic addition procedure. For the phase determination, the center of the cell was used as an origin. The contours are at equally spaced intervals on an arbitrary scale. The small squares and crosses indicate the positions of the atoms after refinement.

a single molecule of formula (II), in space group $P1$ (statistical averages to the contrary) did not succeed.

When two superimposed molecules, related by a center of symmetry, were given half-weight and subjected to a least-squares refinement, the refinement progressed in a satisfactory manner. Fig. 2 shows the superposition of two C_8F_{12} molecules.
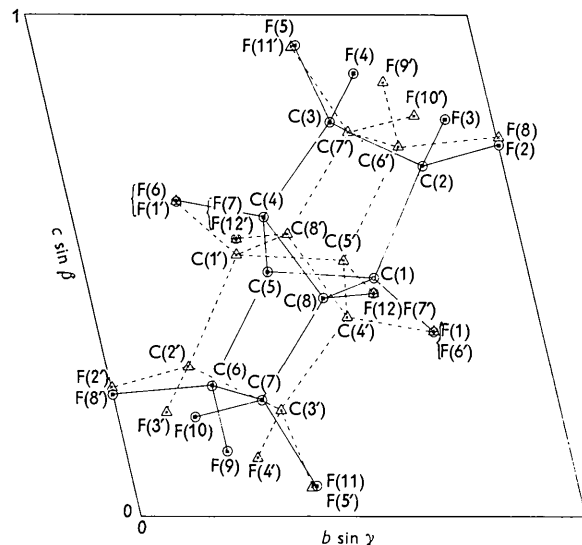

Fig. 2. Superposition of two C_8F_{12} molecules corresponding to the peaks in Fig. 1.

The question arises as to whether the cell is disordered or whether it is a pseudocell with some or all of the axes halved. No extraneous weak reflections were observed to suggest a larger cell, although since the crystal was encased in a glass capillary there is a small possibility that reflections could have been partially absorbed by the glass and be too weak to be observed on the film. However, from packing considerations of neighboring molecules, discussed in a later section, there is no need to have a larger ordered cell. In addition, the related compounds $C_8Cl_4F_8$ and C_6F_{10}, which have physical properties very similar to those of C_8F_{12}, gave X-ray diffraction patterns which were very suggestive of considerable disorder (Schapiro & Hoard, 1954).

Structures comprised of asymmetric molecules, contrary to the requirements of an apparently centrosymmetric space group, have been previously observed for space group $P2_1/a$. For example, in the structures of azulene (Robertson, Shearer, Sim & Watson, 1962) and of acepleiadylene (Hanson, 1960) there were only two molecules per unit cell. Since the space group demanded a center of symmetry whereas the molecules were asymmetric, a satisfactory solution was found only for a disordered structure. In the present investigation, a similar situation exists in space group $P\bar{1}$.

Refinement

The coordinates of the twenty atoms were subjected to a least-squares refinement with the ORFLS program (Busing, Martin & Levy, 1962) which was adapted in our laboratory to the IBM 7030 (STRETCH). Since two molecules occupied the same space in the unit cell, many of the atoms were within a few tenths of 1 Å of each other. To keep pairs of atoms from coalescing, half the atoms were kept in constant positions while one cycle of refinement was performed on the other half. Then the process was reversed, the first half being refined while the second half was kept constant. Although the refinement was slow, the process of alternation kept the matrix from becoming singular. The two groups of atoms were

C(1)C(2)C(3)C(4)F(1)F(2)F(3)F(4)F(5)F(6) and

C(5)C(6)C(7)C(8)F(7)F(8)F(9)F(10)F(11)F(12) .
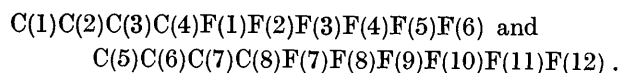
The coordinates of F(1) and F(6) and those of F(7) and F(12) were so closely related by a center of symmetry of the cell, that these two pairs of atoms were refined only as F(1) and F(7) each having double weight.

Early in the refinement, the problem of extinction errors became apparent. Many of the low index reflections had very large $|F_o|$. The computed structure factors for these reflections were much larger in magnitude than the observed ones. No attempt was made to correct for extinction. However, fourteen reflections with large $|F_o|$ were removed from the refinement. The $|F_o|$ of these fourteen reflections were too small by $\frac{1}{3}$ to $\frac{1}{2}$.

Because of the problems of superposition and extinction, this structure should be regarded as only
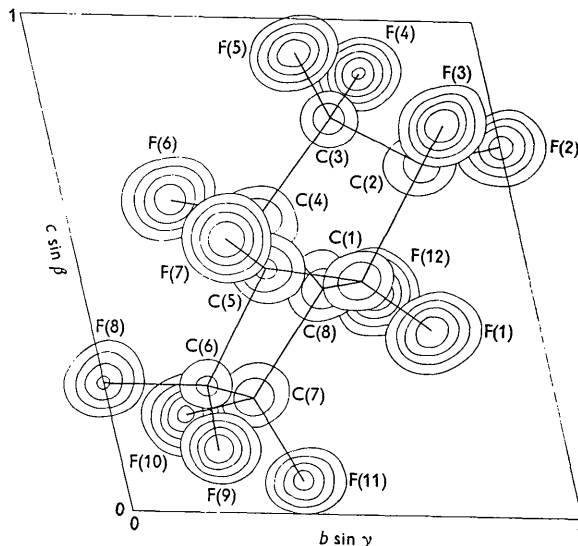

Fig. 3. A composite of two different difference maps to illustrate the electron density of C_8F_{12} in one of its two orientations. The contours are spaced every 2 e.Å^{-3} beginning with the 2 e.Å^{-3} level.

partially refined. The final R value was 17·7%.[*] Table 3 lists the coordinates and temperature factors from the final cycle of least-squares refinement. An electron density map of the molecule in one of the two orientations is illustrated in Fig. 3. This map is a composite of two different difference maps, each

* A microfilm of the observed and computed structure factors has been deposited with The Library of Congress, Exchange and Gift Division, Washington, D.C., U.S.A. The reel number is 9086.

Table 3. *Fractional coordinates for* C_8F_{12}

The thermal parameters are of the form $T = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.
Each thermal parameter is multiplied by 10^4. The origin has been shifted by $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ from that used for the phase determination

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·6084	0·6415	0·4799	226	226	89	48	122	73
C(2)	0·7401	0·8076	0·7048	215	429	130	64	51	33
C(3)	0·5998	0·6326	0·7911	280	360	178	175	122	121
C(4)	0·4445	0·4361	0·6001	251	267	96	94	141	15
C(5)	0·6128	0·4080	0·4862	211	190	97	107	97	−24
C(6)	0·4382	0·2301	0·2666	273	339	148	76	159	50
C(7)	0·2212	0·3327	0·2338	316	300	125	88	97	104
C(8)	0·3408	0·5191	0·4380	237	187	63	69	45	−55
F(1)	0·7046	0·7549	0·3672	354	405	232	89	195	191
F(2)	0·6984	1·0012	0·7447	370	303	188	166	50	0
F(3)	0·9926	0·8929	0·7892	300	245	210	22	78	94
F(4)	0·4648	0·7062	0·8838	524	304	169	238	241	132
F(5)	0·7533	0·5864	0·9323	315	584	125	216	82	162
F(6)	0·2953	0·2451	0·6328	354	405	232	89	195	191
F(7)	0·8125	0·3540	0·5544	300	482	267	251	159	169
F(8)	0·3615	−0·0022	0·2679	342	346	265	131	111	45
F(9)	0·5442	0·2290	0·1337	463	335	176	242	222	117
F(10)	0·0054	0·1774	0·2000	163	212	189	14	20	46
F(11)	0·1837	0·4100	0·0726	263	475	125	174	66	115
F(12)	0·1875	0·6461	0·4456	300	482	267	251	159	169
Standard error									
C	0·0034	0·0034	0·0026	62	64	40	52	43	39
F	0·0020	0·0020	0·0015	42	41	26	34	27	27

computed by eliminating the contribution of half the atoms.

Discussion of structure

Geometry of the molecule

The C_8F_{12} crystal is extremely dense, 2·29 g.cm^{-3}, for an organic substance. It is not surprising, therefore, that the molecule can be contained in an ellipsoid with circular cross-section and that the fluorine atoms are nearly equidistant from each other. Actually, disregarding experimental uncertainty, the symmetry of the molecule is D_{2d}. It has three mutually perpendicular twofold axes, two planes of symmetry bisecting the angles between two of the twofold axes, and the third twofold axis functions as a fourfold inversion axis. The ring system of the molecule consists of a puckered four-membered ring in the middle, fused to five-membered rings on either side (Fig. 4). This configuration has bond angles closer to
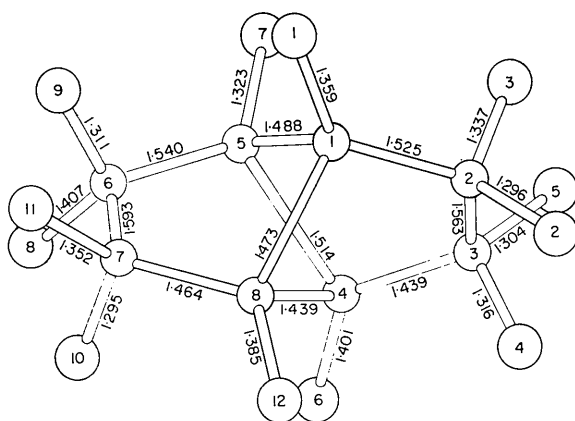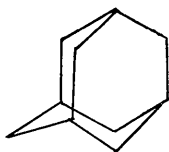
Fig. 4. Bond lengths in C_8F_{12}.

tetrahedral values, and, therefore, less strain than the three fused four-membered rings illustrated in (I). Other somewhat similar tricyclic hydrocarbons have been synthesized in recent years. One is adamantane,

which is free of angle strain since it is composed of four fused, chair-shaped cyclohexane rings (Landa, 1962; Nowacki, 1945). Another is twistane,
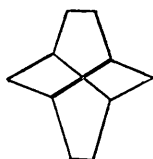
which does have some angle strain since it is made up of half-boat cyclohexane rings (Whitlock, 1962). In all three materials, adamantane, twistane and C_8F_{12}, the surface area of the molecules is extremely small and intermolecular forces must be correspondingly weak; hence all three volatilize very readily.
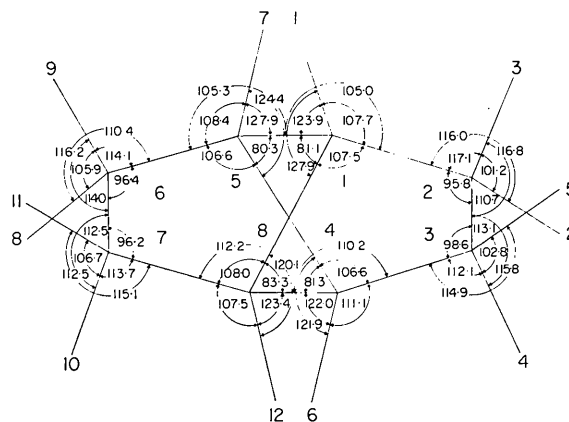
Fig. 5. Bond angles in C_8F_{12}.

The bond lengths and angles for all the atoms in C_8F_{12} are given in Tables 4 and 5 and are shown in Figs. 4 and 5. Although the determination of the bond lengths is not precise, it is interesting to note that the average C–F bond length for one fluorine atom attached to a carbon atom is 1·367 Å as compared with 1·327 Å for the average C–F when two fluorines are attached to a carbon atom. This is in agreement with results obtained from electron diffraction studies of the vapors of fluorocarbons, where monofluorides have an average value of 1·38 Å for the C–F whereas the average value for C–F in polyfluorides is 1·33 Å (see *Interatomic Distances*, 1958).

Table 4. Bond lengths

Bond		Bond	
C(1)–C(2)	1·525 Å	C(1)–F(1)	1·359 Å
C(2)–C(3)	1·563	C(4)–F(6)	1·401
C(3)–C(4)	1·439	C(5)–F(7)	1·323
C(4)–C(5)	1·514	C(8)–F(12)	1·385
C(5)–C(6)	1·540		1·367 av.
C(6)–C(7)	1·593		
C(7)–C(8)	1·464	C(2)–F(2)	1·296
C(8)–C(1)	1·473	C(2)–F(3)	1·337
C(4)–C(8)	1·439	C(3)–F(4)	1·316
C(1)–C(5)	1·488	C(3)–F(5)	1·304
	1·504 av.	C(6)–F(8)	1·407
		C(6)–F(9)	1·311
		C(7)–F(10)	1·295
		C(7)–F(11)	1·352
			1·327 av.

The standard deviation is 0·028 Å for the C–C bond lengths and 0·023 Å for the C–F bond lengths.

The bonds about each carbon atom arrange themselves in as near a tetrahedral array as possible with

Table 5. *Bond angles grouped according to similar environment*

Angle

C(1)–C(5)–C(4)	80·3°	
C(5)–C(4)–C(8)	81·3	cyclobutane
C(4)–C(8)–C(1)	83·3	81·5 av.
C(8)–C(1)–C(5)	81·1	
C(1)–C(2)–C(3)	95·8	
C(2)–C(3)–C(4)	98·6	cyclopentane
C(5)–C(6)–C(7)	96·4	96·7 av.
C(6)–C(7)–C(8)	96·2	
C(8)–C(1)–C(2)	107·5	
C(5)–C(1)–C(2)	105·0	
C(8)–C(4)–C(3)	110·2	
C(5)–C(4)–C(3)	106·6	cyclopentane
C(1)–C(5)–C(6)	105·3	107·7 av.
C(4)–C(5)–C(6)	106·6	
C(1)–C(8)–C(7)	108·0	
C(4)–C(8)–C(7)	112·2	
F(2)–C(2)–F(3)	101·2	
F(4)–C(3)–F(5)	102·8	104·1 av.
F(8)–C(6)–F(9)	105·8	
F(10)–C(7)–F(11)	106·7	
C(8)–C(1)–F(1)	127·9	
C(5)–C(1)–F(1)	123·9	
C(5)–C(4)–F(6)	121·9	
C(8)–C(4)–F(6)	122·0	cyclobutane,
C(4)–C(5)–F(7)	124·4	one F per C
C(1)–C(5)–F(7)	127·9	123·9 av.
C(1)–C(8)–F(12)	120·1	
C(4)–C(8)–F(12)	123·4	
C(2)–C(1)–F(1)	107·7	
C(3)–C(4)–F(6)	111·1	cyclopentane,
C(6)–C(5)–F(7)	108·4	one F per C
C(7)–C(8)–F(12)	107·5	108·7 av.
C(2)–C(3)–F(4)	115·8	
C(2)–C(3)–F(5)	113·1	
C(3)–C(2)–F(2)	110·7	
C(3)–C(2)–F(3)	116·8	
C(7)–C(6)–F(8)	114·0	
C(7)–C(6)–F(9)	116·2	
C(6)–C(7)–F(10)	112·5	
C(6)–C(7)–F(11)	112·5	cyclopentane,
C(1)–C(2)–F(2)	116·0	two F per C
C(1)–C(2)–F(3)	117·1	114·2 av.
C(4)–C(3)–F(4)	112·2	
C(4)–C(3)–F(5)	114·9	
C(5)–C(6)–F(8)	110·4	
C(5)–C(6)–F(9)	114·1	
C(8)–C(7)–F(10)	113·7	
C(8)–C(7)–F(11)	115·1	

The standard deviation for the bond angles ranges from 1·5° to 1·7°.

the constraints imposed by the four-membered ring. The largest deviations from the tetrahedral value occur in the cyclobutane ring where the average CCC angle is 81·5°. Large deviations from the tetrahedral value also occur in the cyclopentane rings since their configurations are constrained by the central four-membered ring. The four CCC angles at either end of the molecule have values between 95·8° and 98·6°. Among the CCF angles, the only large departure from tetrahedral values again occurs with the carbon atoms of the four-membered ring, where the CCF angles average 123·9°.

The puckered configuration of the cyclobutane rings is very similar to that found in the crystal of C_4Cl_8 (Owen & Hoard, 1951) and in the vapor of C_4F_8 (Lemaire & Livingston, 1952); however in C_8F_{12} the four-membered ring is more puckered. The dihedral angles in the carbon ring in C_4F_8 and C_4Cl_8 are $\sim 162°$, whereas the equivalent angle in C_8F_{12} is $\sim 120°$.

The equations for the least-squares planes through atoms

$$C(1)C(2)C(3)C(4)F(1)F(6) \text{ and}$$
$$C(5)C(6)C(7)C(8)F(7)F(12)$$

are, respectively,

$$5·3263X - 4·2318Y + 0·0761Z = 0·5761 \quad (4)$$
$$2·7861X + 4·0284Y - 5·4162Z = 0·6958 \quad (5)$$

where the X, Y and Z values refer to the triclinic axes. The dihedral angle between the two planes is 89°. Deviations of individual atoms from the least-squares planes are:

C(1)	−0·014 Å	C(5)	0·021 Å
C(2)	0·002	C(6)	0·008
C(3)	0·002	C(7)	−0·006
C(4)	−0·008	C(8)	−0·028
F(1)	0·010	F(7)	0·015
F(6)	0·008	F(12)	−0·010

The fluorine atoms in the molecule of C_8F_{12} are so arranged as to be nearly equidistant from each other. Fig. 6 illustrates the average F–F distances between similar pairs of atoms.
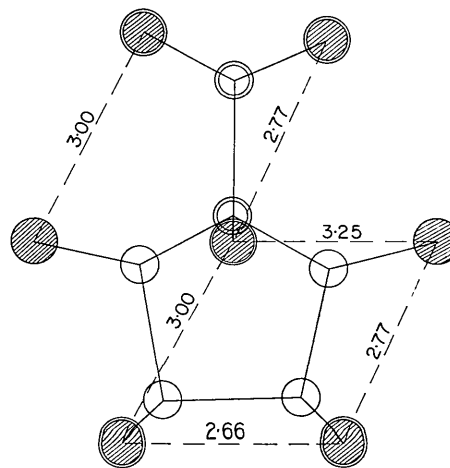

Fig. 6. Non-bonded F–F distances in the molecule. Distances between similar pairs of atoms have been averaged.

Packing of the molecules

The disorder in the crystal corresponds, presumably, to one in which adjacent unit cells are occupied by molecules having the same orientation or one related to it by an inversion through a symmetry center. Successive unit cells are arranged at random or with

Table 6. *The shorter intermolecular contacts*

|		Position of second molecule		
F(5)–F(4')	2·79 Å	$1-x$	$1-y$	$2-z$
F(9)–F(10')	2·79	$1+x$	y	z
F(1)–F(8')	2·91	x	$1+y$	z
F(2)–F(7')	2·91	x	$1+y$	z
F(12)–F(2')	2·91	$1-x$	$2-y$	$1-z$
F(12)–F(8')	2·92	x	$1+y$	z
F(7)–F(7')	2·92	$2-x$	$1-y$	$1-z$
F(4)–F(11')	3·01	x	y	$1+z$
F(3)–F(3')	3·01	$2-x$	$2-y$	$2-z$
F(3)–F(9')	3·02	$2-x$	$1-y$	$1-z$

a limited regularity in some sections of the crystal. Table 6 illustrates that the disorder does not lead to any unusual intermolecular distances. For some arrangements of the molecules, the shortest intermolecular distances are 2·79 Å. This value can be compared to some F–F separations in inorganic compounds, such as 2·65 Å in Na_3TaF_8 (for fluorine atoms in different complex ions) (Hoard, Martin, Smith & Whitney, 1954), 2·84 Å in K_3SiF_7 (Deadmore & Bradley, 1962), and 2·83 Å in ScF_3 (Nowacki, 1939).

Chemistry

The C_8F_{12} compound was formed in two steps by the thermal polymerization of hexafluorobutadiene (Prober & Miller, 1949). In view of the structure of the C_8F_{12} molecule, the probable reactions were first the formation of the cyclooctadiene:

$$2FC=C-C=CF \xrightarrow{\Delta} \text{(ring structure)} ,$$
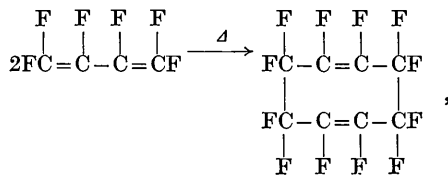
and then the formation of the saturated C_8F_{12}:

$$\text{(reaction scheme)}$$
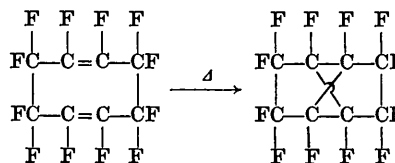
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