

Octafluorocyclooctatetraene at 238 K

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Abstract. C_8F_8 , $M_r = 248.07$, monoclinic, $P2_1/c$, $Z = 4$, $F(000) = 480$; at 238 K, $a = 9.96$ (1), $b = 7.04$ (1), $c = 12.66$ (1) Å, $\beta = 111.6$ (1)°, $V = 825.0$ Å³, $D_x = 2.00$ Mg m⁻³. Full-matrix least-squares refinement resulted in a final conventional R index of 0.044 for 1337 reflections. The C_8 ring of C_8F_8 adopts a tub configuration which is only slightly more flattened than that of C_8H_8 .

Introduction. Octafluorocyclooctatetraene, a potentially useful precursor to other fluorinated organic and organometallic compounds, is prepared by photocycloaddition of dichlorodifluoroethylene to hexafluorobenzene which gives a mixture of tricyclic adducts. Thermal ring opening followed by dechlorination with Zn gives the desired product (Lemal, Buzby, Barefoot, Grayston & Langnis, 1981). The present work has been undertaken to determine the effect of perfluorination on the molecular configuration relative to the hydrocarbon cyclooctatetraene, C_8H_8 (Trætteberg, 1966).

Single crystals of C_8F_8 were grown by vacuum sublimation across a slight temperature gradient. All X-ray measurements were made on a Syntex P2₁ autodiffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation, with the crystal bathed in a stream of dry N_2 at 238 K. In spite of the high sublimation rate at room temperature, it was hoped that the crystal would be stable once it was in the cold stream, so a large single crystal was glued to a glass fiber and transferred as rapidly as possible to the cold stream; when the crystal reached its final location in the stream, it was a spheroidal mass of approximate diameter 0.5 mm. After determination of the space group and unit-cell parameters and verification of crystal quality, it was evident that sublimation was proceeding at a measurable rate, so the unit-cell parameters and orientation matrix based on only 10 rather low-angle reflections ($6.7^\circ < 2\theta < 20.5^\circ$) were accepted and intensity-data collection was begun at a constant scan speed of $12^\circ \text{ min}^{-1}$. Because intensity loss due to sublimation proved to be even more rapid than anticipated, the scan speed was increased to $29^\circ \text{ min}^{-1}$ after measurement of 114 reflections. Even

though the intensities of four standard reflections diminished by about 33% over the 3.7 h of data collection, this fall-off was uniform (Henslee & Davis, 1975), so the intensity data were accepted, corrected accordingly, and the structure was solved and refined. The well behaved refinement and, especially, the excellent agreement among independent equivalent structural features (see below) justify the assertion that no significant structural error has resulted from the sublimation, so redetermination at lower temperature or with the crystal mounted in a capillary, with all of the errors thus introduced, was not considered to be worthwhile. Intensity data processing was as detailed elsewhere (Riley & Davis, 1976), with $p = 0.02$. Other specifics of data collection and processing are listed in Table 1. Structure solution and refinement were carried out with the 1337 reflections for which $I_o \geq 2.0\sigma(I_o)$.

The structure was solved by direct phasing methods, using the *MULTAN* program package (Main, Woolfson, Declercq & Germain, 1974). Full-matrix least-squares refinement of all atoms, isotropic at first, changing later to anisotropic, resulted in convergence with $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.044$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.043$. Refinement for the effects of secondary extinction by Zachariasen's (1968) method led to a final value of $2.4(1) \times 10^{-5}$ for this isotropic parameter. The function minimized was

Table 1. *Data collection at 238 K*

$\lambda(\text{Mo } K\alpha)$	0.71069 Å
Mode	ω scan
Scan range	Symmetrically over 1.0° about $K\alpha_{1,2}$ maximum
Background	Offset 1.0 and -1.0° in from $K\alpha_{1,2}$ maximum
Scan rate	12 or $29^\circ \text{ min}^{-1}$ (see text)
Check reflections	4 remeasured after every 96 reflections; analysis* of these data indicated substantial linear fall-off of intensity with time
Range of time-dependent intensity correction factor	1.000–1.493
2θ range	4.0 – 55.0°
Total reflections measured	2212
Absorption coefficient (Mo $K\alpha$)	0.058 mm^{-1} (not applied)

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* Henslee & Davis (1975).

$\sum w(|F_o| - |F_c|)^2$ where the weighting factor w is the reciprocal square of the standard deviation of each observation $|F_o|$ [i.e. $w = \sigma(|F_o|)^{-2}$]. Neutral-atom scattering factors for C and F (*International Tables for X-ray Crystallography*, 1974) were used. No atom parameter shifted more than 0.02 of its e.s.d. in the final cycle of refinement.

Final atomic coordinates with their estimated standard deviations are listed in Table 2.* Fig. 1 gives a representation with the atom-numbering scheme. Interatomic distances and angles are shown on Figs. 2 and 3 respectively. The packing of the molecules in the crystal is depicted in Fig. 4.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36357 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic fractional coordinates and equivalent isotropic thermal parameters

The atomic numbering scheme is indicated in Fig. 1. Numbers in parentheses are estimated standard deviations in the last digits shown. $U_{eq} = (\frac{1}{3}\pi^2) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^4$)
C(1)	0.8582 (2)	0.9560 (3)	1.1514 (2)	392 (8)
C(2)	0.7644 (2)	0.9554 (3)	1.2028 (2)	396 (8)
C(3)	0.6188 (2)	1.0301 (3)	1.1576 (2)	389 (9)
C(4)	0.5784 (3)	1.2042 (3)	1.1192 (2)	404 (9)
C(5)	0.6713 (3)	1.3593 (3)	1.1154 (2)	437 (9)
C(6)	0.7653 (3)	1.3609 (3)	1.0641 (2)	452 (9)
C(7)	0.7966 (2)	1.2047 (3)	1.0021 (2)	441 (9)
C(8)	0.8359 (2)	1.0300 (3)	1.0391 (2)	419 (9)
F(1)	0.9881 (2)	0.8721 (2)	1.2028 (1)	546 (6)
F(2)	0.8011 (2)	0.8727 (2)	1.3050 (1)	613 (6)
F(3)	0.5167 (2)	0.9044 (2)	1.1584 (1)	605 (6)
F(4)	0.4367 (2)	1.2496 (2)	1.0809 (1)	600 (6)
F(5)	0.6516 (2)	1.5186 (2)	1.1667 (1)	661 (7)
F(6)	0.8398 (2)	1.5203 (2)	1.0645 (1)	719 (8)
F(7)	0.7850 (2)	1.2502 (2)	0.8956 (1)	666 (7)
F(8)	0.8638 (2)	0.9041 (2)	0.9701 (1)	648 (7)

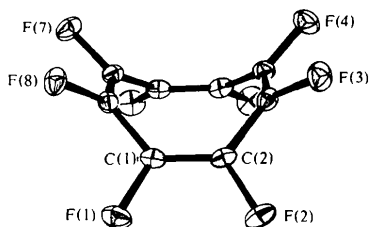


Fig. 1. View of octafluorocyclooctatetraene illustrating the atom-numbering scheme. Thermal ellipsoids are of 20% probability.

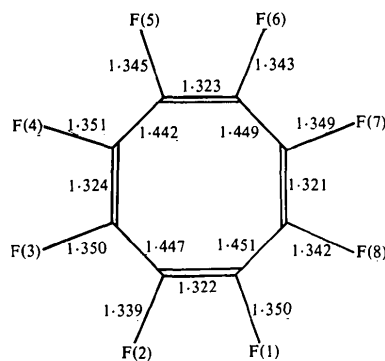


Fig. 2. Bond lengths (\AA). Estimated standard deviations range between 0.002 and 0.004 \AA .

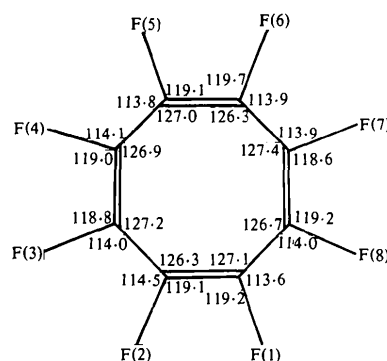


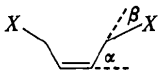
Fig. 3. Bond angles ($^\circ$). All estimated standard deviations are 0.2 $^\circ$.



Fig. 4. Stereoscopic packing diagram of octafluorocyclooctatetraene.

Discussion. The eight-membered ring of octafluorocyclooctatetraene adopts a tub configuration like that of its hydrocarbon counterpart, cyclooctatetraene, but is slightly more flattened. The degree of flattening is indicated by the dihedral angle α (see Table 3) between the plane formed by two non-adjacent double bonds and the plane formed by one of those double bonds and the two single bonds adjacent to it (i.e. as α decreases, the amount of flattening increases). The α value of 41.4 $^\circ$ for C_8F_8 , compared to 43.1 $^\circ$ for C_8H_8 , indicates a slightly more flattened ring in the former. A related compound, octamethylcyclooctatetraene, $\text{C}_8(\text{CH}_3)_8$ (Bordner, Parker & Stanford, 1972), has the same tub configuration as C_8F_8 and C_8H_8 and is reported in the above reference to be flattened with respect to C_8H_8 . However, analysis of the fractional atomic coordinates given by Bordner, Parker & Stanford shows this

Table 3. Comparison of average structural parameters for C_8F_8 with those of related compounds



	$X = H^{(a)}$	$X = F$	$X = CH_3^{(b)}$
$C=C-C$ ($^\circ$)	126.1	126.7	122.2
$C=C-X$ ($^\circ$)	117.6	119.1	123.0
$C-C-X$ ($^\circ$)	116.3	114.0	114.8
$(C=C-X)-(C-C-X)$ ($^\circ$)	1.3	5.1	8.4
$C=C$ (Å)	1.340	1.322	1.326
$C-C$ (Å)	1.475	1.447	1.483
$C-X$ (Å)	1.100	1.346	1.513
$X_i \cdots X_j$ across $C=C$ (Å)	—	2.63	2.97
$X_i \cdots X_j$ across $C-C$ (Å)	—	2.76	3.10
α ($^\circ$)	43.1	41.4	50.9
β ($^\circ$)	—	1.9	0.7–2.5
Torsion; $C=C-C=C$ ($^\circ$)	—	55.8	68.3

Notes: (a) Trætteberg (1966). (b) Calculated from atomic coordinates given by Bordner, Parker & Stanford (1972).

flattened interpretation to be incorrect. The eight-membered ring of $C_8(CH_3)_8$ is, in fact, more puckered than either C_8F_8 or C_8H_8 with α averaging 50.9° . This is as expected, the increased puckering placing the $-CH_3$ groups which are vicinal across a $C-C$ single bond at a greater distance from one another to relieve the steric hindrance of the bulkier groups.

An interesting structural feature of C_8F_8 is that all of the F atoms tilt slightly outward from the tub defined by the carbon ring. The amount of tilt is described by the angle β (see Table 3). In C_8F_8 , β averages about 1.9° which corresponds to a distance of about 0.05 \AA

between each F and the plane formed by the two $C-C$ bonds involving the C to which the F is attached. The methyl groups of $C_8(CH_3)_8$ exhibit a similar outward tilt with β varying from 0.7 to 2.5° .

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References

- BORDNER, J., PARKER, R. G. & STANFORD, R. H. JR (1972). *Acta Cryst.* B28, 1069–1075.
- HENSLEE, W. H. & DAVIS, R. E. (1975). *Acta Cryst.* B31, 1511–1519.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Table 2.2A. Birmingham: Kynoch Press.
- LEMAL, D. M., BUZBY, J. M., BAREFOOT, A. C., GRAYSTON, M. W. & LANGNIS, E. D. (1981). *J. Org. Chem.* In the press.
- MAIN, P., WOOLFSON, M. M., DECLERCQ, J. P. & GERMAIN, G. (1974). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
- RILEY, P. E. & DAVIS, R. E. (1976). *Acta Cryst.* B32, 381–386.
- TRÆTTEBERG, M. (1966). *Acta Chem. Scand.* 20, 1724–1726.
- ZACHARIASEN, W. H. (1968). *Acta Cryst.* A24, 212–216.

Acta Cryst. (1982). B38, 680–682

5-Methylthio-6-oxo-6H-1,2-oxazin-3,4-dicarbonsäure-dimethylester. Ein ungewöhnliches Reaktionsprodukt eines Sydnon mit Acetylendicarbonester

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Abstract. $C_9H_9NO_6S$, monoclinic, $P2_1/c$, $a = 14.933$ (3), $b = 9.265$ (2), $c = 8.425$ (1) Å, $\beta = 92.03$ (1°), $U = 1164.9 \text{ \AA}^3$, $Z = 4$, $D_m = 1.42$, $D_x = 1.478 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$. The structure was solved by direct methods. Anisotropic refinement yielded a conventional R value of 0.036 based on 2122

reflections with $I \geq 2\sigma(I)$ (ω - 2θ scan technique). There are no unusual bond distances or angles.

Einleitung. Als cyclisches Azomethin-imin reagiert das 3-Dimethylamino-4-methylthiosydnon (1) mit Acetylendicarbonsäure-dimethylester bei 353–433 K über das