

The Crystal and Molecular Structure of 1*Ha*:2*He*/4*Ha*:5*He*-Octafluorocyclohexane

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The title compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 5.62$ (1), $b = 7.11$ (1), $c = 11.06$ (1) Å, $\beta = 121.93$ (5)°, $Z = 2$. The molecule possesses crystallographic C_i symmetry. The structure was determined by direct methods and refined by least squares to $R = 4.6\%$ for 547 observed counter amplitudes. Estimated standard deviations average 0.004 Å for bond lengths and 0.25° for bond angles. The ring is in the chair form. Comparison with unsubstituted cyclohexane, however, indicates that it is slightly flatter (mean ring torsion angle 53°), probably owing to repulsive interactions between 1,3-diaxial F substituents.

Introduction

The cyclohexane system is of fundamental importance in organic chemistry and its geometry has been extensively studied by X-ray crystallography (Kahn, Fourme, André & Renaud, 1973), electron diffraction in the gas phase (Davis & Hassel, 1963; Geise, Buys & Mijlhoff, 1971) and theoretical calculations (e.g. Altona & Sundaralingam, 1970; Allinger & Wu, 1971). In a recent survey of the available structural data, Bucourt (1974) has concluded that compared with the ideal chair form with a tetrahedral valence angle and 60° ring torsion angle, cyclohexane adopts a somewhat flattened conformation with the ring bond angle 111° and the ring torsion angle 56°.

Fluorination of benzene with cobalt trifluoride yields a range of polyfluorocyclohexanes (Stephens & Tatlow, 1962). One of these, 1*Ha*:2*He*/4*Ha*:5*He*-octafluorocyclohexane (Nield, Stephens & Tatlow, 1959), formed suitable crystals and an X-ray analysis was carried out in order to assess the effect of F substitution on the geometry of the ring system.

Experimental

A crystal 0.5 × 0.2 × 0.1 mm was mounted inside a Pantak capillary tube and set about the crystallographic z axis. Photographs indicated monoclinic symmetry. Systematic absences corresponded to space group $P2_1/c$. The final cell dimensions and reflexion intensities were measured on a Stoe two-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. With the diffractometer operating in the ω -scan mode, 120 counts of 1 s at intervals of 0.01° were taken for each reflexion on layers 0–2. For the higher

layers a variable scan range was employed; $\Delta\omega$ was calculated from $[A + (B \sin \mu / \tan \theta')]^\circ$, where μ is the equi-inclination angle, $2\theta'$ is the azimuth angle, and A and B were assigned the values 1.0 and 0.5 respectively. Backgrounds were measured for 30 s at each end of the scan. After each layer of data collection, four standard reflexions on the zero layer were remeasured to check the stability of the system. There was no systematic variation of intensity with time. Of 1006 reflexions scanned within the range $0.1 < \sin \theta / \lambda < 0.65$ Å⁻¹, 547 for which $I > 2.5\sigma(I)$ were considered to be observed. Intensities were converted into structure amplitudes in the usual way, but absorption corrections were not applied.

Crystal data

$C_6H_4F_8$, $M_r = 228.1$, monoclinic, $a = 5.62$, $b = 7.11$, $c = 11.06$ Å (all ± 0.01 Å), $\beta = 121.93$ (5)°, $U = 375$ Å³, $Z = 2$, $D_c = 2.02$ g cm⁻³, $F(000) = 224$. Systematic absences: $0k0$, k odd; $h0l$, l odd; space group $P2_1/c$. Molecular symmetry $\bar{1}$ (C_i), Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 1.94$ cm⁻¹.

Determination of the structure

The structure was solved by direct methods (Karle & Karle, 1966) with the *SHELX* programs (Sheldrick, 1975). Phases (0 or 180°) were determined for the 193 reflexions with $E > 1.2$ and from the E map calculated with these phases all the atoms in the asymmetric unit (apart from H atoms) could be located. At this stage R was 31.2% for the 547 observed structure amplitudes and three cycles of least-squares refinement of atomic coordinates and isotropic thermal parameters reduced R to 15%. With the introduction of anisotropic temperature factors a further three cycles of refinement reduced R to 7%. The two H atoms were now located from a difference synthesis and were included in the

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Table 1. Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	4962 (7)	4773 (4)	3691 (3)
C(2)	2798 (7)	5986 (4)	3715 (3)
C(3)	3908 (6)	6748 (4)	5189 (3)
F(1 <i>e</i>)	3853 (5)	3945 (3)	2378 (2)
F(2 <i>a</i>)	444 (3)	4924 (3)	3343 (2)
F(3 <i>e</i>)	1838 (5)	7692 (3)	5215 (3)
F(3 <i>a</i>)	5928 (4)	8023 (2)	5468 (2)
H(1 <i>a</i>)	6487 (66)	5558 (42)	3847 (30)
H(2 <i>e</i>)	2252 (61)	7002 (44)	3065 (35)

least-squares calculations with isotropic temperature factors. The refinement process was terminated when all calculated shifts were $<0.01\sigma$ and *R* was 4.6%. The weighting scheme employed was $w = 1/[\sigma^2(F) + 0.002F^2]$, where $\sigma(F)$ is the standard deviation in the observed amplitudes based on counting statistics. The final atomic coordinates are listed in Table 1.*

Computations were carried out largely on the CDC 7600 computer at the University of Manchester Regional Computer Centre with the *SHELX* system of programs (Sheldrick, 1975).

Results and discussion

Bond lengths, selected non-bonded distances, bond angles and torsion angles are in Table 2. The six-membered ring is in the chair conformation and the full stereochemistry of the molecule is illustrated in Fig. 1, which also shows the atom numbering. F and H atoms are assigned the number of the C atom to which they are linked, with *a* denoting axial and *e*, equatorial. The molecule possesses exact C_i symmetry. In order to conform to the chemical numbering, the atoms which are centrosymmetrically related to those of the asymmetric unit, which bear the numbers 1, 2 and 3, have been labelled 4, 5 and 6 respectively.

The results of analysing the thermal parameters (U_{ij}) of all the atoms of the molecule, except the H atoms, in terms of rigid-body motion (Cruickshank, 1956; Schomaker & Trueblood, 1968) are given in Table 3. The r.m.s. deviation between observed and calculated U_{ij} values is 0.003 \AA^2 , comparable with the estimated standard deviations in the observed thermal parameters. Bond lengths corrected for thermal motion are listed in Table 2 with superscript *c*.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32977 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Molecular dimensions

(a) Bond lengths (Å) with estimated standard deviations in parentheses. Superscript *c* denotes lengths corrected for thermal motion.

C(1)—C(2)	1.502 (4)	1.515 ^c
C(2)—C(3)	1.505 (4)	1.517 ^c
C(3)—C(4)	1.509 (4)	1.521 ^c
C(1)—F(1 <i>e</i>)	1.374 (3)	1.385 ^c
C(2)—F(2 <i>a</i>)	1.383 (3)	1.397 ^c
C(3)—F(3 <i>e</i>)	1.356 (3)	1.368 ^c
C(3)—F(3 <i>a</i>)	1.354 (3)	1.368 ^c
C(1)—H(1 <i>a</i>)	0.958 (32)	
C(2)—H(2 <i>e</i>)	0.948 (32)	

(b) Selected non-bonded distances (Å)

F(3 <i>a</i>)...F(5 <i>a</i>)	2.727	H(1 <i>a</i>)...F(5 <i>a</i>)	2.66
F(1 <i>e</i>)...F(2 <i>a</i>)	2.729	H(1 <i>a</i>)...H(2 <i>e</i>)	2.30
F(2 <i>a</i>)...F(3 <i>e</i>)	2.657	H(2 <i>e</i>)...F(3 <i>a</i>)	2.46
F(3 <i>a</i>)...F(4 <i>e</i>)	2.708	H(2 <i>e</i>)...F(1 <i>e</i>)	2.61
F(3 <i>e</i>)...F(4 <i>e</i>)	2.735	H(2 <i>e</i>)...F(3 <i>e</i>)	2.56
H(1 <i>a</i>)...F(3 <i>a</i>)	2.64	H(4 <i>a</i>)...F(3 <i>e</i>)	2.50

(c) Bond angles (°), with estimated standard deviations in parentheses

C(6)—C(1)—C(2)	112.9 (2)	H(2 <i>e</i>)—C(2)—C(3)	109.2 (18)
F(1 <i>e</i>)—C(1)—C(2)	110.2 (2)	H(2 <i>e</i>)—C(2)—C(1)	111.4 (18)
F(1 <i>e</i>)—C(1)—C(6)	108.6 (3)	H(2 <i>e</i>)—C(2)—F(2 <i>a</i>)	108.4 (18)
H(1 <i>a</i>)—C(1)—C(2)	108.4 (17)	C(2)—C(3)—C(4)	112.6 (2)
H(1 <i>a</i>)—C(1)—C(6)	108.8 (17)	F(3 <i>a</i>)—C(3)—C(4)	110.8 (2)
H(1 <i>a</i>)—C(1)—F(1 <i>e</i>)	107.6 (17)	F(3 <i>a</i>)—C(3)—C(2)	107.8 (2)
C(1)—C(2)—C(3)	110.5 (2)	F(3 <i>e</i>)—C(3)—C(4)	109.3 (3)
F(2 <i>a</i>)—C(2)—C(3)	107.6 (2)	F(3 <i>e</i>)—C(3)—C(2)	109.4 (3)
F(2 <i>a</i>)—C(2)—C(1)	109.6 (2)	F(3 <i>e</i>)—C(3)—F(3 <i>a</i>)	106.7 (2)

(d) Torsion angles (°). Sign convention is as defined by Klyne & Prelog (1960).

C(6)—C(1)—C(2)—C(3)	52.8
C(6)—C(1)—C(2)—F(2 <i>a</i>)	-65.6
C(6)—C(1)—C(2)—H(2 <i>e</i>)	174
F(1 <i>e</i>)—C(1)—C(2)—C(3)	174.5
F(1 <i>e</i>)—C(1)—C(2)—F(2 <i>a</i>)	56.1
F(1 <i>e</i>)—C(1)—C(2)—H(2 <i>e</i>)	-64
H(1 <i>a</i>)—C(1)—C(2)—C(3)	-68
H(1 <i>a</i>)—C(1)—C(2)—F(2 <i>a</i>)	174
H(1 <i>a</i>)—C(1)—C(2)—H(2 <i>e</i>)	54
C(1)—C(2)—C(3)—C(4)	-52.6
C(1)—C(2)—C(3)—F(3 <i>a</i>)	69.9
C(1)—C(2)—C(3)—F(3 <i>e</i>)	-174.4
H(2 <i>e</i>)—C(2)—C(3)—C(4)	-175
H(2 <i>e</i>)—C(2)—C(3)—F(3 <i>a</i>)	-53
H(2 <i>e</i>)—C(2)—C(3)—F(3 <i>e</i>)	63
F(2 <i>a</i>)—C(2)—C(3)—C(4)	67.0
F(2 <i>a</i>)—C(2)—C(3)—F(3 <i>a</i>)	-170.4
F(2 <i>a</i>)—C(2)—C(3)—F(3 <i>e</i>)	-54.7
C(2)—C(3)—C(4)—C(5)	53.9
C(2)—C(3)—C(4)—H(4 <i>a</i>)	67
C(2)—C(3)—C(4)—F(4 <i>e</i>)	-176.6
F(3 <i>e</i>)—C(3)—C(4)—C(5)	175.8
F(3 <i>e</i>)—C(3)—C(4)—H(4 <i>a</i>)	55
F(3 <i>e</i>)—C(3)—C(4)—F(4 <i>e</i>)	-61.6
F(3 <i>a</i>)—C(3)—C(4)—C(5)	-66.9
F(3 <i>a</i>)—C(3)—C(4)—H(4 <i>a</i>)	173
F(3 <i>a</i>)—C(3)—C(4)—F(4 <i>e</i>)	55.7

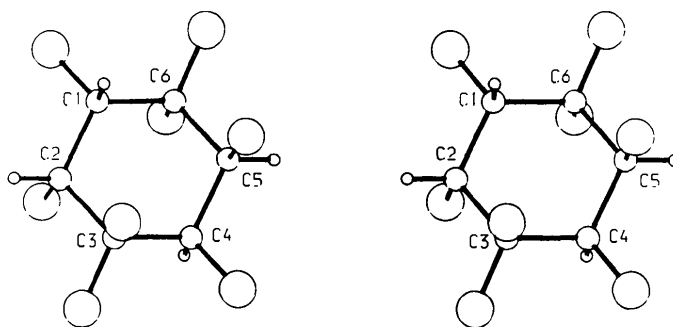


Fig. 1. Stereoscopic view of the molecule. Atoms labelled 4, 5 and 6 are related by a crystallographic centre of symmetry to atoms 1, 2 and 3 respectively.

Table 3. Results of rigid-body-motion analysis

The eigenvectors of the libration tensor **L** and translation tensor **T** are referred, in terms of the corresponding direction cosines, to the orthogonal molecular system defined by the eigenvectors of the molecular tensor of inertia **I**. The eigenvectors of **I** are referred to the unit-cell axes. The origin of the molecular coordinate system is at $x = 0.5000$, $y = 0.5000$, $z = 0.5000$.

	Eigenvalues	Eigenvectors		
I	508 (at. wt Å ²)	0.4710	-0.7292	-0.4965
	721	0.5097	-0.2344	0.8278
	935	-0.7200	-0.6429	0.2613
L	119 ($\times 10^{-4}$ rad ²)	0.0830	-0.9562	-0.2807
	94	0.9953	0.0938	-0.0250
	59	0.0502	-0.2773	0.9595
T	492 ($\times 10^{-4}$ Å ²)	0.6962	-0.6713	-0.2544
	361	-0.6999	-0.7135	-0.0327
	261	-0.1596	0.2008	-0.9665

R.m.s. discrepancy, $\langle \Delta U^2 \rangle^{1/2} = 0.0029$ Å².

C—C bond lengths range from 1.502–1.509 Å (mean 1.505 Å) (uncorrected) and 1.515–1.521 (mean 1.518 Å) (corrected). These are slightly shorter than the C—C bond lengths in cyclohexane as determined by X-ray crystallography (mean 1.526 Å, corrected for thermal motion) and electron diffraction in the gas phase (1.528 Å).

The C—F bonds fall into two categories, C(1)—F(1e) and C(2)—F(2a) involving monofluoro-substituted C atoms, and C(3)—F(3a) and C(3)—F(3e) involving a difluoro-substituted C atom. The former are significantly longer in accord with the generally observed increase in C—F bond distances with decrease in F substitution. The mean values are 1.379 Å (1.391 Å, corrected) and 1.355 Å (1.368 Å, corrected) respectively, slightly longer than similar bonds in the crystal structure of *endo*-1-methoxycarbonyl-3*H*,4*H*-nonafluoronorborene (Hamor & Hamor, 1977). Here there

is one C—F bond involving a monofluoro-substituted C atom of length 1.373 Å (1.381 Å) and eight C—F bonds involving difluoro-substituted C atoms whose mean length is 1.349 Å (1.358 Å).

Bond angles within the ring are in the range 110.5–112.9° (mean 112.0°), slightly greater than the cyclohexane value of 111° (Bucourt, 1974). Consistent with this difference, the ring torsion angles (absolute values 52.6–53.9°, mean 53.1°) are smaller than the cyclohexane value of 56°. The fluorinated ring is thus flatter than the cyclohexane ring. This flattening of the ring system is probably triggered by repulsive 1,3-diaxial interactions, especially between F(3a) and F(5a) and the centrosymmetrically related F(6a) and F(2a), since the effect of the ring flattening is to tilt the axial bonds outwards, so increasing the separations of the axial substituents. Whereas the axial bonds are parallel in the ideal chair form, in the actual, slightly flattened chair form of cyclohexane, these bonds are tilted outwards so as to make an angle of 7° with respect to each other (Bucourt, 1974). In the present structure the axial C—F bonds make an angle of 9.6° with respect to each other, while the two independent angles between axial C—F and C—H bonds are close to the cyclohexane value (6.3 and 7.4°). The effect of the extra flattening of the ring and the large ring bond angle at C(1) is to increase the 1,3-diaxial F...F distance by *ca* 0.2 Å compared with the ideal chair form and by 0.08 Å compared with 'real' cyclohexane to the actual value of 2.727 Å.

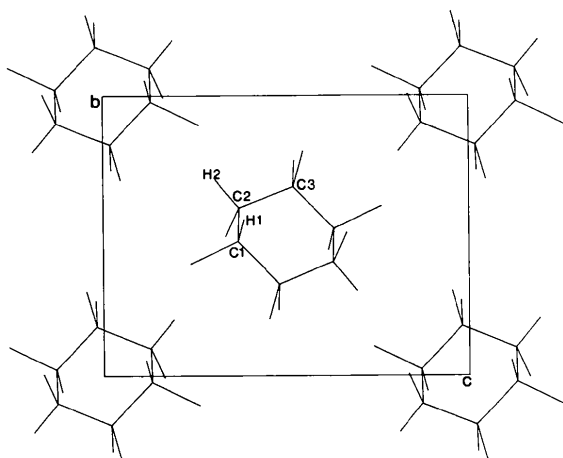
A further effect of the ring flattening is to decrease the separation between axial and equatorial substituents on adjacent C atoms and to increase that between adjacent equatorial substituents. Thus torsion angles of the type F,H(*e*)—C—C—F,H(*a*) are all less than 60° (mean 55°) and those of type F(*e*)—C—C—F,H(*e*) are all greater than 60° (mean 63°). The closest F(*a*)...F(*e*) contact distances, F(2a)...F(3e) 2.657 Å and F(3a)...F(4e) 2.708 Å, are in fact slightly shorter than the F...F 1,3-diaxial distance. Any further flattening of the ring would produce unfavourably short F(*a*)...F(*e*) contacts.

Table 4. Shorter intermolecular contacts (Å)

H(2e)···F(2a ⁱ)	2.56	F(3e)···F(2a ^v)	3.13
H(1a)···F(2a ⁱⁱ)	2.60	F(3e)···F(1e ^{vi})	3.14
H(1a)···F(1e ⁱⁱⁱ)	2.72	F(3a)···F(2a ^{vii})	3.19
H(2e)···F(1e ⁱⁱⁱ)	2.84	F(3a)···F(1e ^{vii})	3.28
F(3a)···F(3a ^{iv})	2.99	F(1e)···C(1 ^{viii})	3.39

Symmetry code

(i)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$	(v)	$-x, 1 - y, 1 - z$
(ii)	$1 + x, y, z$	(vi)	$x, 1\frac{1}{2} - y, \frac{1}{2} + z$
(iii)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	(vii)	$1 + x, 1\frac{1}{2} - y, \frac{1}{2} + z$
(iv)	$1 - x, 2 - y, 1 - z$	(viii)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

Fig. 2. The crystal structure projected along a^* .

The arrangement of molecules in the unit cell is shown in Fig. 2, and the shorter intermolecular distances are in Table 4. None of these is substantially shorter than the sum of the van der Waals radii of the atoms concerned.

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