13. Crystal Structure of 1,1,4,4-Tetrafluorocyclohexane at 95 K

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Summary

The crystal structure of 1,1,4,4-tetrafluorocyclohexane has been determined from X-ray diffraction measurements at 95 K. Internal motion of the CF_2-group can be discerned from analysis of the atomic vibration tensors. The pattern of bond lengths suggests that an anomeric-effect type of interaction between antiperiplanar C,C- and C,F-bonds (as well as between C,H- and C,F-bonds) may be operative in this molecule.

In connection with our interest in the deformation density of C,F-bonds [1] we have carried out a low-temperature crystal-structure analysis of 1,1,4,4-tetrafluorocyclohexane, including an X – X difference map.

Crystal structure of 1,1,4,4-tetrafluorocyclohexane. – $C_6H_8F_4$, $M = 156.12$. Crystals were obtained from Dr. *Klaus Müller*. They are orthorhombic, space group *Pnnm*, $Z = 2$, with cell dimensions: $a = 5.659(2)$, $b = 8.385(2)$, $c = 6.736(2)$ Å at 95 K, $V = 319.6$ Å^3, $D_c = 1.62$ Mg m^{-3}. Intensity measurements were made at 95 K with an *Enraf-Nonius CAD 4* diffractometer equipped with graphite monochromator (Mo*Ka*, $\lambda = 0.7107$ Å) and cooling device; 1050 independent reflexions were measured out to $s = 0.90$ Å^{-1}, 723 with $F > 10\sigma(F)$. No absorption corrections were made ($\mu = 1.85$ cm^{-1}). The structure was solved by direct methods and refined by full-matrix least-squares analysis using a modified weighting scheme with $r = 2.5$ Å^2 [2] and an isotropic extinction correction. The final *R* factor was 0.026.

The molecule has $C_{2h}(2/m)$ site symmetry with the two F-atoms and the substituted C-atom lying on a crystallographic mirror plane. Positional and vibrational parameters are listed in *Table 1*, bond distances and bond angles in *Table 2*. A stereoview of the molecule is shown in *Figure 1*.

Thermal motion analysis. – Comparison of the mean-square vibration amplitudes of pairs of atoms along their respective interatomic vectors [3] suggests that there is an appreciable motion of the F-atoms in the molecular plane relative to the rest of the molecule. This motion could involve the wagging vibration of the CF_2-unit as well as the FCF angle-bending vibration, corresponding to in-phase and out-of-phase motions of the F-atoms. The effect of the combined motion can be simulated by torsion about an axis passing through the C-atom and perpen-

Table 1. *Atomic coordinates and vibration parameters* (all × 10^4) *with standard deviations in parentheses*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1689(1)	1275(1)	0	117(3)	126(2)	151(3)	−4(2)	0	0
C(2)	1250(1)	349(1)	1889(1)	142(2)	162(2)	119(1)	−2(1)	−16(2)	−2(1)
F(1)	3974(1)	1850(1)	0	143(2)	211(3)	233(3)	−63(2)	0	0
F(2)	285(1)	2629(1)	0	211(3)	120(2)	221(2)	33(2)	0	0
H(21)	1510(23)	1072(14)	3011(18)	235(27)					
H(22)	2420(21)	−468(14)	1970(21)	208(26)					

Table 2. *Bond lengths, bond angles and torsion angles with estimated standard deviations in parentheses* (For the bond lengths the first value is uncorrected, the second is corrected for rigid-body and internal vibrational motion)

C(1)–F(1)	1.380(1), 1.384 Å	F(1)–C(1)–F(2)	104.56(6)°	C(2)–C(1)–C(2″)–C(2‴)	54.6(1)
C(1)–F(2)	1.386(1), 1.390	F(1)–C(1)–C(2)	109.48(4)	F(2)–C(1)–C(2″)–C(2‴)	−68.1(1)
C(1)–C(2)	1.511(1), 1.514	F(2)–C(1)–C(2)	109.08(4)	F(1)–C(1)–C(2″)–C(2‴)	178.1(1)
C(2)–C(2′)	1.531(1), 1.533	C(2)–C(1)–C(2″)	114.69(6)	C(1)–C(2)–C(2′)–C(1′)	−52.2(1)
		C(1)–C(2)–C(2′)	110.39(5)		

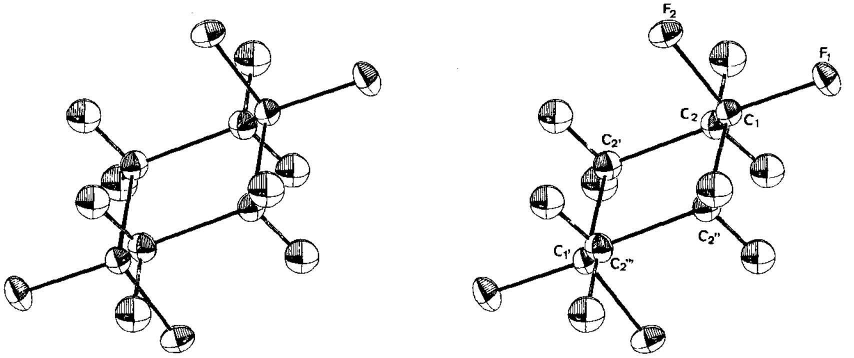

Fig. 1. *Stereoview of 1,1,4,4-tetrafluorocyclohexane molecule with atomic labelling system*

dicular to the molecular mirror-plane, with the resulting motion imparted only to the F-atoms. Introduction of this postulated internal motion into the rigid-body analysis [4] leads to a considerable improvement in the agreement between observed and calculated tensor components: a reduction in the r.m.s. discrepancy from 7.2×10^{-4} Å^2 to 4.6×10^{-4} Å^2 for an increase in the number of adjustable parameters from 8 to 9. The value obtained for the mean-square amplitude of the additional internal motion is 7.65(81) deg^2. For the molecular rigid-body motion the translational tensor is nearly isotropic with eigenvalues of 118, 109 and 95×10^{-4} Å^2: the librational tensor has eigenvalues of 10.0, 5.5 and 4.9 deg^2 with the respective eigenvectors pointing nearly along the molecular inertial axes in order of increasing moment of inertia.

Molecular geometry. – A search of the *Cambridge Structural Database* [5] reveals dimensions for many difluoro-substituted C-atoms. The uncorrected C,F-bond lengths lie mostly in the range 1.34–1.35 Å (average 1.346 Å), only slightly shorter than the microwave value of 1.357 Å in difluoromethane [6]. The C,F-bond lengths found in our study are much longer: 1.380(1) and 1.386(1) Å for the uncorrected values with corrections of +0.004 Å for the combined effects of the internal and rigid-body librational motion. They are by far the longest C, F-distances yet observed at a disubstituted C-atom and probably the most accurate.

The difference of 10° between the exocyclic and endocyclic bond angles at the difluoro-substituted C-atoms is also somewhat extreme, compared with corresponding differences observed in other molecules, although these are always in the same sense, *i.e.* FCF-angle smaller than CCC-angle, except when the C-atom is part of a small ring. From a microwave study of 1,1-difluorocyclohexane [7] the reported angles are 108.7(2)° for FCF and 112.0(7)° for CCC. These cannot be regarded as particularly reliable since the analysis is based on a single isotopic species and involves some questionable assumptions, but rather similar angles (106.8 and 112.6°) are found in a recent X-ray analysis of 1,1,2a,3e,4,4,5a,6e-octafluorocyclohexane [8]. Qualitatively, the small FCF- and the large CCC-angles are nicely accounted for by the *Bent-Walsh* rule [9]: atomic p-character concentrates in orbitals directed towards electronegative substituents. Our values thus show the expected trend although the 10° difference seems a little larger than normal.

The difference found in our analysis between the two types of C, C-bond is also noteworthy (C(2)–C(2′), 1.531(1) Å; C(2)–C(1), 1.511(1) Å for the uncorrected values with corrections of +0.002 Å). It is tempting to ascribe this difference to an anomeric-effect type of interaction between the C(2)–C(2′) bonding orbital and the σ^*-orbital of the antiplanar C, F(1)-bond; such an interaction would lengthen C(2)–C(2′), shorten C(2)–C(1), and lengthen the equatorial C(1), F(1)-bond. In fact, the axial C, F(2)-bond is even slightly longer than the equatorial one. To explain this we would have to invoke a similar anomeric-effect type of interaction between this axial bond and the antiplanar C(2), H-bond. The associated lengthening of the C, H-bond can hardly be expected to be detectable by X-ray analysis. In fact, the C, H(22, axial)-bond seems to be slightly shorter than its equatorial partner (0.95(1) *vs.* 0.98(1) Å with both values showing the systematic shortening of about 0.1 Å in X-H distances determined by X-ray diffraction. In the octafluorocyclohexane molecule mentioned above the analogous anomeric-effect type of interaction should be weaker because of the lowering of the energy of the C(2)–C(2′) bonding orbital due to the F-substituents at these atoms, leading to an increased energy separation between the lower (bonding) orbital and the upper (antibonding C–F σ^*) one. At any rate, this seems at present to be the only plausible explanation for the remarkably long C, F-bonds in the tetrafluorocyclohexane compared with those at the difluoro-substituted C-atoms in the octafluorocyclohexane. This explanation does not, of course, apply to the discrepancy between the C, F-distance found in our study and that from the microwave study of 1,1-difluorocyclohexane [7]. Perhaps the results of the latter study should be discounted until confirmed by a more detailed analysis involving several isotopic species.

A similar but less pronounced shortening of the C(1), C(2)-bond with respect to the C(2), C(2′)-bond is also just discernible from the room-temperature crystal structure analysis of 1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane [10], where the four F-atoms have been replaced by the O-atoms of two ketal rings. The corrected distances there are C(1)–C(2), 1.520(3) Å; C(2)–C(2′), 1.529(3) Å. The OCO- and CCC-angles at the spiro atoms are 105.9(2) and 111.0(2), respectively, and thus also show the same pattern as observed here. To complete the analogy, the axial and equatorial, C,O-distances at the spiro atoms are both 1.437(3) Å (corrected), decidedly on the long side for geminal C,O-bonds.

At the conclusion of the least-squares refinement we calculated X–X difference maps in the C(1)–C(2)–C(2′) and F–C(1)–F planes. We found much stronger peaks at the mid-points of the C,C-bonds than in the C,F-bonds. This result is discussed together with our results for the X–X difference density in tetrafluoroterephthalodinitrile [1].

Crystal packing. – A stereoview of the crystal packing is provided in *Figure 2.* There are no unusually short intermolecular distances, the shortest H···H distance being 2.68 Å between a pair of equatorial H-atoms belonging to molecules separated by the **a** translation. The two shortest H···F distances (2.62 and 2.70 Å) both involve the equatorial F-atom, and also the shortest F···F distance of 3.31 Å is between equatorial F-atoms. The relatively loose packing and the absence of any short intermolecular distances are consistent with the remarkably high volatility of the compound at room temperature.

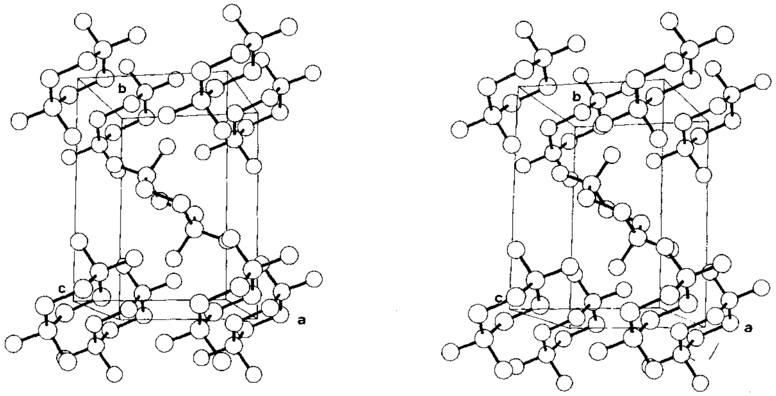

Fig. 2. *Stereoview of crystal packing.* (The origin of the unit cell is at the lower rear left-hand corner)

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