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Structure of Tetrafluoro-1,2-(*RS*)-bis(2,2,3,3-tetrafluorocyclobutyl)ethane

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Abstract

Tetrafluoro-1,2-(*RS*)-bis(2,2,3,3-tetrafluorocyclobutyl)ethane, $C_{10}H_6F_{12}$, crystallizes in space group $P2_1/c$ with $Z = 2$ and cell parameters $a = 5{\cdot}154\ (5)$, $b = 10{\cdot}010\ (7)$, $c = 12{\cdot}559\ (12)$ Å and $\beta = 113°\,45\ (10)'$. The crystal structure has been determined by X-ray diffraction (763 observed reflexions; final R value 0·064). The conformation of the molecule is governed by the steric and electrostatic interactions of the substituents. Steric hindrance is minimized by the adoption of a staggered configuration by the carbon chain. By contrast, the cyclobutane ring is only slightly puckered (torsion angles of 4°) with substituents in the eclipsed conformation. Other adaptations of the molecule to relieve strain involve angular deformations. C—C bond lengths vary from 1·506 (10) to 1·571 (7) Å, whereas the average C—F bond distance is 1·344 (6) Å (range 1·327 to 1·359 Å).

Introduction

In a recent report (Piccardi, Modena & Santoro, 1971) one of us has described the thermal cycloaddition reactions of 3,3,4,4-tetrafluoro-1,5-hexadiene with tetrafluoroethylene to give cyclic mono- and diadducts in addition to the self-dimerization products of the fluoroolefins and a low-molecular-weight polymer of the diene. One of the resulting highly fluorinated products, tetrafluoro-1,2-bis(2,2,3,3-tetrafluorocyclobutyl)ethane (I), has now been subjected to an X-ray crystal structure determination in order to establish exactly the conformation of the molecular structure.

Experimental

The synthesis of (I) was reported by Piccardi *et al.* (1971). Preliminary cell parameters and the space group were obtained from Weissenberg photographs. A small colourless crystal was then mounted on a four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. Accurate cell dimensions together with the best orientation matrix were determined by a least-squares fit of χ, φ, ω and 2θ values from 12 independent reflexions.

Crystal data

$C_{10}H_6F_{12}$, $M_r = 354{\cdot}16$, monoclinic, $a = 5{\cdot}154\ (5)$, $b = 10{\cdot}010\ (7)$, $c = 12{\cdot}559\ (12)$ Å, $\beta = 113°\,45\ (10)'$, $V = 593{\cdot}06$ Å^3, $Z = 2$, $D_c = 1{\cdot}983$ Mg m^{-3}, $F(000) = 348$; space group $P2_1/c$ from systematic absences: $0k0$ for k odd, $h0l$ for l odd.

A crystal of approximately cubic shape (diameter 0·35 mm) was chosen for intensity-data collection on a Picker FACS-1 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) up to $2\theta = 50°$. The moving-crystal–moving-counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of 2·0–2·5° in order to account for $K\alpha_1$–$K\alpha_2$ separation at various 2θ values. Background counts were measured for 10 s at each end of every 2θ scan. During data collection three standards, measured every 50 reflexions, showed a gradual drop in intensity of up to 15%. Of the 1040 independent reflexions measured, 763 were considered observed according to the criterion $I > 2{\cdot}0\sigma\ \{\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, where N_s is the total peak count during the time of scanning t_s, and t_b is the time spent in measuring the N_b background counts$\}$. An arbitrary intensity equal to 0·5 times the observable limit was assigned to the non-significant reflexions. All intensities were corrected for Lorentz and polarization effects but not for absorption [μ(Mo $K\alpha$) = 0·272 mm^{-1}].

The structure was solved by the multi-solution tangent-refinement method *MULTAN* (Germain, Main & Woolfson, 1971) after the observed structure factors had been converted into normalized structure factor amplitudes $|E|$. All $|E| > 1{\cdot}08$ (300 reflexions) were

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Table 1. *Phase angles of the starting set and tangent-formula results*

(*a*) Starting set for the tangent formula

h	*k*	*l*	$\|E\|$	Phase
−3	6	1	3·32	180°
−1	5	8	2·72	180
4	4	1	2·53	360
0	10	4	2·94	*A*
1	2	2	2·81	*B*
−1	8	1	1·95	*C*

(*b*) Tangent-formula results

NUMSET	ABSFOM	ψ_0	RESID	COMBINED FOM
1	0·8918	806	44·94	1·2076
2	0·9100	996	44·22	0·9111
3	0·5834	639	46·09	0·9055
4	0·6809	803	47·94	0·6656
5	1·1312	480	31·61	3·0000
6	0·8168	754	46·37	1·0929
7	0·6757	676	50·02	0·7900
8	0·6616	867	49·19	0·4391

Table 2. *Final fractional coordinates with estimated standard deviations in parentheses*

	x	*y*	*z*
C(1)	0·3827 (8)	0·0430 (4)	0·4549 (4)
C(2)	0·4860 (9)	0·1505 (4)	0·3973 (4)
C(3)	0·5999 (12)	0·2820 (5)	0·4694 (4)
C(4)	0·3857 (11)	0·3619 (4)	0·3719 (4)
C(5)	0·2560 (10)	0·2344 (5)	0·3043 (4)
F(1)	0·2120 (5)	−0·0431 (3)	0·3731 (2)
F(2)	0·2244 (5)	0·0942 (3)	0·5085 (2)
F(3)	0·2058 (8)	0·4318 (5)	0·4013 (4)
F(4)	0·4911 (10)	0·4444 (4)	0·3158 (4)
F(5)	−0·0113 (6)	0·2125 (3)	0·2898 (3)
F(6)	0·2610 (8)	0·2255 (4)	0·1971 (3)
H(2)	0·613 (10)	0·118 (5)	0·355 (4)
H(31)	0·592 (16)	0·277 (7)	0·546 (7)
H(32)	0·759 (16)	0·298 (7)	0·486 (6)

introduced into the calculations together with 50 weak reflexions for the definition of the ψ_0 figure of merit. The total number of phase relationships found was 7789, of which 4990 were retained. The automatically chosen starting set is reported in Table 1. Among the eight possible solutions generated by *MULTAN*, according to the values (π, 2π) of the phase angles *A*, *B* and *C*, the correct one was evident from the highest value of ABSFOM and the lowest value of ψ_0 and of RESID. The corresponding phase angles *A*, *B* and *C* were all 2π. Positional and isotropic thermal parameters of the non-hydrogen atoms were refined to *R* $[=(\sum \|k\|F_o\| - \|F_c\|\|)/\sum k\|F_o\|] = 0{\cdot}12$ by various cycles of block-diagonal least squares minimizing the function $\Delta = \sum w(\|F_o\| - \|F_c\|)^2$ with Immirzi's (1967) program. Atomic scattering factors were calculated from the expression given by Vand, Eiland & Pepinsky (1957) with the parameter values according to Moore (1963). Cruickshank's (1965) weighting scheme $1/w = A + B\|F_o\| + C\|F_o\|^2$ was adopted, where $A = 2F_o(\text{min.})$, $B = 1{\cdot}0$ and $C = 2/F_o(\text{max.})$. After anisotropic refinement the H atoms were introduced in the calculations with their initial coordinates being defined on stereochemical grounds. Refinement then converged to $R = 0{\cdot}064$ for the 763 non-zero reflexions ($R' = 0{\cdot}087$, including unobserved reflexions). The final shifts of the atomic parameters were all well below the corresponding σ values.

The final fractional coordinates and the corresponding standard deviations of the atoms of the independent unit are listed in Table 2.* All calculations were performed on the Univac 1100/20 computer of this Institute using a local program set.

Results and discussion

The molecular and crystal structures of tetrafluoro-1,2-bis(2,2,3,3-tetrafluorocyclobutyl)ethane are given in Figs. 1 and 2, as derived by the *ORTEP* computing and drawing program (Johnson, 1970). Bond data are reported in Table 3.

The molecular structure of (I) is best understood in terms of torsion angles, τ, and non-bonded interactions. The crystallographically imposed molecular symmetry C_i leads to a *trans* arrangement around the central bond C(1)—C(1′) with 1,4 non-bonded interactions F(1)—F(2′) of 2·726 Å. The repulsion forces acting between these highly electronegative substituents are evident from the F(1)—C(1)—C(1′)—F(2′)

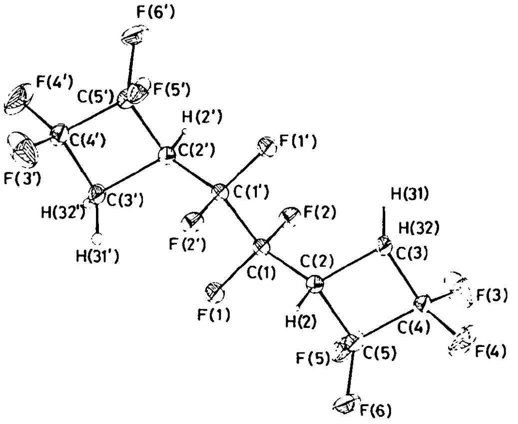

Fig. 1. View of the tetrafluoro-1,2-(*RS*)-bis(2,2,3,3-tetrafluorocyclobutyl)ethane molecule indicating the atom labelling scheme and 30% probability thermal-vibration ellipsoids.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34964 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

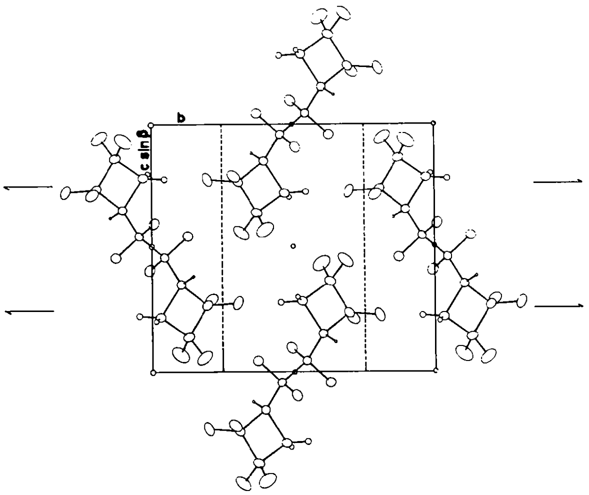

Fig. 2. Packing arrangement of the tetrafluoro-1,2-(*RS*)-bis(2,2,3,3-tetrafluorocyclobutyl)ethane molecules as viewed down the *a* axis of the unit cell.

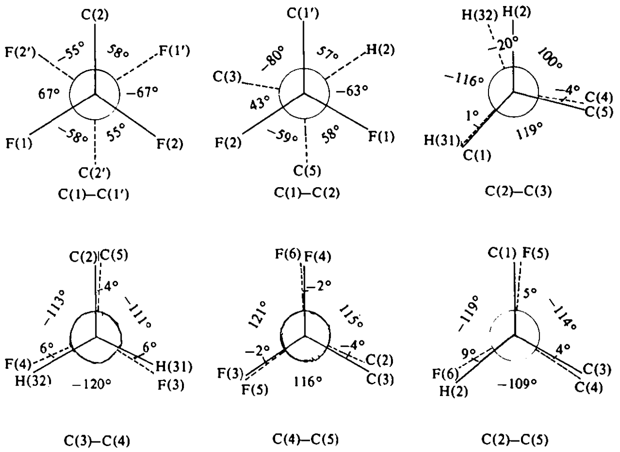

Fig. 3. Newman projections of the C–C bonds of the tetrafluoro-1,2-(*RS*)-bis(2,2,3,3-tetrafluorocyclobutyl)ethane molecule. Estimated standard deviations are *ca* 1·0°. The torsion angles have been calculated according to the convention of Klyne & Prelog (1960).

Table 3. *Geometrical parameters of the independent unit*

Standard deviations are appended as units in the last significant digit. Primes indicate atoms related to those of the independent unit by the inversion centre.

(*a*) Bond lengths (Å)

C(1)–C(2)	1·509 (6)	C(4)–F(3)	1·327 (6)
C(2)–C(3)	1·571 (7)	C(4)–F(4)	1·335 (7)
C(3)–C(4)	1·506 (10)	C(5)–F(5)	1·333 (6)
C(4)–C(5)	1·530 (7)	C(5)–F(6)	1·359 (6)
C(5)–C(2)	1·535 (8)	C(2)–H(2)	1·05 (4)
C(1)–C(1′)	1·543 (10)	C(3)–H(31)	0·98 (9)
C(1)–F(1)	1·358 (6)	C(3)–H(32)	0·80 (9)
C(1)–F(2)	1·351 (4)		

(*b*) Bond angles (°)

C(1′)–C(1)–C(2)	115·3 (2)	C(4)–C(3)–H(32)	117 (3)
C(1′)–C(1)–F(1)	106·2 (2)	C(4)–C(3)–H(31)	121 (3)
C(1′)–C(1)–F(2)	107·3 (2)	H(31)–C(3)–H(32)	102 (5)
F(1)–C(1)–C(2)	109·6 (2)	C(3)–C(4)–C(5)	91·2 (2)
F(1)–C(1)–F(2)	106·3 (2)	C(3)–C(4)–F(3)	114·8 (2)
C(2)–C(1)–F(2)	111·6 (1)	C(3)–C(4)–F(4)	115·9 (2)
C(1)–C(2)–C(3)	116·3 (2)	F(3)–C(4)–F(4)	107·4 (2)
C(1)–C(2)–C(5)	116·2 (2)	F(3)–C(4)–C(5)	113·4 (2)
C(1)–C(2)–H(2)	116 (2)	F(4)–C(4)–C(5)	113·8 (2)
C(3)–C(2)–C(5)	88·6 (2)	C(2)–C(5)–C(4)	90·2 (2)
C(3)–C(2)–H(2)	112 (2)	C(2)–C(5)–F(5)	116·9 (2)
C(5)–C(2)–H(2)	103 (2)	C(2)–F(5)–F(6)	113·6 (2)
C(2)–C(3)–C(4)	89·7 (2)	F(5)–C(5)–C(4)	114·1 (2)
C(2)–C(3)–H(32)	116 (3)	F(5)–C(5)–F(6)	106·5 (2)
C(2)–C(3)–H(31)	111 (3)	F(6)–C(5)–C(4)	115·2 (2)

(*c*) Non-bonded distances (Å)

F(1)–F(2′)	2·726 (6)	H(31)–F(3)	2·60 (10)
F(1)–H(2)	2·71 (5)	F(3)–F(5)	2·602 (6)
F(1′)–H(2)	3·26 (8)	F(5)–C(1)	2·813 (7)
F(2)–H(31)	2·54 (8)	H(2)–H(32)	2·35 (9)
F(2)–F(5)	2·781 (5)	H(32)–F(4)	2·49 (10)
F(2′)–H(2)	2·65 (8)	F(4)–F(6)	2·647 (6)
C(1)–H(31)	2·64 (8)	F(6)–H(2)	2·34 (7)

Table 4. *Coefficients of least-squares-plane equations*

Each plane is represented by an equation of the type $lx + my + nz - p = 0$, referred to an orthogonal system of axes with x along the a^* axis, y in the bc plane and z along the c axis; p is the origin-to-plane distance in Å.

Plane	*l*	*m*	*n*	*p*	σ†
C(5,2,1,1′,2′,5′)	0·0284	0·6455	0·7632	4·0676	0·016
C(2,3,4,5)	−0·6218	−0·0992	0·7768	1·5442	0·055

Interplanar angle: 59·3°

† Root-mean-square deviation in Å.

torsion angle $\tau = 67°$ as opposed to the smaller F–C(1)–C(1′)–C torsion angles (Fig. 3). Non-bonded interactions are again minimized across the C(1)–C(2) link by the assumed staggered conformation (Fig. 3). Consequently, the carbon chain C(5,2,1,1′,2′,5′) is approximately planar (Table 4) with F(5) and F(5′) at 0·10 Å from this plane; the F(2)–F(5) distance is 2·781 Å. Had the alternative stereogeometry with a planar C(3,2,1,1′,2′,3′) skeleton been adopted by the molecule, more severe F–F repulsions (of about 2·4 Å) would have occurred. As a result of the eclipsed C–C bonds (Fig. 3) the minimum 1,2 (vicinal) interactions C–H, H–H, H–F, F–F and C–F of the ring substituents are 2·64, 2·35, 2·34, 2·60 and 2·81 Å, respectively. These values may be compared to the staggered H–F and F–F interactions of 2·71 and 2·73 Å in the same structure.

The cyclobutane moiety of (I) is slightly puckered with C–C–C bond angles in the range 88·6 to 91·2° and C–C–C–C torsion angles of 4°. This is in line with the fact that existing data on simple cyclobutanes indicate that rings which are not centrosymmetrically

Table 5. *Structural data for some simple cyclobutane derivatives*

Only those molecules are included in which the ring is not part of a condensed polycyclic system and is not involved in endo- or exocyclic unsaturation.

Compound*	C–C (Å)	C–C–C (°)	Dihedral angle (°)†	Technique‡	Reference
CB	1·548 (3)	–	–	ED	Almenningen, Bastiansen & Skancke (1961)
CB	–	–	145	NMR	Meiboom & Snyder (1967)
Methyl-CB	1·56 (3)	–	150–160	ED	Lemaire & Livingstone (1952)
Cyclobutyl chloride	1·525–1·550 (5)	90·5 (5)	160	MWS	Kim & Gwinn (1966)
Cyclobutyl bromide	1·540–1·548 (3)	88·1–88·7 (1)	151·6	MWS	Rothschild & Dailey (1962)
Octahydroxy-CB	1·562–1·564 (4)	89·8–90·2 (2)	180	XRD	Bock (1968)
Octafluoro-CB	1·60 (4)	89 (n.d.)	160 (4)	ED	Lemaire & Livingstone (1952)
Octachloro-CB	1·57–1·58 (3)	87·8–88·9 (2·0)	161	XRD	Margulis (1965)
cis,trans,cis-1,2,3,4-Tetraphenyl-CB§	1·566–1·573 (15)	89·4–90·6 (n.d.)	180	XRD	Margulis (1965)
cis,trans,cis-1,2,3,4-CB-tetracarbonitrile	1·547–1·561 (3)	89·8–90·2 (2)	180	XRD	Greenberg & Post (1968)
2,2,4,4-Tetramethyl-*trans*-1,3-CB-diol	1·544–1·545 (5)	91·2 (n.d.)	180	XRD	Margulis (1969)
Tetrafluoro-1,2-bis(2,2,3,3-tetrafluorocyclobutyl)ethane	1·506–1·571 (8)	88·6–91·2 (2)	174·2	XRD	This work
trans-1,2-Dibromo-1,2-dimethoxycarbonyl-CB	1·520–1·580 (27)	87·0–89·4 (n.d.)	153	XRD	Karle, Karle & Britts (1966)
cis-1,2-Dibromo-1,2-dimethoxycarbonyl-CB	1·520–1·580 (27)	85·5–89·3 (n.d.)	150	XRD	Karle, Karle & Britts (1966)
cis,trans,cis-1,2,3,4-CB-tetracarboxylic acid tetramethyl ester	1·541–1·572 (5)	89·0–91·0 (3)	180	XRD	Margulis (1971)
trans-1,2-CB-dicarboxylic acid	1·517–1·553 (4)	87·5–88·8 (2)	149 (2)	XRD	Benedetti, Corradini & Pedone (1970)
cis-1,2-CB-dicarboxylic acid	1·526–1·556 (4)	86·3–90·7 (2)	156	XRD	Van der Helm, Hsu & Sims (1972)
trans-1,3-CB-dicarboxylic acid	1·539–1·555 (10)	88·2–89·3 (5)	155	XRD	Adman & Margulis (1968)
trans-1,3-CB-dicarboxylic acid	1·552–1·567 (6)	89·5–90·5 (3)	180	XRD	Margulis & Fischer (1967)
cis-1,3-CB-dicarboxylic acid	1·548–1·563 (1)	–	149	XRD	Adman & Margulis (1967)
trans-1,3-CB-dicarboxylic acid dianion	1·559–1·567 (6)	–	180	XRD	Adman & Margulis (1968)
Anemonin	1·530–1·545 (15)	87·7–88·6 (8)	152	XRD	Karle & Karle (1966)

* CB: cyclobutane.

† Defined as the angle between normals to two three-carbon-atom planes with the transannular distance common to both planes.

‡ XRD: X-ray diffraction; ED: electron diffraction; NMR: nuclear magnetic resonance; MWS: microwave spectroscopy.

§ Centrosymmetric isomer.

substituted are puckered, whereas rings which are may be planar. However, centrosymmetrically substituted cyclobutanes can also be puckered (*e.g.* cyclobutane, octachlorocyclobutane and *trans*-1,3-cyclobutanedicarboxylic acid). As may be noticed from Table 5, in several compounds ring puckering is quite large (dihedral angles from 145 to 180°). Planar cyclobutane structures, such as *cis,trans,cis*-1,2,3,4-tetraphenylcyclobutane (Margulis, 1965; Dunitz, 1949), *cis,trans,cis*-1,2,3,4-cyclobutanetetracarbonitrile (Greenberg & Post, 1968), octahydroxycyclobutane (Bock, 1968), *trans*-1,3-cyclobutanedicarboxylic acid (Margulis & Fischer, 1967), and its dianion (Adman & Margulis, 1968), and 2,2,4,4-tetramethyl-*trans*-1,3-cyclobutanediol (Margulis, 1969), are invariably centrosymmetric molecules and have as such only been observed in the solid state.

According to a number of researches, the non-planar conformation of the four-membered rings is more favourable than the planar conformation. It is not clear, however, whether planarity is an intrinsic characteristic of a molecule (non-bonding substituent repulsions) or a function of intermolecular forces. It would appear that packing forces in the crystalline state play an important role in fixing the conformation of the cyclobutane ring, consistent with the estimated fairly low potential barrier (about 4 kJ mol^{-1}) between the puckered and the planar conformations of cyclobutane in the gas phase (Rathjens, Freeman, Gwinn & Pitzer, 1953). The case of *trans*-1,3-cyclobutanedicarboxylic acid, which exists in both the planar and puckered forms depending upon its crystalline environment (Adman & Margulis, 1968; Margulis & Fischer, 1967), is illustrative in this regard.

Although the variability of conformation of cyclobutane rings has been discussed (Lambert & Roberts, 1965*a*,*b*) no *a priori* way of predicting the conformation of the ring skeleton after substitution seems available. The extent of deviation from planarity appears to be a function of the nature of the ring substituents. In general, in monosubstituted cyclobutane derivatives the substituents exert less effect on ring conformation and vibrations than in derivatives substituted at more than one ring carbon. It is likely that lack of considerable puckering of the cyclobutane ring of (I) is due to a complex interplay of non-bonded interactions between F(3), F(5), H(31) and F(1), F(1′), F(2) as well as those between H(2), H(32), F(4), F(6).

The set of non-bonded distances, given in Table 3, also partly results from angular rather than conformational distortions. The chain bond angle C(1′,1,2) of 115·3° relieves F(2′)–H(2) to 2·65 Å; further noticeable distortions are found for the exocyclic bond angles C(1,2,3) and C(1,2,5) of 116·3 and 116·2°. Similar values (114·6 and 115·6°) have been calculated for Teflon (Clark & Muus, 1962). The C–C–F angles of the substituted cyclobutane ring average 115·1° (range 113·6–116·9°), at variance with the corresponding angles in the chain (av. 108·7°; range 106·2–111·6°). The former have the effect of increasing the 1,4 non-bonded distances between the cyclobutane substituents. On the other hand, F–C–F angles in (I) are smaller than tetrahedral and range from 106·3 to 107·4° (av. 106·7°), in spite of the differences between ring and chain difluoromethylene groups. Similar bond angles are observed in a variety of compounds, ranging from CF_2H_2 (108° 17′) (Lide, 1952) to polytetrafluoroethylene (108° 30′) (Iwasaki, 1963).

C–C bond distances in tetrafluoro-1,2-bis(2,2,3,3-tetrafluorocyclobutyl)ethane average 1·532 Å as compared to a normal $C(sp^3)$–$C(sp^3)$ single-bond length of 1·537 (5) Å (Sutton, 1965). However, the spread of the individual values, ranging from 1·506 (10) to 1·571 (7) Å, is remarkable. Although the long C–C distance in (I) may not statistically be significantly different from the standard value due to a fairly high e.s.d., the difference between the extreme endocyclic bond lengths, and therefore the asymmetry of the cyclobutane ring, certainly is. This is ascribed to the asymmetric substitution, leading to interactions such as F(2)–H(31), 2·54 Å, and C(1)–H(31), 2·64 Å. It should be noted that long C–C distances are not unusual in cyclobutane derivatives (*cf.* Table 5), as, for example, in perfluorocyclobutane (Lemaire & Livingstone, 1952). The results reported here do not support the suggestion (Churchill & Mason, 1967) that the eclipsing of F atoms lengthens the C–C bond.

The average C–F bond length is 1·344 (6) Å (range 1·327–1·359 Å) and may be compared to 1·343 (8) Å in *cis*-perfluorobicyclo[4.4.0]decane-1,6-diol (Hamor & Hamor, 1976) and in 1,4-dibenzoyldecafluoronorbornane (Hamor & Watkin, 1974), to 1·336 (9) Å in difluoroacetamide (Hughes & Small, 1972), to 1·358 (1) Å in CF_2H_2 (Lide, 1952) and to 1·345 (1) Å in $CHF_2.CH_3$ (Solimene & Dailey, 1954). Hughes & Small (1972) have noticed that there is a variation in C–F bond length depending on the number of F atoms linked to the C atom. In fact, a paraffinic C–F bond of a monofluoro-substituted C is 1·379 (5) Å (Sutton, 1965). This effect has been explained in terms of interatomic charge transfer (Peters, 1963).

There are three non-bonded distances which are smaller than the sum of the van der Waals radii (Bondi, 1964) by 0·2–0·3 Å. These involve C–H, C–F and F–H contacts of 2·64, 2·81 and 2·34 Å, respectively. The shortest non-bonded C–H, C–F, F–F and F–H contacts correspond to interaction energies of –0·0, –0·4, 0·4 and –0·4 kJ mol^{-1}, respectively, as calculated by the method given by Eliel, Allinger, Angyal & Morrison (1965).

It is of interest to compare the molecular structure of (I) with that of other fluorinated alkanes. A planar zigzag carbon configuration as in (I) has also been found in perfluoro-*n*-pentane and perfluoro-*n*-hexane (Bastiansen & Hadler, 1952) but contrasts with the helical chain of poly(tetrafluoroethylene) (13 CF_2 units in six turns, τ = 163·5°; 15 CF_2 units in seven turns, τ = 165·8°) (Clark & Muus, 1962). The tendency towards a planar conformation of the chain is also present in Teflon at high temperatures (Clark & Muus, 1962). The configuration of the asymmetric carbon atoms C(2) and C(2′) in tetrafluoro-1,2-bis(2,2,3,3-tetrafluorocyclobutyl)ethane is (*RS*) and therefore the compound has a *meso* configuration due to the crystallographic inversion centre.

The arrangement of the fluorocarbon (I) in the unit cell is shown in Fig. 2. The shortest intermolecular distances for C–C, C–F, C–H, F–F, F–H and H–H are >4·0, 3·25, 3·65, 2·92, 2·56, and 3·98 Å, as compared to the expected van der Waals distances of 3·60, 3·20, 3·00, 2·80, 2·60 and 2·40 Å, respectively. Noteworthy is the absence of C–C, C–H and H–H contacts, indicating that the packing arrangement is mainly governed by F atoms.

The relevance of this solid-state study to the conformation of tetrafluoro-1,2-bis(2,2,3,3-tetrafluorocyclobutyl)ethane in solution is limited, as NMR studies indicate a variety of unsymmetrically substituted cyclobutanes to exhibit a classical equilibrium between axial and equatorial conformations (Lambert & Roberts, 1965*a*,*b*). Even the parent cyclobutane in solution interconverts rapidly between two nonplanar equilibrium conformations of D_{2d} symmetry (Meiboom & Snyder, 1967). Nevertheless, although there is no clear-cut evidence yet for a truly planar cyclobutane ring, except in the solid state, the extent of puckering of the four-membered ring of (I) leads us to believe that the interpretation of the NMR solution spectrum, as described previously (Piccardi *et al.*, 1971), is correct.

References

ADMAN, E. & MARGULIS, T. N. (1967). *Chem. Commun.* p. 641.

ADMAN, E. & MARGULIS, T. N. (1968). *J. Am. Chem. Soc.* **90**, 4517–4521.

ALMENNINGEN, A., BASTIANSEN, O. & SKANCKE, P. N. (1961). *Acta Chem. Scand.* **15**, 711–712.

BASTIANSEN, O. & HADLER, E. (1952). *Acta Chem. Scand.* **6**, 214–218.

BENEDETTI, E., CORRADINI, P. & PEDONE, C. (1970). *Acta Cryst.* B**26**, 493–498.

BOCK, C. M. (1968). *J. Am. Chem. Soc.* **90**, 2748–2751.

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

CHURCHILL, M. R. & MASON, R. (1967). *Proc. R. Soc. London Ser. A*, **301**, 433–449.

CLARK, E. S. & MUUS, L. T. (1962). *Z. Kristallogr.* **117**, 119–127.

CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, ch. 14, edited by J. S. ROLLETT. London: Pergamon Press.

DUNITZ, J. D. (1949). *Acta Cryst.* **2**, 1–13.

ELIEL, E. L., ALLINGER, N. S., ANGYAL, S. J. & MORRISON, G. A. (1965). *Conformational Analysis*, p. 435. New York: Interscience.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

GREENBERG, B. & POST, B. (1968). *Acta Cryst.* B**24**, 918–924.

HAMOR, M. J. & HAMOR, T. A. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 383–387.

HAMOR, T. A. & WATKIN, D. J. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 140–146.

HUGHES, D. O. & SMALL, R. W. M. (1972). *Acta Cryst.* B**28**, 2520–2524.

IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743–749.

IWASAKI, M. (1963). *J. Polym. Sci. Part A*, **1**, 1099–1104.

JOHNSON, C. K. (1970). Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KARLE, I. L. & KARLE, J. (1966). *Acta Cryst.* **20**, 555–559.

KARLE, I. L., KARLE, J. & BRITTS, K. (1966). *J. Am. Chem. Soc.* **88**, 2918–2921.

KIM, H. & GWINN, W. D. (1966). *J. Chem. Phys.* **44**, 865–873.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

LAMBERT, J. B. & ROBERTS, J. D. (1965*a*). *J. Am. Chem. Soc.* **87**, 3884–3890.

LAMBERT, J. B. & ROBERTS, J. D. (1965*b*). *J. Am. Chem. Soc.* **87**, 3891–3895.

LEMAIRE, H. P. & LIVINGSTONE, R. L. (1952). *J. Am. Chem. Soc.* **74**, 5732–5736.

LIDE, D. R. (1952). *J. Am. Chem. Soc.* **74**, 3548–3552.

MARGULIS, T. N. (1965). *Acta Cryst.* **19**, 857–859.

MARGULIS, T. N. (1969). *Chem. Commun.* pp. 215–216.

MARGULIS, T. N. (1971). *J. Am. Chem. Soc.* **93**, 2193–2195.

MARGULIS, T. N. & FISCHER, M. S. (1967). *J. Am. Chem. Soc.* **89**, 223–226.

MEIBOOM, S. & SNYDER, L. C. (1967). *J. Am. Chem. Soc.* **89**, 1038–1039.

MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.

PETERS, D. (1963). *J. Chem. Phys.* **38**, 561–563.

PICCARDI, P., MODENA, M. & SANTORO, E. (1971). *J. Chem. Soc. C*, pp. 3894–3898.

RATHJENS, W. D., FREEMAN, J., GWINN, W. D. & PITZER, K. S. (1953). *J. Am. Chem. Soc.* **75**, 5634–5642.

ROTHSCHILD, W. G. & DAILEY, B. P. (1962). *J. Chem. Phys.* **36**, 2931–2940.

SOLIMENE, N. & DAILEY, B. P. (1954). *J. Chem. Phys.* **22**, 2042–2044.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Spec. Publ. No. 18. London: The Chemical Society.

VAND, V., EILAND, P. E. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303–306.

VAN DER HELM, D., HSU, I-N. & SIMS, J. M. (1972). *Acta Cryst.* B**28**, 3109–3114.