Geometry of the Fluorinated *cis*-Decalin System: Crystal and Molecular Structure of *cis*-Perfluorobicyclo[4.4.0]decane-1,6-diol

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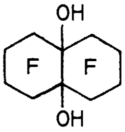
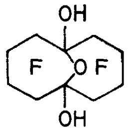
The structure of the title compound has been determined by a single-crystal *X*-ray analysis from three-dimensional counter data. Crystals are orthorhombic, space group *Pbca*, with $Z = 8$ in a cell of dimensions $a = 10.30 \pm 0.01$, $b = 18.50 \pm 0.015$, $c = 14.75 \pm 0.01$ Å. The structure was established by direct methods and refined by least-squares to R 4.7% for 1 210 structure amplitudes. The molecule approximates to C_2 symmetry. Comparison with hydrocarbon analogues indicates that the carbon skeleton is significantly flatter, an effect due mainly to repulsive interactions involving the 2,4,7, and 9(axial)-fluoro-substituents.

FLUORINATION of naphthalene, 1,2,3,4-tetrahydronaphthalene, or bicyclo[4.4.0]decane (decalin) with $CsCoF_4$ results in the formation of perfluorobicyclo[4.4.0]dec-1(6)-ene, which on treatment with acetone–potassium permanganate yields a diol.[1] The structure of this could not be determined with absolute certainty by analytical, chemical, or spectroscopic methods; it most probably had structure (I), with (II) as a possible alternative.[1] Our *X*-ray crystallographic analysis now establishes the *cis*-isomer of structure (I) for the diol. Further, by comparing molecular dimensions with unfluorinated analogues, the effect of substituting fluorine for hydrogen on the geometry of the *cis*-decalin system is assessed.



(I)



(II)

EXPERIMENTAL

Crystallographic Measurements.—Initial cell dimensions were obtained from oscillation and Weissenberg photographs. Final cell dimensions and intensity data were measured with a Stoe two-circle, computer-controlled diffractometer by use of graphite-monochromated Mo-K_α radiation and a scintillation counter. As the crystals were unstable in air, the crystal used, of dimensions $0.55 \times 0.44 \times 0.36$ mm, was mounted inside a Pantak capillary tube, together with a second, larger crystal, and some magnesium perchlorate as dehydrating agent.

The crystal was set about the a axis. Of 3 249 reflections, scanned within the range $0.10 \leqslant \sin\theta/\lambda \leqslant 0.65$, 1 246 having $I > 2.5\,\sigma(I)$ were considered observed. Of these, 1 212 reflections having $\sin\theta/\lambda \leqslant 0.59$ were used in the structure analysis. The ω-scan technique was used, and for layers 0—3, 140 counts of 1 s at intervals of 0.01° were taken for each reflection, backgrounds being measured for 30 s at each end of the scan. For reflections on higher layers, a variable-scan technique was used in order to increase the scan range at low values of the azimuth angle and high values of the equi-inclination angle. The intensities of 3 standard reflections were re-measured at the end of each layer to monitor the stability of the crystal and the *X*-ray tube. In the conversion of intensities to structure amplitudes, the polarisation factor appropriate to monochromated radiation was used, but absorption corrections were not applied.

Crystal Data.—$C_{10}H_2F_{16}O_2$, $M = 458.1$. Orthorhombic, $a = 10.30 \pm 0.01$, $b = 18.50 \pm 0.015$, $c = 14.75 \pm 0.01$ Å, $U = 2\,810.6$ Å^3, $Z = 8$, $D_c = 2.165$, $F(000) = 1\,776$. Systematic absences: $0kl$ when k is odd, $h0l$ when l is odd, $hk0$ when h is odd, space group *Pbca* (D_{2h}^{15}). Mo-K_α radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo-}K_\alpha) = 3.1$ cm^{-1}.

Structure Analysis.—The structure was solved by direct methods [2] by use of a multiple-solution technique [3] and tangent refinement of phases with the automatic phasing program TANFIZ.[4] Phases (0 or 180°) were determined for 186 of the 194 largest E values ($\geqslant 1.65$) and the E map calculated with these phases gave the positions of all the atoms in the molecule (apart from hydrogen atoms). At this stage R was 34.0%. Five cycles of isotropic, full-matrix, least-squares refinement reduced R to 14.9%, after which the atoms were allowed to vibrate anisotropically. A further 4 cycles of refinement reduced R to 5.2%. A Fourier difference synthesis was computed from which the two hydrogen atoms were located. Further least-squares refinement was carried out on the hydrogen atoms (positional parameters only), the oxygen atoms and the 6 adjacent carbon atoms, and finally on the whole molecule, and was terminated when all shifts were $<0.1\sigma$ and R 4.7%. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21560 (8 pp., 1 microfiche).*

The weighting scheme used in the final cycles of refinement was $w^{\frac{1}{2}} = |F_o|/16.5$ if $|F_o| < 16.5$, $w^{\frac{1}{2}} = 1$ if $16.5 \leqslant |F_o| \leqslant 50.0$ and $w^{\frac{1}{2}} = 50.0/|F_o|$ if $|F_o| > 50.0$, chosen to give approximately constant values for the average of $\Sigma w(|F_o| - |F_c|)^2$ when taken in groups of increasing $|F_o|$ and increasing $\sin\theta/\lambda$. Two large low-order reflections (040 $|F_o| = 253.2$, $|F_c| = 280.3$, and 006 $|F_o| = 384.6$, $|F_c| = 408.7$) which showed extinction effects, were omitted from the structure-factor calculations. Atomic scattering factors were taken from ref. 5, except those of hydrogen which were taken from ref. 6.

Computations were carried out on the Birmingham University 1906A computer and on the IBM 370/145 of the Department of Physics, Birmingham University (phase determination and rigid-body thermal-motion analysis).

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[1] R. G. Plevey, I. J. Sallomi, R. Stephens, J. C. Tatlow, J. R. Taylor and D. F. Thomas, unpublished work.

[2] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[3] G. Germain and M. M. Woolfson, *Acta Cryst.*, 1968, **B24**, 91.

[4] O. Kennard, N. W. Isaacs, W. D. S. Motherwell, J. C. Coppola, D. L. Wampler, A. C. Larson, and D. G. Watson, *Proc. Roy. Soc.*, 1971, *A*, **325**, 401.

[5] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

The major computer programs used in the analysis are listed and acknowledged in ref. 7.

RESULTS AND DISCUSSION

The structure of the molecule is illustrated in Figure 1, which also shows the atomic numbering scheme used. Oxygen and fluorine atoms are assigned the number of the carbon atom to which they are linked, with a denoting axial and e, equatorial. Atomic co-ordinates and thermal parameters are listed in Tables 1 and 2, molecular dimensions in Table 3. Estimated standard deviations for lengths, bond angles, and torsion angles (not involving hydrogen atoms) average 0.008 Å, 0.5°, and 0.8°, respectively. The results of analysing the thermal parameters of the heavier atoms in terms of rigid-body motion [8] are shown in Table 4. Bond lengths corrected for thermal motion are listed in Table 3. The two cyclohexyl rings each adopt a chair-like conformation, and, if hydrogen atoms are excluded, the overall geometry of the molecule deviates only slightly from the C_2 symmetry of the idealised *cis*-decalin system. In Table 3, lengths and angles are listed in two columns, such that those in the second are related to the corresponding values in the first by the approximate two-fold axis.

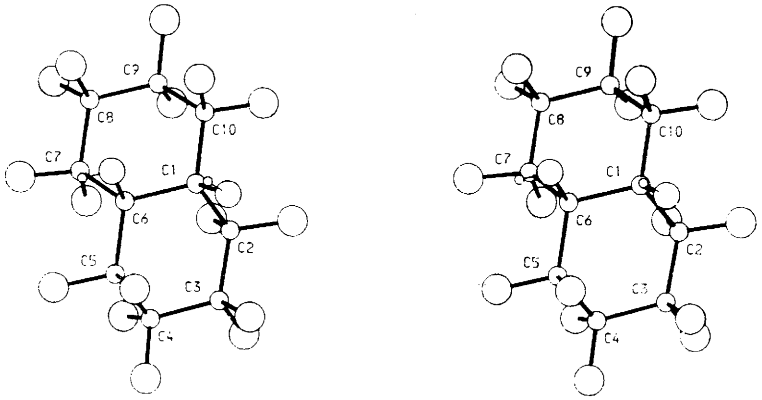

FIGURE 1 Stereoscopic view of the *cis*-perfluorobicyclo[4.4.0]decane-1,6-diol molecule along the *b* axis

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	x	y	z
C(1)	3 365(5)	3 403(3)	5 163(4)
C(2)	4 122(6)	3 914(3)	4 504(4)
C(3)	3 887(6)	3 764(3)	3 495(4)
C(4)	2 460(7)	3 726(4)	3 224(4)
C(5)	1 678(6)	3 230(3)	3 867(4)
C(6)	1 881(5)	3 316(3)	4 913(4)
C(7)	1 012(6)	3 922(3)	5 339(4)
C(8)	1 229(7)	4 032(4)	6 349(5)
C(9)	2 651(8)	4 166(4)	6 595(4)
C(10)	3 558(6)	3 599(4)	6 184(4)
F(2a)	3 797(4)	4 601(2)	4 667(2)
F(2e)	5 403(3)	3 838(2)	4 639(3)
F(3a)	4 463(4)	3 140(2)	3 257(3)
F(3e)	4 460(4)	4 293(2)	3 008(3)
F(4a)	1 957(4)	4 392(2)	3 260(3)
F(4e)	2 348(4)	3 484(2)	2 373(2)
F(5a)	2 017(4)	2 550(2)	3 649(2)
F(5e)	412(4)	3 308(2)	3 669(2)
F(7a)	1 205(4)	4 551(2)	4 913(3)
F(7e)	−239(3)	3 736(2)	5 246(3)
F(8a)	789(4)	3 464(2)	6 830(3)
F(8e)	537(5)	4 617(2)	6 606(3)
F(9a)	3 001(5)	4 827(2)	6 316(3)
F(9e)	2 790(5)	4 140(3)	7 505(3)
F(10a)	3 396(4)	2 988(2)	6 658(2)
F(10e)	4 795(4)	3 818(2)	6 317(3)
O(1)	3 965(4)	2 730(2)	5 014(3)
O(6)	1 556(4)	2 666(2)	5 339(3)
H[O(1)]	3 513(63)	2 422(33)	5 192(44)
H[O(6)]	933(79)	2 552(43)	5 236(56)

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$) for the heavier atoms

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	308	371	468	16	−43	10
C(2)	393	436	514	1	23	74
C(3)	515	543	652	39	168	196
C(4)	625	721	462	−1	−13	91
C(5)	460	586	399	10	−85	−35
C(6)	320	308	520	13	−31	47
C(7)	390	440	560	110	13	−31
C(8)	652	672	559	88	144	−208
C(9)	852	665	565	−41	38	−266
C(10)	573	711	362	−116	−123	22
F(2a)	647	361	814	−68	6	19
F(2e)	369	735	827	−101	−1	125
F(3a)	732	787	733	105	307	−46
F(3e)	851	933	737	−138	234	363
F(4a)	742	761	758	120	−26	313
F(4e)	1 076	1 246	370	−88	−26	10
F(5a)	939	577	531	−97	33	−179
F(5e)	540	1 067	563	−139	−236	108
F(7a)	634	370	926	153	15	70
F(7e)	349	684	991	98	44	−47
F(8a)	906	971	646	−2	347	9
F(8e)	1 061	882	1 185	246	325	−479
F(9a)	1 054	635	914	−139	−20	−307
F(9e)	1 340	1 337	536	−74	−101	−373
F(10a)	775	826	600	60	−103	249
F(10e)	605	1 128	672	−180	−269	−69
O(1)	354	367	710	47	62	88
O(6)	401	393	490	−63	−4	100

* Temperature factors are in the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

Carbon–carbon bond-lengths range from 1.522–1.581 Å (uncorrected) with the central bond C(1)—C(6) the longest (1.581 Å), the other bonds involving C(1) and

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[7] T. A. Hamor and D. J. Watkin, *J.C.S. Perkin II*, 1974, 140.

[8] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754; V. Schomaker and K. N. Trueblood, *ibid.*, 1968, **B24**, 63.

C(6) also rather long (1.562—1.566, mean 1.564 Å) and the six remaining C–C bonds in the range 1.522—1.546 Å (mean 1.531 Å). These last-mentioned are close to the values determined for the C–C bond lengths in cyclohexane by electron diffraction in the gas phase (1.528 Å),[9] *X*-ray crystallography (mean 1.523 Å),[10] and theoretical calculation (1.532 Å).[11] Carbon–fluorine bonds range from 1.335 to 1.352 Å, mean 1.343 Å, in good agreement with those [7] for difluoro-substituted carbon atoms in 1,4-dibenzoyldecafluoronorbornane. Axially oriented bonds are generally slightly shorter than equatorial ones, the former having lengths 1.335—1.347, mean 1.340 Å, and the latter 1.338—1.352, mean 1.346 Å. Corrections for the effect of thermal libration based on the rigid-body model are 0.008—0.011 Å for all bond lengths. Carbon–fluorine bonds corrected on the assumption of riding motion [12] range from 1.354 to 1.396, mean 1.369 Å.

TABLE 3

Molecular dimensions

(*a*) Bonded distances (Å); distances corrected for thermal libration in square brackets

C(1)–C(2)	1.564(8) [1.573]	C(6)–C(7)	1.565(7) [1.576]
C(2)–C(3)	1.533(9) [1.543]	C(7)–C(8)	1.522(9) [1.532]
C(3)–C(4)	1.525(10) [1.534]	C(8)–C(9)	1.529(10) [1.539]
C(4)–C(5)	1.546(9) [1.554]	C(9)–C(10)	1.530(9) [1.541]
C(5)–C(6)	1.566(7) [1.576]	C(10)–C(1)	1.561(8) [1.572]
C(6)–C(1)	1.581(8) [1.591]		
C(1)–O(1)	1.406(6) [1.416]	C(6)–O(6)	1.398(6) [1.406]
C(2)–F(a)	1.335(6) [1.344]	C(7)–F(a)	1.337(6) [1.345]
C(2)–F(e)	1.342(7) [1.351]	C(7)–F(e)	1.340(7) [1.348]
C(3)–F(a)	1.344(7) [1.353]	C(8)–F(a)	1.347(8) [1.355]
C(3)–F(e)	1.350(7) [1.358]	C(8)–F(e)	1.350(7) [1.359]
C(4)–F(a)	1.336(7) [1.345]	C(9)–F(a)	1.339(8) [1.347]
C(4)–F(e)	1.338(7) [1.348]	C(9)–F(e)	1.350(8) [1.359]
C(5)–F(a)	1.344(7) [1.353]	C(10)–F(a)	1.339(7) [1.348]
C(5)–F(e)	1.344(7) [1.353]	C(10)–F(e)	1.352(7) [1.360]
O(1)–H	0.781(63)	O(6)–H	0.692(79)

(*b*) Selected non-bonded distances (Å)

O(1) · · · F(3a)	2.749	O(6) · · · F(8a)	2.765
O(1) · · · F(5a)	2.863	O(6) · · · F(10a)	2.780
F(2a) · · · F(4a)	2.837	F(7a) · · · F(9a)	2.822
F(3a) · · · F(5a)	2.805	F(8a) · · · F(10a)	2.837
F(2a) · · · C(7)	3.285	F(7a) · · · C(2)	3.283
F(4a) · · · C(7)	3.332	F(9a) · · · C(2)	3.366
F(9a) · · · F(2a)	2.600	F(4a) · · · F(7a)	2.576
F(7a) · · · F(2a)	2.697		
F(10e) · · · F(2e)	2.554	F(5e) · · · F(7e)	2.547
O(6) · · · H[O(1)]	2.08		

(*c*) Bond angles (°)

C(6)–C(1)–C(2)	113.5(4)	C(1)–C(6)–C(7)	112.8(4)
C(1)–C(2)–C(3)	114.5(5)	C(6)–C(7)–C(8)	113.9(5)
C(2)–C(3)–C(4)	114.5(5)	C(7)–C(8)–C(9)	113.3(5)
C(3)–C(4)–C(5)	111.6(5)	C(8)–C(9)–C(10)	112.3(5)
C(4)–C(5)–C(6)	118.3(5)	C(9)–C(10)–C(1)	117.7(5)
C(5)–C(6)–C(1)	111.6(4)	C(10)–C(1)–C(6)	111.8(4)
C(2)–C(1)–C(10)	113.3(4)	C(7)–C(6)–C(5)	113.1(4)
O(1)–C(1)–C(10)	107.4(4)	O(6)–C(6)–C(5)	108.9(4)
O(1)–C(1)–C(2)	102.7(4)	O(6)–C(6)–C(7)	107.4(4)
O(1)–C(1)–C(6)	107.4(4)	O(6)–C(6)–C(1)	102.4(4)
F(a)–C(2)–C(1)	109.8(4)	F(a)–C(7)–C(6)	110.5(5)
F(a)–C(2)–C(3)	108.0(5)	F(a)–C(7)–C(8)	108.7(5)
F(e)–C(2)–C(1)	109.5(4)	F(e)–C(7)–C(6)	109.0(4)
F(e)–C(2)–C(3)	106.3(5)	F(e)–C(7)–C(8)	106.0(5)
F(a)–C(2)–F(e)	108.6(4)	F(a)–C(7)–F(e)	108.5(5)
F(a)–C(3)–C(2)	109.9(5)	F(a)–C(8)–C(7)	111.2(5)
F(a)–C(3)–C(4)	108.5(5)	F(a)–C(8)–C(9)	108.9(6)
F(e)–C(3)–C(2)	108.4(5)	F(e)–C(8)–C(7)	107.7(6)
F(e)–C(3)–C(4)	108.4(5)	F(e)–C(8)–C(9)	108.1(5)
F(a)–C(3)–F(e)	106.9(5)	F(a)–C(8)–F(e)	107.5(5)
F(a)–C(4)–C(3)	108.8(5)	F(a)–C(9)–C(8)	109.4(6)
F(a)–C(4)–C(5)	108.7(5)	F(a)–C(9)–C(10)	109.9(6)
F(e)–C(4)–C(3)	110.1(6)	F(e)–C(9)–C(8)	109.4(6)
F(e)–C(4)–C(5)	109.4(5)	F(e)–C(9)–C(10)	107.8(6)
F(a)–C(4)–F(e)	108.1(5)	F(a)–C(9)–F(e)	108.1(5)
F(a)–C(5)–C(4)	105.9(5)	F(a)–C(10)–C(9)	107.2(5)
F(a)–C(5)–C(6)	107.2(4)	F(a)–C(10)–C(1)	107.0(5)
F(e)–C(5)–C(4)	108.0(5)	F(e)–C(10)–C(9)	108.1(5)
F(e)–C(5)–C(6)	109.4(5)	F(e)–C(10)–C(1)	109.3(5)
F(a)–C(5)–F(e)	107.5(5)	F(a)–C(10)–F(e)	107.1(5)
H–O(1)–C(1)	109(5)	H–O(6)–C(6)	113(7)

TABLE 3 (*Continued*)

(*d*) Selected torsion angles (°); estimated standard deviations *ca.* 0.8°

C(6)–C(1)–C(2)–C(3)	−47.7	C(1)–C(6)–C(7)–C(8)	−50.1
C(1)–C(2)–C(3)–C(4)	51.4	C(6)–C(7)–C(8)–C(9)	53.7
C(2)–C(3)–C(4)–C(5)	−48.8	C(7)–C(8)–C(9)–C(10)	−50.4
C(3)–C(4)–C(5)–C(6)	46.2	C(8)–C(9)–C(10)–C(1)	46.5
C(4)–C(5)–C(6)–C(1)	−43.2	C(9)–C(10)–C(1)–C(6)	−43.1
C(5)–C(6)–C(1)–C(2)	42.2	C(10)–C(1)–C(6)–C(7)	43.3
C(10)–C(1)–C(2)–C(3)	−176.5	C(5)–C(6)–C(7)–C(8)	−177.9
C(4)–C(5)–C(6)–C(7)	85.2	C(9)–C(10)–C(1)–C(2)	86.6
C(2)–C(1)–C(6)–C(7)	−86.4		
O(1)–C(1)–C(2)–C(3)	67.9	O(6)–C(6)–C(7)–C(8)	61.9
O(1)–C(1)–C(6)–C(5)	−70.6	O(6)–C(6)–C(1)–C(10)	−71.9
O(1)–C(1)–C(10)–C(9)	−160.7	O(6)–C(6)–C(5)–C(4)	−155.5
O(1)–C(1)–C(6)–C(7)	160.9	O(6)–C(6)–C(1)–C(2)	158.5
F(a)–C(2)–C(1)–C(6)	74.0	F(a)–C(7)–C(6)–C(1)	72.6
F(a)–C(2)–C(3)–C(4)	−71.2	F(a)–C(7)–C(8)–C(9)	−69.9
F(e)–C(2)–C(1)–C(6)	−166.9	F(e)–C(7)–C(6)–C(1)	−168.3
F(e)–C(2)–C(3)–C(4)	172.4	F(e)–C(7)–C(8)–C(9)	173.6
F(a)–C(3)–C(2)–C(1)	−71.0	F(a)–C(8)–C(7)–C(6)	−69.3
F(a)–C(3)–C(4)–C(5)	74.4	F(a)–C(8)–C(9)–C(10)	73.8
F(e)–C(3)–C(2)–C(1)	172.5	F(e)–C(8)–C(7)–C(6)	173.2
F(e)–C(3)–C(4)–C(5)	−169.9	F(e)–C(8)–C(9)–C(10)	−169.7
F(a)–C(4)–C(3)–C(2)	71.2	F(a)–C(9)–C(8)–C(7)	71.8
F(a)–C(4)–C(5)–C(6)	−73.8	F(a)–C(9)–C(10)–C(1)	−75.5
F(e)–C(4)–C(3)–C(2)	−170.4	F(e)–C(9)–C(8)–C(7)	−170.0
F(e)–C(4)–C(5)–C(6)	168.4	F(e)–C(9)–C(10)–C(1)	167.0
F(a)–C(5)–C(4)–C(3)	−74.0	F(a)–C(10)–C(9)–C(8)	−74.0
F(a)–C(5)–C(6)–C(1)	76.3	F(a)–C(10)–C(1)–C(6)	77.5
F(e)–C(5)–C(4)–C(3)	171.1	F(e)–C(10)–C(9)–C(8)	170.8
F(e)–C(5)–C(6)–C(1)	−167.4	F(e)–C(10)–C(1)–C(6)	−166.9
H–O(1)–C(1)–C(2)	−162	H–O(6)–C(6)–C(7)	67
H–O(1)–C(1)–C(6)	−42	H–O(6)–C(6)–C(1)	−174
H–O(1)–C(1)–C(10)	79	H–O(6)–C(6)–C(5)	−56

TABLE 4

Results of rigid-body motion analysis. 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 tensors of inertia *I*. The eigenvectors of *I* are referred to the unit-cell axes. The origin of the molecular co-ordinate system is at $x = 0.2588$, $y = 0.3738$, $z = 0.4957$

	Eigenvalues	Eigenvectors		
I	1 636 (at. wt. Å^2)	−0.2008	0.1428	0.9692
	2 605	0.9782	0.0833	0.1904
	3 095	−0.0535	0.9862	−0.1564
L	87 × 10^{-4} rad^2	0.6572	−0.6469	−0.3867
	55	−0.2455	−0.6688	0.7017
	50	−0.7126	−0.3662	−0.5984
T	406 × 10^{-4} Å^2	0.9960	0.0594	−0.0666
	342	0.0373	−0.9554	−0.2928
	258	−0.0810	0.2892	−0.9538

Root-mean-square discrepancy, $\langle(\Delta U)^2\rangle^{\frac{1}{2}} = 0.0053$ Å^2.

Bond angles within the rings are in the range 111.6—

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118.3, mean 113.8°, significantly greater than the values quoted for cyclohexane (111.05,[9] 111.34,[10] 111.0°[11]). Consistent with the large bond angles, the ring torsion angles (absolute values 42.2—53.7, mean 47.2°), are smaller than in cyclohexane where the mean values are[9-11] in the range 55.1—56.1°. In a survey[11] of the geometries of six mono-, di-, and tri-substituted cyclohexanes as determined by *X*-ray methods, the ring torsion angles range from 50.0 to 60.1°. The cyclohexyl rings of the fluorinated decalin are thus significantly flatter than cyclohexane and its simple derivatives.

To assess the effect of fluorine substitution on the conformation of the carbon skeleton in somewhat greater detail, we have listed in Table 5 selected structural parameters obtained for *cis*-decalin systems by theoretical calculation,[13] electron diffraction,[14] and *X*-ray crystallography. From the rather limited number of *X*-ray studies available we have selected the *cis*-fused A,B-ring system of the steroids 5β-androstane-3α,17β-diol,[15] cholic acid,[16] and 3α,6α-dihydroxy-5β-cholan-24-oic acid,[17] and the *cis*-3-azabicyclo[4.4.0]decane system of the alkaloid reserpine.[18] In an attempt to obtain representative parameters we have also listed the means of the values derived from the four *X*-ray studies (3)—(6) under (7).

TABLE 5

Comparison of structural parameters of *cis*-decalin systems. The atomic numbering is as in Figure 1, so that in the steroids (3)—(5), ring C is fused at C(2), C(3) and the angular methyl group is at C(1). In reserpine (6), the hetero-nitrogen atom occupies the 4-position. Carbon atoms are identified by number only

	(1) *	(2)	(3)	(4)	(5)	(6)	(7)	(8)
(*a*) Bond lengths (Å)								
1–6			1.561	1.55	1.566	1.595	1.568	1.581
Mean 1–2, 5–6, 6–7, 1–10			1.546	1.560	1.544	1.549	1.550	1.564
Mean 2–3, 3–4, 4–5, 7–8, 8–9, 9–10			1.532	1.535	1.527	1.539 [a]	1.533	1.531
Overall mean	1.524_5 [b]	1.536	1.540	1.545	1.537	1.548 [a]	1.543	1.547
(*b*) Bond angles (°)								
Mean ring angle	112.1 [b]	112.0_5	111.1	110.7	111.2	110.1	110.8	113.8
(*c*) Torsion angles (°) [c]								
Mean ring torsion-angle	52.9 [d]	53.1 [d]	55.8 [e]	56.3 [e]	55.6	58.0	56.4	47.2
Mean 2–1–6–7 7–6–5–4 2–1–10–9			69.6	69.4	67.6	67.5	68.5	86.1
Flap angle (deg.) [e,f]			125.4	126.2	123.6	124.0	124.8	132.3

* (1) *cis*-Decalin (theoretical calculation), ref. 13; (2) *cis*-decalin (electron diffraction), ref. 14; (3)—(5) *cis*-fused A,B-ring system of steroids 5β-androstane-3α,17β-diol (ref. 15), cholic acid (ref. 16), and 3α,6α-dihydroxy-5β-cholan-24-oic acid (ref. 17); (6) *cis*-3-azabicyclo[4.4.0]decane system of reserpine (ref. 18); (7) mean of *X*-ray results (3)—(6); (8) present work, uncorrected values for bond lengths.

[a] Excluded from the mean are the two C–N bond lengths. [b] Median of quoted range. [c] Absolute values, ignoring signs. [d] Calculated from mean bond-angle ϕ, using relationship (ref. 9), cos(mean torsion angle) = $-\cos\phi/(1 + \cos\phi)$. [e] Calculated from the published atomic co-ordinates. [f] Angle between planes of C(1), C(3), C(4), C(6) and C(1), C(6), C(8), C(9).

Bond lengths in the unfluorinated decalins (3)—(6) follow the same trend as in the fluorinated decalin (8) with the central C–C bonds, those involving C(1) and C(6), longer than the peripheral ones. This difference is, however, slightly greater in the fluorinated compound. More significant differences occur when bond and torsion angles are considered. Thus the mean ring bond-angle and the mean ring torsion-angle are, respectively, 3° greater and 9.2° smaller in the fluorodecalin than the mean values derived from the *X*-ray studies on the unfluorinated decalins [*cf.* columns (8) and (7) of Table 5]. The three torsion angles C(2)–C(1)–C(6)–C(7), C(2)–C(1)–C(10)–C(9), and C(7)–C(6)–C(5)–C(4), *i.e.* of type C(axial)–C(ring)–C(ring)–C(ring), exhibit an even greater contrast, 85.2—86.6°, mean 86.1° in (8), compared with 63.8—72.9°, mean 68.5° in (3)—(6).

The cyclohexyl rings of the fluorinated compound are thus flatter than the rings in (3)—(6), which are similar to cyclohexane itself. In addition the whole molecule is flattened relative to the decalin systems (3)—(6) by an increase of the angle between the two rings. If the angle between the mean planes through atoms C(1),-C(3),C(4),C(6), and C(1),C(6),C(8),C(9), denoted as the 'flap angle' in Table 5, is used as a measure of this, its value is 132.3° in (8) compared with 123.6—126.2°, mean 124.8°, in (3)—(6).

In a model of the *cis*-bicyclo[4.4.0]decane system constructed on the basis of standard bond lengths and angles (C–C–C 109° 28′), three short transannular[19] H · · · H distances occur, H(9a) · · · H(2a), H(4a) · · · H(7a), and H(7a) · · · H(2a), each *ca.* 2 Å as measured on the model. When the hydrogen atoms are replaced by fluorine

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atoms, assuming C–F 1.35 Å, these separations decrease to *ca.* 1.75 Å. The non-bonded (van der Waals) interaction energy corresponding to such a short F···F distance would be 110 kJ mol^{-1}, calculated by the method given in ref. 20, but taking the van der Waals radius of fluorine to be 1.5 Å.[21] If the *cis*-decalin skeleton of 3α,6α-dihydroxy-5β-cholan-24-oic acid (5) is used as a more realistic model, and fluorine atoms placed in calculated positions, these F···F separations become 1.97, 1.92, and 2.03 Å. The corresponding interaction energies are *ca.* 38, 48, and 28 kJ mol^{-1}, still an unfavourable situation. In the actual structure, however, these separations have increased to 2.600, 2.576, and 2.697 Å [Table 3(*b*)] and the interaction energies have decreased to 0.5, 0.7, and −0.1 kJ mol^{-1}, respectively, a net decrease of 113 kJ mol^{-1}.

The distortion of the carbon skeleton of the fluorodecalin relative to the geometries of the unfluorinated decalins is, therefore, presumably due to the need to increase these transannular F···F separations. The distortion takes the form of a series of comparatively small adjustments in bond angles, torsion angles and bond lengths, the cumulative effect of which is drastically to increase the three short F···F separations. Rough calculations, using the parameters given in ref. 20, indicate that the bond stretching, bond bending, and torsional-strain energies required to change the geometry of the carbon skeleton of the *cis*-decalin system of the steroid (5) to that of the fluorodecalin amount to *ca.* 50 kJ mol^{-1}, very much less than the energy decrease resulting from the more favourable separation of fluoro-substituents F(2a), F(4a), F(7a), and F(9a). On the other hand, the flattening of the cyclohexyl rings has the effect of decreasing the separation between axial and equatorial substituents on adjacent carbon atoms with a concomitant energy increase. This increase is, however, only small, and is partially compensated by a decrease in 1,3-diaxial interaction energies. The total energy increase due to these effects is *ca.* 4.5 kJ mol^{-1}.

TABLE 6

Intermolecular contacts (<3.5 Å for the heavier atoms; <3.0 Å for contacts involving hydrogen atoms)

O(1)···H[O(6^{I})]	2.13	F(10a)···F(4e^{III})	3.11
H[O(1)]···H[O(6^{I})]	2.57	F(3a)···F(4e^{IV})	3.18
H[O(1)]···F(7e^{I})	2.58	F(3e)···F(4a^{IV})	3.19
F(2e)···H[O(6^{I})]	2.64	F(10a)···F(5e^{I})	3.21
O(1)···O(6^{I})	2.82	F(9a)···F(4a^{II})	3.21
O(1)···F(7e^{I})	2.86	F(3e)···F(5e^{IV})	3.23
F(8e)···F(3e^{II})	2.89	F(3a)···F(8a^{I})	3.27
H[O(1)]···F(5e^{I})	2.91	F(10a)···F(3a^{III})	3.34
F(9e)···F(4a^{II})	2.95	F(3a)···O(6^{I})	3.34
F(3a)···H[O(6^{I})]	2.98	F(3e)···F(4e^{IV})	3.38
F(3a)···F(5e^{IV})	3.02	F(10a)···F(5a^{III})	3.41
F(2e)···O(6^{I})	3.03	F(10e)···F(5a^{I})	3.41
O(1)···F(5e^{I})	3.11		

Superscripts refer to the following equivalent positions:

I $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ III $x, \frac{1}{2}-y, \frac{1}{2}+z$
II $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ IV $\frac{1}{2}+x, y, \frac{1}{2}-z$

The arrangement of the molecules in the unit cell is shown in Figure 2. Shorter intermolecular distances are in Table 6. Molecules related by two-fold screw axes at $y=\frac{1}{4}$, $z=\frac{1}{2}$, *etc.*, form zigzag chains parallel to the x axis. These molecules are linked by hydrogen bonds O(1)···H–O(6^{I}), relevant distances being O(1)···O(6^{I}) 2.82 and O(1)···H[O(6)^{I}] 2.13 Å. The angle H[O(6)^{I}]–O(6^{I})···O(1) is 3.4° so that the hydrogen atom lies very close to the O(1)···O(6^{I}) line. The hydrogen atom linked to O(1) is 2.08 Å from O(6), so that there is probably also intramolecular hydrogen bonding O(1)–H[O(1)]···O(6), with the distance O(1)···O(6) 2.53 Å.

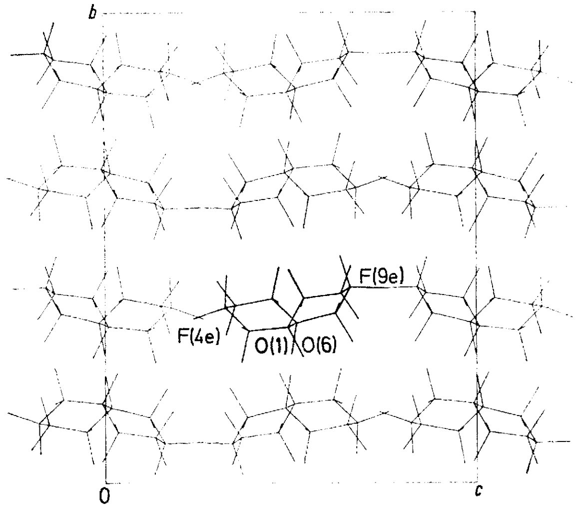

FIGURE 2 The crystal structure projected along the *a* axis

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