Polyfluorobicyclo[2.2.1]heptanes. Part X.[1] Crystal and Molecular Structure of *endo*-1-Methoxycarbonyl-3*H*,4*H*-nonafluoronorbornane

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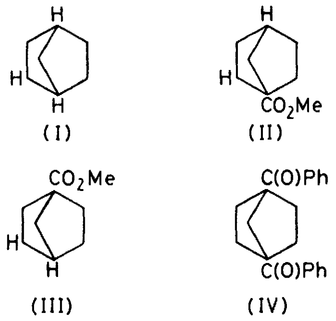
X-Ray crystallographic analysis has established that the major product obtained from *endo*-1*H*,2*H*,4*H*-nonafluoronorbornane (I) by a series of reactions, the first of which is an electrophilic displacement using methyl-lithium, is *endo*-1-methoxycarbonyl-3*H*,4*H*-nonafluoronorbornane (III). The displacement reaction, therefore, takes place predominantly at the 4-position. A minor (*ca.* 7%) constituent of the crystal may have been formed *via* displacement at the other bridgehead position. Crystals are orthorhombic, space group $Pna2_1$, with $Z = 4$ in a cell of dimensions $a = 13.78(1)$, $b = 9.70(1)$, $c = 7.985(10)$ Å. The structure was determined by direct methods and refined by least-squares techniques to R 3.8% for 1 079 observed reflections. The norbornane skeleton shows small but significant deviations from the ideal C_{2v} symmetry due to the unsymmetrical nature of the substitution.

POLYFLUORONORBORNANES with hydrogen at the bridgehead can be converted into carbanionic intermediates which are synthetically useful.[2] Treatment [3] of *endo*-1*H*,2*H*,4*H*-nonafluoronorbornane (I) with methyl-lithium in ether yields a lithium salt involving an electrophilic substitution at either the 1- or 4-position. Addition of CO_2 at −50 °C followed by neutralisation with acid and treatment with diazomethane produces a methoxycarbonyl derivative whose structure is either (II) or (III) depending on whether the electrophilic displacement took place at the 1- or the 4-position.[3] Of these, structure (III) was considered the more likely since the inductive influence of three $>CF_2$ groups would make the hydrogen atom at position 4 the more acidic. This could not, however, be established with certainty by chemical or spectroscopic methods. Our *X*-ray crystallographic analysis now establishes structure (III) for the methoxycarbonyl derivative.

The crystal also contains *ca.* 7.4% of a minor constituent which probably has the alternative structure (II), so that the initial reaction with methyl-lithium probably took place also to a small extent at the 1-position.



(All unmarked substituents are fluorine)

EXPERIMENTAL

Crystallographic Measurements.—As the crystals were unstable in air, the crystal used, of dimensions 1.1 × 0.8 × 0.4 mm, was mounted inside a Pantak capillary tube. Cell dimensions and intensity data were measured with a Stoe two-circle, computer-controlled diffractometer using graphite monochromated Mo-K_α radiation and a scintillation counter. The ω-scan technique was employed with a stepping interval of 0.01° and a step time of 1 s. For layers *hk*0—2 the scan range was 1.4°, and for layers *hk*3—9 a variable-scan technique was used so as to increase the scan range at low values of the azimuth angle and high values of the equi-inclination angle. Backgrounds were measured for 70 s at each end of the scan. The intensities of three *hk*0 reflections were re-measured after each layer of data collection to monitor the stability of the system.

A total of 1 401 reflections were scanned within the range $0.10 < \sin\theta/\lambda < 0.65$, of which 1 079 having $I > 3.5\sigma(I)$ were considered to be observed. In the conversion of intensities to structure amplitudes appropriate layer scale-factors were applied to compensate for slight crystal deterioration.

Crystal Data.—$C_9H_5F_9O_2$, $M = 316.1$. Orthorhombic, $a = 13.78(1)$, $b = 9.70(1)$, $c = 7.985(10)$ Å, $U = 1\,067.3$ Å^3, $Z = 4$, $D_c = 1.967$, $F(000) = 624$. Systematic absences: $0kl$ when $k + l$ is odd, $h0l$ when h is odd, space group $Pna2_1$ (C_{2v}^9) or $Pnam$ (D_{2h}^{16}). $Pna2_1$ established as a result of this investigation. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 2.3 cm^{-1}.

Structure Analysis.—The structure was solved by direct methods using a multiple-solution technique. Phases were determined [4] for 343 of the largest E values and the E map calculated with these phases gave the positions of all the heavier atoms except the terminal methyl carbon and one oxygen atom of the methoxycarbonyl group. These atoms were located from a Fourier difference synthesis. At this stage R was 21.3%. Six cycles of isotropic, full-matrix least-squares refinement,[5] followed by six cycles of anisotropic refinement, reduced R to 6.4%. The five hydrogen atoms were now located from a difference synthesis and included in the least-squares calculations with isotropic temperature factors, thus reducing R to 4.9%.

The two hydrogen atoms directly bonded to the norbornane skeleton were in positions 3-*endo* and 4 consistent with structure (III). The distance C(3)–H(3*n*)† was,

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† Fluorine and hydrogen atoms linked to the norbornane skeleton are assigned the number of the carbon atom to which they are linked with *n* denoting *endo* and *x*, *exo*.

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

[2] S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1965, **21**, 2997; P. J. N. Brown, R. Stephens, J. C. Tatlow, and J. R. Taylor, *J.C.S. Perkin I*, 1972, 937.

[3] J. S. Broughton, R. Stephens, and J. C. Tatlow, unpublished work.

[4] J. R. Carruthers, CRYSTALS, Oxford University Computing Laboratory, 1975.

[5] G. M. Sheldrick, SHELX, University of Cambridge, 1975.

however, 1.38 Å, corresponding rather to a C–F bond length and the temperature factor of H(3*n*) had refined to a near zero value.

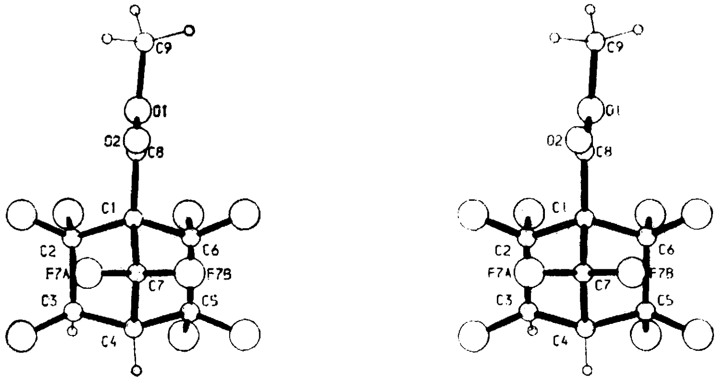

FIGURE 1 Stereoscopic view of the molecule along the normal to the plane of C(2),C(3),C(5),C(6)

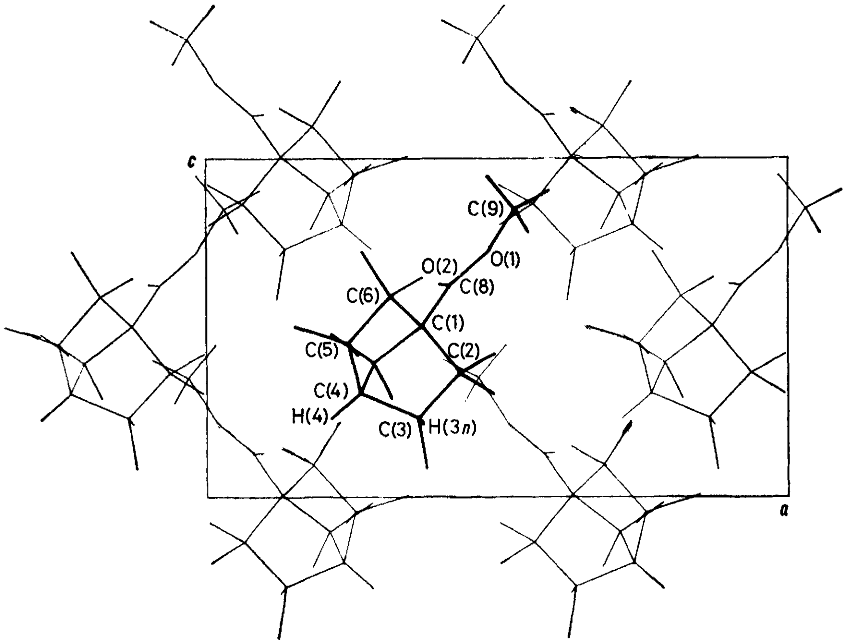

FIGURE 2 The crystal structure projected along the *b* axis

In order to investigate this phenomenon, hydrogen atom H(3*n*) was placed in the expected position 1.08 Å from C(3) and a difference synthesis was computed. This showed a low peak, *ca.* 0.5 Å from H(3*n*), near the extension of the C(3)–H line, suggesting the possibility of disorder in the crystal structure whereby the *endo* site at C(3) is occupied mainly by a hydrogen atom, but also partially by fluorine. Accordingly H(3*n*) was assigned a site occupation factor (s.o.f.) of 0.9 and a fluorine atom F(3n), was placed at the position to which the hydrogen atom had originally refined with s.o.f. = 1 − (s.o.f.)H(3*n*). Refinement was continued with the co-ordinates of F(3*n*) and H(3*n*) fixed. The s.o.f. of H(3*n*) was included in the calculations and it finally converged to a value of 0.926.

The methyl group was refined as a rigid group assuming standard dimensions. The refinement process was terminated when all shifts were $<0.1\sigma$ and *R* 3.8% for the 1 079 observed amplitudes.* Final atom co-ordinates are listed in Table 1, and Figure 1 shows a stereoscopic view of the molecule.

RESULTS AND DISCUSSION

The norbornyl hydrogen atoms have been conclusively found to be in positions 3*n* and 4. The disorder existing at position 3*n* is probably due to the presence of a small proportion (*ca.* 7.4%) of compound (II). It is not possible to confirm this by *X*-ray methods since the low scattering power of hydrogen makes it impossible to

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* Observed and calculated structure amplitudes, the thermal parameters, and the results of mean plane calculations are published in Supplementary Publication No. SUP 22111 (11 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

detect a small proportion of hydrogen at a site mainly occupied by fluorine, and the same overall result would be produced by the presence of any 1-methoxycarbonyl-4*H*-norbornane containing a 3-*endo* fluoro-substituent with the other substituents either fluorine or hydrogen.

TABLE 1

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

	x	*y*	*z*
C(1)	3 710(2)	2 166(3)	5 068(6)
C(2)	4 367(3)	1 552(4)	3 675(6)
C(3)	3 649(3)	989(5)	2 349(7)
C(4)	2 653(3)	1 383(4)	3 065(6)
C(5)	2 444(3)	450(4)	4 553(6)
C(6)	3 160(3)	976(4)	5 945(6)
C(7)	2 888(3)	2 735(4)	3 966(6)
C(8)	4 195(3)	3 177(3)	6 272(6)
C(9)	5 311(3)	3 354(5)	8 523(7)
F(2*x*)	4 946(2)	2 555(3)	3 047(5)
F(2*n*)	4 965(2)	0 550(3)	4 244(5)
F(3*x*)	3 795(2)	1 618(3)	0 830 [c]
H(3*n*) [a]	3 737	−0 110	2 139
F(3*n*) [b]	3 682	−0 440	2 295
H(4)	2 144(27)	1 333(41)	2 300(59)
F(5*x*)	1 516(2)	560(3)	5 071(5)
F(5*n*)	2 613(2)	−905(3)	4 202(6)
F(6*x*)	2 674(2)	1 464(3)	7 274(5)
F(6*n*)	3 722(2)	−52(2)	6 497(5)
F(7a)	3 193(2)	3 732(2)	2 910(5)
F(7b)	2 140(2)	3 257(2)	4 841(5)
O(1)	4 828(2)	2 530(3)	7 221(6)
O(2)	3 999(2)	4 378(3)	6 305(6)
H(9A)	4 836	3 715	9 505
H(9B)	5 928	2 838	9 070
H(9C)	5 557	4 221	7 787

[a] Site occupation factor 0.926(9). [b] Site occupation factor 0.074(9). [c] Held constant to define origin of unit cell.

However, if it is assumed that the starting material for the preparation of the crystals was a pure sample of (I), these possibilities can be excluded.* The positions of the atoms [apart from H(3*n*)] do not seem to be affected by the disorder, and estimated standard deviations are reasonably low, averaging 0.005 Å for bond lengths and 0.3° for bond angles. Thermal parameters are also unexceptional.

TABLE 2

Molecular dimensions *

(*a*) Bond lengths (Å) with estimated standard deviations in parentheses. The second column gives lengths corrected for thermal libration

C(1)–C(2)	1.553(5)	1.563	C(2)–F(2*x*)	1.355(4)	1.363
C(1)–C(6)	1.548(5)	1.558	C(2)–F(2*n*)	1.353(4)	1.363
C(1)–C(7)	1.536(5)	1.546	C(3)–F(3*x*)	1.373(5)	1.381
C(1)–C(8)	1.527(5)	1.534	[C(3)–F(3*n*)	1.388]	
C(2)–C(3)	1.548(6)	1.555	C(3)–H(3*n*)	1.086	
C(3)–C(4)	1.534(6)	1.546	C(4)–H(4)	0.932(43)	
C(4)–C(5)	1.521(6)	1.532	C(5)–F(5*x*)	1.347(4)	1.357
C(4)–C(7)	1.531(5)	1.539	C(5)–F(5*n*)	1.365(5)	1.373
C(5)–C(6)	1.571(5)	1.578	C(6)–F(6*x*)	1.341(5)	1.350
C(8)–O(1)	1.315(5)		C(6)–F(6*n*)	1.338(4)	1.347
C(8)–O(2)	1.196(4)		C(7)–F(7a)	1.350(4)	1.359
C(9)–O(1)	1.471(5)		C(7)–F(7b)	1.345(5)	1.354

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

C(1) · · · C(4)	2.293	F(2*n*) · · · F(6*n*)	2.552
C(2) · · · C(6)	2.523	F(3*x*) · · · F(7a)	2.765
C(3) · · · C(5)	2.476	F(5*x*) · · · F(6*x*)	2.531
C(2) · · · F(7a)	2.731	F(5*x*) · · · F(7b)	2.760
C(3) · · · F(7a)	2.770	F(5*n*) · · · F(6*n*)	2.526
C(5) · · · F(7b)	2.764	F(6*x*) · · · F(7b)	2.710
C(6) · · · F(7b)	2.765	O(2) · · · F(7a)	2.995
F(2*x*) · · · F(3*x*)	2.545	O(2) · · · F(7b)	3.018
F(2*x*) · · · F(7a)	2.674		

TABLE 2 (*Continued*)

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

C(2)–C(1)–C(6)	108.9(3)	C(5)–C(4)–C(7)	100.5(3)
C(2)–C(1)–C(7)	99.0(3)	C(5)–C(4)–H(4)	109.8(25)
C(2)–C(1)–C(8)	116.2(3)	C(7)–C(4)–H(4)	120.8(25)
C(6)–C(1)–C(7)	99.6(2)	C(4)–C(5)–C(6)	103.9(3)
C(6)–C(1)–C(8)	114.1(3)	C(4)–C(5)–F(5*x*)	111.9(3)
C(7)–C(1)–C(8)	116.9(3)	C(4)–C(5)–F(5*n*)	112.3(3)
C(1)–C(2)–C(3)	104.6(3)	C(6)–C(5)–F(5*x*)	110.7(3)
C(1)–C(2)–F(2*x*)	109.5(3)	C(6)–C(5)–F(5*n*)	110.6(3)
C(1)–C(2)–F(2*n*)	113.0(3)	F(5*x*)–C(5)–F(5*n*)	107.5(3)
C(3)–C(2)–F(2*x*)	112.1(3)	C(1)–C(6)–C(5)	103.3(3)
C(3)–C(2)–F(2*n*)	111.4(3)	C(1)–C(6)–F(6*x*)	109.8(3)
F(2*x*)–C(2)–F(2*n*)	106.3(3)	C(1)–C(6)–F(6*n*)	114.9(3)
C(2)–C(3)–C(4)	103.2(3)	C(5)–C(6)–F(6*x*)	111.1(3)
C(2)–C(3)–F(3*x*)	110.7(3)	C(5)–C(6)–F(6*n*)	110.8(3)
[C(2)–C(3)–F(3*n*)	110.6]	F(6*x*)–C(6)–F(6*n*)	106.9(3)
C(2)–C(3)–H(3*n*)	112.4	C(1)–C(7)–C(4)	96.8(3)
C(4)–C(3)–F(3*x*)	110.5(4)	C(1)–C(7)–F(7a)	112.7(3)
[C(4)–C(3)–F(3*n*)	106.9]	C(1)–C(7)–F(7b)	113.8(3)
C(4)–C(3)–H(3*n*)	113.7	C(4)–C(7)–F(7a)	112.7(3)
[F(3*x*)–C(3)–F(3*n*)	114.3]	C(4)–C(7)–F(7b)	113.9(3)
F(3*x*)–C(3)–H(3*n*)	106.5	F(7a)–C(7)–F(7b)	107.1(3)
[F(3*n*)–C(3)–H(3*n*)	8.4]	C(1)–C(8)–O(1)	110.3(3)
C(3)–C(4)–C(5)	108.2(3)	C(1)–C(8)–O(2)	122.7(4)
C(3)–C(4)–C(7)	101.5(3)	O(1)–C(8)–O(2)	127.0(3)
C(3)–C(4)–H(4)	114.6(26)	C(8)–O(1)–C(9)	116.6(3)

(*c*) Selected torsion angles (°); estimated standard deviations *ca.* 0.5°

C(1)–C(2)–C(3)–C(4)	2.2	F(3*x*)–C(3)–C(2)–C(1)	120.2
C(1)–C(6)–C(5)–C(4)	−0.3	F(3*x*)–C(3)–C(4)–C(5)	168.9
C(1)–C(7)–C(4)–C(3)	−54.6	F(3*x*)–C(3)–C(4)–C(7)	−85.4
C(1)–C(7)–C(4)–C(5)	56.5	F(5*x*)–C(5)–C(4)–C(3)	−169.1
C(2)–C(1)–C(6)–C(5)	−68.8	F(5*x*)–C(5)–C(4)–C(7)	85.0
C(2)–C(1)–C(7)–C(4)	55.3	F(5*x*)–C(5)–C(6)–C(1)	−120.3
C(2)–C(3)–C(4)–C(5)	−73.2	F(5*x*)–C(5)–C(6)–F(6*x*)	−2.8
C(2)–C(3)–C(4)–C(7)	32.5	F(5*n*)–C(5)–C(4)–C(3)	−48.0
C(3)–C(2)–C(1)–C(6)	67.4	F(5*n*)–C(5)–C(4)–C(7)	−153.8
C(3)–C(2)–C(1)–C(7)	−35.9	F(5*n*)–C(5)–C(6)–C(1)	120.5
C(3)–C(4)–C(5)–C(6)	71.3	F(5*n*)–C(5)–C(6)–F(6*n*)	−3.2
C(4)–C(5)–C(6)–C(7)	22.6	F(6*x*)–C(6)–C(5)–C(4)	117.1
C(4)–C(7)–C(1)–C(6)	−55.5	F(6*x*)–C(6)–C(1)–C(2)	173.0
C(5)–C(6)–C(1)–C(7)	34.7	F(6*x*)–C(6)–C(1)–C(7)	−83.5
C(6)–C(5)–C(4)–C(7)	−34.5	F(6*n*)–C(6)–C(5)–C(4)	−123.9
C(8)–C(1)–C(2)–C(3)	−161.9	F(6*n*)–C(6)–C(1)–C(2)	52.1
C(8)–C(1)–C(6)–C(5)	159.8	F(6*n*)–C(6)–C(1)–C(7)	155.6
C(8)–C(1)–C(7)–C(4)	−179.2	F(7a)–C(7)–C(1)–C(2)	−63.1
F(2*x*)–C(2)–C(1)–C(6)	−172.0	F(7a)–C(7)–C(1)–C(6)	−174.0
F(2*x*)–C(2)–C(1)–C(7)	84.7	F(7a)–C(7)–C(4)–C(3)	63.2
F(2*x*)–C(2)–C(3)–C(4)	−116.1	F(7a)–C(7)–C(4)–C(5)	174.3
F(2*x*)–C(2)–C(3)–F(3*x*)	1.9	F(7b)–C(7)–C(1)–C(2)	174.9
F(2*n*)–C(2)–C(1)–C(6)	−53.7	F(7b)–C(7)–C(1)–C(6)	64.1
F(2*n*)–C(2)–C(1)–C(7)	−157.0	F(7b)–C(7)–C(4)–C(3)	−174.8
F(2*n*)–C(2)–C(3)–C(4)	124.8	F(7b)–C(7)–C(4)–C(5)	−63.7

* Items in square brackets refer to the minor constituent with a fluorine atom in the 3*n* position.

The thermal parameters of the carbon atoms of the norbornane skeleton and the non-hydrogen atoms directly bonded to them were analysed in terms of rigid-body motion. The root-mean-square deviation between the observed U_{ij} values and those calculated on the basis of the rigid-body model is reasonably low [0.003 5 Å^2], and bond lengths corrected for thermal

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* That the minor constituent is compound (II) is also indicated by re-interpretation of the spectroscopic data.

motion are listed in Table 2, together with other details of molecular geometry.

The norbornane skeleton shows small but highly significant deviations from the ideal C_{2v} symmetry, due, presumably, to the unsymmetrical substitution. The twist angles C(2)–C(1) • • • C(4)–C(3) and C(6)–C(1) • • • C(4)–C(5), which are a measure [6] of the distortion of the system are 1.5 and −0.2°, compared with 0.2 and 0.1° in the symmetrically substituted 1,4-dibenzoyldecafluoronorbornane [1] (IV) and 0° in an undistorted norbornane. The greater degree of distortion of (III) is also apparent from the mean plane calculations.

In discussing the geometry of (IV) it was noted that the distances F(2*n*) • • • F(6*n*) and F(3*n*) • • • F(5*n*) are *ca.* 0.35 Å greater than the corresponding H • • • H distances in norbornane. The increase in the F • • • F separations is brought about by larger than ideal values for bond angles C(1)–C(2)–F(2*n*), C(4)–C(3)–F(3*n*), C(4)–C(5)–F(5*n*), and C(1)–C(6)–F(6*n*), and torsion angles C(4)–C(3)–C(2)–F(2*n*), C(1)–C(2)–C(3)–F(3*n*), C(1)–C(6)–C(5)–F(5*n*), and C(4)–C(5)–C(6)–F(6*n*). These angular distortions were attributed to repulsive interactions between the 2- and 6- and the 3- and 5-*endo*-fluoro-substituents. In the present structure these effects are observed with respect to F(2*n*) and F(6*n*), but not with respect to F(5*n*), probably because of the absence of a 3-*endo*-fluoro-substituent. The flap angle [the angle between the mean planes of atoms C(1)—(4) and C(1), C(4)—(6)] is 113.2°, only slightly larger than that found for norbornane (*cf.* Table 6 of ref. 1), so that the flattening of the norbornane skeleton of (IV), noted previously,[1] is virtually absent here.

The crystal structure is illustrated in Figure 2. None of the intermolecular contact distances is substantially shorter than the sum of the van der Waals radii of the atoms concerned.

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[6] C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1995.