Journal of Fluorine Chemistry, 16 (1980) 417–429

Received: April 25, 1980

THE CRYSTAL AND MOLECULAR STRUCTURE OF *EXO*-1,7-DICHLORO-8,8,9,9,10,10-HEXAFLUORO-3,4-BENZOTRICYCLO[5.3.0.$0^{2,6}$]DECENE-3

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SUMMARY

The crystal structure of the title molecule has been determined by single crystal X-ray diffraction method. The molecule crystallizes in the orthorhombic space group Pbca with unit-cell dimensions a = 21.872(8), b = 11.815(6), c = 10.785(6) Å, and Z = 8. The structure has been solved by MULTAN and refined by least-squares calculations to R = 7.62% for 2088 reflections measured by a diffractometer. The molecule has the *exo* configuration. The central cyclobutane ring is nearly planar. The two five-membered rings are of the envelope conformation. The dihedral angle between the cyclobutane ring and the terminal five-membered ring is 75.5° and that between the cyclobutane ring and the other five-membered ring is 62.2°.

INTRODUCTION

Although photo-cycloaddition reactions are well known and have been extensively employed in organic synthesis, the synthetic utility of the reactions is sometimes diminished by the lack of regioselectivity and stereoselectivity in additions of unsymmetrically substituted olefins. There has been general interest in factors controlling these selectivities. Photocycloaddition of fluoro-olefins has received much less attention than their unique thermal cycloadditions. However, the effect of fluorine recently has become of considerable interest in photochemistry in light of the fact that 5-fluorouracil has been reported to have superior regioselectivity compared with unsubstituted uracil in photo-cycloaddition with several olefins [1]. One of authers examined the photo-cycloaddition of indene to fluoro-olefins and previously reported [2] the acetophenone sensitized addition to cyclic fluoro-olefins in this journal. The title compound, *exo*-1,7-dichloro-8,8,9,9,10,10-hexafluoro-3,4-benzotricyclo[5.3.0.$0^{2,6}$]decene-3, was obtained from the reaction of indene with 1,2-dichlorohexafluorocyclopentene in 97% stereoselectivity. The reaction of indene with 1,2-dichlorotetrafluorocyclobutene or hexafluorocyclobutene showed complete stereoselectivity to give only *exo*-cycloadducts. In contrast, the reaction with chlorofluoroethylenes afforded the corresponding cycloadducts in good regioselectivity and poor stereoselectivity [3]. The configuration of the cycloadducts was estimated on the basis of NMR spectroscopy in the previous papers. Since the structual confirmation of the products should be required in order to discuss the stereochemistry of the reaction, we have made an X-ray investigation of the cycloadduct.

EXPERIMENTAL

Crystal data : $C_{14}H_8F_6Cl_2$, orthorhombic, a = 21.872(8), b = 11.815(6), c = 10.785(6)Å, U = 2787.0(20)$Å^3$, Dc = 1.72gcm^{-3}, Z = 8, space group Pbca, μ(MoKα) = 5.35cm^{-1}, λ(MoKα) = 0.7107Å. Laue symmetry, space group extinctions, and approximate unit-cell dimensions were obtained from Weissenberg photographs. The unit-cell dimensions were refined by the least-squares analysis of 31 θ values automatically centered on a Philips PW1100 diffractometer by the use of MoKα radiation. The intensity data were collected on the diffractometer using graphite monochromated MoKα radiation. The ω-2θ scan method was used. The specimen employed for the data collection had dimensions of 0.53 x 0.45 x 0.38mm. A scan speed of 2°/min in ω and a scan width of $(0.8 + 0.2\tan\theta)^\circ$ were chosen. The background was counted for 10 s at each side of the scan range. A total of 2088 independent reflections with $I > 2\sigma(I)$ were collected and used for the structure analysis. During the data collection, the intensities of 3 standard reflections were monitored every 3 h in order to check the orientation and stability of the crystal. No appreciable decay was observed. The observed intensities were corrected for Lorentz-polarization effects [4] but not for absorption.

Structure determination and refinement

The structure was solved by the use of MULTAN [5] and refined by a block-diagonal least-squares method using anisotropic temperature factors for all the nonhydrogen atoms. The agreement indices R and Rw(= $\Sigma w\Delta F/\Sigma wFo$) were 9.15 and 9.15%. The difference Fourier synthesis computed at this stage clearly showed the positions of all H atoms. Further refinement including all the H atoms resulted in convergence at R = 7.62 and Rw = 7.75%. The function minimized was $\Sigma w(Fo-|Fc|)^2$ and a weighting scheme of $w = (99.0/Fo)^2$ for $Fo > 99.0$ and $w = 1$ for $Fo \leq 99.0$ was used. All the parameter shifts in the final refinement were less than 0.4σ. The atomic scattering factors were taken from ref.[6]. The final difference Fourier map showed no peaks of structural significance. The final atomic coordinates and temperature factors are listed in Table 1. A complete list of the observed and calculated structure factors is preserved by the publisher.

The computer programs used in the calculations were the local version of UNICS [7]. All calculations were performed on a FACOM 230-60 computer at Osaka City University.

RESULTS AND DISCUSSION

A perspective view of the molecule is depicted in Fig. 1. The bond distances and angles are given in Table 2. The deviations of the atoms from least-squares planes, and inter-

TABLE 1

Atomic positional parameters (x 10^4) for nonhydrogen atoms

Atom	x	y	z
Cl(1)	6117.1(7)	7244.3(12)	2136.5(16)
Cl(2)	6124.8(9)	9085.9(16)	4326.8(16)
F(1)	7335.9(15)	9457.8(36)	3559.8(38)
F(2)	6981.3(17)	11126.5(40)	3171.1(41)
F(3)	7803.0(15)	9899.3(38)	1407.7(43)
F(4)	6967.6(16)	10689.6(33)	751.6(38)
F(5)	7306.9(15)	7912.3(32)	1529.7(44)
F(6)	6883.7(17)	8601.1(40)	- 123.3(36)
C(1)	6293(2)	8654(4)	1759(5)
C(2)	5792(2)	9370(5)	1090(5)
C(3)	5147(2)	8931(5)	1173(6)
C(4)	4821(2)	9486(5)	2075(5)
C(5)	5189(3)	10404(5)	2698(7)
C(6)	5834(2)	10271(5)	2139(6)
C(7)	6310(3)	9537(5)	2832(5)
C(8)	6963(2)	10040(5)	2809(6)
C(9)	7193(2)	9874(5)	1488(6)
C(10)	6924(2)	8712(5)	1107(6)
C(11)	4875(3)	8096(5)	441(6)
C(12)	4260(3)	7839(6)	667(7)
C(13)	3941(3)	8392(6)	1570(8)
C(14)	4208(3)	9214(6)	2296(8)

Positional parameters (x 10^3) and isotropic temperature factors for hydrogen atoms

Atom	x	y	z	B
H(1)	592(3)	957(5)	24(5)	2.0(13)
H(2)	600(2)	1103(4)	182(5)	1.0(11)
H(3)	509(3)	776(5)	- 28(6)	2.8(15)
H(4)	414(3)	728(6)	6(7)	4.1(17)
H(5)	356(2)	817(5)	168(5)	1.5(12)
H(6)	398(4)	959(7)	292(7)	6.1(22)
H(7)	519(2)	1032(4)	366(5)	1.1(11)
H(8)	504(4)	1121(6)	257(8)	5.7(20)

Isotropic temperature factors in the form of : $\exp[-B(\sin\theta/\lambda)^2]$

(continued on facing page)

TABLE 1 *(cont.)*

Anisotropic thermal parameters (x 10^5) for nonhydrogen atoms

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	218(3)	523(9)	1221(17)	- 15(10)	- 119(14)	106(22)
Cl(2)	343(5)	1055(16)	823(14)	- 127(16)	117(15)	100(27)
F(1)	213(9)	1278(42)	1291(41)	131(31)	- 429(33)	87(76)
F(2)	254(9)	793(31)	1709(54)	- 201(29)	- 155(38)	- 600(70)
F(3)	142(7)	1324(43)	1771(45)	- 130(30)	64(35)	124(86)
F(4)	227(9)	968(35)	1343(45)	- 169(30)	49(34)	741(68)
F(5)	175(8)	903(34)	2083(61)	273(27)	65(37)	- 200(80)
F(6)	239(9)	1549(47)	990(39)	- 186(36)	249(34)	- 572(75)
C(1)	138(11)	458(35)	872(55)	- 55(33)	4(40)	155(77)
C(2)	120(10)	605(42)	773(51)	- 11(34)	- 25(39)	25(79)
C(3)	138(11)	569(41)	942(58)	- 6(36)	- 201(44)	221(85)
C(4)	156(11)	585(42)	1112(67)	161(37)	54(48)	398(93)
C(5)	160(13)	790(52)	1451(84)	153(43)	63(56)	- 484(117)
C(6)	140(11)	540(40)	1156(67)	6(36)	- 17(47)	- 204(91)
C(7)	173(12)	648(43)	758(54)	49(38)	93(44)	- 127(84)
C(8)	154(12)	724(47)	1135(69)	- 42(41)	- 177(50)	- 173(99)
C(9)	104(10)	881(54)	1178(69)	- 125(40)	54(46)	214(107)
C(10)	137(11)	777(49)	1003(62)	61(40)	73(47)	- 146(97)
C(11)	209(14)	705(50)	1063(70)	- 21(45)	- 256(53)	102(99)
C(12)	203(14)	712(53)	1550(88)	- 116(45)	- 303(62)	158(119)
C(13)	136(13)	913(60)	2079(112)	- 166(45)	- 176(64)	752(141)
C(14)	162(13)	937(60)	1672(96)	47(49)	104(61)	132(134)

Anisotropic thermal parameters in the form of : $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

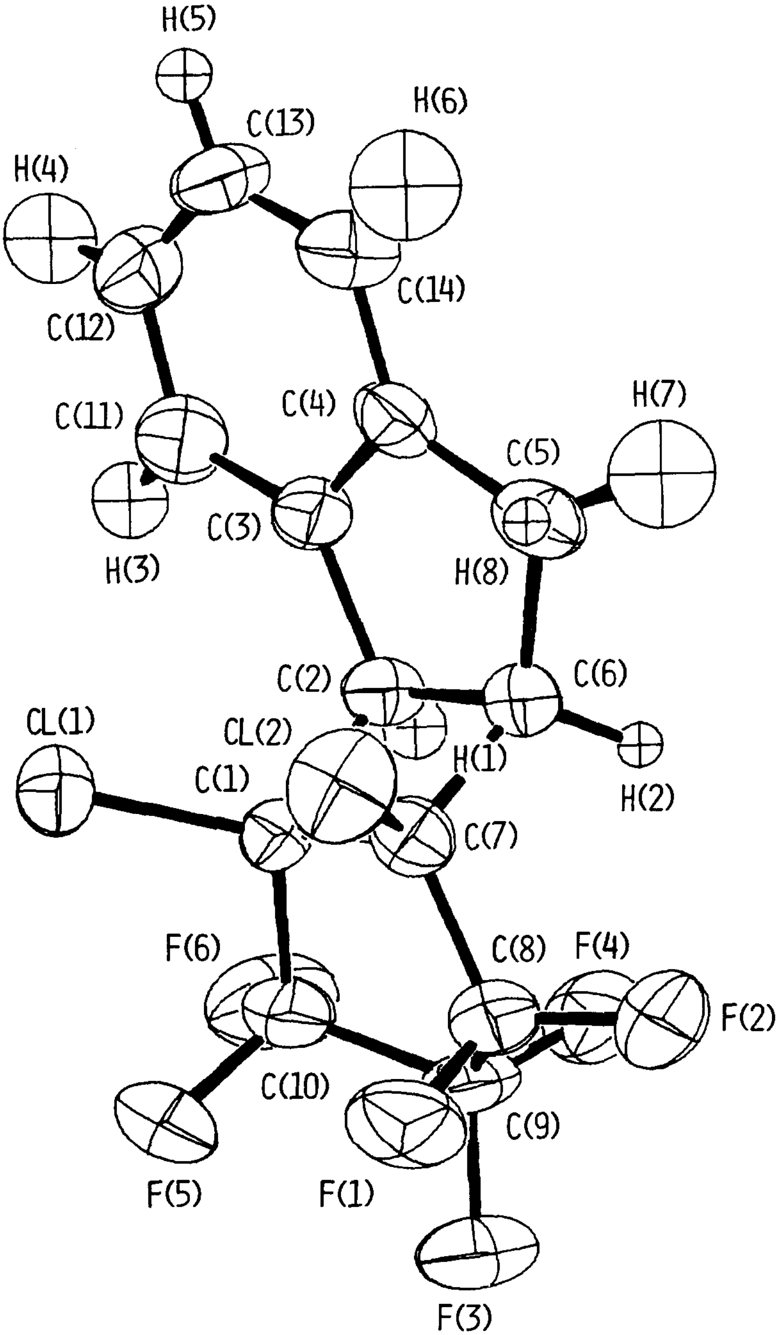


Fig. 1 A perspective view of the molecule.
Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

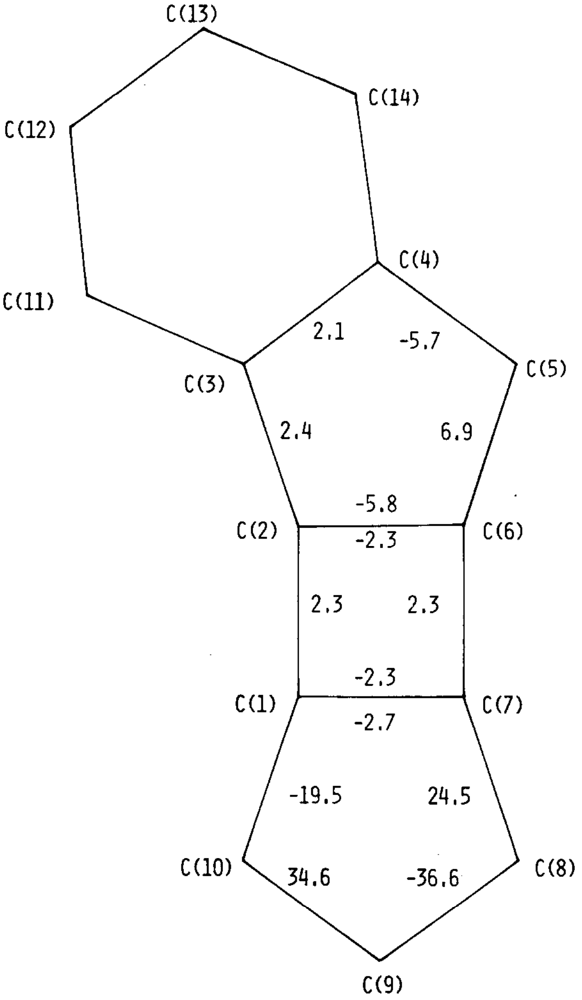
TABLE 2 Bond distances (Å) and bond angles (deg.)

C(1) - C(2)	1.561(7)	C(1) - C(2) - C(6)	89.6(4)
C(1) - C(7)	1.558(8)	C(2) - C(6) - C(7)	90.4(4)
C(2) - C(6)	1.556(8)	C(6) - C(7) - C(1)	90.0(4)
C(6) - C(7)	1.547(8)	C(2) - C(1) - C(7)	89.8(4)
C(7) - C(8)	1.547(8)	C(2) - C(3) - C(4)	111.4(5)
C(8) - C(9)	1.524(9)	C(3) - C(4) - C(5)	112.5(5)
C(9) - C(10)	1.549(9)	C(4) - C(5) - C(6)	103.9(5)
C(10) - C(1)	1.549(8)	C(5) - C(6) - C(2)	107.5(4)
C(2) - C(3)	1.506(7)	C(6) - C(2) - C(3)	104.3(4)
C(3) - C(4)	1.372(8)	C(1) - C(7) - C(8)	105.5(4)
C(4) - C(5)	1.509(9)	C(7) - C(8) - C(9)	105.7(5)
C(5) - C(6)	1.541(8)	C(8) - C(9) - C(10)	103.7(5)
C(3) - C(11)	1.396(8)	C(9) - C(10) - C(1)	104.9(5)
C(11) - C(12)	1.401(9)	C(10) - C(1) - C(7)	106.7(4)
C(12) - C(13)	1.365(11)	C(3) - C(11) - C(12)	117.6(6)
C(13) - C(14)	1.377(11)	C(11) - C(12) - C(13)	120.8(6)
C(4) - C(14)	1.399(8)	C(12) - C(13) - C(14)	121.7(6)
C(1) - Cl(1)	1.757(5)	C(13) - C(14) - C(4)	118.2(6)
C(7) - Cl(2)	1.745(6)	C(14) - C(4) - C(3)	120.5(6)
C(8) - F(2)	1.343(7)	C(4) - C(3) - C(11)	121.2(5)
C(8) - F(1)	1.339(7)	C(2) - C(1) - Cl(1)	117.8(4)
C(9) - F(4)	1.343(7)	C(10) - C(1) - Cl(1)	110.0(4)
C(9) - F(3)	1.337(6)	C(6) - C(7) - Cl(2)	117.5(4)
C(10) - F(6)	1.336(7)	C(8) - C(7) - Cl(2)	110.2(4)
C(10) - F(5)	1.343(7)	C(1) - C(10) - F(6)	112.8(5)
C(2) - H(1)	0.98(6)	C(1) - C(10) - F(5)	111.7(5)
C(6) - H(2)	1.03(5)	C(9) - C(10) - F(6)	112.1(5)
C(11) - H(3)	0.99(6)	C(9) - C(10) - F(5)	107.2(4)
C(12) - H(4)	0.97(7)	F(6) - C(10) - F(5)	108.0(5)
C(13) - H(5)	0.87(5)	C(8) - C(9) - F(4)	109.9(5)
C(14) - H(6)	0.95(8)	C(8) - C(9) - F(3)	112.7(5)
C(5) - H(7)	1.04(5)	C(10) - C(9) - F(4)	109.9(5)
C(5) - H(8)	1.02(8)	C(10) - C(9) - F(3)	112.5(5)
		F(4) - C(9) - F(3)	108.2(5)
		C(7) - C(8) - F(2)	112.9(5)
		C(7) - C(8) - F(1)	110.8(5)
		C(9) - C(8) - F(2)	112.6(5)
		C(9) - C(8) - F(1)	107.4(5)
		F(2) - C(8) - F(1)	107.3(5)

planar angles are listed in Table 3. Torsion angles are given in Fig. 2. It is confirmed that the molecule is of the *exo* form. The dihedral angle between the central cyclobutane ring and the terminal five-membered ring is 75.5° and that between the cyclobutane ring and the other five-membered ring is 62.2°. The cyclobutane ring is nearly planar with all torsion angles smaller than ± 2.3°, typical of fused cyclobutanes. These torsion angles, however, suggest a small distorsion toward a puckered conformation. The average C-C bond length of 1.556(8)Å is slightly longer than the accepted $C(cp^3)$–$C(sp^3)$ bond length (1.537Å), but similar values are found in ref.[8]. The bond angles in the cyclobutane ring are close to 90° in accordance with the planarity of the ring. The terminal five-membered ring is of the envelope conformation, with the C(9) atom deviating 0.55Å from the [C(1), C(7), C(8), C(10)] plane. The [C(8), C(9), C(10)] plane is folded by 35.8° toward the H(1) and H(2) atoms from the [C(1), C(7), C(8), C(10)] plane. The Cl(1), C(1), C(7), Cl(2) torsion angle is - 2.4°. The average value of C-F bond distance is 1.340(7)Å and that of the F-C-F angle is 107.8(5)°. The other five-membered ring is also of the envelope conformation, with the C(6) atom deviating 0.11Å from the [C(2), C(3), C(4), C(5)] plane to the Cl(2) atom. The [C(2), C(3), C(4), C(5)] and [C(2), C(5), C(6)] planes make an angle of 6.6°. The H(1), C(2), C(6), H(2) torsion angle is - 0.2°. The bond distances and bond angles in the phenyl ring are normal.

The arrangement of the molecule in the crystal is shown in Fig. 3. All contacts are of the van der Waals type and intermolecular contacts appear to be normal. Short intermolecular distances are as follows :
Cl(1) (I) – H(8) (II) = 2.83Å, H(5) (I) – F(2) (II) = 2.70Å,
H(6) (I) – F(3) (III) = 2.71Å, F(4) (I) – F(1) (IV) = 2.82Å,
H(4) (I) – H(2) (V) = 2.87Å, H(3) (I) – H(8) (V) = 2.77Å;
Roman numerals refer to the following equivalent positions;
(I) x,y,z (II) 1-x, - 1/2 + y, 1/2 - z (III) - 1/2 + x, y, 1/2 - z (IV) 3/2 - x, 2 - y, - 1/2 + z (V) 1-x, 2-y, - z.

As previously reported [2], the two stereoisomers were obtained in the ratio of 97 : 3 from the addition of indene to



Other torsion angles (deg.)

Cl(1) - C(1) - C(7) - Cl(2)	- 2.4°
H(1) - C(2) - C(6) - H(2)	- 0.2°
H(2) - C(6) - C(5) - H(8)	5.2°
H(2) - C(6) - C(5) - H(7)	- 108.1°

Fig. 2 Torsion angles

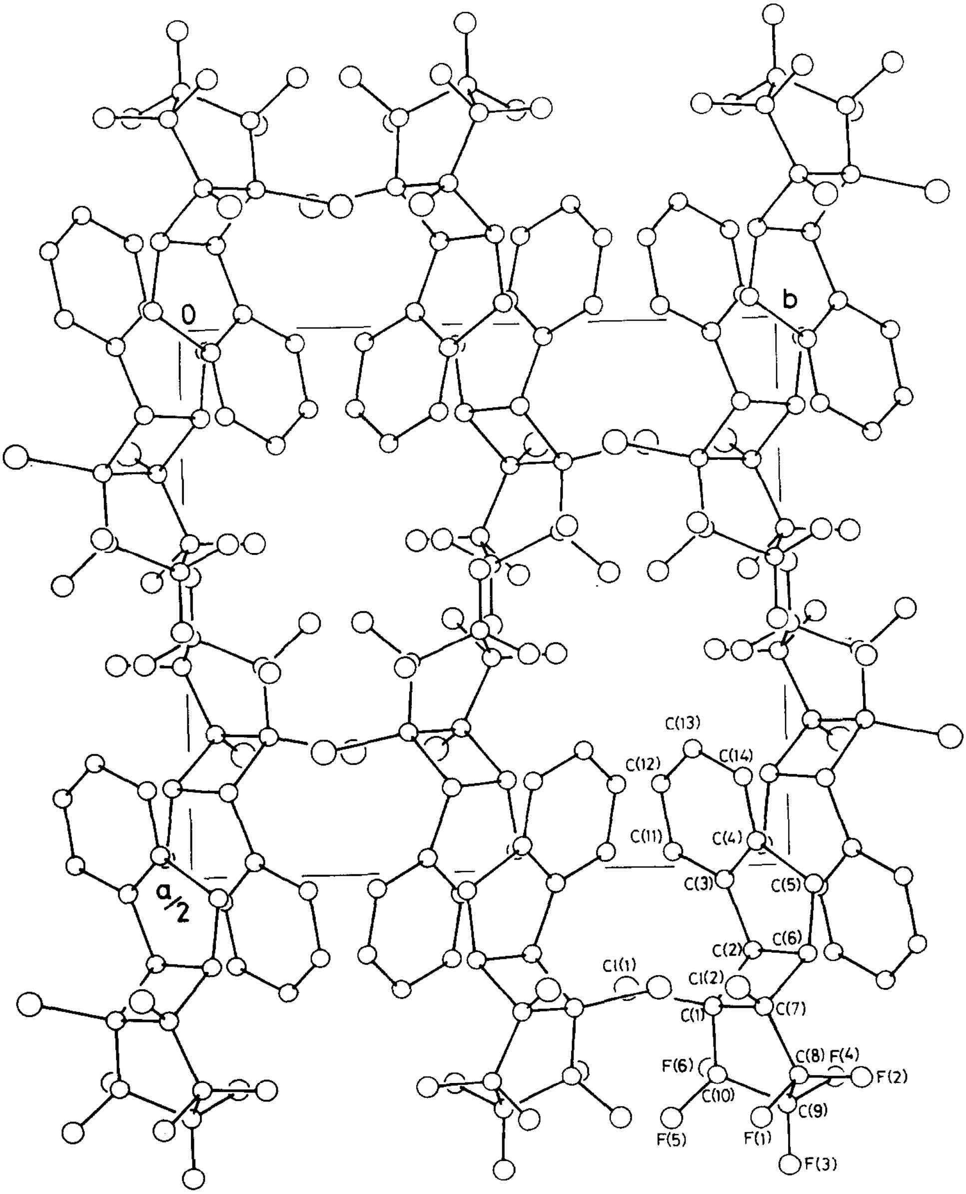


Fig. 3 The crystal structure viewed down the C axis

TABLE 3

Deviations (Å) of atoms from least squares planes and interplanar angles

plane(1) [C(1), C(2), C(6), C(7)]
C(1) 0.016, C(2) - 0.016, C(6) 0.016, C(7) - 0.016

plane(2) [C(1), C(7), C(8), C(9), C(10)]
C(1) - 0.053, C(7) - 0.083, C(8) 0.196, C(9) - 0.232, C(10) 0.171

plane(3) [C(2), C(3), C(4), C(5), C(6)]
C(2) - 0.028, C(3) 0.003, C(4) 0.024, C(5) - 0.040, C(6) 0.041

plane(4) [C(1), C(7), C(8), C(10)]
C(1) 0.016, C(7) - 0.016, C(8) 0.010, C(10) - 0.010

plane(5) [C(8), C(9), C(10)]

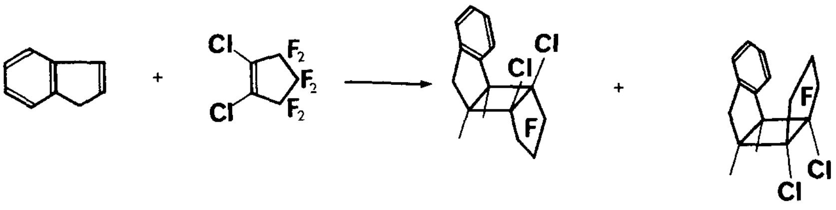
plane(6) [C(2), C(3), C(4), C(5)]
C(2) 0.006, C(3) - 0.011, C(4) 0.011, C(5) - 0.006

plane(7) [C(2), C(5), C(6)]

plane(8) [C(3), C(4), C(11), C(12), C(13), C(14)]
C(3) 0.003, C(4) - 0.005 C(11) 0.000, C(12) 0.000, C(13) - 0.002,
C(14) 0.004

plane(1) - plane(2)	75.5°
plane(1) - plane(3)	62.2°
plane(1) - plane(4)	65.8°
plane(1) - plane(7)	58.2°
plane(4) - plane(5)	35.8°
plane(6) - plane(7)	6.6°
plane(6) - plane(8)	2.6°
plane(3) - plane(8)	1.3°

1,2-dichlorohexafluorocyclopentene. The configuration of the predominant isomer was confirmed to be the *exo* form by this



exo : *endo*
97 : 3

work. From the similarity of the structural assignment on the basis of the NMR spectroscopy, the estimated configuration of other cycloadducts obtained from 1,2-dichlorotetrafluorocyclobutene and hexafluorocyclobutene should be correct. The acetophenone photosensitized addition of indene to the cyclic fluoro-olefins predominantly affords *cis-anti-cis*-2+2-cycloadducts. The triplet photosensitized cycloaddition is explained to proceed *via* biradical intermediates [9] which lead to the cycloadducts by intramolecular coupling. The cyclization of the intermediates would predominantly occur in sterically favorable fashion to give *cis-anti-cis*-2+2-cycloadducts.

Sket and Zupan have reported the photo-cycloaddition of hexafluorobenzene [10]. In contrast with our result, the irradiation (253.7nm) of a cyclohexane solution of indene and hexafluorobenzene without any sensitizer gave *cis-syn-cis*-2+2-cycloadduct exclusively. The stereochemistry of the photo-cycloaddition seems to depend on whether excitation is direct or photosensitized. The photosensitized cycloadditions can be expected to provide a method that might be complementary to the direct photo-cycloaddition with regard to the stereoisomers that can be prepared. We are now trying the direct photo-cycloaddition of indene to 1,2-dichlorohexafluorocyclopentene and the photosensitized addition of indene to hexafluorobenzene.

NMR is a very powerful tool for configurational assignment and the relation between the vicinal H-F coupling constants and their configurations on four-membered ring has been known. However, when the cyclobutane molecules are statically planar or in dynamic equilibrium between nonplanar conformations, the vicinal H-F coupling constants are averaged to become nearly equal having intermediate magnitudes [11]. The values of vicinal H-F coupling constants of the cycloadduct obtained from the addition of indene to hexafluorocyclobutene were 5.9Hz and 7.1Hz [2]. These are in accord with the planarity of the central cyclobutane ring. In this case, no configurational information was obtained from the vicinal H-F coupling constants The NMR spectroscopy alone is sometimes insufficient to establish the structure of the fused polycyclic compounds involving planar four-membered ring formed by the photo-cycloaddition of the cyclic fluoro-olefins.

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