Crystal and Molecular Structure of 2a,3,4,5,6,7,8,8b-Octafluoro-2-methyl-2-(2-methylprop-1-enyl)-1,2,2a,8b-tetrahydrocyclobuta[*a*]napthalene

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The title compound (3) is monoclinic, space group $P2_1/c$, a = 12.006(10), b = 28.532(20), c = 8.993(10) Å, β = 90.10(10)°, Z = 8. The structure was solved from diffractometer data by direct methods and refined to R 0.07 for 2 399 observed reflexions. The two independent molecules in the asymmetric unit exhibit no major structural differences. There is evidence for stacking of aromatic rings.

THE formation of excited molecular complexes (exciplexes) is increasingly being recognized to be a ubiquitous phenomenon that may play a paramount role in many photochemical and photobiological processes.[1] We had earlier suggested that arene–diene exciplexes are intermediates in the photochemical addition of dienes to arenes [2] and that thereby the structures of the arene–diene adducts reflect the configuration of the intermediate arene–diene exciplexes. Detailed product analysis would thus provide information on the structure of the intermediate exciplexes which may hardly be obtained by conventional spectroscopic methods.

Photolysis of perfluoronaphthalene (1) in the presence of 2,4-dimethylpenta-1,3-diene in cyclohexane solution had been found [2d] to yield two addition products, (2) and (3) in equal amounts, whose structures had been assigned on the basis of ^{1}H and ^{19}F n.m.r. data. We present here *X*-ray data for compound (3) which confirm the earlier suggested structure as that expected for an exciplex product where maximum overlap [3] between the two π systems occurs.

EXPERIMENTAL

Crystal Data.—$C_{17}H_{12}F_8$, M = 368.27. Monoclinic, a = 12.006(10), b = 28.532(20), c = 8.993(10) Å, β = 90.10(10)°, U = 3 081(1) Å^3, D_m = 1.588 g cm^{-3}, Z = 8. Space group $P2_1/c$ from systematic absences: $0k0$, k odd, and $h0l$, l odd. Cu-K_α radiation, λ = 1.541 8 Å; μ(Cu-K_α) = 13.1 cm^{-1}.

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[1] J. B. Birks, ' Photophysics of Aromatic Molecules,' Wiley–Interscience, London, 1970; M. Gordon and W. R. Ware, ' The Exciplex,' Academic Press, New York, 1975.

[2] (*a*) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, 1972, **94**, 1405; (*b*) N. C. Yang, J. Libman, and M. Savitzky, *ibid.*, p. 9226; (*c*) N. C. Yang and J. Libman, *Tetrahedron Letters*, 1973, 1409; (*d*) J. Libman, *J.C.S. Chem. Comm.*, 1976, 361.

[3] J. N. Murrell and J. Tanaka, *Mol. Phys.*, 1964, **7**, 363.

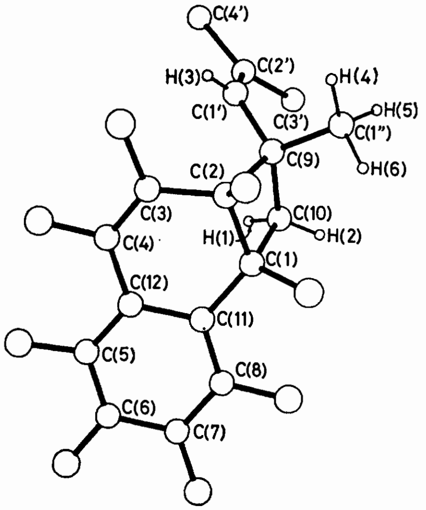

FIGURE 1 Perspective view of molecule (A), showing the atom numbering scheme [H atoms on C(3') and C(4') were not located]. Fluorine atoms are numbered according to the carbon atom to which they are attached

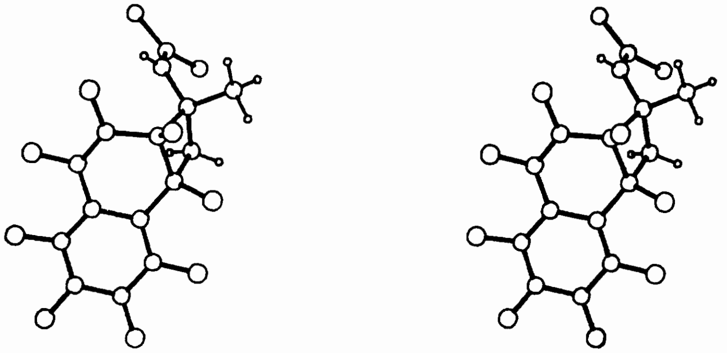

FIGURE 2 Stereoview of molecule (A)

Plate-like colourless crystals were obtained from dichloromethane–methanol.

Systematic absences determined from photographs were misleading since reflexions *hk*0, *h* odd, appeared to be absent. Intensities were measured on an automated Syntex $P2_1$ diffractometer with graphite-monochromated Cu-K_α radiation, for a crystal of dimensions *ca.* 0.4 × 0.2 × 0.04 mm. The diffractometer data showed that some *hk*0 reflexions with *h* odd were weak but present, thus establishing the space group. 3 872 reflexions were collected in the range $0 < 2\theta < 116°$; averaging equivalent reflexions (Lp but no absorption corrections being applied) gave 2 400 unique reflexions with $F > 4\sigma(F)$. The intensity of one check reflexion repeatedly monitored during data collection fell by 30%. The intensities of other reflexions were scaled accordingly. Cell dimensions were obtained by least squares from 15 strong reflexions.

Multisolution Σ_2 sign expansion using the program SHELX was unsuccessful because of the uneven parity group distribution of strong *E* values (very few for odd *l*). The program XCSD (incorporating a pseudotangent refinement to select the starting set [4] and the negative quartet test NQEST [5]) was then used with six odd *l* reflexions forced into the starting set. The best *E* map established positions for 49 of the 50 heavy atoms, only one small peak in the top 50 being incorrect. Figures-of-merit for this solution were NQEST −0.423, R_A (a point-atom *R* factor based on observed peaks) 0.329, R_α (ref. 4) 0.117 (*cf.* the second *E* map, which was also substantially correct; NQEST −0.271, R_A 0.425, R_α 0.237). A difference map showed the remaining heavy-atom position. Isotropic least-squares refinement gave *R* 0.21; large difference peaks near the F atoms suggested considerable thermal motion. Anisotropic refinement (to *R* 0.089), followed by a difference synthesis, gave sites for all hydrogen atoms except methyl hydrogens bonded to sp^2 carbon atoms. These groups presumably exhibit rotational disorder. At this stage the reflexion 020 was omitted as being clearly in error $[F_o - F_c > 30\sigma(F)]$. In the final cycles of refinement, non-methyl hydrogens were allowed to refine freely, the disordered methyl hydrogens were omitted, and the other methyl groups were refined as rigid groups with C–H 1.05 Å, H–C–H 109.5°; separate overall isotropic temperature factors were employed for methyl and non-methyl hydrogens respectively. Convergence was achieved at *R* 0.0697. The corresponding *R'* $[= \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|]$ was

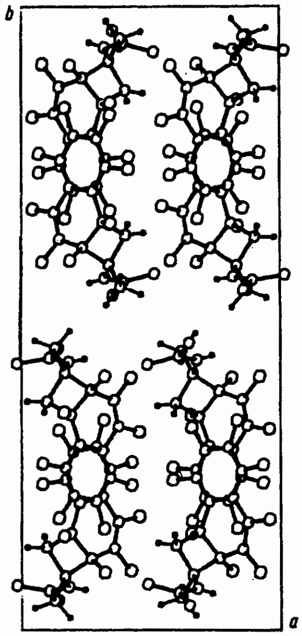

FIGURE 3 Packing diagram: unit cell contents projected down *z*

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[4] P. J. Roberts, R. C. Pettersen, G. M. Sheldrick, N. W. Isaacs, and O. Kennard, *J.C.S. Perkin II*, 1973, 1978.

[5] G. T. de Titta, J. W. Edmonds, D. A. Langs, and H. Hauptman, *Acta Cryst.*, 1975, **A31**, 472.

0.0704, with the weighting scheme $w = 1/[\sigma^2(F) + 0.0005F^2]$. Complex neutral-atom scattering factors were employed. Final atomic co-ordinates and thermal parameters are given in Table 1, and derived interatomic distances and angles in Tables 2 and 3. Diagrams of the structure are given in Figures 1—3. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22089 (24 pp., 1 microfiche).*

TABLE 1

Atom co-ordinates ($\times 10^4$)

Molecule (A)	*x/a*	*y/b*	*z/c*
C(1)	6 875(5)	3 432(2)	1 713(6)
C(2)	7 640(4)	3 851(2)	2 067(6)
C(3)	8 540(5)	3 712(3)	3 111(7)
C(4)	8 733(5)	3 285(3)	3 564(7)
C(5)	8 487(5)	2 453(3)	3 395(7)
C(6)	7 993(6)	2 063(3)	2 803(8)
C(7)	7 087(6)	2 117(3)	1 830(8)
C(8)	6 748(5)	2 562(2)	1 493(6)
C(9)	6 621(4)	4 123(2)	2 692(6)
C(10)	5 979(5)	3 652(2)	2 684(7)
C(11)	7 255(4)	2 949(2)	2 044(6)
C(12)	8 164(5)	2 885(3)	3 030(7)
C(1′)	6 795(5)	4 343(2)	4 210(7)
C(2′)	6 084(5)	4 407(2)	5 315(7)
C(3′)	4 874(5)	4 272(2)	5 220(7)
C(1″)	6 179(5)	4 483(2)	1 593(7)
C(4′)	6 479(6)	4 615(3)	6 809(7)
F(1)	6 562(3)	3 461(1)	214(3)
F(2)	8 130(3)	4 060(1)	831(4)
F(3)	9 193(3)	4 082(2)	3 533(4)
F(4)	9 567(3)	3 233(2)	4 553(4)
F(5)	9 334(3)	2 351(2)	4 337(4)
F(6)	8 328(4)	1 623(2)	3 105(5)
F(7)	6 578(4)	1 739(1)	1 252(5)
F(8)	5 859(3)	2 601(1)	594(4)
H(1)	5 902(36)	3 482(17)	3 724(57)
H(2)	5 276(41)	3 614(17)	2 267(52)
H(3)	7 369(34)	4 419(15)	4 374(45)
H(6)	6 176	4 318	549
H(4)	6 723	4 771	1 569
H(5)	5 371	4 598	1 846
Molecule (B)			
C(1)	8 080(4)	6 536(2)	−870(6)
C(2)	7 312(4)	6 133(2)	−423(6)
C(3)	6 418(5)	6 293(3)	597(7)
C(4)	6 244(5)	6 722(3)	985(7)
C(5)	6 570(5)	7 574(3)	687(7)
C(6)	7 108(7)	7 939(3)	55(9)
C(7)	7 988(7)	7 852(3)	−861(9)
C(8)	8 299(5)	7 401(3)	−1176(6)
C(9)	8 313(5)	5 854(2)	242(6)
C(10)	9 008(5)	6 314(2)	68(7)
C(11)	7 746(4)	7 026(2)	−585(6)
C(12)	6 861(5)	7 125(3)	393(6)
C(1′)	8 169(4)	5 682(2)	1 804(7)
C(2′)	8 912(5)	5 620(2)	2 850(7)
C(3′)	10 159(5)	5 708(2)	2 641(7)
C(1″)	8 582(5)	5 469(3)	4 432(7)
C(4′)	8 697(6)	5 463(2)	−794(7)
F(1)	8 339(3)	6 492(1)	−2 376(3)
F(2)	6 776(3)	5 912(1)	−1 605(4)
F(3)	5 758(3)	5 940(1)	1 114(4)
F(4)	5 433(3)	6 812(2)	1 979(4)
F(5)	5 726(3)	7 687(2)	1 628(5)
F(6)	6 797(4)	8 383(1)	306(5)
F(7)	8 550(4)	8 214(2)	−1 495(5)
F(8)	9 176(3)	7 332(1)	−2 062(4)
H(1′)	9 767(40)	6 312(17)	−491(50)
H(2′)	9 102(38)	6 487(18)	944(55)
H(3′)	7 557(34)	5 634(15)	1 938(46)
H(6)	8 756	5 586	−1 891
H(4)	8 118	5 188	−747
H(5)	9 480	5 342	−441

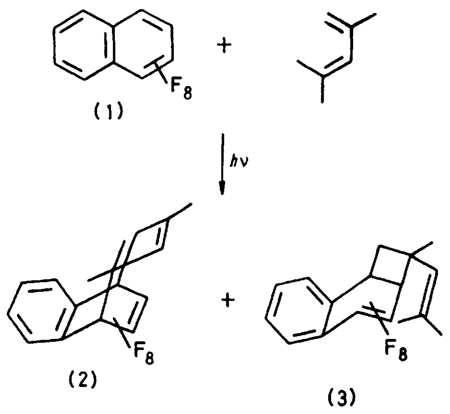
TABLE 2

Bond lengths (Å)

	Molecule (A)	Molecule (B)
C(8)–C(7)	1.366(11)	1.369(12)
C(8)–C(11)	1.355(10)	1.368(10)
C(7)–C(6)	1.403(11)	1.363(12)
C(6)–C(5)	1.369(11)	1.351(11)
C(5)–C(12)	1.332(12)	1.354(11)
C(12)–C(4)	1.415(12)	1.468(11)
C(12)–C(11)	1.416(9)	1.409(9)
C(4)–C(3)	1.305(13)	1.289(13)
C(3)–C(2)	1.484(9)	1.485(9)
C(2)–C(1)	1.541(10)	1.528(10)
C(2)–C(9)	1.555(10)	1.561(10)
C(1)–C(11)	1.483(9)	1.477(9)
C(1)–C(10)	1.522(10)	1.532(10)
C(10)–C(9)	1.548(10)	1.565(11)
C(9)–C(1′)	1.517(10)	1.498(9)
C(9)–C(1″)	1.520(11)	1.524(11)
C(1′)–C(2′)	1.324(9)	1.307(9)
C(2′)–C(3′)	1.505(10)	1.530(10)
C(2′)–C(4′)	1.543(11)	1.538(11)
C(1)–F(1)	1.401(7)	1.395(7)
C(2)–F(2)	1.392(7)	1.392(7)
C(3)–F(3)	1.369(9)	1.365(9)
C(4)–F(4)	1.346(8)	1.347(8)
C(5)–F(5)	1.354(8)	1.360(8)
C(6)–F(6)	1.346(9)	1.343(9)
C(7)–F(7)	1.345(9)	1.359(10)
C(8)–F(8)	1.343(8)	1.336(8)
C(10)–H(1)	1.06(6)	1.04(5)
C(10)–H(2)	0.93(5)	0.94(5)
C(1′)–H(3)	0.74(4)	0.76(4)

DISCUSSION

The two independent molecules forming the asymmetric unit are structurally very similar. (For this reason only one molecule is illustrated in Figures 1 and 2.) Only three pairs of bond lengths are significantly different on the basis of differing by more than the sum of their standard deviations; these are C(7)–C(6), C(2′)–C(3′), and C(12)–C(4). There are several bond-angle differences of *ca.* 2° (typical standard deviations ±0.7°) but none greater than 2.8°; most of these differences involve C–C–F angles. The fluorine atoms display high temperature factors.



Torsion angles around the three rings are shown in Table 4; there are no differences greater than 2.7°. The four-membered ring is appreciably flatter in molecule

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

(B). The strain caused by this ring is presumably responsible for deviation from ideal torsion angles in the central ring.

TABLE 3

Bond angles (°)

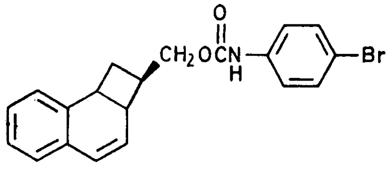
	Molecule (A)	Molecule (B)
C(7)–C(8)–C(11)	122.8(7)	121.5(7)
C(7)–C(8)–F(8)	116.7(7)	118.5(7)
C(11)–C(8)–F(8)	120.5(7)	120.0(7)
C(8)–C(7)–C(6)	118.1(7)	120.5(8)
C(8)–C(7)–F(7)	121.6(7)	119.4(8)
C(6)–C(7)–F(7)	120.3(7)	120.1(8)
C(7)–C(6)–C(5)	119.2(8)	119.1(8)
C(7)–C(6)–F(6)	117.3(7)	119.4(8)
C(5)–C(6)–F(6)	123.5(7)	121.6(8)
C(6)–C(5)–C(12)	122.0(7)	121.6(7)
C(6)–C(5)–F(5)	113.1(8)	115.9(7)
C(12)–C(5)–F(5)	124.9(8)	122.5(7)
C(5)–C(12)–C(4)	121.4(7)	122.7(7)
C(5)–C(12)–C(11)	119.8(7)	120.4(7)
C(4)–C(12)–C(11)	118.7(7)	116.8(7)
C(12)–C(4)–C(3)	124.1(7)	124.2(7)
C(12)–C(4)–F(4)	119.6(8)	117.2(8)
C(3)–C(4)–F(4)	116.2(8)	118.6(8)
C(4)–C(3)–C(2)	125.3(8)	125.2(7)
C(4)–C(3)–F(3)	122.2(7)	121.0(7)
C(2)–C(3)–F(3)	112.5(7)	113.8(7)
C(3)–C(2)–C(1)	110.8(6)	111.6(6)
C(3)–C(2)–C(9)	118.5(6)	118.5(6)
C(1)–C(2)–C(9)	89.6(5)	91.1(5)
C(3)–C(2)–F(2)	108.2(5)	106.1(5)
C(1)–C(2)–F(2)	114.8(5)	114.6(5)
C(9)–C(2)–F(2)	114.2(6)	114.6(6)
C(2)–C(1)–C(11)	119.8(6)	120.1(5)
C(2)–C(1)–C(10)	89.0(5)	89.1(5)
C(11)–C(1)–C(10)	119.1(6)	119.5(6)
C(2)–C(1)–F(1)	108.2(5)	108.9(5)
C(11)–C(1)–F(1)	109.2(5)	108.3(5)
C(10)–C(1)–F(1)	109.8(5)	109.6(5)
C(8)–C(11)–C(12)	118.0(7)	116.9(7)
C(8)–C(11)–C(1)	123.2(6)	122.7(6)
C(12)–C(11)–C(1)	118.8(6)	120.3(6)
C(1)–C(10)–C(9)	90.5(5)	90.8(5)
C(2)–C(9)–C(10)	87.6(5)	86.7(5)
C(2)–C(9)–C(1′)	115.1(5)	115.9(6)
C(10)–C(9)–C(1′)	115.6(6)	115.5(6)
C(2)–C(9)–C(1″)	112.0(6)	111.9(6)
C(10)–C(9)–C(1″)	114.2(6)	113.0(6)
C(1′)–C(9)–C(1″)	110.7(6)	111.7(6)
C(9)–C(1′)–C(2′)	130.0(6)	129.8(6)
H(3)–C(1′)–C(2′)	114.6(33)	121.5(33)
C(1′)–C(2′)–C(3′)	123.2(6)	123.8(6)
C(1′)–C(2′)–C(4′)	120.5(6)	121.8(6)
C(3′)–C(2′)–C(4′)	116.3(6)	114.4(6)
C(1)–C(10)–H(1)	112.3(26)	111.9(27)
C(1)–C(10)–H(2)	111.2(30)	109.5(31)
H(1)–C(10)–H(2)	102.8(39)	107.9(39)
H(1)–C(10)–C(9)	116.0(27)	120.5(28)
H(2)–C(10)–C(9)	123.7(31)	114.9(32)
C(9)–C(1′)–H(3)	115.4(34)	108.7(33)

It is interesting that bond lengths and angles throughout the naphthalene moiety also differ appreciably from ideal values. No highly fluorinated compound of similar tricyclic structure is available for comparison; three studies of octafluoronaphthalene have been published,[6-8] but one[6] gave no atomic co-ordinates while another[7] was inaccurate (*R* 0.35). Aromatic ring C–C bond lengths of the octafluoronaphthalene in the 1 : 1 naphthalene–octafluoronaphthalene complex[8] vary from 1.343 to 1.423 Å, which is very similar to values for the present structure. Bond angles at sp^2 carbon in octafluoronaphthalene (calculated from published co-ordinates[8]) vary from 118.0 to 123.6° (C–C–C) and 118.3 to 120.2° (C–C–F); *cf.* 116.8 to 125.3° (C–C–C) and 112.5 to 124.9° (C–C–F) in the present structure. Some of the discrepancies may be attributed to strain from the four-membered ring. A structure determination of 1,2,2a,8b-tetrahydrobuta[*a*]naphthalen-*endo*-2-ylmethyl *N*-*p*-bromophenylcarbamate[9] [(4), a compound with a tricyclic carbon skeleton identical to that of (3)] also shows some distortion at sp^2 carbon atoms, particularly at the unique double bond, with C–C–C angles from 117 to 127°; however, the standard deviations are rather high (2°).

TABLE 4

Selected torsion angles (°); all e.s.d.s ±1°

Aromatic ring	Molecule (A)	Molecule (B)
C(8)–C(7)–C(6)–C(5)	1.2	2.2
C(7)–C(6)–C(5)–C(12)	−2.8	−2.2
C(6)–C(5)–C(12)–C(11)	2.5	0.3
C(5)–C(12)–C(11)–C(8)	−0.6	1.6
C(7)–C(8)–C(11)–C(12)	−1.0	−1.7
C(11)–C(8)–C(7)–C(6)	0.7	−0.2
Central ring		
C(12)–C(4)–C(3)–C(2)	5.3	4.4
C(4)–C(3)–C(2)–C(1)	4.8	4.8
C(3)–C(2)–C(1)–C(11)	−16.7	−14.0
C(2)–C(1)–C(11)–C(12)	16.9	14.8
C(4)–C(12)–C(11)–C(1)	−5.2	−5.4
C(11)–C(12)–C(4)–C(3)	−6.2	−4.4
Four-membered ring		
C(2)–C(1)–C(10)–C(9)	13.9	11.4
C(1)–C(10)–C(9)–C(2)	−13.8	−11.2
C(1)–C(2)–C(9)–C(10)	13.6	11.2
C(9)–C(2)–C(1)–C(10)	−13.8	−11.4



(4)

TABLE 5

Non-bonded distances <3 Å

$F(1A) \cdots F(6A^{I})$	2.86
$F(1B) \cdots F(6B^{II})$	2.81
$F(4B) \cdots F(7A^{III})$	2.90
$F(7B) \cdots F(4A^{IV})$	2.86
$F(5B) \cdots F(8A^{V})$	2.88
$F(8B) \cdots F(5A^{VI})$	2.87

Roman numeral superscripts refer to the following equivalent positions:

I $x, 0.5 - y, -0.5 + z$
II $x, 1.5 - y, -0.5 + z$
III $1 - x, 0.5 + y, 0.5 - z$
IV $2 - x, 0.5 + y, 0.5 - z$
V $1 - x, 1 - y, -z$
VI $2 - x, 1 - y, -z$

Letters A and B distinguish the two independent molecules.

The packing diagram (Figure 3) shows the stacking of the molecules in the *z* direction, the aromatic rings in

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[6] G. S. Mandel and J. Donohue, Amer. Cryst. Assoc. Abstract Papers (Winter Meeting), 1972, p. 42.

[7] N. A. Akhmed, *Zhur. strukt. Khim.*, 1973, **14**, 573.

[8] J. Potenza and D. Mastropaolo, *Acta Cryst.*, 1975, **B31**, 2527.

[9] R. M. Bowman, C. Calvo, J. J. McCullough, R. C. Miller, and I. Singh, *Canad. J. Chem.*, 1973, **51**, 1060.

projection being approximately superimposed. Within the unit cell, molecule (A) is stacked below a symmetry-generated molecule at x, $\frac{1}{2} - y$, $\frac{1}{2} + z$; molecule (B) below a symmetry-generated molecule at x, $1\frac{1}{2} - y$, $\frac{1}{2} + z$. The stacking distance is hence approximately $\frac{1}{2}z$ (4.5 Å). There are several short non-bonded contacts (see Table 5) between fluorine atoms; only those between F(1) and F(6) are directly due to the stacking. The very close packing is reflected in the high density (1.59 g cm^{-3}); it may also be partly responsible for some of the bond and torsion angle discrepancies already noted.

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