aromatization of Δ^4- and Δ^5-androstene precursors. This reaction involves several successive oxidations and the formation of 19-hydroxy and 19,19-dihydroxy intermediates. There have been conflicting reports concerning the conformational stereochemistry of C(19) in these intermediates (Skinner & Akhtar, 1969; Osawa, 1972). This stereochemistry depends on the conformation of the 19-oxo moiety in the precursor as well as the steric hindrance involved in the various directions of approach to the carbonyl group. The present investigation shows that the conformer in which the oxo group eclipses the C(1)–C(10) bond is the minimum energy form in the solid state of 3β-hydroxy-17-oxo-5-androsten-19-al [torsion angle C(1)–C(10)–C(19)–O(19) = 4·7°]. Comparative analysis of 165 steroids indicates that crystallographically observed conformations are primarily intramolecularly controlled and undistorted by packing forces (Duax, Weeks, Rohrer, Osawa & Wolff, 1975; Duax, Weeks & Rohrer, 1975). While Δ^5-steroids have some flexibility in the *B* ring, substituents such as the 19-aldehyde restrict this flexibility, and the β-axial hydrogen atoms at C(2), C(4), C(8), and C(11) restrict the freedom of rotation of the 19-oxygen substituent. The O(19) atom in five of the six 19-mono-oxygenated steroids examined crystallographically lies between C(1), C(9), and C(11) with the C(19)–O(19) bond ranging from a position eclipsing the C(1)–C(10) bond in the present structure to a position *trans* to the C(5)–C(10) bond (Duax, Weeks & Rohrer, 1975). Consequently, the crystallographically observed conformation of 3β-hydroxy-17-oxo-5-androsten-19-al is suggested as a suitable model upon which to base the development of proposed reaction mechanisms. On the basis of steric considerations alone, the β-hydrogens at C(2), C(4), C(8), and C(11) hinder the approach of reagents to the 19-carbonyl from either the *A* or *C* ring sides. The distances between the β-axial hydrogens H(4β)···H(8) and H(2β)···H(11β) are 4·9 Å and 4·6 Å respectively. Therefore, differentiation between the remaining directions of approach (Fig. 3) is not possible solely on the basis of this structure determination.

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Naphthalene–Octafluoronaphthalene, 1:1 Solid Compound

BY JOSEPH POTENZA AND DONALD MASTROPAOLO

School of Chemistry, Rutgers University, New Brunswick, New Jersey 08903, *U.S.A.*

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Abstract. $C_{10}H_8.C_{10}F_8$, monoclinic, $P2_1/c$, $a=7{\cdot}457$ (5), $b=8{\cdot}503$ (2), $c=12{\cdot}710$ (2) Å, $\beta=99{\cdot}48$ (5)°, $Z=2$, $D_o=1{\cdot}65$ (1), $D_c=1{\cdot}671$ g cm^{-3}. The relative orientation of nearly parallel naphthalene and octafluoronaphthalene molecules within infinite columns closely resembles the stacking found in ordinary, hexagonal graphite. Within experimental error, both molecules exhibit D_{2h} symmetry and chemically equivalent C–C distances in naphthalene are equal to those in octafluoronaphthalene.

Introduction. White needle-like crystals of the title complex [m.p. 132 (1)°C] were prepared by evaporation of an acetone solution containing equimolar amounts of naphthalene and octafluoronaphthalene. Elemental analysis (calculated for $C_{10}H_8.C_{10}F_8$: C 60·01, H 2·01%. Found: C 61·04, H 2·02%) was consistent with formulation of the compound as a 1:1 complex. A single crystal, 0·6 × 0·2 × 0·2 mm, mounted in a sealed glass capillary to prevent sublimation, was used. Preliminary Weissenberg photographs revealed systematic absences $h0l$, $l=2n+1$ and $0k0$, $k=2n+1$, fixing the space group as $P2_1/c$. With the assumption of a half formula unit per asymmetric unit, the observed (flotation) and calculated densities agreed well. Intensities were collected at 21 ± 2°C on a CAD-3 automated diffractometer (θ–2θ scan) with Ni-filtered Cu $K\alpha$ radiation. Of the 1700 diffraction maxima recorded ($4<2\theta<140°$), 970 with $F^2 \geq 2\sigma$ (counting statistics) were considered observed, Lp corrected, and used in the structure solution and refinement. Absorption corrections were not applied (μ for Cu $K\alpha = 14{\cdot}8$ cm^{-1}).

The structure was solved by reiterative application of Sayre's equation with 91 reflections with $|E| \geq 1{\cdot}5$ and a program developed by Long (1965). In addition to three origin-defining reflections, the phases of four reflections were arbitrarily assigned, leading to 16 possible solutions. The true solution gave a consistency index $C = \langle |E_A \sum_{A=B+C} E_B E_C| \rangle / \langle |E_A| \sum_{A=B+C} |E_B|\,|E_C| \rangle$ of 0·87. An F map based on these 91 phases revealed the 14 nonhydrogen atoms in the asymmetric unit with the centers of octafluoronaphthalene and naphthalene molecules at crystallographic centers of symmetry 0,0,0 and $\frac{1}{2}$,0,0 respectively.

The structure was refined by full-matrix least-squares calculations (Potenza, Giordano, Mastropaolo & Efraty, 1974). $R_{wF2} = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$ was minimized and weights were $w = 1/\sigma^2$. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1962). After seven cycles, the last three of which utilized anisotropic thermal parameters, the four unique H atoms were located on a difference map. These were included for further refinement with temperature factors equal to the overall value (3·01 Å^2) obtained by Wilson's method: their temperature factors were not refined. Three additional cycles of all coordinates and heavy-atom anisotropic temperature factors gave final values of 0·13, 0·10 and 0·065 for R_{wF2}, R_{F2} and R_F, respectively.* For the final cycle, all coordinate and thermal parameter changes were less than 0·1 and 1·0 σ, respectively, where σ is the e.s.d. obtained from the inverse matrix. A final difference map showed no significant peaks above a general background of approximately 0·2–0·3 e Å^{-3}. Atomic parameters are shown in Table 1 while views of the complex along **c*** and the normal to the naphthalene plane are shown in Figs. 1 and 2, respectively. Bond lengths are given in Table 2.

* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31139 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. High-melting compounds formed from aromatic fluorocarbons with aromatic hydrocarbons, of which benzene–hexafluorobenzene is a typical example (Patrick & Prosser, 1960), have been known for some

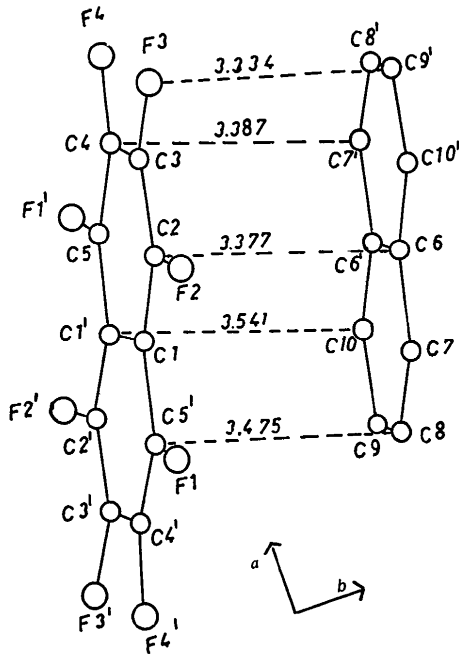

Fig. 1. The $C_{10}H_8.C_{10}F_8$ complex viewed along **c**. Distances between nearly eclipsed atoms are shown.

Table 1. *Final atomic parameters*

Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses. Coordinate and β values are $\times 10^4$. The expression for the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F(1)	725 (3)	2966 (3)	6960 (2)	283 (6)	151 (4)	51 (1)	12 (4)	−7 (3)	−23 (2)
F(2)	2005 (3)	5784 (3)	7189 (2)	265 (6)	162 (4)	43 (1)	−17 (5)	−10 (3)	−7 (2)
F(3)	2343 (4)	8639 (3)	6365 (2)	273 (6)	130 (4)	82 (2)	−52 (5)	6 (3)	−29 (2)
F(4)	1055 (3)	9236 (3)	4304 (2)	332 (7)	100 (3)	83 (2)	23 (5)	39 (3)	−13 (2)
C(1)	357 (5)	4838 (5)	5544 (2)	153 (9)	111 (6)	43 (2)	1 (7)	6 (4)	1 (2)
C(2)	1293 (5)	6054 (5)	6170 (3)	159 (9)	135 (7)	42 (4)	3 (7)	4 (4)	−7 (4)
C(3)	1476 (5)	7499 (5)	5747 (3)	162 (9)	117 (2)	61 (3)	−15 (7)	17 (4)	−19 (4)
C(4)	786 (5)	7800 (4)	4697 (3)	196 (9)	89 (5)	59 (3)	12 (7)	35 (4)	−12 (4)
C(5)	−100 (6)	6690 (5)	4062 (3)	173 (9)	122 (6)	40 (3)	11 (7)	7 (4)	−8 (3)
C(6)	5309 (5)	4868 (5)	5545 (3)	135 (8)	112 (6)	60 (3)	−3 (7)	12 (4)	4 (4)
C(7)	5095 (6)	3347 (5)	5977 (3)	209 (11)	136 (6)	63 (3)	−3 (7)	22 (5)	−15 (4)
C(8)	4290 (6)	2183 (5)	5330 (4)	216 (11)	110 (7)	115 (8)	1 (8)	30 (6)	−13 (5)
C(9)	3663 (6)	2447 (5)	4249 (4)	191 (11)	149 (8)	100 (4)	−25 (8)	20 (5)	−27 (5)
C(10)	3851 (6)	3886 (5)	3808 (4)	176 (11)	136 (7)	69 (3)	−13 (7)	−6 (5)	−12 (4)
H(1)	5553 (58)	3222 (55)	6730 (32)						
H(2)	3916 (60)	1273 (50)	5572 (33)						
H(3)	3050 (61)	1692 (46)	3740 (32)						
H(4)	3405 (57)	4176 (49)	3020 (31)						

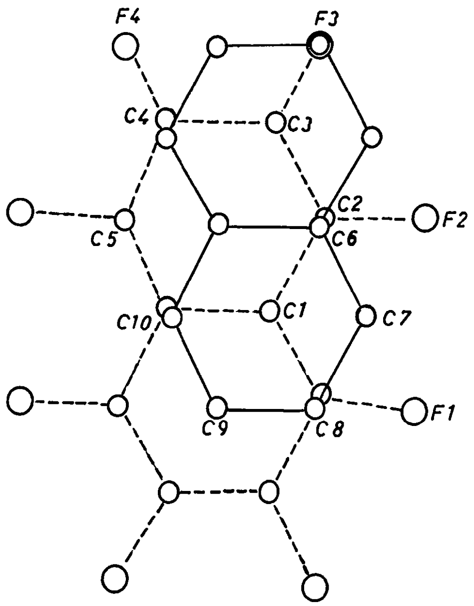

Fig. 2. View of the $C_{10}H_8$–$C_{10}F_8$ complex along the normal to the naphthalene (full lines) plane.

Table 2. *Interatomic distances* (Å)

F(1)–C(5)	1·336 (4)	C(6)—C(6′)	1·405 (7)
F(2)–C(2)	1·336 (5)	C(6)—C(7)	1·423 (7)
F(3)–C(3)	1·342 (5)	C(7)—C(8)	1·357 (7)
F(4)–C(4)	1·344 (5)	C(8)—C(9)	1·390 (6)
C(1)–C(1′)	1·423 (6)	C(9)—C(10)	1·359 (6)
C(1)–C(2)	1·415 (6)	C(10)–C(6′)	1·421 (6)
C(2)–C(3)	1·358 (5)	C(7)—H(1)	0·91 (4)
C(3)–C(4)	1·374 (6)	C(8)—H(2)	0·87 (5)
C(4)–C(5)	1·343 (6)	C(9)—H(3)	0·96 (4)
C(5)–C(1′)	1·419 (6)	C(10)–H(4)	1·00 (4)

time. Several have been studied extensively by thermodynamic (Brennan, Brown & Swinton, 1974) and spectroscopic techniques. The present study was undertaken to help provide a structural basis for examining the stability of these complexes.

Both naphthalene and octafluoronaphthalene molecules exhibit D_{2h} symmetry within experimental error. Further, with the 2σ criterion, chemically equivalent C–C distances in naphthalene are equal to those in octafluoronaphthalene. A comparison of the naphthalene distances with those of the pure compound (Cruickshank, 1957) shows a significant difference only in C(8)–C(9) which is 0·031 Å shorter in the present structure.

In the crystal, naphthalene and octafluoronaphthalene molecules are stacked alternately along **a** and form infinite columns related to each other by the *c* glide plane and the 2_1 axis along **b**. The relative orientation of naphthalene and octafluoronaphthalene molecules (Fig. 2) closely resembles the stacking found in ordinary hexagonal graphite (Wyckoff, 1963) where half the C atoms in a given layer eclipse those in adjacent layers. Between columns H···F contacts, which range from 2·61 to 2·94 Å, are all longer than the sum of the van der Waals radii (*ca* 2·55 Å).

Within experimental error, both molecules are planar; however, deviations of atoms from the least-squares planes are considerably larger for octafluoronaphthalene (av. 0·016, max. 0·033 Å) than for naphthalene (av. 0·001, max. 0·002 Å). The angle between these planes (3·7°) is such as to favor relatively short C···F and C···C contacts between the virtually eclipsed pairs F(3)···C(9′), C(4)···C(7′) and C(2)···C(6). While a specific F(3)···C(9′) interaction may help to stabilize the complex *via* dipole-induced interactions, the mean separation between planes (3·42 Å) is in the range expected for a normal van der Waals separation between aromatic molecules and suggests little, if any, charge transfer. In accord with this suggestion, ultraviolet and laser Raman spectra of the complex failed to reveal peaks which did not arise from the pure components (Mastropaolo, 1974). Similar conclusions regarding charge transfer have been reached both from structural (Dahl, 1973) and thermodynamic (Brennan, Brown & Swinton, 1974) considerations for complexes with hexafluorobenzene.

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