Acta Cryst. (1984). C**40**, 272–274

Structure of a Naphthalene–Perfluorobiphenyl Complex, $C_{10}H_8.C_{12}F_{10}$

By Linda I. Foss, Ashfaquzzaman Syed[*] and Edwin D. Stevens

Department of Chemistry, University of New Orleans, New Orleans, LA 70148, *USA*

and Cheryl L. Klein

Department of Chemistry, Xavier University of Louisiana, New Orleans, LA 70125, *USA*

(*Received* 15 *July* 1983; *accepted* 27 *September* 1983)

Abstract. $M_r = 462{\cdot}29$, monoclinic, $C2/c$, $a = 13{\cdot}355\,(2)$, $b = 6{\cdot}472\,(1)$, $c = 21{\cdot}994\,(3)$ Å, $\beta = 100{\cdot}48\,(1)°$, $V = 1869{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}643$, $D_m = 1{\cdot}642\,(2)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·620 cm^{-1}, $T = 295$ K, $F(000) = 920$, final $R = 0{\cdot}044$ for 652 observed reflections with $F > 3\sigma(F)$. The naphthalene and perfluorobiphenyl are independent molecules held together by van der Waals interactions. The naphthalene molecule is located on a center of symmetry and the perfluorobiphenyl on a twofold axis. The dihedral angle between the two rings of the perfluorobiphenyl molecule is 55·3°.

Introduction. The title compound is one of a series of perfluoroaromatics which have been studied spectroscopically to understand the interactions and dynamics in crystalline complexes (Chen & Prasad, 1977, 1980; Law & Prasad, 1978; Prasad, Law, Bellows & Francis, 1979). Raman spectroscopy of the naphthalene–perfluorobiphenyl complex indicates an ordered structure stabilized by weak van der Waals intermolecular interactions (McCaffrey & Prasad, 1981). In addition, the existence of a phosphorescence from the triplet state of naphthalene, not observed from pure naphthalene crystals, suggests a much different environment for the naphthalene molecules in the complex compared with naphthalene itself (McCaffrey & Prasad, 1981). In order to gain further insight into the interactions and dynamics of this complex, a single-crystal structure determination was undertaken.

Experimental. Sample prepared in Bridgman furnace using ultrapure zone-refined components (McCaffrey & Prasad, 1981). Crystal for data collection obtained by sublimation, approximate dimensions 0·2 × 0·3 × 0·4 mm, sealed in glass capillary. D_m measured by flotation in aqueous ZnI_2 solution. Enraf–Nonius CAD-4 diffractometer, graphite-crystal monochromator, Mo $K\alpha$ radiation. Lattice parameters from 25 reflections with $6{\cdot}8° < 2\theta < 15{\cdot}2°$. Systematic absences: hkl, $h + k = 2n + 1$; $0k0$, $l = 2n + 1$. Absorption as a function of ψ observed to be insignificant and no correction applied. Reflections measured within ranges $2° \le 2\theta \le 50°$, $0 \le h \le 15$, $0 \le k \le 7$, $-26 \le l \le 26$; θ:2θ scans. Intensities of three standard reflections decreased by 6% and used to correct data. 1913 total reflections measured, 1344 unique, 652 considered observed $[F > 3\sigma(F)]$. Correction for Lorentz and polarization effects. Structure determined by direct methods using the program *MULTAN*80 (Main *et al.*, 1980; modified by Frenz, 1982). Peaks corresponding to 16 non-hydrogen atoms located in E map. Structure refined by full-matrix least squares; $\sum w(F_o - F_c)^2$ minimized. H-atom positions calculated on basis of standard geometry. H positions and thermal parameters fixed during refinement; other atoms refined anisotropically. Final $R = 0{\cdot}044$ and $R_w = 0{\cdot}061$ for 146 variables; $w = 1/\sigma(F)^2$ where $\sigma(F^2)^2 = \sigma^2_{\text{c.s.}} + (0{\cdot}03F^2)^2$; $S = 2{\cdot}325$. $(\Delta/\sigma)_{\max} = 0{\cdot}03$. Maximum peak in final difference Fourier map 0·10 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All computer programs from the *SDP* system (Frenz, 1982).

Discussion. Atomic coordinates and thermal parameters are listed in Table 1;[†] Table 2 gives bond distances and angles. The molecular structure and atomic numbering scheme are shown in Fig. 1. The naphthalene molecule is located at a center of symmetry, and is planar, with a maximum deviation from the least-squares plane of only 0·010 (8) Å by C(8). In each of the two rings in the perfluorobiphenyl molecule, which are related by a twofold axis, the maximum deviation from the least-squares plane is 0·014 (4) Å by C(6).

---

[*] On Leave from Tata Iron & Steel Co., Jamshedpur, India.

[†] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38923 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/020272-03$01.50

The perfluorobiphenyl rings are not coplanar, but twisted to avoid unfavorable contacts between F atoms. The dihedral angle between the two rings is 55·3° in perfluorobiphenyl compared with 0·00° in biphenyl itself (Trotter, 1961) at room temperature. The resulting non-bonded contacts are 2·802 (4) Å for F(1)···F(1′) and 2·830 (4) Å for F(5)···F(5′).

A stereoview of the molecular packing in the unit cell is plotted in Fig. 2. Packing of the planar naphthalene with the non-planar perfluorobiphenyl molecules is accomplished by a parallel ordering of naphthalene molecules with perfluorobiphenyl rings at each end of the perfluorobiphenyl molecule. The angle between the least-squares plane of the naphthalene molecule and the closest ring of the perfluorobiphenyl is only 6°. As a result, regions of approximately parallel molecules are formed in the unit cell: one in the center, and the other at the top and bottom of Fig. 2.

A further result of the packing arrangement, evident at the top and bottom of Fig. 2, is that each naphthalene molecule is packed between two perfluorobiphenyl rings. The closest intermolecular contact between rings [C(1)···C(8)] is 3·514 (7) Å. The isolation of naphthalene molecules in the crystal apparently results in weak exciton interaction and exciton–phonon coupling, allowing the observation of a triplet phosphorescence from naphthalene (McCaffrey & Prasad, 1981). The novel spectroscopic properties of the complex are thus explained by the unusual molecular-packing arrangement.

Support of this research by a grant from the Regents of the State of Louisiana is gratefully acknowledged. Funds for the purchase of a diffractometer were provided in part by a grant from the National Science Foundation (CHE8208754).

Table 1. *Positional parameters and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\alpha)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}].$$

	x	y	z	B_{eq}(Å^2)
F(1)	−0·0195 (3)	0·8005 (5)	0·6852 (2)	5·92(9)
F(2)	0·1235 (3)	0·8007 (6)	0·6134 (2)	7·1 (1)
F(3)	0·2525 (3)	0·4748 (7)	0·6160 (2)	7·0 (1)
F(4)	0·2413 (2)	0·1564 (6)	0·6938 (2)	6·6 (1)
F(5)	0·1070(2)	0·1621 (5)	0·7693 (2)	5·42 (8)
C(1)	0·0464 (5)	0·6411 (8)	0·6889 (3)	4·6 (1)
C(2)	0·1182 (5)	0·6405 (9)	0·6513 (3)	4·9 (1)
C(3)	0·1843 (4)	0·479 (1)	0·6531 (3)	4·9 (2)
C(4)	0·1774 (4)	0·3172 (9)	0·6929 (3)	4·7 (1)
C(5)	0·1063 (4)	0·3196 (8)	0·7300 (3)	4·0 (1)
C(6)	0·0379 (4)	0·4802 (8)	0·7295 (2)	4·1 (1)
C(7)	0·6129 (6)	−0·085 (1)	0·4670 (4)	8·2 (2)
C(8)	0·6237 (6)	0·094 (2)	0·4322 (4)	9·1 (2)
C(9)	0·5599 (6)	0·253 (1)	0·4296 (4)	9·1 (2)
C(10)	0·4830 (6)	0·253 (1)	0·4609 (3)	7·5 (2)
C(11)	0·4689 (4)	0·0859 (9)	0·4978 (3)	5·2 (2)

Table 2. *Bond distances* (Å) *and angles* (°)

Numbers in parentheses are estimated standard deviations in the least significant digits.

F(1)–C(1)	1·349 (4)	F(1)–C(1)–C(2)	119·0 (3)
F(2)–C(2)	1·340 (4)	F(1)–C(1)–C(6)	118·9 (3)
F(3)–C(3)	1·329 (4)	C(2)–C(1)–C(6)	112·1 (4)
F(4)–C(4)	1·344 (4)	F(2)–C(2)–C(1)	119·5 (4)
F(5)–C(5)	1·335 (3)	F(2)–C(2)–C(3)	120·3 (4)
C(1)–C(2)	1·376 (5)	C(1)–C(2)–C(3)	120·2 (4)
C(1)–C(6)	1·390 (5)	F(3)–C(3)–C(2)	120·8 (4)
C(2)–C(3)	1·362 (5)	F(3)–C(3)–C(4)	120·3 (4)
C(3)–C(4)	1·380 (5)	C(2)–C(3)–C(4)	118·9 (3)
C(4)–C(5)	1·360 (4)	F(4)–C(4)–C(3)	119·0 (4)
C(5)–C(6)	1·383 (4)	F(4)–C(4)–C(5)	120·6 (4)
C(6)–C(6)	1·472 (6)	C(3)–C(4)–C(5)	120·4 (4)
C(7)–C(8)	1·408 (8)	F(5)–C(5)–C(4)	117·1 (3)
C(7)–C(11)	1·447 (6)	F(5)–C(5)–C(6)	120·4 (3)
C(8)–C(9)	1·333 (8)	C(4)–C(5)–C(6)	122·4 (3)
C(9)–C(10)	1·337 (7)	C(1)–C(6)–C(5)	115·9 (3)
C(10)–C(11)	1·387 (6)	C(1)–C(6)–C(6)	122·6 (3)
C(11)–C(11)	1·382 (7)	C(5)–C(6)–C(6)	121·4 (2)
		C(8)–C(7)–C(11)	117·2 (5)
		C(7)–C(8)–C(9)	122·1 (6)
		C(8)–C(9)–C(10)	121·4 (6)
		C(9)–C(10)–C(11)	120·1 (5)
		C(7)–C(11)–C(10)	120·9 (4)
		C(7)–C(11)–C(11)	117·5 (5)
		C(10)–C(11)–C(11)	121·7 (5)

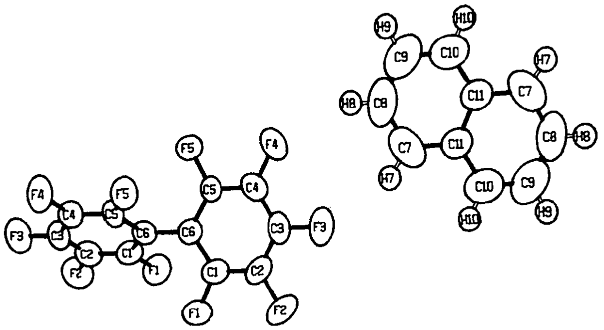

Fig. 1. Plot of the naphthalene and perfluorobiphenyl molecules showing the atomic labeling scheme. Thermal ellipsoids are plotted at the 50% probability level. H atoms have been plotted with arbitrary radii.

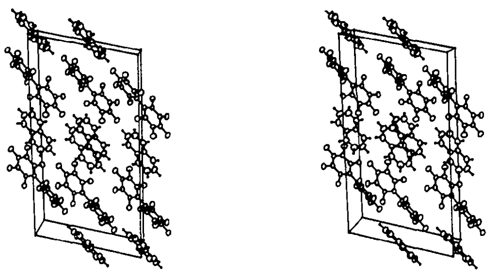

Fig. 2. Stereoview of the molecular packing in the unit cell of the naphthalene–perfluorobiphenyl complex.

References

Chen, F. P. & Prasad, P. N. (1977). *Chem. Phys. Lett.* **47**, 341–345.

Chen, F. P. & Prasad, P. N. (1980). *Chem. Phys. Lett.* **72**, 285–290.

Frenz, B. (1982). *SDP* package of computer programs. Molecular Structure Corp., College Station, Texas, USA.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Law, K. N. & Prasad, P. N. (1978). *Chem. Phys. Lett.* **39**, 105–109.

McCaffrey, R. R. & Prasad, P. N. (1981). *Chem. Phys.* **63**, 13–18.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Prasad, P. N., Law, K. N., Bellows, J. C. & Francis, A. H. (1979). *J. Lumin.* **18/19**, 51–56.

Trotter, J. (1961). *Acta Cryst.* **14**, 1135–1140.

Acta Cryst. (1984). C**40**, 274–277

Benzoyl-3 *p*-Tolylazo-3 Bornanone-2 Dextrogyre, $C_{24}H_{26}N_2O_2$

Par A. Dubourg et R. Roques

Laboratoire de Cristallographie, Faculté des Sciences, 04 *BP* 322 *Abidjan* 04, *Côte d'Ivoire*

Ch. Bertrand, C. Metge et F. Labruyère

Laboratoire de Chimie des Terpènes, Université Paul Sabatier, 118 *Route de Narbonne,* 31062 *Toulouse CEDEX, France*

et J.-P. Declercq et G. Germain

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1348-*Louvain-La-Neuve, Belgique*

(*Reçu le* 18 *juin* 1982, *accepté le* 19 *septembre* 1983)

Abstract. $M_r = 374{\cdot}48$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}868\,(8)$, $b = 11{\cdot}247\,(17)$, $c = 27{\cdot}276\,(39)$ Å, $V = 2107\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}18$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}06$ mm^{-1}, $F(000) = 800$, room temperature. $R = 0{\cdot}089$ for 950 observed reflexions. Two diastereoisomers are obtained by reaction of tolyldiazonium chloride with enolic (1*R*,4*R*)-(+)-3-benzoyl-2-bornanone. The configuration at C(3) has been determined by diffractometric measurement. The molecule is shown to be (1*R*,3*R*,4*R*)-(+)-3-benzoyl-3-*p*-tolylazo-2-bornanone. Moreover, the comparative experimental and theoretical dipole-moment study has confirmed the conformation in solution of the azo and benzoyl groups around C(3), proving that conformational lability of these groups is impossible around the chiral centre. This result has allowed the Cotton effect of the azo chromophore to be related to the stereochemistry of such molecules.

Introduction. Dans le cadre d'une étude sur la synthèse de composés chiraux azoïques nous avons été amenés à faire réagir divers sels de diazonium sur des composés acylés ou aroylés de la bornanone-2-(+) (Bertrand & Bedos, 1954; Guillaumon, Labruyère, Metge & Bertrand, 1973). Dans chaque cas deux isomères sont obtenus; c'est ainsi que le chlorure de phényldiazonium, ou ses homologues, réagissant sur l'acétyl, la benzoyl ou la naphtoyl-3 bornanone-2, donnent par cristallisation dans un solvant non polaire et à faible point d'ébullition, un composé azoïque lévogyre présentant un effet Cotton négatif pour la transition $n \rightarrow \pi^*$ du —N=N—. Ce composé chauffé quelques heures dans un solvant polaire s'isomérise en un dérivé azoïque dextrogyre à effet Cotton positif.

	T_F (K)	$[\alpha]_D^{293\text{K}}$	$\Delta\varepsilon(n\rightarrow\pi^*)$
Benzoyl-3 *p*-tolylazo-3 bornanone-2	414 431	−380 +921	−1,15 +2,28
Naphtoyl-3 *o*-nitrophénylazo-3 bornanone-2	424 449	−27 +593	−0,3 +2,3
Acétyl-3 *o*-nitrophénylazo-3 bornanone-2	481 483	−180 +320	−1,6 +0,8

(Solvant: éthanol; $c = M/50$)

L'étude des spectres de RMN des deux stéréoisomères de la benzoyl-3 *p*-tolylazo-3 bornanone-2 (Parello, Bertrand & Bedos, 1968) montre un cas intéressant de couplage virtuel visible sur le signal du proton 4 en tête de pont et prouve que ce sont bien deux diastéréoisomères.

0108-2701/84/020274-04$01.50