

When no hydrogen bond occurs, the chemical shift of an Az—NH—SO₂—A system (Az = benzofuran moiety, A = tosyl group) is in the range 7.10–7.90 p.p.m. from tetramethylsilane in CDCl₃ solution (Simons, 1978).

The spectral pattern of the aromatic region is different in CDCl₃ and DMSO solutions and more NMR experiments are needed to understand whether the difference is due to conformational changes or to solvent effects.

References

BACHECHI, F., COIRO, V. M., DELFINI, M. & SETTIMI, G. (1988). *Acta Cryst.* **C44**, 1449–1451.

BACHECHI, F., COIRO, V. M., GATTA, F., SETTIMI, G. & DELFINI, M. (1988). *Acta Cryst.* **C44**, 300–303.
 BACHECHI, F., ZAMBONELLI, L. & MARCOTRIGIANO, G. (1977). *J. Cryst. Mol. Struct.* **7**, 11–20.
 CERRINI, S. & SPAGNA, R. (1977). 4th Eur. Crystallogr. Meet., Oxford. Abstracts, p. 7.
 KÁLMÁN, A., CZUGLER, M. & ARGAY, G. (1981). *Acta Cryst.* **B37**, 868–877.
 MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, 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.
 SIMONS, W. W. (1978). Editor. *Sadtler Handbook of Proton NMR Spectra*, p. 601. Philadelphia, London: Sadtler-Heyden.
 TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

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Structure of 4'-Butyl-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile

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Abstract. C₁₇H₁₃F₄N, *M_r* = 307.3, orthorhombic, *P*2₁2₁2₁, *a* = 7.280 (4), *b* = 11.253 (3), *c* = 17.255 (5) Å, *V* = 1413.6 Å³, *Z* = 4, *D_x* = 1.444 g cm⁻³, *Mo Kα*, *λ* = 0.71069 Å, *μ* = 0.79 cm⁻¹, *F*(000) = 632, *T* = 147 K. Final *R* = 0.036 for 1206 observed reflections. The molecular conformation has three planar groups, the cyanotetrafluorophenyl, the phenyl and the butyl groups. The butyl group lies at 13.4 (4)° to the phenyl group and there is an angle of 40.8 (4)° between the tetrafluorophenyl and phenyl groups. In the unit cell, molecules are stacked in pairs (head to tail) with the phenyl ring and the tetrafluorophenyl rings almost exactly overlaying each other. Closest C···C contacts are 3.388 (5) Å within the pairs and 3.380 (5) Å between the pairs.

Introduction. As part of a project involving the synthesis of partially fluorinated analogues of liquid crystalline compounds, a series of 4'-alkyl-2,3,5,6-tetrafluorobiphenyl-4-carbonitriles and 4'-alkyl-2',3',5',6'-tetrafluorobiphenyl-4-carbonitriles have been synthesized and their properties examined. These compounds are not liquid crystals themselves but are potential components of liquid-crystalline

mixtures for use as spectroscopic solvents (Field, Hambley & Pierens, 1990).

Experimental. Synthesis of 4'-butyl-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile proceeded from 4-butylaniline which was converted to the corresponding iodide using standard methods. The aryl—aryl bond was made by coupling the iodide with bromopentafluorobenzene over copper powder at high temperature and the unsymmetrical product, 4-butyl-2',3',4',5',6'-pentafluorobiphenyl, was isolated by fractional distillation. An —NH—NH₂ group was introduced at the 4 position of the fluorinated aromatic ring by direct reaction with hydrazine hydrate and this was transformed sequentially into the corresponding bromide and eventually the required —C≡N group. Details of the synthesis have been published elsewhere (Field, Hambley & Pierens, 1990). Colourless crystals of 4'-butyl-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile were obtained by slow crystallization from hexane.

Cell constants were determined by a least-squares fit to 25 independent reflections in the range 10 < *θ* < 15°, measured and refined on an Enraf-Nonius CAD-4F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table 1. Data were reduced and Lorentz,

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Table 1. Summary of data-collection and processing parameters

Crystal dimensions (mm)	0.30 × 0.04 × 0.10
Data collection range (°)	2 ≤ 2θ ≤ 50
Scan width (°)	1.2 + 0.35tanθ
Horizontal counter aperture (mm)	2.70 + 1.05tanθ
Scan type	ω-θ
Range of hkl	h 0 → 8, k 0 → 13, l 0 → 20
Total data collected	1412
Data with I ≥ 2.5σ(I)	1206
Total variables	252
R = ∑ F _o - F _c /∑ F _o	0.036
wR = ∑(w ^{1/2} F _o - F _c)/∑w ^{1/2} F _o	0.040
Weighting constants*	g = 1.78, k = 0.00051
Max. Δ/σ in final cycle	0.03
Max., min. heights in final Δρ map (e Å ⁻³)	+0.25, -0.21

* Weight $w = g/[\sigma^2(F_o) + kF_o^2]$, g and k refined.

Table 2. Atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters B_{eq} (Å²)

$$B_{eq} = (8\pi^2/3)\sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
N(1)	-0.1155 (4)	0.4307 (3)	0.8541 (2)	2.56
C(1)	-0.1197 (4)	0.3968 (3)	0.7912 (2)	1.72
C(3)	-0.1203 (4)	0.3571 (3)	0.7126 (2)	1.67
C(3)	-0.0608 (4)	0.4296 (3)	0.6529 (2)	1.56
C(4)	-0.0605 (4)	0.3918 (3)	0.5773 (2)	1.52
C(5)	-0.1219 (4)	0.2789 (3)	0.5555 (2)	1.41
C(6)	-0.1809 (4)	0.2068 (3)	0.6162 (2)	1.40
C(7)	-0.1832 (4)	0.2442 (3)	0.6920 (2)	1.47
C(8)	-0.1243 (4)	0.2401 (3)	0.4737 (2)	1.42
C(9)	-0.1790 (4)	0.3189 (3)	0.4159 (2)	1.53
C(10)	-0.1811 (4)	0.2847 (3)	0.3388 (2)	1.49
C(11)	-0.1281 (4)	0.1708 (3)	0.3164 (2)	1.51
C(12)	-0.0752 (4)	0.0918 (3)	0.3751 (2)	1.53
C(13)	-0.0731 (4)	0.1246 (3)	0.4520 (2)	1.50
C(14)	-0.1281 (4)	0.1309 (3)	0.2326 (2)	1.61
C(15)	-0.1508 (5)	0.2285 (3)	0.1723 (2)	1.88
C(16)	-0.1355 (6)	0.1825 (3)	0.0895 (2)	2.38
C(17)	-0.1397 (7)	0.2815 (4)	0.0297 (2)	3.08
F(1)	0.0011 (3)	0.5387 (2)	0.6702 (1)	2.12
F(2)	0.0037 (3)	0.4679 (2)	0.5240 (1)	1.88
F(3)	-0.2473 (2)	0.0983 (2)	0.6014 (1)	1.86
F(4)	-0.2458 (3)	0.1715 (2)	0.7473 (1)	2.01

polarization and decomposition corrections were applied using the Enraf-Nonius *SDP* system (Frenz, 1985). The data were not corrected for absorption effects. The structure was solved by direct methods and was refined by full-matrix least-squares analysis with *SHELX76* (Sheldrick, 1976).^{*} H atoms were refined with isotropic displacement parameters, all other atoms were refined anisotropically. Scattering factors used were the values supplied in *SHELX76*. Non-H-atom coordinates are listed in Table 2 and

* Structure amplitudes, anisotropic displacement parameters of non-H atoms, positional and displacement parameters of H atoms and details of least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53403 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and angles (°)

C(1)—N(1)	1.150 (4)	C(2)—C(1)	1.428 (4)
C(3)—C(2)	1.384 (5)	C(7)—C(2)	1.396 (5)
C(4)—C(3)	1.373 (4)	F(1)—C(3)	1.341 (4)
C(5)—C(4)	1.398 (4)	F(2)—C(4)	1.340 (3)
C(6)—C(5)	1.393 (4)	C(8)—C(5)	1.477 (4)
C(7)—C(6)	1.376 (4)	F(3)—C(6)	1.338 (4)
F(4)—C(7)	1.337 (4)	C(9)—C(8)	1.394 (4)
C(13)—C(8)	1.403 (5)	C(10)—C(9)	1.384 (4)
C(11)—C(10)	1.393 (5)	C(12)—C(11)	1.402 (4)
C(14)—C(11)	1.514 (4)	C(13)—C(12)	1.379 (4)
C(15)—C(14)	1.523 (5)	C(16)—C(15)	1.525 (5)
C(17)—C(16)	1.519 (5)		
C(2)—C(1)—N(1)	178.2 (4)	C(3)—C(2)—C(1)	121.4 (3)
C(7)—C(2)—C(1)	121.9 (3)	C(7)—C(2)—C(3)	116.7 (3)
C(4)—C(3)—C(2)	121.7 (3)	F(1)—C(3)—C(2)	118.7 (3)
F(1)—C(3)—C(4)	119.6 (3)	C(5)—C(4)—C(3)	122.5 (3)
F(2)—C(4)—C(3)	117.0 (3)	F(2)—C(4)—C(5)	120.5 (3)
C(6)—C(5)—C(4)	115.2 (3)	C(8)—C(5)—C(4)	122.0 (3)
C(8)—C(5)—C(6)	122.8 (3)	C(7)—C(6)—C(5)	122.7 (3)
F(3)—C(6)—C(5)	120.0 (3)	F(3)—C(6)—C(7)	117.1 (3)
C(6)—C(7)—C(2)	121.1 (3)	F(4)—C(7)—C(2)	119.2 (3)
F(4)—C(7)—C(6)	119.7 (3)	C(9)—C(8)—C(5)	120.0 (3)
C(13)—C(8)—C(5)	121.7 (3)	C(13)—C(8)—C(9)	118.3 (3)
C(10)—C(9)—C(8)	120.9 (3)	C(11)—C(10)—C(9)	121.3 (3)
C(12)—C(11)—C(10)	117.4 (3)	C(14)—C(11)—C(10)	122.6 (3)
C(14)—C(11)—C(12)	120.1 (3)	C(13)—C(12)—C(11)	121.9 (3)
C(12)—C(13)—C(8)	120.2 (3)	C(15)—C(14)—C(11)	116.0 (3)
C(16)—C(15)—C(14)	112.8 (3)	C(17)—C(16)—C(15)	112.7 (3)

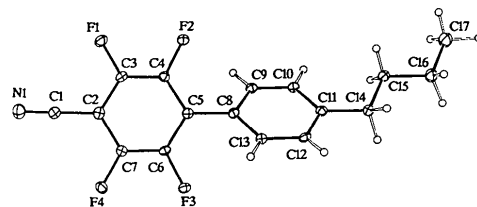


Fig. 1. ORTEP plot of 4'-butyl-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile (30% ellipsoids).

bond lengths and angles are given in Table 3. The atomic nomenclature is defined in the ORTEP (Johnson, 1965) plot given in Fig. 1.

Discussion. A stereoview of the unit cell is shown in Fig. 2. The basic motif of the structure is a pair of molecules stacked antiparallel (head to tail) in which the phenyl ring of one molecule and the tetrafluorophenyl ring of the second molecule almost exactly overlay each other. These pairs are stacked in the *a* direction with shifts in the *b* direction between the pairs. Closest C...C contacts are 3.388 (5) Å within the pairs and 3.380 (5) Å between the pairs. The long axes of the molecules are roughly aligned with the *b* axis and they make head-to-tail contacts in this direction.

The conformation is best described as three planar groups, the cyanotetrafluorophenyl, the phenyl and the butyl groups. The cyanotetrafluorophenyl-group C atoms are coplanar to within 0.008 (3) Å and the attached C, N and F atoms lie within 0.035 (3) Å of

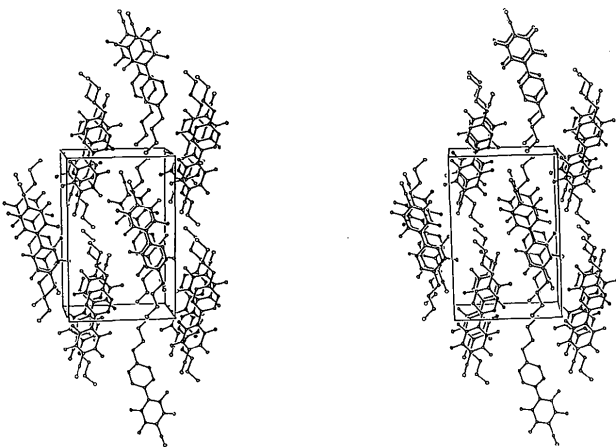


Fig. 2. Stereo plot of the unit cell viewed down the *a* axis with *b* horizontal and *c* vertical.

this plane. The phenyl-group C atoms are coplanar to within 0.006 (3) Å and the attached C atoms lie within 0.018 (3) Å of this plane. The butyl group is less planar, as expected since there are no chemical factors disposing it toward planarity, but the C atoms lie within 0.034 (3) Å of the least-squares plane through them. The butyl group lies at 13.4 (4)° to the phenyl group and there is an angle of 40.8 (4)° between the tetrafluorophenyl and phenyl groups. This latter angle is substantially smaller than the 57.9° in 2,3,5,6-tetrafluorobiphenyl (TFB) (Goodhand & Hamor, 1978) and the 52.9° in 2,3,4,

5,6-pentafluorobiphenyl (PFB) (Brock, Naae, Goodhand & Hamor, 1978) but is similar to the 40.5° in 4'-*n*-butylbiphenyl-4-carbonitrile (Vani, 1983). These results suggest that the inter-ring torsion angle depends at least as much upon crystal-packing effects as upon intramolecular interactions. The inter-ring C—C bond length, 1.477 (4) Å, is shorter than those in TFB and PFB, 1.492 and 1.493 (3) Å, possibly as a consequence of the lower inter-ring torsion angle.

The C—C bonds in the tetrafluorophenyl ring range from 1.373 (4) to 1.398 (4) Å and in the phenyl group from 1.379 (4) to 1.403 (4) Å. In each case, the two shortest bonds are C(2)—C(3) and C(5)—C(6) though the differences are of marginal significance. The C—F bond lengths, average 1.339 Å, are similar to those in the aforementioned compounds.

References

- BROCK, C. P., NAAE, D. G., GOODHAND, N. & HAMOR, T. A. (1978). *Acta Cryst.* **B34**, 3691–3696.
 FIELD, L. D., HAMBLEY, T. W. & PIERENS, G. K. (1990). *Tetrahedron*. In the press.
 FRENZ, B. A. (1985). *Enraf-Nonius Structure Determination Package*. College Station, Texas, USA.
 GOODHAND, N. & HAMOR, T. A. (1978). *Acta Cryst.* **B34**, 1644–1647.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 VANI, G. V. (1983). *Mol. Cryst. Liq. Cryst.* **99**, 21–27.

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Structure of (*E*)-1,2-Dimesitylvinyne Bis(mesitylenecarboxylate)

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Abstract. C₄₀H₄₄O₄, *M_r* = 588.79, triclinic, *P* $\bar{1}$, *a* = 7.9092 (5), *b* = 10.9149 (8), *c* = 11.654 (1) Å, α = 115.100 (7), β = 90.182 (6), γ = 108.597 (5)°, *V* = 852 (4) Å³, *Z* = 1, *D_x* = 1.147 g cm⁻³, $\lambda(\text{Cu } K\alpha)$ = 1.54184 Å, μ = 5.4 cm⁻¹, *F*(000) = 316, *T* = 295 K,

R = 0.048 for 2308 unique reflections with *I* ≥ 2.5σ(*I*). Owing to steric hindrance the dihedral angles between the trimethylphenyl groups and the planes of the bonds to the adjacent *sp*² C atoms are larger than usual. The central ethene fragment is twisted by 7.7 (3)°. The *para*-methyl groups are disordered, while the *ortho* groups are well localized.

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