

Fig. 3. Stereoview of the unit cell. Minimum intermolecular distance: Cl(7a)···Cl(7a') = 3.455 (3) Å.

Cl(6)···Cl(7b) = 3.246 (3) Å are significantly different. This indicates a rotation of the CCl₃ group of about 18° from the expected conformation, already observed in perchloro-*p*-xylene. This rotation is probably due to the molecular packing in the crystal. As can be seen in Fig. 3, the aliphatic Cl atoms form close-packed layers parallel to the (100) plane, while the molecular skeletons are normal to this plane.

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Structure and NMR Spectra of *N*-[2-(α -Hydrazonobenzyl)-3-benzofuranyl]-*p*-toluenesulfonamide

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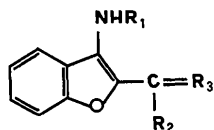
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Abstract. C₂₂H₁₉N₃O₃S, *M_r* = 405.48, monoclinic, *P*2₁/*c*, *a* = 8.296 (3), *b* = 26.859 (8), *c* = 8.820 (4) Å, β = 99.53 (1)°, *V* = 1938.3 Å³, *Z* = 4, *D_x* = 1.389 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 1.87 cm⁻¹, *F*(000) = 848, *T* = 293 K, *R* = 0.056 for 2074 reflections with *I* \geq 3 σ (*I*). The α -hydrazonobenzyl group has a *syn* configuration with respect to N(1). Two hydrogen bonds, involving N and O atoms, are present. In solution, the ¹H mononuclear

NMR spectrum and two-dimensional homonuclear correlated spectroscopy experiments (COSY) confirm the presence of hydrogen bonding.

Introduction. The title compound was prepared by treatment of 2-benzoyl-3-*N*-(*p*-toluenesulfonyl)-benzofuran with hydrazines and was used as the starting material in the synthesis of derivatives with probable psychotropic activity.

Since heterocyclic compounds containing a benzofuran moiety present different reactivity towards hydrazines, an X-ray structural investigation was undertaken on the starting materials and on the intermediates to gain an understanding of the mechanism of formation of the intermediate hydrazones. The crystal structures of compounds (1) and (2), represented below, have been reported in recent papers (Bachechi, Coiro, Gatta, Settini & Delfini, 1988; Bachechi, Coiro, Delfini & Settini, 1988). The present work deals with the crystal structure of (3).



- (1) R₁ = SO₂C₆H₄CH₃ (2) R₁ = H (3) R₁ = SO₂C₆H₄CH₃
 R₂ = CH₃ R₂ = CH₃ R₂ = C₆H₅
 R₃ = O R₃ = O R₃ = N-NH₂

Experimental. Crystals were obtained from a dimethylhydrazine-ethanol solution (1:3 by volume); Nicolet R3 four-circle diffractometer; graphite-monochromated Mo K α radiation; crystal size 0.5 × 0.4 × 0.6 mm; unit-cell dimensions determined using 15 reflections (20 ≤ 2 θ ≤ 26°); 5186 reflections measured in the range 3 ≤ 2 θ ≤ 56°, h = 0 to 10, k = 0 to 34, l = -11 to 11; 2074 reflections with I ≥ 3 σ (I) considered observed; ω -scan mode, with scan rate depending on the intensities. Three standards measured every 100 reflections, no significant change; data processed to yield values of I and σ (I) calculated according the formulae: $I = S[P - (B_1 + B_2)]$ and $\sigma(I) = [S^2(P + B_1 + B_2) + (pI)^2]^{1/2}$, where S is the scan rate, P is the total scan counts, and B₁ and B₂ are the background counts, corrected for the background count-scan time ratio (Bachechi, Zambonelli & Marcotrigiano, 1977); the uncertainty factor p was 0.00046 as calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). Corrections for Lorentz and polarization, but not for absorption. Structure solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least-squares procedures, function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Heavy atoms with anisotropic thermal parameters; H atoms included at calculated positions with fixed coordinates and isotropic thermal parameters (262 parameters refined). Convergence at R = 0.056 ($wR = 0.077$, S = 1.43). (Δ/σ)_{max} = 0.05; final difference map with no peaks exceeding 0.30 e Å⁻³. All calculations performed on an HP 2100 MX mini-computer (CNR Research Area, Rome) using local programs (Cerrini & Spagna, 1977). Scattering

Table 1. Atomic coordinates and isotropic thermal parameters with e.s.d.'s in parentheses

$$U_{eq} = (1/6\pi)\sum_i\sum_j\beta_j a_i \cdot a_j$$

	x	y	z	U _{eq} (Å ²)
S	0.4646 (2)	0.3441 (1)	0.6920 (2)	0.060 (1)
N(1)	0.5184 (5)	0.3853 (2)	0.5697 (5)	0.053 (1)
N(2)	0.4074 (6)	0.3592 (2)	0.2575 (6)	0.057 (3)
N(3)	0.3983 (8)	0.3249 (2)	0.1426 (7)	0.078 (4)
O(1)	0.2155 (4)	0.4686 (1)	0.3663 (4)	0.048 (2)
O(3)	0.4503 (6)	0.3694 (2)	0.8308 (5)	0.077 (3)
O(4)	0.5801 (6)	0.3045 (2)	0.6936 (7)	0.096 (4)
C(2)	0.3109 (6)	0.4260 (2)	0.3797 (6)	0.044 (3)
C(3)	0.4037 (6)	0.4242 (2)	0.5224 (6)	0.045 (3)
C(4)	0.3682 (6)	0.4675 (2)	0.6057 (6)	0.046 (3)
C(5)	0.2497 (7)	0.4932 (2)	0.5069 (6)	0.047 (3)
C(6)	0.1808 (8)	0.5369 (2)	0.5415 (8)	0.059 (4)
C(7)	0.2356 (9)	0.5567 (3)	0.6851 (9)	0.071 (4)
C(8)	0.3548 (9)	0.5325 (3)	0.7880 (8)	0.070 (4)
C(9)	0.4219 (8)	0.4880 (3)	0.7498 (7)	0.061 (4)
C(10)	0.2984 (6)	0.3934 (2)	0.2493 (6)	0.045 (3)
C(11)	0.1600 (7)	0.3997 (2)	0.1186 (6)	0.047 (3)
C(12)	0.2686 (7)	0.3217 (2)	0.6097 (7)	0.049 (3)
C(13)	0.1331 (7)	0.3433 (3)	0.6520 (7)	0.057 (3)
C(14)	-0.0196 (7)	0.3282 (3)	0.5777 (8)	0.061 (4)
C(15)	-0.0354 (8)	0.2925 (2)	0.4645 (8)	0.064 (4)
C(16)	0.1029 (9)	0.2716 (3)	0.4237 (9)	0.071 (4)
C(17)	0.2584 (9)	0.2858 (2)	0.4951 (9)	0.065 (4)
C(18)	-0.2035 (10)	0.2779 (4)	0.3841 (12)	0.109 (6)
C(19)	0.1536 (8)	0.4393 (2)	0.0216 (7)	0.060 (3)
C(20)	0.0227 (9)	0.4470 (3)	-0.0970 (8)	0.068 (4)
C(21)	-0.1042 (8)	0.4129 (3)	-0.1137 (8)	0.069 (4)
C(22)	-0.0998 (8)	0.3724 (3)	-0.0187 (8)	0.069 (4)
C(23)	0.0355 (8)	0.3656 (3)	0.0950 (7)	0.065 (4)

factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic parameters of non-H atoms are given in Table 1.*

¹H NMR spectra were obtained in dimethyl sulfoxide (Me₂SO-*d*₆) solution at room temperature (295 K) on an XL-Varian spectrometer operating at 300 MHz. The concentration of the sample was 5 mg ml⁻¹. The spectral conditions were as follows: spectral width 4000 Hz, pulse width 12 μ s, number of scans 8, acquisition time 2 s, repetition rate 1 s. The two-dimensional spectra (COSY) were obtained with standard software. A total of 128 spectra were collected, each consisting of 16 transients. A 1 s recycle delay (D1) was allowed between each pulse sequence. Heteronuclear correlated two-dimensional spectra were obtained with a spectral width of 2705.6 Hz in the f_1 (¹H) domain and 12594.5 Hz in the f_2 (¹³C) domain. A total of 128 time increments were used and 128 transients were accumulated for each time increment with a delay between transients of 2.0 s.

¹H NMR spectra were also obtained in CDCl₃ solution at room temperature (295 K). The concen-

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and ¹H NMR spectra of the title compound in DMSO and CDCl₃ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53336 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tration of the sample was 5 mg ml⁻¹. The spectral conditions were: spectral width 4000 Hz, pulse width 19 μ s, number of scans 64, acquisition time 3.744 s, repetition rate 0.3 s.

Discussion. Fig. 1 shows the molecular configuration and the atomic numbering. In Table 2 bond lengths and angles are reported. They compare well with those observed in other benzofuran derivatives. The benzofuran moiety is essentially planar, though less so than in (1) and (2). The angle between the mean plane of the benzofuran moiety and that through atoms C(10), C(11), N(2) and N(3) is about 11°. The conformation of the *N*-tosyl group is as expected (Kálmán, Czugler & Argay, 1981). The torsion angles C(2)—C(3)—N(1)—S and C(3)—N(1)—S—C(12) are -106.5 and 52.8°, respectively. One S—O bond is synperiplanar (21°) while the other is -synclinal (-33°) with respect to the phenyl group. The N(1)—S bond is anticlinal with respect to the tosyl group (79°).

There are two hydrogen bonds involving N and O atoms: one of them is intramolecular, between N(1) and N(2) [2.84 (1) Å], the other is intermolecular, between N(3) and O(3') [3.09 (1) Å] (*x*, *y*, *z* - 1). Some short intra- and intermolecular distances, involving C and O or Ni atoms, are also present. N(2)⋯C(17) [3.27 (1) Å] or C(18)⋯O(4) [3.15 (1) Å] (*x* - 1, $\frac{1}{2}$ - *y*, *z* - $\frac{1}{2}$) could be reasonably regarded as hydrogen bonds in the usual sense (Taylor & Kennard, 1982). As already found for compounds (1) and (2), also in (3), according to the geometry around the C(2)—C(10) bond, the hydrazone group assumes the *syn* configuration with respect to the phenyl group.

In DMSO solution the ¹H NMR spectrum of (3) shows a signal at 2.36 p.p.m. due to the methyl protons of the tosyl group. A complex spectral pat-

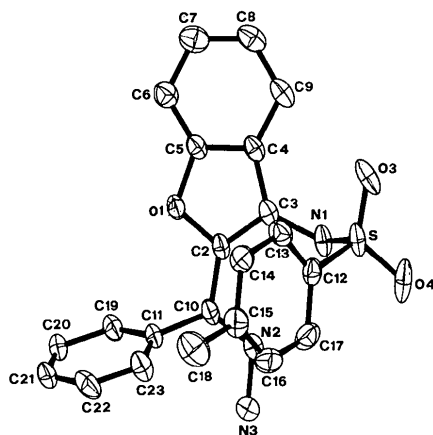


Fig. 1. A perspective view of the molecule. Ellipsoids represent 30% probability.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

O(1)—C(2)	1.385 (7)	S—O(3)	1.422 (5)
O(1)—C(5)	1.394 (7)	S—O(4)	1.430 (6)
C(2)—C(3)	1.363 (8)	S—C(12)	1.773 (6)
C(2)—C(10)	1.434 (8)	C(12)—C(13)	1.371 (8)
C(3)—N(1)	1.429 (8)	C(13)—C(14)	1.387 (11)
C(3)—C(4)	1.431 (8)	C(14)—C(15)	1.374 (10)
C(4)—C(5)	1.387 (8)	C(15)—C(16)	1.378 (11)
C(4)—C(9)	1.389 (9)	C(15)—C(18)	1.508 (12)
C(5)—C(6)	1.360 (9)	C(16)—C(17)	1.392 (11)
C(6)—C(7)	1.380 (11)	C(17)—C(12)	1.389 (9)
C(7)—C(8)	1.389 (11)	C(11)—C(19)	1.362 (9)
C(8)—C(9)	1.384 (10)	C(19)—C(20)	1.393 (10)
C(10)—C(11)	1.496 (8)	C(20)—C(21)	1.385 (10)
C(10)—N(2)	1.284 (8)	C(21)—C(22)	1.371 (11)
N(2)—N(3)	1.362 (8)	C(22)—C(23)	1.388 (10)
N(1)—S	1.658 (5)	C(23)—C(11)	1.370 (9)
C(2)—O(1)—C(5)	106.7 (5)	C(3)—N(1)—S	116.2 (3)
O(1)—C(2)—C(3)	109.6 (5)	N(1)—S—O(3)	108.1 (3)
O(1)—C(2)—C(10)	118.0 (5)	N(1)—S—O(4)	104.6 (3)
C(3)—C(2)—C(10)	132.4 (5)	N(1)—S—C(12)	106.7 (3)
C(2)—C(3)—C(4)	108.3 (5)	O(3)—S—O(4)	119.9 (4)
C(2)—C(3)—N(1)	122.8 (5)	O(3)—S—C(12)	108.3 (3)
N(1)—C(3)—C(4)	128.9 (5)	O(4)—S—C(12)	108.6 (3)
C(3)—C(4)—C(5)	105.5 (5)	S—C(12)—C(13)	118.8 (5)
C(3)—C(4)—C(9)	136.8 (6)	S—C(12)—C(17)	118.4 (5)
C(5)—C(4)—C(9)	117.7 (6)	C(13)—C(12)—C(17)	122.6 (6)
C(4)—C(5)—O(1)	109.9 (5)	C(12)—C(13)—C(14)	118.2 (6)
C(4)—C(5)—C(6)	124.7 (6)	C(13)—C(14)—C(15)	121.2 (6)
O(1)—C(5)—C(6)	125.3 (6)	C(14)—C(15)—C(16)	119.4 (7)
C(5)—C(6)—C(7)	118.8 (6)	C(14)—C(15)—C(18)	119.6 (6)
C(6)—C(7)—C(8)	120.7 (7)	C(16)—C(15)—C(18)	121.1 (7)
C(7)—C(8)—C(9)	121.1 (7)	C(15)—C(16)—C(17)	121.3 (7)
C(8)—C(9)—C(4)	119.0 (6)	C(16)—C(17)—C(12)	117.4 (6)
C(2)—C(10)—N(2)	115.8 (5)	C(19)—C(11)—C(23)	118.5 (6)
C(2)—C(10)—C(11)	119.6 (5)	C(11)—C(19)—C(20)	122.2 (6)
N(2)—C(10)—C(11)	124.6 (5)	C(19)—C(20)—C(21)	117.8 (6)
C(10)—C(11)—C(19)	121.2 (5)	C(20)—C(21)—C(22)	121.2 (7)
C(10)—C(11)—C(23)	120.3 (5)	C(21)—C(22)—C(23)	118.8 (8)
C(10)—N(2)—N(3)	119.4 (6)	C(22)—C(23)—C(11)	121.4 (7)

tern, due to the benzofuran, phenyl and tosyl rings, is present in the range 6.80–7.70 p.p.m. The signals at 7.25 (3H) and 7.45 p.p.m. (2H) are due to the protons of the phenyl group. The signals of the tosyl group are at 6.85 (2H) and 7.45 p.p.m. (2H) partly overlapped with the phenyl group. The benzofuran moiety shows signals at 7.25 (2H), 7.33 (1H) and 7.65 p.p.m. (1H). The spectral multiplicities of the different aromatic groups are similar to those exhibited in analogous compounds previously examined (Bachechi, Coiro, Gatta, Settimj & Delfini, 1988; Bachechi, Coiro, Delfini & Settimj, 1988).

The NH—tosyl and N=NH₂ hydrogen signals are at 9.20 (1H) and 6.93 p.p.m. (2H), respectively. The assignments were confirmed by two-dimensional homonuclear correlated spectroscopy (COSY) and by two-dimensional heteronuclear correlated spectroscopy (HETCOR).

In CDCl₃ solution, the ¹H NMR spectrum shows the signal due to the —NH—SO₂ group at δ = 8.90 (1H). As in compound (1), this shift indicates the presence of an intramolecular hydrogen bond, involving the —NH—SO₂ group, also in solution.

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.

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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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