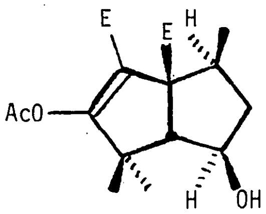
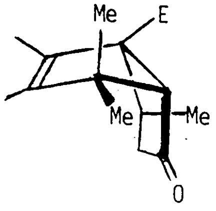
It is of interest that the hydroxyl group of (5), which is the precursor of isomer (2) and is formed as the only product from the sodium borohydride reduction of (4), must have the *exo* configuration. Usually such reactions of bicyclo[3.3.0]octan-2-ones proceed with preferential attack on the *exo* face of the ketone to give the *endo* alcohol (Tabushi, Fujita & Oda, 1970; Paquette, 1979). The exclusive formation of the *endo* product in the case of (4) may result from two factors: (i) reduced steric hindrance to *endo* attack because of an increased fold angle between the rings resulting from the presence of the ethylenic bond and (ii) increased hindrance to *exo* attack because of the secondary *exo*-methyl group. These factors apply only if this methyl group has a pseudoaxial disposition and the *endo* geminal methyl group a pseudoequatorial disposition [*cf.* (6)]. It may be noted, however, that in isomer (2) both the hydroxyl and the secondary methyl groups are pseudoequatorial with dihedral angles C(12)—C(2)···C(4)—O(2) and C(9)—C(7)···C(6)—C(13) of −46 and −21°, respectively.



(5)



(6)

(E = CO_2Me)

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Structure of *N*-(2-Acetyl-3-benzofuranyl)-*p*-toluenesulfonamide

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Abstract. $C_{17}H_{15}NO_4S$, $M_r = 329{\cdot}4$, monoclinic, $P2_1/n$, $a = 11{\cdot}574$ (5), $b = 8{\cdot}375$ (4), $c = 17{\cdot}342$ (8) Å, $\beta = 108{\cdot}0$ (3)°, $V = 1598$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}369$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}11$ cm^{-1}, $F(000) = 688$, room temperature, $R = 0{\cdot}045$ for 2777 observed counter reflections. The structure consists of two planar moieties, the benzofuran system and the *S*-aryl one, which form an angle of about 79°. There is

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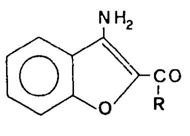
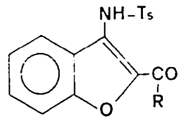
evidence for a hydrogen bond between the N atom of the –NH–SO_2 group and the O atom of the acetyl group, causing the carbonyl group to be *syn* with respect to the N atom.

Introduction. Recently new heterocyclic compounds containing a benzofuran moiety were synthetized (Gatta & Settimj, 1984) in order to check their activity on the central nervous system (Landi Vittory, Gatta, Chiavarelli & Ciriaci, 1964). For this purpose, the reactivity towards hydrazines of 2-acyl-3-aminobenzofurans (I) and of their corresponding 3-*N*-*p*-toluenesulfonylbenzofurans (II), was compared. The results obtained prompted us to study the structures of the starting and resulting compounds for a better knowledge of the different behaviour towards hydrazines of the aforementioned classes of compounds and of the mechanism of formation of the intermediate hydrazone. The present work is part of this structural investigation, carried out by X-ray diffraction and NMR spectroscopy, and reports the crystal and molecular structure of one of the starting materials allowed to react with hydrazine.[*]



(I)



(II)

R=-CH_3

R=-C_6H_5

Experimental. The compound was prepared by adding a cold solution (273 K) of *p*-toluensulfonyl chloride (10·9 g, 0·057 mol) in dry pyridine (30 ml) to a solution of 2-acetyl-3-aminobenzofuran (10 g, 0·057 mol). The resulting reddish solution was kept for 24 h in a refrigerator. The mixture was poured into ice water and the resulting precipitate collected. The crude product (14·0 g) was chromatographed on a silica gel column eluting with a 3:1 *n*-hexane–ethyl acetate mixture to yield 7·6 g of the compound (40·5%). Colourless prismatic crystals were obtained from cyclohexane solution (m.p. 406–407 K). Space group from Weissenberg photographs; crystal size 0·6 x 0·7 x 0·9 mm, Syntex $P2_1$ computer-controlled four-circle diffractometer, graphite monochromator, cell parameters by least squares from setting angles of 15 reflections with $20 \leq 2\theta \leq 30°$. Total of 4445 reflections collected in scan range $2\theta = 3–56°$ ($h = 0$ to 15, $k = 0$ to 11, $l = -22$ to 21); ω-scan mode, with scan rate depending on the intensity; three standards measured every 100 reflections, no significant change; data processed to yield values of I and $\sigma(I)$ (Bachechi, Zambonelli & Marcotrigiano, 1977); in the estimation of $\sigma(I)$ the uncertainty factor was $p = 0·0052$ as calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). Corrections for Lorentz and polarization. Of 4180 independent reflections ($R_{int} = 0·0198$), 2777 with $I \geq 3\sigma(I)$ were considered observed. The structure was solved by direct methods using *MULTAN*80 (Main *et al.*, 1980) and refined by full-matrix least squares, function minimized $w(|F_o|-|F_c|)^2$ with $w = 4F_o^2/\sigma(F_o^2)$. Heavier atoms with anisotropic thermal parameters; H atoms, included at calculated positions, with fixed coordinates and isotropic thermal parameters; the contribution of the H atom of the amide group not considered (208 parameters refined). Convergence at $R = 0·045$ ($wR = 0·045$, $S = 1·38$). $(\Delta/\sigma)_{max} = 0·06$; final difference map with no peaks exceeding 0·30 e $Å^{-3}$. All calculations performed on the HP 2100 MX minicomputer of the CNR Research Area of Rome using local programs. Scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters of the non-hydrogen atoms are given in Table 1.[*]

Table 1. *Final positional parameters* (× 10^4) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	U_{eq}(Å^2)
S	3557·7 (7)	1069·8 (9)	6863·9 (4)	0·045
O(1)	521 (2)	1600 (3)	4162 (1)	0·050
O(2)	3198 (2)	−748 (3)	4629 (1)	0·066
O(3)	4500 (2)	−79 (3)	7151 (1)	0·064
O(4)	2811 (2)	1490 (3)	7346 (1)	0·059
N	2702 (2)	263 (3)	6006 (1)	0·049
C(2)	1567 (3)	838 (4)	4619 (2)	0·047
C(3)	1744 (2)	1057 (3)	5433 (2)	0·043
C(4)	769 (2)	2033 (3)	5504 (2)	0·042
C(5)	47 (3)	2322 (4)	4705 (2)	0·046
C(6)	−1004 (3)	3212 (4)	4489 (2)	0·054
C(7)	−1344 (3)	3855 (4)	5117 (2)	0·060
C(8)	−649 (3)	3607 (4)	5927 (2)	0·060
C(9)	397 (3)	2708 (4)	6131 (2)	0·053
C(10)	2280 (3)	−56 (4)	4221 (2)	0·054
C(11)	1875 (3)	−113 (5)	3312 (2)	0·074
C(12)	4165 (2)	2829 (3)	6605 (1)	0·039
C(13)	5076 (3)	2709 (4)	6242 (2)	0·055
C(14)	5576 (3)	4107 (5)	6063 (2)	0·066
C(15)	5198 (3)	5580 (4)	6227 (2)	0·057
C(16)	4272 (3)	5665 (4)	6575 (2)	0·054
C(17)	3759 (2)	4293 (4)	6765 (2)	0·047
C(18)	5788 (4)	7073 (5)	6055 (3)	0·093

^1H NMR spectra were obtained in dimethyl sulfoxide (Me_2SO–d_6) and in $CDCl_3$ solutions at room temperature (301 K) on a Bruker WH-90 spectrometer operating at 90·1 MHz in the Fourier Transform mode. The

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[*] A preliminary account of this structure has already been given at the XV Congress of the Associazione Italiana di Cristallografia, Monteporzio Catone, Rome, 1984.

[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44410 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

concentration of the sample was 5 mg ml^{-1}. The spectral conditions were as follows: spectral width 1200 Hz, computer 8 K memory, pulse width 1·3 μs (30° pulse), number of scans 20.

Discussion. A perspective view of the molecule is shown in Fig. 1, and a selection of bond distances and angles is given in Table 2. Bond distances and angles are normal and compare well with those found in analogous compounds.

The structure consists of two planar moieties, the benzofuran system and the *S*-aryl one, which form an angle of about 79°. As evident from the angles between the relevant least-squares planes of the molecule, the spatial arrangement of the tosyl group relative to the benzofuran moiety does not differ from the majority of arylsulfonylamido compounds (Kálmán, Czugler & Argay, 1981). The N atom and the acetyl group are coplanar with the benzofuran moiety. The C(3)—N and C(2)—C(10) bond distances show a partial double-bond character as indicative of a conjugation of the N atom and the C=O group with the π system of the benzofuran moiety.

The short N···O(2) contact [2·756 (4) Å] is indicative of a hydrogen bond between the N atom and the O atom of the carbonyl group.

The values of the N—S bond distance [1·655 (3) Å] and of the two N—S—O angles [102·7 (1) and 109·1 (1)°] seem to indicate an sp^3 rather than an sp^2 hybridization of the N atom, according to the analysis of Kálmán *et al.* (1981).

The title compound can exist as *syn* or *anti* isomers. According to the geometry of the C(2)—C(10) bond the carbonyl group must be assigned the *syn* configuration with respect to the N atom.

The conformation around the N—S and S—C(12) bonds agrees with those found in other compounds possessing the *N*-tosyl fragment (Kálmán *et al.*, 1981). It is characterized by (i) coplanarity of the S atom with the tosyl group; (ii) the position of the O atoms with respect to the tosyl group so that one S—O bond is +synclinal with respect to C(12)—C(13) and the other S—O bond is —synperiplanar with respect to C(12)—C(17); (iii) the position of the N atom such that the S—N bond is anticlinal with respect to C(12)—C(13).

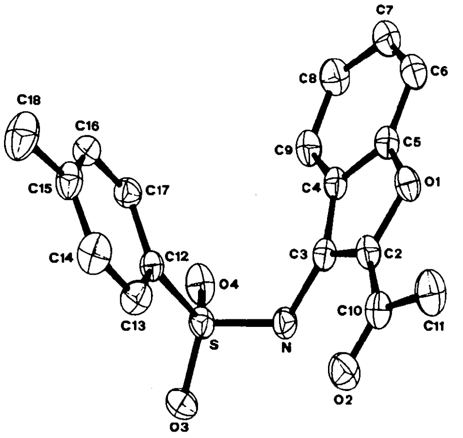

Fig. 1. Perspective view of a molecule of the title compound. The ellipsoids represent 30% probability.

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

O(1)—C(2)	1·381 (4)	C(10)—O(2)	1·225 (5)
O(1)—C(5)	1·369 (3)	N—S	1·655 (3)
C(2)—C(3)	1·374 (4)	S—O(3)	1·424 (3)
C(2)—C(10)	1·438 (4)	S—O (4)	1·420 (2)
C(3)—N	1·406 (4)	S—C(12)	1·750 (3)
C(3)—C(4)	1·429 (4)	C(12)—C(13)	1·389 (4)
C(4)—C(5)	1·400 (5)	C(13)—C(14)	1·383 (5)
C(4)—C(9)	1·407 (4)	C(14)—C(15)	1·368 (5)
C(5)—C(6)	1·376 (5)	C(15)—C(16)	1·385 (4)
C(6)—C(7)	1·377 (4)	C(15)—C(18)	1·499 (6)
C(7)—C(8)	1·402 (6)	C(16)—C(17)	1·380 (4)
C(8)—C(9)	1·376 (5)	C(17)—C(12)	1·371 (4)
C(10)—C(11)	1·500 (5)		

C(2)—O(1)—C(5)	106·0 (2)	O(2)—C(10)—C(11)	121·6 (3)
O(1)—C(2)—C(3)	110·7 (2)	C(3)—N—S	124·3 (2)
O(1)—C(2)—C(10)	119·7 (3)	N—S—O (3)	102·7 (1)
C(3)—C(2)—C(10)	129·5 (3)	N—S—O (4)	109·1 (1)
C(2)—C(3)—C(4)	107·1 (3)	N—S—C (12)	106·8 (1)
C(2)—C(3)—N	119·8 (3)	O(3)—S—O(4)	120·1 (1)
N—C(3)—C(4)	132·9 (3)	O(3)—S—C(12)	109·5 (1)
C(3)—C(4)—C(5)	105·0 (2)	O(4)—S—C(12)	108·0 (1)
C(3)—C(4)—C(9)	137·3 (3)	S—C(12)—C(13)	118·5 (2)
C(5)—C(4)—C(9)	117·7 (3)	S—C(12)—C(17)	120·7 (2)
C(4)—C(5)—O(1)	111·2 (3)	C(13)—C(12)—C(17)	120·8 (3)
C(4)—C(5)—C(6)	124·2 (3)	C(12)—C(13)—C(14)	118·0 (3)
O(1)—C(5)—C(6)	124·2 (3)	C(13)—C(14)—C(15)	122·2 (3)
C(5)—C(6)—C(7)	116·2 (3)	C(14)—C(15)—C(16)	118·6 (3)
C(6)—C(7)—C(8)	121·3 (3)	C(14)—C(15)—C(18)	121·0 (3)
C(7)—C(8)—C(9)	121·7 (3)	C(16)—C(15)—C(18)	120·4 (3)
C(8)—C(9)—C(4)	118·4 (3)	C(15)—C(16)—C(17)	120·6 (3)
C(2)—C(10)—O(2)	119·6 (3)	C(16)—C(17)—C(12)	119·8 (3)
C(2)—C(10)—C(11)	118·8 (3)		

In solution the ^{1}H NMR spectrum shows two signals at $\sigma = 2\cdot36$ (3*H*) and 2·50 p.p.m. (3*H*), due to the methyls of the tosyl and acetyl groups respectively.

In the range 7·10–8·60 p.p.m. a complicated multiplet (8*H*) due to the overlapping of the resonances of the aromatic protons of the tosyl group and of benzofuran is present. Moreover, the signal due to the —NH—SO$_2$ group is at $\delta = 9\cdot50$ p.p.m.(1*H*). This confirms the presence of an intramolecular hydrogen bond between the H atom of —NH—SO$_2$ and the O atom of acetyl —CO. In fact, when a hydrogen bond does not occur, the chemical shift of the Az—NH—SO$_2$-*A* group is in the range 7·1–7·90 p.p.m. from tetramethylsilane in CDCl$_3$ solution (*Sadtler Handbook of Proton NMR Spectra,* 1978). No splitting of the methyl of the tosyl group is present and this indicates the presence of only one conformer in solution at room temperature.

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The Structures of Polymorph I at 181 K and Polymorph II at 297 K of the Bis(water–dichloropicric acid)–1,4,7,10,13,16-Hexaoxacyclooctadecane Complex, $2[H_2O.C_6(NO_2)_3Cl_2(OH)].(CH_2CH_2O)_6$

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Abstract. $2C_6HCl_2N_3O_7.C_{12}H_{24}O_6.2H_2O$. Polymorph I, $M_r = 896·35$, monoclinic, $P2_1/a$, $a = 8·519\ (12)$, $b = 24·901\ (14)$, $c = 9·592\ (6)$ Å, $\beta = 113·46\ (9)°$, $Z = 2$, $V/Z = 933·2\ (30)$ Å^3, $D_x = 1·595\ (5)$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 4·07$ cm^{-1}, $F(000) = 920$, $T = 181\ (5)$ K, $R = 0·046$ for 4084 reflections. Polymorph II, $M_r = 896·35$, monoclinic, $C2/c$, $a = 23·069\ (7)$, $b = 12·078\ (3)$, $c = 15·740\ (2)$ Å, $\beta = 120·65\ (2)°$, $Z = 4$, $V/Z = 943·2\ (8)$ Å^3, $D_m = 1·589\ (3)$, $D_x = 1·578\ (2)$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 4·03$ cm^{-1}, $F(000) = 1840$, $T = 297\ (2)$ K, $R = 0·043$ for 1747 reflections. The structure of polymorph I at room temperature [Britton, Chantooni, Wang & Kolthoff (1984). *Acta Cryst.* C**40**, 1584–1587] is disordered and the H atoms near the O atom of the water molecule could not be found. The complex was reported as the hydronium picrate complex on chemical grounds. Polymorph II at room temperature and polymorph I at low temperature are both ordered and the H atoms have been located. Both are properly described as the water–picric acid complex. The principal difference between the two polymorphs is in the orientation of the picric acid portions with respect to the crown ring; there are no significant chemical differences. In each polymorph the complex is centrosymmetric with each water molecule weakly hydrogen bonded to two O atoms of the crown ether and strongly hydrogen bonded to the H atom of a dichloropicric acid molecule. There are no unusual bond distances or angles.

Introduction. In a previous paper (Britton, Chantooni, Wang & Kolthoff, 1984) we reported the room-temperature crystal structure of polymorph I of the title compound, which we then described, on chemical grounds, as the hydronium dichloropicrate complex (all of the H atoms involved in hydrogen bonding were disordered and not located in the structure determination). In an attempt to prepare the known complex with one water and one dichloropicric acid per crown ether we obtained crystals of a second polymorph, polymorph II, whose structure we determined and which we report here. To anticipate, the structure of polymorph II is ordered, the H atoms in the hydrogen bonds could be located and the observed structure is the water–dichloropicric acid complex. Given this result it appeared desirable to repeat the determination of the structure of polymorph I at low temperature (which was not available locally at the time of the original determination). This has been done and we also report this structure here.

Experimental. Crystals of polymorph II suitable for diffraction were obtained by dissolving the compound previously prepared from aqueous solution in a hot 1:7 1,2-dichloroethane:cyclohexane mixture and allowing the mixture to cool. D_m was measured by flotation in aqueous KI solution. Crystals of polymorph I suitable for diffraction were obtained by recrystallization from hot water; well formed crystals of both polymorphs were present in the recrystallized sample. D_m was not measured for I.

II. A crystal 0·30 × 0·30 × 0·35 mm was coated with a thin layer of epoxy cement to prevent loss of

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