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N-[2-(1-Hydrazonoethyl)-3-benzofuranyl]-*p*-toluenesulfonamide

Fiorella Bachechi,[a]* Vincenza M. Coiro[a] and Maurizio Delfini[b]

[a]*Istituto di Strutturistica Chimica 'Giordano Giacomello', CNR, Area della Ricerca di Roma, PO Box 10, I-00016 Monterotondo Stazione (Rome), Italy, and* [b]*Dipartimento di Chimica, Universitá di Roma 'La Sapienza', Rome, Italy. E-mail: fior@isc.mlib.cnr.it*

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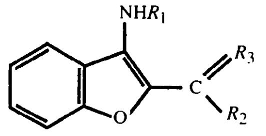
Abstract

The structure of the title compound, $C_{17}H_{17}N_3O_3S$, has been determined. It consists of two planar moieties, the benzofuran and *S*-aryl systems, which form an angle of 65.6 (1)° with one another.

Comment

Heterocyclic compounds containing a benzofuran moiety have been studied because they are active on the central nervous system. 2-Acetyl-3-aminobenzofurans and their corresponding 3-*N*-*p*-toluenesulfonyl derivatives were allowed to react with hydrazines in order to prepare the related hydrazones as starting materials for the synthesis of compounds which were expected to have psychotropic activity. Since only the *N*-*p*-toluenesulfonylbenzofurans gave hydrazones in good yield, X-ray structural investigations on the starting compounds and products of this preliminary synthesis were carried out in order to gain a better understanding of the mechanism of the reaction with hydrazines. So far, the structures of the starting compounds (1) (Bachechi, Coiro, Gatta, Settimj & Delfini, 1988) and (2) (Bachechi, Coiro, Delfini & Settimj, 1988), and of the product (3) (Bachechi, Coiro, Delfini & Settimj, 1991) have been reported. The present work deals with the crystal structure of another product, *N*-[2-(1-hydrazonoethyl)-3-benzofuranyl)]-*p*-toluenesulfonamide, (4), which was easily prepared by treatment of the acetyl derivative (1) with hydrazine.



(1) $R_1 = SO_2C_6H_4CH_3$; $R_2 = CH_3$; $R_3 = O$
(2) $R_1 = H$; $R_2 = CH_3$; $R_3 = O$
(3) $R_1 = SO_2C_6H_4CH_3$; $R_2 = CH_6H_5$; $R_3 = N{-}NH_2$
(4) $R_1 = SO_2C_6H_4CH_3$; $R_2 = CH_3$; $R_3 = N{-}NH_2$

A perspective view of (4) with the atom-numbering scheme is shown in Fig. 1. Bond distances and angles are normal and compare well with those of the analogous compounds (1), (2) and (3).

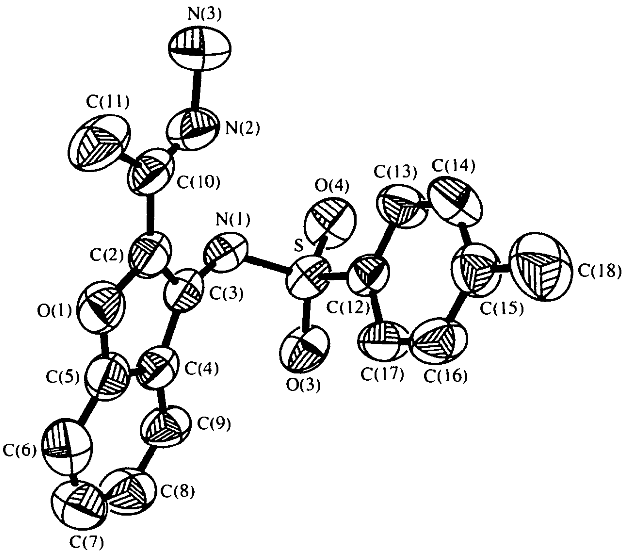


Fig. 1. A perspective view of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 30% probability level.

The structure consists of two planar moieties, the benzofuran and the *S*-aryl systems, which form an angle of 65.6 (1)° with one another. The benzofuran moiety can be considered planar as is the case in the corresponding starting compound, (1). The mean plane through the benzofuran ring forms an angle of 3.5 (1)° with the plane through atoms C(10), C(11), N(2) and N(3) (Table 3). The C=N double bond thus lies in the plane of the benzofuran moiety.

An intramolecular hydrogen bond of 2.817 (4) Å is present between atoms N(1) and N(2). The hydrazone group assumes a *syn* configuration with respect to N(1) around the C(2)—C(10) bond and an *anti* configuration around the C(10)—N(2) bond, as in the analogous compound (3).

Considering the structures of the four compounds, (1), (2), (3) and (4), some similar features are evident. They have a *syn* configuration of the hydrazone or carbonyl group around the C(2)—C(10) bond and an intramolecular hydrogen bond between N(1) and the O atom of the carbonyl group in compounds (1) and (2), and between N(1) and atom N(2) of the hydrazone group in compounds (3) and (4). In addition, in the *S*-aryl derivatives (1), (3) and (4), the C(3)—N(1)—$SO_2C_6H_4CH_3$ moieties are similarly oriented, as seen from the values of C(3)—N(1)—S—C(12) (~−55°) and N(1)—S—C(12)—C(13) (~−85°) (Table 3).

Quite surprisingly, the main differences between the four compounds relate to the benzofuran system and, in the toluenesulfonyl derivatives (1), (3) and (4), its conformation around the N(1)—C(3) bond. These differences can be rationalized only when correlated with the hydrogen bonding present in the four compounds. In the starting compounds (1) and (2), the N(1)···O(2) distances have obviouslyly different values [2.756 (4) in (1) and 2.853 (3) Å in (2)] while in the products (3) and (4), the N(1)···N(2) distances have intermediate values [2.843 (6) in (3) and 2.817 (4) Å in (4)]. As shown in Table 3, as the strength of the hydrogen-bond increases in the sequence (3) → (4) → (1), there is a large increase in the value of the S—N(1)—C(3)—C(2) torsion angle which brings the H atom closer to the acceptor. Other structural parameters can be related to the strength of the hydrogen bond, for example, the S—N(1)—C(3) and N(1)—C(3)—C(2) angles, and the angle between the benzofuran plane and the plane through the substituent at C(2). Their variations in the sequence (2) → (3) → (4) → (1) also favour the directionality of the hydrogen bond as can be seen from the values of the N(1)—H···*X* angle [*X* is O(2) in compounds (1) and (2), and N(2) in (3) and (4)] and from the degree of coplanarity between the plane of the substituents at N(1) [C(3), N(1), S(1)] and that of the hydrogen-bond acceptor [*i.e.* C(2), C(10), C(11) R_3 (considered the plane of the lone pair)] (Table 3).

Only a few structural features are of interest in the starting materials (1) and (2). The main difference between them is seen in the N(1)···O(2) hydrogen-bond distance, which may indicate a lower tendency towards hydrogen-bond interaction of the carboxyl group in compound (2). The poor polarizability of the C=O bond in compound (2), which is lost in the *N*-*p*-toluenesulfonyl derivative, (1), may also account for the observed difference in reactivity towards hydrazine of the two starting materials.

Experimental

The title compound was prepared by adding 98% hydrazine hydrate to a warm solution of compound (1) in 50% aqueous ethanol. The resulting solution was then allowed to stand for 2 h at room temperature and then overnight in a refrigerator. Small crystals of (4) were obtained from $CHCl_3$/methanol solution.

Crystal data

$C_{17}H_{17}N_3O_3S$
$M_r = 343.4$
Monoclinic
$P2_1/n$
$a = 8.160 (2)$ Å
$b = 22.289 (4)$ Å
$c = 9.461 (2)$ Å
$\beta = 96.51 (3)°$
$V = 1709.6 (6)$ Å^3
$Z = 4$
$D_x = 1.334$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14–18°$
$\mu = 0.21$ mm^{-1}
$T = 295$ K
Prism
0.5 × 0.3 × 0.2 mm
Transparent colourless

Data collection

Syntex $P2_1$ four-circle diffractometer
Profile data from ω scans
Absorption correction: none
6681 measured reflections
4543 independent reflections
2289 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.0336$
$\theta_{\rm max} = 28.0°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 29$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0525$
$wR = 0.0593$
$S = 1.0785$
2289 reflections
285 parameters
Weighting scheme based on measured e.s.d.'s; $w = 1/[\sigma^2(F^2)]$

$(\Delta/\sigma)_{\rm max} = 0.153$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.2C, 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S(1)	0.88417 (9)	0.12343 (4)	0.30650 (8)	4.0
N(1)	0.9306 (3)	0.0741 (1)	0.1877 (3)	4.0
N(2)	0.8897 (4)	0.0964 (1)	−0.1073 (3)	5.2
N(3)	0.9154 (4)	0.1305 (2)	−0.2271 (3)	6.8
O(1)	0.6760 (3)	−0.0344 (1)	−0.0160 (2)	4.7
O(3)	0.8569 (3)	0.0913 (1)	0.4324 (2)	5.1
O(4)	1.0133 (3)	0.1672 (1)	0.3112 (3)	5.6
C(2)	0.7674 (3)	0.0177 (1)	0.0005 (3)	3.9
C(3)	0.8213 (3)	0.0271 (1)	0.1407 (3)	3.6
C(4)	0.7641 (3)	−0.0221 (1)	0.2201 (3)	3.8
C(5)	0.6751 (4)	−0.0579 (1)	0.1179 (3)	4.4
C(6)	0.5973 (4)	−0.1103 (2)	0.1487 (4)	5.9
C(7)	0.6169 (5)	−0.1282 (2)	0.2904 (4)	6.4
C(8)	0.7097 (4)	−0.0942 (2)	0.3936 (4)	6.0
C(9)	0.7818 (4)	−0.0414 (2)	0.3626 (3)	4.8
C(10)	0.7977 (4)	0.0498 (2)	−0.1278 (3)	4.4
C(11)	0.7251 (4)	0.0259 (2)	−0.2697 (3)	6.1
C(12)	0.6978 (3)	0.1584 (3)	0.2411 (3)	3.6

C(13)	0.6993 (4)	0.2065 (3)	0.1483 (3)	4.8
C(14)	0.5540 (4)	0.2337 (4)	0.0978 (4)	5.5
C(15)	0.4045 (4)	0.2148 (3)	0.1388 (3)	4.8
C(16)	0.4058 (4)	0.1667 (4)	0.2311 (4)	5.4
C(17)	0.5518 (4)	0.1385 (3)	0.2828 (3)	4.6
C(18)	0.2444 (4)	0.2440 (4)	0.0794 (4)	7.2

Table 2. *Selected geometric parameters (Å, °)*

S(1)—N(1)	1.648 (3)	C(4)—C(9)	1.407 (4)
S(1)—O(3)	1.428 (2)	C(5)—C(6)	1.378 (5)
S(1)—O(4)	1.433 (3)	C(6)—C(7)	1.390 (6)
S(1)—C(12)	1.758 (3)	C(7)—C(8)	1.390 (5)
N(1)—C(3)	1.413 (4)	C(8)—C(9)	1.362 (5)
N(2)—N(3)	1.401 (4)	C(10)—C(11)	1.502 (4)
N(2)—C(10)	1.284 (5)	C(12)—C(13)	1.387 (4)
O(1)—C(2)	1.379 (4)	C(12)—C(17)	1.370 (4)
O(1)—C(5)	1.372 (4)	C(13)—C(14)	1.369 (5)
C(2)—C(3)	1.366 (4)	C(14)—C(15)	1.387 (5)
C(2)—C(10)	1.453 (4)	C(15)—C(16)	1.381 (5)
C(3)—C(4)	1.438 (4)	C(15)—C(18)	1.510 (5)
C(4)—C(5)	1.392 (4)	C(16)—C(17)	1.386 (4)
O(3)—S(1)—N(1)	107.7 (1)	C(6)—C(5)—O(1)	124.8 (3)
O(4)—S(1)—N(1)	104.5 (1)	C(6)—C(5)—C(4)	123.7 (3)
O(4)—S(1)—O(3)	119.9 (1)	C(7)—C(6)—C(5)	116.3 (3)
C(12)—S(1)—N(1)	108.2 (1)	C(8)—C(7)—C(6)	121.0 (4)
C(12)—S(1)—O(3)	107.8 (1)	C(9)—C(8)—C(7)	122.3 (3)
C(12)—S(1)—O(4)	108.2 (1)	C(8)—C(9)—C(4)	118.1 (3)
C(3)—N(1)—S(1)	121.6 (2)	C(2)—C(10)—N(2)	115.1 (3)
C(10)—N(2)—N(3)	117.1 (3)	C(11)—C(10)—N(2)	125.8 (3)
C(5)—O(1)—C(2)	106.0 (2)	C(11)—C(10)—C(2)	119.1 (3)
C(3)—C(2)—O(1)	110.5 (2)	C(13)—C(12)—S(1)	119.7 (2)
C(10)—C(2)—O(1)	117.4 (2)	C(17)—C(12)—S(1)	120.1 (2)
C(10)—C(2)—C(3)	132.0 (3)	C(17)—C(12)—C(13)	120.2 (3)
C(2)—C(3)—N(1)	122.8 (3)	C(14)—C(13)—C(12)	119.6 (3)
C(4)—C(3)—N(1)	129.2 (2)	C(15)—C(14)—C(13)	121.5 (3)
C(4)—C(3)—C(2)	107.6 (3)	C(16)—C(15)—C(14)	117.9 (3)
C(5)—C(4)—C(3)	104.4 (2)	C(18)—C(15)—C(14)	121.1 (3)
C(9)—C(4)—C(3)	136.9 (3)	C(18)—C(15)—C(16)	121.0 (3)
C(9)—C(4)—C(5)	118.6 (3)	C(17)—C(16)—C(15)	121.4 (3)
C(4)—C(5)—O(1)	111.5 (3)	C(16)—C(17)—C(12)	119.4 (4)

Table 3. *Geometric parameters (Å, °) of the related benzofuran derivatives (1), (2), (3) and (4)*

The atoms used to calculate the mean planes are in square brackets. R_3 is one of the substituents at C(10) (see *Scheme*). *X* is O(2) in compounds (1) and (2), and N(2) in compounds (3) and (4).

	(1)	(4)	(3)	(2)
[O(1)–C(9)]^ [S(1), C(12)–C(17)]	77.4 (1)	65.6 (1)	46.1 (2)	
[O(1)–C(9)]^ [C(11), C(10), R_3]	0.7 (1)	3.5 (1)	11.1 (2)	7.9 (1)
C(3)—N(1)—S—C(12)	−55.2 (3)	−57.4 (3)	−52.8 (4)	
N(1)—S—C(12)—C(13)	−72.9 (3)	−83.7 (4)	−95.2 (4)	
N(1)—S—C(12)	106.8 (1)	108.2 (1)	106.7 (3)	
S—N(1)—C(3)—C(2)	140.8 (3)	124.8 (2)	106.5 (3)	
N(1)—H···*X*	2.756 (4)	2.817 (4)	2.843 (6)	2.853 (3)
S—N(1)—C(3)	124.3 (2)	121.6 (2)	116.2 (3)	
C(2)—C(3)—N(1)	119.8 (3)	122.8 (3)	122.8 (5)	126.4 (3)
N(1)—H···*X*	106	92	80	
[C(2), C(10), C(11), R_3]^ [C(3), N(1), S(1)]	41.2 (1)	56.1 (1)	79.5 (2)	

The structure was solved by direct methods (*SHELXTL-Plus*; Sheldrick, 1991) and refined by full-matrix least-squares methods. All the non-H atoms were refined anisotropically. The H atoms of the methyl groups were introduced at geometrically idealized positions. All other H atoms could be located on a difference Fourier map. All H atoms were refined riding on their parent atoms.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1246). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Polymorphic Forms of 3-Hydroxy-2-methyl-4*H*-pyran-4-one (Maltol)

JOHN BURGESS,[a] JOHN FAWCETT,[a] DAVID R. RUSSELL,[a] ROBERT C. HIDER,[b] M. BILAYET HOSSAIN,[c] CINDY R. STONER[c] AND DICK VAN DER HELM[c]

[a]*Department of Chemistry, University of Leicester, Leicester LE1 7RH, England,* [b]*School of Life, Basic Medical and Health Sciences, Kings College London, Campden Hill Road, Kensington, London W8 7AH, England, and* [c]*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, USA. E-mail: jxf@leicester.ac.uk*

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Abstract

The crystal structures of two polymorphic forms of maltol, $C_6H_6O_3$, have been determined. The polymorphs exhibit different crystal-packing arrangements through intermolecular hydrogen bonding involving the hydroxyl H atoms. Form (1) has a near-planar chain of molecules linked by hydrogen bonds while form (2) has mutually hydrogen-bonded dimers. In both polymorphic forms there are also weaker C—H···O bonds which give greater stability to the chains of form (1) and link the dimers in form (2).

Comment

In the structures of both polymorphic forms, the hydroxyl atoms H1 bonded to the O1 atoms are involved in intermolecular hydrogen bond to a carbonyl atom, O2. In the case of polymorph (1), there are two crystallographically unique molecules (*A* and *B*) arranged

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