Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1324). Services for accessing these data are described at the back of the journal.

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X-ray investigations of sulfur-containing fungicides. I. 4′-{[Benzoyl(4-tolyl-hydrazono)methyl]sulfonyl}acetanilide

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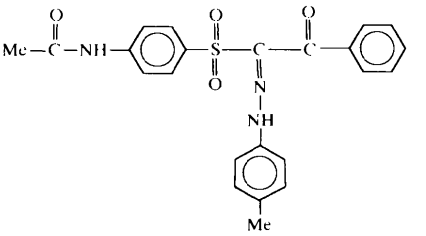
Abstract

The conformation of the title compound, $C_{23}H_{21}N_3O_4S$, is stabilized by a strong intramolecular hydrogen bond assisted by resonance connecting the hydrazone moiety and the sulfonyl group. The most important electronic interaction is electrostatic attraction of the oppositely charged carbonyl and sulfonyl groups which counteracts the strongly electron-withdrawing character of the latter group.

Comment

Sulfones, similarly to sulfonamides, show strong *in vitro* and *in vivo* antibacterial activity and for almost 60 years have been used successfully in medicine (Mandell & Sande, 1985). Certain sulfones also exhibit fungicidal activity. Preliminary tests have proved that substituted (2-oxo-2-phenylethyl) phenyl sulfones show fungicidal activity comparable to, or better than, commercial fungicides (Zakrzewski, 1996). The present work is part of a larger project in which we aim to identify molecular features which are responsible for the antimycotic action and to construct the best fungicide. The most effective way to fight fungi is to attack spores before they manage to germinate (Hassall, 1982). This requires long and continuous action of a fungicide. The goal of this project is to construct compounds which undergo slow photodynamic degradation in the presence of daylight and reduce themselves to compounds similar to (2-oxo-2-phenylethyl) phenyl sulfones. Although there are almost 100 β-keto sulfones in the Cambridge Structural Database (Allen *et al.*, 1979), to the best of my knowledge there has been no X-ray structure determination so far of the α-hydrazone-β-keto sulfones described in the scientific literature.



(I)

A view of the title compound (I) with atom numbering is shown in Fig. 1. The S=O2 sulfonyl double bond, the carbonyl group and the *p*-methylphenylhydrazone moiety are roughly coplanar. The molecular conformation of these three fragments is similar to that observed in β-diketo-arylhydrazones (Bertolasi, Gilli *et al.*, 1994) and can be defined as *EZE*. The three-letter symbol was initially introduced to describe the conformation of 2,2-diacylethenamines (Gómez-Sánchez *et al.*, 1987) and was further applied to β-diketo-arylhydrazones. In the title compound, the above three letters indicate, relative to the C1=N1 bond, the positions of the carbonyl C2=O3 and the sulfonyl S=O2 double bonds as well as the N2—C17 bond bearing the aryl substituent.

The central part of the molecule is stabilized by a strong intramolecular hydrogen bond, assisted by resonance (RAHB), connecting the hydrazone moiety and the sulfonyl group. With two π bonds and an n_p nitrogen lone pair this practically planar (mean deviation from the O2,S,C1,N1,N2,H2 plane is 0.03 Å) cyclic system follows Hückel's rule of aromaticity (March, 1992). Although several publications exist on

the strong intramolecular resonance-assisted hydrogen bonds connecting the hydrazone and carbonyl groups (Bertolasi, Nanni *et al.*, 1994, and references therein), to the best of my knowledge there have been no reports on similar planar cyclic systems in which the carbonyl group is replaced by a sulfonyl moiety.

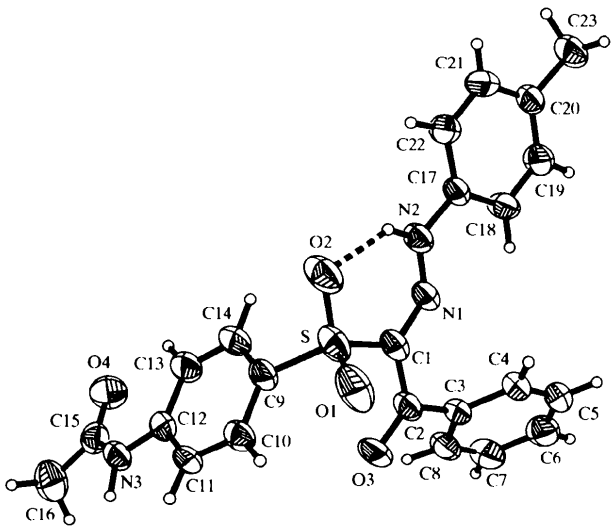


Fig. 1. Molecular structure of compound (I). Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is indicated by a dashed line.

The separation of the carbonyl-O3 and sulfonyl-S atoms [2.955 (2) Å] is less than the sum of their respective van der Waals radii (3.32 Å; Bondi, 1964). Shortening of this interatomic distance has often been observed in α,α-unsubstituted β-ketosulfones and is usually explained by hyperconjugative cross-interaction involving the π^*(C=O3)—σ(S—C1) and π(C=O3)—σ^*(S—C1) pairs of bonding and non-bonding molecular orbitals (Dal Colle *et al.*, 1995; Distefano *et al.*, 1996, and references therein). According to general theory of the anomeric effect (Kirby, 1983; Juaristi & Cuevas, 1992), the largest overlapping of these orbitals should occur when the interacting polar bonds are situated in the *gauche* position. However, in compound (I) the S—C1 and C2=O3 bonds are almost *syn*-periplanar [the S—C1—C2—O3 torsion angle is 7.7 (3)°]. The only existing *gauche* interactions involve S=O1 with the C1—C2 and C1—N1 bonds. The former is not a typical polar bond while the latter already participates in strong RAHB. In addition, the O1···N1 non-bonding distance [3.681 (2) Å] is much longer than the sum of the respective van der Waals radii (3.07 Å). Therefore, the main electronic interaction should be the Coulombic type, electrostatic attraction of the negatively charged carbonyl group and the highly positive S atom. This effect counteracts the strong electron-withdrawing character of the phenylsulfonyl group as confirmed by the highly positive value of its Hammett σ constant (0.70; Hansch & Leo, 1979).

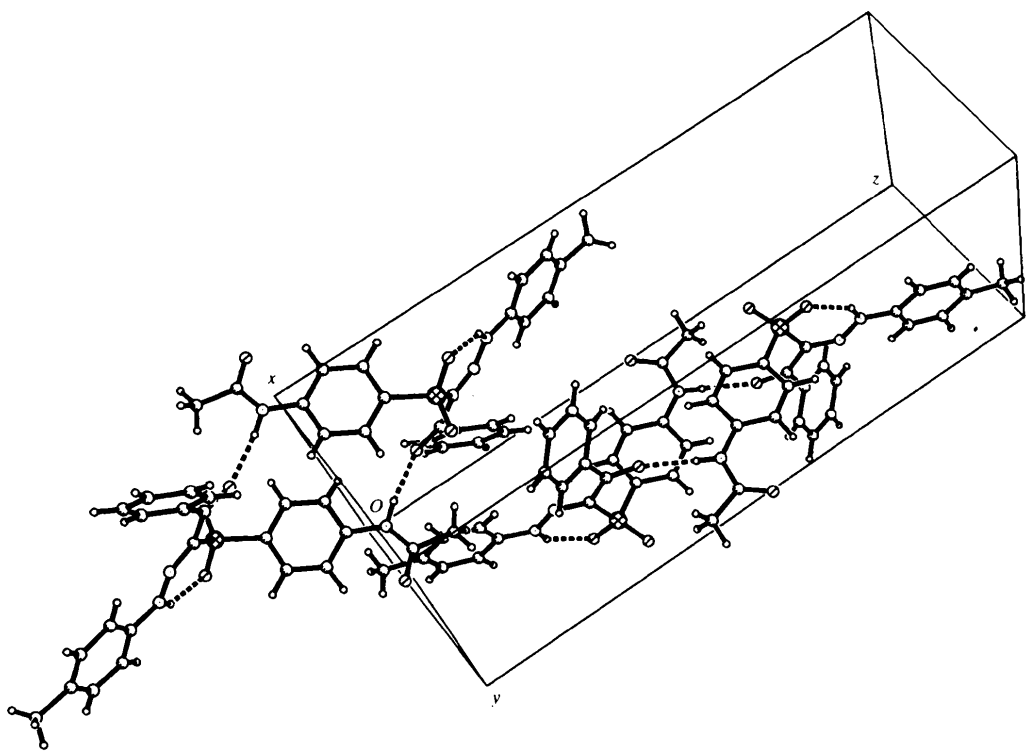


Fig. 2. Packing diagram showing centrosymmetric dimers linked by intermolecular hydrogen bonds. Hydrogen bonds are indicated by dashed lines.

Bond lengths are consistent with values reported in *International Tables for Crystallography* (Allen *et al.*, 1992), and indicate the high level of electron-density delocalization which exists within the carbonyl group and the hydrazone moiety. The main exception is the S—C1 bond [1.795 (2) Å] which is longer than a typical S—Csp^3 single bond (1.779 Å; Allen *et al.*, 1992). The lengthening of this bond, along with the relatively short C1—C2 bond [1.462 (3) Å] resembles the characteristic bond-length changes induced by the anomeric effect. It suggests that, despite the unfavoured *syn*-periplanar arrangement, there is a weak stereoelectronic interaction which is responsible for the electron-density transfer from the sulfonyl towards the carbonyl group. The carbonyl group is not coplanar with the terminal phenyl ring. Also, the C2—C3 bond length [1.499 (3) Å] is closer to the value reported for a Csp^3—C$_{aryl}$ (1.506 Å) than a Csp^2—C$_{aryl}$ bond (1.470 Å) (Allen *et al.*, 1992). Therefore, the stereoelectronic and π delocalizations involving the carbonyl group are directed towards the sulfonyl and hydrazone moieties to such an extent that the influence of the terminal phenyl group is limited to an inductive effect only.

Molecules of compound (I) form centrosymmetric dimers which are connected by intermolecular hydrogen bonds involving the β-carbonyl O3 atoms and the N3—H3 bonds of the terminal acetamide moieties, details are summarized in Table 2. In terms of Etter's graph-set terminology (Etter, 1990), this bond system can be described as $R_2^2(20)$. Outside the hydrogen bonding regions, the packing arrangement is not influenced significantly by steric interactions as identified by sums of the respective van der Waals radii (Fig. 2).

Experimental

Compound (I) was synthesized by reaction of *p*-acetanilidephenacyl sulfone with *p*-toluenediazonium chloride in alkaline ethyl alcohol solution (Zakrzewski, 1996). Crystals used for the data collection were obtained by vapour diffusion. A sample of (I) dissolved in a 3:1 mixture of chloroform and isopropyl alcohol was equilibrated at room temperature against pure isopropyl alcohol for ten days.

Crystal data

$C_{23}H_{21}N_3O_4S$
M_r = 435.49
Monoclinic
$P2_1/n$
a = 11.687 (2) Å
b = 7.576 (1) Å
c = 24.153 (3) Å
β = 95.91 (1)°
V = 2127.2 (5) Å^3
Z = 4
D_x = 1.360 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 45 reflections
θ = 5–14.5°
μ = 0.188 mm^{-1}
T = 293 (2) K
Prism
0.60 × 0.50 × 0.35 mm
Yellow

Data collection

Siemens *P*3 diffractometer
ω–2θ scans
Absorption correction: none
5897 measured reflections
4821 independent reflections
3666 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 27.56°
h = −15 → 15
k = −1 → 9
l = −1 → 31
3 standard reflections
every 97 reflections
intensity decay: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.171
S = 1.020
4821 reflections
364 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.112P)^2 + 0.4735P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.026
$\Delta\rho_{max}$ = 0.260 e Å^{-3}
$\Delta\rho_{min}$ = −0.344 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S—O1	1.435 (2)	N1—C1	1.314 (2)
S—O2	1.4453 (19)	N2—C17	1.412 (2)
S—C9	1.754 (2)	O3—C2	1.229 (2)
S—C1	1.795 (2)	C1—C2	1.462 (3)
N1—N2	1.296 (2)	C2—C3	1.499 (3)
O1—S—O2	118.03 (12)	N1—N2—C17	119.72 (16)
O1—S—C9	108.68 (10)	N1—C1—C2	117.71 (17)
O2—S—C9	108.61 (11)	N1—C1—S	124.84 (16)
O1—S—C1	109.07 (11)	C2—C1—S	117.45 (14)
O2—S—C1	105.41 (9)	O3—C2—C1	119.92 (18)
C9—S—C1	106.44 (10)	O3—C2—C3	118.81 (19)
N2—N1—C1	125.16 (17)	C1—C2—C3	121.25 (16)
S—C1—C2—O3	7.7 (3)	O1—S—C1—N1	−120.00 (19)
S—C1—N1—N2	−2.3 (3)	O2—S—C1—C2	−172.10 (17)
O1—S—C1—C2	60.24 (19)	O2—S—C1—N1	7.7 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O2	0.90 (3)	1.91 (3)	2.654 (3)	139 (3)
N3—H3···O3^i	0.90 (2)	2.06 (2)	2.949 (3)	169 (2)

Symmetry code: (i) 1 − x, −y, −z.

All H atoms were located on a difference Fourier map calculated after three cycles of anisotropic refinement. Their positional and isotropic displacement parameters were allowed to refine freely. Two reflections recognized as outliers were not included into the refinement.

Data collection: *P*3 *Diffractometer Control Program* (Siemens, 1989). Cell refinement: *P*3 *Diffractometer Control Program*. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SYBYL* (TRIPOS, 1996) and *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1293). Services for accessing these data are described at the back of the journal.

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Intermolecular C—H···N and C—H···O interactions in (2*S*,4*S*,5*R*)-(−)-3,4-dimethyl-5-phenyl-2-(1,3-thiazol-2-yl)-1,3-oxazolidine

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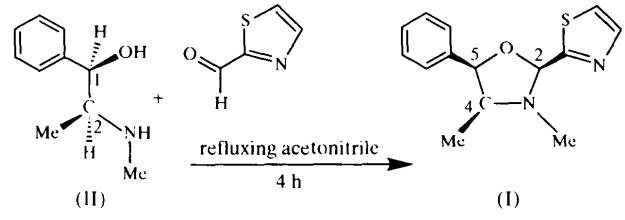
Abstract

The title compound, $C_{14}H_{16}N_2OS$, prepared from (1*R*,2*S*)-(−)-ephedrine, contains the oxazolidine ring in an envelope conformation, with the nitrogen atom 0.623 (2) Å from the plane of the other four oxazolidine-ring atoms. Intermolecular C—H···N and C—H···O interactions generate a two-dimensional hydrogen-bonded network, with shortest C···N and C···O distances of 3.403 (3) and 3.463 (2) Å, respectively.

Comment

Amino acid derivatives continue to be an important class of chiral compounds with applications in asymmetric synthesis and catalysis. The title compound, (I), a derivative of (1*R*,2*S*)-(−)-ephedrine, (II), is of current interest as a chiral auxiliary and as a new potentially bidentate ligand with an O,N or O,S donor-atom set for use in coordination chemistry.



(II) (I)

Bond lengths and angles are unexceptional and in accord with anticipated values (Orpen *et al.*, 1994). The absolute structure can be deduced from (II) and by analysis of our X-ray data. The oxazolidine ring adopts an envelope conformation with N3 0.623 (2) Å from the (O1,C2,C4,C5) plane, which is at angles of 74.18 (6) and 86.99 (6)° to the phenyl and thiazole rings, respectively. The phenyl ring is oriented at an angle of 41.15 (8)° to the thiazolyl group. The molecular geometry in (I) compares with (2*S*,4*S*,5*R*)-(−)-2-(1*H*-imidazol-2-yl)-3,4-dimethyl-5-phenyl-1,3-oxazolidine, (III) (Gallagher