

4'-[[Benzoyl(4-nitrophenylhydrazono)methyl]-
sulfonyl]acetanilide

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Key indicators

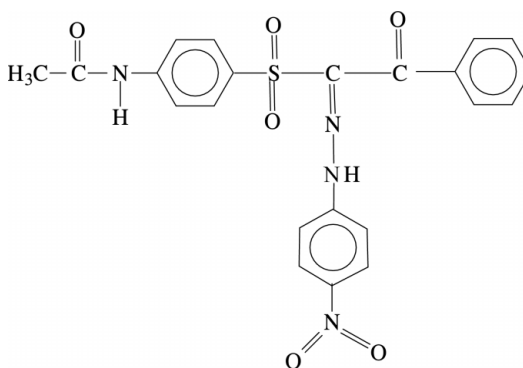
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$
 R factor = 0.056
 wR factor = 0.180
Data-to-parameter ratio = 7.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The conformation of the title compound, $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_6\text{S}$, is stabilized by a strong resonance-assisted intramolecular hydrogen bond linking the hydrazone moiety and the sulfonyl group. The resulting six-membered ring is practically planar. Short intramolecular contacts link oppositely charged atoms of the sulfonyl and β -carbonyl groups. The crystal packing is influenced by intermolecular hydrogen bonds involving the β -carbonyl O atoms and the N—H bonds of the terminal acetamide moieties.

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Comment

The present work is part of a project aimed at structural studies of modified β -ketosulfones. The investigated compounds have bactericidal and fungicidal activity (Zakrzewski & Kacała, 1998; Zakrzewski, 1999). In this paper, the X-ray structure of 4'-[[benzoyl(4-nitrophenylhydrazono)methyl]sulfonyl]acetanilide, (I), is reported. The title compound, (I), shows a high rate of photodynamic decay. Freshly grown crystals decompose within approximately two weeks of being exposed to daylight.



(I)

The solid-state conformation of all five α -phenylhydrazone- β -ketosulfones reported in the scientific literature (Wolf, 1999, 2001*a,b*) are constrained either by strong intramolecular resonance-assisted hydrogen bonds (abbreviated hereafter RAHB) (Jeffrey, 1997) or by non-stereospecific electrostatic attraction of the oppositely charged sulfonyl S and β -carbonyl C atoms. Electron-withdrawing terminal substituents linked to the α -phenylhydrazone group restrict the electron-density transfer from the hydrazone moiety towards the positively charged S and β -carbonyl C atoms. This effect strengthens the RAHB and prompts the simultaneous intensification of the intramolecular electrostatic attraction (Wolf, 2001*a*, and references therein).

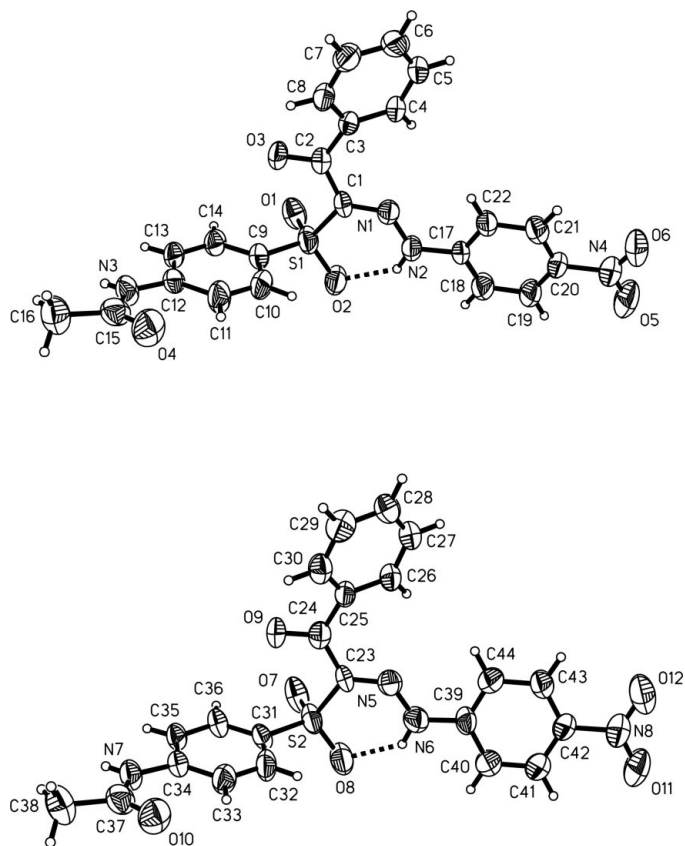


Figure 1

The molecular structures of both molecules of the asymmetric unit of (I). The displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bonds are indicated by dashed lines.

Compound (I) crystallizes in the triclinic space group $P\bar{1}$. Two molecules constitute the asymmetric unit. A view with the atom-numbering is shown in Fig. 1. The superposition of both independent molecules clearly reveals the strong similarity of their conformations (Fig. 2). The root-mean-square deviation calculated from the least-squares fit of all respective non-H atoms is 0.23 Å.

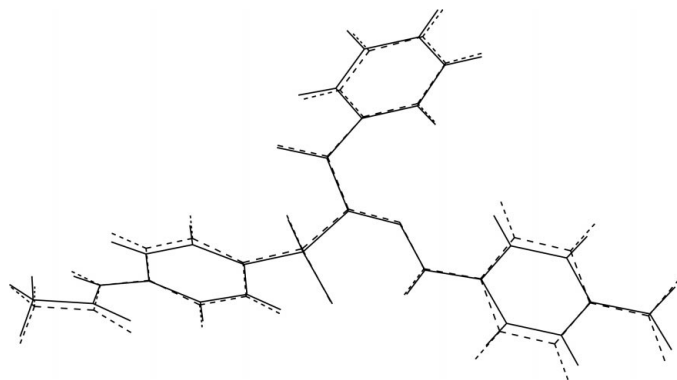


Figure 2

The superposition of both molecules of the asymmetric unit of (I). The second molecule is shown with dashed lines. The least-squares fit was based on all non-H atoms.

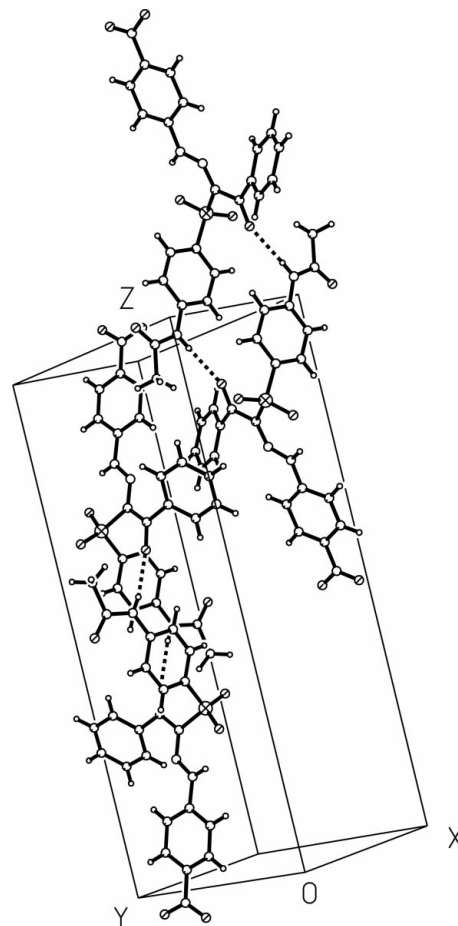


Figure 3

The packing diagram showing centrosymmetric dimers linked by intermolecular hydrogen bonds. Hydrogen bonds are indicated by dashed lines.

In both independent molecules, one of the sulfonyl double bonds (S1=O2 and S2=O8), the β -carbonyl groups and the phenylhydrazone moieties are approximately coplanar. According to Bertolasi *et al.* (Bertolasi, Gilli *et al.*, 1994; Bertolasi, Nanni *et al.*, 1994), their configuration may be defined as *EZE*. The three letters indicate, relative to the C=N bond, the positions of the carbonyl C=O and sulfonyl S=O double bond, as well as the N–C bond bearing the phenyl ring.

Central fragments of both molecules are fixed by the strong intramolecular RAHB's. These bonds connect the hydrazone and sulfonyl groups. The six-membered RAHB rings in both molecules are practically planar; the root-mean-square deviations from the O2/S1/C1/N1/N2/H2 and O8/S2/C23/N5/N6/H61 planes are 0.05 and 0.04 Å, respectively. The intramolecular N2...O2 and N6...O8 distances [2.620 (6) and 2.651 (7) Å, respectively] are much shorter than the sum of the respective van der Waals radii, 3.07 Å (Bondi, 1964).

Large positive atomic charges are located on atoms S1, S2, C2 and C24 (1.32, 1.31, 0.51 and 0.50 e, respectively). All O atoms are negatively charged. The atomic charges of O1, O2

and O3 range between -0.53 and -0.71 e. The electrostatic potential derived atomic charges were calculated, with *GAUSSIAN98* (Frisch *et al.*, 1998) at the *RHF/6-311+G(d,p)* level for the X-ray determined coordinates. Grid points were selected according to the *CHELPG* procedure of Breneman & Wiberg (1990). Electrostatic attraction of the oppositely charged atoms generates intramolecular contacts between $S \cdots O3$ and $O1 \cdots C2$ atom pairs; details are summarized in Table 2.

The bond-length distribution in (I) is close to that observed in all related compounds (Wolf, 1999, 2000, 2001*a,b*). In particular, the $S1-C1$ and $S2-C23$ bonds are longer [1.793 (6) and 1.783 (6) Å, respectively] than the conventional $S-Csp^2$ single bond, 1.751 Å (Allen *et al.*, 1992). Similar bond elongation in all α -phenylhydrazono- β -ketosulfones was explained by the hyperconjugative (Juaristi & Cuevas, 1995; Graczyk & Mikołajczyk, 1994; Cramer, 1996) interactions involving $\sigma(S-C1) - \pi^*(C=O3)$ bonding and non-bonding atomic orbitals. Similar intramolecular interactions were also observed in α -unsubstituted β -ketosulfones and β -keto-sulfoxides (Distefano *et al.*, 1991, 1996; Dal Colle *et al.*, 1995; Olivato *et al.*, 1998, 2000; Wolf, 2001*c*).

In the crystal lattice, molecules of (I) form elongated centrosymmetric dimers, which are connected by intermolecular hydrogen bonds involving the β -carbonyl atoms O3 and O7, and the $N3-H3$ and $N7-H71$ bonds of the terminal acetamide moieties (Fig. 3). According to Etter's graph-set terminology (Etter *et al.*, 1990; Bernstein *et al.*, 1995), these bond systems can be described as $R_2^2(20)$.

Experimental

The title compound was synthesized by the reaction of *p*-acetanilide benzoylmethyl sulfone with 4-nitrophenyldiazonium chloride. The reaction was carried out in alkaline ethyl alcohol solution (Zakrzewski, 1996). The crystal used for data collection was obtained by vapour diffusion; the sample was dissolved in a 2:1 mixture of chloroform and isopropyl alcohol and equilibrated at room temperature against pure isopropyl alcohol for 15 d.

Crystal data

$C_{22}H_{18}N_4O_6S$	$Z = 4$
$M_r = 466.46$	$D_x = 1.454 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 7.461$ (1) Å	Cell parameters from 50 reflections
$b = 11.663$ (2) Å	$\theta = 5-25^\circ$
$c = 24.621$ (5) Å	$\mu = 1.78 \text{ mm}^{-1}$
$\alpha = 94.31$ (3)°	$T = 293$ (2) K
$\beta = 90.88$ (3)°	Ellipsoid, yellow
$\gamma = 94.01$ (3)°	$0.45 \times 0.35 \times 0.35 \text{ mm}$
$V = 2130.7$ (6) Å ³	

Data collection

Kuma KM-4 diffractometer	$R_{\text{int}} = 0.052$
$\omega-2\theta$ scans	$\theta_{\text{max}} = 50.1^\circ$
Absorption correction: ψ scan	$h = -7 \rightarrow 7$
(<i>XEMP</i> ; Siemens, 1989)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.463$, $T_{\text{max}} = 0.537$	$l = 0 \rightarrow 24$
4490 measured reflections	3 standard reflections
4354 independent reflections	every 100 reflections
2363 reflections with $I > 2\sigma(I)$	intensity decay: 46%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1040P)^2 + 0.8456P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.180$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
4354 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
596 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0027 (4)

Table 1

Selected geometric parameters (Å, °).

$S1-O1$	1.440 (5)	$S2-O7$	1.439 (5)
$S1-O2$	1.445 (4)	$S2-O8$	1.448 (5)
$S1-C1$	1.793 (6)	$S2-C23$	1.783 (6)
$S1-C9$	1.732 (6)	$S2-C31$	1.749 (6)
$O3-C2$	1.234 (6)	$O9-C24$	1.228 (7)
$N1-N2$	1.311 (6)	$N5-N6$	1.305 (7)
$N1-C1$	1.316 (7)	$N5-C23$	1.302 (7)
$N2-C17$	1.400 (7)	$N6-C39$	1.411 (8)
$C1-C2$	1.461 (8)	$C23-C24$	1.472 (8)
$C2-C3$	1.493 (8)	$C24-C25$	1.491 (8)
$O5-N4$	1.207 (8)	$O11-N8$	1.174 (7)
$O6-N4$	1.211 (8)	$O12-N8$	1.208 (8)
$N4-C20$	1.457 (8)	$N8-C42$	1.462 (8)
$N3-C12$	1.396 (8)	$N7-C34$	1.407 (8)
$N3-C15$	1.355 (8)	$N7-C37$	1.371 (8)
$O4-C15$	1.209 (8)	$O10-C37$	1.200 (8)
$C15-C16$	1.521 (9)	$C37-C38$	1.518 (9)
$O1-S1-O2$	117.4 (3)	$O7-S2-O8$	118.3 (3)
$O1-S1-C1$	109.3 (3)	$O7-S2-C23$	108.6 (3)
$O1-S1-C9$	109.2 (3)	$O7-S2-C31$	109.7 (3)
$O2-S1-C1$	105.2 (3)	$O8-S2-C23$	105.3 (3)
$O2-S1-C9$	109.2 (3)	$O8-S2-C31$	107.8 (3)
$C1-S1-C9$	105.5 (3)	$C23-S2-C31$	106.5 (3)
$N2-N1-C1$	123.8 (5)	$N6-N5-C23$	124.4 (5)
$N1-N2-C17$	119.9 (5)	$N5-N6-C39$	120.7 (6)
$N1-C1-C2$	117.6 (5)	$S2-C23-N5$	125.8 (5)
$S1-C1-N1$	124.7 (5)	$S2-C23-C24$	117.6 (5)
$S1-C1-C2$	117.6 (4)	$N5-C23-C24$	116.6 (5)
$O3-C2-C1$	117.8 (5)	$O9-C24-C23$	118.1 (6)
$O3-C2-C3$	119.4 (5)	$O9-C24-C25$	119.1 (6)
$C1-C2-C3$	122.8 (5)	$C23-C24-C25$	122.8 (5)
$O5-N4-O6$	122.6 (7)	$O11-N8-O12$	122.2 (7)
$O5-N4-C20$	117.8 (8)	$O11-N8-C42$	119.0 (7)
$O6-N4-C20$	119.5 (7)	$O12-N8-C42$	118.7 (7)
$C12-N3-C15$	128.7 (6)	$C34-N7-C37$	127.8 (6)
$O4-C15-N3$	124.0 (7)	$O10-C37-N7$	123.7 (7)
$O4-C15-C16$	121.7 (7)	$O10-C37-C38$	122.5 (7)
$N3-C15-C16$	114.3 (6)	$N7-C37-C38$	113.8 (6)
$S1-C1-C2-O3$	7.9 (8)	$S2-C23-C24-O9$	8.4 (8)
$S1-C1-N1-N2$	-1.3 (8)	$S2-C23-N5-N6$	-4.6 (9)
$O1-S1-C1-C2$	59.9 (5)	$O7-S2-C23-C24$	60.5 (5)
$O1-S1-C1-N1$	-117.4 (5)	$O7-S2-C23-N5$	-117.9 (5)
$O2-S1-C1-C2$	-173.2 (5)	$O8-S2-C23-C24$	-171.8 (5)
$O2-S1-C1-N1$	9.4 (6)	$O8-S2-C23-N5$	9.8 (6)

Table 2

Contact distances (Å).

$S1 \cdots O3$	2.916 (4)	$S2 \cdots O9$	2.926 (5)
$S1 \cdots N2$	3.091 (5)	$S2 \cdots N6$	3.104 (6)
$O1 \cdots C2$	3.230 (7)	$O7 \cdots C24$	3.218 (8)
$O2 \cdots C2$	3.915 (7)	$O8 \cdots C24$	3.920 (8)

Table 3

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2···O2	0.86	1.92	2.620 (6)	138
N3—H3···O3 ⁱ	0.86	2.15	2.993 (6)	166
N6—H61···O8	0.86	1.95	2.651 (7)	138
N7—H71···O9 ⁱⁱ	0.86	2.14	2.980 (7)	167

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, -y, 2 - z$.

All H atoms were placed in calculated positions and were treated as riding on the adjacent N or C atom. They were refined with individual isotropic displacement parameters equal to 1.2 times the value of the equivalent displacement parameters of the parent N or C atom.

Data collection: *KM-4 User's Guide* (Kuma, 1991); cell refinement: *KM-4 User's Guide*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SYBYL* (Tripos, 1996) and *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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