Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1,2-Diphenyl-2-(phenyldiazenyl)-2-tosylethanone, an example of a fungicide containing a sulfonyl group

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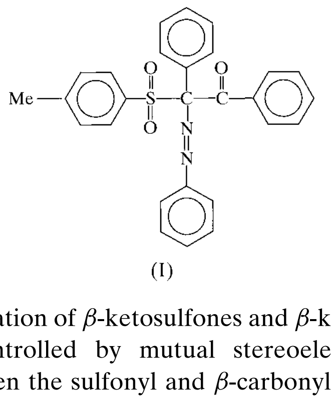
Received 31 May 2000
Accepted 22 August 2000

The molecule of the title compound, $C_{27}H_{22}N_2O_3S$, adopts an irregular propeller shape with the tetrahedral C1 atom pivotal. The α-azophenyl and α-phenyl moieties are approximately coplanar. Electrostatic attraction of the oppositely charged atoms generates several short intramolecular contacts involving the sulfonyl, azo and carbonyl groups. Characteristic bond-length distribution of the central part of the molecule indicates that the Coulombic charge transfer is supplemented by hyperconjugation involving donation of electron density from the azo moiety towards the sulfonyl and carbonyl groups.

Comment

The title compound, (I), represents a new group of α-phenylazo-β-ketosulfones characterized by a substantial antimycotic activity (Zakrzewski & Kacała, 1998; Zakrzewski, 1999), which arises from the photodynamic degradation of a fungicide. In the presence of daylight, the original compound splits into fragments which are toxic to the fungal mycellium. The present work is part of a larger project carried out in collaboration with A. Zakrzewski (Technical and Agricultural Academy, Bydgoszcz, Poland). Our aim is to identify molecular features which are responsible for the antymycotic activity and to prepare the best fungicide (Wolf, 1999).



(I)

The conformation of β-ketosulfones and β-ketosulfoxides is very often controlled by mutual stereoelectronic charge transfers between the sulfonyl and β-carbonyl groups (Distefano *et al.*, 1996; Olivato *et al.*, 2000, and references therein). These interactions reduce the large positive charge present on the S atom and partially counteract the strong electron-withdrawing capacity of the phenylsulfonyl group. The latter is confirmed by the highly positive value of the Hammett σ_p constant, 0.70 (Hansch & Leo, 1979). Attractive Coulombic interactions prompt the oppositely charged atoms to be positioned closer than the sums of their van der Waals radii. Indeed, short intramolecular contacts have often been observed in β-ketosulfones and β-ketosulfoxides (Kucsman & Kapovits, 1985).

A view of compound (I) with the atom-numbering scheme is shown in Fig. 1. Selected geometric parameters are given in Table 1. The molecule adopts an irregular propeller shape with the tetrahedral C1 atom pivotal. The α-azophenyl and α-phenyl moieties are approximately coplanar.

The electrostatic potential derived atomic charge distribution (S 1.18, O1 −0.59, O2 −0.60, O3 −0.45, N1 −0.14, N2 −0.27, C1 −0.07 and C2 0.46 e) clearly shows that within the central part of a molecule the positive charges are located on the S and carbonyl C2 atoms only. Electrostatic attraction of the oppositely charged atoms generates several short intramolecular contacts as listed in Table 2. In particular, the sulfonyl S atom forms a short contact with the carbonyl O3 atom [2.946 (2) Å], and the carbonyl C2 atom is positioned close to the azo N2 atom [2.693 (2) Å]. The sums of the respective van der Waals radii are 3.32 and 3.25 Å (Bondi, 1964). Shortening of the former distance has often been observed in α,α-unsubstituted-β-ketosulfones and, in addition to the electrostatic charge transfer, it is also attributed to the anomeric overlapping of the $\pi^*(C2{=}O3)$–$\sigma(S{-}C1)$ and $\pi(C2{=}O3)$–$\sigma^*(S{-}C1)$ pairs of bonding and non-bonding molecular orbitals (Distefano *et al.*, 1991; Dal Colle *et al.*, 1995). By analogy, the short intramolecular S···N2 contact which exists in (I) can be influenced by the $\pi^*(N1{=}N2)$–$\sigma(C1{-}C2)$ and $\pi(N1{=}N2)$–$\sigma^*(C1{-}C2)$ cross interactions. The anomeric effect is most effective when interacting polar bonds are positioned *gauche* with respect to each other

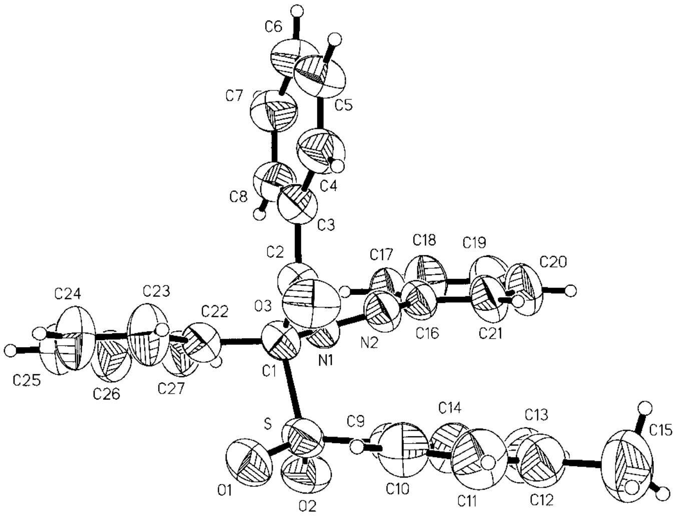


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

(Juaristi & Cuevas, 1995, and references therein). Indeed, 12 out of 14 non-cyclic α,α-unsubstituted β-ketosulfones which are reported in the Cambridge Structural Database (Allen *et al.*, 1979) adopt conformations which are dominated by *gauche* arrangements of their S—C1—C2═O3 moieties. In compound (I), the S—C1 and C2═O3 bonds are almost synperiplanar, while the conformation of the N1═N2 and C1—C2 bonds is much closer to *gauche* [the S—C1—C2═O3 and N2═N1—C1—C2 torsion angles are −13.9 (2) and 39.8 (2)°, respectively]. This suggests that the latter system is more affected by the anomeric effect while interactions between the S—C1 and C2═O3 bonds are dominated by the non-stereospecific electrostatic Coulombic interactions.

The azo moiety adopts the *trans* conformation. The N1═N2 bond [1.2445 (18) Å] is slightly longer than reported in *International Tables for Crystallography* (Allen *et al.*, 1992) (1.222 Å). C1—N1 [1.474 (2) Å] is shorter than the respective bond in the standard Csp^3—N═N system (1.493 Å). A very long S—C1 bond [1.8875 (17) Å] is accompanied by a stretched C1—C2 bond [1.539 (2) Å]. The former is much longer than the typical single S—C bond, 1.78 Å. The latter exceeds the single C—C bond, as has been found in the aliphatic ketones, C—C(O)—C (1.511 Å). These systematic bond differences resemble the characteristic pattern of bond-length changes induced by an anomeric effect (Kirby, 1983; Graczyk & Mikołajczyk, 1994). This effect is partially responsible for the donation of electron density from the azo N2 atom towards the S and carbonyl C2 atoms. The resulting hyperconjugative (March, 1992) increase of π character of the C1—N1 bond can be stabilized by conjugation with the α-phenyl ring borne by the C1 atom (Wolf, 2000). This explains the odd conformation of a molecule as characterized by an approximate coplanarity of the α-phenyl and α-phenylazo fragments located opposite each other.

The azo and carbonyl groups are approximately coplanar with their parent phenyl rings. The C2—C3 bond length [1.501 (2) Å] is closer to the value reported for a $Csp^3—C_{\rm aryl}$ (1.506 Å) than a $Csp^2—C_{\rm aryl}$ bond (1.470 Å). The N2—C16 bond length [1.430 (2) Å] is very similar to the $C_{\rm aryl}$—N═N bond length (1.431 Å). The distribution of the endocyclic bond lengths and valency angles in the terminal phenyl rings is uniform and does not resemble quinoid-type structures (Domenicano, 1992). This indicates that the stereoelectronic and the π-electron delocalization involving the carbonyl and azo groups are directed towards the central part of a molecule. The influence of the terminal phenyl rings is restricted to a small inductive effect only. All typical bond lengths quoted throughout this paper are taken from Allen *et al.* (1992).

Examination of intermolecular distances shows that the packing arrangement is not significantly influenced by steric interactions as identified by the sums of the respective van der Waals radii (Bondi, 1964).

Experimental

The title compound was synthesized by reaction of the benzoylphenylmethyl *p*-tolyl sulfone with phenyldiazonium chloride in alkaline ethyl alcohol solution (Zakrzewski, 1996). The crystal used for the data collection was obtained by vapour diffusion. A sample of (I) dissolved in a 2:1 mixture of chloroform and isopropyl alcohol was equilibrated at room temperature against pure isopropyl alcohol for 10 d.

Crystal data

$C_{27}H_{22}N_2O_3S$
$M_r = 454.53$
Monoclinic, $P2_1/c$
$a = 11.824$ (2) Å
$b = 17.573$ (2) Å
$c = 11.960$ (2) Å
$\beta = 110.24$ (1)°
$V = 2331.6$ (6) Å^3
$Z = 4$
$D_x = 1.295$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 80 reflections
$\theta = 5$–12°
$\mu = 1.487$ mm^{-1}
$T = 292$ (2) K
Ellipsoidal shape, yellow
0.49 × 0.41 × 0.32 mm
0.40 mm (radius)

Data collection

Kuma Diffraction KM-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1991)
$T_{\rm min} = 0.522$, $T_{\rm max} = 0.621$
9632 measured reflections
5074 independent reflections
3880 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 80.88°$
$h = -15 \rightarrow 15$
$k = -22 \rightarrow 0$
$l = -15 \rightarrow 15$
3 standard reflections every 100 reflections intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.133$
$S = 1.034$
5074 reflections
387 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.2920P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0011 (2)

Table 1
Selected geometric parameters (Å, °).

S—O1	1.431 (1)	N1—C1	1.474 (2)
S—O2	1.437 (1)	N2—C16	1.430 (2)
S—C9	1.755 (2)	C1—C22	1.521 (2)
S—C1	1.888 (2)	C1—C2	1.539 (2)
O3—C2	1.211 (2)	C2—C3	1.501 (2)
N1—N2	1.245 (2)		
O1—S—O2	118.93 (9)	N1—C1—C2	113.0 (1)
O1—S—C9	108.16 (9)	C22—C1—C2	111.3 (1)
O2—S—C9	107.67 (9)	N1—C1—S	105.7 (1)
O1—S—C1	107.41 (8)	C22—C1—S	104.6 (1)
O2—S—C1	103.80 (8)	C2—C1—S	111.7 (1)
C9—S—C1	110.74 (8)	O3—C2—C3	120.9 (2)
N2—N1—C1	111.7 (1)	O3—C2—C1	112.0 (2)
N1—N2—C16	113.7 (1)	C3—C2—C1	119.1 (1)
N1—C1—C22	110.1 (1)		
S—C1—C2—O3	−13.9 (2)	O2—S—C1—N1	−38.5 (1)
S—C1—N1—N2	−82.7 (1)	O2—S—C1—C22	77.8 (1)
S—C1—C2—C3	168.9 (1)	N1—C1—C2—O3	−132.9 (2)
O1—S—C1—C2	71.5 (1)	N1—C1—C2—C3	49.9 (2)
O1—S—C1—N1	−165.3 (1)	N2—N1—C1—C22	165.0 (1)
O1—S—C1—C22	−49.0 (1)	N2—N1—C1—C2	39.8 (2)
O2—S—C1—C2	−161.7 (1)		

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 [C—H 0.79 (4)–1.18 (2) Å], only the C19—H19 distance was

Table 2
Contact distances (Å).

S···O3	2.946 (2)	O2···N1	2.789 (2)
O1···C2	3.315 (2)	O2···N2	3.397 (2)
S···N2	3.175 (2)	N2···C2	2.693 (2)

restrained to 1.00 (1) Å. Electrostatic potential derived atomic charges were calculated with *TURBOMOLE* (MSI, 1996) at the HF/6–31G** level for the X-ray determined coordinates. The van der Waals fit has been applied.

Data collection: *KM*-4 *User's Guide* (Kuma Diffraction, 1991); cell refinement: *KM*-4 *User's Guide*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *INSIGHT*II (MSI, 1997) and *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL*97.

The author is indebted to Dr Andrzej Zakrzewski (Technical and Agricultural Academy, Bydgoszcz, Poland) for his valuable comments and a sample of compound (I). Quantum chemical calculations were performed in the ACK CYFRONET Kraków, Poland; support through computational grants 030/1999 and 050/1999 is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1053). Services for accessing these data are described at the back of the journal.

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