

X-ray investigations of sulfur-containing fungicides. IV.¹
4'-[[Benzoyl(4-chlorophenylhydrazono)methyl]sulfonyl]acetanilide and
4'-[[benzoyl(4-methoxyphenylhydrazono)methyl]sulfonyl]acetanilide

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Received 1 June 2001

Accepted 26 June 2001

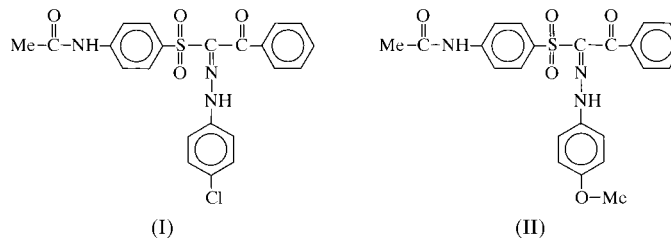
The conformations of the two approximately isomorphous structures 4'-[[benzoyl(4-chlorophenylhydrazono)methyl]sulfonyl]acetanilide, C₂₂H₁₈ClN₃O₄S, and 4'-[[benzoyl(4-methoxyphenylhydrazono)methyl]sulfonyl]acetanilide, C₂₃H₂₁N₃O₅S, are stabilized by resonance-assisted intramolecular hydrogen bonds linking the hydrazone moieties and sulfonyl groups. The stronger bond is observed in the former compound. The difference in electronic properties between the Cl atom and the methoxy group is too small to significantly alter the non-bonding interactions of the sulfonyl and β-carbonyl groups.

Comment

X-ray and *ab initio* molecular-orbital investigations of phenyl benzoyl(phenylhydrazono)methyl sulfones have shown that strongly electron-withdrawing substituents bonded to the phenylhydrazone moiety increase the strength of the intramolecular resonance-assisted N—H···O=S hydrogen bonds (Jeffrey, 1997) and prompt simultaneous contraction of the intramolecular contacts between the oppositely charged atoms of the sulfonyl and β-carbonyl groups (Wolf, 2001a, and references therein). The latter effect promotes electron density back-donation towards the S atoms and therefore reduces the strongly electron-withdrawing character of the sulfonyl groups. In this paper, the isomorphous crystal structures of 4'-[[benzoyl(4-chlorophenylhydrazono)methyl]sulfonyl]acetanilide, (I), and 4'-[[benzoyl(4-methoxyphenylhydrazono)methyl]sulfonyl]acetanilide, (II), are reported. Their terminal substituents attached to the α-phenylhydrazone group have opposite electronic properties. The *para*-Cl atom in (I) shows electron-withdrawing ability, whereas the *para*-methoxy group in (II) has electron-donating character. The

¹Part III: Wolf (2001b).

Hammett σ_p constants are 0.23 and -0.27, respectively (Hansch *et al.*, 1995). An interesting feature of (I) and (II) is their antimycotic activity, which increases after exposing fungi colonies with added fungicide to radiation characteristic of daylight (Wolf, 1999, 2000; Zakrzewski & Kacała, 1998; Zakrzewski, 1999).



The molecular structures of (I) and (II) are shown in Figs. 1 and 2. The superposition of both structures (Fig. 3) clearly shows the similarity of their conformations; the root-mean-square deviation calculated from the least-squares fit of all relevant non-H atoms is 0.27 Å.

In (I) and (II), the S=O₂ sulfonyl double bonds, carbonyl groups and phenylhydrazone moieties are approximately coplanar. Their configuration can be defined as *EZE*. This three-letter symbol was initially used to describe the conformation of 2,2-diacylethenamines (Gómez-Sánchez *et al.*, 1987) and was applied further to β-diketoarylhydrazones (Bertolasi, Gilli *et al.*, 1994; Bertolasi, Nanni *et al.*, 1994). In the compounds investigated, the above three letters indicate, relative to the C1=N1 bond, the positions of the carbonyl C2=O3 bond, the sulfonyl S=O2 bond and the N2—C17 bond bearing the phenyl ring.

The central fragments of both molecules are constrained by strong intramolecular hydrogen bonds assisted by resonance (resonance-assisted hydrogen bonds, RAHB). These bonds connect the hydrazone and sulfonyl groups. The six-membered RAHB rings in (I) and (II) are practically planar (r.m.s. deviations from the O2/S/C1/N1/N2/H2 planes are 0.03 and 0.07 Å, respectively). The N2···O2 distance in (I) [2.647 (4) Å] is shorter than that in (II) [2.663 (3) Å]. On the other hand, the S=O2 bond in (I) is longer [1.451 (3) Å] than that in (II) [1.438 (2) Å]. This characteristic variation of bond lengths and *D···A* distances indicates that a stronger RAHB exists in (I) (Gilli *et al.*, 1994).

Atomic charges derived from electrostatic potentials were calculated using 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 Merz–Singh–Kollman procedure (Bessler *et al.*, 1990; Singh & Kollman, 1984). Large positive atomic charges are located on atoms S and C2 [1.25 and 0.52 e, and 1.26 and 0.47 e for (I) and (II), respectively]. All O atoms are negatively charged; atomic charges on O1, O2 and O3 are in the range -0.52 to -0.68 e. Electrostatic attraction of the oppositely charged atoms generates intramolecular contacts between the atom pairs S···O3 and O1···C2; details are summarized in Tables 2 and 5.

A similar situation was observed in the three α-hydrazono-β-ketosulfones reported in the Cambridge Structural Data-

base (Allen & Kennard, 1993), 4'-[[benzoyl(4-tolylhydrazono)methyl]sulfonyl]acetanilide, (III) (Wolf, 1999), phenyl benzoyl(phenylhydrazono)methyl sulfone, (IV), and phenyl benzoyl(4-nitrophenylhydrazono)methyl sulfone, (V) (Wolf, 2001a). In (V), the strongly electron-withdrawing *para*-nitro group attached to the phenylhydrazone moiety hinders electron density redistribution from the hydrazone fragment towards the electron-deficient S and β -carbonyl C atom, and thus helps to conserve large positive charges on those atoms. This effect strengthens intramolecular hydrogen bonding and, in addition, favours electrostatic attraction of the oppositely charged atoms of the sulfonyl and carbonyl dipoles. Finally, it results in a significant shortening of the intramolecular S \cdots O3 contact in (V) [2.818(3) Å] compared with (IV) [2.976(1) Å]. In the title compounds, (I) and (II), the S \cdots O3 distances are significantly contracted below the van der Waals limit (3.32 Å; Bondi, 1964). Nevertheless, both contacts are practically equal [2.954(3) and 2.952(2) Å]. This observation indicates that the divergence of the electronic properties of the Cl atom and the methoxy group was too small to alter the non-bonding interactions of the sulfonyl and β -carbonyl groups significantly.

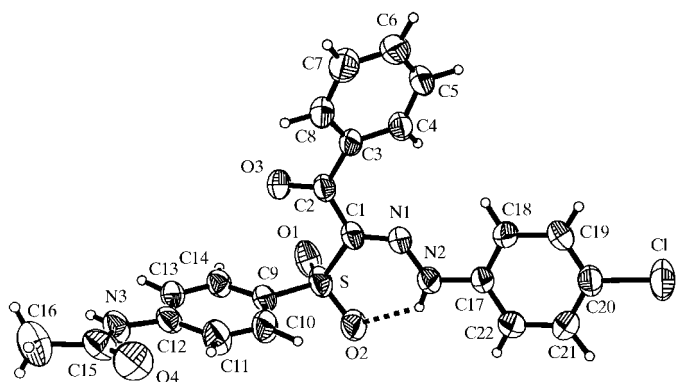


Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the intramolecular hydrogen bond is indicated by a dashed line.

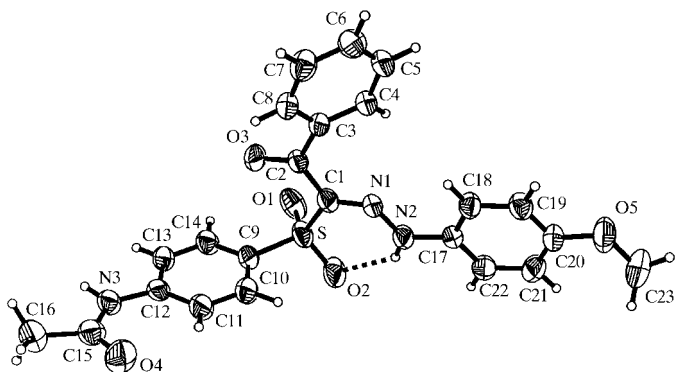


Figure 2
The molecular structure of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and the intramolecular hydrogen bond is indicated by a dashed line.

Bond lengths in (I) and (II) are close to those observed in related compounds (Wolf, 1999, 2001a). In particular, the S—C1 bonds are longer [1.792(3) and 1.787(2) Å, respectively] than the conventional S—Csp³ single bond (1.779 Å; Allen *et al.*, 1992). Similar bond elongation in (III), (IV) and (V) [1.795(3), 1.798(2) and 1.784(1) Å, respectively] was attributed to hyperconjugative (Juaristi & Cuevas, 1995; Graczyk & Mikołajczyk, 1994; Cramer, 1996) interactions involving σ (S—C1)— π^* (C=O3) bonding and non-bonding atomic orbitals. The resulting transfer of electron density from S towards O3 increases charge separation between the sulfonyl and carbonyl groups and, finally, intensifies the electrostatic attraction of the oppositely charged S and O3 atoms. A similar pattern of intramolecular interactions was observed in α -unsubstituted β -ketosulfones and β -ketosulfoxides (Distefano *et al.*, 1991, 1996; Dal Colle *et al.*, 1995; Olivato *et al.*, 1998, 2000; Wolf, 2001b).

In the crystal lattice, molecules of (I) and (II) form centrosymmetric dimers, which are connected by intermolecular hydrogen bonds involving the β -carbonyl O3 atoms and the N3—H2 bonds of the terminal acetamide moieties. According to Etter's graph-set terminology (Etter *et al.*, 1990; Bernstein *et al.*, 1995), these bond systems can be described as $R_2^2(20)$. Additionally, the O4 atoms of the acetamide groups are involved in three close contacts with the surrounding H atoms of the phenyl rings. According to the liberal definition of Desiraju & Steiner (1999), these contacts could be classified as C—H \cdots O hydrogen bonds. Details are summarized in Tables 3 and 6.

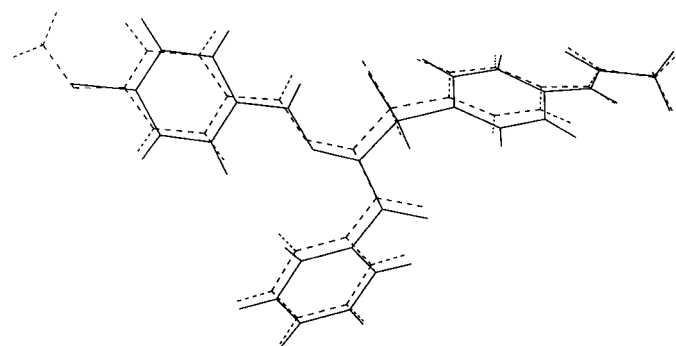


Figure 3
The superposition of (I) and (II), with (II) plotted as dashed lines. The least-squares fit was based on all common non-H atoms, *i.e.* the terminal Cl and methoxy substituents were not considered. The r.m.s. deviation was 0.27 Å.

Experimental

Compounds (I) and (II) were synthesized by the reaction of *p*-acetanilide benzoylmethyl sulfone with *p*-chlorophenyldiazonium chloride and *p*-methoxyphenyldiazonium chloride, respectively. The reactions were carried out in alkaline ethyl alcohol solutions (Zakrzewski, 1996). The crystals used for data collection were obtained by vapour diffusion: samples were dissolved in a 2:1 mixture of chloroform and isopropyl alcohol, and equilibrated at room temperature against pure isopropyl alcohol for 6 and 14 d, respectively.

Compound (I)

Crystal data

$C_{22}H_{18}ClN_3O_4S$	$D_x = 1.434 \text{ Mg m}^{-3}$
$M_r = 455.90$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 60 reflections
$a = 11.603 (4) \text{ \AA}$	$\theta = 5\text{--}15^\circ$
$b = 7.5960 (10) \text{ \AA}$	$\mu = 0.32 \text{ mm}^{-1}$
$c = 24.110 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 96.44 (2)^\circ$	Prism, yellow
$V = 2111.6 (9) \text{ \AA}^3$	$0.50 \times 0.45 \times 0.30 \text{ mm}$
$Z = 4$	

Data collection

Kuma KM-4 diffractometer	$h = -13 \rightarrow 13$
$\omega/2\theta$ scans	$k = -1 \rightarrow 9$
4434 measured reflections	$l = 0 \rightarrow 28$
3719 independent reflections	3 standard reflections
2531 reflections with $I > 2\sigma(I)$	every 100 reflections
$R_{\text{int}} = 0.036$	intensity decay: 10%
$\theta_{\text{max}} = 25^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 3.1336P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.135$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
3719 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
306 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

S—O1	1.431 (3)	N2—C17	1.408 (4)
S—O2	1.451 (3)	C1—C2	1.467 (5)
S—C1	1.792 (3)	C2—C3	1.502 (5)
S—C9	1.746 (4)	N3—C12	1.400 (5)
O3—C2	1.231 (4)	N3—C15	1.352 (5)
N1—N2	1.289 (4)	O4—C15	1.212 (5)
N1—C1	1.306 (4)	Cl—C20	1.742 (3)
O1—S—O2	118.2 (2)	N1—C1—C2	117.6 (3)
O1—S—C1	109.28 (18)	S—C1—N1	125.0 (3)
O1—S—C9	109.02 (17)	S—C1—C2	117.4 (2)
O2—S—C1	104.82 (16)	O3—C2—C1	119.7 (3)
O2—S—C9	108.63 (18)	O3—C2—C3	119.0 (3)
C1—S—C9	106.19 (17)	C1—C2—C3	121.3 (3)
N2—N1—C1	125.7 (3)	C15—N3—C12	128.8 (3)
N1—N2—C17	120.1 (3)		
S—C1—C2—O3	7.4 (5)	O1—S—C1—N1	-120.2 (3)
S—C1—N1—N2	-3.1 (6)	O2—S—C1—C2	-172.8 (3)
O1—S—C1—C2	59.5 (3)	O2—S—C1—N1	7.5 (4)

Table 2

Contact distances (\AA) for (I).

S...O3	2.954 (3)	O1...C2	3.222 (5)
S...N2	3.115 (3)	O2...C2	3.918 (5)

Table 3

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D\text{---}H\text{---}A$	$D\text{---}H$	$H\text{---}A$	$D\text{---}A$	$D\text{---}H\text{---}A$
N2—H2...O2	0.83 (4)	2.01 (4)	2.647 (4)	132 (3)
N3—H3...O3 ⁱ	0.86 (4)	2.10 (4)	2.959 (4)	178 (4)
C11—H11...O4	0.82	2.35	2.873 (6)	123
C21—H21...O4 ⁱⁱ	0.98	2.54	3.254 (5)	130
C14—H14...O4 ⁱⁱⁱ	0.88	2.39	3.107 (5)	139

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, 1 + y, z$.

Compound (II)

Crystal data

$C_{23}H_{21}N_3O_5S$	$D_x = 1.380 \text{ Mg m}^{-3}$
$M_r = 451.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 48 reflections
$a = 11.4897 (12) \text{ \AA}$	$\theta = 4.5\text{--}10.2^\circ$
$b = 7.4158 (9) \text{ \AA}$	$\mu = 0.19 \text{ mm}^{-1}$
$c = 25.507 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.53 (3)^\circ$	Plate, yellow
$V = 2172.5 (4) \text{ \AA}^3$	$0.55 \times 0.35 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Siemens P3 diffractometer	$h = -1 \rightarrow 13$
$\omega/2\theta$ scans	$k = -1 \rightarrow 8$
5473 measured reflections	$l = -30 \rightarrow 30$
3823 independent reflections	3 standard reflections
2647 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.052$	intensity decay: 18%
$\theta_{\text{max}} = 25^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.2858P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
3823 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
317 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 4

Selected geometric parameters (\AA , $^\circ$) for (II).

S—O1	1.441 (2)	C1—C2	1.459 (3)
S—O2	1.438 (2)	C2—C3	1.501 (3)
S—C1	1.787 (2)	N3—C12	1.401 (3)
S—C9	1.751 (3)	N3—C15	1.358 (3)
O3—C2	1.228 (3)	O4—C15	1.211 (3)
N1—N2	1.291 (3)	O5—C20	1.361 (3)
N1—C1	1.309 (3)	O5—C23	1.408 (4)
N2—C17	1.415 (3)		
O1—S—O2	118.15 (13)	N1—C1—C2	117.82 (19)
O1—S—C1	109.04 (11)	S—C1—N1	124.71 (17)
O1—S—C9	108.56 (12)	S—C1—C2	117.40 (16)
O2—S—C1	104.97 (11)	O3—C2—C1	120.2 (2)
O2—S—C9	108.87 (12)	O3—C2—C3	118.9 (2)
C1—S—C9	106.67 (12)	C1—C2—C3	120.89 (19)
N2—N1—C1	125.93 (19)	C15—N3—C12	128.9 (2)
N1—N2—C17	120.15 (18)	C20—O5—C23	118.1 (2)
S—C1—C2—O3	8.4 (3)	O1—S—C1—N1	-114.9 (2)
S—C1—N1—N2	-1.4 (4)	O2—S—C1—C2	-170.4 (2)
O1—S—C1—C2	62.1 (2)	O2—S—C1—N1	12.6 (3)

Table 5

Contact distances (Å) for (II).

S...O3	2.952 (2)	O1...C2	3.234 (3)
S...N2	3.114 (2)	O2...C2	3.894 (3)

Table 6

Hydrogen-bonding geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O2	0.86 (3)	1.98 (3)	2.663 (3)	135 (2)
N3—H3...O3 ⁱ	0.89 (3)	2.10 (3)	2.991 (3)	174 (2)
C11—H11...O4	0.89	2.29	2.867 (4)	122
C21—H21...O4 ⁱⁱ	0.94	2.55	3.474 (4)	167
C14—H14...O4 ⁱⁱⁱ	0.95	2.46	3.144 (3)	129

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, 1+y, z$.

All H atoms were located in a difference Fourier map calculated after three cycles of anisotropic refinement. The positional and isotropic displacement parameters of H2 and H3 in both (I) and (II) were allowed to refine freely. The positional parameters of all remaining H atoms were constrained using *AFIX* 44 and *AFIX* 134 in *SHELXL97* (Sheldrick, 1997) for the phenyl and methyl groups, respectively [$C-H = 0.82-1.04$ and $0.89-0.99$ Å for (I) and (II), respectively]. Common displacement parameters were applied to H atoms of the individual phenyl and methyl groups.

For compound (I), data collection: *KM-4 Software* (Kuma, 1991); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1995). For compound (II), data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *INSIGHTII* (Molecular Simulations, 1997) and *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1471). Services for accessing these data are described at the back of the journal.

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