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Preferred conformations in the solid state of some *α*-(*p*-phenylsulfinyl)-*p*-substituted acetophenones

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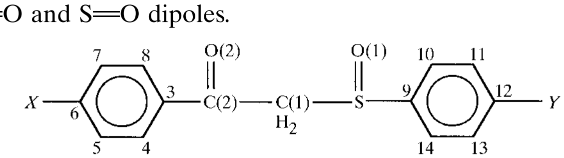
Information on the geometrical structures of α-(p-phenylsulfinyl)-p-substituted acetophenones X—PhC(O)CH_2S(O)Ph—Y [X = OMe, Y = H (1); X = NO_2, Y = OMe (2); X = OMe, Y = NO_2 (3); IUPAC names: (1) 4-methoxyphenyl phenylsulfinylmethyl ketone; (2) 4-nitrophenyl 4-methoxyphenylsulfinylmethyl ketone; (3) 4-methoxyphenyl 4-nitrophenylsulfinylmethyl ketone] have been obtained from X-ray diffraction analyses. A comparison of these results with those previously obtained from X-ray diffraction and *ab initio* computations of α-methylsulfinylacetophenone, PhC(O)CH_2-S(O)Me, indicated that (1) and (2) adopt in the crystal a cis_1 conformation and (3) assumes a *quasi-gauche* geometry. The stabilization of these conformations in the crystal is discussed in terms of the dipole moment coupling, Coulombic and intramolecular charge transfer interactions between the oppositely charged atoms of the C=O and S=O dipoles. The p-substituted benzene ring is *quasi*-coplanar with the sulfinyl group for (1) and (3), but is *quasi*-perpendicular for (2). Conjugation and repulsion between the sulfinyl sulfur lone pair and the π-benzene ring seem to be responsible for the observed geometries.

1. Introduction

Our previous IR and X-ray diffraction studies supported by 6-31G** *ab initio* calculations of some α-alkylsulfinylacetophenones (Olivato *et al.*, 1998; Distefano *et al.*, 1996), PhC(O)CH_2S(O)R (R = Me, Et and Bu^t), have shown that these compounds adopt a cis_1 conformation in the solid state, for which the O atoms of the S=O and C=O dipoles are close to each other. The stabilization of the cis_1 conformation in the crystal has been ascribed to dipole moment coupling along with Coulombic attraction, and intramolecular charge transfer between the negatively charged carbonyl O atom and the positively charged sulfinyl S atom [$O^{\delta-}$(CO)$\cdots S^{\delta+}$(SO)], which should overcome the repulsive field effect between C=O and S=O dipoles.



(I)

In order to further investigate the nature of the electronic and Coulombic interactions which occur in the solid state of α-sulfinylacetophenones the present paper reports the X-ray structures of some α-(p-phenylsulfinyl)-p-substituted acetophenones (I): X = OMe and Y = H for (1); X = NO_2, Y = OMe for (2) and X = OMe, Y = NO_2 for (3).

These model compounds were chosen in order to verify how the variation on the conjugation involving the *para* substituents at the phenacyl and phenylsulfinyl groups should influence the stabilization of the *cis* or *gauche* rotamers of the title compounds in the solid state.

2. Experimental

2.1. Synthesis, NMR and CHN analyses

α-(*p*-Phenylsulfinyl)-*p*-substituted acetophenones X—$PhC(O)CH_2S(O)Ph$—Y [(1)–(3)] were prepared by the following procedure: to a solution of the correseponding α-(*p*-phenylthio)-*p*-substituted acetophenone (Olivato & Guerrero, 1992) in acetic acid, cooled to 273 K, was added dropwise an equivalent amount of 30% hydrogen peroxide. The stirred reaction mixture was kept at room temperature until all the ketosulfide had reacted. After the reaction work-up, the pure solids were obtained from recrystallization in methanol. Crystals for the X-ray analysis were obtained by diffusion from chloroform–*n*-hexane solution. The α-arylsulfinylacetophenones (2) and (3) are new compounds. Although (1) has already been described in the literature (Lamm & Samuelsson, 1970) its melting point deviates reasonably from ours. (1) (X = OMe; Y = H): m.p. 357–361 K (Lamm & Samuelsson, 1970; m.p. 352–353 K); ^{1}H NMR ($CDCl_3$): δ 7.86 [*d*, 2H, ArC(O), J = 9.0 Hz], 7.71–7.65 [*m*, 2H, ArS(O)], 7.52–7.47 [*m*, 3H, ArS(O)], 6.90 [*d*, 2H, ArC(O), J = 9.0 Hz], 4.24 (*d*, 1H, CH_2, J = 14.0 Hz), 3.92 (*d*, 1H, CH_2, J = 14.0 Hz), 3.85 (*s*, 3H, OCH_3). Anal.: calc. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.61; H,5.09. (2) (X = NO_2; Y = OMe): m.p. 379–383 K; ^{1}H NMR ($CDCl_3$): δ 8.25 [*d*, 2H, ArC(O), J = 8.9 Hz], 8.01 [*d*, 2H, ArC(O), J = 8.9 Hz], 7.55 [*d*, 2H, ArS(O), J = 8.9 Hz], 6.96 [*d*, 2H, ArS(O), J = 8.9 Hz], 4.50 (*d*, 1H, CH_2, J = 13.6 Hz), 4.14 (*d*, 1H, CH_2, J = 13.6 Hz), 3.80 (*s*, 3H, OCH_3). Anal.: calc. for $C_{15}H_{13}NO_5S$: C, 56.42; H, 4.10; N,4.39. Found: C, 56.77; H, 3.95; N, 4.73. (3) (X = OMe; Y = NO_2): m.p. 443–448 K; ^{1}H NMR ($CDCl_3$): δ 8.35 [*d*, 2H, ArS(O), J = 8.8 Hz], 7.90 [*d*, 2H, ArC(O), J = 8.8 Hz]; 7.85 [*d*, ArS(O), J = 8.8 Hz], 6.93 [*d*, 2H, ArC(O), J = 8.8 Hz], 4.56 (*d*, 1H, CH_2, J = 14.5 Hz), 4.38 (*d*, 1H, CH_2, J = 14.5 Hz), 3.88 (*s*, 3H, OCH_3). Anal.: calc. for $C_{15}H_{13}NO_5S$: C, 56.42; H, 4.10; N,4.39. Found: C, 56.05; H, 4.09; N, 4.29.

The conditions for recording the ^{1}H NMR spectra have already been described (Olivato *et al.*, 1997).

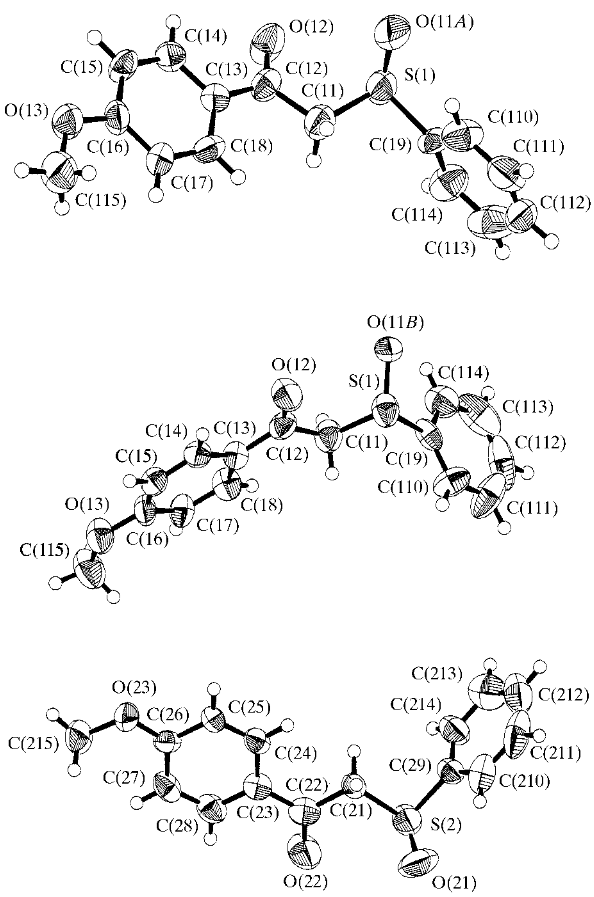


Figure 1

Crystal structure of (1) showing the three molecules. The molecule with O(11*A*) corresponds to the *R* form and that with O(11*B*) to the *S* form of one of the independent molecules. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

2.2. Crystal structures

In all cases the measurements were carried out in a CAD-4-Mach3 Enraf–Nonius diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at room temperature (T = 293 K), using the $\theta/2\theta$ scan method. H atoms were located on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they were attached. Software used: data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *MolEN* (Fair, 1990); structures were solved using *SHELXS*86 (Sheldrick, 1990) and refined on F^2 using *SHELXL*97 (Sheldrick, 1997), molecular graphics: *ZORTEP* (Zsolnai, 1995); preparation of material for publication and deposition: *SHELXL*97 (Sheldrick, 1997) and *PARST*95 (Nardelli, 1995). Specific details of the structure analyses are given in Table 1.[1]

The compounds are shown in Figs. 1–3. In (1) two independent molecules were found in the asymmetric unit. A difference-Fourier map showed two relatively high peaks at bond distances from the S atom which indicated that there was some statistical disorder concerning the O atom in one of the molecules. This disorder could be satisfactorily described by a simple model postulating two different configurations, with the O atom alternatively occupying one of the two positions. The s.o.f.s (site occupancy factor) of these positions were refined constraining their sum to be equal to 1.00, thus refining to 0.625 (9) for the *S* form and 0.375 (9) for the *R* form,

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0095). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{15}H_{14}O_3S$	$C_{15}H_{13}NO_5S$	$C_{15}H_{13}NO_5S$
Chemical formula weight	274.32	319.32	319.32
Cell setting	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P\overline{1}$
a (Å)	10.4698 (9)	5.5704 (8)	6.7468 (8)
b (Å)	10.2770 (9)	8.619 (1)	7.4303 (7)
c (Å)	25.449 (2)	30.356 (5)	15.201 (2)
α (°)	90	90	85.25 (1)
β (°)	98.429 (1)	90	79.56 (1)
γ (°)	90	90	75.39 (1)
V (Å^3)	2708.7 (4)	1457.4 (4)	724.64 (15)
Z	8	4	2
D_x (Mg m^{-3})	1.345	1.455	1.463
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	20	25	25
θ range (°)	8.06–11.98	8.15–13.41	8.12–17.23
μ (mm^{-1})	0.239	0.246	0.247
Temperature (K)	293	293	293
Crystal form	Irregular	Irregular	Irregular
Crystal size (mm)	0.25 × 0.22 × 0.10	0.20 × 0.15 × 0.08	0.25 × 0.15 × 0.10
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	None
No. of measured reflections	3670	1615	3188
No. of independent reflections	3162	1615	2930
No. of observed reflections	1198	688	2503
Criterion for observed reflections	$F^2 > 2\sigma F^2$	$F^2 > 2\sigma F^2$	$F^2 > 2\sigma F^2$
R_{int}	0.1327	0	0.0097
θ_{max} (°)	21.64	25.48	26.29
Range of h, k, l	$-10 \rightarrow h \rightarrow 10$	$0 \rightarrow h \rightarrow 6$	$0 \rightarrow h \rightarrow 8$
	$0 \rightarrow k \rightarrow 10$	$0 \rightarrow k \rightarrow 10$	$-8 \rightarrow k \rightarrow 9$
	$-26 \rightarrow l \rightarrow 0$	$0 \rightarrow l \rightarrow 36$	$-18 \rightarrow l \rightarrow 18$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 60 min	Every 60 min	Every 60 min
Intensity decay (%)	−1	−0.4	−1.1
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0568	0.1067	0.0412
$wR(F^2)$	0.1044	0.2887	0.1129
S	0.929	1.009	1.076
No. of reflections used in refinement	3162	1615	2930
No. of parameters used	355	201	200
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0495)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.2000)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0648)^2 + 0.2154P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.003	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.350	1.549	0.264
$\Delta\rho_{min}$ (e Å^{-3})	−0.217	−0.511	−0.318
Extinction method	None	*SHELXL*97 (Sheldrick, 1997)	None
Extinction coefficient	–	0.003 (7)	–
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

resulting in an enantiomeric excess of the *S* form. As the rotational energy barrier between the carbonyl group and the phenyl ring is low, the methyl moiety of the *para*-methoxy substituent appears either in the same side or the opposite one with respect to the carbonyl O atom of the phenacyl moiety. In fact, the two *S* forms show the methyl group in opposite sides. In (2) a final difference-Fourier map showed a relatively high peak close to S, O1 and C1 atoms, which could not be modelled and can be ascribed to the rather poor diffracting quality of the crystals and to the fact that when the data

Table 2
Selected X-ray geometrical data of some α-(*p*-substituted phenylsulfinyl)-*p*-substituted acetophenones $X-PhC(O)CH_2S(O)Ph-Y$ [(1)–(3)] and the corresponding X-ray data along with the population, dipole moments and the selected torsion angles optimized for different *cis* (*c*) and *gauche* (*g*) conformers for the α-methylsulfinyl acetophenone (from Distefano *et al.*, 1996) (4) Ph—C(O)CH$_2$S(O)Me at the 6-31G** level.

P indicates the molar fraction of the *cis* and *gauche* rotamers as a percentage; the labelling of the atoms are shown in (I); dihedral angles: α = O(2)—C(2)—C(1)—S; β = C(2)—C(1)—S—C(9); γ = C(2)—C(1)—S—O(1); γ′ = O(1)—S—C(9)—C(10); δ = O(2)—C(2)—C(3)—C(8); sum of van der Waals radii for C(2)···O(1) = 3.22 Å and for O(2)···S = 3.32 Å.

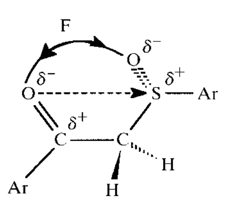
						Torsion angles (°)						
Compound	*X*	*Y*	Conformation	*P* (%)	μ/D	α	β	γ	γ′	δ	C(2)···O(1) (Å)	O(2)···S (Å)
(1) *S*2*S*†	MeO	H	c_1	–	–	3.0 (9)	167.9 (6)	−84.6 (6)	−6.8 (8)	1 (1)	3.40 (1)	2.869 (6)
(1) *S*1*R*†	MeO	H	c_1	–	–	13.5 (9)	175.6 (6)	68.0 (7)	16.1 (8)	168.7 (8)	3.16 (1)	2.822 (5)
(1) *S*1*S*†	MeO	H	c_1	–	–	13.5 (9)	175.6 (6)	−81.2 (8)	158.0 (8)	168.7 (8)	3.42 (1)	2.822 (5)
(2)†	NO_2	OMe	c_1	–	–	−12 (2)	174 (1)	−75 (1)	111 (1)	−4 (2)	3.22 (1)	2.83 (1)
(3)†	OMe	NO_2	*q-g*‡	–	–	−51.1 (3)	−175.1 (2)	−65.7 (2)	−1.6 (2)	5.3 (3)	3.077 (3)	2.947 (2)
(4)†	–	§	c_1	–	–	−8.8 (7)	−178.7 (5)	−71.0 (4)	–	–	3.246 (7)	2.874 (3)
¶			c_1	0.4	6.44	−15.7	172.4	−78.9	–	–	3.304	2.873
¶			c_2	63.1	5.37	8.2	−72.2	178.5	–	–	3.972	2.940
¶			*g*	26.3	2.08	88.7	−51.5	60.2	–	–	3.265	3.481

† X-ray. ‡ From Distefano *et al.* (1996). § *q-g* refers to the *quasi-gauche* conformation. ¶ 6-31G**.

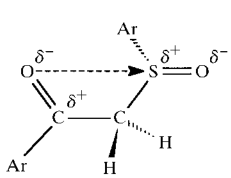
collection was started the crystal was transparent and colourless, and by the end it was stained owing to some moisture adsorption at the surface. In spite of the rather poor diffraction quality of (1) and (2) the main aim of the work was achieved, which was obtaining the relevant structural information.

3. Discussion

The torsion angles α, β, γ, γ′ and δ of the compounds are listed in Table 2 along with the O(2)···S and C(2)···O(1) interatomic distances. For the sake of comparison this table includes the corresponding X-ray geometrical data for the α-methylsulfinylacetophenone compound (4) in Table 2, together with the values obtained by fully optimized *ab initio* 6-31G** calculations for cis_1, cis_2 and *gauche* conformations (Distefano *et al.*, 1996). The most polar and least stable cis_1[2] rotamer for (4), obtained by *ab initio* calculations, has similar geometry to that of (1) and (2) with respect to α, β and γ torsion angles (II). As pointed out previously (Distefano *et al.*, 1996), the molecular structure of (4) has an α torsion angle close to that of the cis_2[3] rotamer (Table 2), but the β and γ



(II)



(III)

angles are interchanged with respect to those of the cis_2 rotamer (III). Thus, in the cis_1 rotamer the angle between the C═O and S═O dipoles is small, leading to a large repulsive field effect, *F* (Bellamy, 1978; Katritzky & Topsom, 1989), between the negatively charged O atoms of the referred dipoles. This agrees with the decrease of the negative charge at the carbonyl and sulfinyl O atoms in the cis_1 rotamer compared with the cis_2 rotamer for the parent α-methylsulfinylacetophenone (4) (Table 3).

The cis_1 rotamer of (4) possesses a higher dipole moment than that of the cis_2 rotamer (Table 2). The stabilization of the *cis* rotamers in (1) and (2), which have geometries similar to that of the cis_1 rotamer of (4), may be ascribed, as previously proposed, to a larger energy gain derived from dipole moment coupling. Moreover, Table 2 shows that the *cis* conformations of (1), (2) and (4) present a short contact between O(2)···S atoms, whose interatomic distances are shorter than the sum of the van der Waals radii, allowing a O(CO) → S(SO) intramolecular charge transfer which should also contribute to the stabilization of the cis_1 conformation in crystal (II). As expected from this geometry, the C(2)···O(1) interatomic distances for (1), (2) and (4) are in general larger than the sum of the van der Waals radii (Table 2).

On the other hand, (3) assumes a *quasi-gauche* (*q-g*) geometry (α ≃ 51°) in crystal (IV), but the β and γ torsion angles are close to those of the cis_1 rotamer for (1), (2) and (4)

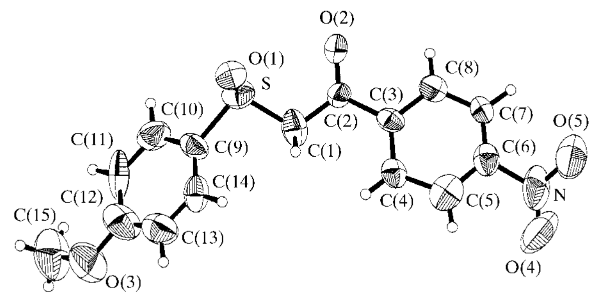
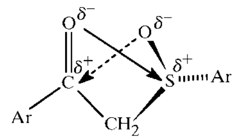


Figure 2
Crystal structure of (2) showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

[2] For the cis_1 rotamer the S═O group is *quasi*-perpendicular to the plane defined by O═C—CH$_2$—S bonds (II).
[3] For the cis_2 rotamer the S═O dipole belongs to the O═C—CH$_2$—S plane and is almost in the opposite direction with respect to the C═O dipole (III).

(Table 2). Consequently, these β and γ angles differ significantly from those of the *gauche* rotamer of (4), which is observed only in organic solvent solution (Olivato *et al.*, 1998).



(IV)

It should be pointed out that the *quasi-gauche* geometry of (3) not only allows a short contact between the O(2)$\cdots$S atoms [2.947 (2) Å], but also between the C(2)$\cdots$O(1) atoms [3.077 (3) Å]. In fact, the shortening of 0.38 Å between O(2)$\cdots$S atoms and 0.14 Å between C(2)$\cdots$O(1) atoms with respect to the sum of their van der Waals radii originate a through space-crossed charge transfer and attractive electrostatic interactions between the oppositely charged atoms of the C=O and S=O dipoles, which should stabilize the *quasi-gauche* geometry of (3) in crystal (IV).

The stronger O(CO) $\rightarrow$ S(SO) interaction with respect to the O(SO) $\rightarrow$ C(CO) interaction may be ascribed to the higher electron density at the carbonyl O atom owing to the conjugation which occurs in the *para*-methoxyphenacyl moiety and to the increased positive charge at the sulfinyl S atom in the *para*-nitrophenylsulfinyl moiety owing to the direct conjugation between the sulfinyl sulfur lone pair and the *para*-nitrophenyl group (see below).

It can also be noticed, in Table 2, that the carbonyl group and the phenyl ring of the acetophenone moiety are *quasi*-coplanar for (1)–(3) (δ in the range 5 to -11°), irrespective of the nature of the *para* substituent (MeO, NO_2 or H). Similarly, the sulfinyl group and phenyl ring of the phenylsulfinyl moiety is *quasi*-coplanar for (1) and (3) (γ' in the range -2 to -22°), for which the *para* substituents are H and NO_2, respectively (Table 2). However, in the case of (2), for which the *para* substituent at the phenylsulfinyl group is OMe, the sulfinyl group is *quasi*-perpendicular to the phenyl ring (γ' = 111°; Table 2). This behaviour may be explained as outlined below.

In the case of the *para*-nitrophenylsulfinyl derivative (3) it may be assumed that there is a stronger conjugation between the sulfinyl sulfur lone pair and the π system of the *para*-nitrophenyl group leading to the stabilization of the *quasi*-planar conformation. Similarly, the conjugation between the sulfinyl sulfur lone pair and the π-system of the phenyl ring should also be responsible for the *quasi*-coplanarity of the sulfinyl group and the phenyl ring for the phenylsulfinyl derivative (1), but obviously to a minor extent in comparison to (3).

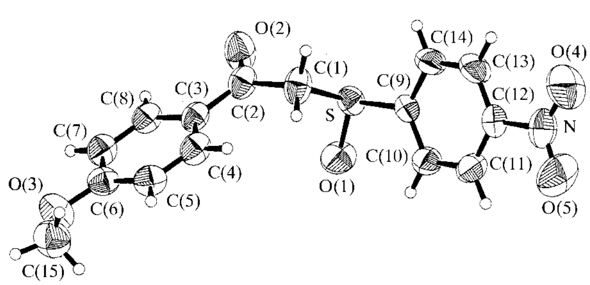


Figure 3
Crystal structure of (3) showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Table 3
Charges at selected atoms (e) for α-methylsulfinyl acetophenone (from Distefano *et al.*, 1996), $PhC(O)CH_2S(O)Me$ (4), obtained by *ab initio* 6-31G** computations (a minus sign indicates an excess of negative charge).

Conformer	e/C C(CO)	O(CO)	S(SO)	O(SO)
c_1	0.553	−0.523	1.018	−0.785
c_2	0.540	−0.545	1.004	−0.798
g†	0.549	−0.542	0.963	−0.787

† g corresponds to the most stable g_3 conformer of the original article.

As for (2), the conjugation between the methoxyl oxygen lone pair and the π system of the phenyl ring increases the electron density at C(9) of the benzene ring of the *p*-methoxyphenylsulfinyl moiety, leading to a stronger repulsion with the sulfinyl sulfur lone pair [see (I)]. This effect forces the sulfinyl sulfur lone pair to rotate, leading to a *quasi*-perpendicular geometry of the sulfinyl group in relation to the benzene ring of the *p*-methoxyphenylsulfinyl moiety.

Finally, X-ray data shows that the *para*-nitro and *para*-methoxy substituents, either at the phenacyl or at the phenylsulfinyl moiety, are almost coplanar with the benzene rings for (1)–(3). In fact, as for the *para* substituents at the phenacyl moiety, the δ' torsion angle[4] is in the range (-4 to 14°), and as for the *para* substituent at the phenylsulfinyl moiety, the γ'' torsion angle[5] is in the range (-6 to 9°).

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[4] δ' = $H_3C-O-C(6)-C(7)$ or $O-N-C(6)-C(7)$.
[5] γ' = $H_3C-O-C(12)-C(11)$ or $O-N-C(12)-C(11)$.

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