Experimental and theoretical study of the intramolecular interactions determining the conformation of β-carbonyl sulfoxides

Giuseppe Distefano,*[,a] Maurizio Dal Colle,[a] Marcello de Palo,[a] Derek Jones,[b] Gabriella Bombieri,[c] Antonio Del Pra,[c] Paulo R. Olivato[d] and Mirta G. Mondino[d]

[a] *Dipartimento di Chimica, Università di Ferrara, via Borsari 46, 44100 Ferrara, Italy*
[b] *ICoCEA-CNR, Area della Ricerca di Bologna, via P. Gobetti 101, 40129 Bologna, Italy*
[c] *Istituto di Chimica Farmaceutica, Università di Milano, Viale Abruzzi 42, 2013 Milano, Italy*
[d] *Instituto de Química, Universidade de São Paulo, Brazil*

Information on the geometrical and electronic structures of α-methylsulfinylacetophenone, $C_6H_5C(O)CH_2S(O)CH_3$ 2, have been obtained from X-ray diffraction analysis, UV photoelectron spectroscopy and *ab initio* 6-31G calculations. A comparison of the results with those obtained from the spectra and the computations on α-methylthioacetophenone, $C_6H_5C(O)CH_2SCH_3$ 1 and α-methylsulfonylacetophenone, $C_6H_5C(O)CH_2SO_2CH_3$ 3, together with previous results on β-keto sulfides and β-keto sulfones indicates that the CH_2–S(O) bond in 2 is *quasi-cis* to the carbonyl group in the gas and solid phase, at variance with the other β-carbonyl thioderivatives which adopt a *gauche* conformation. Eigenvector analysis, electron charge distribution at various atoms and/or groups and geometric parameters indicate that the *cis* conformation of 2 is stabilized by a strong non-bonded interaction between the negatively charged carbonyl oxygen and the positively charged sulfur atom from which it is separated by a distance (2.8–2.9 Å) much shorter than the sum of the van der Waals radii. The predominant charge transfer interaction in 3 and related sulfones occurs in the opposite direction ($O_{SO_2}\rightarrow C_{CO}$). The inversion of the direction of the charge transfer (and the change of the *cis*/*gauche* orientation of the thio group) from sulfone to sulfoxide is associated with an increase of electron affinity of the thio group in the latter, and could explain its smaller thermal stability.**

Ab initio **3-21G* calculations on several conformations of the bis-thioderivatives $C_6H_5C(O)CH(SCH_3)S(O)CH_3$ 4, $C_6H_5C(O)CH(SR)SO_2R$ (R = Me 5 and Ph 6) and $C_6H_5C(O)CH(SOCH_3)SO_2CH_3$ 7, together with X-ray diffraction (4, 6 and 7) and photoelectron spectroscopy (4) analyses confirmed the *cis* (SOR) and *gauche* (SR and SO_2R) preferred orientation of the thio groups with respect to the carbonyl group as observed in the monosubstituted derivatives. In 4 and 7 the S_{SO} atom is about 30° out of the *cis* plane [O(1)–C(2)–C(3)].**

Over the last few years we have investigated the interplay between the geometric and electronic structures of β-substituted carbonyl derivatives, $RC(O)CH_2X$ (R = alkyl, aryl, heterogroup; X = halogen, SR, SO_2R) in the gas and condensed phases. In particular, the results of IR, UV–VIS and ^{13}C NMR spectroscopies indicated[1–8] that the above compounds in solution prefer a *gauche* conformation, the quantity of the *cis* one being generally 10–20% of the former. The higher stability of the *gauche* rotamer has been mainly ascribed to the π_{CO}–σ_{C-S} and π^*_{CO}–σ^*_{C-S} hyperconjugative interactions, which alter the electronic distribution and, consequently, the ν_{CO} stretching frequencies, $\pi^*_{CO}\leftarrow n$ transition energies, NMR chemical shifts, *etc.* are modified with respect to the parent compounds where X = H or an alkyl group.

Ultraviolet photoelectron (PE) and electron transmission (ET) spectroscopy measure, respectively, the ionization energies (E_i) and the attachment energies (E_a) of bands and resonances related to various valence (filled and empty) molecular orbitals (MOs). These techniques offer, in principle, the possibility of isolating components of the total electronic effect of a substituent. We have used these electron spectroscopies, coupled with semiempirical, *ab initio* pseudopotential[9–13] or 3-21G* calculations on selected derivatives, to investigate the effects of the R and X substituents on the gas phase conformation of β-substituted carbonyls. In addition to the above mentioned hyperconjugative interactions detected in solution analyses, the PE and ET results indicate significant orbital mixing between the X heteroatom lone pair(s) and the π,π* and n_{CO} orbitals of the R–CO group. These interactions compete with the mesomeric interaction between the (substituted) R group and the carbonyl group to determine the most stable conformation.[14–18] The balance of the above interactions generally also results in the dominance of the *gauche* conformation in the gas phase, the stabilization energy deriving from X_{lp} and/or σ_{C-X} to π* MOs charge transfer (CT) interactions. In some cases the variation of the R group or even of the nature of its *para*-substituents from donor to acceptor, may sizeably modify the interaction between the X and CO group, or even stabilize the *cis* conformation.[15–18]

When X is a sulfonyl group (SO_2R', R′ = alkyl or aryl), most samples crystallize at room temperature, allowing X-ray diffraction analysis. The β-carbonyl sulfones prefer the *gauche* conformation in the gas, solid and liquid phases irrespective of the two substituents on the $-C(O)CH_2SO_2-$ fragment.[8,19–22] Energy levels, bond distance and electron charge distribution analyses indicate that this conformation is characterized by two short non-bonding distances between pairs of oppositely charged atoms: (i) the carbonyl carbon atom (δ+) and one of the oxygen atoms (δ−) of the SO_2 group, and (ii) the carbonyl oxygen atom (δ−) and the sulfur atom (δ+). The former distance, sizeably shorter than the sum of the van der Waals radii, allows through-space and through-bond[23] mixing between the MOs of the R–C(O) and SO_2 groups. In particular, a strong CT interaction from the SO_2 to the C(O) group occurs which, in part, counteracts the electron withdrawing inductive effect of the SO_2R group. The $-I_{SO_2}$ effect and the $\pi^*_{CO} \leftarrow O_{SO_2}$ CT interaction, therefore, appear to become stronger synergistically, forcing the dominance of the most propitious conformation.[21,22]

Both β-carbonyl sulfone and β-carbonyl sulfide derivatives, therefore, appear to prefer a *gauche* conformation which is stabilized by electron charge donation from the thio to the carbonyl group. In this context, we present here the results of an X-ray diffraction, PE spectroscopy and theoretical (*ab initio* 3-21G* and 6-31G**) study of the electronic and geometric structure of α-methylsulfinylacetophenone, $C_6H_5C(O)CH_2S(O)CH_3$ **2**, of the bis-thiosubstituted derivatives $C_6H_5C(O)CH(SCH_3)S(O)CH_3$ **4**, $C_6H_5C(O)CH(SR)SO_2R$ (R = Me **5** and Ph **6**) and $C_6H_5C(O)CH(SOCH_3)SO_2CH_3$ **7**, and of the related molecules α-methylthioacetophenone, $C_6H_5C(O)CH_2SCH_3$ **1** and α-methylsulfonylacetophenone, $C_6H_5C(O)CH_2SO_2CH_3$ **3**, in order to elucidate the conformation and the dominant electronic interactions present in the fragments C(O)–CH$_2$S(O)– and C(O)–CH(SO$_n$)SO$_m$–R (n = 0, 1; m = 1, 2).

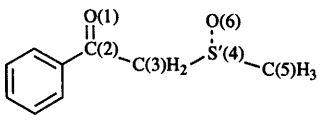
Experimental

Photoelectron (PE) spectra

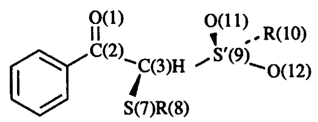
The He(I) spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer connected to a Datalab DL4000 signal analysis system. The bands, calibrated against rare-gas lines, were located using the position of their maxima, which were taken as corresponding to the vertical E_i values. The accuracy of the E_i values was estimated to be better than 0.05 eV (except for shoulders). The assignment of PE spectra is based on the composite-molecule approach and the substituent effect, using as reference compounds dimethyl sulfoxide, $CH_3S(O)CH_3$ **9**,[24] and acetophenone, $C_6H_5C(O)CH_3$ **8**,[15,25] for **2**, simple related molecules[17,22] for **1** and **3**, and **2** and dimethyl sulfide, CH_3SCH_3 **10**,[26] for the bisubstituted derivative **4**. The samples were available from previous studies.[8,22]

Calculations

The valence orbital energy and localization properties, the electron charge distribution at the various atoms and/or groups and the geometric parameters of compounds **1**–**7** were computed at *ab initio* levels using the GAUSSIAN 92 series of programs.[27] To determine the preferred conformation of **2** we have optimized 12 different starting geometries at the *ab initio* 3-21G* level. The starting conformations had the C(3)–S′(4) bond in the O(1)–C(2)–C(3) plane (*cis* conformations) or perpendicular to it (*gauche* conformations) and the methyl carbon, the sulfinyl oxygen or the sulfur lone pair lying in this plane. The geometry of the five lowermost conformations (c1, c2, g1, g2 and g3, see Table 1) was then optimized at the 6-31G** level (*d* functions on S and C and *p* functions on H), allowing complete relaxation. The dihedral angles α, β and γ are defined in the diagram below. Fully optimized 6-31G** computations were carried out also for **1** and **3** to compare the results with those obtained for **2**. Previous 3-21G* calculations indicated[22] that **3** prefers a *gauche* conformation corresponding to the solid state data obtained from X-ray diffraction analysis[28] (see Table 2). In addition, a *gauche* conformation has been generally found to be the most stable for β-carbonyl sulfides,[18] and thus only *gauche* conformations were optimized for **1** and **3**. Only frozen ring 3-21G* calculations (forcing the benzene ring to be planar with bond angles of 120°) were performed on the bisubstituted derivatives.



α = O(1)–C(2)–C(3)–S′(4)
β = C(2)–C(3)–S′(4)–C(5)
γ = C(2)–C(3)–S′(4)–O(6)



α = O(1)–C(2)–C(3)–S(7)
β = C(2)–C(3)–S(7)–R(8)
α′ = O(1)–C(2)–C(3)–S′(9)
β′ = C(2)–C(3)–S′(9)–R(10)
γ′ = C(2)–C(3)–S′(9)–O(11)

The conformation of **4** was optimized starting from X-ray diffraction data, **4a**; additional minima were found from this optimized geometry by exchanging the value of the two α angles **4c** or exchanging β with γ **4b**. To optimize the sulfide, sulfone derivatives **5** and **6** we started from the X-ray data for **6** using *cis* and *gauche* arrangements for the SMe and SO$_2$Me groups, respectively (**5a** and **6a**), and then the α and α′ values were interchanged (**5b** and **6b**). Finally, five different starting conformers were used for **7**, differing in the values of the α, β and γ angles of the two substituents. In the conformer optimized by starting from the experimental geometry (**7b**) the C=O bond lies in the space formed by the angle O(11)–S′(9)–O(12) (see Fig. 1 for the atom numbering), while in the other sulfonyl derivatives the carbonyl group lies outside this space both experimentally and theoretically (see the β′ and γ′ values in Table 3). For this reason, we also optimized a conformation (**7a**) whose starting geometry for the two thio substituents was taken from those of

Table 1 Relative energy dipole moment (*pl*), selected dihedral angles and non-bonded distances optimized for different *cis* (c) and *gauche* (g) conformers of $PhC(O)CH_2S(O)CH_3$ (**2**) at the 6-31G** and 3-21G* (frozen ring) levels and corresponding X-ray geometrical data (in italics), and sum of the relevant van der Waals radii

			Dihedral angles[a]/°				
	Relative energy/kJ mol^{-1}	μ/D	α	β	γ	C(2)···O(6)[b]/Å	O(1)···S′(4)[c]/Å
X-Ray	—	—	−8.8(7)	−178.7(5)	−71.0(4)	3.246(7)	2.874(5)
3-21G*	**2a**, c1: 19.58	6.56	−6.4	169.8	−80.6	3.335	2.834
frozen ring	**2b**, c2: 4.60	5.26	8.3	−71.5	177.8	3.974	2.917
	2c, g1: 14.54	3.66	90.1	−75.7	173.1	3.987	3.425
	2d, g2: 6.77	2.55	98.5	−161.7	88.8	3.495	3.537
	2e, g3: 0.00	0.89	101.1	−31.3	81.2	3.519	3.632
6-31G**	**2a**, c1: 12.41	6.44	−15.7	172.4	−78.9	3.304	2.873
optimized	**2b**, c2: 0.00	5.37	8.2	−72.2	178.5	3.972	2.940
	2c, g1: 7.18	3.83	88.8	−76.4	173.4	3.980	3.416
	2d, g2: 5.60	3.16	88.7	−166.5	84.4	3.409	3.403
	2e, g3: 2.17	2.08	88.8	−51.5	60.2	3.265	3.481

[a] α = O(1)–C(2)–C(3)–S; β = C(2)–C(3)–S–R; γ = C(2)–C(3)–S–O. [b] Sum of van der Waals radii = 3.22 Å. [c] Sum of van der Waals radii = 3.32 Å.

Table 2 Valence region E_i (eV; in italics), values and corresponding *ab initio* MO energies ($-\varepsilon_i$/eV) for compounds **1–4** and experimental data for the reference compounds **8–10**

		n_S	π_R	π_R	π_{SO}	n_{CO}	Next band
1, $C_6H_5C(O)CH_2SCH_3$	*Exp*	*8.55*	*9.41*	*9.69*		*9.41*	*11.28*
	6-31G**	9.19	9.32	9.58		11.35	
2, $C_6H_5C(O)CH_2S(O)CH_3$	*Exp*	*8.69*	*9.58*	*9.58*	*9.8*	*10.69*	
2a, c1	6-31G**	9.19	9.65	9.78	11.08	11.80	
2b, c2 (min.)	6-31G**	9.64	9.68	9.84	11.04	12.08	
2c, g1	6-31G**	9.95	9.60	9.70	11.15	12.05	
2d, g2	6-31G**	10.13	9.25	9.35	11.25	11.81	
2e, g3	6-31G**	9.94	9.27	9.37	11.43	11.80	
3, $C_6H_5C(O)CH_2SO_2CH_3$	*Exp*		*9.77*	*9.77*		*10.0*	*10.80*
	6-31G**		9.54	9.64		11.70	
4, $C_6H_5C(O)CH(SCH_3)S(O)CH_3$	*Exp*	*8.62*	*9.48*	*9.6(5)*	*10.0sh*	*10.85*	*11.29*
		9.0(5)					
4a	3-21G*	9.43	9.65	9.80	11.24	11.77	
		10.22					
4b	3-21G*	9.37	9.81	9.89	10.77	11.83	
		10.15					
8, $C_6H_5C(O)CH_3$[a]	*Exp*		*9.38*	*9.8*		*9.57*	*>11.5*
9, $CH_3S(O)CH_3$[b]	*Exp*	*9.1*			*10.17*		*12.57*
10, CH_3SCH_3[c]	*Exp*	*8.72*					*11.30*

[a] From ref. 15. [b] From ref. 24. [c] From ref. 26.

Table 3 Relative energies (ΔE) of various conformers, experimental and theoretical (3-21G*) values of the dihedral angles for compounds **1–7**, PhC(2)[O(1)]C(3)H(SO$_n$R)S′O$_m$R (n = 0, 1; m = 1, 2); X-ray values are reported in italics

				Dihedral angles[a]/°					
	X	X′	ΔE/kJ mol^{-1}	α	β	γ	α'	β'	γ'
1	H	SMe					92.8	−70.6	
2a	H	SOMe	19.58				−6.4	169.8	−80.6
		X-ray, c1					*−8.8(7)*	*−178.7(5)*	*−71.0(4)*
2b		c2	4.6				8.27	−71.53	177.8
		$(\beta'\leftrightarrow\gamma')$[c]							
2e		g3	0.0				101.1	−31.3	81.2
3a	H[b]	SO_2Me					83.4	−65.6	49.4
		X-ray					*80.1(7)*	*−73.6(5)*	178.8
									43.1(6)
									171.7(5)
3b	H[c]	SO_2Ph					93.8	−59.8	55.5
		X-ray					*89.8(2)*	*−43.3(2)*	−174.7
									72.2(2)
									−158.8(1)
4a	SMe	SOMe	0.0	−93.0	57.4		30.9	163.7	61.4
		X-ray		*−90(3)*	*53(3)*		*35(4)*	*165(3)*	*55(3)*
4b		$(\beta'\leftrightarrow\gamma')$[d]	4.01	−97.5	63.4		25.7	57.0	175.6
4c		$(\alpha\leftrightarrow\alpha')$[d]	19.85	14.5	64.1		−105.4	−147.0	109.8
5a	SMe	SO_2Me	0.0	113.6	−48.8		−11.9	−50.9	65.9
									−164.6
5b	SMe	SO_2Me	1.97	−92.8	23.4		37.7	−70.3	46.3
		$(\alpha\leftrightarrow\alpha')$[d]							174.1
6a	SPh	SO_2Ph	0.0	110.6	−29.1		−15.2	−57.4	59.9
		X-ray		*94(1)*	*−50.4(8)*		*−35(1)*	*−47.1(9)*	−169.9
									70.1(9)
									−160.6(8)
6b		$(\alpha\leftrightarrow\alpha')$[d]	8.74	−103.14	87.5		126.7	−148.8	−34.8
									97.3
7a	SOMe	SO_2Me[e]	0.0	38.1	157.2	54.3	−86.6	59.8	−53.6
									176.7
7b			1.31	−15.2	−67.4	−169.4	108.3	−157.3	−39.5
		X-ray		*−23(1)*	*−83(6)*	*176(4)*	*95(4)*	*152(6)*	90.2
									89(4)
									42(4)
7c		$(\beta\leftrightarrow\gamma)$[d]	30.16	−41.7	−175.4	−57.9	83.0	131.1	−112.3
									18.3
7d	SOMe	SO_2Me	22.79	−105.7	150.9	44.8	22.2	43.4	−72.3
		$(\alpha\leftrightarrow\alpha')$[d]							159.1
7e	SOMe	SO_2Me	17.93	38.8	−86.8	167.8	−95.4	34.12	−78.4
		$(\beta'\leftrightarrow\gamma')$[d]							152.0

[a] α = O(1)–C(2)–C(3)–S; α' = O(1)–C(2)–C(3)–S′; β = C(2)–C(3)–S–R; β' = C(2)–C(3)–S′–R; γ = C(2)–C(3)–S–O; γ' = C(2)–C(3)–S′–O. [b] From ref. 28. [c] From ref. 22. [d] For each compound the optimization started from the experimental data. Additional minima were found from these optimized geometries modified by exchange of the torsion angles related by ↔ in column 3. [e] The starting geometry was taken from compounds **2** and **3**, see text.

the monosubstituted compounds **2** and **3**. Conformer **7a** was found to be slightly (1.31 kJ mol^{-1}) more stable than **7b**. The results of the calculations are collected in Tables 1–5 together with the relevant experimental data.

In order to contain the computational costs at manageable levels (for example, compound **6** at the 3-21G* level needs 277 basis functions), a search for the absolute energy minimum for the bis-thioderivatives was not pursued. Our efforts were directed to reproduce the experimental conformation and to investigate the variations caused by a limited number of changes in the orientation of the thio substituents.

Crystal data

$C_9H_{10}O_2S$ 2. $M = 182.2$; orthorhombic; *Pbca*, $a = 9.458(2)$, $b = 19.885(2)$, $c = 9.498(1)$ Å; $V = 1786.3(7)$ Å^3; $Z = 8$; $D_x = 1.35$ Mg m^{-3}; λ(Mo-Kα) = 0.710 69 Å; $R = 0.045$ ($R_w = 0.050$) for 670 observed reflections [$I > 3\sigma(I)$].

$C_{10}H_{12}O_2S_2$ 4. $M = 228.3$; monoclinic; *C2/c*, $a = 27.78(1)$, $b = 5.518(7)$, $c = 15.707(9)$ Å; $\beta = 115.37(4)$°; $V = 2176(3)$ Å^3; $Z = 8$; $D_x = 1.39$ Mg m^{-3}; λ(Mo-Kα) = 0.710 69 Å; $R = 0.13$ ($R_w = 0.14$) for 650 observed reflections [$I > 2\sigma(I)$].

$C_{20}H_{16}O_3S_2$ 6. $M = 368.5$; monoclinic; $P2_1/n$, $a = 10.384(4)$, $b = 16.165(2)$, $c = 11.601(4)$ Å; $\beta = 112.61(2)$°; $V = 1797.6(9)$ Å^3; $Z = 4$; $D_x = 1.36$ Mg m^{-3}; λ(Mo-Kα) = 0.710 69 Å; $R = 0.064$ ($R_w = 0.068$) for 965 observed reflections [$I > 3\sigma(I)$].

$C_{10}H_{12}O_4S_2$ 7.[29] $M = 260.3$; triclinic; $P_{\bar{1}}$, $a = 5.31(2)$, $b = 13.40(2)$, $c = 17.83(3)$ Å; $\alpha = 103.3(1)$, $\beta = 98.6(1)$, $\gamma = 101.4(1)$°; $Z = 4$; $D_x = 1.46$ Mg m^{-3}; λ(Mo-Kα) = 0.710 69 Å.

Data collection, processing and refinement

CAD4 diffractometer ω–2θ scan technique, graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å), $T = 295$ K. Solution by direct methods (SHELX-86).[30] Full matrix least-squares refinement. Anisotropic thermal parameters for all non-hydrogen atoms were applied for compound **2**. For compounds **4** and **6** anisotropy was applied only to the non-phenyl atoms which were refined as isotropic rigid groups. The H-atoms were introduced in calculated positions with fixed isotropic thermal parameters ($U = 0.07$ Å^2). The weighting scheme $w = [\sigma^2 F_o{}^2 + PF_o2]^{-1}$ was applied, with $P = 0.005\,543$ for **2**, $P = 0.015\,074$ for **4** and $P = 0.025\,82$ for **6**. Scattering factors were taken from ref. 31. Structure refinement and final geometrical calculations were carried out with SHELX-76[32] and PARST[33] programs. Drawings were produced using ORTEP II.[34]

Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **2**, **4** and **6** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/11.

Results and discussion

α-Methylsulfinylacetophenone 2

The molecular structure determined by X-ray diffraction is shown in Fig. 1. The value for the dihedral angles α, β and γ are presented in Table 1, together with the corresponding values obtained by fully optimized *ab initio* 6-31G** and frozen ring 3-21G* calculations for the five conformations c1, c2, g1, g2 and g3. Table 1 also lists the experimental and computed O(1) ··· S′(4) and O(6) ··· C(2) interatomic distances compared with the corresponding sums of the van der Waals radii.[35]

The most stable minimum occurs for the *quasi-cis* conformation, c2, which has $\alpha = 8.17$° (6-31G**), in agreement with the solid phase value, $\alpha = -8.4$°. However, the β and γ values of c2 are interchanged with respect to the X-ray diffraction data. The conformer which reproduces the experimental β and γ values lies higher in energy by 12.41 kJ/mol^{-1} (6-31G**). The three *gauche* conformations have intermediate energy. From the 6-31G** relative energies of Table 1, the intensity of the *gauche* rotamers in the gas phase is about 50% of that of the prevalent c2 conformer. This figure can be compared with 45% and 65% derived from the analysis of the IR spectrum in CCl_4 and hexane, respectively.[36] (The 3-21G* calculations are unable to reproduce the correct ordering of the first two conformers, see Table 1.) There are no intermolecular short contacts in the crystal which could justify the higher stability of the c1 conformer. However, both c1 and c2 possess high dipole moments (6.44 and 5.37 D,† respectively, 6-31G**) and the stabilization of the c1 over the c2 form could be associated with a larger energy gain deriving from dipole moment coupling in the crystal. Therefore, the β-carbonyl sulfoxide group –C(O)CH_2S(O)– in **2** prefers a *cis* conformation where the C(3)–S′(4) bond is nearly coplanar with the O(1)–C(2) bond. This result is at odds with those of **1** and **3** (see Table 3), which prefer[21,22] a *gauche* arrangement. The *gauche* conformation of the sulfide is stabilized by the crossed $\sigma^*_{C-S} \leftarrow \pi_{CO}$ and $\pi^*_{CO} \leftarrow \sigma_{C-S}$ MO CT interactions. The largest contribution to the stabilization of a *gauche* conformer for the sulfone derivative originates from electrostatic and CT intramolecular interactions between the SO_2 and the CO groups. These interactions are made possible by the short non-bonded distance between a partially negatively charged oxygen atom of the SO_2 group [O(6)] and the positively charged C(2) (see Tables 4 and 5). An interesting observation from the data of Table 1 is that the O(6) ··· C(2) contact distance in **2** is longer than the sum of the corresponding van der Waals radii, while the O(1) ··· S′(4) contact distance is significantly (*ca.* 0.4 Å) shorter in the *cis* derivatives in both gas and solid phases.

The PE spectra of derivatives **1**–**4** are presented in Fig. 2. The E_i values that are lower than about 11.5 eV are collected in Table 2, together with the corresponding *ab initio* MO energies and the relevant values from the spectra of reference compounds **8**, **9** and **10**. On the basis of the assignment of the spectra of **8**[15,25] and **9**,[24] five ionizations are expected in the low (< 11 eV) E_i region of **2**. It shows, in fact, three bands of relative intensity 1 : 3 : 1 (see Fig. 2). As shown by the partial energy level correlation diagram in Fig. 3(*a*), the splitting between the first and the third bands in **2** (1.9 eV) is larger than the corresponding value in the component molecules **8** and **9** (*ca.* 1 eV), indicating a sizeable interaction between the two moieties of **2**. Strong orbital mixing is confirmed by eigenvector analysis. In order to test the ability of the *ab initio* calculations to reproduce the electronic structure of this class of compounds, the computed valence MO ordering of compounds **1** and **3** has been compared with the E_i ordering obtained from the PE spectra. The computations closely reproduce, in the Koopmans' approximation, the π-ring E_i values (see Table 2), but the n_S (in **1**) and, particularly, the n_{CO} (in **3**) orbitals are computed to be too stable by 0.6 and 2.0 eV, respectively. This indicates that the conformation of **2** in the gas phase does not correspond to g3, g2 or g1, because the n_S orbital is computed to lie below the π-ring orbitals for these rotamers, in disagreement with the spectrum which begins with an isolated band (whose shape is characteristic for an n_S orbital). The intensity ratio of the photoelectron bands indicates an upper limit of 10% for the contribution of the *gauche* rotamers to the spectral intensity. At variance with the other rotamers, the n_S and the two π-ring orbitals are deeply mixed in c2, explaining the experimental destabilization of the HOMO of **2** with respect to **9** [see Fig. 3(*a*)]. The computations indicate also, that in c2 the n_{CO} and π_{SO} orbitals of the two fragments are deeply mixed, through the CH_2 bridge,[37] and that the fourth and fifth MOs are mainly localized at the sulfinyl and carbonyl oxygen, respectively. The calculations suggest, therefore, that the n_{CO}/π_{SO} ordering in **2**

---

† D ≈ 3.335 64 × 10^{-30} C m.

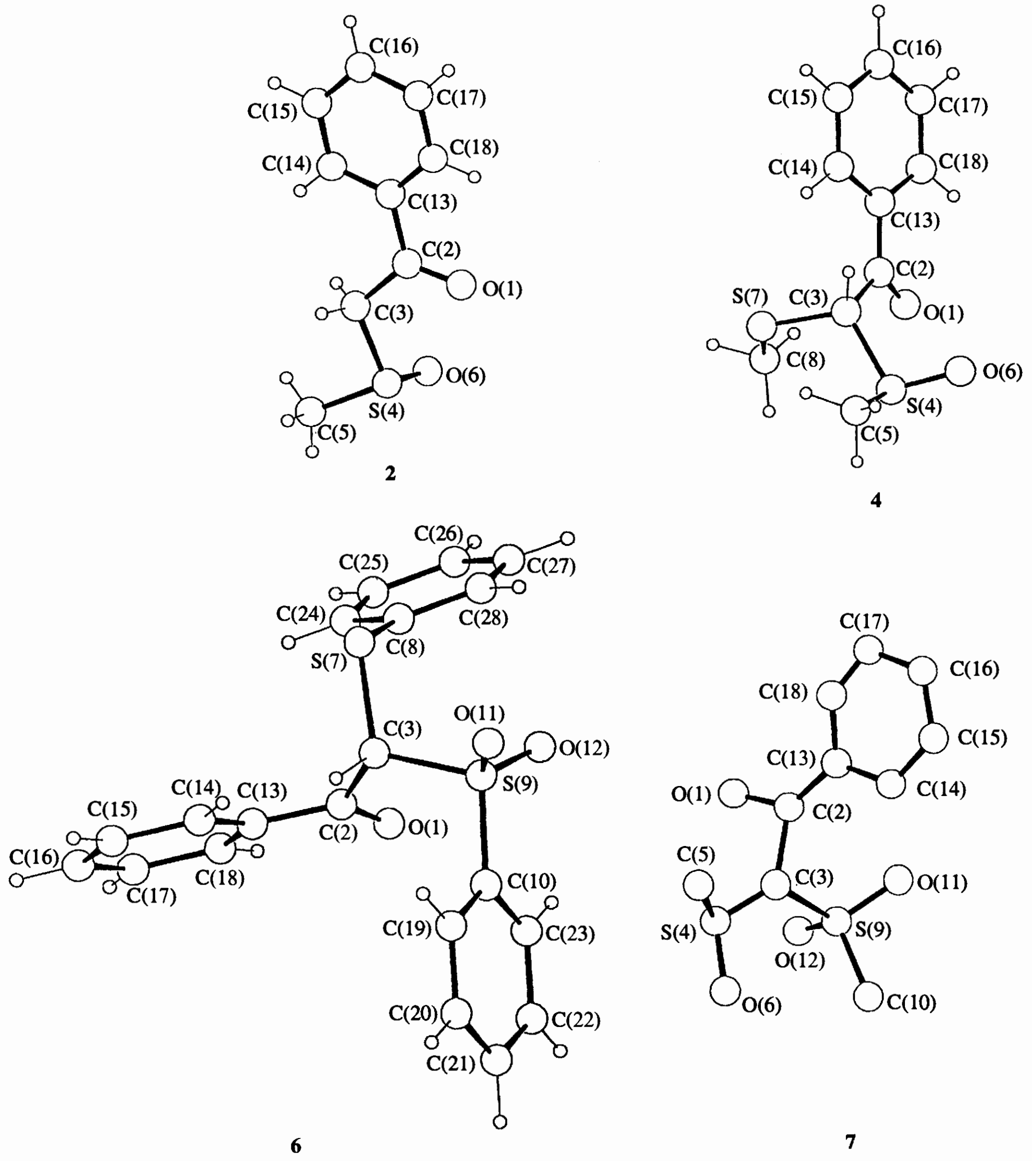
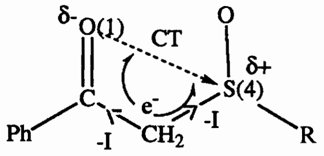
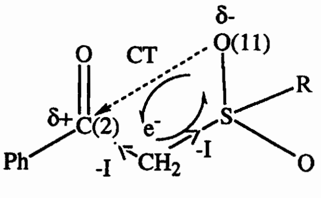


Fig. 1 Crystal structures of compounds **2**, **4**, **6** and **7** with heavy atom labelling. The size of the atoms is arbitrary. In **7**, hydrogen atoms are omitted (see text).

(n_{CO} = 10.69, π_{SO} = 9.8 eV) is reversed with respect to the component fragments (n_{CO} in **8** = 9.57 or 9.8, π_{SO} in **9** = 10.17 eV). A comparison between the PE spectra of $C_6H_5SOCH_3$ (two π-ring and π_{SO} bands at 9.6–10.1 eV)[24] and $C_6H_5COCH_3$ (two π-ring and n_{CO} bands at 9.4–9.8 eV)[15] indicates that the inversion cannot be ascribed to the slightly larger electron-withdrawing effect of the CH_3SO group compared to the CH_3CO group. The rationalization of these findings can be found in the geometric structure and charge distribution of **2b** (see Tables 1 and 5). The carbonyl oxygen atom, in fact, bears a negative charge (-0.55 e$^-$) and is separated from the positively charged ($+1.0$ e$^-$) sulfur atom by a distance (*ca.* 2.9 Å) much shorter than the sum of the van der Waals radii (3.32 Å). So that, in addition to the through-bond mixing between the n_{CO} and the π_{SO} orbitals, there is also a strong electrostatic interaction between the O(1) and S′(4) atoms, coupled with a (small in the ground state) O(1)⟶S′(4) charge transfer. The direction of the CT interaction in **2** occurs in the reverse direction to the prevailing CT interaction [O(11)⟶C(2)] in sulfone **3**, explaining the increase of the E_{nCO} value in the former (see Table 2). Finally, the relaxation of the negative charge from O(1) towards the SO group upon π_{SO} ionization contributes to the reduction of the $E_{\pi SO}$ value in **2** with respect to **9** (see Table 2).



2



3

A reason for the peculiar conformational behaviour of β-carbonyl sulfoxide **2** with respect to β-carbonyl sulfide **1** and β-carbonyl sulfone **3** can be found in the higher electron affinity of the thio group in the former compound. In fact, the lowest

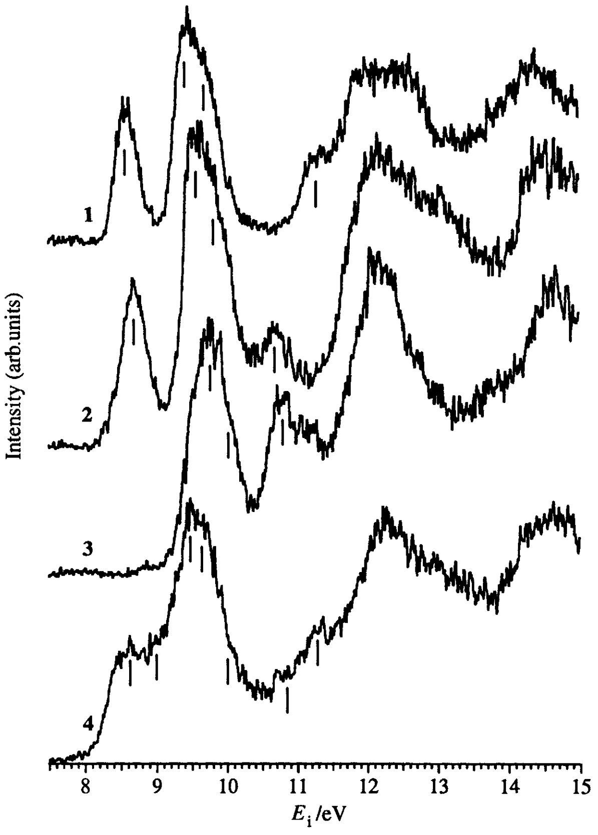


Fig. 2 Photoelectron spectra of compounds $C_6H_5C(O)CH_2SCH_3$ **1**, $C_6H_5C(O)CH_2S(O)CH_3$ **2**, $C_6H_5C(O)CH_2SO_2CH_3$ **3** and $C_6H_5C(O)CH(SCH_3)S(O)CH_3$ **4**

attachment energy (E_a) value of the corresponding dimethyl derivatives decreases in the order: SMe_2 = 3.25,[38] SO_2Me_2 = 3.10[39] and $SOMe_2$ = 2.30 eV.[40]

We noticed that derivative **2** slowly decomposes even if stored at low temperature, producing compounds deriving from the breaking of the C(3)–S′(4) and C(2)–C(3) bonds, while **3** is much more stable in the same conditions. Both the thiosubstituents have strong electron-withdrawing inductive effects, so that the different stability might be due to the opposite direction of the dominant CT interaction between the thio and the carbonyl groups. As far as the charge density at the C(2)–C(3) and C(3)–S′(4) bonds is concerned, the dominant CT interaction in **3** counteracts the strong $-I_{SO_2R}$ effect, while in **2** the CT interaction cooperates with the electron-withdrawing effect of the SOR group weakening the bond strength and thus facilitating the detachment of the sulfinyl group.

An analysis of the crystal structure of **2** indicates, in addition, that the molecular packing is characterized by some relatively short contacts between either the phenyl or the methylenic hydrogens of adjacent molecules and the O(6) of the sulfoxide group of the order of 2.4–2.6 Å. Despite the methylene group lying between two electron-withdrawing groups, there is no evidence of intramolecular hydrogen bonds, and tautomeric forms are not possible because of the conformation. This result is in agreement with the analysis of the computed (6-31G**) geometry of the *cis* rotamers, where the shortest H···O contact, which occurs with O(6) (2.72 Å), is longer than the sum of the van der Waals radii (2.6 Å). Clearly, the O(1)→S′(4) interaction dominates and determines the prevailing *cis* conformation of **2**. Similarly, in the structure of **3**, intramolecular short contacts between the methylenic hydrogens and the oxygen atoms have not been detected either in the crystals[28] or in the computations. In the computed (6-31G**) structure of the gl conformer the shortest H···O contact (2.527 Å) is to O(1).

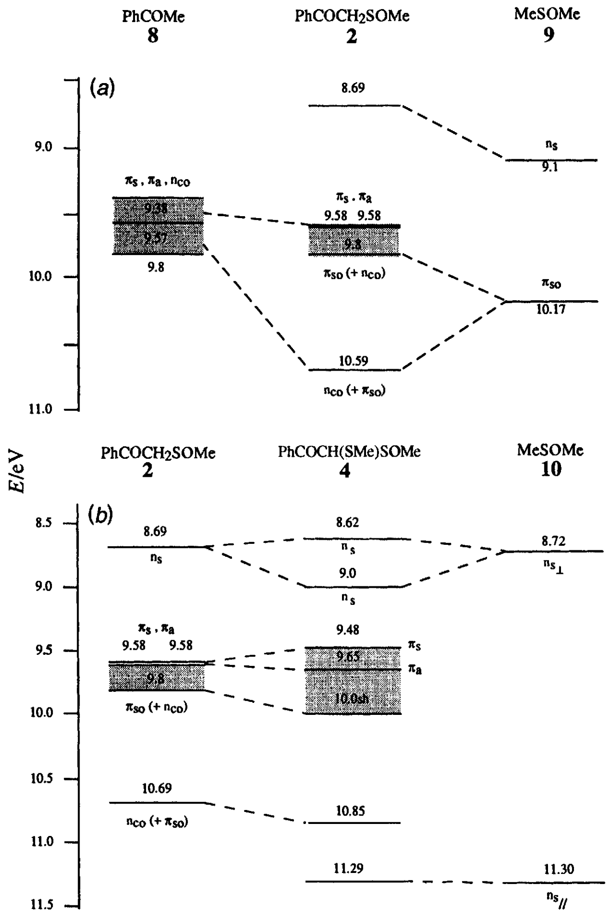


Fig. 3 Partial energy level correlation diagrams for (*a*) compounds **8**, **2** and **9**, and (*b*) compounds **2**, **4** and **10** ($n_{S\perp}$ and $n_{S\parallel}$ indicate the sulfur lone pair orbitals of **10** lying, respectively, perpendicular to and in the C–S–C plane)

Bisubstituted derivatives 4–7, PhC(O)CH(SO$_n$R)S′O$_m$R (n = 0, 1; m = 1, 2)

The X-ray structures of compounds **4**, **6** and **7**[29] are shown in Fig. 1. The values of the dihedral angles α, β, γ, α′, β′ and γ′ obtained by X-ray diffraction are presented in Table 3 together with those obtained from 3-21G* calculations for the various conformers of compounds **1**–**7**. In Tables 3–5, the two α-substituents of the basis compound acetophenone, $PhC(O)CH_3$, are named X and X′. The former symbol refers to H or to the less oxidized thiosubstituent, the latter to the more oxidized one. Table 3 also reports the relative energies of the various conformers of each compound. Table 4 lists the experimental and computed contact distances between C(2) and the oxygen atoms of the thio groups and between O(1) and the sulfur atoms, together with selected bond lengths. A satisfactory agreement exists between the experimental and the computed data, except for **7**, for which only preliminary structural data are available. The charges at various atoms and groups for compounds **1**–**7**, obtained by *ab initio* 3-21G** calculations, are presented in Table 5. A minus sign indicates an excess of negative charge. The most stable computed geometry for the bis-thioderivatives **4** and **6** matches that obtained by X-ray diffraction. The computations also reproduce (**7a** and **7b**) the *quasi-cis* and *gauche* orientation of the SO and SO_2 groups, respectively, while the optimized β and γ values differ somewhat from the corresponding data in the crystals. In the two lowest energy conformations of the S, SO bisubstituted derivative **4**, the orientations of the thio groups are nearly the same as those of the respective monosubstituted compounds, *i.e.* the SO group is *quasi-cis* with respect to the carbonyl, while the S one is *gauche* (see Table 3). The exchange of the positions of the

Table 4 Experimental and theoretical (3-21G*) values of selected bond lengths and interatomic distances for compounds **1**–**7**, PhC(2)[O(1)]C(3)H(SO$_n$R)S′O$_m$R (n = 0, 1; m = 1, 2); X-ray values in italics

			Bond lengths and interatomic distances/Å							
	X	X′	C(2)O(1)	C(2)C(3)	C(3)S	C(3)S′	C(2)O	C(2)O′	SO(1)	S′O(1)
1	H	SMe	1.218	1.515		1.826				3.444
2a	H	SOMe, c1	1.214	1.522		1.804		3.335		2.834
		X-ray	*1.219(8)*	*1.492(8)*				*3.246(7)*		2.874(5)
2b		$(\beta'\leftrightarrow\gamma')$, c2	1.217	1.513		1.805		3.974		2.917
2c		$(\beta'\leftrightarrow\gamma')$, g1	1.218	1.518		1.817		3.987		3.425
2d		g2	1.215	1.528		1.812		3.495		3.537
2e		g3	1.216	1.525		1.816		3.519		3.632
3a	H^a	SO$_2$Me	1.217	1.525		1.77		3.04 3.945		3.368
		X-ray	*1.216(8)*	*1.524(8)*		*1.787(8)*		*2.991(8)*		*3.308(8)*
3b	H^b	SO$_2$Ph	1.214	1.525		1.773		3.162 3.953		3.507
		X-ray	*1.211(2)*	*1.518(3)*		*1.782(2)*		*3.306(2)*		*3.426(2)*
4a	SMe	SOMe	1.217	1.525	1.818	1.815		3.10	3.445	2.869
		X-ray	*1.27(4)*	*1.50(5)*	*1.82(3)*	*1.82(4)*		*3.09(4)*	*3.36(3)*	*2.94(2)*
4b		$(\beta'\leftrightarrow\gamma')^c$	1.222	1.518	1.822	1.832		3.988	3.468	2.973
4c		$(\alpha\leftrightarrow\alpha')^c$	1.212	1.534	1.815	1.849		3.654	2.97	3.583
5a	SMe	SO$_2$Me	1.216	1.520	1.830	1.796		3.281 3.930	3.647	2.968
5b		$(\alpha\leftrightarrow\alpha')^c$	1.216	1.521	1.831	1.793		3.001 3.927	3.50	3.02
6a	SPh	SO$_2$Ph	1.213	1.517	1.842	1.795		3.25 3.93	3.642	2.994
		X-ray	*1.20(2)*	*1.53(1)*	*1.82(1)*	*1.80(1)*		*3.36(1)* >*3.5*	*3.455(8)*	*3.044(7)*
6b		$(\alpha\leftrightarrow\alpha')^c$	1.215	1.484	1.832	1.785		2.954 3.563	3.554	3.729
7a	SOMe	SO$_2$Me^d	1.217	1.533	1.832	1.775	3.0	3.02 3.94	2.891	3.356
7b			1.217	1.536	1.830	1.797	3.944	2.93 3.40	2.763	3.553
		X-ray	*1.3(1)*	*1.6(1)*	*1.6(1)*	*1.8(1)*	>*3.5*	*2.9(1)* *3.2(1)*	*3.0(1)*	*3.3(1)*
7c		$(\beta'\leftrightarrow\gamma')^c$	1.211	1.541	1.845	1.785	2.967	3.60 2.74	2.879	3.273
7d		$(\alpha\leftrightarrow\alpha')^c$	1.214	1.530	1.865	1.789	2.946	3.29 3.91	3.521	2.945
7e		$(\beta'\leftrightarrow\gamma')^c$	1.219	1.530	1.845	1.790	3.96	3.312 3.937	2.882	4.274 4.471

[a] From ref. 28. [b] From ref. 22. [c] For each compound the optimization started from the experimental data. Additional minima were found from these optimized geometries modified by exchange of the torsion angles related by ↔ in column 3. [d] The starting geometry was taken from compounds **2** and **3**, see text.

two substituents of the sulfinyl group $(\beta'\leftrightarrow\gamma')$ in the input geometry of **4a** is associated with a small (4.01 kJ mol^{-1}) energy increase of the optimized conformation (**4b**). However, when the torsions of the two thiogroups are exchanged $(\alpha\leftrightarrow\alpha')$, the total energy increases by about 20 kJ mol^{-1}, indicating that some important stabilizing interaction is lost in this operation. With respect to the monosubstitued derivatives, in **4a** the electron charge at the carbonyl carbon atom, C(2), is less (+0.630 e, +0.596 e, +0.584 e in **4a**, **1** and **2b**, respectively) and the non-bonding contact between C(2) and O(6) is shorter [*ca.* 3.1 (**4a**) and 3.974 Å (**2b**)], becoming shorter than the sum of their van der Waals radii. The presence of the O(6)⟶C(2) charge transfer in addition to the strong O(1)⟶S(4) CT interaction [$d_{O(1)/S'(4)}$ = 2.87 Å, see Table 4] is related to an increase of the α value from 8° (**2**) to about 30° (**4a** and **4b**) and appears to increase the molecular stability. In fact, the (vapour phase) PE spectrum of **4** does not show any decomposition product. The spectrum, however, does show an increased interaction between the various group orbitals with respect to **2**, as indicated by the spreading out of the energy levels in the correlation diagram [Fig. 3(*b*)] amongst the uppermost E_i values of **2**, **4** and **10**. Interestingly, the HOMO of **4** is only slightly destabilized with respect to **2**, likely because the above mentioned O(6)⟶C(2) CT interaction stabilizes the MOs mainly localized at the SO group. The assignment of the next five bands is shown in Fig. 3(*b*). Taking into account the above mentioned downward shift, with respect to the π-ring orbitals, of the computed energy of the heteroatom lone pair orbitals, the *ab initio* energy level ordering (see Table 2) supports the experimental assignment. In particular, the π-ring and π_{SO} orbitals agree better with the results of the computations for the **4b** conformer.

Both the X-ray and the theoretical data indicate that, also in compound **7**, the thio groups have the same conformation as in the respective monosubstituted derivatives. Namely, the SO group assumes a *quasi-cis* orientation with respect to the carbonyl group and the SO$_2$ group a *gauche* one. The SO *gauche*-SO$_2$ *cis* conformer, **7d**, has significantly (*ca.* 22.8 kJ mol^{-1}) higher energy. As in **2**, the O$_{CO}$–S$_{SO}$ distance in **7** is sizeably shorter (2.89 Å) than the sum of van der Waals radii, so that the O(1)⟶S(4) charge transfer is still strongly active in the bisthiosubstituted compound. In analogy with **4**, in **7a** there is a strong O(6)$^{\delta-}$ ··· C(2)$^{\delta+}$ interaction, determined by the increase of positive charge at C(2) with respect to the monosubstituted derivative and by the value of the O$_{SO}$–C$_{CO}$ distance, which in **7a**, but not in **7b**, is quite shorter than the sum of the respective van der Waals radii. Once again, the presence of two crossed CT interactions could be a leading stabilizing factor, as already seen in **4**. The behaviour of the SO$_2$ substituent of **7a** is the same as that in the corresponding

Table 5 Charges at various atoms and groups (*e*) for compounds **1**–**7**, PhC(O)CHSO$_n$RS′O$_m$R (n = 0, 1; m = 1, 2), obtained by *ab initio* 3-21G* computations (a minus sign indicates an excess of negative charge)

			e/C								
	X	X′	XCHX′	C_{CO}	O_{CO}	Ph	S	SO	SO_2	SO	SO_2
1	H	SMe	−0.006	0.596	−0.584	−0.019	0.200				
2a	H	SOMe c1 (X-ray)[a]	−0.038	0.604	−0.561	−0.005		1.07		−0.680	
2b		c2 ($\beta' \leftrightarrow \gamma'$)[b]	−0.008	0.584	−0.582	0.007		1.066		−0.699	
2e		g3	0.010	0.588	−0.570	−0.028		1.031		−0.669	
3a	H	SO_2Me (X-ray)[a]	−0.184	0.571	−0.568	0.180			1.527		−0.591 −0.600
3b	H	SO_2Ph (X-ray)[a]	−0.021	0.574	−0.554	0.001			1.657		−0.605 −0.605
4a	SMe	SOMe (X-ray)[a]	−0.076	0.630	−0.569	0.015	0.228	1.067		−0.680	
4b		($\beta' \leftrightarrow \gamma'$)[b]	−0.026	0.605	−0.588	−0.008	0.260	1.054		−0.651	
4c		($\alpha \leftrightarrow \alpha'$)[b]	−0.057	0.603	−0.543	0.003	0.304	1.024		−0.650	
5a	SMe	SO_2Me	−0.076	0.606	−0.566	0.036	0.272		1.577		−0.587 −0.601
5b		($\alpha \leftrightarrow \alpha'$)[b]	−0.087	0.628	−0.578	0.037	0.263		1.568		−0.593 −0.600
6a	SPh	SO_2Ph (X-ray)[a]	−0.093	0.629	−0.559	0.022	0.363		1.706		−0.588 −0.616
6b	S	($\alpha \leftrightarrow \alpha'$)[b]	−0.086	0.633	−0.556	0.009	0.337		1.695		−0.588 −0.608
7a	SOMe	SO_2Me[c]	−0.102	0.617	−0.564	0.049		1.062	1.538	−0.670	−0.591 −0.587
7b		(X-ray)[a]	−0.098	0.614	−0.554	0.038		1.090	1.545	−0.701	−0.569 −0.603
7c		($\beta \leftrightarrow \gamma$)[b]	0.120	0.646	−0.545	0.019		1.102	1.562	−0.650	−0.582 −0.578
7d		($\alpha \leftrightarrow \alpha'$)[b]	−0.100	0.616	−0.547	0.031		1.041	1.575	−0.636	−0.575 −0.613
7e		($\beta' \leftrightarrow \gamma'$)[b]	−0.059	0.585	−0.564	0.038		1.068	1.573	−0.654	−0.565 −0.599

[a] The starting geometry was taken from X-ray diffraction data. [b] For each compound the optimization started from the experimental data. Additional minima were found from these optimized geometries modified by exchange of the torsion angles related by ↔ in column 3. [c] The starting geometry was taken from compounds **2** and **3**.

monosubstituted derivative **3**. In fact the C_{CO}–O_{SO_2} non-bonding distance is still much shorter than the van der Waals contact, while the O_{CO}–S_{SO_2} one is nearly equal to it, *i.e.* a strong $SO_2 \rightarrow CO$ charge transfer operates.

In the sulfide, sulfone compounds **5** (R = Me) and **6** (R = Ph), the SR group maintains the *gauche* orientation of the corresponding monomer. The displacement of the SO_2 group from the *gauche* (**3**) to a *quasi-cis* orientation (**5** and **6**) causes a sizeable shortening of the $O_{CO} \cdots S_{SO_2}$ contact, which becomes the shortest non-bonded distance between pairs of atoms bearing opposite charges. The direction of the strongest CT interaction between the CO and the SO_2 groups is, consequently, reversed in **5** and **6** with respect to **3**.

Finally, it can be observed that the oxygen atoms present in the molecules of **4** have relatively short contacts with the hydrogens of the adjacent phenyls in the range 2.36(7)–2.45(4) Å, while the molecular packing of **6** is characterized by some relatively short contact involving either the S(7) atom or O(11) of the sulfonyl moiety and hydrogens of adjacent molecules. The C(22)–H ⋯ S(7) contact is significantly short [2.819(7) Å] and can contribute a significant driving force in building the crystal lattice.

Conclusions

X-Ray diffraction and He(I) PE spectral analyses, together with fully relaxed *ab initio* 6-31G** SCF calculations, have been used to determine the preferred conformation of α-methylsulfinylacetophenone **2**. The results have been compared with those obtained for the corresponding sulfide **1** and sulfone **3**, and for the three bis-thiosubstituted acetophenones **4**–**7**. The main results can be summarized as follows.

In the crystal of **2** the CH_2–S bond is nearly coplanar with the carbonyl C=O bond. A *quasi-cis* conformation is also the most stable one computed at the 6-31G** level of computation. This conformation differs from that previously found for sulfides and sulfones, which prefer a *gauche* arrangement. In particular, the preferred conformation of β-carbonyl sulfones is mainly determined by a strong CT interaction from one of the oxygen atoms of the SO_2 group [O(11)] towards the carbonyl C atom [C(2)]. These two atoms bear opposite charges and lie at a distance significantly shorter than the sum of the corresponding van der Waals radii. Interestingly, in **2** the computed O(6) ⋯ C(2) contact distance is longer than the corresponding van der Waals value, while, in the *cis* derivatives, the O(1) ⋯ S′(4) non-bonded distance is significantly shorter than the sum of the van der Waals radii and this vicinity occurs between oppositely charged atoms. The analysis of the He(I) PE spectra of **1**–**3** coupled with the analysis of the computed IE values for the various conformations and with the assignment of reference spectra indicate that *gauche* conformers are unlikely to contribute to the observed spectrum of **2**, thus confirming the results of the computations and of the X-ray diffraction analysis. The stabilizing CT in **2** occurs in the reverse direction to the prevailing CT interaction in sulfones, probably because of the higher electron affinity of the sulfinyl group. The CT interaction in **3** counteracts the $-I_{SO_2}$ effect, strengthening synergically the CH_2–SO_2 bond. The most important CT interaction in **2** cooperates with the electron-withdrawing effect of the SOR group in reducing the negative charge density at

C(3). The detachment of the methylsulfinyl group is, thus, facilitated in accordance with the greater thermal lability of **2** compared with **3**.

The preferred *cis* or *gauche* orientation of the C–SO_nR (n = 0, 1, 2) bonds with respect to the carbonyl group observed in the monosubstituted derivatives **1–3** is, by preference, maintained also in the disubstituted compounds **4–7**. In fact, in the sulfide, sulfoxide and sulfone, sulfoxide derivatives both the X-ray structure and the *ab initio* 3-21G* calculations indicate that the C–SR (**4**) and the C–SO_2R (**7**) bonds prefer a *gauche* orientation, while the C–SOR bond prefers a *quasi-cis* one. In both compounds, the $O_{CO} \cdots S_{SO}$ distance is very short (2.9–3.0 Å) as in **2**. With respect to the corresponding monosubstituted derivative **2**, the O(6) $\cdots$ C(2) non-bonded distance contracts in **4** and **7** to 3.0–3.1 Å. The shortening is due to an increase of the α value and is accompanied by an increase in the positive charge at C(2). So that, in addition to the peculiar interaction of the monosubstituted sulfinyl derivative, an SO→CO retrodonation is also present in the disubstituted compounds which likely contributes to the observed higher stability with respect to **2**.

In the sulfide, sulfone compounds **5** (R = Me) and **6** (R = Ph) the SR group maintains the *gauche* orientation of the monomer **1**. The displacement of the SO_2R group from the *gauche* (**3**) to a *quasi-cis* orientation (**5** and **6**) causes a sizeable shortening of the $O_{CO} \cdots S_{SO_2}$ distance. The direction of the prevalent CT interaction appears, therefore, to be related not only to the electron affinity of the SO_nR group (which reaches a maximum for n = 1), but also to the relative orientation of the thio substituents and to their steric hindrance.

References

1 P. R. Olivato, H. Viertler, B. Wladislaw, K. C. Kole and C. Sandorfy, *Can. J. Chem.*, 1976, **54**, 3026.
2 B. Wladislaw, H. Viertler, P. R. Olivato, I. C. C. Calegão, V. L. Pardini and R. Rittner, *J. Chem. Soc.*, *Perkin Trans. 2*, 1980, 453.
3 S. A. Guerrero, J. R. T. Barros, B. Wladislaw, R. Rittner and P. R. Olivato, *J. Chem. Soc.*, *Perkin Trans. 2*, 1983, 1053.
4 P. R. Olivato, B. Wladislaw and S. A. Guerrero, *Phosphorus*, *Sulfur Relat. Elem.*, 1987, **33**, 135.
5 P. R. Olivato, F. Oike and J. C. D. Lopes, *Phosphorus*, *Sulfur*, *Silicon Relat. Elem.*, 1990, **47**, 391.
6 P. R. Olivato, R. Nanartonis, J. C. D. Lopes and Y. Hase, *Phosphorus*, *Sulfur*, *Silicon Relat. Elem.*, 1992, **71**, 107.
7 P. R. Olivato, B. Wladislaw, S. A. Guerrero and D. Russowsky, *Phosphorus*, *Sulfur Relat. Elem.*, 1985, **24**, 225.
8 H. Lumbroso, D. M. Bertin, P. R. Olivato, É. Bonfada, M. G. Mondino and Y. Hase, *J. Mol. Struct.*, 1989, **212**, 113.
9 J. C. Berthelat, P. G. Durand and A. Serafini, *Mol. Phys.*, 1977, **33**, 159.
10 PHSONDO is a modified version of the HONDO program (M. Dupuis, J. Rys and H. F. King, QCPE 336) which includes pseudopotentials.
11 *Calculates atomique et Moleculaires ab-initio: Manuel d'utilisation pour 'Atelier d'Initiation aux Techniques de Pseudopotential'*, Tolouse, 1981.
12 J. C. Berthelat and J. P. Daudey, *PSATOM Manual*, 1978.
13 B. Ross, C. Salez, A. Veillard and E. Clementi, *Tech. Rep. RJ518*, IBM Research, 1968.
14 P. R. Olivato, S. A. Guerrero, A. Modelli, G. Granozzi, D. Jones and G. Distefano, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 1505.
15 G. Distefano, G. Granozzi, R. Bertoncello, P. R. Olivato and S. A. Guerrero, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, 1459.
16 G. Distefano, M. Guerra, D. Jones, A. Modelli, P. R. Olivato and S. A. Guerrero, *J. El. Spectr. Rel. Phen.*, 1989, **49**, 281.
17 R. Bertoncello, G. Granozzi, P. R. Olivato, S. A. Guerrero and G. Distefano, *J. Chem. Soc.*, *Perkin Trans. 2*, 1989, 143.
18 D. Jones, A. Modelli, P. R. Olivato, M. Dal Colle, M. de Palo and G. Distefano, *J. Chem. Soc. Perkin Trans. 2*, 1994, 1661.
19 P. R. Olivato and M. G. Mondino, *Phosphorus*, *Sulfur*, *Silicon Relat. Elem.*, 1991, **59**, 219.
20 P. R. Olivato, É. Bonfada and R. Rittner, *Magn. Res. Chem.*, 1992, **30**, 81.
21 G. Distefano, M. Dal Colle, V. Bertolasi, P. R. Olivato, É. Bonfada and M. G. Mondino, *J. Chem. Soc.*, *Perkin Trans. 2*, 1991, 1195.
22 M. Dal Colle, V. Bertolasi, M. de Palo, G. Distefano, D. Jones, A. Modelli and P. R. Olivato, *J. Phys. Chem.*, 1995, **99**, 15011.
23 R. Hoffmann, *Acc. Chem. Res.*, 1971, **4**, 1.
24 H. Bock and B. Solouki, *Chem. Ber.*, 1974, **107**, 2299.
25 J.-F. Gal, S. Geribaldi, G. Pfister-Guillouzo and D. G. Morris, *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, 103.
26 G. Wagner and H. Bock, *Chem. Ber.*, 1974, **107**, 68.
27 Revision B, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. Steward and J. A. Pople, GAUSSIAN 92, Gaussian Inc., Pittsburgh, PA, 1992.
28 J. S. Grosset, P. K. Dubey, G. H. Gill, T. S. Cameron and P. A. Gardner, *Can. J. Chem.*, 1984, **62**, 798.
29 For 7 only approximate results are available due to the lack of a consistent scattering power from the crystals available despite all the attempted crystallization processes. The low quality of the crystals allowed only the determination of the triclinic cell and the formulation of a molecular structure consistent with the chemical formula. Two distinct molecules constitute the asymmetric units but the differences between the two is just within the limit of the very high ESDS. For this reason only one molecule is reported (see Fig. 1).
30 E. M. Sheldrick, SHELX 86 Crystallographic Computing 3, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985.
31 *International Tables for X-Ray Crystallography*, 2nd edn., Kynoch Press, Birmingham, 1974, vol. 4, p. 101.
32 E. M. Sheldrick, SHELX 76, University of Cambridge, UK, 1976.
33 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
34 C. K. Johnson, *ORTEP Report ORNL 5138*, Oak Ridge National Laboratory, TS, USA, 1976.
35 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
36 P. R. Olivato and S. G. Mondino, unpublished results.
37 R. Hoffmann, *Acc. Chem. Res.*, 1971, **4**, 1.
38 A. Modelli, D. Jones, G. Distefano and M. Tronc, *Chem. Phys. Letters*, 1991, **181**, 361.
39 H.-D. Martin, R. Iden, H. Landen, B. Mayer, G. Distefano, A. Modelli and R. Gleiter, *J. Electron Spectrosc. Relat. Phenom.*, 1986, **41**, 385.
40 A. Modelli, unpublished results.

Paper 6/00680I
Received 29*th January* 1996
Accepted 20*th March* 1996