

Spectroscopic and theoretical studies of some 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates

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ABSTRACT

The analysis of the IR ν_{CO} bands of the 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates 4'-Y-C₆H₄SC(O)CH₂S(O)Et (Y = NO₂ **1**, Cl **2**, Br **3**, H **4**, Me **5**, OMe **6**) supported by B3LYP/6-31G(d,p) calculations along with the NBO analysis for **1**, **4** and **6** and X-ray analysis for **3**, indicated the existence of four *gauche* (*q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn*) conformers for **1–6**. The calculations reproduce quite well the experimental results, i.e. the computed *q-g-syn* and *g₃-syn* conformers correspond in the IR spectrum (in solution), to the ν_{CO} doublet higher frequency component of larger intensity, while the computed *g₁-anti* conformer correspond to the ν_{CO} doublet lower frequency component (in solution). NBO analysis showed that the $n_{\text{S}} \rightarrow \pi_{\text{C}_1=\text{O}_2}^*$, $n_{\text{O}(\text{CO})} \rightarrow \sigma_{\text{C}_1-\text{S}_3}^*$, $n_{\text{O}(\text{CO})} \rightarrow \sigma_{\text{C}_1-\text{C}_4}^*$ orbital interactions are the main factors which stabilize the *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers for **1**, **4** and **6**. The $n_{\text{O}(\text{CO})} \rightarrow \sigma_{\text{C}_1-\text{S}_3}^*$ interaction which stabilizes the *q-g-syn*, *g₃-syn* and *q-g₂-syn* conformers into a larger extent than the *g₁-anti* conformer, is responsible for the larger ν_{CO} frequencies of the former conformers relative to the latter one. The *q-g-syn*, *g₃-syn* and *q-g₂-syn* conformers are further stabilized by $\sigma_{\text{C}_4-\text{S}_5} \rightarrow \pi_{\text{CO}}^*$ (strong), $\pi_{\text{CO}}/\sigma_{\text{C}_4-\text{S}_5}^*$, $n_{\text{O}(\text{CO})} \rightarrow \sigma_{\text{C}_6-\text{H}_{17}[\text{Et}]}^*$ (weak) and $\pi_{\text{CO}}/\sigma_{\text{C}_4-\text{S}_5}^*$ (strong) orbital interactions. The *g₁-anti* conformer is also stabilized by $\sigma_{\text{C}_4-\text{S}_5} \rightarrow \pi_{\text{CO}}^*$ (strong), $\pi_{\text{CO}}/\sigma_{\text{C}_4-\text{S}_5}^*$, $n_{\text{O}(\text{CO})} \rightarrow \sigma_{\text{C}_6-\text{H}_{17}[\text{Et}]}^*$, $\pi_{\text{C}_9=\text{C}_{11}[\text{Ph}]} \rightarrow \sigma_{\text{C}_4-\text{H}_{16}[\alpha-\text{CH}_2]}^*$ (weak), $n_{\text{O}(\text{SO})} \rightarrow \sigma_{\text{C}_{11}-\text{H}_{23}[\text{o-Ph}]}^*$ (medium) and $\pi_{\text{CO}}/\sigma_{\text{C}_4-\text{S}_5}^*$ (strong) orbital interactions. The *q-g-syn* conformer is further stabilized by $\text{O}_{(\text{CO})}^{\delta-} \cdots \text{S}_{(\text{SO})}^{\delta+}$ attractive Coulombic interaction while the *q-g₂-syn* conformer is destabilized by the $n_{\text{S}_5} \cdots \text{O}_{(\text{CO})}^{\delta-}$ repulsive Coulombic interaction. This analysis indicates the following conformer stabilization order: *q-g-syn*; *g₃-syn* > *g₁-anti* >> *q-g₂-syn*. X-ray single crystal analysis of **3** indicates that it assumes in the solid a distorted *q-g₂-syn* geometry which is stabilized through almost the same orbital and Coulombic interaction which takes place for the *q-g₂-syn* conformer, in the gas, along with dipole moment coupling and a series intermolecular C—H \cdots O interactions.

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1. Introduction

Preceding spectroscopic (IR, ¹³C NMR, UV and UPS) and X-ray studies supported by theoretical calculations on some β -carbonyl-sulfoxides XC(O)CH₂S(O)R have shown that the *gauche* conformer is the most stable for the α -sulfinylketones (X = Me; R = Et, 4-Y-C₆H₄) [1–3] and α -sulfinylesters (X = 4-Y-C₆H₄O; R = Et) [4], while the *cis* conformer becomes the predominant for α -sulfinylacetophenones and α -sulfinylamides (X = 4-Y-C₆H₄, Et₂N; R = Alkyl, 4-Y-C₆H₄ [5–8]. As for the α -sulfinyl *N*-methoxy-*N*-methyl amides (X = N[Me][MeO]; R = 4-Y-C₆H₄) [9] the *cis* conformer prevails for the *diastereomer₁*, while the *gauche* conformer predominates for

the *diastereomer₂* [9]. In general the stabilization of the *gauche* conformers has been attributed to the $\pi_{\text{CO}}/\sigma_{\text{C}-\text{S}}$ and, to a minor extent, to the $\pi_{\text{CO}}/\sigma_{\text{C}-\text{S}}^*$ orbital interactions, while the larger stabilization of the *cis* conformers of the α -alkylsulfinylacetophenones and α -phenylsulfinylamides relative to the α -alkyl- and α -aryl-sulfinylacetones has been ascribed to the $\pi_{\text{Ph}}-\pi_{\text{CO}}$ and $n_{\text{N}}/\pi_{\text{CO}}$ conjugation, which originates stronger intramolecular electrostatic and charge transfer interactions between $\text{C}^{\delta+}=\text{O}^{\delta-}$ and $\text{S}^{\delta+}=\text{O}^{\delta-}$ dipoles ($n_{\text{O}(\text{CO})}/\sigma_{\text{S}=\text{O}}^*$ orbital interaction).

In the MeC(O)X series [10] there is a progressive increase of the experimental carbonyl oxygen lone pair (n_{O}) ionization energy going from amide ($E_{\text{i}} = 9.20$ eV) to acetophenone ($E_{\text{i}} = 9.34$ eV) to butanone ($E_{\text{i}} = 9.46$ eV) to thioester ($E_{\text{i}} = 9.64$ eV) and to ester ($E_{\text{i}} = 10.45$ eV), for X = NEt₂, Ph, Et, SEt and OEt, respectively, which in turn is accompanied by a corresponding decrease of the negative

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charge on the carbonyl oxygen atom in this direction. Moreover, there is a progressive increase of the electron affinity of the π_{CO}^* orbital going from amide ($E_{\text{ae}} = 2.26$ eV) to ester ($E_{\text{ae}} = 2.09$ eV) to butanone ($E_{\text{ae}} = 1.26$ eV) and to thioester ($E_{\text{ae}} = 0.95$ eV).

Therefore, it seems reasonable to expect a larger stabilization of the *gauche* conformer for the α -sulfinyl-thioesters relative to the same conformation of the other α -sulfinyl derivatives, due to stronger $\pi_{\text{CO}}^*/\sigma_{\text{C-S(O)}}$ orbital interaction which should operate in the *gauche* conformation of the sulfinyl-thioesters, once the $n_{\text{O(CO)}}/\sigma_{\text{S-O}}^*$ orbital interaction should stabilize the *cis* conformation only into a minor extent due to the large ionization energy of the carbonyl oxygen lone pair.

Aiming to throw more light on the nature of the different electronic interactions which may stabilize the *cis* and *gauche* conformers of the α -sulfinylthioesters, this paper reports the IR study of some 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates [11] 4'-Y-C₆H₄SC(O)CH₂S(O)Et bearing in 4'-position electron-attracting, hydrogen and electron-donating substituents, i.e. Y = NO₂ **1**, Cl **2**, Br **3**, H **4**, Me **5**, OMe **6** (Scheme 1) along with density functional theory (DFT) and Natural Bond Orbital (NBO) calculations of **1**, **4** and **6** and X-ray diffraction analysis of compound **3**.

These compounds were chosen taking into account that the orbital and Coulombic interactions, which could operate in their *cis* and *gauche* conformers, should be affected by changes in the $n_{\text{S}}/\pi_{\text{CO}}^*$ conjugation involving the 4'-substituent at the phenylthio-carboxy group, and consequently should influence the stabilization of the referred conformers.

2. Experimental

2.1. Materials

All solvents for IR measurements were spectrograde and were used without further purification. The 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates 4'-Y-C₆H₄SC(O)CH₂S(O)Et (Y = NO₂ **1**, Cl **2**, Br **3**, H **4**, Me **5**, OMe **6**) are novel compounds and were prepared as follows: to a stirred solution of the appropriate thioester-sulfide (10 mmol) in glacial acetic acid (2.2 mL; 40 mmol) at 0 °C, a solution of hydrogen peroxide (10 mmol; 30%) was added slowly. The reaction mixture was maintained below 10 °C until all the thioester-sulfide has been reacted (ca. 2 h), then, 13 mL of dichloromethane was added, and the solution was neutralized with an aqueous solution of sodium bicarbonate. After stirring for 5–10 min, a

saturated aqueous sodium chloride solution was added and then the product was extracted with CH₂Cl₂. The organic layer was dried over anhydrous magnesium sulphate. The solvent was removed under vacuum without heating, and the obtained crude solid was dissolved with dichloromethane and crystallized through the slow addition of *n*-hexane, at room temperature. Suitable crystals for X-ray analysis were obtained by vapour diffusion from chloroform/*n*-hexane at room temperature for **3**. The physical, ¹H and ¹³C NMR, and elemental analysis of the thioester-sulfoxides **1–6** are presented in Table 1. The starting 2-ethylthio-(4'-substituted) phenylthioacetates 4'-Y-C₆H₄SC(O)CH₂SEt were prepared as previously described [12].

2.2. IR measurements

The IR spectra were recorded with a FTIR Nicolet Magna 550 FTIR spectrometer, with 1.0 cm⁻¹ resolution, at a concentration of 1.0 × 10⁻² mol dm⁻³ in *n*-hexane, carbon tetrachloride, chloroform, and acetonitrile solutions, using a 0.519 mm sodium chloride cell, for the fundamental carbonyl region (1800–1600 cm⁻¹). The spectra for the carbonyl first overtone region (3600–3100 cm⁻¹) were recorded in carbon tetrachloride solution (1.0 × 10⁻² mol dm⁻³), using a 1.00 cm quartz cell. The overlapped carbonyl bands (fundamental and first overtone) were deconvoluted by means of the Grams/32 curve fitting program, version 4.04, Level II [13]. The populations of the *gauche* and *quasi-gauche* conformers were estimated from the maximum of each component of the resolved carbonyl doublet, expressed in percentage of absorbance, assuming equal molar absorptivity coefficients for the referred conformers.

2.3. NMR measurements

¹H NMR and ¹³C NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.947 and 75.423 MHz, respectively, for 0.1 mol/dm³ solutions in chloroform-*d*. ¹H and ¹³C chemical shifts are reported in ppm relative to TMS, as internal standard.

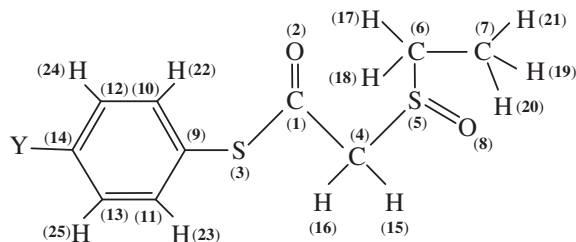
2.4. X-ray measurements

2.4.1. Data collection, structure solution and refinement

X-ray diffraction experiments were performed at room temperature (*T* = 290 K) on a MACH3 four-circle diffractometer. MoK α radiation and $\omega/2\theta$ scanning mode were applied. Three standard reflections showed no significant intensity fluctuation (ca. 0.4%) throughout the experiments. The intensities were corrected for Lorentz and polarization and ψ -scan based absorption was applied. The structure was solved by direct methods using SIR97 [14] and refined against *F*² with SHELXL97 program [15]. The hydrogen atoms were added geometrically and refined with the riding model. Details of the data collection, structure solution and refinement are shown in Table 2. The crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 777718.

2.5. Theoretical calculations

All calculations were carried out (at 298 K) using methods and basis sets implemented in the Gaussian package of programs (G03-E01) [16]. The hybrid Hartree–Fock density functional B3LYP method [17] with the 6-31G(d,p) basis set was used [18]. Full geometry optimizations and analytical vibrational frequency calculations were performed on all the *gauche* or *quasi-gauche* orientations of the α -sulfur atom with respect to the carbonyl group resultant from a systematic conformational search, allowing



Y = NO₂ **1**, Cl **2**, Br **3**, H **4**, Me **5**, OMe **6**

$\alpha = \text{O}(2)-\text{C}(1)-\text{C}(4)-\text{S}(5)$
 $\beta = \text{C}(1)-\text{C}(4)-\text{S}(5)-\text{C}(6)$
 $\gamma = \text{C}(1)-\text{C}(4)-\text{S}(5)-\text{O}(8)$
 $\delta = \text{O}(2)-\text{C}(1)-\text{S}(3)-\text{C}(9)$
 $\phi = \text{C}(1)-\text{S}(3)-\text{C}(9)-\text{C}(11)$
 $\epsilon = \text{C}(4)-\text{S}(5)-\text{C}(6)-\text{C}(7)$

Scheme 1. Atoms labelling of 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates and assignment of relevant dihedral angles.

Table 1
Physical, ^1H NMR and elemental analysis data for 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates 4'-Y-C₆H₄SC(O)CH₂S(O)Et (**1–6**).

Comp.	Y	^1H NMR ^a	^{13}C NMR ^a	Mp (°C)	Molecular formula	Elemental analysis/%	
						C	H
1	NO ₂	8.31–8.27 (2H, m), 7.67–7.63 (2H, m), 4.03 (2H, s), 3.00–2.90 (2H, m), 1.41 (3H, t, $^3J = 7.4$ Hz)	186.98, 148.59, 134.73, 126.41, 124.46, 62.33, 46.55, 6.60	101–104	C ₁₀ H ₁₁ NO ₄ S ₂	Calc. Found	43.94 40.6
2	Cl	7.44–7.39 (2H, m), 7.36–7.31 (2H, m), 3.94 (2H, s), 3.00–2.80 (2H, m), 1.37 (3H, t, $^3J = 7.5$ Hz)	188.22, 136.48, 135.41, 129.60, 120.67, 62.11, 46.30, 6.32	93–96	C ₁₀ H ₁₁ ClO ₂ S ₂	Calc. Found	43.71 42.2
3	Br	7.60–7.53 (2H, m), 7.45–7.28 (2H, m), 3.95 (2H, s), 2.79–2.67 (2H, m), 1.39 (2H, t, $^3J = 7.2$ Hz)	188.16, 132.69, 135.69, 125.37, 124.89, 62.17, 46.42, 6.42	99–101	C ₁₀ H ₁₁ BrO ₂ S ₂	Calc. Found	45.58 40.4
4	H	7.42 (5H, m), 3.93 (2H, s), 2.99–2.77 (2H, m), 1.35 (3H, $^3J = 7.5$ Hz)	188.65, 134.15, 129.91, 129.28, 126.28, 62.13, 46.17, 5.83	59–62	C ₁₀ H ₁₂ O ₂ S ₂	Calc. Found	52.60 5.30
5	CH ₃	7.33–7.30 (2H, m), 7.26–7.22 (2H, m), 3.95 (2H, s), 3.00–2.70 (2H, m), 2.38 (3H, s), 1.36 (3H, $^3J = 7.5$ Hz)	189.27, 140.50, 134.22, 130.27, 122.83, 62.12, 46.26, 21.25, 6.29	98–100	C ₁₁ H ₁₄ O ₂ S ₂	Calc. Found	52.55 5.09
6	OCH ₃	7.34–7.31 (2H, m), 6.96–6.93 (2H, m), 3.93 (2H, s), 3.81 (3H, s), 3.00–2.70 (2H, m), 1.37 (3H, t, $^3J = 7.5$ Hz)	189.77, 135.86, 116.90, 116.09, 115.03, 61.91, 55.26, 46.20, 6.25	98–102	C ₁₁ H ₁₄ O ₃ S ₂	Calc. Found	54.40 5.71
						Calc. Found	51.14 5.46
						51.21	5.19

^a H chemical shifts in ppm relative to TMS and coupling constants in Hz, in CDCl₃.

complete relaxation of all internal parameters. Frequency analyses were carried out to verify the nature of the minimum state of all the stationary points obtained and to calculate the zero-point vibrational energies (ZPVE) corrections. The NBO 3.1 program [19] was used as implemented in the Gaussian 03 package, and the reported NBO delocalization energies (E2) are those given by second-order perturbation theory.

3. Results and discussion

Table 3 lists the stretching frequencies and the absorbance percentage of the analytically resolved carbonyl band for the 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates **1–6** in solvents of increasing relative permittivity [20], i.e. *n*-hexane ($\epsilon = 1.9$), carbon tetrachloride ($\epsilon = 2.2$), chloroform ($\epsilon = 4.8$), and acetonitrile ($\epsilon = 38$). A carbonyl doublet is shown for the majority of the studied compounds, in all solvents, excepting **1** (CCl₄ and CHCl₃), **2** (*n*-C₆H₁₄) and **3** (CH₃CN), for which only a singlet is detected. In the first overtone region of compounds **1, 2, 4–6**, in CCl₄, only singlets are observed, excepting compound **3** for which a doublet is observed. In general the doublet higher frequency component is significantly more intense than the lower component along the series **1–6**, in all solvents. Therefore, the lack of the lower frequency component in the carbonyl first overtone region for derivatives **1, 2, 4–6**, may be ascribed to the fact that the half-band width of this band is twice larger than that of the carbonyl stretching band, in the fundamental region. Thus, the low intensity carbonyl band component is hidden under the higher intensity carbonyl band component.

It should be pointed out that there is not any clear solvent effect on the intensity of each doublet component as the solvent polarity varies. However, it may be noticed a discrete increase of the intensity of the higher frequency component with respect to the lower one, going from **6** to **1** or **2**, in *n*-C₆H₁₄, CCl₄ and CHCl₃. The solvent effect on the carbonyl band components for **3**, as a prototype for compounds **1–6** is illustrated in Fig. 1. Although the observed solvent effect is not an evidence of rotational isomerism, the occurrence of two carbonyl bands in the first overtone region of **3** at frequencies twice those of the fundamental unless ca. 25 cm^{−1} (which corresponds two times the mechanical anharmonicity [21]), and with practically the same relative intensity ratios, may be taken as an evidence for the existence of two stable conformers [22,23] in solution for the whole series **1–6** (see above).

Aiming to determine the geometries for the stable conformations of series **1–6**, computations at the B3LYP/6-31G(d,p) level of theory for the 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates **1, 4** and **6** were performed. Table 4 presents the relevant data for these compounds which indicate the existence of four stable conformations, i.e., *quasi-gauche-syn* (*q-g-syn*), *g₃-syn*, *g₁-anti*, *quasi-gauche₂-syn* (*q-g₂-syn*). The *q-g-syn* and *g₃-syn* conformers present almost the same computed carbonyl frequencies of ca. 1702 cm^{−1}, 1696 cm^{−1}, 1695 cm^{−1} for derivatives **1, 4** and **6**, respectively, while the *g₁-anti* conformer present the lowest carbonyl frequency of ca. 1687 cm^{−1}, 1678 cm^{−1}, 1676 cm^{−1} for derivatives **1, 4** and **6**, respectively. The *q-g₂-syn* conformer presents the highest computed carbonyl frequency of ca. 1715 cm^{−1}, 1710 cm^{−1}, 1712 cm^{−1} for derivatives **1, 4** and **6**, respectively. Furthermore, the summing up of molar fraction of the *q-g-syn* and *g₃-syn* conformers varies with the nature of the 4'-substituent, i.e. from ca. 85% to 74% and to 65%, for derivatives **1** (NO₂), **4** (H), **6** (OMe), respectively. Simultaneously, the molar fraction of the *g₁-anti* conformer increases in the same direction, i.e. from ca. 12% to 24% and to 33%, for derivatives **1, 4** and **6**, respectively. The molar fraction of the least stable *q-g₂-syn*

Table 2

Crystal data and structure refinement of 2-ethylsulfinyl-4'-bromophenyl thioacetate 4'-Br-C₆H₄SC(O)CH₂S(O)Et (**3**).

Empirical formula	C ₁₀ H ₁₁ BrO ₂ S ₂
Formula weight	307.22
Temperature (K)	290(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions (Å)	
<i>a</i>	4.9385(9)
<i>b</i>	28.760(2)
<i>c</i>	8.770(1)
Volume (Å ³)	1245.6(3)
Z, Calc. density (Mg m ⁻³)	4, 1.638
Absorption coefficient (mm ⁻¹)	3.613
<i>F</i> (0 0 0)	616
Crystal size (mm)	0.12 × 0.10 × 0.05
Theta range for data collection (°)	1.42–26.00
Limiting indices	–6–6, 0–35, 0–10
Reflections collected	2630, 2435
Completeness to $\theta = 26^\circ$	100.00%
Absorption correction	Ψ -scan
Max and min transmission	0.835, 0.655
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2435/1/137
Goodness-of-fit on <i>F</i> ²	1.022
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0487, 0.1266
<i>R</i> indices (all data)	0.1267, 0.1642
Largest diff. peak and hole (e Å ⁻³)	0.481, –0.447

conformer remains almost constant for derivatives **1**, **4** and **6**, of ca. 2%. Fig. 2 presents a qualitative diagram which illustrates well this trend. It should be pointed out that the calculations reproduce quite well the experimental results. Actually, the *q-g-syn* and *g₃-syn* conformers which present very close computed frequencies should correspond in the IR spectrum, in solution, to the carbonyl doublet higher frequency component of larger intensity while the *g₁-anti* conformer should correspond to the carbonyl doublet lower frequency component of smaller intensity. Moreover, in solution, the intensity of the higher frequency carbonyl doublet component changes from (100%, CCl₄; 100%, CHCl₃) for **1** to (90%, CCl₄; 83%, CHCl₃) for **6** while the intensity of the lower carbonyl frequency component changes from (0%, CCl₄; 0%, CHCl₃) for **1** to (10%, CCl₄; 17%, CHCl₃) for **6**. As expected, the least stable *q-g₂-syn* conformer of low molar fraction, in the gas, is not detected in solution.

Table 4 shows that the *q-g-syn* conformer is the more stable (*E*_{rel.} = 0.0 kJ mol⁻¹; 42.0%) for **4** and (*E*_{rel.} = 0.0 kJ mol⁻¹; 38.6%) for **6**, while is the second more stable (*E*_{rel.} = 1.59 kJ mol⁻¹;

29.4%) for **1**. The *q-g-syn* conformer displays the 2-sulfinyl ($\alpha \cong +56^\circ$) substituent in a *syn-clinal* or *quasi-gauche* geometry with respect to the carbonyl group. The *syn* and *anti* suffixes indicate that the δ dihedral angle [C(Ph)–S–C=O] is close to 0° and 180°, respectively.

The *g₃-syn* conformer is the more stable (*E*_{rel.} = 0.0 kJ mol⁻¹; 55.7%) for **1** and is the second (*E*_{rel.} = 0.69 kJ mol⁻¹; 31.8%) and third (*E*_{rel.} = 0.92 kJ mol⁻¹; 26.3%) stable conformer for **4** and **6**, respectively. The *g₃-syn* conformer displays the 2-sulfinyl ($\alpha \cong +75^\circ$) substituent in a *syn-clinal* or *gauche* geometry with respect to the carbonyl group.

The *g₁-anti* is the third stable conformer (*E*_{rel.} = 3.9 kJ mol⁻¹; 11.7%) and (*E*_{rel.} = 1.42 kJ mol⁻¹; 23.7%) for **1** and **4**, respectively, and is the second (*E*_{rel.} = 0.41 kJ mol⁻¹; 32.7%) stable conformer for **6**. The *g₁-anti* conformer displays the 2-sulfinyl ($\alpha \cong +78^\circ$) substituent in a *syn-clinal* or *gauche* geometry with respect to the carbonyl group.

The *q-g₂-syn* conformer is the least stable (*E*_{rel.} \cong 7.1 kJ mol⁻¹; 2.3%) conformer for **1**, **4** and **6**. The *q-g₂-syn* conformer displays the 2-sulfinyl ($\alpha \cong +60^\circ$) substituent in a *syn-clinal* or *quasi-gauche* geometry with respect to the carbonyl group, whose geometry is similar to that of the *q-g-syn* conformer. Fig. 3 illustrates the computed molecular structures of the *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers of **4**, taken as a prototype for compounds **1–6**.

Table 5 shows the CHELPG charges at the selected atoms at the B3LYP/6-31G(d,p) level for compounds **1**, **4** and **6**. Table 6 displays the interatomic distances between some selected atoms and the difference between these contacts and the sum of the van der Waals radii ($\sum v dW$ radii) (ΔI) for the same compounds.

In order to understand the nature of the orbital interactions which act stabilizing the *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers for the title compounds, the NBO analysis [19] was performed. Table 7 presents selected NBO interactions for **1**, **4** and **6** [24]. It can be observed in this Table that the more important orbital interactions for *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers are: (a) the LP_{S3} \rightarrow $\pi^*_{C=O_2}$, which corresponds to the [O=C–S \leftrightarrow O=C=S⁺] conjugation, whose mean energy value is ca. 31 kcal mol⁻¹; (b) the LP_{O2} \rightarrow σ^*_{C-S} and LP_{O2} \rightarrow σ^*_{C-C} (though bond coupling) whose mean energy value is of ca. 35 kcal mol⁻¹ and 18 kcal mol⁻¹, respectively. Nevertheless, the LP_{O2} \rightarrow σ^*_{C-S} mean energy value which is ca. 36 kcal mol⁻¹ for *q-g-syn*, *g₃-syn*, and *q-g₂-syn* conformers is ca. 5 kcal mol⁻¹ higher than the same interaction for the *g₁-anti* conformer.

The stronger LP_{O2} \rightarrow σ^*_{C-S} orbital interaction for the *syn* (*q-g*, *g₃*, and *q-g₂*) conformers relative to that for the *anti* (*g₁*) conformer originates an increase of the carbonyl bond order and thus in the

Table 3

Frequencies (ν , cm⁻¹) and intensities of the carbonyl stretching bands in the IR spectra of 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates 4'-Y-C₆H₄SC(O)CH₂S(O)Et (**1–6**).

Comp.	Y	<i>n</i> -C ₆ H ₁₄		CCl ₄		CHCl ₃		CH ₃ CN	
		ν	<i>P</i> ^a	ν	<i>P</i>	ν^b	<i>P</i>	ν	<i>P</i>
1	NO ₂	– ^c	–	1702	100.0	3384	100.0	1700	100.0
		– ^c	–	–	–	–	–	1695	16.7
2	Cl	1704	100.0	1699	91.7	3376	100.0	1695	91.7
		–	–	1682	8.3	–	–	1666	8.3
3	Br	1704	76.9	1699	84.3	3377	78.0	1696	92.2
		1684	13.1	1687	15.7	3344	22.0	1675	7.8
4	H	1702	92.3	1697	92.6	3373	100.0	1692	88.9
		1685	7.7	1682	7.4	–	–	1665	11.1
5	Me	1700	90.4	1696	91.7	3369	100.0	1691	82.6
		1683	9.6	1674	8.3	–	–	1668	17.4
6	OMe	1700	92.6	1695	90.1	3368	100.0	1687	83.6
		1683	7.4	1675	9.9	–	–	1667	16.4

^a Intensity of each component of the carbonyl doublet expressed in percentage of absorbance.

^b First overtone.

^c Compound slightly soluble in this solvent.

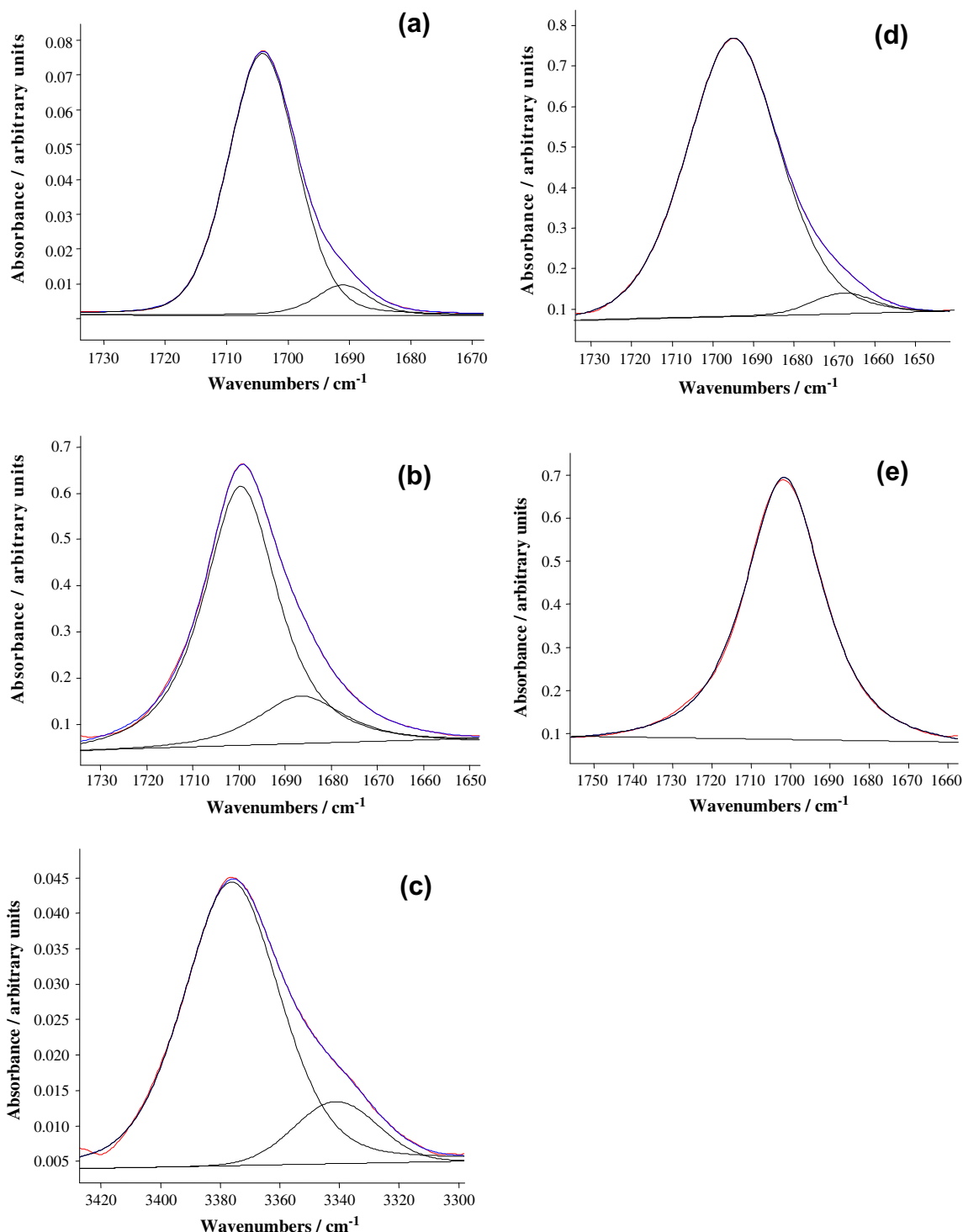


Fig. 1. IR spectra of 2-ethylsulfinyl-4'-bromophenylthioacetate (**3**) showing the analytically resolved carbonyl stretching band, in: *n*-hexane (a), carbon tetrachloride [fundamental (b) and first overtone (c)], chloroform (d) and acetonitrile (e).

ν_{CO} frequencies of the former conformers with respect to the latter one. Fig. 4 illustrates the $n_{(\text{S}_3)}/\pi_{\text{C}_1-\text{O}_2}^*$, $n_{\text{O}_2(\text{CO})}/\sigma_{\text{C}_1-\text{S}_3}^*$ and $n_{\text{O}_2(\text{CO})}/\sigma_{\text{C}_1-\text{C}_4}^*$ orbital interactions with their corresponding representations in the Valence Bond Theory. The NBO mean energy value of the $\sigma_{\text{C}_1-\text{S}_3}^*$ orbital for *syn* (*q-g*, *g*₃, and *q-g*₂) indicate that it is more stable than the same orbital for *g*₁-*anti* conformer by *ca.* 2 kcal mol⁻¹. This behaviour is responsible for the observed slightly stronger $n_{\text{O}_2(\text{CO})}/\sigma_{\text{C}_1-\text{S}_3}^*$ orbital interaction of the *syn* conformers with respect to the *anti* conformer.

The *syn* (*q-g*, *g*₃, *q-g*₂) conformers for **1**, **4** and **6** (Structure 1, Scheme 2) present short intramolecular contacts between the $\text{O}(2)_{[\text{CO}]} \cdots \text{C}(9)_{[\text{Ph}]}$ atoms whose distances are shorter than the $\sum v$ dW radii by $\Delta l \cong -0.25$ Å. The eigenvector analysis of the relevant orbitals indicates the existence of the $n_{\text{O}(\text{CO})}/\pi_{\text{Ph}}^*$ charge transfer for the referred conformers which should contribute for the stabilization of the *syn* conformers. However, the $\text{LP}_{\text{O}_2} \rightarrow \pi_{\text{C}_9=\text{C}_{11}}^*$ interaction was not detected in the NBO analysis, probably because its value should be slightly smaller than 0.5 kcal mol⁻¹. On the

Table 4
Relative energy (E , kJ/mol⁻¹), dipole moment (μ , D), selected dihedral angles ($^\circ$), carbonyl frequencies (ν , cm⁻¹) optimized for the minimum energy conformations of 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates 4'-Y-C₆H₄SC(O)(CH₂S(O)Et) (1), (4), (6) at the B3LYP/6-31G(d,p) level, and X-ray geometrical data of 2-ethylsulfinyl-4-bromophenylthioacetate 4-Br-C₆H₄SC(O)(CH₂S(O)Et) (3).

Comp.	Y	Conf. ^{a,b}	E^c	μ^d	ν_{CO}^e	Dihedral angles ^f				γ	δ	ϕ	ϵ
						α	β	γ	δ				
3	Br(X-ray)	<i>q-g₂-syn</i>	–	–	–	–51.9(9)	–177.5(5)	–65.4(5)	–0.1(8)	72.2(7)	74.6(7)		
1	NO ₂	<i>q-g-syn</i>	1.59	2.30	1701.2	57.6	–80.6	169.3	3.5	–53.3	–179.2		
		<i>g₃-syn</i>	0.0	6.71	1703.7	75.2	–76.6	33.8	–10.3	–59.1	–171.2		
		<i>g₁-anti</i>	3.87	4.59	1686.6	78.5	–65.9	45.3	179.8	72.7	172.2		
		<i>q-g₂-syn</i>	7.02	7.53	1715.0	64.8	178.3	68.6	1.6	–53.1	–173.6		
4	H	<i>q-g-syn</i>	0.0	3.82	1697.1	53.4	–80.0	169.9	3.5	–63.3	–178.8		
		<i>g₃-syn</i>	0.69	2.50	1696.4	74.7	–73.6	37.2	–5.7	–64.9	171.3		
		<i>g₁-anti</i>	1.42	4.05	1678.3	78.3	–66.4	44.7	179.3	77.4	171.6		
		<i>q-g₂-syn</i>	7.10	3.18	1710.6	60.5	–177.0	73.5	2.1	–61.3	–171.9		
6	OMe	<i>q-g-syn</i>	0.0	4.59	1695.2	57.7	–80.1	169.9	3.7	–66.4	–179.5		
		<i>g₃-syn</i>	0.92	2.08	1695.3	74.7	–73.6	37.0	–6.5	–69.0	170.9		
		<i>g₁-anti</i>	0.41	4.40	1676.1	78.8	–65.8	45.4	179.3	79.8	171.6		
		<i>q-g₂-syn</i>	7.25	1.99	1712.0	57.1	–177.3	73.2	2.7	–67.4	–172.1		

^a Conformer assignment.

^b *syn* and *anti* refer to the δ dihedral angles which are close to 0° and 180°, respectively.

^c Relative energy.

^d Molar fraction in percentage.

^e Scaling factor of 0.954.

^f See Scheme 1.

other hand, the *anti* (g_1) conformer (Structure II, Scheme 2) present short intramolecular contacts between the oppositely charged $\text{H}^{\delta+}(16) \cdots \text{C}^{\delta-}(9)_{[\text{Ph}]}$ atoms whose distances are shorter than the $\sum v$ dW radii by Δl values which vary from -0.28 \AA to -0.33 \AA and to -0.34 \AA for **1**, **4** and **6**, respectively. This trend is in line with the $\pi_{\text{C9}=\text{C11}} \rightarrow \sigma_{\text{C4-H16}}^*$ orbital interaction whose value is the maximum ($\Delta E = 0.64 \text{ kcal mol}^{-1}$) for the methoxy derivative **9** (highest HOMO of π_{Ph} orbital), and the minimum for the nitro derivative **1** whose ΔE value is smaller than $0.50 \text{ kcal mol}^{-1}$ (lowest HOMO of π_{Ph} orbital). A further short contact which takes place in the *anti* (g_1) conformer is between the oppositely charged $\text{O}^{\delta-}(8)_{[\text{SO}]} \cdots \text{H}^{\delta+}(23)_{[\text{O-Ph}]}$ atoms whose distances are shorter than the $\sum v$ dW radii by Δl values which vary from -0.34 \AA to -0.35 \AA and to -0.45 \AA for **6**, **4** and **1**, respectively. This tendency is in agreement with the progressive increase of the ($\text{LP}_{\text{O8}(3)} \rightarrow \sigma_{\text{C11-H23}}^*$; $\text{LP}_{\text{O8}(1)} \rightarrow \sigma_{\text{C11-H23}}^*$) orbital interactions (hydrogen bond) whose energy values vary from (1.3; $1.0 \text{ kcal mol}^{-1}$) to (1.5; $1.0 \text{ kcal mol}^{-1}$) and to (2.3; $1.6 \text{ kcal mol}^{-1}$) for **6**, **4** and **1**, respectively. Thus, the *anti* (g_1) conformer is stabilized by both $\pi_{\text{C9}=\text{C11}}[\text{Ph}] \rightarrow \sigma_{\text{C4-H16}}^*[\alpha\text{-CH}_2]$ (weak) and $\text{LP}_{\text{O[SO]}} \rightarrow \sigma_{\text{C11-H23}}^*[\text{O-Ph}]$ (medium) orbital (hydrogen bond) and electrostatic interactions.

The *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers for **1**, **4** and **6** which display very short $\text{S}(5) \cdots \text{C}(1)$ contacts between α -sulfinyl sulfur and the carbonyl carbon atoms (Δl mean value of $ca. -0.70 \text{ \AA}$), are responsible for the stabilization of the referred *gauche* conformers through the $\sigma_{\text{C4-S}}/\pi_{\text{CO}}^*$, $\pi_{\text{CO}}/\sigma_{\text{C-S}}^*$ and $\pi_{\text{CO}}^*/\sigma_{\text{C-S}}^*$ orbital interactions.

In general, the $\sigma_{\text{C4-S}}/\pi_{\text{C1=O}_2}^*$, $\pi_{\text{CO}}/\sigma_{\text{C-S}}^*$ and $\pi_{\text{CO}}^*/\sigma_{\text{C-S}}^*$ interactions are stronger for the *g₃-syn* and *g₁-anti* conformers (α dihedral angle of $ca. 77^\circ$) and weaker for the *q-g-syn* and *q-g₂-syn* conformers (α dihedral angle of $ca. 60^\circ$). In fact, there is a better overlap between the relevant orbitals for the former conformers with respect to the latter ones. Thus, the $\sigma_{\text{C4-S}} \rightarrow \pi_{\text{C1=O}_2}^*$ interaction mean energy value is $ca. 5.3 \text{ kcal mol}^{-1}$ for *g₃-syn* and *g₁-anti* conformers and $ca. 3.8 \text{ kcal mol}^{-1}$ for *q-g-syn* and *q-g₂-syn* conformers for **1**, **4** and **6** derivatives. In the same way, the unusual $\pi_{\text{C1=O}_2} \rightarrow \sigma_{\text{C4-S}_5}^*$ interaction [25] mean energy value is $ca. 7.2 \text{ kcal mol}^{-1}$ for *g₃-syn* and *g₁-anti* conformers and $ca. 5.0 \text{ kcal mol}^{-1}$ for *q-g-syn* and *q-g₂-syn* conformers for **1**, **4** and **6** derivatives. The $\pi_{\text{C1=O}_2} \rightarrow \sigma_{\text{C4-S}_5}^*$ interaction mean energy value is the weakest for the $\pi^*(\pi)/\sigma^*(\sigma)$ interaction series, i.e. $ca. 2.2 \text{ kcal mol}^{-1}$ for *g₃-syn* and *g₁-anti* conformers and $ca. 1.4 \text{ kcal mol}^{-1}$ for *q-g-syn* and *q-g₂-syn* conformers, for **1**, **4** and **6** derivatives.

It should be pointed out, that there is a slight progressive increase of the $\sigma_{\text{C4-S}_5} \rightarrow \pi_{\text{C1=O}_2}^*$ mean interacting energy value, for the four conformers, going from **6** to **1** which vary from 4.3 to $5.2 \text{ kcal mol}^{-1}$. Actually, the electron-donating 4'-methoxy substituent which destabilizes the $\pi_{\text{C1=O}_2}^*$ orbital gets it far apart from the $\sigma_{\text{C4-S}_5}$ orbital, while the electron attracting 4'-nitro substituent which stabilizes the $\pi_{\text{C1=O}_2}^*$ orbital gets it closer to the $\sigma_{\text{C4-S}_5}$ orbital. Therefore, the former substituent act decreasing the $\sigma_{\text{C4-S}_5} \rightarrow \pi_{\text{C1=O}_2}^*$ orbital interaction energy while the latter substituent makes it stronger.

The geometry of *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers allows intramolecular contact between the oppositely charged $\text{O}^{\delta-}(8)_{[\text{SO}]} \cdots \text{C}^{\delta+}(1)_{[\text{CO}]}$ atoms whose distances are shorter than the $\sum v$ dW radii by Δl mean values of -0.27 \AA for **1**, -0.16 \AA for **4** and -0.05 \AA for **6**. This contact becomes larger than the $\sum v$ dW radii for the *q-g-syn* conformer as the sulfinyl oxygen atom becomes far apart from the carbonyl carbon atom ($\gamma \cong 170^\circ$) (Table 4). Nevertheless, the weak $\text{LP}_{\text{O8}(3)} \rightarrow \pi_{\text{C1=O}_2}^*$ orbital interaction of $0.5 \text{ kcal mol}^{-1}$ is the only one detected for the *g₃-syn* conformer for the 4'-nitro derivative **1** which possess the shortest intramolecular contact ($\Delta l = -0.34 \text{ \AA}$) and should have the closest $\pi_{\text{C1=O}_2}^*$ orbital energy with respect to that of the

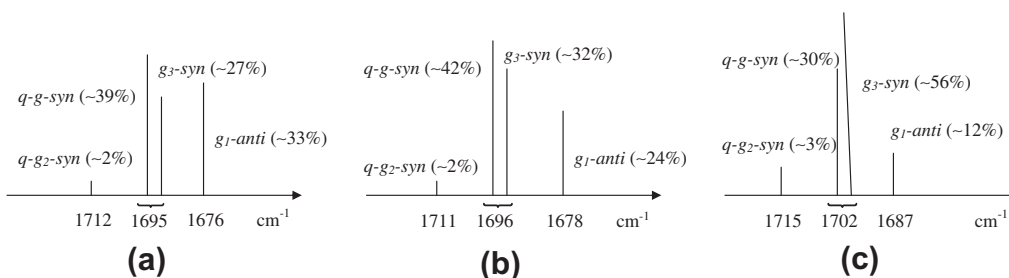


Fig. 2. Diagram showing the frequency and the relative intensity of the carbonyl band components for the *q-g-syn*, *g3-syn*, *g1-anti* and *q-g2-syn* conformers of 4'-methoxy (a), 4'-hydrogen (b), 4'-nitro (c) 2-ethylsulfinyl-phenylthioacetates computed at the B3LYP/6-31G(d,p) level.

$\sigma_{C_4-S_5}$ orbital, as above discussed. It may be concluded that the $O^{\delta-}(8)_{[SO]} \cdots C^{\delta+}(1)_{[CO]}$ electrostatic interaction is the main factor which contributes for the stabilization of the *g3-syn*, *g1-anti* and *q-g2-syn*, whose strength follows the order $1 > 4 > 6$, along with a weaker contribution of the $LP_{O8(3)} \rightarrow \pi_{C_1=O_2}^*$ orbital interaction.

A further short contact is found between the oppositely charged $O^{\delta-}(2)_{[CO]} \cdots H^{\delta+}(17)_{[CH_2]}$ atoms whose distances are shorter than the $\sum v dW$ radii by Δl mean value of ca. -0.36 \AA for *q-g-syn*, *g3-syn*, *g1-anti* conformers for **1**, **4** and **6**. The $O^{\delta-}(2)_{[CO]} \cdots H^{\delta+}(17)_{[CH_2]}$ contact is responsible for $LP_{O2} \rightarrow \sigma_{C_6-H_{17}[Et]}^*$ orbital interaction whose mean energy value is of ca. $1.2 \text{ kcal mol}^{-1}$ for the referred conformers. However, this contact is significantly larger than the $\sum v dW$ radii for the *q-g2-syn* as the ethyl group becomes far apart from the carbonyl oxygen atom. Thus, the electrostatic and orbital (hydrogen bond) interactions contribute for the stabilization of the *q-g-syn*, *g3-syn*, *g1-anti* conformers almost to the same extent.

It should be pointed out that appropriate geometry for the *q-g-syn* conformer ($\alpha \cong 55^\circ$; $\beta \cong -80^\circ$; $\gamma \cong 170^\circ$) brings closer the oppositely charged $O^{\delta-}(2)_{[CO]} \cdots S^{\delta+}(5)_{[SO]}$ atoms whose contact is smaller than $\sum v dW$ radii by $\Delta l \cong -0.10 \text{ cm}^{-1}$. This geometry is similar to that of the β -carbonyl-sulfoxides ($\alpha \cong 10^\circ$; $\beta \cong -73^\circ$; $\gamma \cong 180^\circ$) [5–7], but do not allows the $LP_{O2} \rightarrow \sigma_{S-O}^*$ interaction as the slightly larger α dihedral angle precludes the occurrence of this

orbital overlap. Thus, the *q-g-syn* conformer is significantly stabilized through the Coulombic $O^{\delta-}(2)_{[CO]} \cdots S^{\delta+}(5)_{[SO]}$ interaction. Similarly, the *q-g2-syn* conformer presents an α angle of ca. 60° , which is close to that of the *q-g-syn* conformer, but the $\gamma \cong 70^\circ$ and $\beta \cong 178^\circ$ dihedral angles for the *q-g2-syn* conformer are interchanged with respect to those of the *q-g-syn* conformer. This geometry should also stabilize electrostatically the *q-g2-syn* conformer through the $O^{\delta-}(2)_{[CO]} \cdots S^{\delta+}(5)_{[SO]}$ short contact, whose interatomic distance is smaller than the $\sum v dW$ radii by $\Delta l \cong -0.13 \text{ cm}^{-1}$. However, the *q-g2-syn* conformer (Structure III, Scheme 2; Fig. 2) brings the sulfinyl sulphur lone pair close to the negatively charged carbonyl oxygen atom ($LP_{S5} \cdots O^{\delta-}(2)_{[CO]}$) which originates a strong repulsive Coulombic interaction between them, leading to a significant destabilization of *q-g2-syn* conformer. Moreover, this repulsive interaction seems to be responsible for an increase of the carbonyl bond order and consequently to the rising of the ν_{CO} stretching frequency of *q-g2-syn* conformer with respect to the ν_{CO} frequencies of the *g3-syn*, *g1-anti* and *q-g2-syn* conformers as found in the calculations (Table 4).

The mean summing up values of all selected orbital interaction energies of the *q-g-syn* ($96.2 \text{ kcal mol}^{-1}$), *g3-syn* ($102.0 \text{ kcal mol}^{-1}$), *g1-anti* ($97.8 \text{ kcal mol}^{-1}$) and *q-g2-syn* ($97.7 \text{ kcal mol}^{-1}$) conformers for **1**, **4** and **6** (Table 7) indicate that the *g3-syn* conformer is the

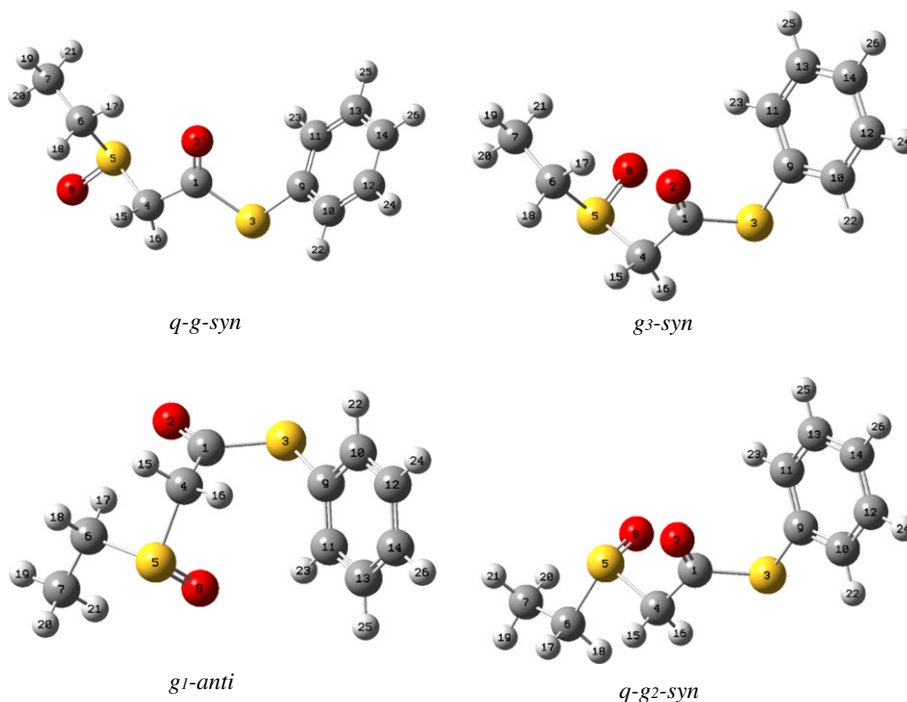


Fig. 3. Molecular structures of the conformers of **4** obtained at the B3LYP/6-31-G(d,p) level.

Table 5CHELPG charges (e) at selected atoms obtained at the B3LYP/6-31G(d,p) level for 4'-Y-C₆H₄SC(O)CH₂S(O)Et (**1**), (**4**), (**6**).

Comp.	Y	Conf.	O(2) _[CO]	C(1) _[CO]	S(3)	C(9) _[Ph]	H(23) _[Ph]	S(5) _[SO]	O(8) _[SO]	H(17) _[CH₂]	H(16) _[α-CH₂]
1	NO ₂	<i>q-g-syn</i>	-0.385	0.379	-0.267	0.263	0.140	0.190	-0.425	0.035	0.140
		<i>g₃-syn</i>	-0.430	0.465	-0.228	0.201	0.139	0.184	-0.407	0.089	0.139
		<i>g₁-anti</i>	-0.392	0.454	-0.191	0.120	0.059	0.192	-0.380	0.089	0.038
		<i>q-g₂-syn</i>	-0.435	0.511	-0.250	0.215	0.166	0.259	-0.421	0.055	0.129
4	H	<i>q-g-syn</i>	-0.408	0.405	-0.295	0.261	0.124	0.185	-0.433	0.040	0.133
		<i>g₃-syn</i>	-0.451	0.505	-0.269	0.223	0.128	0.185	-0.410	0.103	0.132
		<i>g₁-anti</i>	-0.408	0.462	-0.219	0.138	0.046	0.165	-0.384	0.085	0.035
		<i>q-g₂-syn</i>	-0.459	0.543	-0.297	0.254	0.153	0.249	-0.425	0.053	0.125
6	OMe	<i>q-g-syn</i>	-0.412	0.404	-0.294	0.208	0.129	0.185	-0.433	0.040	0.131
		<i>g₃-syn</i>	-0.457	0.495	-0.262	0.169	0.140	0.181	-0.410	0.098	0.129
		<i>g₁-anti</i>	-0.415	0.450	-0.220	0.093	0.066	0.165	-0.391	0.091	0.024
		<i>q-g₂-syn</i>	-0.467	0.560	-0.306	0.194	0.148	0.245	-0.426	0.067	0.122

Table 6Selected interatomic distances (Å) for the minimum energy conformations of 4'-Y-C₆H₄SC(O)CH₂S(O)Et (**1**), (**4**), (**6**) at the B3LYP/6-31G(d,p) level, and X-ray geometrical data for 4'-Br-C₆H₄SC(O)CH₂S(O)Et (**3**).

Comp	Y	Conf. ^a	S ₅ ...C ₁	ΔI ^c	O ₂ ...S ₅	ΔI	C ₁ ...O ₈	ΔI	C ₉ ...O ₂	ΔI	O ₂ ...H ₁₇	ΔI	O ₈ ...H ₂₃	ΔI	H ₁₆ ...C ₉	ΔI	H ₁₆ ...C ₁₁	ΔI
3	Br	X-ray	2.699(7)	-0.80	3.095(5)	-0.23	3.124(8)	-0.10	2.909(9)	-0.31	^d							
1	NO ₂	<i>q-g-s</i>	2.822	-0.68	3.224	-0.10	4.031	0.71	2.987	-0.23	2.439	-0.28	-	-	-	-	-	-
		<i>g₃-s</i>	2.783	-0.72	3.336	0.02	2.978	-0.34	2.943	-0.28	2.356	-0.36	-	-	-	-	-	-
		<i>g₁-a</i>	2.837	-0.66	3.423	0.10	3.145	-0.18	4.030	0.81	2.331	-0.39	2.266	-0.45	2.617	-0.28	2.855	-0.05
		<i>q-g₂-s</i>	2.763	-0.74	3.218	-0.10	3.245	-0.08	2.989	-0.23	-	-	-	-	-	-	-	-
4	H	<i>q-g-s</i>	2.824	-0.68	3.212	-0.11	4.037	0.72	2.969	-0.25	2.409	-0.31	-	-	-	-	-	-
		<i>g₃-s</i>	2.806	-0.69	3.360	0.04	3.038	-0.28	2.954	-0.27	2.328	-0.39	-	-	-	-	-	-
		<i>g₁-a</i>	2.839	-0.66	3.422	0.10	3.152	-0.17	4.025	0.81	2.323	-0.40	2.366	-0.35	2.574	-0.33	2.884	-0.02
		<i>q-g₂-s</i>	2.770	-0.73	3.185	-0.14	3.305	-0.02	2.978	-0.24	-	-	-	-	-	-	-	-
6	OMe	<i>q-g-s</i>	2.819	-0.68	3.239	-0.08	4.037	0.82	2.967	-0.25	2.415	-0.31	-	-	-	-	-	-
		<i>g₃-s</i>	2.806	-0.69	3.358	0.04	3.038	-0.18	2.948	-0.27	2.324	-0.40	-	-	-	-	-	-
		<i>g₁-a</i>	2.840	-0.66	3.429	0.11	3.161	-0.06	4.022	0.80	2.324	-0.40	2.385	-0.34	2.565	-0.34	2.920	0.02
		<i>q-g₂-s</i>	2.772	-0.73	3.161	-0.16	3.307	0.09	2.970	-0.25	-	-	-	-	-	-	-	-
		Σrv dW ^b	3.50		3.32		3.22		3.22		2.72		2.72		2.90		2.90	

^a Conformer designation.^b Sum of the van der Waals radii.^c Difference between nonbonded atoms distance and the sum of the van der Waals radii.^d Interatomic distance larger than the sum of the van der Waals radii.**Table 7**Comparison of significant NBO energies (kcal mol⁻¹) of the corresponding interacting orbitals for the gauche(*g*) or quasi-gauche (*q-g*) conformers of 4'-Y-C₆H₄SC(O)CH₂S(O)Et (**1**), (**4**), (**6**) at the B3LYP/6-31G(d,p) level.

Orbitals	Y = NO ₂ (1)				Y = H (4)				Y = OMe (6)			
	<i>q-g-s</i>	<i>g₃-s</i>	<i>g₁-a</i>	<i>q-g₂-s</i>	<i>q-g-s</i>	<i>g₃-s</i>	<i>g₁-a</i>	<i>q-g₂-s</i>	<i>q-g-s</i>	<i>g₃-s</i>	<i>g₁-a</i>	<i>q-g₂-s</i>
LPS ₃ → π _{C₁=O₂}	30.7	30.5	28.9	30.7	31.8	32.2	30.5	32.0	32.0	32.2	30.8	31.9
LPO ₂ → σ _{C₁-S₅}	36.7	36.5	31.5	37.2	35.7	35.3	30.5	36.2	35.5	35.0	30.3	36.2
LPO ₂ → σ _{C₁-C₄}	17.7	18.2	18.3	18.8	18.1	18.5	18.5	19.2	18.1	18.5	18.6	19.3
LPO ₂ → σ _{C₆-H₁₇}	1.3	1.3	0.8	^a	1.5	1.3	0.9	-	1.4	1.4	0.8	-
σ _{C₄-S₅} → π _{C₁=O₂}	3.9	6.1	5.1	5.0	3.2	5.4	5.0	4.2	3.3	5.4	4.9	3.8
π _{C₁=O₂} → σ _{C₄-S₅}	1.4	2.0	2.3	1.5	1.3	2.0	2.3	1.3	1.4	2.0	2.4	1.2
π _{C₁=O₂} → σ _{C₄-S₅}	4.7	7.2	7.2	5.2	4.2	7.2	7.2	4.8	4.8	7.3	7.3	4.5
LPO ₈ (3) → π _{C₁=O₂}	-	0.5	-	-	-	-	-	-	-	-	-	-
LPO ₈ (3) → σ _{C₁₁-H₂₃}	-	-	2.3	-	-	-	1.5	-	-	-	1.3	-
LPO ₈ (1) → σ _{C₁₁-H₂₃}	-	-	1.6	-	-	-	1.0	-	-	-	1.0	-
π _{C₉=C₁₁} → σ _{C₄-H₁₆}	-	-	-	-	-	-	-	-	-	-	0.6	-

^a Interaction energy lower than 0.5 kcal mol⁻¹.

most stable, followed by *g₁-anti* and *q-g₂-syn* conformers, being the *q-g-syn* conformer the slightly less stable. The *q-g-syn* conformer is further stabilized through the O^{δ-}(2)_[CO] · S^{δ+}(5)_[SO] attractive Coulombic interaction while the *q-g₂-syn* conformer is destabilized by the LP_{S5} · O^{δ-}(2)_[CO] repulsive Coulombic interaction. This analysis is in line with the computed relative conformer population which indicates that both the *q-g-syn* and *g₃-syn* conformers are the more stables, followed by the *g₁-anti* conformer, while the *q-g₂-syn* is the least stable (Fig. 2 and Table 4).

The computed population of the *q-g-syn*, *g₃-syn* and *g₁-anti* conformers changes going from the electron attracting 4'-nitro derivative **1** to the electron-donating 4'-methoxy derivative **6**. Nevertheless, the low population of the *q-g₂-syn* remains practically constant going from **1** to **6** (Table 4). It should be pointed out that there is not a straightforward explanation to justify the facts: that the *q-g-syn* conformer population increases going from **1** (29.4%) to **6** (39%), the *g₃-syn* conformer decreases its population going from **1** (39%) to **6** (27%) while the *g₁-anti* population

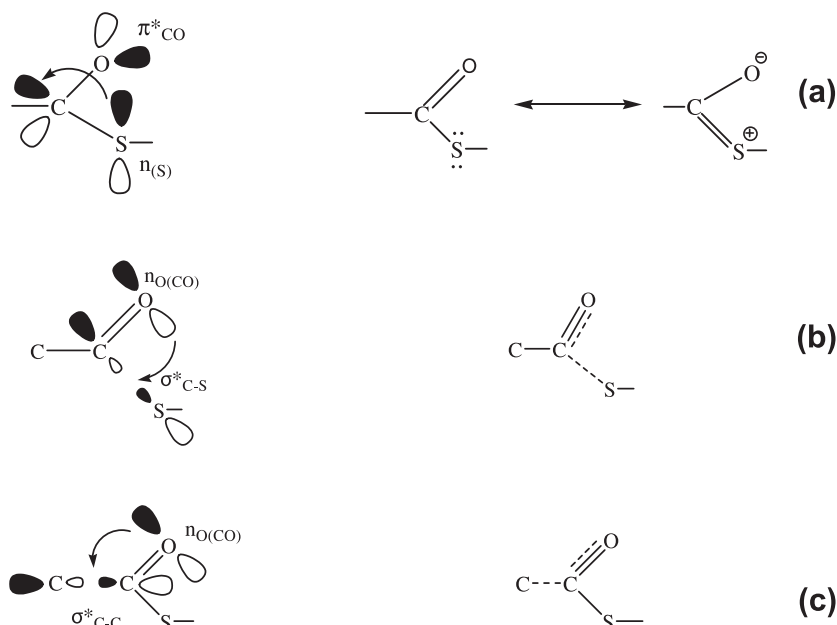


Fig. 4. $n_{(S3)}/\pi^*_{C_1-O_2}$ (a), $n_{O_2(CO)}/\sigma^*_{C_1-S_3}$ (b) and $n_{O_2(CO)}/\sigma^*_{C_1-C_4}$ (c) orbital interactions with their corresponding representations in the Valence Bond Theory.

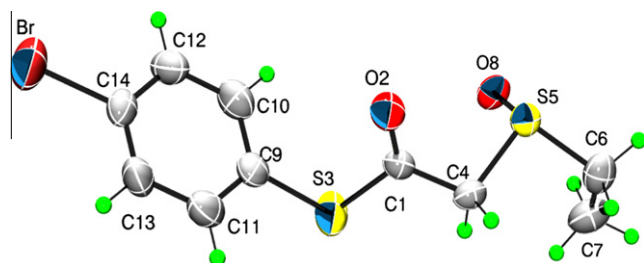


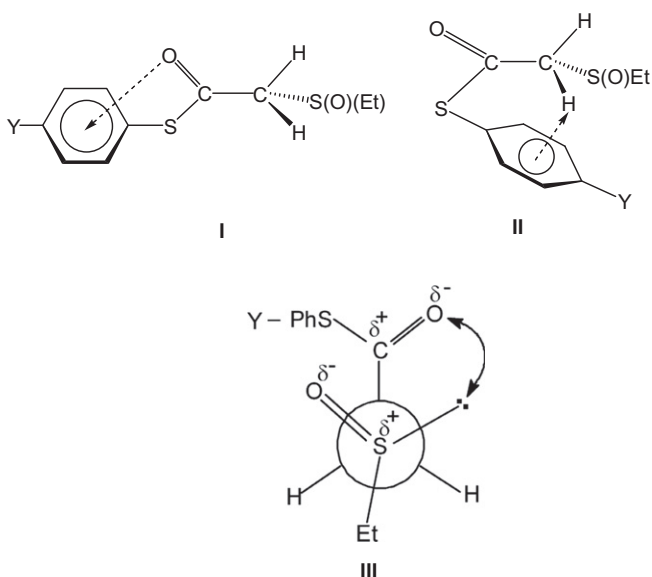
Fig. 5. X-ray crystal structure of 2-ethylsulfinyl-4'-bromophenylthioacetate (**3**) with the heavy atoms labelling. Displacements ellipsoids are drawn at 50% probability level and H atoms are shown as spheres of arbitrary radii.

Table 8

Intermolecular hydrogen-bond geometry (\AA , $^\circ$) for the single crystal of 2-ethylsulfinyl-4'-bromophenylthioacetate 4'-Br-C₆H₄SC(O)CH₂S(O)Et (**3**).

D—H...A	D—H	H...A ^a	D...A	D—H...A
C ₄ —H ₄ A...O ₈ ⁱ	0.97	2.58	3.546(9)	175
C ₇ —H ₇ B...O ₈ ⁱ	0.96	2.65	3.563(11)	158
C ₆ —H ₆ B...O ₈ ⁱⁱ	0.97	2.58	3.323(9)	134
C ₄ —H ₄ B...O ₈ ⁱⁱ	0.97	2.48	3.273(8)	139
C ₁₀ —H ₁₀ ...O ₂ ⁱⁱⁱ	0.93	2.64	3.500(11)	154
Symmetry operations: i = $-x + 1/2 + 1$, $-y + 1$, $+z - 1/2$				
ii = $x - 1$, y , z				
iii = $x + 1$, y , z				

^a Sum of the van der Waals radii: 2.72 \AA .



Scheme 2. Relevant intramolecular short contact in *syn* (q - g , g_3 , q - g_2) conformers (I), *anti* (g_1) conformer (II) and q - g_2 -*syn* conformer (III) of 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates 4'-Y-C₆H₄SC(O)CH₂S(O)Et.

increases going from **1** (12%) to **6** (33%). Actually, the different orbital and electrostatic interactions which stabilize the referred conformers may act in opposite directions making difficult to rationalize these trends (see above).

X-ray single crystal analysis, performed for **3** (Fig. 5) shows that the dihedral angles α , β , γ , δ , φ (Table 4) indicate that this compound exists in the solid state in a geometry which is reasonably close to the less stable q - g_2 -*syn* gas conformation for derivatives **1**, **4** and **6**. However, the ε dihedral angle in the crystal for **3** (74.6°) deviates significantly from the same angle for **1**, **4** and **6**, in the gas phase ($\varepsilon \cong -173^\circ$). It should be noted, that in the solid of **3**, the difference between the intramolecular contacts and the sum of the van der Waals radii (Δl) (Table 6) for $S_5 \cdots C_1$ (ca. -0.80 \AA), $O_2 \cdots S_5$ (ca. -0.23 \AA), $C_1 \cdots O_8$ (ca. -0.10 \AA), $C_9 \cdots O_2$ (ca. -0.32 \AA) are similar to the corresponding (Δl) values found in the gas phase for **1**, **4** and **6**. Therefore, these short contacts stabilize almost into the same extent the distorted q - g_2 -*syn* conformer of **3** in the solid through the same orbital and Coulombic interactions which take place for the q - g_2 -*syn* conformer in the gas phase for **1**, **4** and **6**.

In order to obtain a larger energy gain from crystal packing, the slightly distorted q - g_2 -*syn* geometry of **3** is stabilized in the solid through dipole moment coupling along with a series of C—H...O interactions whose H...O interatomic distances are close or shorter than the sum of their van der Waals radii as shown in Table 8.

4. Conclusions

The preferred conformations of some 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates bearing as substituents NO₂ **1**, Cl **2**, Br **3**, H **4**, Me **5**, OMe **6** were determined by ν_{CO} IR analysis, B3LYP/6-31G(d,p) calculations along with the NBO analysis for **1**, **4** and **6** and X-ray analysis for **3**. Theoretical data indicated the existence of four *gauche* conformers, i.e. the *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers for **1**, **4** and **6** derivatives. The *q-g-syn* and *g₃-syn* conformers present almost the same computed ν_{CO} frequencies while the *g₁-anti* conformer presents the lowest ν_{CO} frequency. The *q-g₂-syn* conformer shows the highest computed ν_{CO} frequency. The calculations reproduce quite well the experimental results. In fact the *q-g-syn* and *g₃-syn* conformers correspond in the IR spectrum (in solution) to the ν_{CO} doublet higher frequency component of larger intensity while the *g₁-anti* conformer correspond to the ν_{CO} doublet lower frequency component of smaller intensity.

The NBO analysis showed that the *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers for **1**, **4** and **6** are strongly stabilized by LP_{S3} → $\pi^*_{\text{C}_1=\text{O}_2}$ (conjugative), LP_{O2} → $\sigma^*_{\text{C}_1-\text{S}_3}$ and LP_{O2} → $\sigma^*_{\text{C}_1-\text{C}_4}$ (through bond coupling) interactions whose mean energy values are of ca. 31 kcal mol⁻¹, 35 kcal mol⁻¹ and 18 kcal mol⁻¹, respectively. The LP_{S3} → $\pi^*_{\text{C}_1=\text{O}_2}$ and LP_{O2} → $\sigma^*_{\text{C}_1-\text{C}_4}$ orbital interactions stabilize all the conformers into the same extent while the (*q-g*, *g₃* and *q-g₂*)-*syn* conformers are more stabilized than the *g₁-anti* conformer by ca. 5 kcal mol⁻¹ through the LP_{O2} → $\sigma^*_{\text{C}_1-\text{S}_3}$ orbital interaction. The stronger LP_{O2} → $\sigma^*_{\text{C}_1-\text{S}_3}$ interaction for the (*q-g*, *g₃* and *q-g₂*)-*syn* conformers relative to that of the *g₁-anti* conformer originates an increase of the carbonyl bond order and thus in the ν_{CO} frequencies of the former conformers relative to the latter one.

The *q-g-syn*, *g₃-syn* and *q-g₂-syn* conformers are further stabilized by $\sigma_{\text{C}_4-\text{S}_5} \rightarrow \pi^*_{\text{C}_1=\text{O}_2}$ (strong), $\pi_{\text{C}_1=\text{O}_2} \rightarrow \sigma^*_{\text{C}_4-\text{S}_5}$, LP_{O2} → $\sigma^*_{\text{C}_6-\text{H}_{17}[\text{Et}]}$ (weak) and $\pi^*_{\text{C}_1=\text{O}_2} / \sigma^*_{\text{C}_4-\text{S}_5}$ (strong) orbital interactions. The *g₁-anti* conformer is stabilized by $\sigma_{\text{C}_4-\text{S}_5} \rightarrow \pi^*_{\text{C}_1=\text{O}_2}$ (strong), $\rightarrow \pi_{\text{C}_1=\text{O}_2} / \sigma^*_{\text{C}_4-\text{S}_5}$, LP_{O2}[CO] → $\sigma^*_{\text{C}_6-\text{H}_{17}[\text{Et}]}$, $\pi_{\text{C}_9=\text{C}_{11}[\text{Ph}]} \rightarrow \sigma^*_{\text{C}_4-\text{H}_{16}[\text{Z-CH}_2]}$ (weak), LP_{O8}[SO] → $\sigma^*_{\text{C}_{11}-\text{H}_{23}[\text{O-Ph}]}$ (medium) and $\pi^*_{\text{C}_1=\text{O}_2} / \sigma^*_{\text{C}_4-\text{S}_5}$ (strong) orbital interactions.

The mean summing up values of all selected orbital interaction energies of the *q-g-syn*, *g₃-syn*, *g₁-anti* and *q-g₂-syn* conformers for **1**, **4** and **6** indicate that the *g₃-syn* conformer is the most stable, followed by *g₁-anti* and *q-g₂-syn* conformers, being the *q-g-syn* conformer the slightly less stable. However, the *q-g-syn* conformer is further stabilized through the O^{δ-}(2)_[CO] · · S^{δ+}(5)_[SO] attractive Coulombic interaction while the *q-g₂-syn* conformer is destabilized by the LP_{S5} · · O^{δ-}(2)_[CO] repulsive Coulombic interaction. This analysis is in line with the computed relative conformer population which indicates the following order: *q-g-syn*, *g₃-syn* > *g₁-anti* >> *q-g₂-syn*.

X-ray single crystal analysis, performed for **3** shows that this compound assumes a geometry reasonably close to the less stable *q-g₂-syn* conformation in the gas phase for **1**, **4** and **6**.

In the solid, **3** presents similar S₅ · · C₁, O₂ · · S₅, C₁ · · O₈, C₉ · · O₂ intramolecular short contacts found in the gas phase for **1**, **4** and **6**. These contacts stabilize the distorted *q-g₂-syn* conformer of **3** through the same orbital and Coulombic interactions which take place for the *q-g₂-syn* conformer in the gas phase for **1**, **4** and **6**. The energy gain for the crystal packing of **3** is obtained through dipole moment coupling along with a series of C—H · · O interactions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.07.035.

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