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

Paulo R. Olivato a,*, Mário L.T. Hui a, Alessandro Rodrigues a, Carlos R. Cerqueira Jr. a, Julio Zukerman-Schpector b, Roberto Rittner c, Maurizio Dal Colle d

a Conformational Analysis and Electronic Interactions Laboratory, Institute of Chemistry, USP, CP 26077, 05513-970 São Paulo, SP, Brazil
b Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil
c Physical Organic Chemistry Laboratory, Chemistry Institute, State University of Campinas, Campinas, SP, Brazil
d Dipartimento di Chimica, Università di Ferrara, Ferrara, Italy

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A B S T R A C T

The analysis of the IR νCO bands of the 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates 4'-Y-C₆H₄SCO(O)CH₂S(O)Et (Y = NO₂, 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 (g-g-syn, g-s-anti and g-g-anti) conformers for 1–6. The calculations reproduce quite well the experimental results, i.e. the computed g-g-syn and g-g-anti conformers correspond in the IR spectrum (in solution), to the νCO doublet higher frequency component of larger intensity, while the computed g-s-anti conformer correspond to the νCO doublet lower frequency component (in solution). NBO analysis showed that the n(O) → π* (r) → π* (r) → σ* (r) → σ* (r) orbital interactions are the main factors which stabilize the g-g-syn, g-s-anti and g-g-anti conformers for 1, 4 and 6. The n(O=O) → π* (r) interaction which stabilizes the g-g-syn, g-s-anti and g-g-anti conformers in a larger extent than the g-s-anti conformer, is responsible for the larger νCO frequencies of the former conformers relative to the latter one. The g-g-syn, g-s-anti and g-g-anti conformers are further stabilized by π(σ r) → π(σ r) (strong), π(σ r) → π(σ r) (weak) and π(σ r) → π(σ r) (strong) orbital interactions. The g-a-anti conformer is also stabilized by π(σ r) → π(σ r) (strong), π(σ r) → π(σ r) (medium) and π(σ r) → π(σ r) (weak) orbital interactions. The g-g-anti conformer is further stabilized by O₅(CO) → S₆(CO) attractive Coulombic interaction while the g-g-anti conformer is destabilized by the n₅(CO) → O₅(CO) repulsive Coulombic interaction. This analysis indicates the following conformer stabilization order: g-g-syn; g-s-anti; g-g-anti; g-g-anti. X-ray single crystal analysis of 3 indicates that it assumes in the solid a distorted g-g-anti geometry which is stabilized through almost the same orbital and Coulombic interaction which takes place for the g-g-anti conformer, in the gas, along with dipole moment coupling and a series intermolecular C···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-carbonylsulfoxides XC(O)CH₂S(O)R have shown that the gauche conformer is the most stable for the α-sulfynylketones (X = Me; R = Et, 4-Y-C₆H₄) [1–3] and α-sulfynylesters (X = 4-Y-C₆H₄O; R = Et) [4], while the cis conformer becomes the predominant for α-sulfynylacetonophenes and α-sulfynylamides (X = 4-Y-C₆H₄, Et₂N; R = Alkyl, 4-Y-C₆H₄) [5–8]. As for the α-sulfynyl N-methoxy-N-methyl amides (X = N(Me)₂[MeO]; R = 4-Y-C₆H₄) [9] the cis conformer prevails for the diastereomer 1, while the gauche conformer predominates for the diastereomer 2. In general the stabilization of the gauche conformers has been attributed to the π(CO)/σ(C–S) and, to a minor extent, to the π(CO)/σ(C–S) orbital interactions, while the larger stabilization of the cis conformer of the α-alkylsulfynylacetonophenes and α-phenylsulfinylamides relative to the α-alkyl- and α-aryl-sulfynylacetophenes has been ascribed to the π(πσ) → n(O=O) and nπ πσ(CO) conjugation, which originates stronger intramolecular electrostatic and charge transfer interactions between C⁺=O⁻⁻ and S⁺⁺=O⁻⁻ dipoles (n(O=O)/σ(C–S) orbital interactions).

In the MeC(O)X series [10] there is a progressive increase of the experimental carbonyl oxygen lone pair (nπ) ionization energy going from amide (Eπ = 9.20 eV) to acetophenone (Eπ = 9.34 eV) to butanone (Eπ = 9.46 eV) to thiophene (Eπ = 9.64 eV) and to ester (Eπ = 10.45 eV), for X = NEt₂, Ph, Et, SET and OEt, respectively, which in turn is accompanied by a corresponding decrease of the negative

* Corresponding author. Tel.: +55 11 3091 2167; fax: +55 11 3815 5579.
E-mail address: prolivat@iq.usp.br (P.R. Olivato).

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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 $\pi_{CO}$ orbital going from amide ($E_{am} = 2.26$ eV) to ester ($E_{es} = 2.09$ eV) to butanone ($E_{b} = 1.26$ eV) and to thioester ($E_{t} = 0.95$ eV).

Therefore, it seems reasonable to expect a larger stabilization of the gauche conformer for the $\alpha$-sulfinyl-thioesters relative to the same conformation of the other $\alpha$-sulfinyl derivatives, due to stronger $\pi_{CO}/\sigma_{C-S(0)}$ orbital interaction which should operate in the gauche conformation of the sulfinyl-thioesters, once the $\pi_{CO}$/$\sigma_{C-S(0)}$ 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 $\alpha$-sulfinylthioesters, this paper reports the IR study of some 2-ethylsulfinyl-$(4'-$substituted$)$-phenylthioacetates [11] 4'-Y-C$_6$H$_5$SC(O)CH$_2$SEt bearing in 4'-position electron-attracting, hydrogen and electron-donating substituents, i.e. Y = NO$_2$, Cl, 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 $\beta$/$\pi_{CO}$ 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 prepared without further purification. The 2-ethylsulfinyl-$(4'$-substituted$)$-phenylthioacetates 4'-Y-C$_6$H$_5$SC(O)CH$_2$SEt (Y = NO$_2$, 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 and to this mixture was slowly added sodium bicarbonate. After stirring for 5–10 min, a saturated aqueous sodium chloride solution was added and then the product was extracted with CH$_2$Cl$_2$. 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, $^1$H and $^{13}$C NMR, and elemental analysis of the thioester-sulfoxides 1–6 are presented in Table 1. The starting 2-ethylthio-$(4'$-substituted$)$ phenylthioacetates 4'-Y-C$_6$H$_5$SC(O)CH$_2$SEt were prepared as previously described [12].

2.2. IR measurements

The IR spectra were recorded with a FTIR Nicolet Magna 550 FTIR spectrometer, with a 1.0 cm$^{-1}$ resolution, at a concentration of 1.0 $\times$ 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 $\times$ 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

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 299.947 and 75.423 MHz, respectively, for 0.1 mol/dm$^3$ solutions in chloroform-d. $^1$H and $^{13}$C 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$\alpha$ 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 $\psi$-scan based absorption was applied. The structure was solved by direct methods using SIR97 [14] and refined against $F^2$ with SHEXL97 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 $\alpha$-sulfur atom with respect to the carbonyl group resultant from a systematic conformational search, allowing
Table 1

<table>
<thead>
<tr>
<th>Physical, 1H NMR and elemental analysis data for 2-ethylsulfinyl-(4-Y-C6H4SC(O)CH2S(O)Et</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Y</td>
<td>1H NMR&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7.44–7.49 (2H, m), 7.36–7.31 (2H, m), 3.94 (2H, s), 3.00–2.80 (2H, m), 1.37 (2H, t), 1.27 (2H, t), 1.36</td>
</tr>
<tr>
<td>Cl</td>
<td>7.60–7.53 (2H, m), 7.45–7.28 (2H, m), 3.95 (2H, s), 2.79–2.79 (2H, m), 1.35 (2H, t), 1.33 (2H, t), 1.33</td>
</tr>
<tr>
<td>Br</td>
<td>7.41 (5H, m), 3.93 (2H, s), 2.89–2.77 (2H, m), 1.35 (3H, t), 1.33 (3H, t), 1.33</td>
</tr>
<tr>
<td>H</td>
<td>7.42 (5H, m), 3.93 (2H, s), 2.89–2.77 (2H, m), 1.35 (3H, t), 1.33 (3H, t), 1.33</td>
</tr>
</tbody>
</table>

<sup>a</sup> H chemical shifts in ppm relative to TMS and coupling constants in Hz, in CDCl<sub>3</sub>.
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 g₁-anti conformers which present very close computed frequencies should correspond to the carbonyl doublet lower frequency component of smaller intensity while the g₁-anti conformer should correspond to the carbonyl doublet lower frequency component of smaller intensity. Moreover, in solution, quite well the experimental results. Actually, the g₁-anti conformer remains almost constant for derivatives 1, 4, and 6, respectively. The g₁-anti conformer displays the 2-sulfinyl (ζ = 74°) substituent in a syn-clinal or quasi-gauche geometry with respect to the carbonyl group.

Table 2

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

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C₁₀H₁₁BrO₂S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>307.22</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>290(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Orthorhombic, P2₁2₁2₁</td>
</tr>
<tr>
<td>Unit cell dimensions (Å)</td>
<td>a = 4.9385(9), b = 28.760(2), c = 8.770(1)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1245(6)</td>
</tr>
<tr>
<td>Z, Calc. density (Mg m⁻³)</td>
<td>4.1638</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>3.613</td>
</tr>
<tr>
<td>F(0 0 0)</td>
<td>616</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.1 ≤ 0.10 ≤ 0.05</td>
</tr>
<tr>
<td>Theta range for data collection (°)</td>
<td>1.42–26.00</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>–6–6, 0–35, 0–10</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>2630, 2435</td>
</tr>
<tr>
<td>Completeness to θ = 26°</td>
<td>100.00%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>ψ-scan</td>
</tr>
<tr>
<td>Max and min transmission</td>
<td>0.835, 0.655</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2435/1/137</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.022</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>0.0487, 0.1266</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>0.1267, 0.1642</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å⁻³)</td>
<td>0.481, –0.447</td>
</tr>
</tbody>
</table>

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).

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Y</th>
<th>n-C₆H₄+</th>
<th>CCl₄</th>
<th>CHCl₃</th>
<th>CH₂CN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν [cm⁻¹]</td>
<td>p [a]</td>
<td>ν [cm⁻¹]</td>
<td>ν [cm⁻¹]</td>
<td>ν [cm⁻¹]</td>
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<tr>
<td>1</td>
<td>NO₂</td>
<td>&lt;c</td>
<td>1702</td>
<td>100.0</td>
<td>3384</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td>1704</td>
<td>100.0</td>
<td>1699</td>
<td>91.7</td>
</tr>
<tr>
<td>3</td>
<td>Br</td>
<td>1704</td>
<td>76.9</td>
<td>1699</td>
<td>84.3</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>1702</td>
<td>92.3</td>
<td>1697</td>
<td>92.6</td>
</tr>
<tr>
<td>5</td>
<td>Me</td>
<td>1700</td>
<td>90.4</td>
<td>1696</td>
<td>91.7</td>
</tr>
<tr>
<td>6</td>
<td>OMe</td>
<td>1700</td>
<td>92.6</td>
<td>1695</td>
<td>90.1</td>
</tr>
</tbody>
</table>

[a] Intensity of each component of the carbonyl doublet expressed in percentage of absorbance.
[b] First overtone.
[c] Compound slightly soluble in this solvent.
CO frequencies of the former conformers with respect to the latter one. Fig. 4 illustrates the $n_\text{CO}/\pi_\text{C=C}$, $n_\text{CO}/\pi_\text{C=O}$ and $n_\text{CO}/\sigma_\text{C=C}$ orbital interactions with their corresponding representations in the Valence Bond Theory. The NBO mean energy value of the $\sigma_\text{C=S}$ orbital for $\text{syn}(q\cdot g, g_3, q\cdot g_3)$ indicates that it is more stable than the same orbital for $\text{anti}(q\cdot g, g_3, q\cdot g_3)$ conformer by ca. 2 kcal mol$^{-1}$. This behaviour is responsible for the observed slightly stronger $n_\text{CO}/\pi_\text{C=C}$ orbital interaction of the $\text{syn}$ conformers with respect to the $\text{anti}$ conformer.

The $\text{syn}(q\cdot g, g_3, q\cdot g_3)$ conformers for 1, 4 and 6 (Structure I, Scheme 2) present short intramolecular contacts between the O(2)$\cdot$C(9)$\cdot$C(11) atoms whose distances are shorter than the $\sum v dW$ radii by $\Delta l \approx -0.25 \, \AA$. The eigenvector analysis of the relevant orbitals indicates the existence of the $n_\text{CO}/\pi_\text{W}$ charge transfer for the referred conformers which should contribute for the stabilization of the $\text{syn}$ conformers. However, the $\text{LP}_{\text{C}=\text{C}} \rightarrow \pi_\text{C=C}$ interaction was not detected in the NBO analysis, probably because its value should be slightly smaller than 0.5 kcal mol$^{-1}$. On the

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).
other hand, the anti (g₁) conformer (Structure II, Scheme 2) presents short intramolecular contacts between the oppositely charged H²(16)···C₆H₄(9)] atoms whose distances are shorter than the \( \sum \nu \) \( dW \) radii by ΔL values which vary from −0.28 Å to −0.33 Å and to −0.34 Å for 1, 4 and 6, respectively. This trend is in line with the π°C=CH – πC₆H₄-S⁻ orbitals interaction whose value is the maximum (ΔE = 0.64 kcal mol⁻¹) for the methoxy derivative 9 (highest HOMO of πC=CH orbital), and the minimum for the nitro derivative 1 whose ΔE value is smaller than 0.50 kcal mol⁻¹ (lowest HOMO of πC=CH orbital). A further short contact which takes place in the anti (g₁) conformer is between the oppositely charged O⁴⁺(8)[OS] – H₁¹(3)[O₆₃] atoms whose distances are shorter than the \( \sum \nu \) \( dW \) radii by ΔL values which vary from −0.34 Å to −0.35 Å and to −0.45 Å for 6, 4 and 1, respectively. This tendency is in agreement with the progressive increase of the \( \text{LP}_{O₆₃}(3) \rightarrow \pi C_{c₈-h₅₆}; \text{LPO}_{₆₃}(1) \rightarrow \pi C_{c₈-h₅₆} \) orbital interactions (hydrogen bond) whose energy values vary from (1.3; 1.0 kcal mol⁻¹) to (1.5; 1.0 kcal mol⁻¹) and to (2.3; 1.6 kcal mol⁻¹) for 6, 4 and 1, respectively. Thus, the anti (g₁) conformer is stabilized by both \( \pi C_{C₈-H₅₆}[O₆₃] \rightarrow \pi C_{C₈-H₅₆}[O₆₃] \) (weak) and \( \text{LP}_{O₆₃}(3) \rightarrow \pi C_{C₈-H₅₆}[O₆₃] \) (median) 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 S(5)···C(1) contacts between α-sulfinyl sulfur and the carbonyl carbon atoms (ΔL mean value of ca. −0.70 Å), are responsible for the stabilization of the referred gauche conformers through the \( \pi C₆H₄-S⁻/\pi C=CH \) and \( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ \) interactions.

In general, the \( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ \) and \( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ \) interactions are stronger for the g₃-syn and g₁-anti conformers (π dihedral angle of ca. 77°) and weaker for the q-g-syn and q-g₂-syn conformers (π dihedral angle of ca. 60°). In fact, there is a better overlap between the relevant orbitals for the former conformers with respect to the latter ones. Thus, the \( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ \), interaction mean energy value is ca. 5.3 kcal mol⁻¹ for g₁-syn and g₁-anti conformers and ca. 3.8 kcal mol⁻¹ for q-g-syn and q-g₂-syn conformers for 1, 4 and 6 derivatives. In the same way, the unusual \( \pi C₆H₄-O₂ \rightarrow \pi C₆H₄-S⁻ \) interaction [25] mean energy value is ca. 7.2 kcal mol⁻¹ for g₁-syn and g₁-anti conformers and ca. 5.0 kcal mol⁻¹ for q-g-syn and q-g₂-syn conformers for 1, 4 and 6 derivatives. The \( \pi C₆H₄-O₂ \rightarrow \pi C₆H₄-S⁻ \) interaction mean energy value is the weakest for the \( \pi C₆H₄-O₂/\pi C₆H₄-O₂ \) interaction series, i.e. ca. 2.2 kcal mol⁻¹ for g₂-syn and g₁-anti conformers and ca. 1.4 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 \( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ \) mean interacting energy value, for the four conformers, going from 6 to 1 which vary from 4.3 to 5.2 kcal mol⁻¹. Actually, the electron-donating 4'-methoxy substituent which destabilizes the \( \pi C₆H₄-O₂ \) orbital gets it far apart from the \( \pi C₆H₄-S⁻ \) orbital, while the electron attracting 4'-nitro substituent which stabilizes the \( \pi C₆H₄-O₂ \) orbital gets it closer to the \( \pi C₆H₄-S⁻ \) orbital. Therefore, the former substituent act decreasing the \( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ \) orbital interaction energy while the latter substituent makes it stronger.

The geometry of g₁-syn, g₁-anti and q-g₂-syn conformers allows intramolecular contact between the oppositely charged O⁴⁺(8)[OS] – C₆H₄(1)[C(1)] atoms whose distances are shorter than the \( \sum \nu \) \( dW \) radii by ΔL mean values of −0.27 Å for 1, −0.16 Å for 4 and −0.05 Å for 6. This contact becomes larger than the \( \sum \nu \) \( dW \) radii for the q-g₂-syn conformer as the sulfinyl oxygen atom becomes far apart from the carbonyl carbon atom (\( \gamma \approx 170° \)) (Table 4). Nevertheless, the weak \( \text{LP}_{O₆₃}(3) \rightarrow \pi C₆H₄-O₂ \) orbital interaction of 0.5 kcal mol⁻¹ is the only one detected for the g₁-syn conformer for the 4'-nitro derivative 1 which possess the shortest intramolecular contact (ΔL = −0.34 Å) and should have the closest \( \pi C₆H₄-O₂ \) orbital energy with respect to that of the

### Table 4

<table>
<thead>
<tr>
<th>Comp</th>
<th>( E / \text{M} \text{mol}^{-1} )</th>
<th>( \sum \nu ) ( dW ) radii</th>
<th>ΔL</th>
<th>( \gamma )</th>
<th>( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ )</th>
<th>( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ )</th>
<th>( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.95</td>
<td>71.92</td>
<td>0.01</td>
<td>170°</td>
<td>0.25</td>
<td>0.32</td>
<td>0.67</td>
</tr>
<tr>
<td>2</td>
<td>32.95</td>
<td>71.92</td>
<td>0.01</td>
<td>170°</td>
<td>0.25</td>
<td>0.32</td>
<td>0.67</td>
</tr>
</tbody>
</table>

- \( E / \text{M} \text{mol}^{-1} \): Molar fraction in percentage.
- \( \sum \nu \) \( dW \) radii: Selected dihedral angles (°), carbonyl frequencies (cm⁻¹), optimized for the minimum energy conformations of 2-ethylsulfinyl(4,5-substituted)phenoxyacetates 4-Y. 
- ΔL: Molar fraction in percentage.
- \( \gamma \): Molar fraction in percentage.
- \( \pi C₆H₄-S⁻/\pi C₆H₄-O₂ \): See Scheme 1.
\( \sigma_{C_4-S} \) orbital, as above discussed. It may be concluded that the O\(^{\delta+}(8)_{35O1} \cdot \sigma^\text{orbital interaction} \) is the main factor which contributes for the stabilization of the \( g_1\text{-syn}, g_1\text{-anti} \) and \( q\text{-g}_2\text{-syn} \), whose strength follows the order \( 1 > 4 > 6 \), along with a weaker contribution of the LP\(_{8}(3) \) electrostatic interaction.

A further short contact is found between the oppositely charged \( \sigma_{C_4-H_2} \) orbital interaction whose mean energy value is of ca. 1.2 kcal mol\(^{-1} \) for the referred conformers. However, this contact is significantly larger than the \( \sum \nu \) dW radii by \( \Delta \) mean value of ca. –0.36 Å for \( q\text{-g}_2\text{-syn}, g_1\text{-syn}, g_1\text{-anti} \) conformers for 1, 4 and 6. The O\(^{\delta-}(2)_{31C0} \cdot \sigma^\text{orbital interaction} \) contact is responsible for LP\(_{82} \) – \( \sigma_{C_4-H_2} \) short contact, whose interatomic distance is smaller than the \( \sum \nu \) dW radii by \( \Delta \) mean value of ca. 0.13 Å for the referred conformers. However, the \( \sum \nu \) dW radii for the \( q\text{-g}_2\text{-syn} \) 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 \( q\text{-g}_2\text{-syn}, g_1\text{-syn}, g_1\text{-anti} \) conformers almost to the same extent.

It should be pointed out that appropriate geometry for the \( q\text{-g}_2\text{-syn} \) conformer (\( \alpha \approx 55^\circ; \beta \approx 30^\circ; \gamma \approx 170^\circ \)) brings closer the oppositely charged O\(^{\delta-}(2)_{31C0} \cdot \sigma^\text{orbital interaction} \) whose contact is smaller than the \( \sum \nu \) dW radii by \( \Delta \) mean value of ca. –0.10 cm\(^{-1} \). This geometry is similar to that of the \( \mu\text{-carbonyl-sulfoxides} \) (\( a \approx 10^\circ; \beta \approx 73^\circ; \gamma \approx 180^\circ \)) \[5–7\], but do not allows the LP\(_{82} \) – \( \sigma_{C_4-O} \) interaction as the slightly larger \( \alpha \) dihedral angle precludes the occurrence of this orbital overlap. Thus, the \( q\text{-g}_2\text{-syn} \) conformer is significantly stabilized through the Coulombic O\(^{\delta-}(2)_{31CO} \cdot \sigma^\text{orbital interaction} \) interaction. Similarly, the \( q\text{-g}_2\text{-syn} \) conformer present an \( \alpha \) angle of ca. 60°, which is close to that of the \( q\text{-g}_2\text{-syn} \) conformer, but the \( \gamma \approx 70^\circ \) and \( \beta \approx 178^\circ \) dihedral angles for the \( q\text{-g}_2\text{-syn} \) conformer are interchanged with respect to those of the \( q\text{-g}_2\text{-syn} \) conformer. This geometry should also stabilize electrostatically the \( q\text{-g}_2\text{-syn} \) conformer through the O\(^{\delta-}(2)_{31C0} \cdot \sigma^\text{orbital interaction} \) short contact, whose interatomic distance is smaller than the \( \sum \nu \) dW radii by \( \Delta \) mean value of ca. –0.13 Å. However, the \( q\text{-g}_2\text{-syn} \) conformer (Structure III, Scheme 2; Fig. 2) brings the sulfinyl sulphur lone pair close to the negatively charged carbonyl oxygen atom (LP\(_{84} \cdot \sigma^\text{orbital interaction} \)) which originates a strong repulsive Coulombic interaction between them, leading to a significant destabilization of \( q\text{-g}_2\text{-syn} \) conformer. Moreover, this repulsive interaction seems to be responsible for an increase of the carbonyl bond order and consequently to the rising of the \( \nu_{CO} \) stretching frequency of \( q\text{-g}_2\text{-syn} \) conformer with respect to the \( \nu_{CO} \) frequencies of the \( g_1\text{-syn}, g_1\text{-anti} \) and \( q\text{-g}_2\text{-syn} \) conformers as found in the calculations (Table 4).

The mean summing up values of all selected orbital interaction energies of the \( q\text{-g}_2\text{-syn} \) (96.2 kcal mol\(^{-1} \)), \( g_1\text{-syn} \) (102.0 kcal mol\(^{-1} \)), \( g_1\text{-anti} \) (97.8 kcal mol\(^{-1} \)) and \( q\text{-g}_2\text{-syn} \) (97.7 kcal mol\(^{-1} \)) conformers for 1, 4 and 6 (Table 7) indicate that the \( g_1\text{-syn} \) conformer is the

**Fig. 2.** Diagram showing the frequency and the relative intensity of the carbonyl band components for the \( q\text{-g}_2\text{-syn}, g_1\text{-syn}, g_1\text{-anti} \) and \( q\text{-g}_2\text{-syn} \) conformers of 4’-methoxy (a), 4’-hydrogen (b), 4’-nitro (c) 2-ethylsulfanyl-phenylthiocacetates computed at the B3LYP/6-31G(d,p) level.

**Fig. 3.** Molecular structures of the conformers of 4 obtained at the B3LYP/6-31-G(d,p) level.
most stable, followed by the $g_r$-anti and $q_g$-syn conformers, being the $q_g$-syn conformer the slightly less stable. The $q_g$-syn conformer is further stabilized through the $O^1 (2\bar{\text{E}})$ and $S^1 (3\bar{\text{R}})$ attractive Coulombic interaction while the $g_r$-syn conformer is destabilized by the $\text{LP}_{35} - O^1 (2\bar{\text{E}})$ repulsive Coulombic interaction. This analysis is in line with the computed relative conformer population which indicates that both the $q_g$-syn and $g_r$-syn conformers are the more stable, followed by the $g_r$-anti conformer, while the $q_g$-syn conformer is the least stable (Fig. 2 and Table 4).

The computed population of the $q_g$-syn, $g_r$-syn and $g_r$-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 $q_g$-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 $g_r$-syn conformer decreases its population going from 1 (39%) to 6 (27%) while the $g_r$-anti population
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 \( \alpha, \beta, \gamma, \delta, \phi \) (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 \( \epsilon \) dihedral angle in the crystal for 3 (74.6\(^\circ\)) deviates significantly from the same angle for 1, 4 and 6, in the gas phase (\( \epsilon \approx -173^\circ \)). 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 (Table 6) for S\( \cdots \)C\(1\) (ca. -0.80 Å), O\(2\)\(\cdots\)S\(3\) (ca. -0.23 Å), C\(1\)\(\cdots\)O\(8\) (ca. -0.10 Å), C\(9\)\(\cdots\)O\(2\) (ca. -0.32 Å) are similar to the corresponding (\( \Delta l \)) 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.

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**Table 8**

<table>
<thead>
<tr>
<th></th>
<th>D–H·A</th>
<th>D–H·A*</th>
<th>D–A</th>
<th>D–H·A</th>
</tr>
</thead>
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<td>C(\cdots)H(1)(\cdots)–O(2)(\cdots)</td>
<td>0.97</td>
<td>2.58</td>
<td>3.546(9)</td>
<td>175</td>
</tr>
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<td>C(\cdots)H(2)(\cdots)–O(2)(\cdots)</td>
<td>0.96</td>
<td>2.65</td>
<td>3.583(11)</td>
<td>158</td>
</tr>
<tr>
<td>C(\cdots)H(3)(\cdots)–O(2)(\cdots)</td>
<td>0.97</td>
<td>2.58</td>
<td>3.323(9)</td>
<td>134</td>
</tr>
<tr>
<td>C(\cdots)H(4)(\cdots)–O(2)(\cdots)</td>
<td>0.97</td>
<td>2.48</td>
<td>3.273(8)</td>
<td>139</td>
</tr>
<tr>
<td>C(\cdots)H(5)(\cdots)–O(2)(\cdots)</td>
<td>0.93</td>
<td>2.64</td>
<td>3.500(11)</td>
<td>154</td>
</tr>
</tbody>
</table>

Symmetry operations: i = –x + 1/2 + 1, –y + 1, –z – 1/2

\( * \) Sum of the van der Waals radii: 2.72 Å.

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**Fig. 4.** \( n(S_3)/p(C_3)C_1 —O_2 \) (a), \( nO_2(CO)/r(C_3)C_1 —S_3 \) (b) and \( nO_2(CO)/r(C_3)C_1 —C_4 \) (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.

**Scheme 2.** Relevant intramolecular short contact in \( q-g_2-syn \) conformers (I), anti (\( g_1 \)) conformer (II) and \( q-g_2-syn \) conformer (III) of 2-ethylsulfinyl-(4'-substituted)-phenylthioacetates \( 4-Y-C_6H_4SC(O)CH_2S(O)Et \).
4. Conclusions

The preferred conformations of some 2-ethylsulfinyl-(4-substituted)-phenylthiocarbamates bearing as substituents NO2, 1, Cl 2, Br 3, H 4, Me 5, OMe 6 were determined by vcr 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, g1-syn, g1-anti and q-g2-syn conformers for 1, 4 and 6 derivatives. The q-g-syn and g1-syn conformers present almost the same computed vcr frequencies while the g1-anti conformer presents the lowest vcr frequency. The q-g2-syn conformer shows the highest computed vcr frequency. The calculations reproduce quite well the experimental results. In fact the q-g-syn and g1-syn conformers correspond in the IR spectrum (in solution) to the vcr doublet frequency component of larger intensity while the g1-anti conformer correspond to the vcr doublet lower frequency component of smaller intensity.

The NBO analysis showed that the q-g-syn, g1-syn, g1-anti and q-g2-syn conformers for 1, 4 and 6 are strongly stabilized by LP C1—O2 → πC1—C2 (conjugative), LP O2 → πC1—S2 and LP O2 → πC1—C4 (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 C1—O2 and LP O2 → πC1—C4 orbital interactions stabilize all the conformers into the same extent while the (q-g, g1 and q-g2)-syn conformers are more stabilized than the g1-anti conformer by ca. 5 kcal mol⁻¹ through the LP O2 → πC1—C4 orbital interaction. The stronger LP O2 → πC1—C4 interaction for the (q-g, g1 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 vcr frequencies of the former conformers relative to the latter one.

The q-g-syn, g1-syn and q-g2-syn conformers are further stabilized by πC1—C4 → πC1—C2 (strong), πC1—C2/πC1—C4, LP O2 → πC1—H1 (weak) and πC1—πC1/πC1—C4 (strong) orbital interactions. The g1-anti conformer is stabilized by πC1—C5 → πC1—C2 (strong), πC1—C2/πC1—C5, LP O2(CO) → πC1—H3, πC1—H4/πC1—H5 (weak), LP O2(SO3) → πC1—H3/πC1—H4 (medium) and πC1—πC1/πC1—C4 (strong) orbital interactions.

The mean summing up values of all selected orbital interaction energies of the q-g-syn, g1-syn, g1-anti and q-g2-syn conformers for 1, 4 and 6 indicate that the g1-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 0° (2)CO → S1°(5)SO3 attractive Coulombic interaction while the q-g2-syn conformer is destabilized by the LP C1—O2 → 0°(2)CO repulsive Coulombic interaction. This analysis is in line with the computed relative conformer population which indicates the following order: q-g-syn, g1-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-g-syn conformation in the gas phase for 1, 4 and 6.

In the solid, 3 presents similar S5—C3—C4—O2—S3—C1—O6 (C3—O2—S3—C1—O6) intramolecular short contacts found in the gas phase for 1, 4 and 6. These contacts stabilize the distorted q-g-syn conformer of 3 through the same orbital and Coulombic interactions which take place for the q-g-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.

References