Spectroscopic and theoretical studies on the conformation of some α-sulfanylacetophenones

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IR νCO and νSO frequencies of some α-sulfanylacetophenones [PhC(O)CH₂S(O)R: R = Me 1, Et 2, Prt 3, Ph 4 and Bu’ 5] have been measured and their conformations are estimated with the help of ab initio 6-31G** calculations and X-ray diffraction analyses. The anomalous negative carbonyl frequency shifts for the cis, rotamer together with the decrease of the νSO frequency of some α-sulfanylacetophenones PhC(O)CH₂S(O)R, with the sulfinyl R = methyl, aryl; R’ = alkyl, aryl but the cis rotamer is more stable for some acetophenone derivatives (R = phenyl; R’ = methyl, phenyl). Our recent study on α-methylsulfanylacetophenone by X-ray diffraction, UV photoelectron spectroscopy and ab initio 6-31G** calculations along with the IR results for the methylsulfanyl- and phenylsulfanyl-acetophenones have indicated that the CH₂-S(O) bond is quasi-cis to the carbonyl group in the gas and solid phases and in solution, and that the cis conformation is stabilized by electrostatic and charge transfer interactions, between the negatively charged carbonyl oxygen atom and the positively charged sulfur atom. In order to further investigate the stability of the cis rotamer of the acetophenone sulfoxides, this paper reports on α-sulfanylacetophenones PhC(O)CH₂S(O)R, with the sulfur group substituent of increasing size, i.e. R = methyl 1, ethyl 2, isopropyl 3, tert-butyl 5 and phenyl 4, by means of IR spectroscopy, X-ray diffraction and ab initio calculations.

Materials
The (spectrograde) solvents for IR measurements were used without further purification. α-Methylsulfinyl-, 1,13 ethylsulfinyl-, 2,14 phenylsulfinyl-, 415 and tert-butylsulfinyl-516 acetophenones were prepared by literature procedures. α-Isopropylsulfanylacetophenone, 3, is a new compound and was obtained by the oxidation of the α-(isopropylthio)acetophenone with an equivalent amount of 30% hydrogen peroxide dissolved in acetic acid at 0°C over 10 h. After the reaction work-up, 82% yield of the pure colourless oil was obtained from a silica gel chromatographic column using hexane-acetone as eluent: δ(δ(CDC1) 1.35 [d, 3H, J 6.6, CH(CH₃)₂], 1.34 [d, 3H, J 6.6, CH(CH₃)₂], 2.68–3.08 [septet, 1H, J 6.6, CH(CH₃)₂], 4.22 (d, 1H, J 14, CH₃), 4.34 (d, 1H, J 14, CH₃), 7.44–7.65 (m, 3H, ArH), 7.98 (d, 2H, ArH) (Found: C, 62.70; H, 6.76. Calc. for C₁₅H₁₄O₃S: C, 62.83; H, 6.71%). The α-(tert-butylthio)acetophenone is a new compound and was obtained in 61% yield, following a literature procedure.17 Bp 92–93°C (0.15 Torr); δ(δ(CDC1) 1.34 [s, 9H, C(CH₃)₃], 3.82 (s, 2H, CH₂), 7.79–7.50 (m, 3H, ArH), 7.92–7.95 (m, 2H, ArH) (Found: C, 69.27; H, 7.77. Calc. for C₁₉H₁₆O₃S: C, 69.19; H, 7.74%).

IR measurements
The IR spectra were obtained on an FTIR Nicolet Magna 550

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The overlapped carbonyl stretching bands were deconvoluted by a curve fitting program based on the unrestricted Cauchy-Gauss sum functions on H. Minor modifications were introduced by using the half band width and the Cauchy-Gauss shape ratio as input parameters. The non-linear baseline was optimized by the introduction of an additional component having a Gaussian profile and a very large half-width.

The relative concentrations of the cis-gauche rotamers for 1-5 were estimated from the absorbance ratio at the maxima (a/a-g) of the carbonyl band components, assuming equal molar absorptivity coefficients for the various rotamers.

NMR measurements

$^1$H NMR spectra were recorded at 200 MHz on a Bruker AC-200 spectrometer in deuteriochloroform using TMS as an internal standard. $^1$J values are given in Hz.

Calculations

The geometric parameters and the electron charge distribution at the various atoms of tert-butylsulfinyl- and ethylsulfinyl-acetophenone were computed at the ab initio level using the GAUSSIAN92 series of programs. To determine the preferred conformations of 2 and 5 we optimized at the HF/6-31G** level (of functions on S, C and O and p functions on H) four starting conformations corresponding to the lowermost cis and the two lowermost trans conformations previously obtained for the corresponding methyl derivative, 1. The dihedral angles $\alpha$, $\beta$, and $\gamma$ are defined below ($\alpha = 0^\circ$: cis conformation). Complete relaxation of all the internal parameters was allowed for the ethyl derivative, while for 5, the C-H bond distances of the tert-butyl group were kept equal in a conformer, and the HCC bond angles, equal in a methyl group, were allowed to change for different groups. These restrictions provided C-H bond distances (1.0842–1.0847 Å) and HCC angles (110.5–111.2°) values close to those fully optimized for the various conformers of 2 (1.0836–1.0846 Å and 110.5–110.6°, respectively).

Crystal data

Only low quality hygroscopic crystals were obtained after many attempts by diffusion methods from chloroform–n-hexane solutions.†

$\text{C}_4\text{H}_8\text{O}_2\text{S}$, (2) $M = 196.27$, monoclinic, space group $\text{P}2_1$/a, $a = 10.330(2)$, $b = 12.974(4)$, $c = 15.702(6)$ Å, $\beta = 106.31(3)^\circ$, $V = 2080(1)$ Å$^3$, $Z = 8$, $D_{\text{calc}} = 1.29$ mg m$^{-3}$, $\lambda$(Mo-Ka) = 0.710 69 Å, $R = 0.146$.

$\text{C}_5\text{H}_8\text{O}_2\text{S}$, (5) $M = 224.32$, monoclinic, space group $\text{P}2_1$/n, $a = 5.852(1)$, $b = 11.524(4)$, $c = 18.804(3)$ Å, $\beta = 90.95(2)^\circ$, $V = 1267.9(5)$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.18$ mg m$^{-3}$, $\lambda$(Mo-Ka) = 0.710 69 Å, $R = 0.121$.

Data collection and processing

X-Ray diffraction data were recorded on a CAD4 diffractometer with 0/2θ scan technique, graphite monochromated Mo-Kα radiation ($\lambda = 0.710 69$ Å, $T = 295$ K). Solution by direct methods (SIR 92). Full matrix least-squares refinement. For 2 the 4527 measured reflections ($2\theta_{\text{max}} = 52^\circ$) yielded 4098 unique and 1398 reflections with $F^2 > 4\sigma F^2$. Anisotropic thermal parameters for all non-hydrogen atoms were applied and two unique isotopic thermal parameters ($U = 0.05$ Å$^2$ for non-methyl and $U = 0.07$ Å$^2$ for methyl hydrogens) were assigned to the hydrogen atoms introduced in the calculated positions. 265 parameters were refined (mean $\sigma(a) = 0.02$) and the final conventional $R$ was 0.146 [$R = \Sigma|F_0| - |F'|/\Sigma|F_0|$. (The average esd of a C-C bond was 0.02 Å). For 5 the 1568 measured reflections ($2\theta_{\text{max}} = 42^\circ$) yielded 1310 unique and 630 reflections with $F^2 > 4\sigma F^2$. Anisotropy was applied only to the non-phenyl atoms which were refined as isolated rigid groups and to the non-methyl groups. The H-atoms were introduced in calculated positions with isotropic thermal parameters 20% higher than the attached carbon. 88 parameters were refined and the

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Table 1

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<th>Solid</th>
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<td>$\nu$cm$^{-1}$</td>
<td>$\alpha/\alpha_{ga}$</td>
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<td>1691.0</td>
<td>—</td>
<td>3362.5</td>
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</table>

$^a$ Ratio of the absorbances of the high and low frequency components of the analytically resolved doublet. $^b$ Subscripts c and g indicate cis and gauche rotamers. $^c$ First overtone. $^d$ Single symmetrical band. $^e$ Compound 3 is a liquid. $^f$ Refers to two gauche rotamers. $^g$ Ratios of the absorbances of the highest and the lowest triplet frequency components in relation to the absorbance of the most intense middle frequency component.

$^*$Acetophenone.

Table 1 Frequencies and intensities of the carbonyl stretching bands in the IR spectra of $n$-sulfinylacetophenones PhCl(O)CH$_2$S(O)R 1-5 and the frequencies of acetophenone 6

final conventional \( R \) was 0.121 \( [R = \sum |F_{o}|-|F_{c}|]/\sum |F_{c}|] \). Structure refinement and final geometrical calculations were carried out with SHELXL-93\textsuperscript{24} and PARST\textsuperscript{25} programs. Drawings were produced using ORTEP II.\textsuperscript{26}

**Results and discussion**

Table 1 collects the stretching frequencies and the absorbance ratios of the analytically resolved carbonyl bands for the \( \alpha \)-alkylsulfinyl- (1–3, \( 5 \)) and \( \alpha \)-phenylsulfinyl- (4) acetophenones in \( n \)-hexane, carbon tetrachloride (fundamental and first overtone), chloroform, acetonitrile, dimethyl sulfoxide and in the solid state. The frequencies of the parent acetophenone \( 6 \) are included for comparison. Compounds 1–5 show in all solvents a doublet, except in \( n \)-hexane where 4 and 5 have a single symmetrical band and a triplet, respectively. The intensity ratio of the components of the doublet for compounds 1–4 varies slightly in solvents of low relative permittivity \( \varepsilon \) (\( n \)-hexane, \( \varepsilon = 1.9 \); carbon tetrachloride, \( \varepsilon = 2.2 \); and chloroform, \( \varepsilon = 4.8 \)), where the higher frequency component is the more intense. However, in high relative permittivity solvents (acetonitrile, \( \varepsilon = 38 \); and dimethyl sulfoxide, \( \varepsilon = 47 \)) there is a significant increase of the lower frequency component. For compound 5 the lower frequency component is more intense in solvents of low polarity and less intense in solvents of high polarity.

The solvent effect on the carbonyl band components for 1, as a prototype for compounds 1–4, and 5 is illustrated in Fig. 1. The behaviour of 5 shows the presence of conformational isomerism,\textsuperscript{28a} while an anomalous solvent effect is observed for 1. However, the occurrence of two carbonyl bands in the first overtone region at frequencies approximately twice those in the fundamental region and of about the same intensity ratios is evidence of \( cis \)--\textit{gauche} rotational isomerism\textsuperscript{29} for the whole series 1–5. As outlined below, it seems reasonable to attribute the higher frequency component of the doublet to the more polar \( cis \) rotamer (structure I) and the lower one to the less polar \( gauche \) rotamer (structure II). In addition, the single carbonyl band (4) and the lowest frequency component of the triplet (for 5) observed in \( n \)-hexane correspond to the \( cis \) and a second \( gauche \) rotamer, respectively.

The X-ray molecular structures of 2 and 5 are shown in Fig. 2. The dihedral angles \( \alpha \), \( \beta \) and \( \gamma \) are listed in Table 2, together

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Fig. 1 IR analytically resolved carbonyl stretching bands of the \( \alpha \)-methylsulfinylacetophenone 1 and of \( \alpha \)-tert-butylsulfinylacetophenone 5: in \( n \)-hexane (\( a \)), (\( e \)); carbon tetrachloride (\( b \)), (\( f \)); chloroform (\( c \)), (\( g \)); and acetonitrile (\( d \)), (\( h \)), respectively.
Table 2 Relative energy, dipole moments and selected dihedral angles optimized for different cis (c) and gauche (g) conformers of some PhC(O)CH₂S(O)R at the 6-31G** level and corresponding X-ray geometrical data, and the sum of the relevant van der Waals radii.

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<th>Comp. R</th>
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<th>X-Ray (c₁)</th>
<th>Relative energy/ Dihedral angles(^a/b)</th>
<th>X-Ray (c₁)</th>
<th>Relative energy/ Dihedral angles(^a/b)</th>
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<td>P(^{a}) (%)</td>
<td>(\mu) D</td>
<td>(\alpha)</td>
<td>(\beta)</td>
<td>(\gamma)</td>
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<td>1 Me(^+) 6-31G**</td>
<td>12.41</td>
<td>0.4</td>
<td>6.44</td>
<td>(-8.8(7))</td>
<td>(-71.0(4))</td>
<td>3.246(7)</td>
</tr>
<tr>
<td>2 Et 6-31G**</td>
<td>11.77</td>
<td>0.6</td>
<td>6.31</td>
<td>(-15.2)</td>
<td>(-79.7)</td>
<td>3.315</td>
</tr>
<tr>
<td>3 Bu(^+) 6-31G**</td>
<td>8.44</td>
<td>2.6</td>
<td>6.15</td>
<td>(-15.7)</td>
<td>(-162.9)</td>
<td>3.293</td>
</tr>
</tbody>
</table>

\(^a\) Molar fraction of each rotamer in percentage. \(\alpha = C(1) - C(2) - C(3) - S; \beta = C(2) - C(3) - S - R; \gamma = C(2) - C(3) - S - O.\) \(^b\) Sum of van der Waals radii = 3.22 \(\AA\). \(^c\) Sum of the van der Waals radii = 3.32 \(\AA\). \(^d\) From ref. 10.

The C(2) \(\cdots\) O(6) and O(1) \(\cdots\) S(4) non-bonded interatomic distances are also reported. The pre-dicted distribution of the two more stable conformers cis\(_2\) (ca. 60\%) and gauche\(_c\) (ca. 30\%) of 1 and 2 is very close to that obtained from the intensity ratios of the high and low frequency carbonyl doublet components in \(\eta\)-hexane (Table 1; 65\% and 35\%, respectively). Therefore, it may be assumed that the high and low frequency components of the carbonyl doublet correspond to the cis\(_2\) and gauche\(_c\) conformers, respectively, not only for 1 and 2 but also for 3 and 4. This assignment is supported by the frequencies of each carbonyl doublet component in all solvents, and also by the similar solvent effect on the relative intensities of the carbonyl doublet as described above (see Table 1).

For compound 5 (Table 2) the gauche\(_c\) conformer is the most stable (ca. 77\%, HF/6-31G**) in agreement with the very intense middle component of the carbonyl triplet in \(\eta\)-hexane (ca. 75\%, Table 1). The second and third stable conformers are the gauche\(_c\) and cis\(_2\) (13 and 8\%, respectively). Although the highest frequency component of the carbonyl triplet in \(\eta\)-hexane is slightly more intense than the lowest component (see Fig. 1), the former is ascribable to the more polar cis\(_2\) rotamer (\(\mu = 5.02\) D) and the latter to the less polar gauche\(_c\) rotamer (\(\mu = 1.08\) D) in agreement with the disappearance of the lowest frequency triplet component in polar solvents.

The most polar and least stable cis\(_2\) rotamers for 1, 2 and 5 obtained by \(\textit{ab initio}\) calculations have about the same geometry of the crystals and are the only rotamers present in solid state (Fig. 2), in agreement with the single carbonyl band observed in the IR spectra (Table 1). The molecular structures have a dihedral angles close to that of the cis\(_2\) rotamers (Table 2). However, the \(\beta\) and \(\gamma\) values are interchanged with respect to those of the cis\(_2\) rotamers. Thus, in the cis\(_2\) rotamers the angle between the C-O and S-O dipoles is small (Table 2) leading to a large repulsive field effect\(^2\) between them. This agrees with the decrease of the negative charge on the carbonyl and sulfanyl oxygen atoms in the cis\(_2\) in comparison with the cis\(_2\) rotamers (Table 3). Both cis\(_1\) and cis\(_2\) rotamers possess high dipole moments (ca. 6.30 and 5.20 D, respectively), and the stabilization of the cis\(_1\) over the cis\(_2\) form in the crystals may be associated with a larger energy gain deriving from dipole moment coupling. Therefore, it can be concluded from the X-ray analysis and \(\textit{ab initio}\) calculation for the \(\beta\)-keto sulfoxides 1, 2 and 5 together with the IR data for the whole series, that the cis\(_1\) conformation is preferred in the solid state for 1-5. In the gas phase and in solvents of low polarity, the cis\(_1\) and gauche\(_c\) conformations prevail for 1-4 and 5, respectively. The higher stabil-
ity of the polar cis rotamer for 1–4 agrees with its geometry (structure III) which allows short-range intramolecular contact between the carbonyl oxygen and the sulfur atom. In fact, in 1 and 2 the carbonyl oxygen has a negative charge \( (ca. -0.52 e) \) and is separated from the sulfur, positively charged \( (ca. +1.03 e) \), by a distance of about 2.9 Å, shorter than the sum of the van der Waals radii (3.32 Å) (Table 2).

The carbonyl frequency shifts with respect to the parent compound 6 (\( \Delta \nu \)) in n-hexane, carbon tetrachloride and chloroform, for the cis and gauche rotamers of the \( \beta \)-keto sulfoxides 1–5, are listed in Table 4. Both the cis (\( \Delta \nu_c \)) and gauche (\( \Delta \nu_g \)) shifts are negative, the latter being, in general, much larger than the cis ones. The cis shifts for 1–5 refer to the cis \( \delta \) rotamers. The gauche shifts for 1–4 and the more negative one for 5 in n-hexane correspond to the gauche \( \delta \) rotamers, whilst the remaining \( \Delta \nu_g \) value for 5 corresponds to the gauche \( \gamma \) rotamer as shown below.

The significant negative gauche shifts agree with the prevalence of the \( \sigma_{CCO} - \sigma_{CSO} \) orbital interactions over the \( -1 \) effect of the alkylsulfanyl or phenylsulfanyl groups \( \left[ \sigma_{ROR}, \sigma_{SOPh} \right] \geq 0.50 \)[38], leading to a decrease in the carbonyl force constant and, therefore, in the \( \nu_{CO} \) frequencies with respect to the parent acetophenone 6.

On the other hand, the anomalous approximately constant negative cis shifts (Table 4) along with the unexpected decrease of the population of the more polar cis rotamer in solvents of high polarity for 1–4 (Table 1) support the existence of a strong intramolecular interaction between the carbonyl oxygen and the sulfur atoms (see structure IV) responsible for the decrease in the carbonyl frequencies. Moreover, the cis–gauche equilibrium is shifted towards the less polar gauche form only in solvents of high polarity, because in conformation V the C=O dipole is further away from the sulfanyl sulfur. This geometry allows a better solvation of the oxygen atom of the C=O dipole, as the oxygen atom of the S=O dipole seems to be solvated by approximately the same amount in both rotamers.

The \( \Delta \nu \) values for compound 5 agree with the peculiar relative stabilities of its rotamers. The larger steric hindrance[39] between the R and the carbonyl group in the cis\( \delta \) rotamer of 5 with respect to 1–4 causes a rotation of the sulfanyl group of about 20° around the C(3)–S bond (see Table 2 and structures VI and VII). As a consequence, the O(1)···S distance increases (by about 0.03 Å), decreasing the stabilizing charge transfer and electrostatic interactions, and then cis\( \delta \) is no longer the most stable conformer. The rotation of the sulfanyl group also increases the repulsive field effect between the negatively charged carbonyl oxygen and the sulfur lone pair[40] causing a slight decrease of the negative charge at O(1) and an increase in the carbonyl frequency, in agreement with the smaller \( \Delta \nu_g \) value for the cis\( \delta \) rotamer of 5.

In addition, there is a closer proximity between the carbonyl oxygen and the alkyl group in structure VIII (gauche\( \delta \)) than in IX (gauche\( \gamma \)). The bulky Bu' group, therefore, perturbs the gauche\( \delta \) geometry \( (\Delta \nu \approx 10^3) \) more than the gauche\( \gamma \) one \( (\Delta \nu \approx 5^3) \) compared to the less hindered derivatives (see Table 2). So, gauche\( \delta \) is the most stable conformer for 5, explaining its peculiar \( \Delta \nu_g \) value in all solvents.

The higher carbonyl frequency in the gauche\( \delta \) than in the gauche\( \gamma \) rotamer for 5 can be explained by the smaller electrostatic attraction between C(2) and O(6) and also by the larger repulsive field effect between the sulfur lone pair and the negatively charged carbonyl oxygen (see Tables 3 and 4).

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**Table 3** Charges at selected atoms \( (e) \) for compounds 1, 2 and 5, PhC(O)CH\( _2 \)S(O)R obtained by \( \text{ab initio} \) 6-31G** computations (a minus sign indicates an excess of negative charge)

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<tr>
<th>Comp.</th>
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<th>Conformer</th>
<th>( \sigma_{CCO} )</th>
<th>( \sigma_{OCC} )</th>
<th>( \delta_{SO} )</th>
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<tr>
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**Table 4** Carbonyl frequency shifts \( (\Delta \nu) \) for the cis (\( \Delta \nu_c \)) and gauche (\( \Delta \nu_g \)) rotamers of the \( \alpha \)-sulfanylacetophenones PhC(O)CH\( _2 \)S(O)R

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<td></td>
<td>5</td>
<td>Bu’</td>
<td>-3.6</td>
<td>-11.6*</td>
</tr>
</tbody>
</table>

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*\( \Delta \nu_c \) and \( \Delta \nu_g \) refers to the difference: \( \nu_{PC(O)CH\( _2 \)S(O)R} - \nu_{PC(O)CH\( _2 \)S(O)R} \).
Finally, the higher stabilization of the cis rotamers for a-sulfinylacetophenones 1-4 with respect to the cis rotamers of a-sulfinylacetones\(^{33,34}\) (see the Introduction) may be explained by the larger relaxation of the benzene ring π-electron charge with respect to the aliphatic systems, as the \(n\text{O}_{\text{C=O}}\) ionization energy for acetonophenone (9.38 eV)\(^{35}\) and propane (9.71 eV)\(^{36}\) indicate.

The stretching frequency of the S=O band in carbon tetrachloride for compounds 1-4 is practically constant (1067.7–1068.8 cm\(^{-1}\)) irrespective of the inductive effect of the R substituent of the sulfinyl groups, while the \(v\text{O}_{\text{O=O}}\) for the tert-buty1 derivative 5 is 1061.2 cm\(^{-1}\). This result agrees with the fact that the more abundant rotamer is the higher carbonyl frequency component cis for 1-4 and the lower carbonyl frequency component gauche for 5.

Conclusions

The preferred conformation of a-phenylsulfinylacetophenones, PhC(O)CH\(_2\)S(O)R (R = Me, Et, Pr, Ph and Bu\(^t\)) has been determined by IR spectroscopy and X-ray diffraction analyses and \(ab\ initial\) calculation. In the gas phase, in solutions of less polar solvents and in the solid state the cis rotamer (ca. 60%) prevails for 1-4 over the gauche rotamer (ca. 30%) owing to stabilizing intramolecular electrostatic and charge transfer interactions between the oppositely charged O(1) and S atoms.

In 5 the gauche (ca. 77%) is more stable than the cis rotamer (ca. 8%) for which a significant steric hindrance between the carbonyl oxygen atom and the bulky tert-butyl group takes place (structure VI). Thus, in order to reduce this hindrance the tert-butyl group moves away while the sulfur lone pair comes nearer the carbonyl oxygen lone pair. This new cis\(_2\) conformation for 5 (structure VII) is destabilized by a significant electrostatic and lone pair–lone pair repulsion between the negatively charged oxygen atom and the sulfur lone pair compared with the cis\(_2\) conformation for 1-4. Furthermore, the gauche rotamer of 5 (structure IX) which is free from steric hindrance becomes more stable than the sterically hindered gauche rotamer (structure VIII).

In conclusion, the bulky tert-butyl group destabilizes the cis\(_2\) rotamer to a higher degree than does the gauche\(_2\) rotamer. Thus the delicate balance of the mentioned stereoelectronic effects is responsible for the predominance of the gauche\(_2\) rotamer in the conformational equilibrium of 5 to the detriment of the cis\(_2\) rotamer, which in turn is the more stable rotamer for the majority of the studied acetonaphenol sulfoxides 1-4, as expected.

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References

24 G. M. Sheldrick, SHELXL-93: Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1993.
30 C. Hansch and A. Leo, Substituent constants for the correlation analysis in Chemistry and Biology, Wiley, NY, 1970.
32 The mixing of the sulfur lone pair with other group orbitals is not negligible, so that the sp\(^3\) hybridization assumed in the present discussion and in structures VI-IX is only an approximation. However, the HOMO of the studied compounds has prevailing sulfur character in agreement with the experimental UPS data\(^{36}\) for compound I.

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