

## Electronic Interactions in 2-(Ethylsulphonyl) Ketones studied by Ultraviolet Photoelectron Spectroscopy

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The bands present in the low ionization energy region ( $E_i \leq 12$  eV) of the (He I and He II) photoelectron spectra of some aromatic (R = NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, **4**; C<sub>6</sub>H<sub>5</sub>, **5**; MeOC<sub>6</sub>H<sub>4</sub>, **6**;  $n = 1$ ) and aliphatic (R = Me, and  $n = 1$ , **2**; or 2, **3**) ethylsulphonyl ketones, RC(O)(CH<sub>2</sub>)<sub>*n*</sub>SO<sub>2</sub>Et, have been assigned to the corresponding molecular orbitals by comparison with the assignments reported for simpler related molecules. The comparison has been assisted by the determination of the geometric structure of **6** (by X-ray diffraction) and of the model compounds HC(O)CH<sub>2</sub>SO<sub>2</sub>H and *p*-C<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>SO<sub>2</sub>CH<sub>3</sub> (by semiempirical calculations). Oppositely charged atoms of the carbonyl and ethanesulphonyl groups are separated by distances shorter than the sum of the van der Waals radii, allowing crossed charge-transfer interactions. Low symmetry allows a deep through-space and through-bond mixing among the various group orbitals, as indicated by experimental  $E_i$  values and theoretical calculations.

We have undertaken a multidisciplinary approach to the study of the electronic interactions between the carbonyl and the alkylsulphonyl groups in compounds of the general formula RC(O)CH<sub>2</sub>SO<sub>2</sub>R. The most relevant results hitherto obtained<sup>1,2</sup> can be summarized as follows. (i) According to molecular-mechanics calculations (MMC) (R = CH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>), a *gauche* conformer with the dihedral angles  $\alpha = \text{O}=\text{C}-\text{CH}_2-\text{S} \approx 90^\circ$  and  $\beta = \text{Me}-\text{S}-\text{CH}_2\text{C}(=\text{O}) \approx -60^\circ$ , is predominant (*ca.* 90%). (ii) for this conformer, the <sup>13</sup>C NMR chemical shifts of the  $\alpha$ -methylene and carbonyl carbon atoms, and the CO and SO<sub>2</sub> stretching frequency variations with respect to simple ketones and dimethyl sulphone can be rationalized by invoking the presence of  $\pi(\text{CO})/\sigma^*(\text{C}-\text{SO}_2)$  and  $\pi^*(\text{CO})/\sigma(\text{C}-\text{SO}_2)$  interactions. These results imply that the alkylsulphonyl substituent, in addition to a strong inductive stabilizing effect, can also exert an electron donation towards the carbonyl group stronger than that of an alkyl group.

For a fuller understanding of the electronic interaction between the carbonyl and the alkylsulphonyl groups in this class of compound, we now present an ultraviolet photoelectron (PE) spectroscopy analysis of some 2-(ethylsulphonyl)-acetophenones, YC<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>SO<sub>2</sub>Et (Y = NO<sub>2</sub>, **4**; H, **5**; OCH<sub>3</sub>, **6**) and of the simpler compounds 2-(ethylsulphonyl)-propanone, MeC(O)CH<sub>2</sub>SO<sub>2</sub>Et (**2**) and 4-(ethylsulphonyl)-butan-2-one, MeC(O)(CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>Et (**3**).

PE spectroscopy, measuring the ionization energy ( $E_i$ ) of bands related to various valence molecular orbitals (MOs), offers, in principle, the possibility of isolating components of the total electronic effect of a substituent. This technique, therefore, is well suited to the investigation of substituent effects. We have already used PE spectroscopy, in combination with theoretical calculations, to study the electronic and steric interactions in compounds containing the -C(O)CH<sub>2</sub>X group (X = hetero substituent) and this approach has worked successfully.<sup>3-6</sup>

The relative orientation of the two groups of interest in this class of compounds has been determined by X-ray diffraction on **6** and by semiempirical MINDO/3 calculations on the model compounds HC(O)CH<sub>2</sub>SO<sub>2</sub>H and *p*-C<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>SO<sub>2</sub>CH<sub>3</sub>. The results of the calculations have also given information on the mixing among orbitals mainly localized at the CO and SO<sub>2</sub> groups.

### Experimental and Calculations

**PE Spectra.**—He I and He II PE spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer equipped with a Helectros He II lamp. The spectra were calibrated against noble-gas lines. The error in the  $E_i$  values given is  $\pm 0.05$  eV for well resolved bands, and  $\pm 0.1$  eV for shoulders.

The assignment of the PE spectra has been based on the composite-molecule approach and the substituent effect, using as reference compounds dimethyl sulphone, CH<sub>3</sub>SO<sub>2</sub>CH<sub>3</sub> (**1**), for the SO<sub>2</sub>  $E_i$  values,<sup>7-9</sup> and pentan-2-one<sup>3</sup> and  $\alpha$ -ethylthioacetophenones,<sup>5</sup> YC<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>SEt (Y = NO<sub>2</sub>, **7**; H, **8**; OCH<sub>3</sub>, **9**), for the carbonyl lone pair ( $n_o$ ) and the  $\pi$ -ring  $E_i$  values. The assignment of ionization bands has been confirmed by the analysis of the intensity variations of corresponding bands on changing the ionizing radiation. On going from He I to He II spectra, the bands corresponding to MOs rich in O *p* atomic orbitals increase in intensity, those related to MOs of mainly C 2*p* character are almost unaffected, and the intensity of those rich in S *p* orbitals decreases.<sup>10-14</sup>

**Crystal Data.**—C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>S,  $M = 242.30$ , orthorhombic,  $a = 5.273(1)$ ,  $b = 10.544(5)$ ,  $c = 21.030(5)$  Å,  $U = 1169(1)$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range  $8 \leq \theta \leq 12$ ), space group  $P2_12_12_1$  (No. 19),  $Z = 4$ ,  $D_c = 1.388$  g cm<sup>-3</sup>. Colourless prismatic crystal of dimensions 0.12 × 0.24 × 0.25 mm.  $\mu(\text{Mo-K}\alpha) = 2.60$  cm<sup>-1</sup>;  $F(000) = 512$ .

**Data Collection and Processing.**—CAD4 diffractometer  $\omega/2\theta$  scan technique, graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å); 2304 reflections measured ( $2 \leq \theta \leq 27$ ,  $+h$ ,  $+k$ ,  $+l$ ), out of which 937 having  $I \geq 2\sigma(I)$  were used in the refinement;  $T = 295$  K.

**Structure Analysis and Refinement.**—Solution by direct methods (MULTAN82<sup>15</sup>). Full-matrix least-squares refinement with non-hydrogen atoms anisotropic and hydrogen atoms isotropic. The weighting scheme,  $w = 4F_o^2/[\sigma(F_o^2) + (0.05F_o^2)^2]$ , with  $\sigma(F_o)$  from counting statistics, gave satisfactory agreement. Final  $R$  and  $R_w$  values are 0.049, 0.051; max shift/error = 0.3; largest  $\Delta F$  peak 0.25 e Å<sup>-3</sup>;  $S$  (esd of an

**Table 1** Positional parameters and their estimated standard deviations (in parentheses)

Atom	x	y	z
S	0.598 6(3)	0.225 8(1)	0.124 10(6)
O(1)	0.550 2(8)	0.010 4(3)	0.233 2(2)
O(2)	0.865 8(7)	0.203 8(5)	0.130 0(2)
O(3)	0.513 8(9)	0.341 0(4)	0.095 2(2)
O(4)	1.361 4(7)	0.259 0(4)	0.415 7(2)
C(1)	1.184 1(9)	0.218 7(5)	0.373 5(2)
C(2)	1.137(1)	0.094 6(5)	0.358 4(2)
C(3)	0.950(1)	0.065 5(5)	0.315 1(2)
C(4)	0.804 9(9)	0.159 6(5)	0.286 5(2)
C(5)	0.854(1)	0.285 5(5)	0.302 3(2)
C(6)	1.041(1)	0.314 6(5)	0.346 0(3)
C(7)	0.605(1)	0.119 3(4)	0.241 2(2)
C(8)	0.467 1(9)	0.219 4(5)	0.202 3(2)
C(9)	0.463(1)	0.094 6(5)	0.083 5(3)
C(10)	0.578(2)	0.083 0(7)	0.107 6(3)
C(11)	1.510(1)	0.166 1(6)	0.446 4(3)

**Table 2** Bond distances (Å) with esds in parentheses

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S	O(2)	1.433(4)	C(5)	C(6)	1.380(7)
S	O(3)	1.428(4)	C(5)	H(5)	0.99(5)
S	C(8)	1.785(5)	C(6)	H(6)	0.94(4)
S	C(9)	1.777(6)	C(7)	C(8)	1.520(7)
O(1)	C(7)	1.195(6)	C(8)	H(81)	0.89(5)
O(4)	C(1)	1.358(6)	C(8)	H(82)	0.96(4)
O(4)	C(11)	1.410(7)	C(9)	C(10)	1.517(9)
C(1)	C(2)	1.368(7)	C(9)	H(91)	0.96(6)
C(1)	C(6)	1.388(7)	C(9)	H(92)	0.79(5)
C(2)	C(3)	1.377(8)	C(10)	H(101)	0.99(7)
C(2)	H(2)	0.90(4)	C(10)	H(102)	0.84(7)
C(3)	C(4)	1.388(7)	C(10)	H(103)	0.94(10)
C(3)	H(3)	0.93(5)	C(11)	H(111)	0.96(6)
C(4)	C(5)	1.392(7)	C(11)	H(112)	0.81(5)
C(4)	C(7)	1.483(7)	C(11)	H(113)	0.97(8)

observation of unit weight) = 1.96. All calculations performed using the CAD4-SDP<sup>16</sup> and PARST<sup>17</sup> program systems; scattering factors from ref. 18.\* Full lists of non-hydrogen atom co-ordinates, bond lengths and bond angles are given in Tables 1–3.

**Calculations.**—We have performed semiempirical MINDO/3 calculations on the model compounds HC(O)CH<sub>2</sub>SO<sub>2</sub>H, allowing complete relaxation, and pY-C<sub>6</sub>H<sub>4</sub>C(O)CH<sub>2</sub>SO<sub>2</sub>CH<sub>3</sub> (Y = NO<sub>2</sub>, **4b**; H, **5b**; and OCH<sub>3</sub>, **6b**). For the latter compounds the geometry has been optimized forcing the benzene ring to be planar and with angles of 120°. In addition, from previous experience,<sup>4,5</sup> the carbonyl group has been assumed to lie in the plane of the benzene ring. Considering that the results obtained for the relevant geometric parameters were quite close to those provided by X-ray diffraction analysis on **6** and **5b**,<sup>19</sup> and by MMC<sup>1,2</sup> for the predominant conformer of 2-(methylsulphonyl)propanone, **2b**, and **5b**, we did not attempt more sophisticated calculations. Semiempirical calculations were also performed on H<sub>2</sub>C(O) and CH<sub>3</sub>SO<sub>2</sub>H to assist the assignment of the PE bands.

The samples were available from previous studies.<sup>1,2</sup>

\* Full lists of hydrogen atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data centre. For details, see 'Instructions for Authors (1991)', *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

**Table 3** Bond angles (°) with esds in parentheses

Atom 1	Atom 2	Atom 3	Angle
O(2)	S	O(3)	118.8(3)
O(2)	S	C(8)	107.2(2)
O(2)	S	C(9)	108.2(3)
O(3)	S	C(8)	107.6(2)
O(3)	S	C(9)	109.3(3)
C(8)	S	C(9)	104.9(3)
C(1)	O(4)	C(11)	117.7(4)
O(4)	C(1)	C(2)	125.1(5)
O(4)	C(1)	C(6)	114.8(5)
C(2)	C(1)	C(6)	120.0(5)
C(1)	C(2)	C(3)	119.7(5)
C(1)	C(2)	H(2)	121(3)
C(3)	C(2)	H(2)	120(3)
C(2)	C(3)	C(4)	121.5(5)
C(2)	C(3)	H(3)	118(4)
C(4)	C(3)	H(3)	121(4)
C(3)	C(4)	C(5)	118.3(5)
C(3)	C(4)	C(7)	117.8(4)
C(5)	C(4)	C(7)	123.9(4)
C(4)	C(5)	C(6)	120.2(5)
C(4)	C(5)	H(5)	120(3)
C(6)	C(5)	H(5)	120(3)
C(1)	C(6)	C(5)	120.3(5)
C(1)	C(6)	H(6)	121(3)
C(5)	C(6)	H(6)	119(3)
O(1)	C(7)	C(4)	122.5(5)
O(1)	C(7)	C(8)	118.3(5)
C(4)	C(7)	C(8)	119.2(4)
S	C(8)	C(7)	109.7(4)
S	C(8)	H(81)	107(3)
S	C(8)	H(82)	101(3)
C(7)	C(8)	H(81)	107(3)
C(7)	C(8)	H(82)	122(3)
H(81)	C(8)	H(82)	109(4)
S	C(9)	C(10)	109.9(4)
S	C(9)	H(91)	108(4)
S	C(9)	H(92)	96(3)
C(10)	C(9)	H(91)	120(4)
C(10)	C(9)	H(92)	121(3)
H(91)	C(9)	H(92)	99(5)
C(9)	C(10)	H(101)	105(4)
C(9)	C(10)	H(102)	119(5)
C(9)	C(10)	H(103)	109(5)
H(101)	C(10)	H(102)	103(7)
H(101)	C(10)	H(103)	95(7)
H(102)	C(10)	H(103)	121(8)
O(4)	C(11)	H(111)	114(4)
O(4)	C(11)	H(112)	113(4)
O(4)	C(11)	H(113)	103(5)
H(111)	C(11)	H(112)	110(5)
H(111)	C(11)	H(113)	100(6)
H(112)	C(11)	H(113)	116(7)

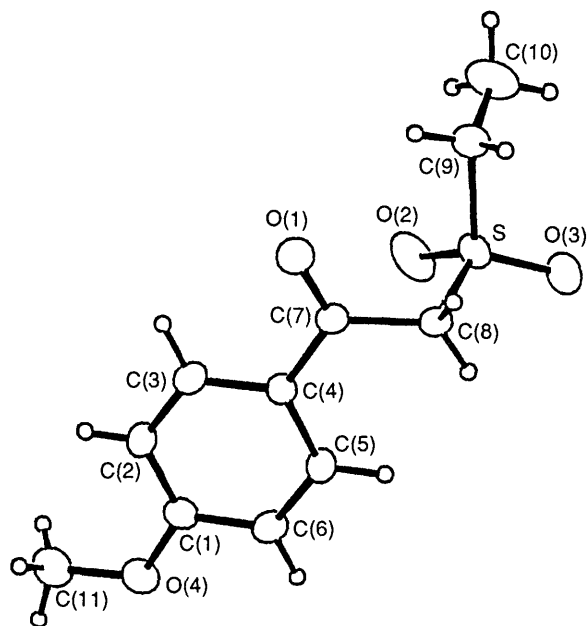
## Results and Discussion

**Analysis of the Geometric Structure.**—Fig. 1 shows the molecular structure determined by X-ray diffraction of **6**. The values for the dihedral angles  $\alpha = \text{O}(1)\text{—C}(7)\text{—C}(8)\text{—S}$  and  $\beta = \text{C}(9)\text{—S—C}(8)\text{—C}(7)$  are presented in Table 4 together with the corresponding values computed by MINDO/3 on the model compounds and those previously determined by X-ray diffraction on **5b**.<sup>19</sup> Table 4 also lists the experimental and computed S—O(1) and C(7)—O(2) interatomic distances compared with the sum of the van der Waals radii, and the computed charges at selected atoms.

The MINDO/3 values for the dihedral angles show good agreement with the experimental data confirming that  $\alpha$  and  $\beta$  are nearly equal in the aliphatic and aromatic derivatives, as found by MMC,<sup>1,2</sup> and that, in the most stable conformer, the C(8)—S bond is *gauche* ( $\alpha \approx 80^\circ$ ) to the  $\pi(\text{CO})$  MO allowing hyperconjugative interaction. The preferred conformation, in

**Table 4** Experimental and theoretical values of the dihedral angles  $\alpha = \text{O}(1)\text{-C}(7)\text{-C}(8)\text{-S}$  and  $\beta = \text{R-S-C}(8)\text{-C}(7)$  ( $^\circ$ ) for 2-(alkylsulphonyl) ketones,  $\text{RC}(\text{O})\text{CH}_2\text{SO}_2\text{R}'$ , 1-4, interatomic distances, sums of the relevant van der Waals radii ( $\text{\AA}$ ) and computed charges on atoms (e)

	MINDO/3				Sum of the vdW radii	X-ray	
	(R' = CH <sub>3</sub> )					R = MeOC <sub>6</sub> H <sub>5</sub> R' = Et	R = C <sub>6</sub> H <sub>6</sub> <sup>a</sup> R' = Me
	R = R' = H	R = C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	R = C <sub>6</sub> H <sub>6</sub>	R = C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>			
$\alpha$	78.39	75.0	74.2	78.09		78.8	80.05
$\beta$	-69.44	-78.45	-78.27	-80.93		-79.2	-73.56
S-O(1)	3.47	3.35	3.35	3.39	3.32	3.236	3.308
C(7)-O(2)	3.15	3.09	3.09	3.05	3.22	2.857	2.991
Charges							
S	1.68	1.58	1.58	1.59			
O(1)	-0.46	-0.55	-0.54	-0.52			
C(7)	0.63	0.61	0.59	0.59			
O(2)	-0.66	-0.72	-0.72	-0.71			

<sup>a</sup> From ref. 19.**Fig. 1** ORTEP view (with thermal ellipsoids at the 30% probability level) of the molecular structure of **6** showing the atom numbering

addition, allows the  $\pi(\text{CO})/\sigma^*(\text{C-SO}_2)$  and  $\pi^*(\text{CO})/\sigma(\text{C-SO}_2)$  charge-transfer interactions proposed to rationalise IR and NMR data, and the  $\pi^*(\text{CO})/\sigma^*(\text{C-SO}_2)$  mixing invoked to explain the trend of the  $\pi^*(\text{CO}) \leftarrow n_{\text{O}}$  transition energy.<sup>1</sup>

An interesting observation from the data of Table 4 and Fig. 1 is that the S-O(1) and (particularly) the C(7)-O(2) interatomic distances are shorter than the sum of the van der Waals radii and that these contacts occur between pairs of oppositely charged atoms. Strong through-bond and through-space<sup>20</sup> interactions are expected, therefore, in the PE spectra of these compounds.

The expectations based on geometric data are confirmed by MINDO/3 eigenvector analysis: (i) the  $\pi(\text{CO})$  MO contains contributions from orbitals of the CH<sub>2</sub> and SO<sub>2</sub> groups, (ii) the  $\pi^*(\text{CO})$  MO is stabilized by mixing with vacant orbitals localized at the SO<sub>2</sub> group, (iii) the  $n_{\text{O}}(\text{CO})$  orbital is mixed with the two uppermost filled SO<sub>2</sub> group orbitals; this mixing destabilizes the  $n_{\text{O}}$  orbital by 0.4 eV on going from H<sub>2</sub>CO to HC(O)CH<sub>2</sub>SO<sub>2</sub>H.

**PE Spectra.**—The PE spectra of selected derivatives are presented in Fig. 2. The lower  $E_i$  values of all the compounds

examined are collected in Table 5 together with the relevant values taken from the spectra of the reference compounds.

We begin our analysis of the PE data by considering the aliphatic derivatives. The spectra of compounds **2** and **3** can be considered to derive from those of **1** and pentan-2-one. The spectrum of **1** shows four  $E_i$  values below 12 eV ascribed to ionization from MOs mainly localized at the SO<sub>2</sub> group, see Table 5. The uppermost  $E_i$  values of pentan-2-one at 9.46 [ $n_{\text{O}}(\text{CO})$ ] and 11.74 [ $\pi(\text{CO})$ ] eV.<sup>3</sup> The strong electron-withdrawing inductive effect of the sulphone group has been estimated<sup>7-9</sup> to stabilize cation states by some 1.0–1.3 eV and, therefore, the  $\pi(\text{CO})$  ionization in **2** and **3** will likely occur at  $E_i$  values larger than 12 eV. We then expect the presence of five bands (the four SO<sub>2</sub> and the  $n_{\text{O}}$  bands) in the low-energy region ( $\leq 12$  eV) of the spectra of **2** and **3**.

A comparison of the  $E_i$  values and of the relative band intensity with those of **1**,<sup>7-9</sup> allows a straightforward assignment of  $E_{i,2} - E_{i,5}$  of compounds **2** and **3** to ionization from the MOs mainly localized at the SO<sub>2</sub> group. The first band, whose relative intensity significantly increases in the He II spectra, is therefore assigned to ionization from the  $n_{\text{O}}$  orbital.

The stabilization of the  $n_{\text{O}}$  orbital in **2** and **3** with respect to the corresponding orbital in pentan-2-one, ca. 0.6 eV, is smaller than expected on the basis of the inductive effect of the sulphone group. These  $E_i$  values are in line with the presence of a retrodonating interaction which transfers negative charge from the SO<sub>2</sub> towards the CO group. As reported above, the very short distance between an oxygen atom of the SO<sub>2</sub> group and the carbonyl carbon atom (MINDO/3 charges in the model compound -0.66 and +0.63, respectively, see Table 4) confirms this possibility.

This interaction is reduced by the introduction of a second CH<sub>2</sub> group between the two interacting groups. In fact, on going from **2** to **3**, corresponding SO<sub>2</sub>-ionization values decrease by 0.3–0.4 eV. The largest variations are shown by the two uppermost values, whose corresponding MOs, in **2**, are mixed with the  $n_{\text{O}}$  orbital according to the calculations.

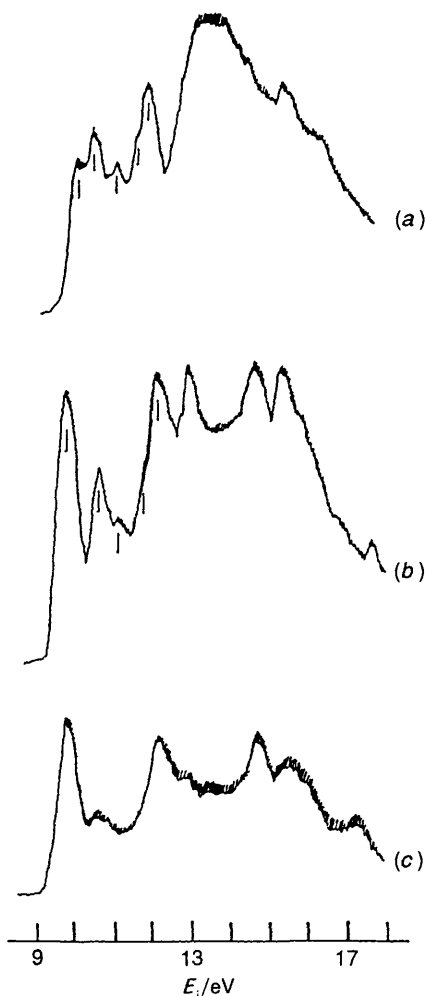
Note that the carbonyl stretching frequency,  $\nu(\text{CO})$ , exhibits a parallel behaviour:<sup>1</sup> it increases by only 1 cm<sup>-1</sup> on going from pentan-2-one to **2**, (while, on the basis of the  $\sigma_1$  value of the ethylsulphonyl group, a stabilization larger by one order of magnitude would be expected), and it increases by 5 cm<sup>-1</sup> on going from **2** to **3** despite the fact that in the latter the sulphonyl group is in the  $\beta$  position.

Now we turn to the aromatic derivatives **4–6**. A comparison with the  $E_i$  values of the reference compounds **7–9**<sup>5</sup> and **1** (see Table 5) indicates that  $E_i$  values  $\leq 10.15$  eV can be related to

**Table 5** Ionization energy values (eV) of compounds 1-9

Compound	$\pi$ -ring and $n_o$ orbitals			$SO_2$ -group orbitals			
1 $CH_3SO_2CH_3^a$				10.65	11.18sh	11.65sh	12.0
2 $CH_3COCH_2SO_2CH_2CH_3$			10.10	10.81	11.31	11.75sh	12.06
3 $CH_3COCH_2CH_2SO_2CH_2CH_3$			10.0	10.40	10.95	11.5sh	11.74
4 $NO_2C_6H_4COCH_2SO_2CH_2CH_3$	10.15	10.15	10.15	10.91	11.35 <sup>b</sup>	12.15	13.03 <sup>b</sup>
5 $HC_6H_4COCH_2SO_2CH_2CH_3$	9.71	9.71	9.71	10.55	11.15	11.7sh	12.1 <sup>b</sup>
6 $CH_3OC_6H_4COCH_2SO_2CH_2CH_3$	8.78	9.60	9.60	10.47	10.94	11.36 <sup>b</sup>	11.8
7 $NO_2C_6H_4COCH_2SCH_2CH_3^c$	10.15	10.15	10.15				
8 $HC_6H_4COCH_2SCH_2CH_3^c$	9.4	9.60	9.60				
9 $CH_3OC_6H_4COCH_2SCH_2CH_3^c$	8.63	9.44	9.44				

<sup>a</sup> From refs. 7-9. <sup>b</sup> This peak contains contributions from other ionization processes. <sup>c</sup> From ref. 5. sh: shoulder.



**Fig. 2** He I PE spectra of 4-(ethylsulphonyl)butan-2-one,  $MeC(O)CH_2CH_2SO_2Et$  (a), and He I (b) and He II (c) PE spectra of  $\omega$ -ethylsulphonylacetophenone,  $C_6H_5C(O)CH_2SO_2Et$

ionization from the two uppermost  $\pi$ -ring and the  $n_o$  orbitals, while the four bands between *ca.* 10.5 and 12 eV can be ascribed to ionization from the  $SO_2$  MOs. MINDO/3 data confirm the ordering of  $n_o$  and  $\pi$ -ring ionizations above  $SO_2$  ionizations and reproduce the trend of the  $\pi$ -ring and  $n_o$  orbitals with the *para* substituent.

The relative band intensity of the  $SO_2$  ionizations, however, does not exactly follow the pattern shown by the aliphatic compounds indicating that ionization from other groups contributes to this energy region. A comparison with the spectra of 7-9<sup>5</sup> indicates that these contributions can mainly be ascribed to ionization from MOs localized at the Y substituent, while

ionization from the uppermost  $\sigma$ -ring orbitals is likely to occur above 12 eV (see Table 2 and Figs. 1 and 2 of ref. 5).

Although band overlap makes uncertain detailed speculations, it is possible to observe that ionization from the sulphone group in 5 gives rise to bands at nearly the same energy values as in 1, and that corresponding bands are slightly (0.1-0.3 eV) destabilized in 6 and stabilized in 4 with respect to 5. Eigenvector analysis indicates the presence of through-bond mixing between the filled  $n_o$  and  $SO_2$  orbitals. In addition, the opposite charge carried by the S and O (CO) atoms and their separation close to (or, in 6, slightly shorter than) the sum of the van der Waals radii (see Table 4) suggest the presence of (a small) charge-transfer CT, interaction. The latter interaction is facilitated by a *para* electron-releasing substituent (which increases the negative charge density at the carbonyl oxygen) and hindered by the nitro group.

The presence of an interaction which transfers negative charge from the carbonyl towards the  $SO_2$  group is in line with the IR results.<sup>1</sup> The asymmetric  $SO_2$  stretching frequency in *para*-substituted 2-(ethylsulphonyl)acetophenones is higher than in  $EtSO_2Et$  reflecting the inductive effect of the benzoyl group. The decrease observed on going from Y = H to Y =  $NH_2$  has been ascribed to the  $SO_2 \leftarrow CO$  CT interaction which decreases the S-O force constant. (This stretching frequency remains practically constant on going from Y = H to Y =  $NO_2$ .)

A comparison of the  $E_i$  values related to the  $n_o$  and  $\pi$ -ring orbitals of 4-6 with the corresponding  $E_i$  values of 7-9 shows that the introduction of the  $-SO_2Et$  for the  $-SEt$  group has no effect (Y =  $NO_2$ ) or only a small (0.1-0.3 eV) stabilizing effect in spite of the strong inductive effect of the sulphone group.<sup>9,21</sup> This observation, together with the values of the computed charges at the C(7) and O(2) atoms and the experimental and computed C(7)-O(2) distances which are significantly shorter than the sums of the van der Waals radii (see Table 4), allows speculation of the existence of a retrodonating mechanism from the  $SO_2$  group orbitals towards the carbonyl group, in line with the observation made for the aliphatic compounds.

## Conclusions

The preferred conformation of 2-(ethylsulphonyl) ketones has been determined by X-ray diffraction analysis on the aromatic derivative  $CH_3OC_6H_5C(O)CH_2SO_2Et$  and by semiempirical calculations on the model compounds  $HC(O)CH_2SO_2H$  and  $RC(O)CH_2SO_2CH_3$  (R =  $C_6H_5OCH_3$ ,  $C_6H_6$  and  $C_6H_5NO_2$ ). The two methods, in line with previous MM calculations, indicate that in these compounds the C(8)-S bond is *gauche* to the carbonyl group, the C(7)-O(1) and S-C(9) bonds are nearly eclipsed ( $\alpha \approx -\beta$ ), and the positively charged atoms S and C(7) have contacts shorter than the sums of the van der Waals radii with the negatively charged atoms O(1) and O(2), respectively.

This conformation allows hyperconjugative and charge-transfer interactions between the CO and the SO<sub>2</sub> groups. Orbital mixing is shown by eigenvector analysis and is reflected by shifts (with respect to reference compounds) of  $E_i$  values related to orbitals mainly localized at the two interacting groups. In summary, it is possible to say that both the RC(O) and the SO<sub>2</sub>Et groups inductively stabilize the orbitals mainly localized at the other moiety, and that hyperconjugative and CT interactions acting in the opposite direction in part counteract the stabilizing inductive effects.

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