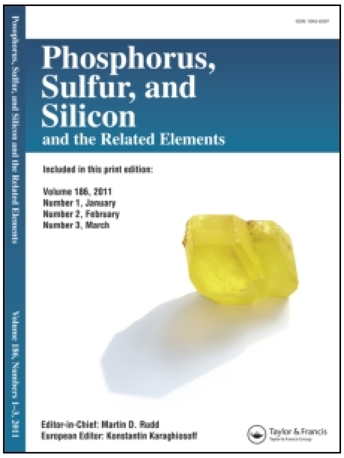

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INTERACTION BETWEEN THE CARBONYL GROUP AND A SULFUR ATOM. PART XI PHOTOELECTRON SPECTRA OF SOME 2-ALKYLTHIOCYCLOPENTANONES

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INTERACTION BETWEEN THE CARBONYL GROUP AND A SULFUR ATOM. PART XI[†]

PHOTOELECTRON SPECTRA OF SOME 2-ALKYLTHIOCYCLOPENTANONES

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The helium I photoelectron spectra of some 2-alkylthio-cyclopentanones are reported. The IP's related to the sulfur and carbonyl lone pairs are compared to those in the corresponding cyclopentanones and cyclopentyl alkyl sulfide. The observed stabilization of both orbitals cannot be explained by the mutual inductive effects of the sulfur and carbonyl group. The conformational dependence of this effect is discussed.

Recent studies[1,2] have shown that the 2-alkylthio-substituted ketones exhibit a decrease of the frequency of the i.r. carbonyl band in comparison with the corresponding unsubstituted ketones. It was observed that this shift of ν_{CO} has a conformational dependence, reaching its maximum value in the alkylthio open-chain or cyclic ketones, in which the C—S bond, preponderantly gauche or axial, respectively, is approximately aligned with the π_{CO} system. Hyperconjugative interaction has been tentatively suggested as responsible for the decrease of the force constant of the carbonyl group and, therefore, for the shift of ν_{CO} to lower frequencies.

In order to obtain additional information about the molecular ground state of these compounds photoelectron measurements were carried out. Previous reports[3] described the IP's for the open-chain 2-alkylthio-ketones. In this work photoelectron measurements on some α-alkylthio-cyclopentanones are reported.

It was considered relevant to investigate the compounds (1) to (5). (Table I).

The He I photoelectron spectra of the compounds studied are given in Figures 1 and 2. The Table lists the lone pair orbital ionization potentials.

Cyclopentanone (1) has its first band at 9.30 eV. It is known[4,5] to correlate to ionization from the carbonyl oxygen lone pair ($\bar{O}_{(CO)}$). For (2) substitution of a n-propyl group in position 2 induces a shift of 0.2 eV to lower energy. In the spectrum of (3) the sharp sulfur lone pair band ($\bar{S}$) is found at 8.18 eV.[6] The spectra

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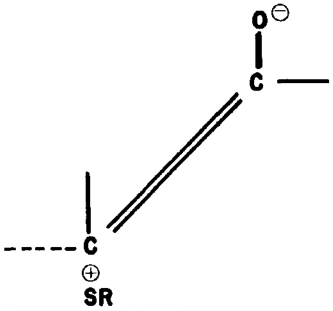
[†] Presented at the Tsukuba Mini-Symposium on Chemistry of Organosulfur and Related Compounds, Japan, August 1982.

TABLE I

Photoelectron spectra of some cyclopentanones and related sulfide

No.	Compounds	IP's (eV)	
		$\bar{O}_{(CO)}$	$\bar{S}$
(1)	Cyclopentanone	9.30	—
(2)	2-*n*-Propylcyclopentanone	9.10	—
(3)	Ethylcyclopentyl sulfide	—	8.18
(4)	2-Methylthiocyclopentanone	9.62	8.65
(5)	2-Ethylthiocyclopentanone	9.50	8.50
(6)			

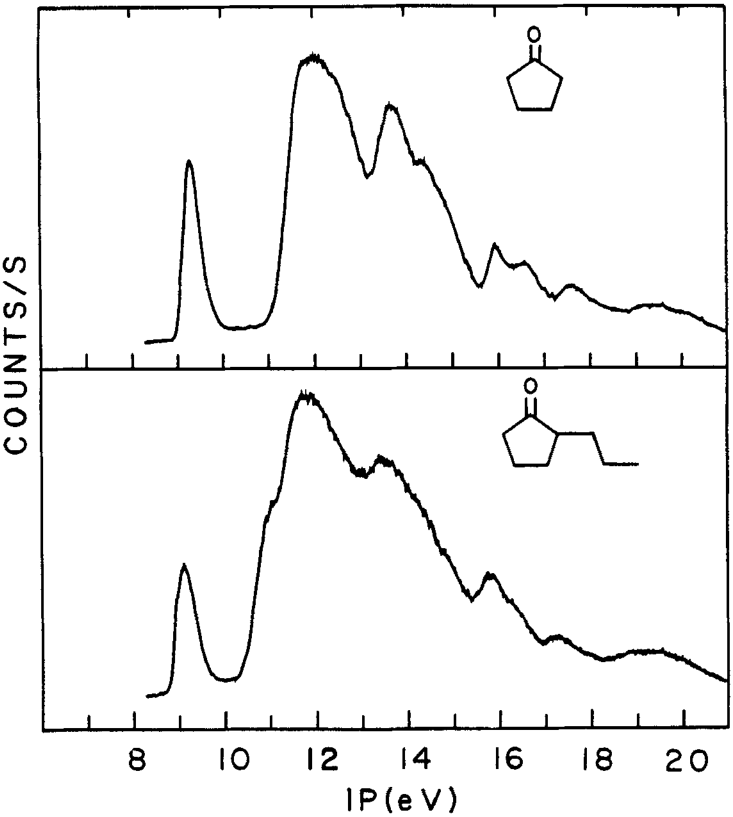


FIGURE 1 The He I photoelectron spectra of cyclopentanone (1) and 2-*n*-propylcyclopentanone (2).

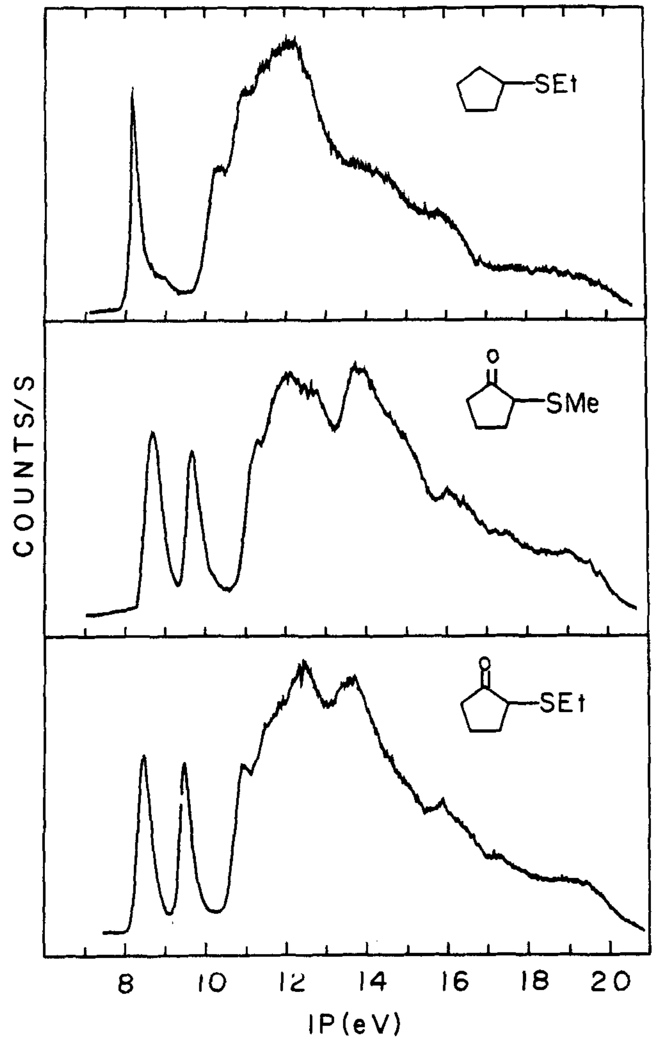


FIGURE 2 The He I photoelectron spectra of ethylcyclopentyl sulfide (3), 2-methylthiocyclopentanone (4) and 2-ethylthiocyclopentanone (5).

of our target compounds (4) and (5), which contain both sulfur and carbonyl, are to be compared to those of the former three compounds. Similarly to the open-chain sulfur substituted ketones[3] the first photoelectron bands in (4) and (5) (8.50 eV and 8.65 eV) may be related to ionization from the sulfur lone pair and the second ones (9.50 eV and 9.62 eV) to that from the carbonyl oxygen lone pair orbital. This would indicate that due to the simultaneous presence of sulfur and carbonyl group both, the carbonyl oxygen lone pair and sulfur lone pair orbitals underwent stabilization. These assignments are supported by the results of our previous measurements of the basicity of the carbonyl group for the series of the open-chain and cyclic α-alkylthio-substituted ketones, in comparison with the corresponding unsubstituted ketones.[7,1] The decrease of basicity constants observed for these compounds is parallelled by the trend in the IP's. A switchover of the levels would result in a decrease of IP of the carbonyl oxygen lone pair and, therefore, would be in disaccord with the basicity results.

The stabilizations of $\overline{O}_{(CO)}$ and $\overline{S}$ in compound (5), in comparison with those in (2) and (3) (table I) are to be compared with the stabilizations which can be estimated roughly from the mutual inductive effects of the carbonyl group and the sulfur atom. It may be seen that the replacement of —CH_2— group by S leads to the shifts of both, sulfur and carbonyl oxygen lone pair bands to higher energies, 0.32 eV and 0.40 eV, respectively. The inductive effect of the carbonyl group, was estimated[8] from the average ionization potential of $\overline{O}_{(CO)}$ in 1,3-cyclopentanedione and that in cyclopentanone as 0.71 eV. The inductive effect of the sulfur atom, similarly estimated[9] from 1,3-dithiolane and thiophane or 1,3-dithiane and thiane is 0.30 eV and 0.36 eV respectively. Therefore, while the $\overline{S}$ should be strongly stabilized due to the inductive effect of the carbonyl group, the $\overline{O}_{(CO)}$ should undergo only a slight stabilization due to the weak inductive effect of the sulfur atom. This is in disagreement with the ionization potential data, which do not show much difference in the stabilizations of $\overline{S}$ and $\overline{O}_{(CO)}$. It may be seen that although the stabilization of $\overline{O}_{(CO)}$ by 0.40 eV corresponds roughly to the inductive effect of sulfur the stabilization of $\overline{S}$ by 0.32 eV is much less than would be expected from the inductive effect of the carbonyl group. Similar results were obtained previously[7] for $CH_3SCH_2COCH_3$, in which $\overline{S}$ and $\overline{O}_{(CO)}$ levels are stabilized by 0.35 eV and 0.45 eV respectively.

The fact that in the 2-alkylthio-cyclopentanones and open-chain ketones the C—S bond is predominantly axial and gauche, respectively, makes the hypothesis of through-space interaction between the two lone pairs on $\overline{O}_{(CO)}$ and $\overline{S}$ suggested previously[3] of little viability, as this geometry does not favour the overlapping of the corresponding orbitals. The smaller stabilization of the sulfur lone pair might be in line with the hyperconjugative interaction between σ_{C-S} and π_{CO} orbitals, proposed for the ground state of these molecules[1,2] (Structure 6). It seems reasonable to suggest that two factors, which originate from the contribution of (6) to the structure of the molecule, may affect the $\overline{S}$ level—the decrease of the importance of the polarized structure $C^+—O^-$, responsible for the inductive effect of the carbonyl group on sulfur, and the weakening of the C—S bond. Both factors may be responsible for the smaller stabilization of $\overline{S}$ in comparison with the estimated value from the inductive effect of the carbonyl group.

It is noteworthy that the stabilization of 0.7 eV, observed[3] for the ether $\overline{O}$ level in $CH_3OCH_2COCH_3$, corresponds to the estimated value from the inductive effect of the carbonyl group. This is a quite expected result considering the small polarizability of the C—O bond as compared with the C—S bond and is in accord with our recent conformational studies on the α-heterosubstituted acetones,[2] which showed that the strength of the hyperconjugative interaction follows the order: C—F < C—O < C—N < C—Cl < C—Br < C—S < C—I.

It should be also mentioned that the stabilization of the $\pi_{C=C}$ level, reported for the 3-cyclopentenone in comparison with cyclopentene, attributed[10] to the inductive effect of the carbonyl group, was of the approximately same order (0.8 eV) as in 1,3-cyclopentanedione and methoxyacetone. Both examples, for oxygen substituted and β,γ-unsaturated ketones, seem to indicate that the carbonyl group (unless its polarization is modified) exerts the inductive effect of similar order on the different groups.

We will refrain from pushing the arguments further. Theoretical work is clearly needed.

EXPERIMENTAL

The photoelectron spectra were measured on a Perkin-Elmer PS-16 instrument with a He(I) source. All ionization potentials cited in the paper are vertical values.
Products: 2-ethylthiocyclopentanone,[11] 2-methylthio-cyclopentanone,[12] 2-*n*-propylcyclopentanone[13] and ethyl cyclopropyl sulfide,[14] were prepared by literature procedures and identified by n.m.r. and i.r. spectroscopy. All compounds were analysed by g.l.c. to assess their purity.

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REFERENCES AND NOTES

1. B. Wladislaw, H. Viertler, P. R. Olivato, I.C.C. Calegão, V. L. Pardini and R. Rittner, *J. Chem. Soc. Perkin II*, **1980**, 453.
2. S. A. Guerrero, J. R. T. Barros, B. Wladislaw, R. Rittner and P. R. Olivato, *J. Chem. Soc. Perkin II*, in press.
3. P. R. Olivato, H. Viertler, B. Wladislaw, K. C. Cole and C. Sandorfy, *Can. J. Chem.*, **54**, 3026 (1976).
4. A. D. Bain and D. C. Frost, *Can. J. Chem.*, **51**, 1245 (1973).
5. S. H. Jerson, S. D. Worley, N. Bodor, J. J. Kaminski and T. W. Flechtner, *J. Electron Spectrosc.*, **13**, 421 (1978).
6. A. Schweig and W. Thiel, *Mol. Phys.*, **27**, 265 (1974).
7. K. C. Cole, C. Sandorfy, M. T. Fabi, P. R. Olivato, R. Rittner, C. Trufem, H. Viertler and B. Wladislaw, *J. Chem. Soc. Perkin II*, **1977**, 2025.
8. K. N. Houk, L. P. Davis, G. R. Newkome, R. E. Duke Jr. and R. V. Nauman, *J. Am. Chem. Soc.*, **95**, 8364 (1973).
9. D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, **94**, 3599 (1972).
10. W. Schäter, A. Schweig, G. Maier and T. Sayrac, *J. Am. Chem. Soc.*, **96**, 279 (1974).
11. M. Mousseron, R. Jacquier and A. Fontaine, *Bull. Soc. Chim. Fr.*, **1952**, 767.
12. P. G. Gassman, T. J. Bergen, D. P. Gilbert and B. W. Cue Jr., *J. Am. Chem. Soc.*, **96**, 5495 (1974).
13. H. C. Brown, N. W. Rathke, G. W. Kabalka and M. M. Rogic, *J. Am. Chem. Soc.*, **90**, 4166 (1968).
14. R. L. Hopkins and H. T. Rall, *J. Am. Chem. Soc. Div. Petrol., Chem. Preprints* 2, **1**, 231 (1957).