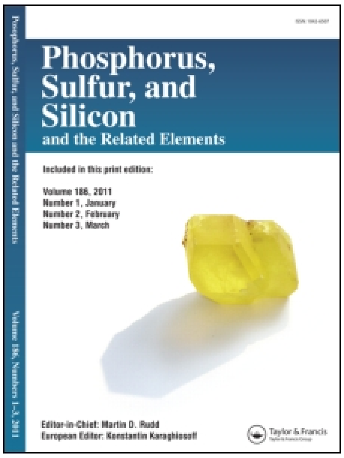

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# PHOTOELECTRON SPECTRA OF THE ALKYL PHENYL DISULFIDES

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# PHOTOELECTRON SPECTRA OF THE ALKYL PHENYL DISULFIDES

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The He I and He II spectra of the alkyl phenyl disulfides were recorded and interpreted in terms of a composite-molecule model in which the sequence of the first four ionisation energies is: $\pi_S - n_S < n_S < \pi_A < \pi_S + n_S$. This sequence is contrary to the STO-3G* calculations, but in agreement with the more extensive 3-21G* calculations. Furthermore, analysis of the intensity variations on going from He I to He II radiation validates the composite-molecule model and therefore suggests that the sulfur lone-pairs adjacent to the alkyl moiety are localised on the sulfur atom, whereas the sulfur lone-pairs adjacent to the ring are delocalised within the $\pi$ system of the phenyl ring.

*Key words:* Alkyl phenyl disulfides; photoelectron spectra; m.o. calculations.

## INTRODUCTION

The disulfide link is commonly found in natural products. Furthermore, in extracellular proteins disulfide bonds (S—S) provide the cross-links which are thought to be responsible for the initial folding of proteins.[1] The biochemical importance of the S—S link lies in the fact that the bond may be easily formed or broken under reasonable biological conditions.[2]

Interest in elucidating the geometric structure of compounds containing a S—S link remains unabated, due to the importance of sulfur lone-pair interactions with the aliphatic or aromatic moieties. In general, alkyl disulfides are found to have zig-zag structures, whereas for the diaryl disulfides the torsional angle between the Aryl-S—S planes is rigid and is 90°.[2] These observations are further substantiated by quantum mechanical calculations.[3]

Ultraviolet photoelectron spectroscopy (UPS) directly measures the valence electronic structure of most compounds. Moreover, when invoking Koopmans' approximation (KA) it is a powerful tool in assessing the degree of lone-pair repulsion on adjacent sulfur atoms and so gives insight into the mechanisms that affect the torsional strain. Hence, it has been used to investigate the isomerization surface of the disulfur dihalides[4] and the conformation analysis of such compounds as di-2-pyridyl and diphenyl dichacogenides,[5] diphenyl disulfides,[5,6] 1,4-dithiepane,[7] 1,5-dithiocane,[7] 1,5 dithionane,[7] 1,4,7-trithionane[7] and 1,6-dithiecane.[7]

UPS also provides valuable insight into the degree of interaction (i.e. the degree of localisation or delocalisation) of equivalent orbitals. This is particularly so when comparing ionisations arising from He I and He II radiation sources. The photoionisation cross-section from a sulfur 3p atomic orbital (AO) has been shown both experimentally[8] and theoretically[9] to be substantially reduced when compared

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with ionisation from a carbon 2p AO on going from He I to He II radiation. It is therefore possible with He I/He II studies to assign whether ionisations are from an orbital localised on the sulfur atom or from an orbital composed mainly of carbon 2p AOs. Hence, depending on the sulfur-carbon interaction, composite orbitals give variations in cross-sections from these two extremes. In this vein, Gleiter and Spanger-Larsen[10] have compared the He I/He II spectra of carbon subsulfide, whereas Glass et al.[11] have compared the same ratio for a number of thiols.

A useful interpretative model in UPS is the composite-molecule model, which utilizes interactions between orbitals that are localised on different fragments of a molecule. In the case of the disubstituted disulfides the sequence of ionisation energies (IEs) measured in UPS can be thought of as arising from interactions involving orbitals localised on the sulfur atoms with orbitals localised on the aryl or alkyl moieties. Giordan and Bock[6] have used such an analysis for interpreting the He I spectra of diphenyl disulfide as have Glass *et al.*[11] for several thiols. For these molecules the low IEs can be modelled in terms of the $e_{2g}$ ($\pi$) molecular orbitals (MOs) localised on the benzene moiety interacting with orbitals localised on the sulfur atom. The asymmetric $\pi$ MO (labelled $\pi_A$) with a node at the substituent site remains unshifted in the composite-molecule model, whereas the symmetric $\pi$ MO (labelled $\pi_S$) with electron density on the substituent site has a resonant interaction with sulfur 3p AOs to produce composite orbitals of antibonding and bonding character. The sequence of IEs for these molecules has been shown to reflect the ordering given by the composite-molecule model.

As an extension of our earlier work on the electronic structure of the alkylbenzenes,[12,13] halo-toluenes[14,15] and the oxy-[16,17] and thio bispyridines,[18] we have investigated the He I/He II UPS of ethyl-, propyl- and iso-propyl phenyl disulfide in order to discern (within a composite-molecule model) the ionisations arising from the sulfur *p*-type orbitals and carbon $\pi$-molecular orbitals. Furthermore, we have employed STO-3G* and 3-21G* calculations, at standard geometries, to give KA IE sequences. Of the two models, the 3-21G* calculations will be shown to be more useful for interpretation of these spectra.

## RESULTS AND CALCULATIONS

The He I and He II photoelectron spectra of ethyl phenyl disulfide, propyl phenyl disulfide and iso-propyl phenyl disulfide together with their integrated curves are shown in Figure 1. Band intensities obtained from integrated curves are scaled in Table I for use in a density-of-state analysis. The density-of-state analysis assumes that the band intensity is a measure of orbital degeneracy so that where bands are strongly overlapped the total band area in each separable region of the spectrum is related to the number of occupied molecular orbitals.

The lowest four vertical ionisation energies (IEs) are listed in Table II, together with the composite-molecule model assignment based on the eigenvalues and eigenvectors obtained from Pople et al.[23] GAUSSIAN 88 suite of programmes using the STO-3G* (s=p) and 3-21G* MO basis sets. The calculations were performed at the Hartree-Fock level and so rely heavily on Koopmans' approximation in order

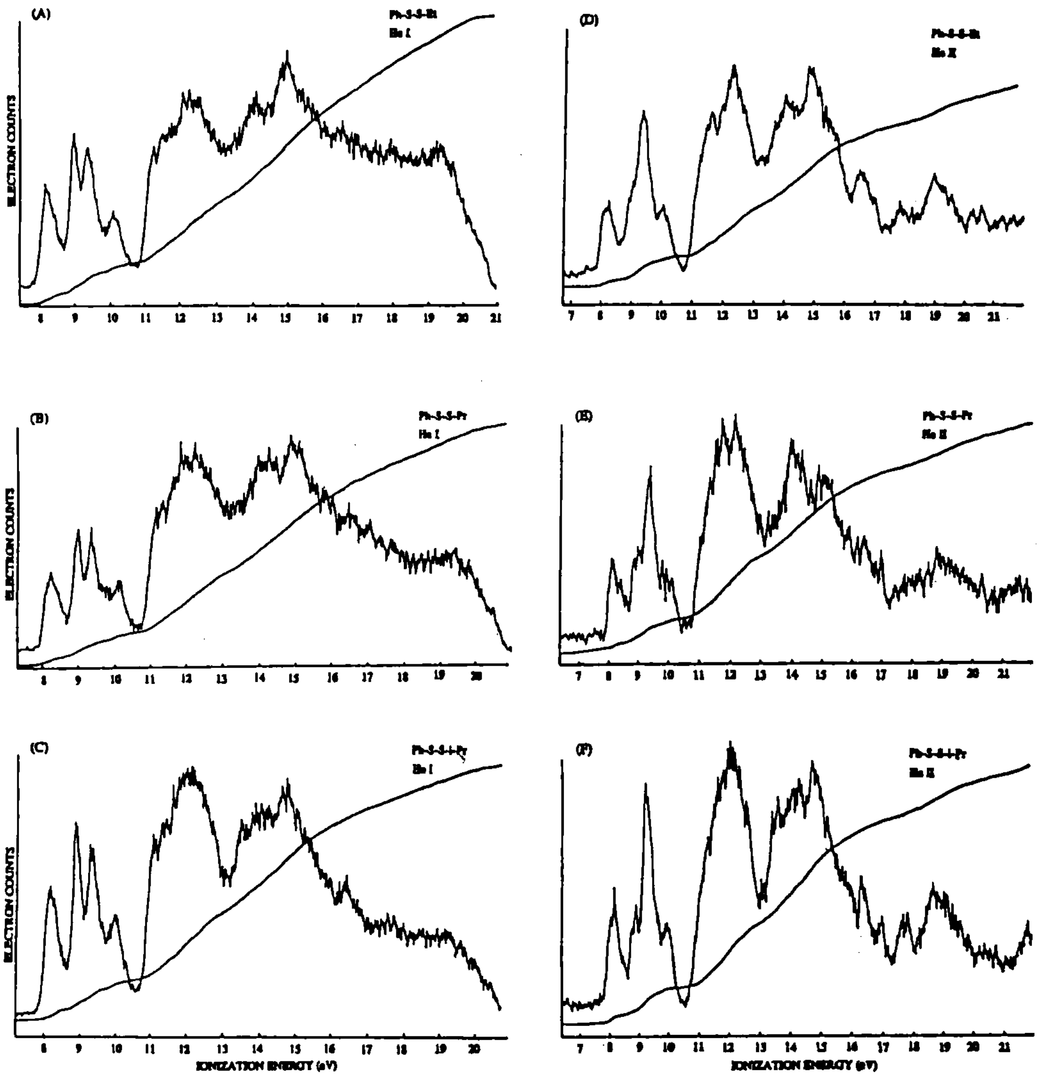

FIGURE 1 Integrated and differential spectra of: (A) He I of ethyl phenyl disulfide; (B) He I of n-propyl phenyl sulfide; (C) He I of iso-propyl phenyl sulfide; (D) He II of ethyl phenyl disulfide; (E) He II of n-propyl phenyl sulfide; (F) He II of iso-propyl phenyl sulfide.

to accurately mimic experimental IE sequences. Poor cancellation of relaxation with correlation errors renders Koopmans' approximation invalid.[24] Nevertheless, Koopmans' approximation does serve as a useful first-order interpretation of UPS spectra.[24] As the 3-21G* basis set is a double valance $\zeta$ basis, with six $d$ polarisation functions, it would be expected to yield more reliable orbital energies than the STO-3G* (which is only a minimal basis set augmented with just five cartesian $d$-functions[25]).

In all calculations standard geometries for the phenyl ring and alkyl chain were employed.[26-27] The S—S bondlength was fixed at 2.04 Å for the alkyl phenyl disulfides, which was based on the S—S bondlength of dimethyl disulfide.[27] For

TABLE I

Experimental relative photoelectron band intensities and ratios for alkyl phenyl disulfide

| Band | IE Range (/eV) | Experimental Band Intensities | | |
|---|---|---|---|---|
| | | He I | He II | % Change[a] |
| *Ethyl Phenyl Disulfide* | | | | |
| 1 | 7.95 - 8.65 | 1.03 | 0.81 | -21 |
| 2 | 8.65 - 9.09 | 0.86 | 0.35 | -59 |
| 3 | 9.09 - 9.66 | 1.24 | 2.12 | 71 |
| 4 | 9.66 - 10.49 | 0.87 | 0.72 | -17 |
| *n-Propyl Phenyl Disulfide* | | | | |
| 1 | 7.91 - 8.67 | 0.97 | 1.02 | -5 |
| 2 | 8.67 - 9.19 | 0.90 | 0.21 | -77 |
| 3 | 9.19 - 9.82 | 1.15 | 1.94 | 69 |
| 4 | 9.82 - 10.72 | 0.98 | 0.83 | -15 |
| *Iso-Propyl Phenyl Disulfide* | | | | |
| 1 | 7.93 - 8.63 | 1.02 | 0.96 | -6 |
| 2 | 8.63 - 9.14 | 0.89 | 0.47 | -47 |
| 3 | 9.14 - 9.72 | 1.21 | 1.91 | 58 |
| 4 | 9.72 - 10.68 | 0.88 | 0.66 | -25 |

a) See equation (2) in text for further details.

di-p-bromophenyl disulfide the torsional angle in the crystal structure between the two phenyl rings is 86°.[27] For diphenyl disulfide n.m.r.,[28] dipole moment[29] and x-ray photoelectron[30] studies all indicate that the dihedral angle is 90°. Generally, it is found for RSSR molecules the dihedral angle between the two functional groups is near this angle and since UPS cannot discern between conformers with energy barriers smaller than the energy available from ambient surroundings (i.e. ~2.5 kJ $mol^{-1}$)[17,18] the dihedral angles between the phenyl ring and alkyl chain in all calculations were fixed at 90°.

## DISCUSSION

An effective assignment tool is to use the IE distributions based on the *s-p* separation rule.[31] The number of *p*-based bands below 18 eV is given by,

$$N_T = N_C + 2.0N_S + 0.5N_H \qquad (1)$$

For benzene, Equation (1) would predict 9 *p*-based bands. However, it is well

TABLE II

Comparison of theoretical and experimental ionisation energies (in eV) and preferred assignments for alkyl phenyl disulfides

| Exp. | | Assign./ | $IE_{CALC.}$ | |
|---|---|---|---|---|
| $IE_{VERT.}$ | | MO Subst. | STO-3G* | 3-21G* |
| *Ethyl Phenyl Disulfide* | | | | |
| $IE_1$ | 8.22 | $\pi_S$-$n_S$ | 6.68 | 9.33 |
| $IE_2$ | 8.94 | $n_S$ | 6.52 | 9.47 |
| $IE_3$ | 9.29 | $\pi_A$ | 7.68 | 9.52 |
| $IE_4$ | 10.17 | $\pi_S$+$n_S$ | 7.30 | 9.83 |
| *n-Propyl Phenyl Disulfide* | | | | |
| $IE_1$ | 8.17 | $\pi_S$-$n_S$ | 6.66 | 9.31 |
| $IE_2$ | 8.92 | $n_S$ | 6.50 | 9.45 |
| $IE_3$ | 9.33 | $\pi_A$ | 7.67 | 9.51 |
| $IE_4$ | 10.08 | $\pi_S$+$n_S$ | 7.28 | 9.78 |
| *Iso-Propyl Phenyl Disulfide* | | | | |
| $IE_1$ | 8.20 | $\pi_S$-$n_S$ | 6.68 | 9.30 |
| $IE_2$ | 8.91 | $n_S$ | 6.49 | 9.42 |
| $IE_3$ | 9.34 | $\pi_A$ | 7.68 | 9.51 |
| $IE_4$ | 10.08 | $\pi_S$+$n_S$ | 7.32 | 9.84 |

known that there is a cross-over of a *s*- and *p*-based band in the 15–18 eV region, giving a total of 10 bands below 18 eV.[32] Hence for ethyl-, propyl and iso-propyl phenyl disulfide, equation (1) would predict 18, 20 and 20 bands respectively. The STO-3G* calculations yield exactly that number of IEs below 18 eV. However, the first four predicted IEs (as shown in Table II) are in poor agreement with experiment, with in fact six bands predicted below 10.7 eV. On the other hand, the 3-21G* is in reasonable agreement with the *s-p* separation rule giving seventeen, nineteen and nineteen bands, respectively, but with the *s*-based band predicted above 18 eV. Moreover, the 3-21G* low IEs are better distributed, when compared with experiment, with four bands predicted below 10.7 eV.

Table I gives a density-of-state analysis. The total integrated band intensities have been scaled to the total number of four bands below ~10.7 eV, consistent with the 3-21G* calculations. The integrated intensities are not scaled for transmission effects of the electrostatic analyser,[33] since there is evidence of a slight rising background from the low to the high IE region from recorded background spectra. The He I band intensities are therefore more reliable in reflecting the expected molecular orbital degeneracy due to the larger signal recorded for these spectra, which will ensure that the density-of-state analysis and subsequent scaling will not be so sensitive to the background signal. Table I indicates 3-21G* IE distribution is reasonable below 10.7 eV, when compared with experiment, since the band areas are ~1. Assuming six bands below 10.7 eV (which would be consistent with the STO-3G* calculations) yields far poorer intensity distribution.

Due to the large number of overlapping cationic states at higher energies, the KA assignments of the photoelectron spectra of the alkyl phenyl disulfides are given in Table II, for only the lowest four IEs. The assignments are given in terms of a composite-molecule model which assumes that the MOs are linear combinations of strongly localised orbitals. For the alkyl phenyl disulfides these originate from the phenyl/alkyl fragments and from the sulfur atoms. The $e_{2g}$ MOs of benzene are at 9.24 eV.[32] Since the $\pi_A$ does not have correct symmetry for overlap with the sulfur 3*p* AO perpendicular to the ring, the composite orbital remains essentially benzene in character and so is not shifted by resonance. Nevertheless, it is inductively shifted from the benzene value. On the other hand, the $\pi_S$ MO does have the correct symmetry and so interacts with the adjacent sulfur 3*p* AO to form composite orbitals of anti-bonding and bonding character. The sulfur atom attached to the alkyl chain has a 3*p* AO which is essentially unshifted in a resonance sense and so can be considered as essentially a sulfur lone-pair. This is further supported by the fact that the sulfur-sulfur bond is a long bond (i.e., 2.04 to 2.17 Å[27]) and so is mainly of $\sigma$ character. The alkyl chain serves to inductively shift the sulfur lone-pair. Figure 2 gives the general composite-molecule model for the alkyl phenyl disulfides. Hence, using the composite-molecule model we would anticipate for the alkyl phenyl disulfides the following IE sequence: $\pi_S - n_S < n_S < \pi_A < \pi_S + n_S$. From Table II it is evident that the 3-21G* IE sequence is in exact agreement with the composite-molecule model, whereas the STO-3G* gives the IE sequence: $n_S < \pi_S - n_S < \pi_S + n_S < \pi_A$.

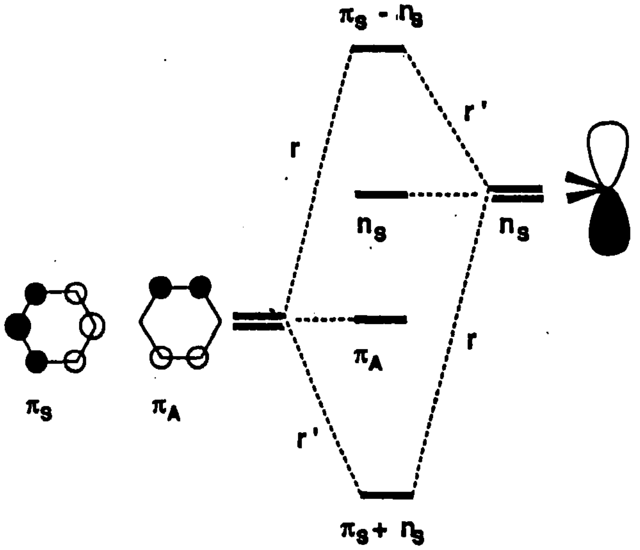

FIGURE 2 Orbital diagram indicating the composite-molecule model of alkyl phenyl disulfides. The labels *r* and *r'* indicate the extent of the resonance interactions between the sulfur lone-pair $n_S$ and the fragment orbital $\pi_S$ localised on the benzene moiety.

The composite-molecule model would also predict that all three alkyl phenyl disulfides should exhibit similar He I and He II spectra in the low IE region (8-11 eV), more or less independent of the alkyl pendant group. Moreover, that the photoionisation cross-section of the second IE would be anticipated to be markedly reduced on comparing He I with He II spectra, since it is essentially a sulfur lone-pair, whereas the third band would be the least reduced as it is mainly composed from the benzene $\pi_A$ MO.

A measure of relative He I/He II intensities is given by the formula[34]:

$$\% \text{ Change} = [\{\text{He II area/He I area}\} - 1] \times 100 \qquad (2)$$

where a large negative percentage change reflects a decrease in intensity on going from He I to He II radiation and so is indicative of ionisation from an MO largely of sulfur $3p$ AO character, whereas a large positive percentage change is indicative of ionisation from a $\pi$ MO, composed on C $2p$ AO character. Table I indicates that for all the alkyl phenyl disulfides investigated here the second and fourth IEs are ionisation from MOs mostly of sulfur character, whereas the first and third IEs arise from ionisation from MOs mostly of carbon character. Furthermore, the second IE shows the most pronounced reduction which is in accord with a $n_S$ assignment, whereas the third IE has the most pronounced enhancement, which is also in accord with ionisation largely from the phenyl ring $\pi_A$ MO. Hence, the intensity analysis on going from He I to He II radiation is in complete agreement with both the composite-molecule model and with the 3-21G* calculations.

In conclusion, the sequence of the first four ionisation energies (as given by the UPS spectra) of the alkyl phenyl disulfides can be interpreted in terms of a composite-molecule model in which the sequence is: $\pi_S - n_S < n_S < \pi_A < \pi_S + n_S$. This sequence is contrary to the STO-3G* calculations, but in agreement with the more extensive 3-21G* calculations and with the analysis of the band intensity variations on going from He I to He II radiation. Furthermore, the composite-molecule model suggests that the sulfur lone-pair adjacent to the alkyl moiety is localised on the sulfur atom, whereas the sulfur lone-pair adjacent to the alkyl moiety is localised on the sulfur atom, whereas the sulfur lone-pair adjacent to the ring is delocalised within the $\pi$ system of the phenyl ring.

## EXPERIMENTAL

All of the alkyl phenyl disulfides were synthesized in our laboratory using procedures reported in the literature.[19,20] The purity of each compound was confirmed from GC, IR and NMR studies, although mass spectra analysis did indicate contamination from diphenyl disulfide when the probe was heated well in excess of 400 K. Alkyl phenyl disulfide disproportionates into a mixture of the dialkyl and diphenyl disulfide even at room temperature. Hence, diphenyl disulfide is often present in small amounts in the mass spectra of the alkyl phenyl disulfides.[21]

All spectra were recorded using a Perkin-Elmer PS 16/18 spectrometer modified with a Helectros helium source. All compounds required a heated inlet probe as they are solids or low volatile liquids at room temperature. For example, the boiling point of ethyl phenyl disulfide is 339 K[22] at 0.1 torr compared with diphenyl disulfide which has a melting point of 331 K.[19] The diphenyl disulfide spectra were recorded at ~364 K. Due to the possibility of small contamination from the diphenyl disulfide, the alkyl phenyl disulfide spectra were recorded in the low temperature range of 300–310 K. For all the spectra the vapour pressure in the ionisation region was ~0.1 torr. Further, due to the absence of the characteristic band of diphenyl disulfide at 13.35 eV in all of the alkyl phenyl sulfides and because of vast differences in the distribution of the cationic states above 11 eV, we can discount significant presence (> 5%) of diphenyl disulfide in the alkyl phenyl disulfide spectra.

Under He I conditions, the operating resolution was between 25 and 35 meV for all of the spectra in Figure 1. The He I and He II spectra were accumulated for 20 minutes with maximum intensity in the region of 400–1000 and 0–100 c.p.s. respectively. For each compound a number of spectra were recorded over ~3 hours in order to ensure that the intensities were reproducible under the existing operating conditions. The spectra were calibrated using butadiene and nitrogen gas mixtures.

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