

DISTINGUISHING IONIZATION FROM SULFUR P-TYPE LONE PAIR ORBITALS AND
CARBON π -MOLECULAR ORBITALS BY He I/He II PHOTOELECTRON SPECTROSCOPY

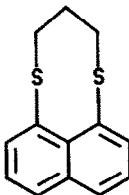
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(Received in USA 9 August 1988)

Abstract: He I and He II photoelectron spectra of methylthiomethylbenzene (2), 2-(1-methylethylthio)ethylbenzene (3), 1-naphthalenemethanethiol (4), 1,1-dimethylethylthiobenzene (5), benzenethiol (6), and methylthiobenzene (7) are reported. Comparison of the He I and He II band areas for each compound provide a reliable basis for assigning the bands as due to photoionization from a carbon π -molecular orbital, sulfur p-type lone pair orbital, or mixed orbital. Ionization from a molecular orbital localized on sulfur results in a large decrease in intensity using He II compared with He I as the source relative to ionization from carbon π -molecular orbitals. Mixed orbitals with both sulfur and carbon character also give rise to diminished intensities in the He II versus He I spectra relative to pure carbon orbitals, but proportionately less decrease than pure sulfur orbitals.

Photoelectron spectroscopy is a powerful method for quantitatively assessing the degree of interaction of equivalent orbitals.¹⁻⁵ This method has been used with mesocyclic polythioethers.⁶ The conformations of several such compounds (1,4-dithiepane, 1,5-dithiocane, 1,5-dithionane, 1,4,7-trithionane, and 1,6-dithiepane) have been deduced by a comparison of the splittings of the sulfur lone pair orbitals measured by this technique with those obtained by semi-empirical molecular orbital calculations and molecular mechanics analysis.⁶ Naphtho[1,8-b,c]dithiocin, 1, was studied by photoelectron spectroscopy with the intent of determining



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the magnitude of the lone pair interaction between the p-type lone pair orbitals on each of the sulfur atoms.⁷ It was hypothesized that the extent of this interaction would be unprecedentedly large owing to its geometry. However, it proved difficult to unequivocally assign the ionization potentials measured to specific molecular orbitals. This paper presents the validation of a little used method for experimentally distinguishing ionizations from aromatic and sulfur lone pair based orbitals. This method consists of comparing the He I and He II photoelectron spectra for the compound in question. The cross section for ionization from a sulfur 3p orbital has been shown experimentally⁸ to be reduced substantially more than that for ionization of a carbon 2p orbital on going from He I to He II sources. As pointed out by Gleiter and Spanget-Larsen in their review,¹ comparison of the He I and He II photoelectron

spectra of carbon subsulfide⁹ provides a means for assigning the ionizations to an orbital predominantly centered on carbon or sulfur atoms. The spectra show relative intensity changes such that the more diffuse molecular orbitals predominantly localized on sulfur give rise to more intense bands in the He I spectrum than in the He II spectrum relative to the more contracted molecular orbitals predominantly on carbon atoms. As evidence for the validity of this method, these assignments are in agreement with those obtained by other criteria.

We were interested in expanding this methodology to investigate whether this technique would work in distinguishing ionizations from aromatic molecular orbitals and those from sulfur lone pair molecular orbitals, and even those from molecular orbitals that were mixtures of sulfur lone pair and aromatic orbitals.

RESULTS AND DISCUSSION

The He I and He II photoelectron spectra of methylthiomethylbenzene 2, 2-(1-methylethylthio)ethylbenzene, (3), and 1-naphthalenemethanethiol, (4), are shown in Fig. 1, and the results presented in Table 1. In each of the He II spectra, the area of the band

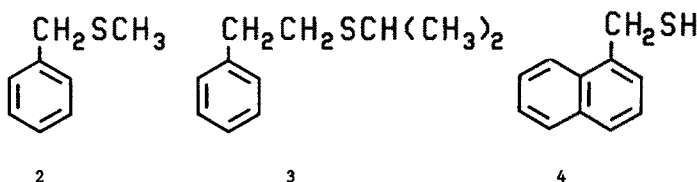


Table 1

Compound	Band	I.P. (eV) ^a	Relative Area ^b		Relative Area Change ^c
			He I	He II	
2	a	8.41	0.57	0.19	-66%
	b+c	9.0	1.00	1.00	
		9.4			
3	a	8.26	0.62	0.16	-74%
	b+c	8.9	1.00	1.00	
		9.3			
4	a	8.04 ^d			+16% ^f
	a' ^e	8.22	0.94 ^f	1.09 ^f	
	a'' ^e	8.38			
	b	8.83	1.00	1.00	
	c	9.09	1.33	0.53	
	d	9.85*	0.94	0.98	

^a Vertical ionization potentials

^b Areas relative to bands assigned to all carbon π

^c [(He II area/ He I area) - 1] 100%

^d Adiabatic ionization potential

^e Bands (a), (a'), and (a'') are the ionization potentials of the vibrational progression of 1365cm⁻¹ within band (a) as shown in Fig. 1 (c).

^f Refers to the sum of bands (a), (a'), and (a'').

assigned to 100% aromatic π -molecular orbital is normalized to the corresponding band in the He I spectrum. All other bands are then given areas relative to this 100% aromatic π -band. In these compounds, the aromatic π -molecular orbitals and sulfur lone pair orbitals, are insulated from each other precluding direct π -type resonance. The He I photoelectron spectrum of methylthiomethylbenzene has been reported before¹⁰ as has the spectrum of the related α -toluenethiol¹¹ and our He I photoelectron spectrum is comparable to that obtained previously.

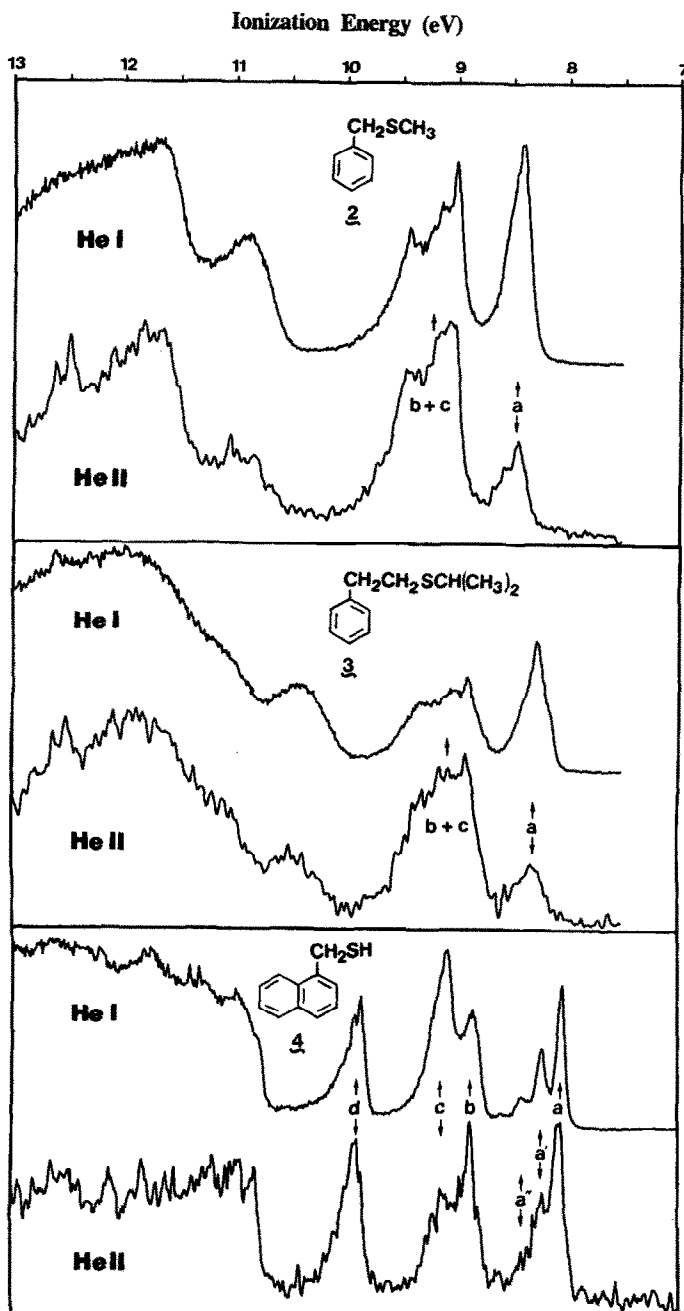


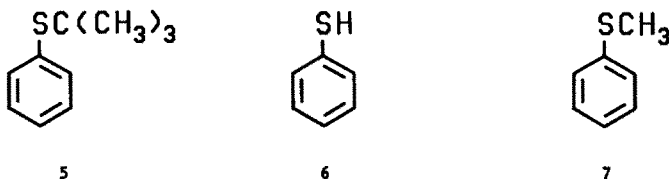
Fig. 1. He I and He II photoelectron spectra for (A) methylthiomethylbenzene, 2, (B) 2-(1-methylethylthio)ethylbenzene 3, and (C) 1-naphthalenemethanethiol, 4.

The ionization potentials for compound 2 has been previously assigned¹⁰ on the basis of comparison with models and oxygen analogues as follows: band (a) is due to ejection of an electron from the p-type lone pair orbital on sulfur and bands (b) and (c) are due to ionization of an electron in e_{1g} (S) and e_{1g} (A) π -orbitals of benzene whose degeneracy has been broken by substitution on the benzene ring. It should be noted that band (a) is close to the first ionization potential of dimethyl sulfide (8.65,¹¹ 8.68¹²⁻¹⁵eV), and bands (b) and (c) are close to those of toluene (first I.P.=8.81eV, second I.P.=9.13 eV).^{16,17} In this way, the ionization potentials in 3 and 4 can be assigned readily as follows. Band (a) in 3 is close to the first ionization potential in 2,2'-thiobispropane (8.26eV)¹⁵ and, therefore, is assigned to the p-type nonbonding orbital on sulfur. Bands (b) and (c) in this compound are close to the first two ionization potentials in toluene and, therefore, are assigned to π -orbitals. Bands (a), (b), and (d) in 4 roughly correspond in energy to the first three ionization potentials of naphthalene (8.18, 8.88, and 10.15eV),¹⁰ (8.15, 8.88, and 10.10eV)¹⁸ and are assigned as due to photoejection of electrons from π -orbitals. Band (c) is 0.32eV lower in energy than the first ionization potential of methanethiol (9.41eV)^{13,14,19} and, in analogy with the 0.27eV lowering in ionization potential in 2 for the p-type lone pair electrons on sulfur compared with dimethyl sulfide, band (c) is assigned to ionization of a p-type lone pair electron on sulfur. The vibrational fine structure of 1365 cm^{-1} in band (a) of compound 4 confirms this assignment as a naphthalene π -band because nonbonding sulfur lone-pair orbitals are not expected to show prominent vibrational fine structure.¹ The infrared spectrum of 4 shows C-C stretching vibrations at 1594 and 1508 cm^{-1} . Ejection of an electron from a bonding naphthalene π -molecular orbital weakens the C-C bond resulting in a lowered frequency for this vibration. Vibrational fine structure of 484 cm^{-1} is observed in band (d) of compound 4 also confirming its assignment as a naphthalene band. Compound 4 shows strong bands due to aromatic C-H out-of-plane bending modes^{20,21} at 798 and 776 cm^{-1} in its infrared spectrum. The lowering in frequency of the vibration in the ion state as compared with the neutral ground state is consistent with ejection of an electron from a bonding π -molecular orbital. Vibrational analysis cannot be used in assigning the third π -molecular orbital because neither bands (b) or (c) show vibrational fine structure.

Perusal of Fig. 1 and Table 1 reveal that band (a) in compound 2 decreases in intensity relative to bands (b) and (c), which remain the same relative to each other. Comparing the relative areas of the bands in the He II spectrum to those in the He I spectrum reveals that band (a) decreases approximately 66% in intensity relative to bands (b) and (c). Similarly, in compound 3 bands (b) and (c) remain the same in intensity relative to each other but band (a) increases by ca. 74% relative to bands (b) and (c). In compound 4, bands (a) and (d) decrease slightly in intensity relative to band (b), but band (c) decreases markedly by about 60% relative to band (b). In all of these cases, the ionizations from a π -type molecular orbital on carbon atoms remain the same in intensity relative to each other on changing from He I to He II photons, but that due to photoionization from a 3p lone-pair orbital on sulfur decreases by approximately two-thirds. In this regard, it is worth noting that the cross section for He I

photoejection of electrons from a carbon 2p and sulfur 3p orbital are 6.128 and 4.333, respectively, and for He II photoejection of electrons from these orbitals 1.875 and 0.6028, respectively.²² The percentage change in intensities due to photoionization of a carbon 2p and sulfur 3p orbital on going from a He I to He II source expected on this basis is 55%. Interestingly, this expected change is comparable to that observed in compounds 2-4 despite the delocalized nature of the π -molecular orbitals derived from the carbon 2p orbitals.

This study was extended to compounds in which direct resonance between the sulfur lone pair and π -molecular orbitals is possible. Specifically, 1,1-dimethylethylthiobenzene, 5, benzenethiol, 6, and methylthiobenzene, 7, were studied and the results given in Fig. 2



and Table 2. The He I photoelectron spectra for all of these compounds has been reported and

Table 2

Compound	Band	I.P. (eV) ^a	Relative Area ^b		Relative Area Change ^c
			He I	He II	
5	a	8.36	0.51	0.18	-65%
	b+c	9.2	1.00	1.00	
		9.4			
6	a	8.40	0.96	0.70	-27%
	b	9.38	1.00	1.00	
	c	10.64	0.73	0.47	
7	a	8.01	0.85	0.45	-45%
	b	8.61	0.22	0.11	
	c	9.25	1.00	1.00	
	d	10.17	0.75	0.54	

^a Vertical ionization potential

^b Areas relative to bands assigned to all carbon π

^c [(He II area/ He I area)-1] 100%

analyzed before (5,²³ 6,²³ and 7^{10,23-25}) as have some analogous naphthalene compounds^{26,27} by several methods including comparison with model compounds, comparisons in homologous series, theoretical computational methods, and vibrational analysis. Our He I spectra agree with those previously reported, but in some cases, we have observed vibrational fine structure for the first time, which further confirm the earlier assignments.

Mellor and coworkers²³ have interpreted the photoelectron spectra of compounds 5-7 in terms of two conformers: planar conformer 8 in which the dihedral angle between the benzene and CSC planes is 0°, and perpendicular conformer 9 in which that dihedral angle is 90°. In planar

conformer 8, the sulfur p-type orbital can mix with the aromatic molecular orbitals, but in conformer 9, the sulfur p-type orbital is orthogonal to the aromatic π -molecular orbitals and there is no overlap between these orbitals. Owing to steric factors, compound 5 exists predominantly (95:5) as perpendicular conformer 9. The orbital assignments involving the non-interacting sulfur p-type orbital and the two π -molecular orbitals of highest energy for the predominant conformer of this compound are as follows. Band (a) is due to the sulfur p-type

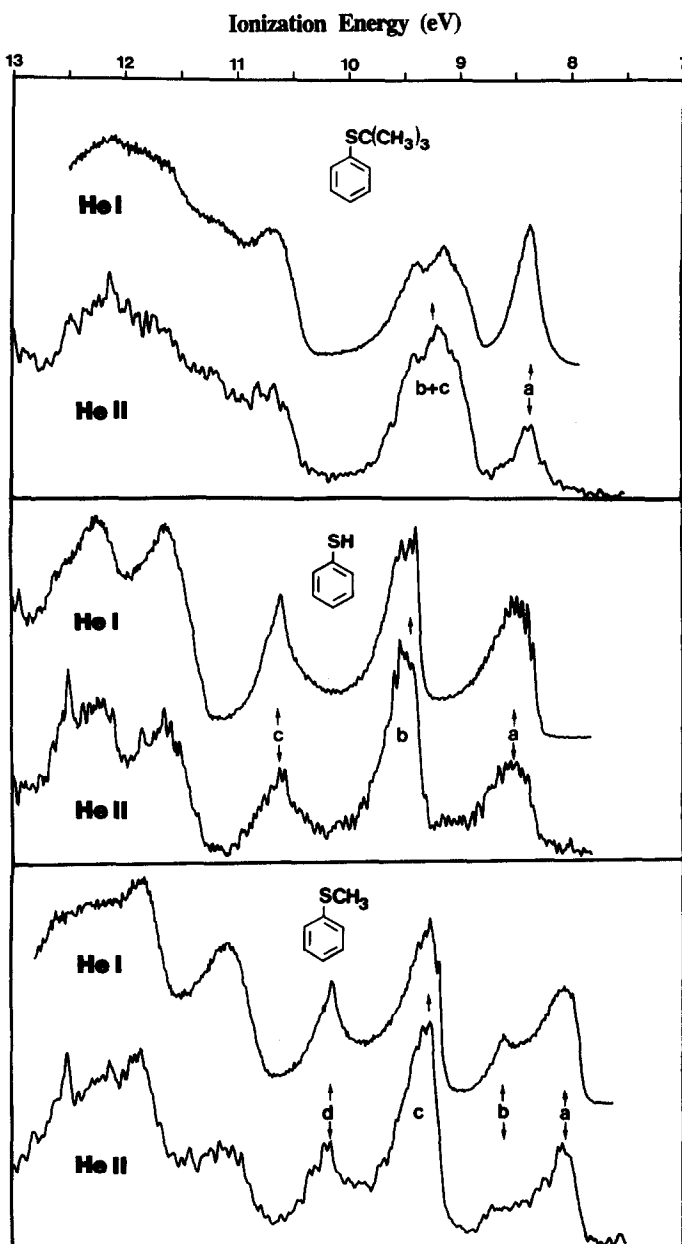
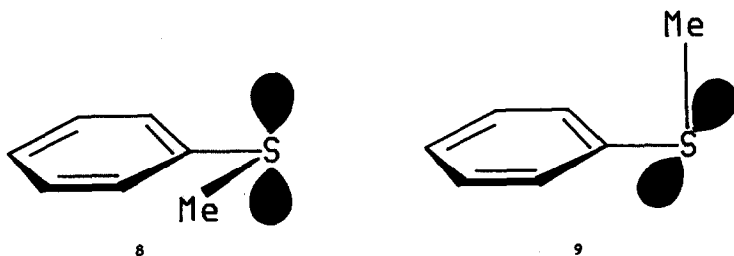


Fig. 2 He I and He II photoelectron spectra for (A) 1,1-dimethylethylthiobenzene, 5, (B) benzenethiol, 6 and (C) methylthiobenzene 7.



lone pair and bands (b) and (c) are due to the $e_{1g}(S)$ and $e_{1g}(A)$ benzene π -molecular orbitals (analogous to those in compounds 2 and 3). Compound 6 exists exclusively as conformer 8 in which there is mixing between the sulfur p-type orbital and the π -molecular orbital. This mixing has been discussed previously^{1-5,23,24,28,29} and is shown schematically in Fig. 3. The sulfur p-type orbital mixes extensively with the $e_{1g}(S)$, but not the $e_{1g}(A)$ orbital of benzene because the latter has a node at the carbon atom bearing the sulfur substituent. The result is that the highest and third highest occupied molecular orbitals have mixed sulfur and carbon character but the occupied molecular orbital of second highest energy has only carbon character. In accordance with this description, the assignments for compound 6 are; band (a) and (c) result from removal of an electron from sulfur p- and carbon π mixed orbitals, and band (b) is due to the noninteracting carbon π molecular orbital. Compound 7 exists as an equilibrium mixture of conformers 8 and 9 in a ratio of 9:1 at room temperature.²³ Variable temperature photoelectron spectroscopic studies support this interpretation of two conformers in equilibrium in compound 7.²⁵ It has also been suggested³⁰ that there should be a continuum of conformers each contributing to the observed photoelectron spectrum rather than two distinct conformations. Nevertheless, the two suggested conformational minima have their appeal from a qualitative point of view although they may be deficient for quantitative analysis. The bands in the

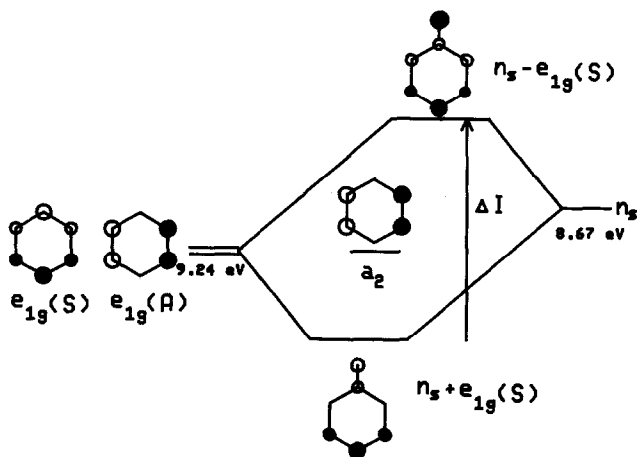


Fig. 3. Orbital diagram illustrating the mixing of sulfur p-type lone pair orbital (n_s) with degenerate e_{1g} orbitals of benzene in methylthiobenzene.

photoelectron spectrum of 7 are assigned as follows. Band (a) is due to ionization from the n_s - e_{1g} orbital of predominant conformer 8. Band (b) is due to photoionization from the sulfur p-type nonbonding orbital of minor conformer 9. Band (c) is due to removal of an electron from both the a_2 orbital of the major conformer 8 and from the noninteracting e_{1g} carbon π -molecular orbitals of minor conformer 9. Band (d) is due to photoejection of an electron from the n_s+e_{1g} orbital of major conformer 8.

Comparison of the He I and He II photoelectron spectra for compound 5 shows that band (a) diminishes in intensity relative to bands (b) and (c) by 65% (owing to the overlap of bands (b) and (c), it is not possible to definitively determine whether the intensity ratios of bands (b) and (c) change relative to each other). In compound 6, the intensity of bands (a) and (c) diminish relative to band (b) in the He II spectrum compared with the He I spectrum. Band (a) diminishes approximately 27% relative to band (b) and band (c) diminishes a comparable amount (35%). For compound 7 bands (a), (b), and (d) diminish relative to band (c) by 45, 50, and 28%, respectively. The overlap of bands (a) and (b) cause the percent reduction values to have more inherent error than the other bands because of the difficulty fitting overlapping bands. In all of these cases, as before, the ionizations from a π -molecular orbital on carbon atoms remain the same relative to each other on changing from He I to He II ionization, but that due to photoionization from a 3p lone pair orbital on sulfur decreases dramatically. In addition, in general, orbitals that result from mixing of sulfur lone pair orbitals and carbon π -molecular orbitals decrease roughly half that for unmixed sulfur lone pair orbitals.

In conclusion, comparison of relative intensities of bands obtained in He I versus He II photoelectron spectra provides a valid method for assigning the character of the orbital from which the electron is ejected as predominantly carbon aromatic π , sulfur 3p-type lone pair, or mixed. This method appears to be qualitatively reliable and, perhaps, even useful semiquantitatively for the two series studied despite the caution that bond contributions are neglected.¹

EXPERIMENTAL

General Methods

Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model PE 983 Spectrophotometer. ¹H NMR spectra were measured at 250 MHz, with a Bruker WM250 spectrometer.

Materials

All reagents and methylthiomethylbenzene (2), benzenethiol (6) and methylthiobenzene (7) were obtained from Aldrich Chemical Company, Milwaukee, WI, and used as received unless specified otherwise. 1-Naphthalenemethanethiol (4) was prepared according to the method of Givens *et al.*³¹ 1,1-Dimethylethylthiobenzene (5) was prepared according to the method of Ipatieff *et al.*³²

2-(1-Methylethylthio)ethylbenzene (3)

This synthesis was based on adoption of the general method of Ono, *et al.*³³ A sample of freshly cut sodium metal (0.48g, 21 mmol) was added to absolute ethanol (15 mL) at room

temperature under an argon atmosphere. After completion of the reaction, 2-propanethiol (1.93 mL, 1.58g, 21 mmol) was added dropwise. The light yellow solution was stirred at room temperature under an argon atmosphere for several minutes. A sample of the p-toluenesulfonate of 2-phenylethanol (2.25g, 8.1 mmol) prepared by the general method of Tipson³⁴ and having a mp 39-40°C (lit.³⁵ 35.5-36.6) was added in one portion and the reaction mixture stirred overnight. The mixture was filtered and concentrated to about one-quarter of the original volume under reduced pressure. Water (50 mL) was added and the mixture extracted with dichloromethane (3x75 mL). The organic extracts were combined, dried (MgSO₄), concentrated on a rotary evaporator and chromatographed on a silica gel column eluting with 5% ethyl acetate in hexanes to afford 2-(1-methylethylthio)ethylbenzene (3) as an oil: IR (neat) 3025, 2956, 2922, 2863, 1602, 1495, 1452, 1380, 1363, 1243, 1223, 1155, 1052, 734, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 1.30 (6H, d, J=6.7Hz, CH₃), 2.89 (5H,m), 7.29 (5H,m); MS (m/z) calcd for C₁₁H₁₆S 180.0973, found 180.0976.

Photoelectron Spectroscopy

All photoelectron spectra were taken on a modified McPherson 36 ESCA Photoelectron Spectrometer,³⁶ and are the result of a sum of individual scans through the use of a LSI-11 computer interfaced with the instrument.³⁷ Each individual scan was calibrated prior to collection to the ²P_{3/2} Argon line (15.759 eV) in He I mode and the He line (24.587 eV) in the He II mode. Spectral resolution was maintained at less than 20 meV in He I and less than 30 meV in He II on each of the calibrant peaks. Spectra of compounds 5, 6, and 8 were run using a PES cell developed by Mark E. Jatcko equipped with a heater and thermocouple for accurate adjustment of cell temperature. Spectra of the liquids were run from a glass tube attached to the instrument via a stainless steel needle valve to regulate sample introduction.

The PES data is presented in analytical form in the tables using an asymmetric Gaussian representation for the ionization bands from the program GFIT.³⁸ The function form is $C(E) = A \exp\{-k[(E-P)/W]^2\}$, where C(E) is the electron counts at binding energy E, A is the peak amplitude, P is the peak position (vertical I.P.), $W = W_h$, the half-width when $E > P$ (on the high binding energy side of the peak), or $W = W_l$, the half-width when $E < P$ (on the low binding energy side of the peak), and $k = 4\ln 2$. The reproducibility of the vertical ionization energies by these techniques is about ± 0.02 eV. The relative integrated peak areas are reproducible to about 5% in the He I and about 10% in the He II for individual peaks. If two peaks overlap and are overlapping such that there is not a clear inflection between their maxima, the peaks are constrained to have the same shape. In the spectra containing the two ionization potentials of the benzene ring E set, (compounds 2, 3 and 5) due to the extensive overlapping of vibrational modes, as many as four (4) asymmetric gaussians were used to accurately account for the total area under these bands. The resulting areas were then summed and ratioed to 1.00 relative to the other bands in the spectrum. Overlapping peaks are included in the fit of a band only if they are needed for a statistically significant representation of the band contour and produce reasonable band shapes. Because of the correlation between parameters in an overlapping band, there is greater uncertainty in the true vertical ionization energy for each peak (about ± 0.1 eV in worst cases). Thus, ionization potentials are only reported to the 0.1 eV or as a range

of I.P. values. In the compounds reported here, it was essential to get an accurate representation of the peak areas no matter how complex the bandshape. Vibrational frequencies were obtained from the energy spacing between maxima and minima in the individual points of the raw data collection and are good to $\pm 50 \text{ cm}^{-1}$.

Acknowledgments: The authors gratefully acknowledge support of this work by the National Institutes of Health (Grant No. HL 15104). We also thank Professor Dennis Lichtenberger of the University of Arizona for helpful discussions. The photoelectron spectra were measured in the Laboratory for Electron Spectroscopy and Surface Analysis.

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