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Photoelectron Spectra of Alkyl Aryl Selenides. Electronic and Steric Factors in the Observation of Rotamers

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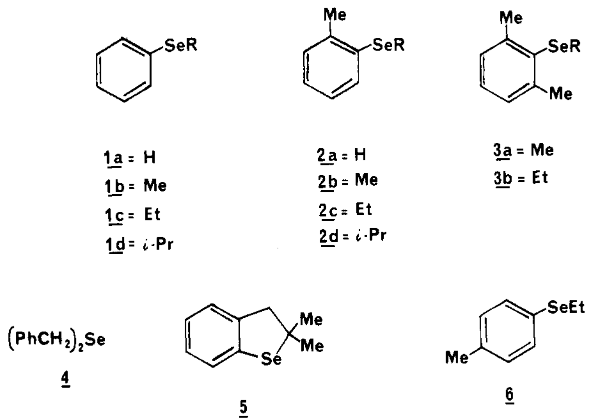
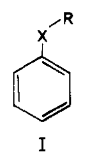
The photoelectron spectra of several aryl alkyl selenides have been measured. Several of the spectra show evidence for the existence of two predominant rotamers, one with maximum p–π overlap and one with minimal overlap. Using the interaction model developed here, we show how steric factors effect rotamer populations and demonstrate that electronic effects determine whether or not different rotamers can be detected by the photoelectron technique.

The photoelectron spectra of benzene derivatives have provided copious information about electronic and steric effects in these species. For molecules such as phenols, phenyl ethers, and anilines, the low ionization potential (IP) region of the spectrum is readily assigned[1] by reference to a molecular orbital energy level diagram in which one has allowed the p orbital on the substituent to interact with the benzene B_1 orbital. The tacit assumption in such cases is that it is necessary only to consider a planar or nearly planar conformation in which the substituent p orbital is oriented for maximum overlap with the phenyl B_1 orbital. Lack of complexity in the low-IP regions of the photoelectron spectra of such compounds generally support this assumption, since the presence of rotameric forms far removed from the planar form would result in either the observation of additional photoelectron bands or in bands appreciably broader than those actually observed. Nevertheless, it is also to be expected that large substituent groups could alter this picture. Indeed, the photoelectron spectra of *tert*-butyl phenyl ether[3,4] and of other compounds with large ortho substituents[5] do reflect the steric constraints placed on these molecules.

A particularly interesting situation arises with phenyl chalcogenides, since both theoretical[6] and experimental studies, including photoelectron studies,[8,9] suggest that in some cases there may be a fairly close balance in energy between two extreme rotameric forms, designated as planar (I) and perpdicular (II). Earlier calculations[6] had suggested that this might be the case even for anisole, but the lack of complexity in the low IP region of the photoelectron spectrum does not support this contention. However, the corresponding portion of the spectrum of thioanisole is more complicated. In fact, early attempts to interpret the spectrum proved incorrect[10,11] until credence was taken of the two rotamer hypothesis. Two groups considered this possibility, and approached the problem differently. Schweig and Thon[9] developed a variable-temperature inlet system for their spectrometer in an attempt to probe the temperature dependence of the photoelectron spectrum. Changes were indeed observed in the range of 20–500 °C which could be rationalized in terms of an increase in abundance of the perpendicular form as the temperature was raised. Mellor and co-workers[8] studied a family of alkyl phenyl sulfides by photoelectron spectroscopy, and again their results supported the notion of there being two predominant conformers. They found that the importance of the less conjugated conformer increases monotonously through the series H, Me, Et, *i*-Pr, *t*-Bu. These previous studies on the spectra of alkyl phenyl sulfides were made difficult because the bands due to the planar and perpendiular forms strongly overlap. Arguments then must rest on the appearance of shoulders and relative changes in the appearances of these shoulders.

Chart I





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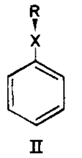

II

In the present study, we have examined the photoelectron spectra of several alkyl phenyl selenides. For these

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Table I. Summary of Ionization Potentials Measured from Photoelectron Spectra of Selenium Compounds[a]

compd	1st band(s)	higher IP bands
1a	8.9 (a)	9.8, 10.3, 11.6, 12.4, 13.0
1b	8.0, 8.3	9.3, 9.9, 10.9, 11.8, 12.6
1c	8.3	9.5 (a), 10.8, 11.6 (b), 12.3
1d	8.3	9.4, 9.6, 11.0 (b), 12.1
2a	8.4	9.3, 10.4, 11.4, 12.1
2b	7.8, 8.2	8.9, 9.2 (b), 9.8, 10.5
2c	8.0, 8.3	9.0, 9.4 (b), 9.8 (b), 10.6, 11.3
2d	7.9 (b), 8.2	9.1, 9.4 (b), 9.8 (b), 10.5 (b), 10.7, 11.0
3a	8.7	9.3, 10.4, 11.5
3b	8.3	9.3, 10.4, 11.5
4	7.96	8.98, 9.22, 10.50
5	7.6	9.0, 9.8, 10.4, 11.1
6	8.0 (b), 813	9.4 (a), 10.7 (b), 11.4 (b)(?), 11.7 (b)

[a] (a) designates center of a broad band, and (b) designates shoulder or inflection. Values are in electron volts.

Table II. Summary of IP Data Measured from Photoelectron Spectra of Oxygen and Sulfur Compounds[a]

compd	1st band(s)	higher IP bands
7	8.4	9.1, 11.0, 11.4 (b), 13.0 (a)
8	8.4	9.3, 11.1, 11.6, 12.6 (a), 14.0 (a)
9	7.8, 8.4	9.5, 10.5, 10.9, 11.4, 12.4 (a)

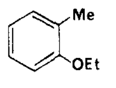
[a] (a) designates center of a broad band, and (b) designates shoulder or inflection. Values are in electron volts.

substances, the contributions from different rotamers to the overall photoelectron spectrum are more apparent. Thus, we have been able to study in a fairly detailed way the effects of steric constraints on rotamer population and the effects of electronic factors in allowing one to observe different rotamers by photoelectron spectroscopy.

Results and Discussion

The selenium compounds shown in Chart I have been examined by photoelectron spectroscopy.

In addition, the following oxygen and sulfur compounds (7–9), not previously studied, were examined by photoelectron spectroscopy for comparison purposes.



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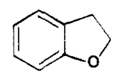

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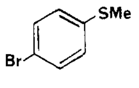

9

The lowest IP band for each selenium compound corresponds to the HOMO, which is of predominantly Se 4p character. In some cases, this band is broad and relatively featureless (e.g., spectrum of **1a**), and in others it is relatively narrow (e.g., spectrum of **3a**). In still others there is distinct doublet character to the first band (e.g., spectra of **1b** and **2b–d**), the relative intensities of which vary from compound to compound. Some representative spectra are shown in Figure 1. IP values derived from the low ionization energy regions of the various photoelectron spectra are shown in Tables I and II. By analogy with the situation existing for phenyl alkyl sulfides, we inferred that some of our spectra might provide information about rotamer populations, especially when the first band showed clear doublet character. Comparison of the photoelectron spectra of **1b** and **5** seems to confirm this view.

Compound **5** is unable to undergo torsional isomerization because structural constraints make the perpendicular conformer unattainable. Thus a simplification is expected in the spectrum of **5** compared to that of **1b**. Such a simplification is indeed seen in that the doublet structure apparent in **1b** has collapsed in the spectrum of **5**. The single, relatively narrow band observed for **5** is consistent with the presence of just one rotamer. Accordingly, the low-IP region of the spectrum of **5** is readily interpreted. The first band (IP = 7.6 eV), which occurs at the lowest IP value for any Se compound reported here, is predominantly due to the Se lone pair, but with some benzene π character (Se 4p − B_1). The second band (IP = 9.0 eV) corresponds to the noninteracting benzene π orbital, which is destabilized compared to the corresponding orbital in benzene itself as a consequence of subsequent inductive effects (A_2). The third band (IP = 9.8 eV) corresponds to ionization from the benzene π orbital which has interacted with the Se lone-pair orbital and thereby acquired some Se 4p character and become somewhat stabilized (Se 4p + B_1).

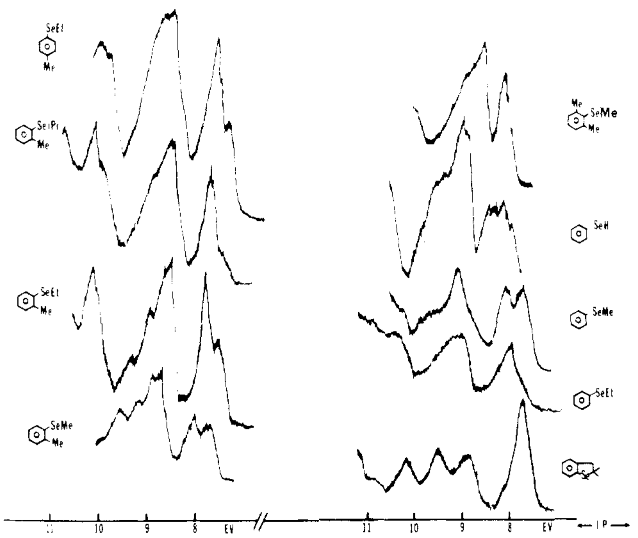

Figure 1. Photoelectron spectra (58.4 nm) of some alkyl phenyl selenides.

The interpretation of the spectrum of phenyl methyl selenide (**1b**) serves as a prototype for other spectra where some degree of doublet structure is present in the lowest IP band. For this compound, the lowest IP component of the doulet appears at IP = 8.0 eV, and this must be assigned to the HOMO of the planar rotamer I. The second component of the doublet, IP = 8.3 eV, is assigned to the rotamer that allows minimal overlap between the Se 4p orbital and the π system (II). Judging by the relative intensities of the photoelectron peaks, the relative abundances of the two rotamers are in a ratio of about 1:1. The corresponding ratio for thioanisole is about 3:2. The difference must be at least in part related to the longer C–X bond in the selenium compound.

It is certainly to be expected that any steric factors which destabilize the planar rotamer of phenyl methyl selenide would be increased in importance in phenyl ethyl selenide (**1c**) and phenyl isopropyl selenide (**1d**). Thus, it is at first surprising to see no evidence for doublet structure in the lowest IP bands of these compounds, especially when the spectra of the corresponding *o*-tolyl compounds are examined. These spectra (see Figure 1) show a consistent decrease in importance of the planar conformer as the size of the alkyl group of the selenium atom increases. It is also curious that the lowest ionization potential of phenyl methyl selenide is lower than that of the ethyl- or isopropyl-substituted compounds. Normally a decrease in IP accompanies an increase in size of alkyl group.

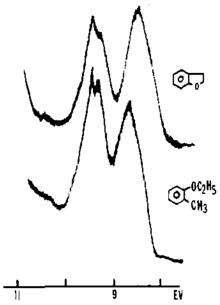

Figure 2. Photoelectron spectra (58.4 nm) of **7** and **8**.

We believe that a subtle electronic effect is responsible for both our inability to observe the two rotamers of phenyl ethyl selenide (**1c**) and phenyl isopropyl selenide (**1d**) by photoelectron spectroscopy, as well as the IP inversion described above. Changing from a methyl substituent to larger alkyl substituents on the selenium atom will raise the "basis" energy of the Se 4p orbital, thereby increasing the energy gap between the Se 4p and phenyl π orbitals. Thus conjugative interaction is lessened, and, as a consequence, the ionization potentials of the perpendicular and planar rotamers become too similar to be resolved. In the *o*-tolyl compounds, however, the raising in energy of the Se 4p basis orbital is matched by a comparable raising of the energy of the phenyl π orbitals by the methyl group in the ring. Thus the energy gap between the Se 4p and phenyl π orbitals is maintained at a value appropriate for an interaction large enough to distinguish between the planar and perpendicular rotamers.

Confirmation of this can be obtained from the spectrum of **6**. In this compound the energies of the "basis" Se 4p and phenyl π orbitals can be assumed to be approximately the same as in **2c**, while the steric effects in **6** must be equivalent to those in **1c**. The photoelectron spectrum of **6** shows the expected doublet structure for the lowest IP band, strongly suggesting that electronic factors are responsible for the lack of any observable doublet structure in **1c** and **2c**.

In order to confirm that the photoelectron spectra of phenyl alkyl ethers do not show evidence for different rotameric forms, we examined compounds **7** and **8** (Figure 2). As can be seen, there is only a slight simplification (sharpening of peaks) in the spectrum of **8** as compared to **7**, in complete contrast to the situation in, for example, **2c** and **5**.

Thus, examination by PES of an appropriate series of compounds can provide useful information on rotamer populations, and the factors which govern relative populations of rotamer. Since both steric and electronic effects influence the stability of any given rotamer, an extensive series of investigations is necessary to evaluate specific effects. It is tempting to make certain simplifying assumptions, but only more detailed studies can validate them. For example, in common with previous workers dealing with conformational issues in PES, it is tempting to suppose that the relative photoionization cross sections for the planar and perpendicular rotamers are similar, thereby enabling one to estimate rotamer populations from peak heights or areas. Furthermore, one might suppose that in molecules such as those under study here, the main perturbations to rotamer population are steric in nature.

Examination of the spectra of thioanisole and *p*-bromothioanisole lend limited support to these ideas. Shweig and Thon had reported that at room temperature the relative abundances of the planar and perpendicular forms are in the ratio 1.54:1 (overlapping bands). In the spectrum of *p*-bromothioanisole (Figure 3) one expects to see a better resolution of the planar and perpendicular forms since the bromo substituent will raise the basis energy of the phenyl π orbitals and thereby increase the interaction with the S 3p lone pair in the planar rotamer. Moreover, if it is indeed true that such an electronic perturbation has little effect on rotamer populations, one should still observe a ratio close to 3:2 for the two components of the doublet within the first photoelectron band. Experimentally this is found to be the case. A possible complication had been anticipated in that the HOMO of the *p*-bromo compound contains some Br 4p character, which might be expected to result in an increase in photoionization cross section compared to the nonsubstituted parent compound. However, this effect is evidently small since no significant deviation in the 3:2 peak ratios are observed.

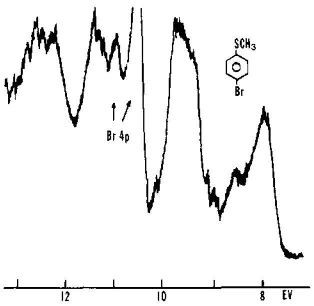

Figure 3. Photoelectron spectrum (58.4 nm) of **9**.

Table III. MINDO/3 Calculations on Phenol and Thiophenol at Various Dihedral Angles

	HXCC dihedral angle, deg	heat of formation, kcal/mol	calcd HOMO IP, eV
PhOH	0	−29.21	8.46
PhOH	45	−27.62	8.60
PhOH	90	−26.19	8.77
PhSH	0	21.21	8.47
PhSH	45	22.03	8.63
PhSH	90	22.67	8.99

The last point which must be addressed involves the fact that for a given series of oxygen, sulfur, and selenium-substituted aromatics, the ability to observe rotamers via photoelectron spectroscopy follows the order oxygen < sulfur < selenium. The implications of this trend are as follows. For oxygen substituents the planar rotamer I must be substantially more stable than its perpendicular counterpart II. However, as one moves to sulfur and ultimately to selenium, the preference for rotamer I should gradually decrease. Moreover, when additional steric perturbations are placed on sulfur- and selenium-substituted aromatics (e.g., ortho substituents), the relative amounts of rotamer I should be further decreased.

In order to better understand these results, we have performed MINDO/3 calculations on phenol and thiophenol.[12] The results of these calculations are listed in Table III. With the exception of the dihedral angle in question, each of these listings has been energy optimized with respect of its geometry. For phenol, the planar form is over 3 kcal/mol more stable than the perpendicular form. Since this corresponds to an equilibrium population of greater than 99:1 I/II, it is easy to understand why predominantly nonplanar oxygen-substituted aromatics

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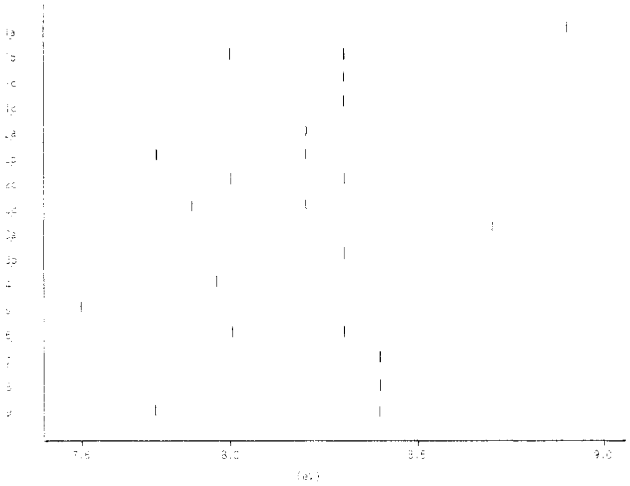

Figure 4. Low IP region of the photoelectron spectra of 1-9.

are only observed in cases of severe steric hindrance (see Figure 4). For thiophenol, the energy difference between the planar and perpendicular forms is only half as large (~1.5 kcal/mol). Presumably, for selenium-substituted aromatics the corresponding energy differences are even smaller. When these electronic factors are coupled with the previously discussed steric factor, the trends reported in this study appear quite reasonable.

In summary, then, it appears that relative peak heights measured from the photoelectron spectra give a reasonable estimation of rotamer populations if distinct features attributable to the different rotamers can be identified. In the compounds examined here, the observation of such distinct features depends on the existence of a significant interaction between the substituent lone pair and the phenyl π orbitals.

Experimental Section

Photoelectron spectra were obtained on a modified Perkin-Elmer PS16 spectrometer.[13] Compounds were either commercially available or synthesized by standard methods.

Acknowledgment. The Emory group thanks the NIH for financial support.

Registry No. 1a, 645-96-5; **1b**, 4346-64-9; **1c**, 17774-38-8; **1d**, 22233-89-2; **2a**, 37773-21-0; **2b**, 1528-88-7; **2c**, 37773-42-5; **2d**, 78805-16-0; **3a**, 78805-17-1; **3b**, 78805-18-2; **4**, 1842-38-2; **5**, 60096-27-7; **6**, 37773-43-6; **7**, 614-71-1; **8**, 496-16-2; **9**, 104-95-0; phenol, 108-95-2; benzenethiol, 108-98-5.

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Cycloaddition of Substituted Bicyclo[3.2.1]octa-2,6-diene with 4-Phenyl-1,2,4-triazoline-3,5-dione

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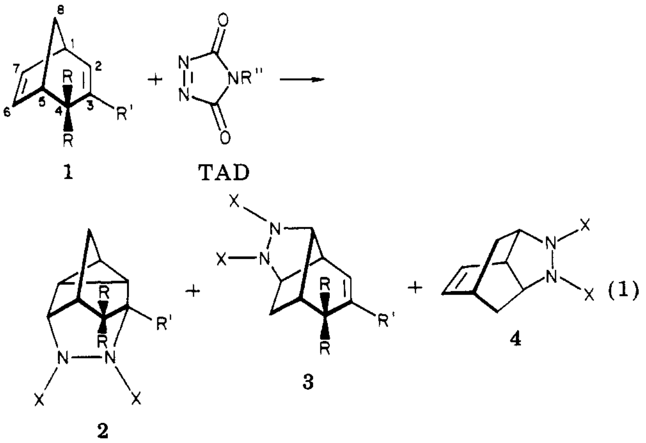
4,4-Dimethylbicyclo[3.2.1]octa-2,6-diene (**1b**) reacts with 4-phenyl-1,2,4-triazoline-3,5-dione to give the rearranged urazole **3b** (via dipolar cycloaddition at the more strained C_6–C_7 double bond) as the only isolable (22% yield) product, while 3-bromobicyclo[3.2.1]octa-2,6-diene (**1c**) affords the ene adduct **7** as the major product (60% yield) together with a 10% yield of the rearranged urazole **3c**. Both dimethyl substitution at the C_4 position and bromo substitution at the C_3 position suppress effectively homocycloaddition and dipolar cycloaddition at the less strained C_2–C_3 double bond. The ene reactivity of the bromo diene **1c** is surprising, since neither the parent diene **1a** nor the dimethyl diene **1b** exhibit this cycloaddition behavior.

Recently we observed[1] that the parent hydrocarbon bicyclo[3.2.1]octa-2,6-diene (**1a**) reacted with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) to give the urazoles **2–4** (eq 1). Urazole **2a** is the product of homocycloaddition at the C_3–C_6 site, while **3a** and **4a** result from dipolar cycloaddition,[2] respectively, at the C_6–C_7 and C_2–C_3 double bonds. The fact that dipolar cycloaddition competed effectively with the usually preferred homocycloaddition[3] is unique for this dienic substrate and stimulated our interest to examine the reaction of substituted derivatives of 1 with TAD. On one hand, we chose the 4,4-dimethyl derivative **1b** in an attempt to suppress the homocycloaddition mode on grounds of steric blocking of homoattack at the C_3–C_6 site; on the other hand, we chose the 3-bromo derivative **1c** to suppress dipolar attack on the C_2–C_3 double bond. We report here on the synthesis of the hitherto unknown diene **1b** and the cycloaddition reactivity of dienes **1b** and **1c** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD).



a, R = R = H; b, R = Me, R' = H; c, R = H, R' = Br; X + X = -CONR"CO-; R" = Me, Ph

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[3] Adam, W.; De Lucchi, O. *Angew, Chem., Int. Ed. Engl.* **1980**, *19*, 762.