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CONFORMATION, ELECTRONIC STRUCTURE AND REACTIVITY AS PROBED BY PHOTOELECTRON SPECTROSCOPY

City University of New York PH.D. 1980

CONFORMATION, ELECTRONIC STRUCTURE AND REACTIVITY AS PROBED BY PHOTOELECTRON SPECTROSCOPY

by

GARO HOROZOGLU ARMEN

A dissertation submitted to the Graduate Faculty in Chemistry in Partial fulfillmant of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1980

This manuscript has been read and accepted for the Graduate Faculty in Science in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

CONFORMATION, ELECTRONIC STRUCTURE AND REACTIVITY AS PROBED BY PHOTOELECTRON SPECTROSCOPY

by

Garo Horozoglu Armen

Adviser: Professor A.D. Baker

In this work, photoelectron spectroscopy is applied to three separate areas; conformational analyses, electronic structure and chemical reactivity.

Conformational studies were carried out on selenium systems, in which the interaction of the lone pair orbitals of selenium with other lone pair orbitals on adjacent pi systems was investigated.

The He(I) photoelectron spectra of complexes of Co(III) with acetylacetone and several derivatives are reported. The ionization potentials of metal localized d-electrons and ligand pi-orbitals are used to probe the extent of **metal-to-ligand** pi-bonding and possible aromatic character in the chelate ring.

Finally PES results are used in the investigation of reactivities of chemical systems. In one set of experiments, the frontier molecular orbital theory was applied in comparing reactivities of nitrones and azoxy compounds. The possibility of modifying structure, based on PES results, in order to enhance chemical reactivity is suggested. In a separate study, ionization potential data is used to elucidate complexation phenomena involving crown ethers, cryptates and related substances. Through-bond interaction appears to be an important phenomena in the chemistry of certain crown compounds.

IN MEMORY

OF

MY FATHER AND MOTHER

AND

VALERIE'S DADDY

ACKNOWLEDGEMENTS

It is with deep sense of gratitude that I express my sincere thanks to the following people for having made integral contributions to my work.

Prof. A.D. Baker, for his guidance and constant encouragement, and for having made my graduate work pleasant and rewarding. His expertise in the field of spectroscopy is only surpassed by his infinite good humor and patience.

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Valerie H. Armen, my wife, for her support and patience through the years.

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INTRODUCTION

In recent years chemists have become more orbital conscious because of the growing number of applications of molecular orbital theory in probing chemical problems. Therefore, to gather information on molecular orbital energies has become an important task for many chemists. Experimentally, however, the only directly measurable quantity is the ionization or binding energy of an electron occupying the orbital. According to Koopmans' Theorem, which disregards the changes in the energies of the molecular orbitals during the electron ejection process, the binding energy (IP) is equal in magnitude to the orbital energy (E).

$$E = - IP$$

Photoelectron spectroscopy has proved to be the only direct method of measuring all of the ionization energies of a molecule. The technique can be used to measure IP's of valence shell as well as inner shell electrons. The method basically uses a beam of monoenergetic light to interact with a sample thereby ejecting electrons; the kinetic energies of the electrons which are ejected are then measured and recorded. The following equation can be used in correlating ionization energy with the kinetic energy of the electron.

$$KE = h\nu - IP$$

In the PE spectrum obtained each band corresponds to ionization from a single molecular orbital, and therefore, by scanning all the electron energies a spectrum of bands is obtained. Each band corresponds to one molecular orbital of a given species.

PES is a versatile technique. It can be used as a tool in analyzing chemical systems as well as explaining observed chemical behaviour, or simply to gain insight into the molecular orbital structure of a molecule. There are two main branches of the technique: (a) UV-PES and (b) X-ray PES.

(a) UV-PES measures the energies of the valence shell orbitals. It is used to probe mainly non-analytical aspects of a system. The details of the instrumentation are discussed in Chapter 1. The applications of this technique to practical aspects of chemistry range from conformational analysis to predicting relative reactivities of chemical systems. In this thesis, Chapters 2-5 deal with numerous applications of this technique to chemical systems. Each chapter, being isolated from the other in terms of its contents, will contain its own introduction.

(b) X-ray PES -- This technique which has numerous analytical applications utilizes an X-ray source to ionize inner shell electrons. Since inner shell orbitals of an atom are not perturbed much in the formation of a molecule, their energies are representative of the nature of the atom itself regardless of its environment. Therefore, the technique is a very useful tool in elemental analysis. X-ray PES has been used extensively in structural determination and surface studies, since it can be used to study solid samples.

In this thesis all the work done is concentrated in the area of UV-PES.

CHAPTER 1

INSTRUMENTAL DEVELOPMENT

IMPROVEMENTS ON THE PERKIN-ELMER PS-16 SPECTROMETER.

The PS 16 spectrometer at Queens College which had been disassembled, has been altered in design and rebuilt (see Figure 1).

The original instrument was a self-contained unit which incorporated the vacuum system as well as all the electronic and the electrical components and the recorder. Presently, the instrument has been converted to three separate units; one consisting of the vacuum system; the second having the electronics of the analyzer, the detection system, and the recorder; and the third consisting of the control and monitoring components of the vacuum and the cooling systems. These changes make the components of the instrument readily accessible in case of mechanical difficulties and/or other malfunctions.

In addition to the above changes, several components were redesigned and constructed somewhat differently for the purpose of improving the vacuum system, the cooling system, and the sweep circuit of the analyzer. Coolant liquid and calibration gas inlet ports of the main vacuum chamber have been also modified to make these parts more serviceable.

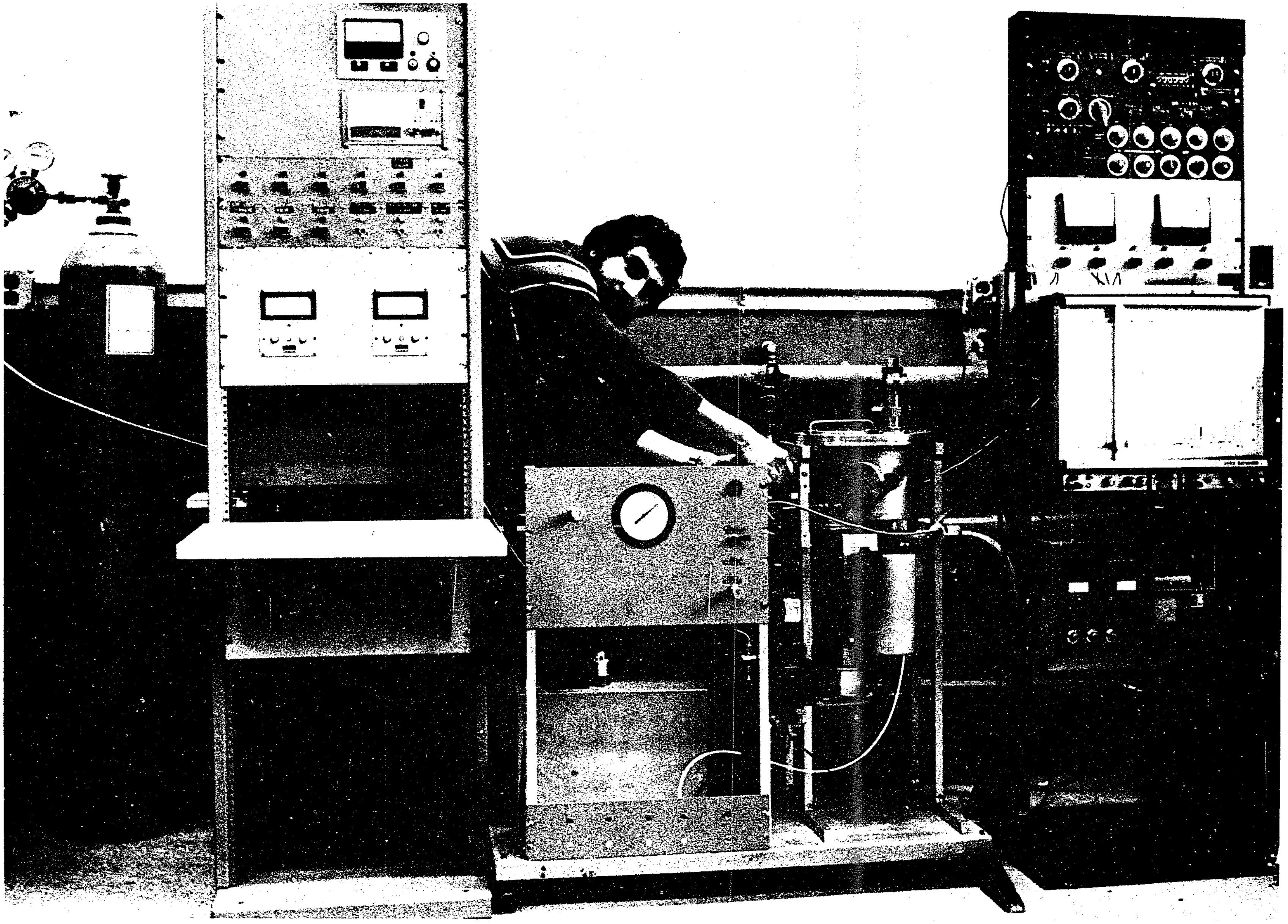

Fig. 1 - The Modified Perkin Elmer PS-16 Photoelectron Spectrometer

To improve the vacuum capability of the instrument, the light source connections from the He tank to the cathode were redesigned (see Figure 2). Upon reproduction of the original design, major leaks were discovered when the light source line was tested for vacuum independently from the rest of the system. Cajon glass connectors and a slightly wider capillary were used in the reconstruction process, and these improved the vacuum significantly. The helium line going from the He tank to the metering valve was provided with a shut-off valve, which alleviated the necessity of readjusting the helium pressure for optimum resolution each time a spectrum was obtained.

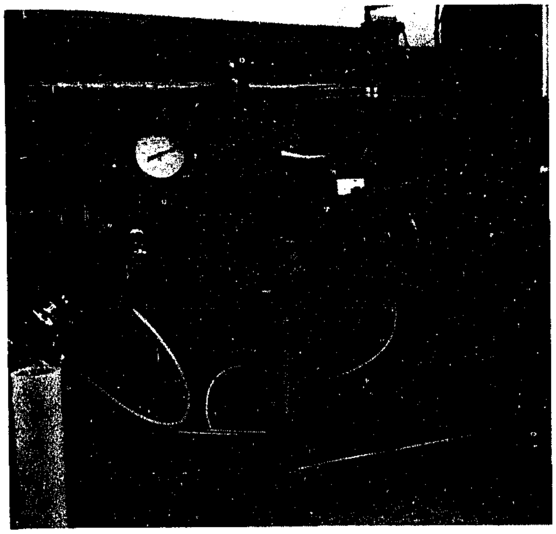

Fig. 2 - Light source connections.

The cooling systems on Perkin-Elmer photoelectron spectrometers are rather poorly designed. Since for optimum resolution and accuracy spectra have to be run at constant temperature, it is very important to be able to accurately monitor and control the temperature of the sample being studied. The original instrument was equipped with a water cooling system which used tap system as its water source, and with the temperature of this water being typically below 15° C, the Perkin-Elmer design did not provide very good control even at very low flow rates of the coolant (water, being a highly efficient coolant when used at low temperatures, cools the system much too rapidly, not allowing enough time for a complete spectrum to be obtained at constant temperature) .

The cooling system was improved significantly by the introduction of a Lauda MGW model temperature bath which was modified to our specifications by the company. Major difficulties with the original system were experienced especially when constant temperatures above sixty degrees were desired. With the temperature of the water source of the cooling system now being controllable anywhere between 5-90 degrees, it is possible to get constant temperatures of 60-275 degrees for considerable lengths of time without much difficulty. The modified cooling system was put together in much the same way as it was in the original instrument. Water from the bath circulates through the anode tip of the light source and flow rate is controlled by two rotameters (one with course and the other with fine adjusments). In the new system the flow rate of water is no longer as critical as it was in the old system, and the adjustable temperature feature of the waterbath provides an excellent means of controlling the temperature of the sample within a narrow range. In Table I are tabulated typical values for the temperature of the bath vs the temperature of the sample chamber at constant flow rate of the coolent water.

TABLE I

Temp of Bath in °C	Temp of Sample in °C
50	63
60	81
70	103
80	134
90	160

For temperatures above 160 degrees lower flow rates are used. It should be noted that coolants other than water can also be used as long as the viscosity of the liquid used is within an acceptable range.

The best results with the new system are achieved when one first obtains the approximate desired temperature by adjusting the rotameters, and then uses the temperature control of the bath for further fine adjustments to arrive at the exact desired temperature.

Sample temperature monitoring was accomplished by using a digital meter and a probe calibrated to 0.5°C. These components were purchased from Thermoelectric Inc.

The original design of the sweep circuit of the analyzer plates did not provide us with the ability to alter the sweep range continuously. Such a feature would be very useful for expanding and contracting the spectrum within any range. Trouble shooting in the original instrument was also impossible because of the inaccesibility of the components involved. The new design incorporates a sweep circuit (see Figure 3), which through the use of a number of potentiometers makes it possible to offset the zero reference point and continuously change the sweep range. In addition to this a number of test points have been constructed (for the purpose of trouble shooting) , which are a permanent part of the sweep circuit panel (see Figure 4).

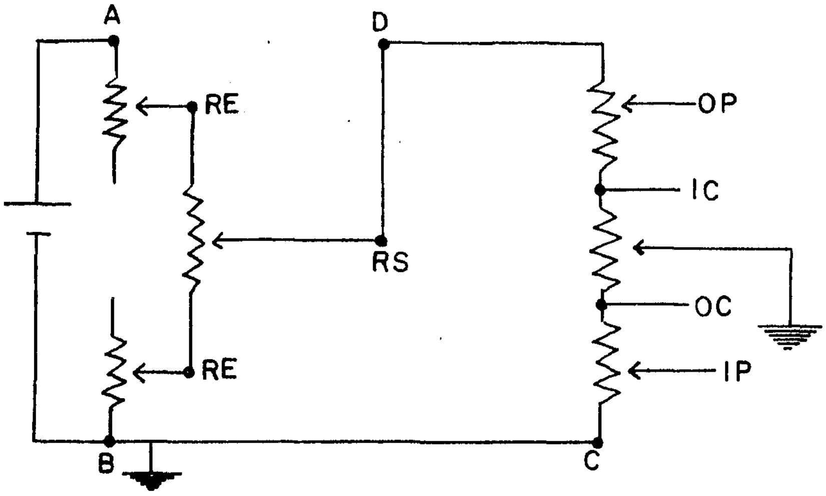

Fig. 3 - The sweep circuit of the analyzer plates.

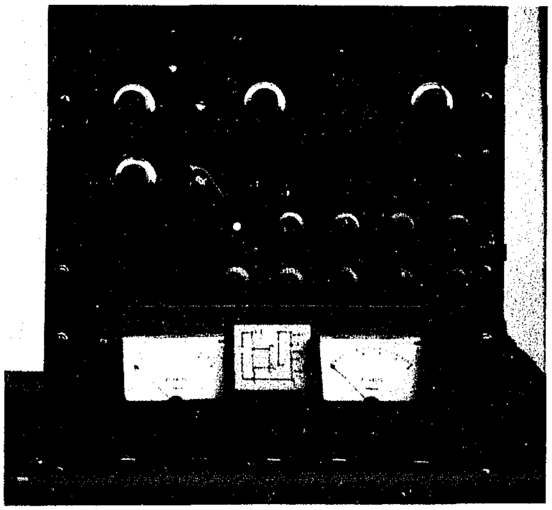

Fig. 4 - The sweep circuit panel.

MODIFICATION OF THE PS-16 FOR ELECTRON IMPACT EXPERIMENTS

(A) THEORY

Electron transmission spectroscopy has become an important technique for chemists since it provides the most reliable and direct experimental method of measuring energies of unoccupied molecular orbital levels. One of the applications of the technique to chemical systems is discussed in Chapter two.

Electron transmission spectroscopy was developed by the late G.J. Schulz and his collaborators at Yale university (1-3). In the Schulz type of a spectrometer the electron beam generated by an electron gun is sent through an electron monochromator into the collision chamber, where the intensity of the electron beam is attenuated due to absorption of electrons by the sample. By varying the electron energies continuously, one can determine the energies at which electrons attach to the sample by locating the points at which a drop in transmitted electron intensity occurs. These points yield the electron affinities of the sample compound.

Reports on the use of glow discharge lamps as electron sources for electron impact excitation have appeared (4). According to these reports it has been possible to utilize the plasma in the discharge lamp of a conventional ultraviolet photoelectron spectrometer as an electron source for low energy electron impact excitation. These experiments were carried out with a standard Perkin-Elmer photoelectron Spectrometer. Except for the operation of the discharge lamp, the spectrometer was used in exactly the same manner as for the measurements of photoelectron spectra. When the lamp was operated to produce He(I) radiation, a pressure of 0.2-0.5 torr is used. In this pressure range electrons from the discharge plasma cannot reach the entrance slit to the collision chamber because of inelastic collisions between the electrons and He molecules. However, to operate the light source as an electron gun, the plasma was intentionally diluted to increase the mean free path of the electrons. This was accomplished by lowering the pressure in the discharge while monitoring the background electron count.

Our attempts to generate electrons in this manner were successful. However, the method itself did not prove to be a successful and reliable means of obtaining electron transmission spectra, despite its definite practical advantages, for the following reasons.

The electrons generated in the plasma follow a Maxwellian distribution of electrons (Fig. 5a). It was hoped to see a modification of this distribution (Fig. 5b) when a sample was introduced into the sample chamber; the inverse peaks would correspond to the electron affinities of the sample. However, we were unable to get a very stable baseline during the course of an experiment, because of the extreme sensitivity of electron energies to very small

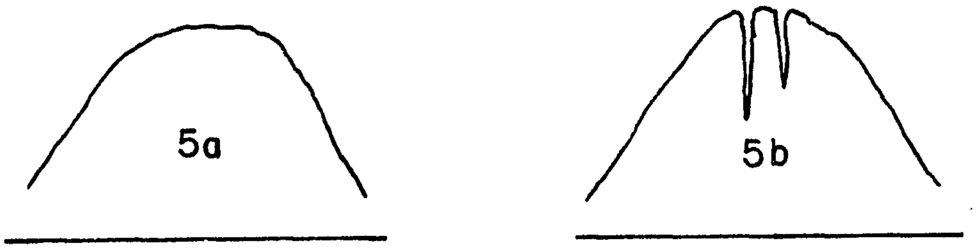

Fig. 5 - Maxwellian distribution of electrons before and after the introduction of a sample in electron impact experiments.

fluctuations in the pressure of the plasma gas. Thus, we encountered a very large signal-to-noise ratio, and although the method seems feasible in principle, rather major effort will be needed to make it practicable.

Because of the definite disadvantages of this method vs Schulz's it was decided to use the basic Schulz design with some modifications to make the PS-16 compatible with electron transmission experiments. However it should be noted that the observation of the plasma electrons is a very interesting discovery, and this field is wide open for further research and other applications where our stringent requirements are not very important.

(B) EXPERIMENTAL:

The main vacuum chamber of the PS-16 has been modified to be compatible with a source for electron impact experiments. This source consists of an electron gun and a lens system (see Figure 6). Electrons having been generated here go through the same kinetic energy analyzer used for PES measurements and pass through the adjustable slit into the collision chamber, where monochromatic electrons of proper enegy are absorbed by the sample and the rest go through the exit slit into the detecter. Detection, amplification and recording are accomplished using the components of the modified PS-16. The electron gun and modified target chamber have not yet been installed; nevertheless the major design features have been considered and are described here.

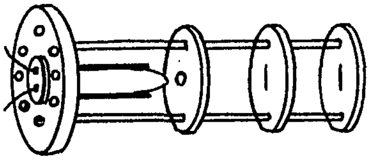

Fig. 6 - An electron gun and a lens system.

The collision chamber is much like the one used for PS measurements except in that it has two slits, one allowing electrons to enter and the other to exit. The sample chamber is introduced into the instrument with a simple adapter (see Fig. 7) which goes between the analyzer and the detecter compartments and is provided with the same probe inlet mechanism used in the PS-16. This collision chamber compartment is pumped differentially in order to remove the sample vapors before they diffuse into the analyzer and the detector compartments (for proper operation a pressure of 10^{-4} torr should be maintained in these compartments).

Our new sweep circuit design is also compatible for electron impact experiments since changing the sweep range and offsetting the zero reference point are readily accomplished by simply readjusting the potentiometers of the sweep circuit. A digital Fluke multimeter (which has a high enough impedence to give reliable readings) is used for all adjustments.

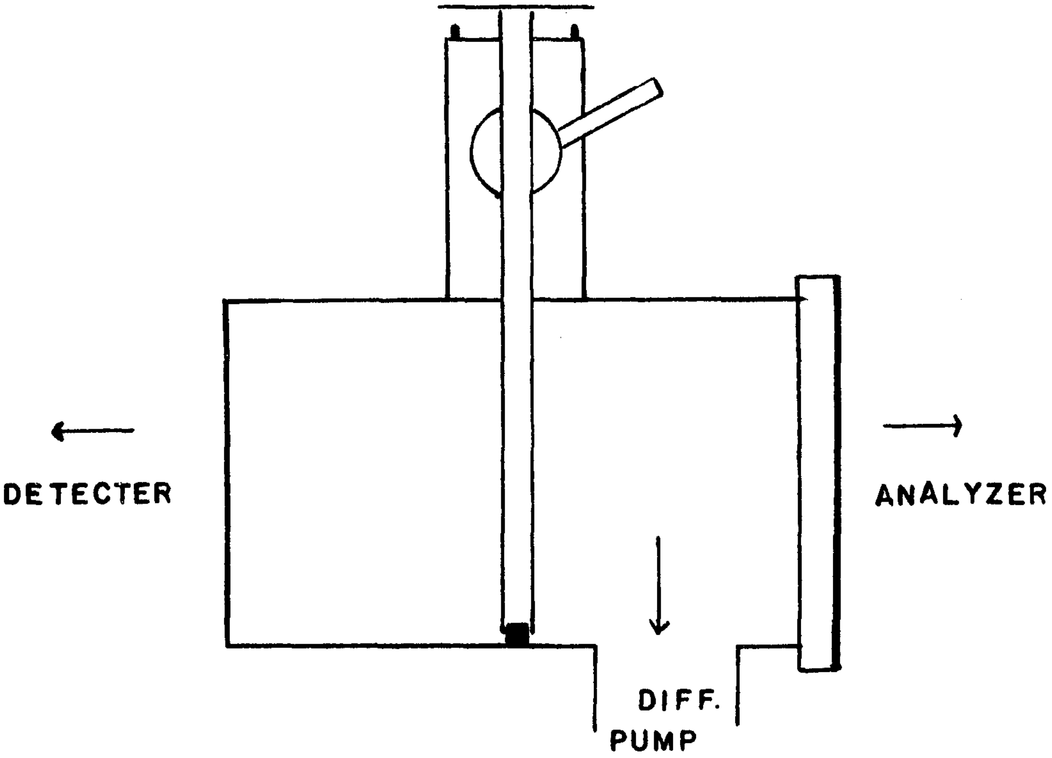

Fig. 7 - Sample chamber adapter

An alternative and somewhat simpler design can also be considered for electron impact experiments utilizing the PS-16. This involves having the electron beam interact with the sample before sending it through the KE analyzer. This design eliminates the necessity of having an additional compartment for the introduction of the sample , which can now be introduced in the same manner as it was for PES measurements using the probe with two slits described above. However, in this design the collision chamber is adjacent to the electron gun compartment, which has to be pumped differentially in order to eliminate the possibility of burning out the filament at elevated pressures. Although one does not expect to get as good a resolution with this design compared to previous one , the spectrum obtained should be respectable.

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CHAPTER 2

FRONTIER ORBITALS AND CHEMICAL REACTIVITY

Qualitative molecular orbital theory has become a very powerful tool for organic chemists especially since the introduction of the Woodward-Hoffman rules. More recently, quantitative molecular orbital theory has been utilized in probing other aspects of reactivity besides the simple "allowedness" of reactions. This work is based on the perturbation treatment of molecular orbital theory and was first introduced by Coulson and Longuet-Higgins (1); it is also known as the frontier orbital theory of Fukui (2).

Earlier theories on reactivity concerned themselves mainly with the product-like character of the transition state. The frontier orbital theory, however looks at how the orbitals of the initial reactants influence the energy of the transition state. Although one could not have direct knowledge of the extent of orbital interaction in the transition state, the energy of the transition state can be estimated from the initial slope of the energy curve (Fig. 1). Therefore the initial stages of the orbital interaction can be taken as indicative of the situation in the transition state. Both the new and the the old theories are important and should be considered complementary to each other if a full understanding of the factors underlying chemical reactivity is desired.

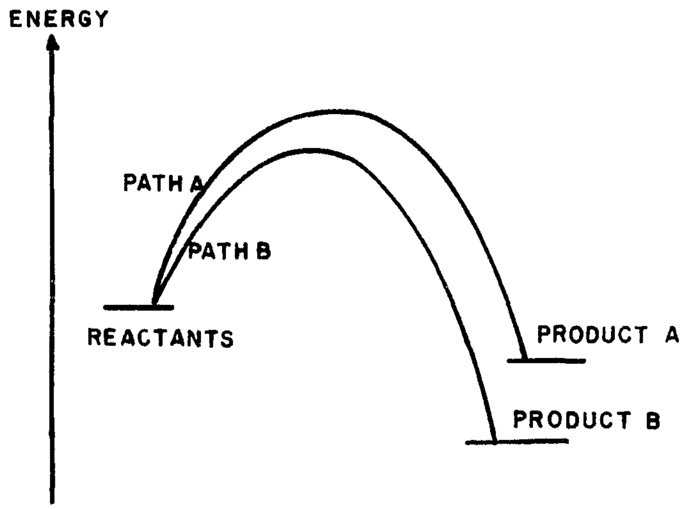


Fig. 1 - Energy along two possible reaction coordinates

In order to understand chemical reactivity from the perspective of the frontier orbital theory, one would have to consider two molecules which will react by a simple one step mechanism. Obviously, as the molecules approach each other their valence shell orbitals are perturbed. This perturbation of the orbitals will result in bonding and antibonding types of interactions much in the same way as atomic orbitls interact to form MO's. As the two molecules approach each other the first order interactions will be between their filled orbitals. Interactions of the unfilled orbitals will also occur, but as there are no electrons in these orbitals their interaction will have no effect on the energy of the system. Formation of bonding orbitals is a favorable process (exothermic), whereas the formation of antibonding orbitals is a unfavorable process (endothermic); however, the energies involved in these two processes are not equal. In fact, the destabilization effect due to antibonding interactions is always greater than the stabilization due to bonding interactions, E* > E . To understand this, let us consider the bonding and antibonding interactions of the hydrogen 1s orbitals to form the MO's in H_2 (Fig. 2). In the absence of any electrons both E and E* will be equal; however,if a pair of electrons are placed in either the sigma or both the sigma and the sigma* orbitals, the energies of the orbitals involved will be raised due to the destabilization introduced by the electron-electron repulsions. This will undoubtedly make E* greater than E, which will in turn make the overall interaction process an unfavorable one if both the sigma and the sigma* orbitals are filled. This is the reason why He atoms do not combine to form He_2. It is this net increase in the energy of the

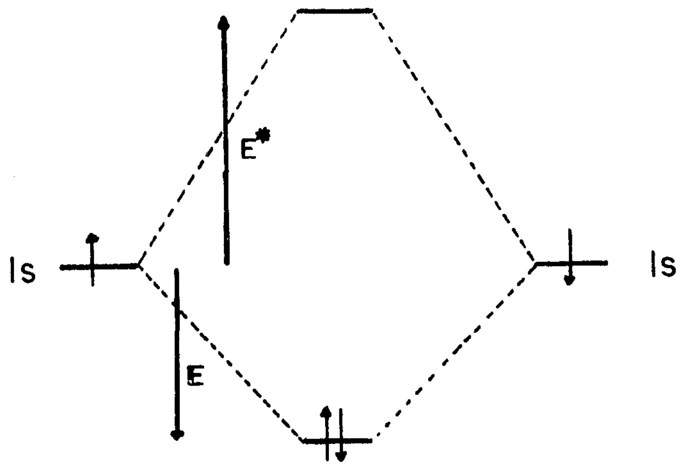


Fig. 2 - Orbitals of hydrogen.

interacted system(due to the interaction of the filled orbitals) that gives rise in part to the activation energy in many systems.

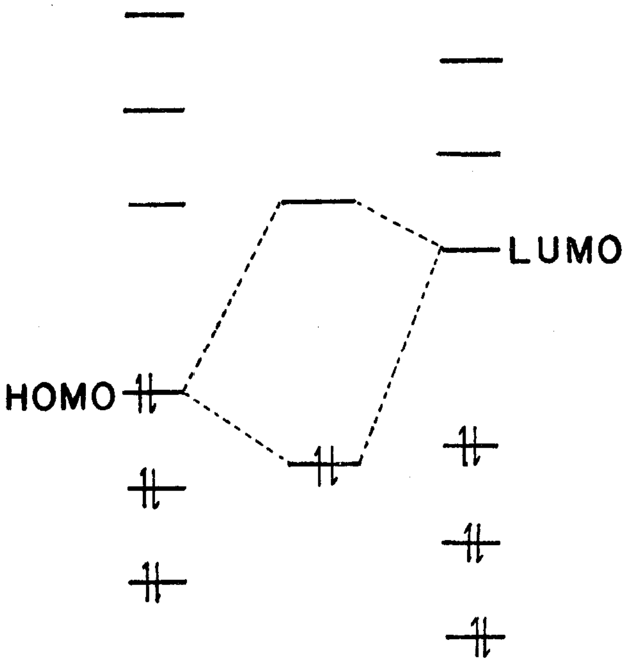
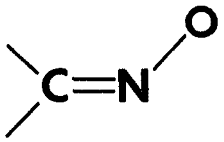


Fig. 3 - The interaction of HOMO of one molecule with LUMO of another.

The interactions which have the effect of lowering the energy of the transition state are the ones betwen the filled orbitals of one molecule with the unfilled orbitals of the other (Fig.3). Here the bonding combinations of the orbitals will contribute to the lowering of the activation energy, and the antibonding combinations will have no effect on the energy of the system, since there are no electrons occupying these orbitals. These interactions are generally of secondary importance because of the larger energy separation between the filled orbitals of one molecule and the unfilled orbitals of another. However the greatest of all such interactions will be the ones between the HOMO of one molecule and the LUMO of another, since the splitting of these levels is the smallest. These HOMO-LUMO interactions are, therefore, very important because of their contribution to the lowering of the transition state energy.

In view of all these facts, it follows that all other conditions being the same, the smaller this HOMO-LUMO separation is, the more favorable the reaction process will be. Thus, a method of measuring these orbital energies will be of great help in probing relative reactivities of molecules. One such method is photoelectron spectroscopy (PES), which is the only direct method of measuring valence shell orbital energies. Much work is also being done in developing a technique of measuring unfilled orbital energies (see Chapter one). Ideally one would like to be able to correlate HOMO-LUMO separation with reactivities of chemical systems; however, this is not always possible due to the lack of data on LUMO energy levels. Instead one could correlate only the HOMO energies with reactivity if one of the reacting species is unchanged throughout the study. By keeping the LUMO energy constant, the HOMO-LUMO separation would be proportional to the energy of the HOMO itself, the higher the HOMO energy, the smaller will be the HOMO-LUMO splitting and the more favorable the reaction process will be.

So far, only the influence of the HOMO-LUMO splitting on chemical reactivity has been discussed. There are obviously other factors that will influence reactivity as well as the selectivity of the reactive sites. Among these factors are coulombic forces, which, for example, favor reactions between polar species over nonpolar ones. Other factors such as relative strengths of bonds being broken and formed, disturbances in conjugation, entropy considerations, steric effects, solvent effects etc. are not accounted for in the frontier orbital theory. Therefore one has to be cautious in applying this theory to systems where the above factors dominate reactivity. In fact, ideally, gas phase reactions would be very suitable for the application of this theory, although one can still get relatively good results by limiting the application of the frontier orbital theory to systems where the influence of all the other effects on reactivity is kept at a minimum or at a constant level. In our work we intend to apply FMO theory to such systems.



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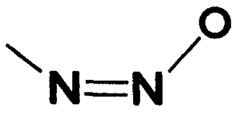
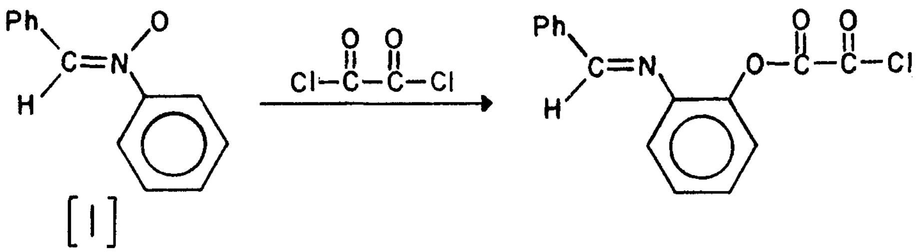


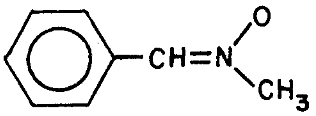
[b]

There has been considerable recent interest in the chemistry of nitrones [a] and azoxy compounds [b]. In this work an attempt will be described to use photoelectron spectroscopy to probe the effects of substituents on particular reactions of these systems, with a view of modifying structure to increase reactivity. For nitrones two kinds of reactions have been explored in this project; (a) 1,3 dipolar cycloadditions (3), and (b) ortho substitution reactions of N-aryl nitrones with certain acid and aryl halides and other reagents (4). One example of the latter type is the reaction of alpha,N-diphenylnitrone [1] with oxalyl chloride (equation 1). While nitrones undergo these reactions, (a) and (b), with relative ease, azoxy compounds are essentially inert. It was not until 1973 that the first report of a 1,3-dipolarcycloaddition reaction of an azoxy compound (benzo[c]cinnoline-N-oxide [7] with dimethylacetylenedicarboxylate) was made (5). On comparison of a nitrone with a corresponding azoxy compound, the diminished reactivity of the latter in cycloaddition and other similar reactions can be understood qualitatively in terms of the replacement of the methine group in nitrone by the more electronegative nitrogen atom in the azoxy compound. This replacement will tend to stabilize the

(1)



orbitals of an azoxy compound relative to the corresponding nitrone. Quantitatively, such stabilization can be measured by PES. For example comparison of the spectra of alpha,N-diphenylnitrone [1] and azoxybenzene [5] show the first ionization potential of the latter to exceed that of the former by ca. 0.8 eV (Table 1).



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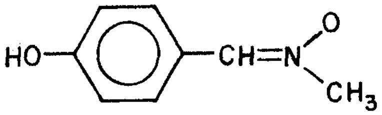

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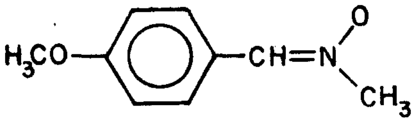

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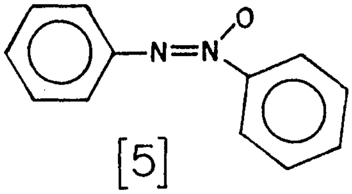

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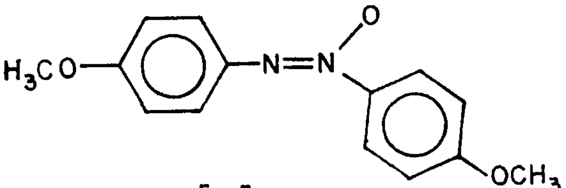

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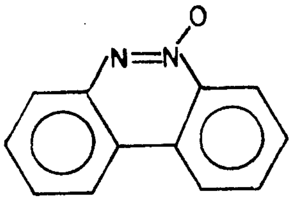


[7]

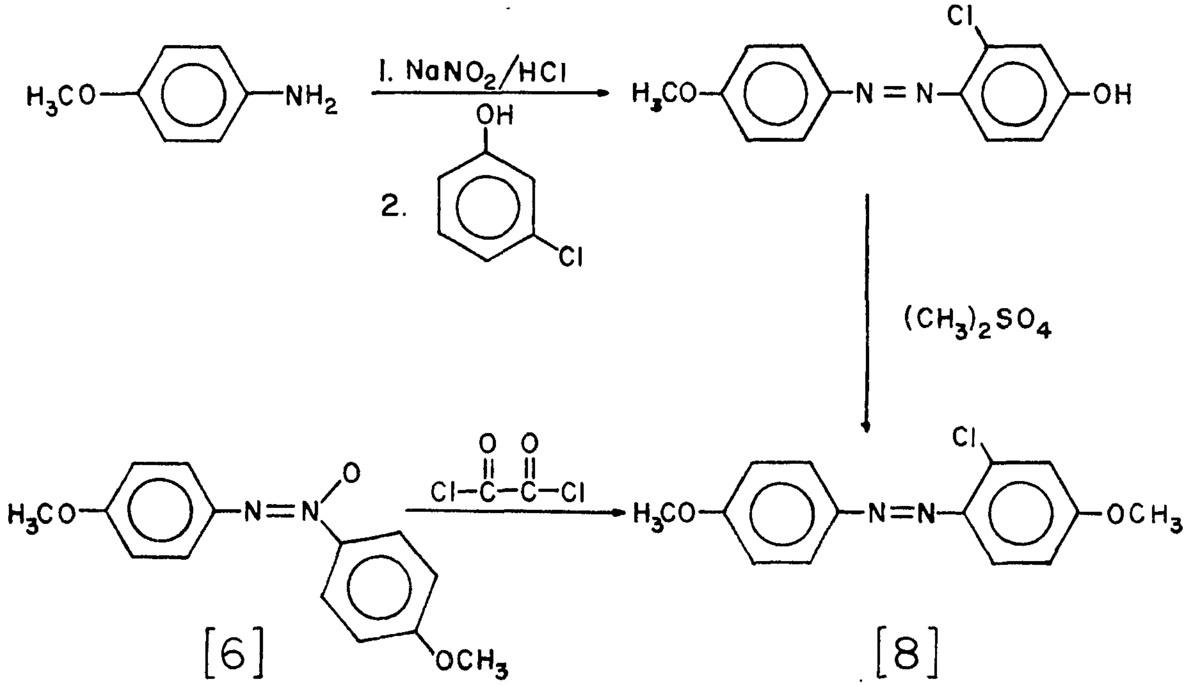
TABLE 1

FIRST IONIZATION POTENTIALS OF SELECTED NITRONES AND AZOXYCOMPOUNDS.

COMPOUND	IONIZATION POTENTIAL (eV)
[1]	7.75
[2]	8.01
[3]	7.76
[4]	7.60
[5]	8.55
[6]	8.00
[7]	8.10

The first IP of the phenyl 1,3-dipoles relates to the HOMO orbital ($\pi 4b_1$) which is localized partly on the oxygen atom (6). From the results obtained for compounds 3 and 4 in Table 1 one can see that significant lowering of the IP (i.e. raising of the HOMO energy) can be achieved by the introduction of a para -OH or $-OCH_3$ substituent in the phenyl ring. For azoxy compounds it is, therefore, to be expected that a corresponding HOMO destabilization should be observed if appropriate -OH or $-OCH_3$ groups are introduced. The objectives in this work were to verify this prediction and to find out if enhanced reactivity might accompany such raising of HOMO energy. In addition an attempt is made to account for the reactivity of benzo[c]cinnoline-N-oxide in 1,3 dipolar reactions. The IP's of compounds 5 and 6 show that the expected HOMO destabilization was observed upon the substitution of the proper groups in azoxy compounds. To see if this destabilization is accompanied with an increase in reactivity, pertinent reactions were run.

Dichloromethane solutions of azoxybenzene and of azoxyanisole [6] were mixed in separate experiments with oxalyl chloride. Azoxybenzene showed no reaction even after several hours, while a deep red coloration appeared immediately upon the addition of the oxalyl chloride to azoxyanisole. Upon work up, an orange product, mp 94-96°was isolated. Mass spectrometry of the product showed it contained one chlorine atom per molecule and had a molecular weight of 276 (M^{+2} at 278). The position of the chlorine atom was determined by an independent synthesis :



The yield of [8] from [6] was essentially quantitative . Thus the reactivity of azoxybenzene towards oxalyl chloride is dramatically enhanced by the introduction of para $-OCH_3$ groups. Increased reactivity was observed towards phosgene, thionyl chloride, and ethyl oxalyl chloride (azoxybenzene itself is inert to all these reagents). However, it was suprising that oxalyl chloride yields a different product with azoxyanisole than with N-aryl nitrones, giving ortho-chlorination rather than the formation of an ortho-chloroglyoxalate (equation 1). Ethyl oxalyl chloride in reaction with azoxyanisole also gives [8] in low yield, indicating Cl^- may be the chlorinating species. To further verify our prediction that the HOMO energy levels can be correlated with reactivity in azoxy compounds we have measured the HOMO energy level in benzo[c]cinnoline-N-oxide. The first IP of this compound is 8.10 eV. This value is appreciably lower than that reported for azoxybenzene, perhaps because of the locking in of the conformation in [7]. This low value for the first IP is consistent with the observed capability of benzo[c]cinnoline-N-oxide to undergo 1,3-dipolar addition reactions as do nitrones.

We believe that the application of the frontier orbital theory in comparing the reactivities of nitrones with azoxy compounds is especially appropriate ; since the structures of these compounds are so similar, changes in other factors influencing reactivity are kept at a minimum. The results also show the real possibility of using photoelectron spectroscopy to help design molecules that will react in a new and useful fashion.

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CHAPTER 3

PHOTOELECTRON SPECTRA OF SELENIUM COMPOUNDS. THE EFFECT OF CONFORMATION ON THE INTERACTIONS OF THE SELENIUM LONE PAIRS WITH ADJACENT PI SYSTEMS

INTRODUCTION

In certain cases, it is possible to use ultraviolet photoelectron spectroscopy (UPS or PES) to study conformational problems, and this represents a most useful organic application of the technique. One class of compounds amenable to such studies are organic derivatives of the elements of Group VIA. The spectra of certain of these compounds e.g. peroxides and disulphides (1,2), provide information on dihedral angles, while the spectra of others, e.g. thioanisole (3), have previously been interpreted in terms of two rotomeric forms in equilibrium with each other. In this section a brief review of existing work is presented, followed by a study on the related selenium and diselenium systems.

For the systems described above, conformational information is obtained from studies of the interaction of heteroatom lone pair orbitals either with other lone pair orbitals or with pi orbitals. Conclusions are based on the usual criteria that the degree of any such through-space interaction depends on the energy gap between the interacting orbitals, the distance between the centers of interaction, and their relative orientations.

In the case of peroxides, disulphides, and diselenides, the two highest energy (lowest IP) orbitals arise from bonding and antibonding combinations of the heteroatom p-orbitals (4). Differing energy splittings between the pi and pi* orbitals for peroxides and disulphides (2), have been interpreted in terms of differing dihedral angles. Particularly useful in the interpretation of such effects are Walsh diagrams (5) which display orbital energies as a function of dihedral angle. Walsh diagrams for some disulphides and peroxides appear in a previous paper by Kimura et al. (2,6).

Of course in reality, no molecule is locked into one particular conformation with a unique defining dihedral angle. Rather the molecule will have a spectrum of conformations, and the PES spectrum will reflect a weighted mean of all conformations. In the case where there is one well defined energy minimum, there will be a particular dihedral angle characteristic of this minimum. In reality, it is more reasonable to speak of this as the average dihedral angle, such that the molecule will spend most time in conformations with dihedral angle close to this mean value. Naturally any departure from the mean dihedral angle

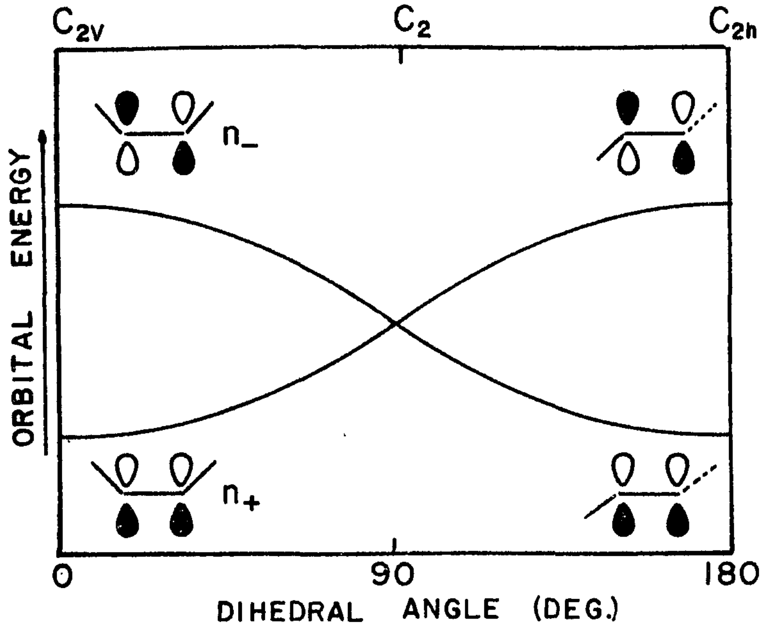


Fig.1 - Qualitative orbital corrolation diagram (Walsh diagram) for Two pure p orbitals on adjacent heteroatoms as a function of dihedral angle.

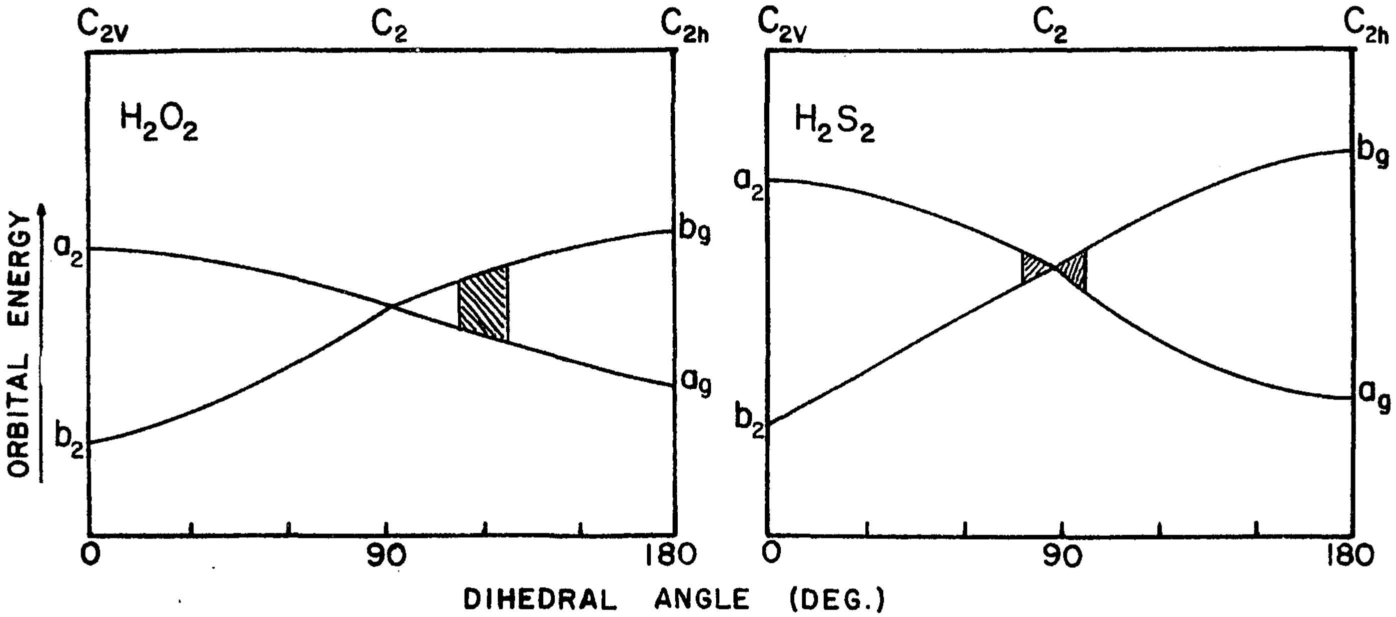


Fig. 2 - Walsh diagrams for H_2O_2 and H_2S_2. The shaded areas designate the regions around the mean dihedral angles where the molecules spend most their time.

will result in strain and the strain energy will be greater in the case of systems under some geometric constraint, such as bridged polycyclic molecules. Considering the case of two pure p-orbitals on adjacent heteroatoms, no interaction is expected if the dihedral angle is 90°, and the Walsh diagram will be of the form shown in Figure 1 (6). Thus, if the mean dihedral angle is close to 90°, only a small splitting is expected betweem the pi and pi* bands in a PES spectrum, as is the case with H_2S_2, while a larger splitting is seen in H_2O_2 with a mean dihedral angle of 120° (see Figure 2) (2) This is an interesting example, since for any given dihedral angle other than 90 degrees there is a greater pi-pi* splitting in H_2S_2 than in H_2O_2.

Wagner and Bock have interpreted the spectra of a series of dialkyl disulphides and 1,2-dithiane (8). The experimental splittings of the first two bands in dimethyl, diethyl and dipropyl disulphides were measured to be in the range of 0.25 eV; however for di-t-butyl disulphide and 1,2-dithiane the splittings were 0.65 and 0.95 eV respectively. Results of the EHMO calculations for 1,2-dithiane gives a splitting of 0.42 eV, and consequently the authors concluded that part of the experimentally observed splitting is due to through bond interactions. However we note that the splitting of the first two bands in $(CH_3CH_2)_2S$ (the open chain analog of 1,2-dithiane) at the same dihedral angle as in 1,2-dithiane is 0.85 eV (8). In light of this, it appears questionable to invoke through bond interactions based solely on the results of EHMO calculations.

Photoelectron spectra of CH_3SH, $(CH_3)_2S$, C_6H_5SH and $C_6H_5CH_3SH$ have been studied in terms of the bonding between carbon and sulfur by Frost, McDowell et.al. (9). Two of the 3p pi orbitals on sulfur participate in sigma bonding and the third with two electrons remains as a lone pair 3p orbital. The first ionization band in the PE spectra of divalent sulfur compounds is assigned to the 3p sulfur orbital unless one of the R groups on a molecule of the type R-S-R possesses an energy level near the energy of the sulfur 3p orbital like in benzenethiol (in selenium compounds this is not a problem since lone pair of the Se is at a lower IP than benzene orbitals).

Ionization potentials reported for H_2S, CH_3SH and $(CH_3)_2S$ are 10.47, 9.44 and 8.67 eV respectively; the shifts observed are mainly due to the sigma inductive effect of the electron donating CH_3 group. In such cases where sulfur is bonded to an alkyl group the interaction of the S lone pair with carbon "p" is very small. However, in benzenethiol where sulfur is attached to the benzene ring there is considerable through space interactions between the S lone pair and benzene pi system.

These deductions have been demonstrated by Frost et.al. in comparing the PES spectrum of benzenethiol with that of toluenethiol. In benzene the lowest IP due to ionization from the pi E_{1g} orbitals is at 9.25 eV (10), while in toluene these orbitals are split into two. Since only one of these orbitals interacts with the substituent, the other, having its node in this position, remains virtually unaffected. In toluene the first IP observed is at 8.81 eV, which represents ionization from the b1 orbital, and the second band at 9.25 eV is due to ionization from an unperturbed a2 orbital (11). Toluenethiol has its first band at 8.85 eV and the second at 9.25 eV (9). There is no appreciable change in IP's going from toluene to toluenethiol, except in the superposition of the sulfur lone pair band with the a2 band of toluene. All these facts point out that there is no overlap between the the S lone pair and the benzene pi system when they are separated by a CH_2 group. In going from benzene to benzenethiol, however, a drastic a change in their spectra is observed. Benzenethiol has three bands in the region below 11 eV; the band at 9.38 e V undoubtedly corresponds to the benzene a2 which does not interact. Bands at 8.28 and 10.65 eV correspond to the + and - combinations of the sulfur lone pair with the b1 orbital of benzene.

Variable temperature studies associated with a spectroscopic tool represent a classical approach to studying conformational problems. Recently Schweig at al. (3). have added PES to the list of spectroscopic techniques that can be used in a variable temperature study. Particularly interesting results were obtained with thioanisole, for which it has been suggested that there is a equilibrium between two predominant conformations , one being essentially planar, and one non-planar. They observed spectral changes on changing the temperature from 20-500°C, which they rationalized in terms of torsional isomerism in the molecule. Although the observed changes in peak intensities seem to have significant meaning in this case, the validity of any quantitative study involving PES peak intensities is generally questionable, since intensities are not necessarily a quantitative measure of electron population in a given orbital. Thus, other ways for probing the torsional isomerism is desirable. Such a study is described in this work.

Dewar et al. (12). have also interpreted the spectra of aryl alkyl ethers and sulfides in terms of their rotomeric forms. In phenol and anisole interaction between the lone pair and aromatic pi system was reported to be at a maximum (planar form). However, in t-butyl phenyl ether and 2,6-disubstituted aryl ethers steric interactions between the ortho groups and the alkyl moiety destabilizes the conformer with maximum p-pi orbital overlap by forcing the alkyl group out of the plane of the benzene ring. In sulfur analogues the same effect is observed through other spectroscopic observations.

In the remainder of this section the spectra of a number of selenium compounds will be considered in light of the above studies and conclusions.

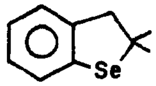
EXPERIMENTAL

Spectra were obtained using the modified Perkin-Elmer PS-16 spectrometer earlier described. Compounds were either comercially available or synthesized.

RESULTS AND CONCLUSIONS

PES data for the compounds studied are summarized in Table 1.

TABLE 1

	COMPOUND	1st IP	2nd IP	3rd IP	4th IP	5th IP
1	$(CH_3)_2Se$	8.38	11.00	12.05	---	---
2	$(CH_3)_2Se_2$	8.54	8.82	10.73	11.76	12.48
3		7.68	8.96	9.80	10.40	11.05
4	$PhSeCH_3$	7.92	8.32	9.30	9.68	10.85
5	PhSePh	7.81	9.26	9.92	10.81	11.27
6	PhSeBz	8.05	8.74	9.27	10.63	11.38
7	BzSeBz	7.96	8.98	9.22	10.50	---
8	PhSeSePh	8.00	8.46	9.28	9.65	11.11
9	BzSeSeBz	8.00	8.24	8.83	9.15	10.44
10	Bz_2Cl_2Se	9.29	9.58	10.94	11.92	12.37
11	BzSeCN	9.41	9.68	11.57	---	---
12	CH_3-S-CH_3	8.68	11.20	12.60	---	---
13	CH_3-S-S-CH_3	8.97	9.21	---	---	---

(A) Dimethyl Selenide and Dimethyldiselenide

Spectra of these compounds are shown in Figure 3. They are similar to the corresponding sulfur compounds. The first IP of the diselenide, 8.54 eV, is actually higher than that of the monoselenide (8.38 eV) despite, the interaction of the Se lone pairs in the former, which destabilizes the HOMO. Apparently the electron withdrawing inductive effect associated with each $-SeCH_3$, which causes a stabilization, dominates over the destabilization caused by interaction of the Se lone pairs. A similar effect is observed on going from Me_3S to Me_3S_2.

(B) Phenylmethylselenide and Related Compounds

The PES spectrum of thioanisole has already been considered in terms of two predominant equilibrated rotomeric forms. Principal evidence for this assignment came from the number of peaks and shoulders in the spectrum, and from variable temperature studies. Interpretation of the spectrum depends on the recognition that, of the two extreme rotomeric forms one is planar with through-space interaction of the heteroatom p- and phenyl pi- orbitals at a maximum, while the other has these orbitals at 90 degrees to each other. The spectrum of phenylmethylselenide[4] (Figure 4a) appears qualitatively similar to that of thoianisole. This suggests that a common explanation for the two spectra is likely. However, features which appear as shoulders in the thioanisole spectrum are actual peaks in

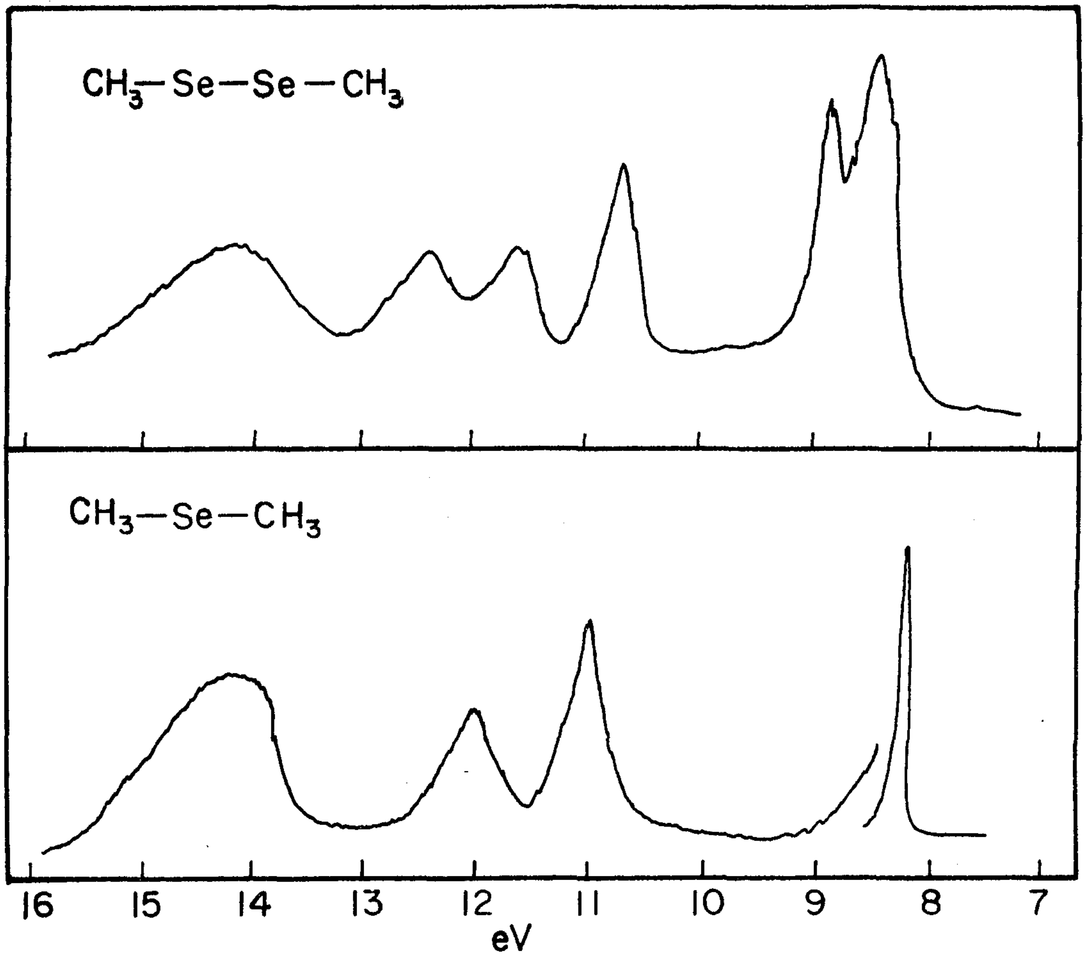


Fig. 3 - Photoelectron spectra of dimethyl selenide and dimethyl diselenide.

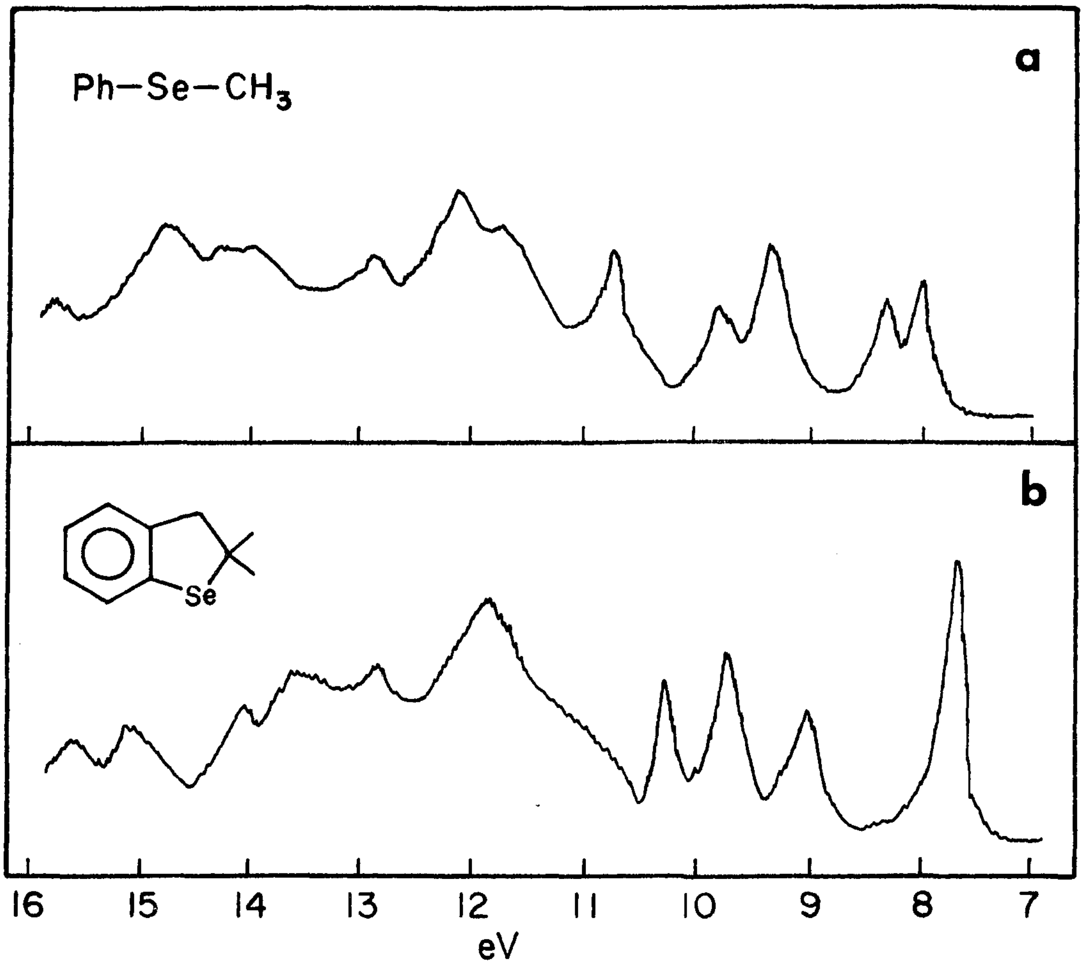
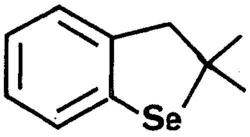


Fig. 4 - Photoelectron spactra of phenylmethyl selenide and compound 3.

the spectrum of phenylmethylselenide, and, accordingly, assignments for the selenium compound can be placed on a surer footing. Wishing to use an alternative to the variable temperature approach to confirm the conformational assignaments, it was decided to investigate the spectrum of compound 3, which, because of geometric factors cannot undergo torsional isomerization.



[3]

Thus, if the conformational arguments already presented were correct, one should find a simplification in the spectrum of [3] (13) compared to that of phenylmethylselenide. Comparison of Figures 4 a and b do indeed show this effect.

Therefore, PES results for [3] can be interpreted as follows. The first band (IP = 7.6 eV), which occurs at the lowest value for any Se derivative studied herein, is predominantly Se 4p lone pair. The second band (IP = 8.96 eV) corresponds to ionization from the non interacting benzene pi orbital, which is destabilized compared to the corresponding orbital in benzene itself owing to the inductive effect of the ring fused onto positions 1 and 2, and the third band (IP = 9.80 eV) is due to the benzene pi-orbital which has interacted with the Se lone pair and thereby become stabilized.

Going back to the more complicated spectrum of phenylmethylselenide, two distinct bands are observed in the region below 8.5 eV, both of which must correspond to ionizations from Se lone pair orbitals. The first band (7.92 eV) must be due to the planar rotomer, while the second (8.32 eV) is assigned to the rotomer that allows no or minimal overlap between the Se lone pair and the benzene pi system. Judging from the relative intensities of the PES bands, the relative intensities of the two rotomeric states are about 1:1. Clearly there must be a significant energy barrier separating the two rotomers, otherwise only one broad Se lone pair peak would have been observed, peaking near the average of the two peaks actually seen.

(C) Dibenzyl, Diphenyl, and Phenylbenzyl Selenides

The first ionization potential of diphenyl selenide [5] is observed at 7.81 eV. Based on this value and on steric considerations, a planar conformation for this molecule is ruled out, since in the planar form a much larger destabilization of the HOMO energy would be expected owing to the interaction of the Se lone pair with the two phenyl pi systems. Another extreme conformation for this molecule is shown in Figure 5, where the Se lone pair interacts with the orbitals of one of the phenyl rings and is orthogonal to the orbitals of the second ring. Although the PES spectrum is not incompatible with this formulation, Figure 5 represents only one of several possible conformations that might also be consistent with the PES spectrum, since there would be a whole range of conformations where the sum of the contributions from each individual phenyl pi system would be equal to the contribution of the single interacting phenyl pi system in the structure showen in Fig. 5. In reality, a weighted average of the spectra of several different contributing rotomers is what is seen.

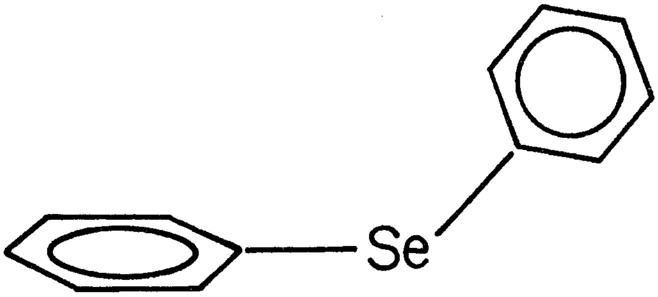


Fig. 5 - An extreme conformation for diphenyl selenide in which the rings are at 90 to each other.

In dibenzylselenide (14) we would not expect any through space interactions between the benzene orbitals and the Se "p" orbital, since such interactions were ruled out in sulfur compounds where the benzene ring is removed from the heteroatom by at least one CH_2 group. Thus, the band due to Se lone pair ionization is moved down to 7.96eV due to sigma inductive effects of the electron donating benzyl group. Such effects seem to be in the order of 0.2 eV for each benzyl group, with respect to methyl groups. Bands at 8.98 eV and 9.22 eV belong to the benzene b1 and a2 orbitals respectively.

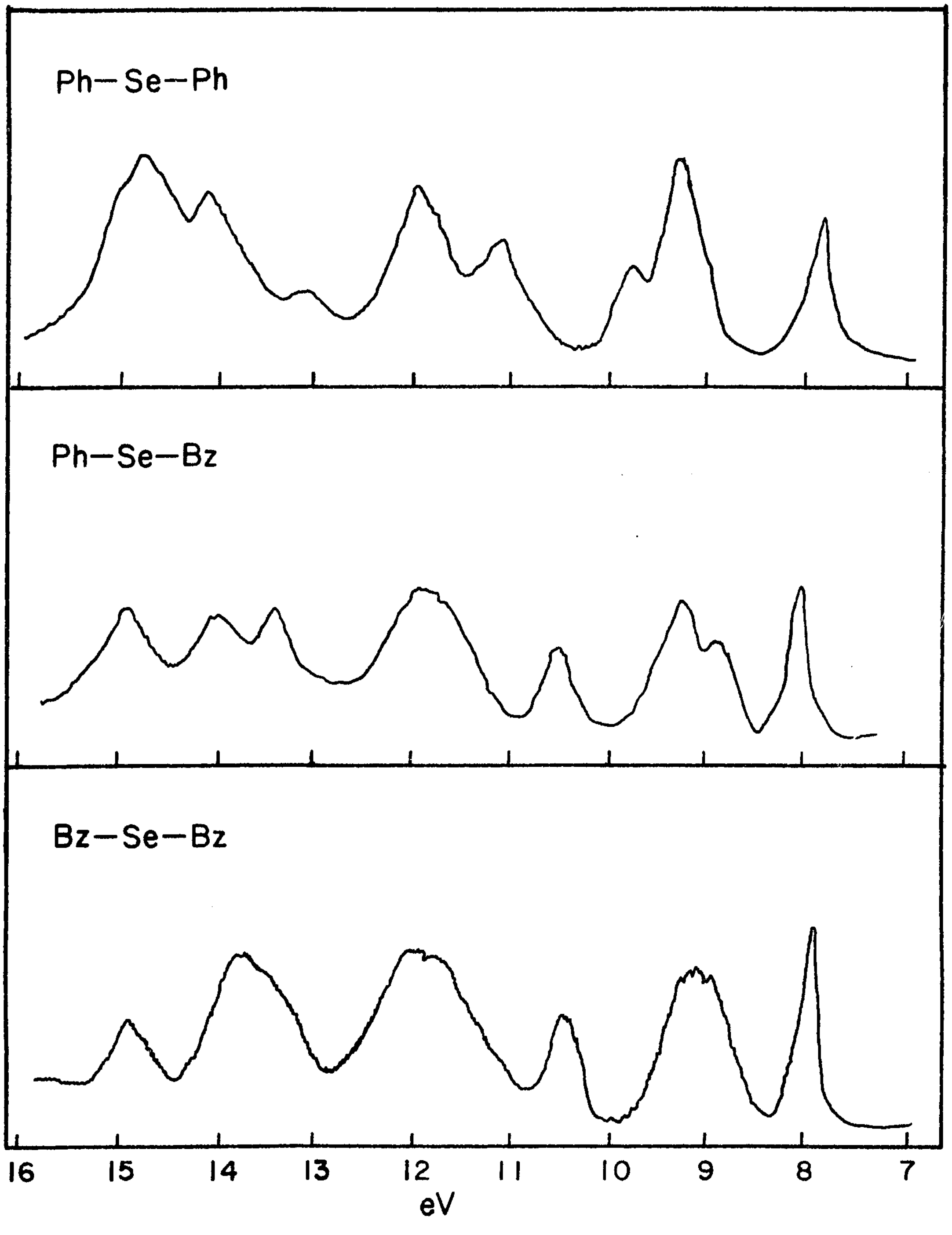


Fig. 6 - Photoelectron spactra of diphenyl, phenylbenzyl and dibenzyl selenides.

Looking at the spectrum of phenylbenzylselenide, there does not seem to be appreciable p-pi interaction since the position of the Se lone pair band at 8.05 eV is mostly accounted for by the inductive effect of the benzyl group. (A larger shift due to p-pi interaction would have been expected if such was allowed by the geometry of the conformer.) Bands at 8.74 eV and 9.27 eV are again due to benzene orbitals, split due to substitution.

(D) Diphenyl Diselenide and Dibenzyl Diselenide

In the interpretation of the spectra of these two compounds dimethyl diselenide has been used as our model system. In dibenzyl diselenide (14) we would not expect any through space interactions between the benzyl pi systems and the Se lone pairs since the two are separated by CH_2 groups. Therefore, the only conjugative interactions will be those of the Se lone pairs with each other. Thus, the spectrum of this compound should be similar to that of dimethyl diselenide except that additional bands are seen as a result of the phenyl rings present. PES results are in accordance with expectations. The first two bands (8.00 and 8.24 eV) originate from + and - combinations of the Se lone pair orbitals, and the bands at 8.83 and 9.15 eV correspond to the HOMO orbitals of the phenyl system, which are split because of methyl substitution as in toluene. Since splittings between the first two bands in dimethyl diselenide and dibenzyl diselenide are 0.24 and 0.28 eV,

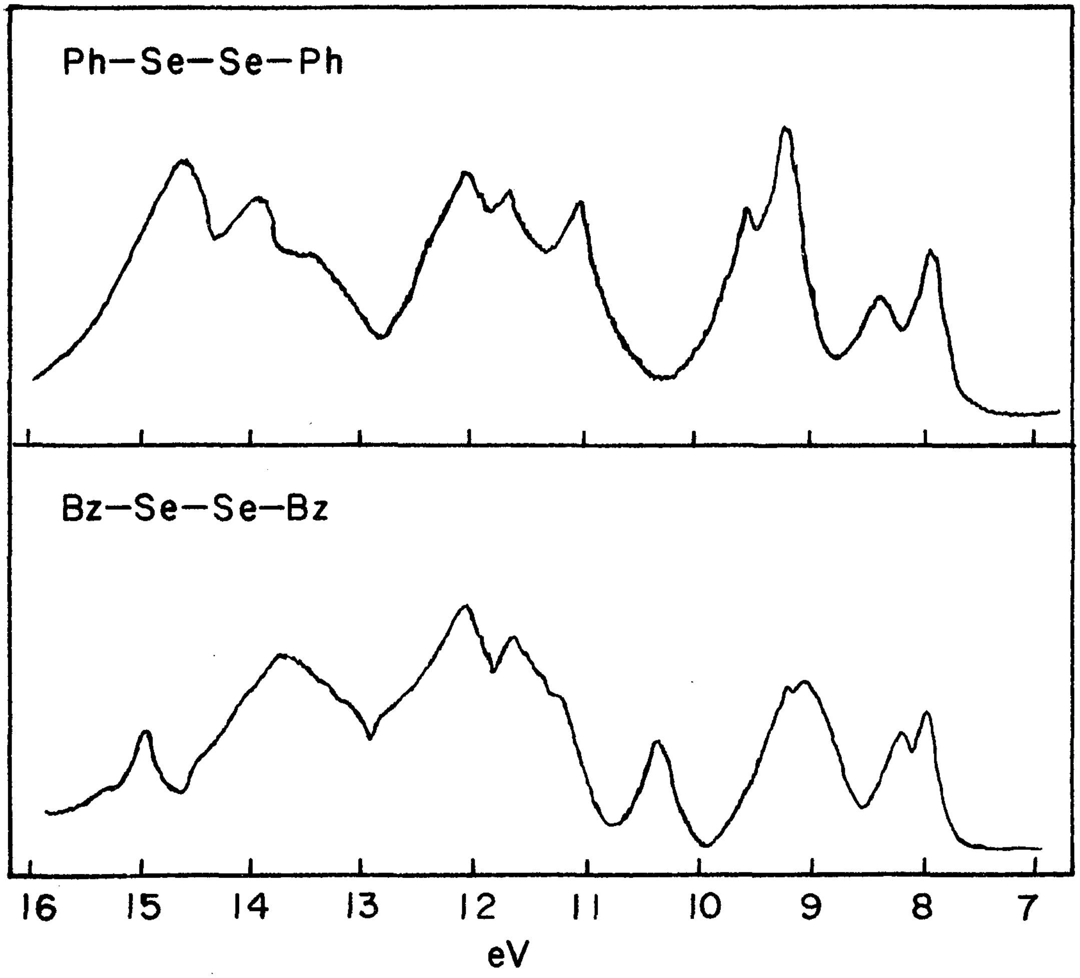


Fig. 7 - Photoelectron spectra of diphenyl and dibenzyl diselenides.

both molecules have similar dihedral angles and, therefore, comparable conformations. The shifts observed in the spectrum of dibenzyl diselenide result from sigma inductive effects of phenyl groups, which are in the order of 0.25 eV.

Interpretation of the spectrum of diphenyl diselenide would appear to pose a greater challenge, in that there are four systems that are potentialy capable of interacting with each other . Nevertheless, the assignments for bands in the spectrum of this compound are made readily. The first two bands again belong to + and - combinations of Se lone pair orbitals. The 9.28 eV band is due to the non-interacting benzene a2 orbitals , and partly to b1 orbitals which are not capable of interacting because of their symmetry (orthogonal to Se lone pair orbitals). The Band at 9.65eV is clearly due to the benzene b1 orbital that interacts with the Se lone pair and is moved down in energy. Splitting between the first two bands in this molecule is determined to be .46 eV from the PES spectrum. This splitting would not be expected to be greatly influenced by interaction with the phenyl pi system, since both of these selenium lone pair like orbitals would be shifted to the same direction (the one closer to the energy of the HOMO of benzene would be effected slightly more). Thus, the dihedral angle for diphenyl diselenide is clearly smaller than in dibenzyl diselenide.

(E) Dichloro Dibenzylselenide and Benzyl Selenocyanate

The interpretation of the spectrum of dichloro dibenzylselenide is simplified because there are no orbitals availible for conjugative interactions. Bands observed at 9.29 and 9.58 eV are due to ionization from benzene a2 and b1 like orbitals, which are slightly stabilized (by about 0.30 eV) with respect to toluene orbitals. The 10.94 eV band is rather sharp and can be assigned to chlorine 3p orbitals which remain virtually unperturbed.

For many thiocyanates detailed UPS characterization of the electronic structure is difficult. In aromatic thiocyanates the ionization energies of the highest occupied benzenoid pi orbitals are close to those of sulfur based "n", and, therefore, the resulting bands have strongly intermixed character and escape detailed one-to-one assignments. This was found to be the case with aromatic selenocyanates. A Selenium lone pair which would ordineraly appear around 8.35 eV in dimethyl selenide is shifted to 9.68 eV in methyl thiocyanate. This indicates the presence of very strong inductive interactions between the CN moiety and the selenium atom, which causes the stabilization of the Se lone pair by more than 1.3 eV despite possible conjugative interactions between the pi of CN and n of Se; the latter would destabilize the Se lone pair orbital. In view of all these facts, the interpretation of the PES results obtained for benzyl selenocyanate can now be made.

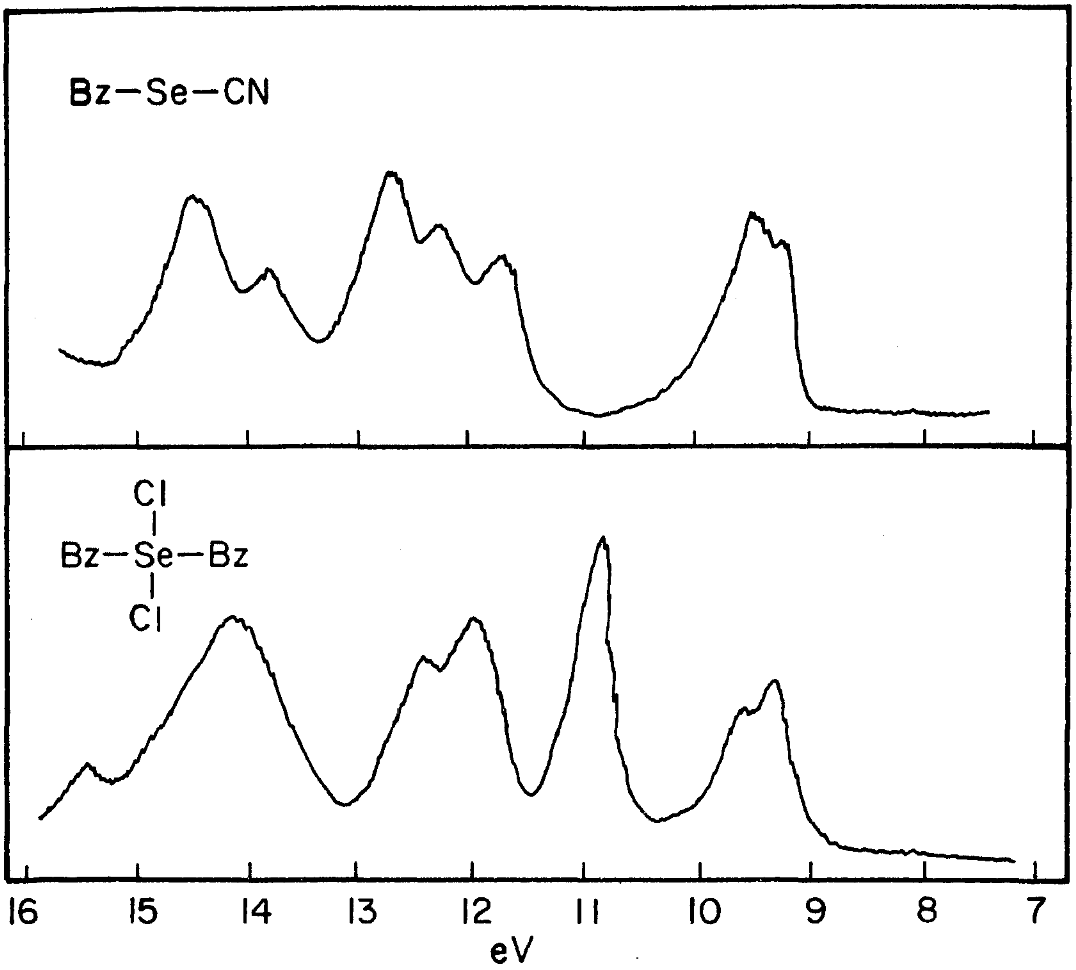


Fig. 8 - Photoelectron spectra of benzyl selenocyanate and dichloro dibenzyl selenide.

In benzyl selenocyanate the only possible conjugative interactions are the ones between the selenium lone pair orbital and CN pi system. Since there is cylindrical orbital symmetry about the CN group, regardless of the conformation of the molecule, the magnitude of the interaction of Se lone pair with CN pi system will be the same. The broad band observed from 9.00 to 9.80 in the PES spectrum is due to the benzene orbitals and to the Se lone pair orbital stabilized by the strong inductive effect of the CN group. Although there are through space interactions between CN and Se orbitals, the magnitude of this is small, since there is a large energy separation between the lone pair orbital of Se and the pi system of CN; therefore, the strong inductive interactions dominate and the Se lone pair is stabilized apprechiably. The peak at 11.57 eV is due to ionization from the cyano group, the position of this peak giving another indication that the magnitude of the through space interactions in this case is expected to be very small.

In conclusion it could be stated that PES of selenium compounds can be assigned on the basis of the spectra of sulfur analogues, provided one takes into account the lower IP of selenium 4p orbitals compared to sulfur 3p orbitals. It is also evidenced that the conformation effects play an important role in determining the details of the spectrum, which must sometimes be interpreted in terms of two or more distinct rotomers.

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CHAPTER 4

CROWN ETHER COMPLEXATION STUDIES USING PES

INTRODUCTION

During the past decade there has been much interest in the complexing of alkali and alkaline earth metal ions with macrocyclic polyethers and the effect of this on ion pair structure in various solvents (1). Because of their strong complexing ability, crown ethers have proved to be extremely important chemical reagents. Typically, crown ethers provide a cavity which can be altered in size and structure to accommodate metal ions, and other polar species of different size and charge. The resulting complexes are of great synthetic interest since enhanced solubilities and reactivities of ionic species in non polar solvents result. For example, by increasing the solubilities of electrolytes in non-polar media, the crown ethers can act as phase transfer catalysts and provide anions in poorly solvated conditions, with concomitant increase in reactivities. The crown ethers are also becoming popular as model compounds in the study of selective transport across membranes, biological or otherwise. The natural selectivity which biological systems show towards Na^+ and K^+ can be paralleled by a series of diverse macrocyclic polyethers. Structural determinations have shown that the main feature by which crown complexes differ from naturally occuring antibiotics that incorporate a cyclic polyether, is that in crown compounds the oxygen atoms are arranged in a plane around the central ion and the axial positions are available for interactions with other molecules or ions. In the naturally occuring antibiotics the central ion can be completely enclosed in a cubical or octahedral environment. This type of complexing is observed in only very large and flexible crown compounds.

Crown ethers have also been of considerable interest in other fields of chemistry such as in solvent extraction and isotope separation, and a wide variety of other uses are being discovered for these compounds as more information is gathered on their structure as well as chemical properties. The crown ethers derive their strong complexing ability from their arrays of oxygen atoms , and their selectivity for different metal ions is thought to be derived primarily from the size of the ring cavity which must match the size of the cation. Although for the most part, M-macrocycle (M=metal) systems have been discussed in terms of cavity size of the macrocycle and the radius of the cation, recently attempts have been made to explain these systems in terms of the charge density of the cations and the conformation of the ligand. There have also been attempts to explain the stability of the cationic complexes of macrocycles in terms of the effect of the counter-anion (2). According to this argument, the stability of the complex increases with diminishing basicity of the anion. The aim of the work herein has been to explore the electronic structures of crown ethers and related compounds, using photoelectron spectroscopy and M.O. calculations. It is hoped to show tnat such considerations can be quite important in obtaining a full understanding of the complexing abilities of these compounds. Some new explanations for aspects of crown-ether chemistry suggest themselves, based on our findings. To begin this discussion, a brief review is given of the existing work and observations made on crown ether, cryptates and some macrocyclic nitrogen and sulfur complexes.

Most ordinary macrocyclic polyethers are rings of different sizes containing four to 12 oxygen atoms, usually each oxygen atom separated from its neighbor by two carbon atoms. A large number of these compounds have been prepared for use as ligands for group IA cations (M^+). These systems have been thoroughly studied in solution and in the solid state. Group IIA cationic complexes of cyclic polyethers, however, were relatively less known until recently, when complexing between the crowns and magnesium and calcium was discovered (3,4). Nevertheless, a few crown-M^{+2} systems are well defined compounds. In some cases the difficulty of complexation in M^{+2} systems has been attributed to the strong solvation of M^{+2} ions (5), but solution stability data (6) has shown this not to be the predominant factor.

The naming of crown ethers is conventionally formulated as follows: A number, referring to the total number of atoms in the macrocyclic ring is followed by the word crown (or C), which in turn is followed by a second number referring to the number of oxygens in the ring (e.g. 18C6 refers to a 18 membered macrocyclic ring containing 6 oxygens).

Among group IA elements, it is known that Li^+ is the best for complexation with the 14C4 system, Na^+ for 15C5 system and K^+ for 18C6 (7). On the other hand, of all crown ethers synthesized, benzo14C4, benzo15C5, 18C6 and dibenzo18C6 have been found to be the best ligands among the small to medium sized macrocycles, for both alkali and alkaline earth cations (8). Comparison of the stability data for 18C6-K^+ , 15C5-Na^+ and 14C4-Li^+ indicates that 18C6-K^+ is the most stable system of the three (9). This observation cannot be explained simply in terms of the relative values of the ionic radii vs the size of the cavity, since in all three cases we have a good match of ion-size to ligand cavity. Therefore, it is clear that other factors must also be considered in determining the formation and the relative stabilities of crown-M systems.

In order for complexation to occur, the crown ligand must compete successfully with other molecules present in the solution, including the solvent molecules. "Hard-soft" acid/base rationalizaions can be used to discuss relative stabilities of complexes in certain cases. For example, it has been observed that highly charged actinide ions display a striking preference for ligands in which the oxygen sites are polar and hard, such as H_2O and NO_3^- (10). The presence of such ligands in the medium provides an unfavorable situation with respect to crown ether complexation. Avoidance of such conditions, therefore, enhances crown complex formation for these metal ions.

It is believed that through variation of molecular parameters such as dipole moment, polarizibility of the binding sites, and the van der Waals radii of the ligand atoms, interaction selectivity may be influenced considerably . Calculations (11) done on complexes of hypothetical molecules with cations indicate that an increase in the dipole moment (and/or the polarizibility) together with a decrease in the radius of the ligand atoms leads to an increase in the stability of the complex. The results can be summarized in terms of small and polar binding sites that generally prefer metal ions such as Ca^{+2} over Na^+ and Ba^{+2}. This of course applies to situations where other effects such as solvent or anion-cation interactions do not overwhelm these effects. (Ideally the results would be most applicable to gas phase systems.) In calculations of hypothetical systems, it is possible to vary one of the parameters and keep all the others constant, but in real systems one can not do this. Therefore, an experimental method which gives an indication of some of the above parameters would be most helpful. As described in the next section PES studies of crown ethers and realated compounds provide a correlation with the polarizibilities of the oxygen sites, and it is demonstrated how this can be used to predict stabilities of complexes and explain the already observed trends.

In addition, PES studies can be used to explain the effects of the substituents on the crown molecules. For example, why is it that the complexes of benzo15C5 are more stable than those of 15C5, and why is there little difference between the stabilities of complexes of 18C6 and dibenzo18C6?

EXPERIMENTAL

The saturated compounds are colorless viscous liquids or low melting solids . They are soluble in a variety of solvents, because of their hydrophilic interior and hydrophobic exterior. A good number of these compounds dissolve in water as well as in petroleum ether. Aromatic macrocyclic polyethers, on the other hand, are colorless crystalline compounds and their solubility decreases with an increasing number of aromatic rings. Those with two aromatic rings are nearly insoluble or very slightly soluble in polar solvents, but they readily dissolve in most non-polar organic solvents.

A point should be made about the toxicity of the crown compounds. Although all of the facts about the physiological effects of crowns are not yet known, it is almost certain that fatality results if prolonged and/or excessive ingestion occurs (12). Therefore , utmost caution should be excersized in the handling of all crowns , and contact with skin and inhalation of vapors should be especially avoided.

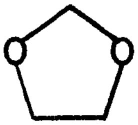
Some of the compounds used in our experiments have been synthesized by Prof. Charles Liotta and his associates at Georgia Tech , and the rest have been purchased from PCR Research Chemicals Inc.

We have run the PES of some 17 crown and other macrocycles, along with three open chain polyethers. The spectra were obtained with the modified Perkin Elmer PS16 equipped with a temperature controlled cooling system, as described earlier in this thesis. All twenty compounds studied appeared to be thermally stable at moderately high temperatures. All the spectra were obtained using a heated probe at temperatures ranging from 70° to 150° C. Most saturated crowns sublimed 20-30 degrees below their normal melting point; aromatic macrocyles had to be heated near their normal melting point to record the PE spectrum.

RESULTS AND DISCUSSION

It is appropriate to begin by considering the spectra of relatively small ring compounds containing two or more heteroatoms. Spectra for five and six membered cyclic compounds containing oxygen or sulfur atoms can be interpreted in terms of through-bond or through-space interactions of the lone pair p-orbitals located on the heteroatoms (13,14). Table 1 summarizes I.P. data. In these molecules lone pair orbitals are the highest in energy of the filled molecular orbitals. To probe the mechanism by which lone pair orbitals interact in oxygen and sulfur systems it is instructive to compare the splittings of the highest two levels in compounds in which the positions of the heteroatoms and the size of the ring are systematically altered.

The photoelectron spectrum showed that the splitting in 1,3-dioxolane [1] was .55 eV . This rather large splitting can not be accounted for in terms of through space interactions alone, especially since a splitting of only 0.25 eV is seen for 1,3-dioxane, the geometry of which is more favorable for such through-space interactions. Turner (14) looked for a through-bond mechanism to explain the large splitting in 1,3-dioxolane. To investigate this he divided the sigma orbital network into orbitals localized between the ring carbon and oxygen atoms and into orbitals localized along C-H bonds. He then determined that C-H localized orbitals of "a" symmetry interact with the lone pair "a" orbital to produce the rather large splitting observed between the first two peaks in the spectrum of 1,3 dioxolane (Fig. 1). In 1,3-dioxane, on the other hand, the overlap is not as good because the C-H bonds, through which the interaction occurs, are staggered with respect to the lone pair p orbitals and, therefore, measured splitting is much less.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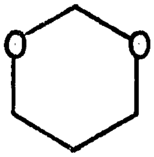
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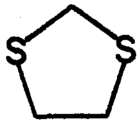
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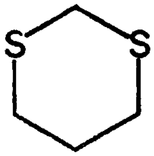
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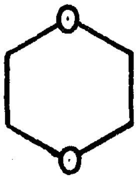
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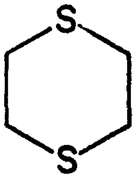
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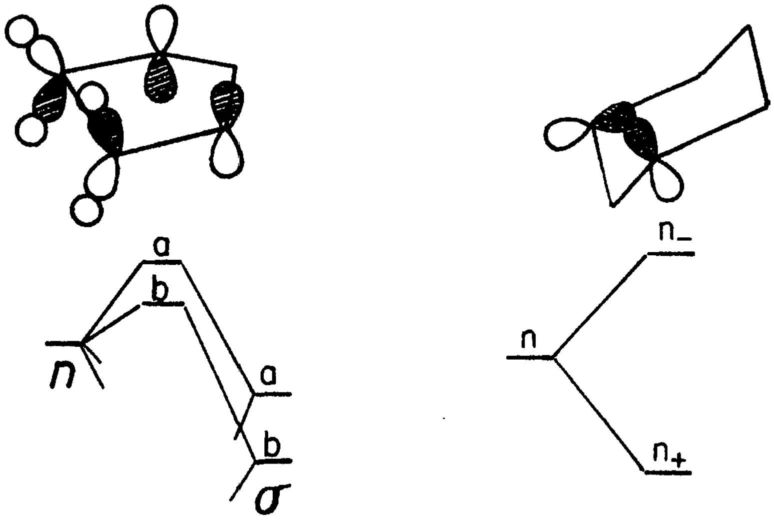


Fig. 1 - The splitting of the lone pairs in 1,3-dioxalane and 1,3-dioxane.

TABLE 1

LONE PAIR IP'S IN SOME OXYGEN AND SULFUR HETEROCYCLES

COMPOUND	1st IP	2nd IP	D(IP2-IP1)
[1] 1,3-dioxolane	10.10	10.65	0.55
[2] 1,3-dioxane	10.10	10.35	0.25
[3] 1,3-dithiolane	8.75	9.05	0.30
[4] 1,3-dithiane	8.54	8.95	0.41
[5] 1,4-dioxane	9.43	10.65	1.22
[6] 1,4-dithiane	8.58	9.03	0.45

In the sulfur analogs of the above two compounds just the opposite trend is observed. Because of more diffused sulfur 3p orbitals here, through-space interactions have become more pronounced. In addition, through-bond interactions in the sulfur compounds are small or nonexistent owing to the relatively large energy separation between the sulfur 3p and the sigma orbitals. In earlier work from this laboratory, it was shown that the values for the splittings of the first two peaks in the spectra of 1,3 dithiolane and 1,3-dithiane are, respectively, 0.30 and 0.41 eV.

The photoelectron spectra of 1,4-dioxane and 1,4-dithiane show splittings of 1.22 and .45 eV. This provides further proof of the dominance of the through-bond over through-space interactions in oxygen heterocycles. Both of these molecules are known to exist in the chair conformation in the gas phase. Since the direct overlap of the lone pair orbitals is unlikely due to geometrical considerations, a through-bond mechanism is needed to explain the large splitting observed in 1,4-dioxane vs the small splitting in 1,4-dithiane. Turner suggested (14) that the through bond interactions are possible here with the intermediacy of the C-C sigma orbitals and not the C-H orbitals, since in the chair conformation of the molecule these bonds are staggered (Fig. 2).

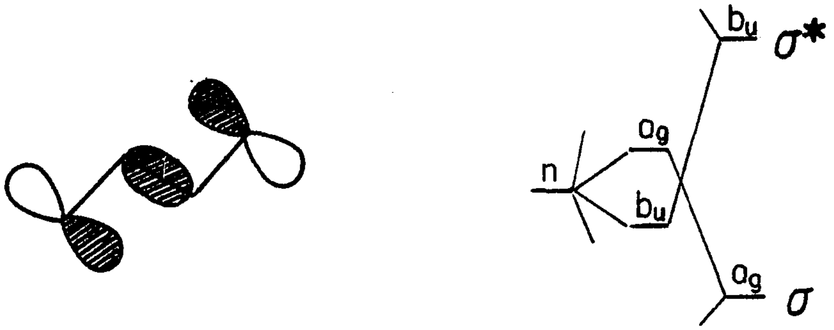


Fig. 2 - The splitting of the lone pair orbitals in 1,4-dioxane and 1,4-dithiane.

In view of the above results, it would be safe to conclude that the intermediacy of the C-C sigma bonds leads to a more effective through-bond interaction than that of the C-H sigma bonds, since the splitting observed in the former case is much larger. We shall now use these observations to help in the interpretation of the photoelectron spectra of oxygen, sulfur and nitrogen macrocycles.

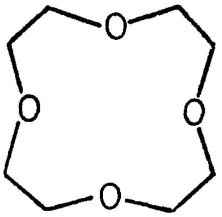
Since crown ethers are generally described as compounds of oxygen in which oxygen atoms are separated from each other with two methylene groups, one can consider 1,4-dioxane the simplest prototype crown ether and, as such, a possible model for explaining the kinds of orbital interactions that can occur. A particularly notable characteristic of 1,4-dioxane is its low ionization potential, 9.4 eV; ordinary ethers have their first IP at around 10 eV. This low IP is of course due to the extensive through-bond interactions just discussed in connection to this molecule. This trend is even more pronounced in some larger crown ethers, as shall be seen from the photoelectron spectral results obtained.

(A) Photoelectron Spectra of Dimethoxyethane, Diglyme, Triglyme and 12crown4

An important common characteristic in the PE spectrum of all these compounds is the broadness of the lowest IP band. Usually the highest energy oxygen electrons are essentially nonbonding, and in such cases, the corresponding PE bands are rather sharp. Consequently, the broadness of the lowest IP bands in the spectra of the three open chain polyethers and 12C4 is an indication of extensive interactions of oxygen lone pair orbitals in these molecules. Since molecular models indicate that the direct through-space overlap of the oxygen lone pairs is not likely to be important, the observed broadness of the bands is herein attributed to through-bond interactions. Two different types of through-bond interactions have already been discussed, one with the intermediacy of the C-C sigma bonds and the other with C-H bonds. To pinpoint exactly which mechanism is in effect is an impossibility in the case of the open chain polyethers without the help of more extensive investigation; the extremely flexible structure of these molecules makes this the case. In all probability, however, both of these mechanisms are in operation. Furthermore, the observed bands result from an averaging effect of the interactions in all possible orientations of the molecule. Therefore, in situations where there is good overlap, through-bond interactions would increase with an increase in the rigidity of the molecule. Notably, at least one of the two posible interactions would be enhanced in a rigid molecule.

$CH_3{-}O{-}\left[CH_2{-}CH_2{-}O\right]_n{-}CH_3$

n=1 , DME [7]
n=2 , DIGLYME [8]
n=3 , TRIGLYME [9]



12C4 [10]

TABLE 2

COMPOUND	1st IP	2nd IP	3rd IP	4th IP
[7] DME	9.9 (9.2)	11.70	12.90	-
[8] Diglyme	9.8 (9.0)	-	-	-
[9] Triglyme	9.8 (8.8)	11.50	-	-
[10] 12C4	9.3 (8.6)	9.60	9.90	11.40

Vertical IP's of DME, diglyme and triglyme are all in the neighborhood of 9.8 eV, whereas the adiabatic IP's are 9.2 , 9.0 and 8.8 eV respectively . These results indicate increasing through-bond interactions with an increase in the number of of oxygen atoms. The other bands observed in the spectra of these compounds originate from ionizations from sigma type molecular orbitals, and their assignment is difficult because of the overlap of these bands.

The PE spectrum of 12C4 reveals the presence of even more extensive through-bond interactions in this molecule. The first band in the spectrum of 12C4 is broader than it is in its open chain analogue, triglyme , indicating these interactions are more pronounced in 12C4. Since this molecule is more rigid than triglyme this result is not too suprising. There are four oxygens in 12C4, and the first band should be split into four peaks. Because of the overlapping of bands, only three, hardly identifiable peaks in the first band are observed. From molecular models one can see that C-H through-bond interactions are favored over

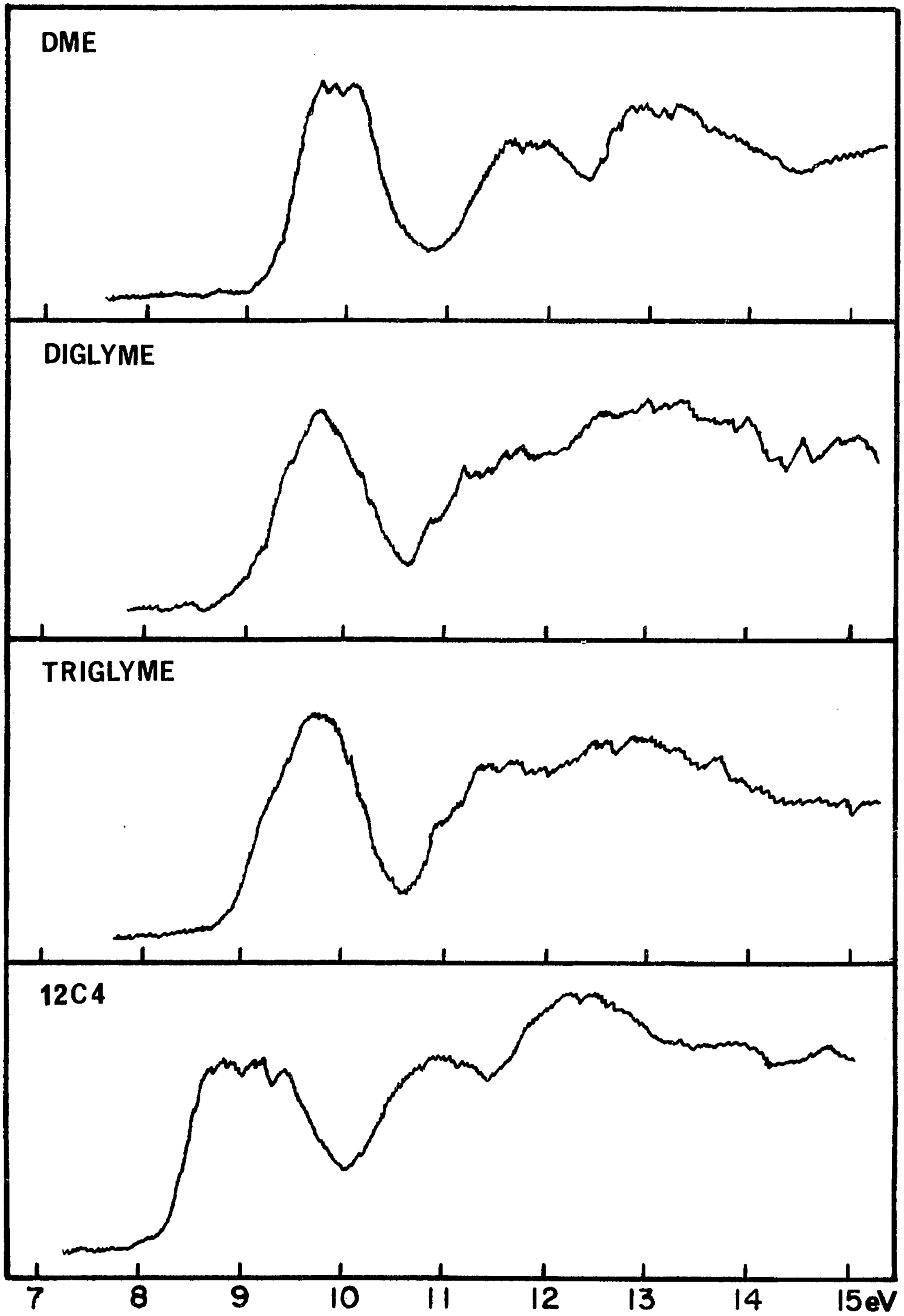


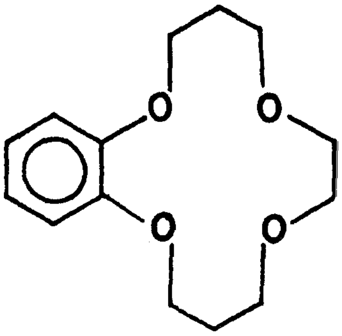
Fig. 3 - Photoelectron spectra of DME, diglyme, triglyme and 12C4.

C-C ones, and, therefore, the former provides the primary mechanism responsible for lone pair interactions. The adiabatic IP is observed at 8.6 eV, and the first band is split into three components with peaks at 9.25, 9.60 and 9.90 eV. In view of this data alone, indicating a relatively small splitting for the oxygen peaks, it can be concluded that the mechanism of the through - bond interactions is most likely via C-H bonds. A much larger splitting would have been expected in the case of C-C through-bond interactions, as was the case in 1,4-dioxane where the splitting is in the order of 1.2 eV.

(B) Photoelectron Spectra of Cyclohexo14C4, Benzo14C4, 15C5 and Benzo15C5

The PE spectra of cyclohexo14C4 and 15C5 are very similar, and both resemble the spectrum of 12C4, except that the first bands in the spectra of the former two are much smoother. The first bands in all three are equally broad, and one might assume similar interactions operate in all three cases. The IP of the first band in CY14C4 is 9.3 eV, whereas that of 15C5 is 9.60 eV. The difference can be attributed to the strong electron donating effect of the cyclohexyl ring on the 14-membered crown, which would raise the energy of the highest MO, thus lowering its IP.

Upon the introduction of a benzene system into the crown ring, the first IP decreases drastically. The first band observed in the spectra of B15C5 and B14C4 are at 8.00 and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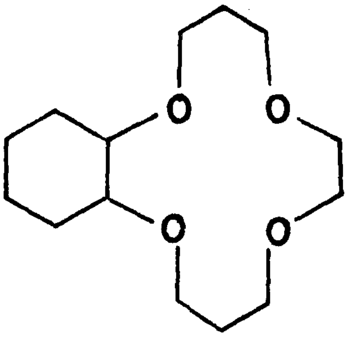
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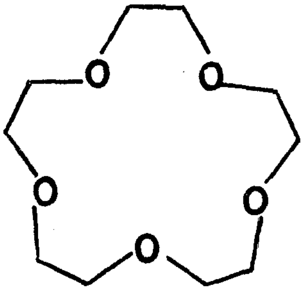
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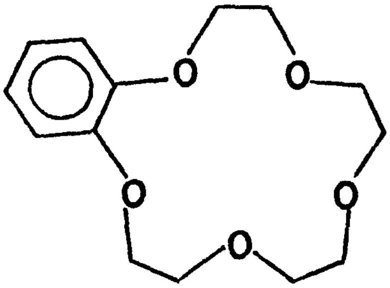
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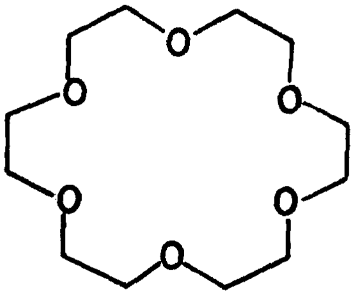
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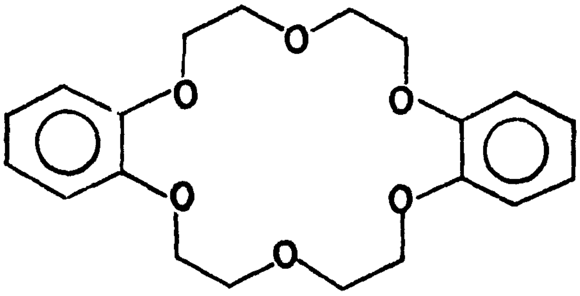
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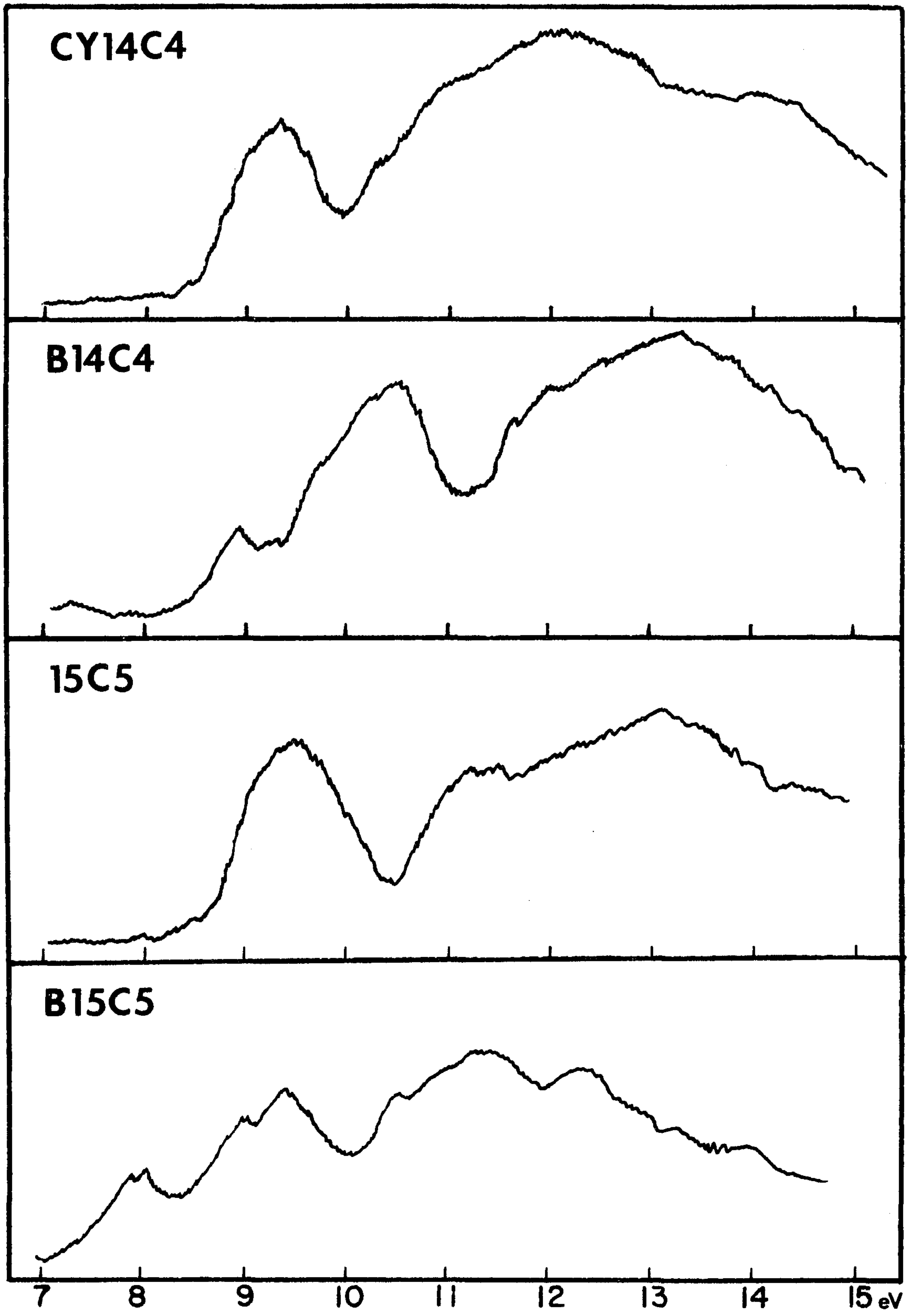


Fig. 4 - Photoelectron spectra of cyclohexo14crown4, benzo14crown4, 15crown5 and benzo 15crown5.

8.05 eV. Assignments made here will apply to both compounds because of the similarity in their structures. The first band in both compounds can be assigned to molecular orbitals that would be formed from the - combinations of the benzene-pi and oxygen-lone pair orbitals. Since the initial energies of the uninteracted orbitals are very similar, this MO would be localized on the benzene ring, and to an almost equal extent, on the oxygen atoms adjacent to the ring. One can see this from the qualitative MO diagram in Fig. 3. The second band observed in each of the spectra corresponds to the second highest MO and is assigned to ionization from the oxygen lone pair orbitals that are not adjacent to the benzene ring, and therefore, not capable of interacting with the pi-system. This assignment is supported by the fact that the IP in both cases is comparable to that for lone pairs in unsubstituted crown ethers. The third band in the spectrum is most probably due to ionizations from the molecular orbital resulting from the + combination of the orbitals that make up the HOMO. The degenerate benzene-pi orbitals will no doubt interact unequally because of substitutions in 1 and 2 positions of the ring, and therefore, after interactions these levels would be slightly split. This effect is not resolved in the spectra, however, probably as a result of the overlap of bands in that region.

TABLE 3

COMPOUND	1st IP	2nd IP	3rd IP	4th IP
[11] CY14C4	9.3	-	-	-
[13] 15C5	9.43	11.30	-	-
[14] B15C5	8.00	9.60	10.65	-
[15] 18C6	8.25	8.93	9.68	10.28
[16] DB18C6	8.05	8.65	9.53	-

The above qualitative assignments are in agreement with the subsequent INDO MO calculations done on B15C5. According to these calculations the highest MO is indeed localized on both the benzene ring and the oxygens adjacent to it. The calculations also indicate that the second MO is mainly localized on the oxygens not adjacent to the benzene ring, and the third MO is localized on both the benzene ring and adjacent oxygen.

(C) Photoelectron Spectra of DB18C6 and 18C6

Fig. 5a shows the photoelectron spectrum of 18C6. The broad band observed from 8 eV to 11 eV is no doubt due to ionization from MO's that have resulted from the extensive interactions of the oxygen lone pair orbitals through the sigma framework. This broad band is divided into at least six visible smaller peaks, each of which can be visualized to have resulted from different combinations of the lone pair orbitals. This is rather reminiscent of benzene

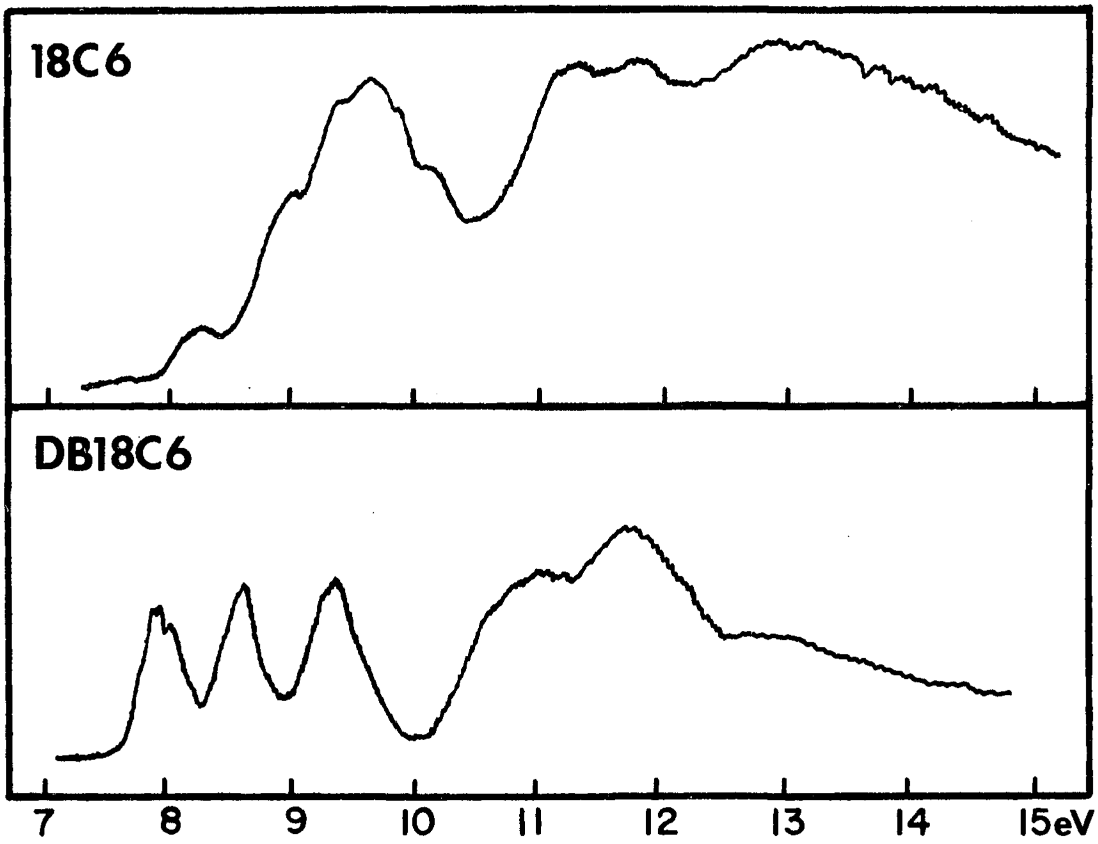


Fig. 5 - Photoelectron spectra cf 18crown6 and dibenzo18crown6.

orbitals that result from the through-space interactions of the carbon p's in the pi system. However, in the crown all six orbitals are filled and their interaction is via a through-bond mechanism. This leads to the conception that the through-bond interactions here involve the intermediacy of both C-C and C-H bonds. The geometry of this crown molecule allows a larger degree of C-C through-bond interactions than in smaller crowns because the O-C-C-O dihedral angle is approximately 60 degrees, and this provides the molecule with a conformation similar to that of 1,4-dioxane in which the through-bond interaction has been assigned to the C-C type. The presence of this strong through-bond interaction, especially of the C-C category, makes this a very unique unsubstituted polyether, with ionization from oxygen localized orbitals leading to its unusually low IP. As will be seen later, this provides the molecule with a set of properties not possessed by ordinary straight chain polyethers.

The first band observed in this spectrum of DB18C6 at 8.05 eV undoubtedly arises from ionization from the - combinations of benzene-pi and oxygen lone pair orbitals. In the case of B15C5 and B14C4 the highest MO was localized equally on the benzene ring and the oxygen atoms; however, in DB18C6 this same orbital is probably localized mainly on the oxygens adjacent to the benzene ring. This argument can be justified by considering the initial energies of the orbitals in question before their interaction. The HOMO of

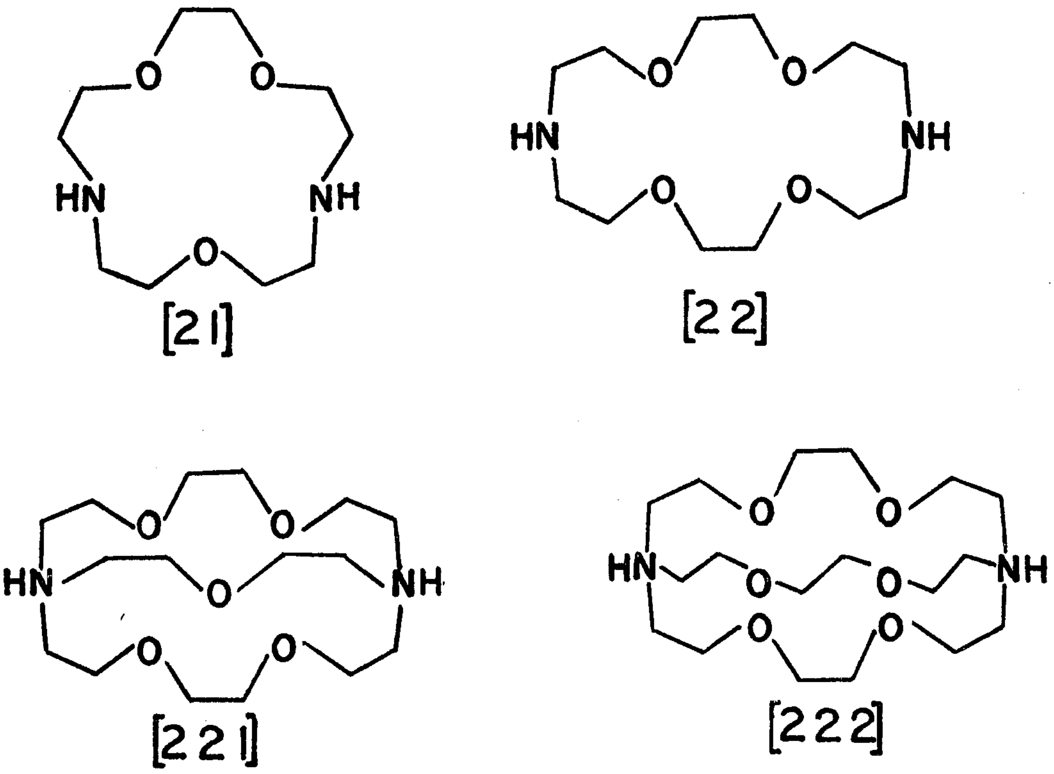
18C6 is at 8.25 eV and that of benzene is at 9.27 eV; therefore, it is not at all surprising that the resultant orbital at 8.05 eV would have mainly oxygen lone pair character. The second band in the spectrum is probably due to ionization from oxygen lone pair orbitals not interacting with the benzene-pi system, and the band at 9.53 is due to ionization from mainly benzene localized MO's that result from the + combinations of the orbitals that participate in the formation of the HOMO in this molecule.

At this juncture it should be pointed out that the substitution of the benzene ring(s) does not change the HOMO energy of the crown in the 18-membered ring very much (a change of only 0.2 eV). However, the change upon substitution is appreciable for the 15 and 14 membered crowns (ca. 1.4 eV)

(D) Photoelectron Spectra of Kryptofix 21, 22, 221, 222

The structures of cryptates studied here are given in Fig. 6. As Fig. 7 shows, the PE spectra of all four cryptates are very similar; accordingly, the assignments made will apply to all four compounds. The interpretation of the spectrum of 21 and 22 which are nonbicyclic cryptates will be advanced first.

One could look at nonbicyclic cryptates as amine analogues of macrocyclic ethers in which, generally, two non-adjacent oxygens have been replaced by nitrogen atoms. For example, kryptofixes 21 and 22 are analogous to 15C5 and



[21] [22]

[221] [222]

Fig. 6 - The structures of kryptofixes 21, 22, 221, 222.

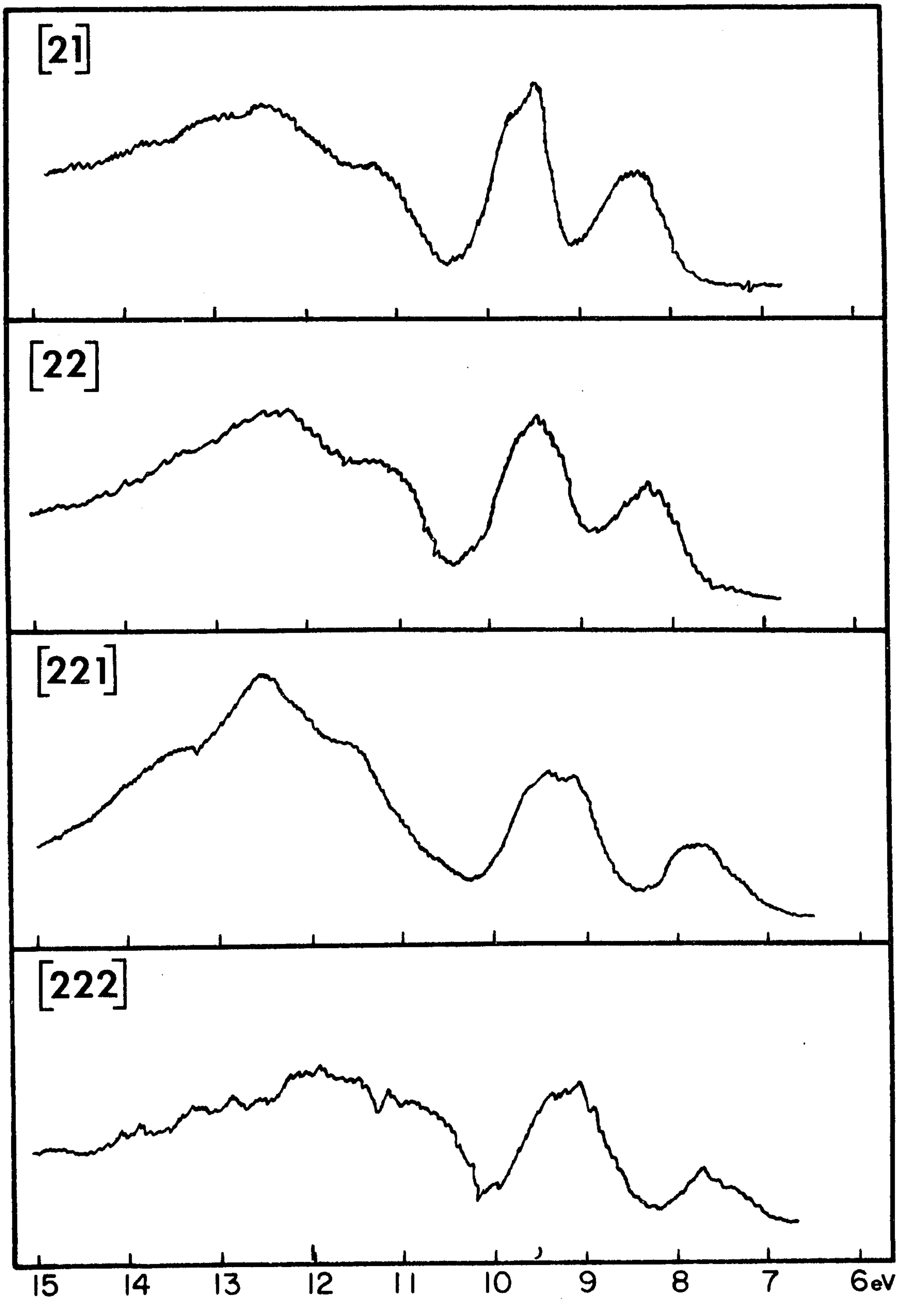
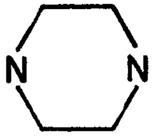


Fig. 7 - Photoelectron spectra of Kryptofixes 21, 22, 221, 222.

18C6 respectively. With the introduction of the nitrogen atoms into the crown ring the mechanism of the through-bond interactions of the oxygen lone pair orbitals is interrupted, because nitrogen lone pairs are of much higher energy, and therefore, not capable of interacting with C-C or C-H sigma orbitals nearly as effectively as those in oxygen. This supposition is confirmed by the small interaction seen in [17]. Consequently, through-bond interactions in [21] and [22] are more localized and they do not extend to any oxygens past a nitrogen atom. In view of these facts, the best way to interpret the spectra of these compounds would be to consider the interaction between



[17]

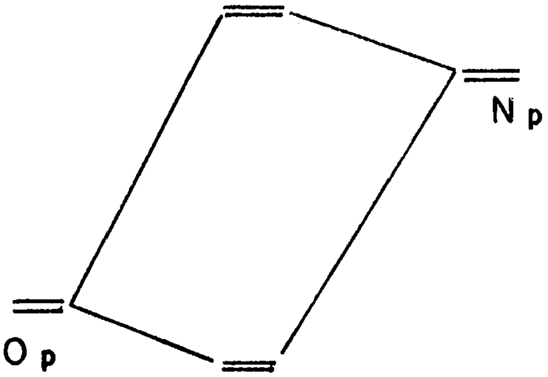


Fig. 8 - Interaction between oxygen and nitrogen lone pair orbitals in cryptates.

orbitals of molecular fragments. For example, we can consider the interaction between the orbitals of two dimethoxyethanes and those of secondary amine nitrogens to yield the MO's of crytofix 22 (Fig. 8). The HOMO IP of DME is 9.9 eV and that of secondary amine nitrogen lone pairs is 8.2 - 8.4 eV. Because of the large energy difference between these two orbitals, there should be practically no interaction and the results of the PE spectrum confirm this. The smaller peak due to ionization from the practically unperturbed nitrogen lone pair appears at 8.35 eV and the band due to ionization from oxygen orbitals at 9.58; this band is slightly broader than its equivalent in the spectrum of DME. This and the lower value of the IP in [22] can be attributed to better through-bond interaction between the two oxygens owing to the increased rigidity of the bonds in kryptofix 22.

TABLE 4

COMAPOUND	1st IP	2nd IP	3rd IP	4th IP
[21]	8.44	9.68	11.35	-
[22]	8.35	9.58	11.20	-
[221]	7.70	9.32	11.00	12.35
[222]	7.80	9.47	11.27	-

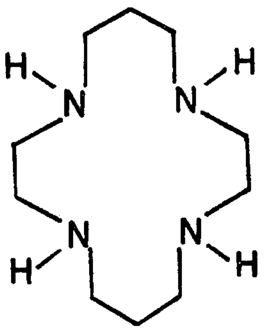
The interpretation of the spectrum of kryptofix 21 is almost identical; although, here the interaction is between a dimethoxyethane segment and an ether oxygen with the nitrogen lone pairs, and, as one can see, there is no big shift of peaks in the spectrum of [21] relative to that in [22]. A 0.1 eV increase in the first IP can be attributed to a lesser interaction between the nitrogen and oxygen orbitals since we have reduced the number of oxygens in the ring by one.

Bicyclic cryptates have slightly lower 1st and 2nd IP's. This is due to the presence of tertiary amine nitrogen lone pairs which have energies 0.2-0.4 eV higher than those of secondary amine nitrogen lone pairs. However, D(IP1-IP2) is larger in Kryptofix 221 as well as 222 indicating that the interaction of the two orbitals that form the MO's is slightly greater in the bridgehead compounds. This is probably due to the presence of the larger number of oxygens, which would also increase the number of possible orientations for effective overlap.

Generally, we observe that bicyclic cryptates have lower first IP's than those of macrocyclic polyethers.

(E) Photoelectron Spectra of Nitrogen Macrocycles

Photoelectron spectra of cyclam, Me_3cyclam, Me_4cyclam and benzocyclam (Fig. 9) have been obtained. The assignment of bands in the spectrum of these compounds is fairly straightfoward. In cyclams there is not much likelihood of through-space interactions of the nitrogen lone pair orbitals as one could see from molecular models. As to through-bond interactions, they are very small because



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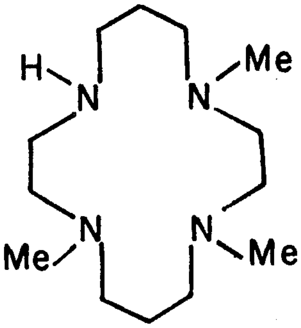

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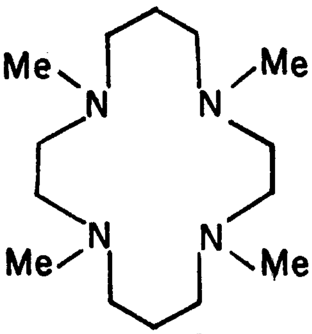

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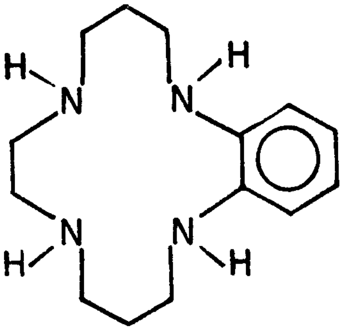

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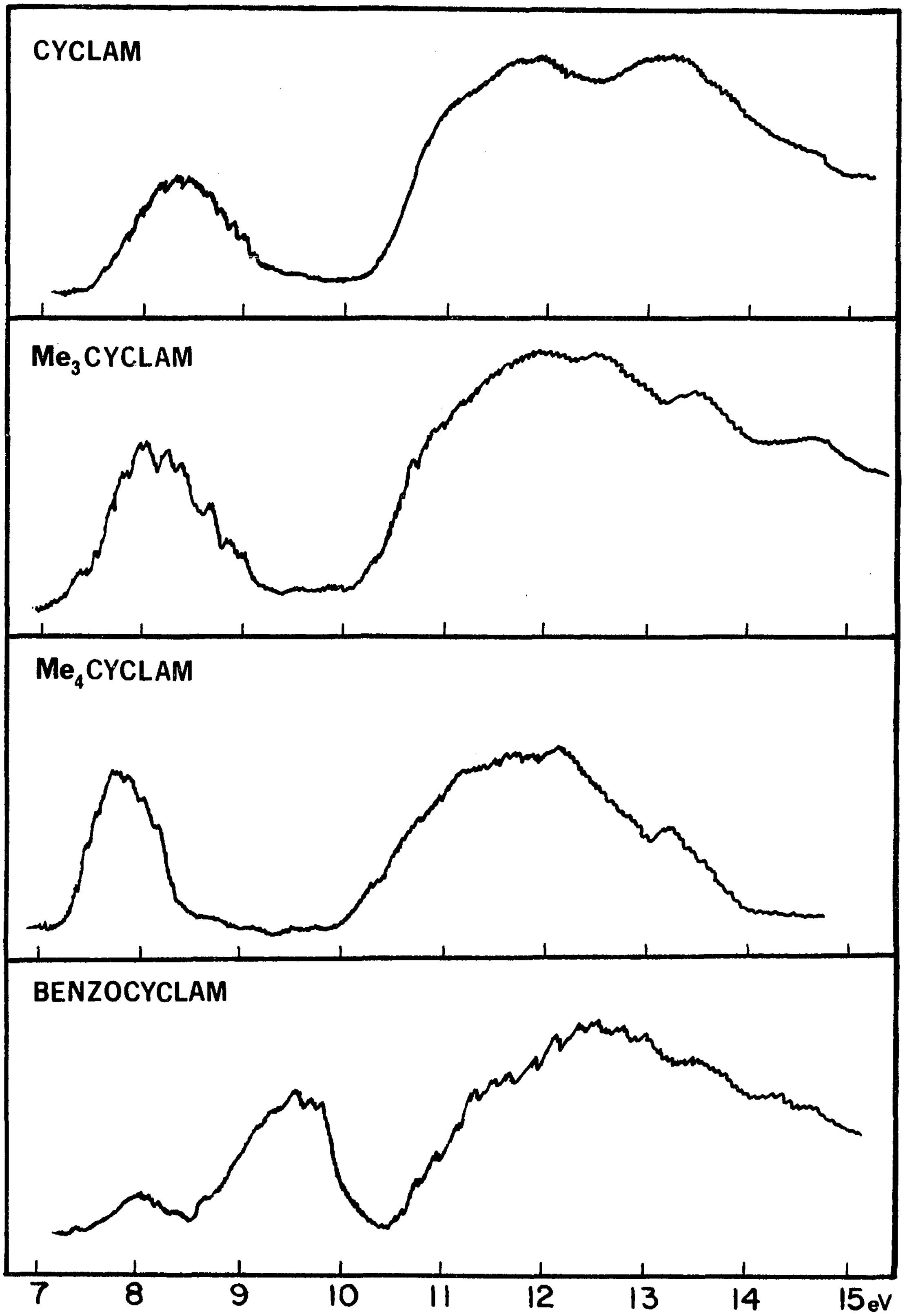


Fig. 9 - Photoelectron spectra of cyclam, trimethylcyclam, tetramethylcyclam and benzocyclam.

of the large separation between the energies of the orbitals involved. A distinctive characteristic of these spectra is the presence of what appeares to be vibrational fine structure of the bands due to ionization from nitrogen lone pair like orbitals. This vibrational structure may be a result of umbrella inversion about the nitrogen center. Even though typical lone pair orbitals (in O, S, etc.) produce characteristically sharp peaks in the PE spectra (reflecting AO character), nitrogen lone pair orbitals produce broad bands, owing to symmetry based mixing of the lone pair orbitals with sigma bands of nitrogen. The first band observed in the spectra of the first three cyclams is due to nitrogen lone pair like orbitals. There appears to be a gradual decrease in the IP of this first band upon substitution of methyl groups. This is demonstrated in the spectra of cyclam, Me_3cyclam and Me_4cyclam, which has the lowest IP. This effect is due to the strong inductive effects of the Me groups (electron donating).

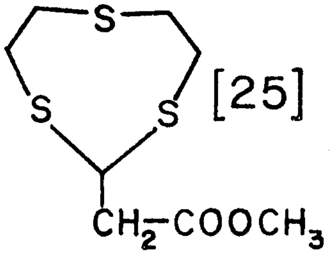
TABLE 5

COMPOUND	1st IP	2nd IP	3rd IP	4th IP
[18]	8.50	11.20	-	-
[19]	8.02	10.80	-	-
[20]	7.90	10.80	-	-
[23]	8.05	9.00	9.55	9.85

The PE spectrum of benzocyclam is much like that of B15C5. The presence of vibrational structure is noticeable in the first two bands of this spectrum. The MO's in benzocyclam can be qualitatively constructed, as was done in B15C5, considering the interaction of the nitrogen lone pair orbitals with the benzene HOMO's. The first band is due to the - combinations of these orbitals, but, unlike B15C5, in benzocyclam this MO, because of the relative energies of the interacting orbitals, has mostly nitrogen lone pair character. The IP due to this MO is lower than the first IP in cyclam by 0.45 eV. The second and third bands are due to + combinations of the above orbitals; here the splitting between the interacted benzene orbitals a2 and b1 are resolved. These second and third bands also exhibit some vibrational structure, which is indicative of some nitrogen lone pair character of these MO's.

(F) Photoelectron Spectra of Sulfur Oxygen Heterocycles

In the spectrum of [24] two broad bands are observed in the low IP region. These bands result from the interaction of the two sulfur-lone pair orbitals. The mechanism of this interaction is through-space, since sulfur is not capable of interacting through-bond very effectively, given the large separation in the energies of the sigma and the lone pair orbitals (this was demonstrated for 1,3- and 1,4-dithiane). In addition through-space orbital interactions are favored for sulfur because of its large and diffused lone pair



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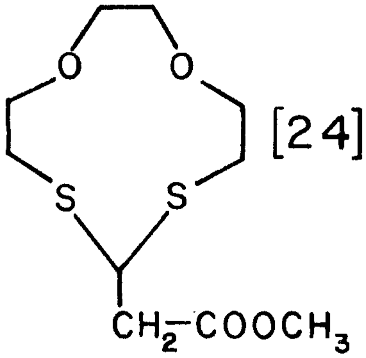


[24]

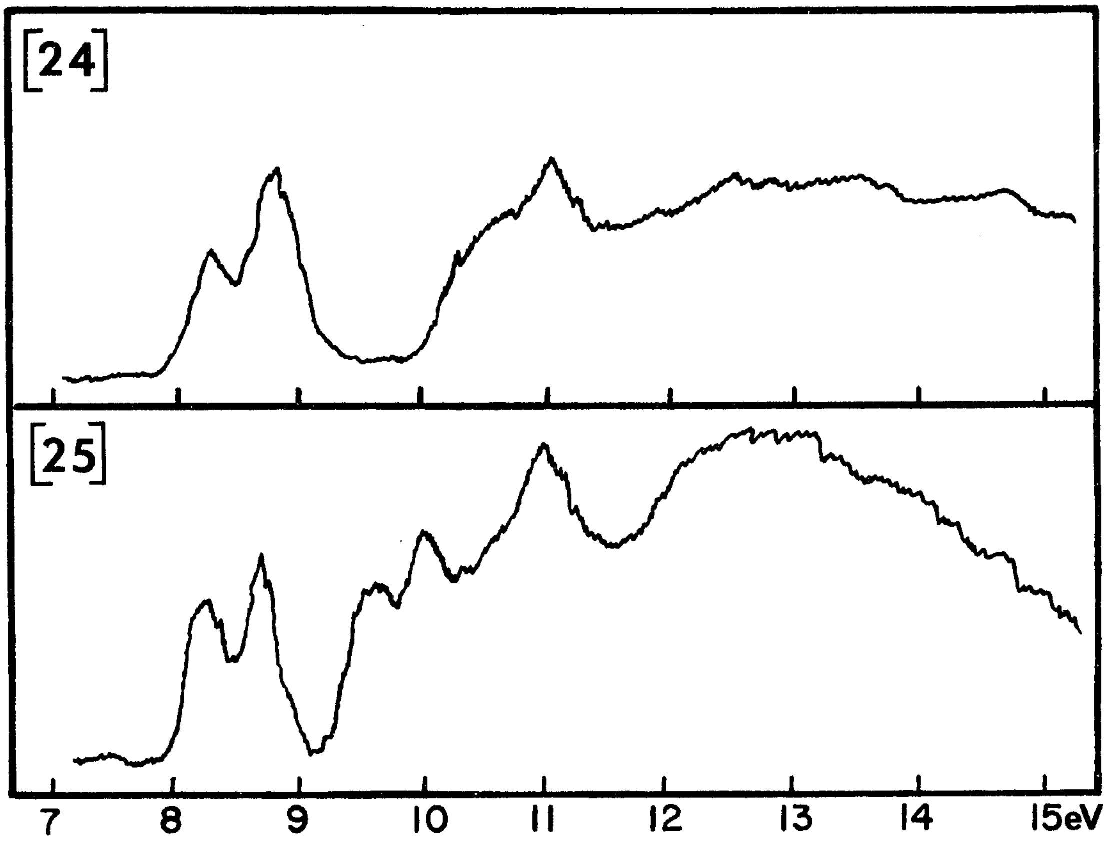


Fig. 10 - Photoelectron spectra of compounds 24 and 25.

orbitals, as long as they are within interacting distance of each other. In compound [24] this seems to be the case; the second band which is due to ionization from oxygen lone pair orbitals is also split into two. Here, however, through-bond interactions are responsible for the appearance of the two peaks. The situation with oxygen is somewhat similar to that in crown ethers, but, the two peaks appear distinctively unlike those in DME. This is probably because only one type of through-space interactions is dominant, and from molecular models this interaction appears to be via the C-C sigma bonding orbitals.

TABLE 6

COMPOUND	1st IP	2nd IP	3rd IP	4th IP
[24]	6.27	8.78	10.61	11.02
[25]	8.16	8.61	9.50	9.95

In view of the assignments made in the spectrum of [24], the interpretation of the spectrum of [25] is as follows. Obviously the two lone pair orbitals on sulfurs close to the carbonyl group are split by means of through-space interactions as was the case in [24]. The third sulfur in the molecule is two carbons away from the other two sulfur atoms, and therefore, this sulfur is not within the interaction range and will remain essentially in a 3p atomic orbital. The first band is clearly due to the MO which is the result of the - combinations of the two 3p lone pair orbitals on the sulfur atoms close to the carbonyl group. The second broader band, however, represents two overlapping bands: one due to ionization from the MO which is formed from the + combinations of these same lone pair orbitals and the other corresponding to the uninteracted sulfur lone pair orbital on the third sulfur. These assignments are made on the basis of comparison of the spectrum of [24] with that of [25] and also on the basis of the relative intensities of the first and second bands in the spectrum of compound [25].

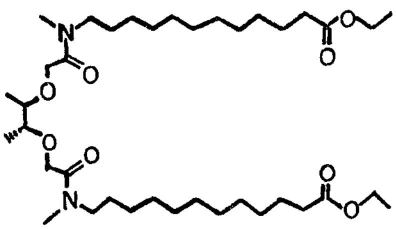
CONCLUSIONS

The most important application of the assignments thusfar made would seem to be in shedding light on the nature of the ligand binding centers in crown ethers. A literature scan shows that up to now, it has been assumed that the oxygens behaved as hard spheres in crown ethers (15); this view will have to be changed by the PES results just described. It now appeares that unlike ordinary ethers crowns have unusually low ionization potentials; this, as explained, is primarily due to the through-bond interactions of the oxygen lone pair orbitals. The value of the ionization potential is an indication of how tightly the electrons are bound by the nucleus; the lower the IP, the less tightly bound are the electrons. Thus the ionization potentials can be correlated to the extent of electron cloud diffusibility, and therefore, to polarizibility of the sites holding the molecular orbital responsible for the low IP band.

Chemists have attributed the complexing of alkali metals with crown ethers to the "macrocyclic effect" but no one has elaborated on the exact nature of this macrocyclic effect or how it operates. In crowns this macrocyclic effect seems to be partially attributable to the increased polarizibility of the oxygen molecules, which in this case seem to show more preference for binding with alkali metals than alkaline earth or transition metal cations.

To explain the stabilities of ordinary metal ligand systems, metal ions and ligands have been classified as soft and hard species according to their preference (16). It has been shown that hard metal ions which are classified as being highly electronegative with low polarizibility prefer ligands which are also hard, like O, F, etc. On the other hand, soft metal ions which are highly polarizable and have low electronegativities prefer ligands which are also soft in the donor position (I, Br, Cl). Crown systems, on the other hand, have not been looked at from the perspective of this hard-soft model. If oxygen atoms in crown ethers were assumed to be hard centers, any attempts made to establish the validity of the hard-soft model would fail because of the initial mistaken assumption. However, in view of our findings, it would be possible to extend the use of the soft-hard models to crown systems. This is already supported with existing observations made on crown-M complexes as shall be described below. Caution, however, should be excersised in the application of this approach in the absolute sense, since there are other forces that operate in competition with the ones in the hard-soft model. In addition, the softness or hardness of a species is not a measurable quantity -- it is a relative concept; therefore, the arguments made here will be in a relative sense only.

It has already been pointed out that highly charged (hard) actinide metal ions prefer to pair up with hard centers such as oxygen sites in H_2O and NO_3^-, rather than form complexes with crown ethers, where according to our arguments the oxygen sites are softer. Here, hard-hard stability clearly prevails. Alkali metal ions such as K^+ (which is relatively soft) by contrast prefer to form complexes with crown ethers in the presence of the same molecules or ions with hard oxygen centers; in this case soft-soft interactions are responsible for complex formation. The same considerations can also account for the greater stability of the softer alkali crown complexes compared to harder alkali earth complexes of crown ethers (17). The presence of the softer oxyen sites in benzo15C5 (lower 1st IP 8.05) is clearly responsible for the stabilities of complexes of this ligand with alkali metals ($\log \beta 1 = 2.0$ where β is the formation constant) over the complexes of 15C5 (higher 1st IP 9.4) with the same cations (log $\beta1=0.3$). Benzo substituted ligands which otherwise do not have a very soft oxygen center appear to have a greater affinity for alkali metals, whereas the unsubstituted crowns such as 15C5 have a greater affinity for harder cations such as Sr^{+2} or Tl^{+3}. The fact that there is not much difference in the stabilities of 18C6 (logK=2.06) and DB18C6 (logK=2.18) is an indication that complexes with alkali metal ions can be attributed to the relatively small difference (0.20 eV) in their IP's.

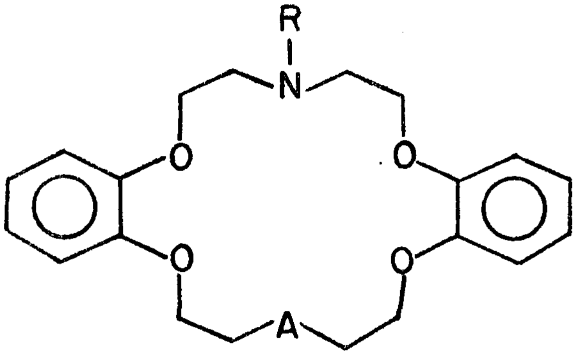


[26]

In other systems such as ionophore [26], which shows extremely high selectivity for Ca^{+2} in membranes, it is thought that the presence of highly polar amide carbonyl coordinating sites (which are harder centers with higher 1st IP's) ensure the interaction of the ligand with a cation like Ca^{+2} over alkali metal cations (18). From this it appears that more polar binding sites lead to the preference of divalent over monovalent cations of the same size, and small cations of the same charge are also preferred over larger ones. This is another demonstration of the applicability of the hard-soft model to crown and like systems.

It is now possible to look at the effect of the substituents on the ionization potential and how to correlate this with the stabilities of some macrocyclic complexes. Some substituents have been found to produce pronounced effects on selectivity towards various cations. From this alone , it appears that the energies of the oxygen lone pair orbitals, which are altered upon substitution, are one of the determining factors in the complexation process.

Reported data (19) on rate constants show that the presence of electron-withdrawing species such as a nitro group on the benzene ring of cis 4,4-DB18C6 slows down the complex formation and destabilizes the complex ion. This is consistent with the fact that increasing the first IP would destabilizie complex formation, and the IP in DB18C6 is clearly increased by the substitution of the strongly electron-withdrawing nitro groups.



COMPOUND	R	A
X	n–C_8H_{17}	O
Y	H	O
Z	H	N-H

Frensdorf (20) has found that in methanol, the logK for potassium complexes of DB18C6, X, Y, Z, are, respectively, 5, 4.1, 3.2 and 1.63 . In this series one could see that the ionization potentials increase in order of decreasing stabilities. Substituents on the donor atoms seem to be responsible for the observed changes in the stabilities of the crown complexes by altering the IP's.

The replacement of aliphatic ether links with aromatic ones (which decrease the basicity of oxygen atoms and, thereby, raise the 1st IP of the molecule) is also observed to diminish the complexing power with t-BuNH^{+3} (21).

It is also possible to attempt to explain stochiometries of complexes in terms of this approach to stabilities of crown systems. It is believed by many that the stochiometry of a complex can be predicted by the Ion-Cavity-Radius Concept (22-25), such that if the cation fits nicely into the cavity of the ligand 1:1 complexes are formed. In cases where the cation is larger than the cavity 1:2 complexes would form. However, the discovery of 1:2 complexes of cations which are much smaller than the macrocycle cavity has discredited the use of this concept in its simple form.

It has been observed that as the cavity size of the crown increases for a given size of M (in cases where 1:1 complexes are formed) the ligand tends to be folded around the cation (25). It appears that the folding of the ligand occurs with large and flexible macrocycles and with cations of high charge density (hard cations such as Mg^{+2}). For the formation of stable complexes (with ligands containing soft centers) it would appear that the charge on the cation has to be delocalized extensively, and therefore, hard cations need a large number of coordination sites for this purpose. Thus, it is not at all surprising that Mg^{+2} forms sandwich complexes with B15C5, although the size of the cation is much smaller than the cavity. Alternatively, bimetallic complexes are observed in cases where the ligand is a very large macrocycle and the cation is relatively polarizable (low charge density), as in potassium.

These arguments can be extended to cryptate systems as well. For example, bicyclic cryptates form more stable complexes with M^{+2} ions than do crowns (27); however, the stabilities of such complexes are much lower than in cryptate-M^{+} systems. The stabilities of bicyclic cryptate-M^{+2} systems probably result from the increase in the number of coordination sites. IP's of cryptates can also be correlated with the stabilities of their complexes. In general, bicyclic cryptates have lower 1st IP's than do crown ethers.

The establishment of correlations of ionization potentials with stability data in nitrogen and sulfur macrocycles is much more difficult because of the lack of availability of stability data on complexes of these systems. In addition, there seems to be some evidence that the nature of bonding in these cases is different than that in crown ethers and cryptates; the possibility of covalent bonding is being explored.

In summary, it appeares that IP data may be very useful in elucidating complexation phenomena involving crowns, cryptates and related substances. Further, more extensive studies are obviously in order so that the correlations elucidated thusfar can be put on a more rigorous basis. It appeares that it may be possible to custom design ligands on the basis of known types of through-bond and substituent effects, thereby making better and more specific ligands.

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CHAPTER 5

THE He(I) PHOTOELECTRON SPECTRA OF SOME GAMMA SUBSTITUTED Co(III) ACETYLACETONATE COMPLEXES

INTRODUCTION

HE(I) Photoelectron Spectroscopy has offered considerable insight in the study of the valence molecular orbital structure of metal complexes. In this work the ionization potentials of metal-localized d-electrons and ligand pi-orbitals are used to probe the extent of metal-to-ligand pi bonding and possible aromaric character in the chelate ring of some metal acetylacetonate complexes (Fig. 1).

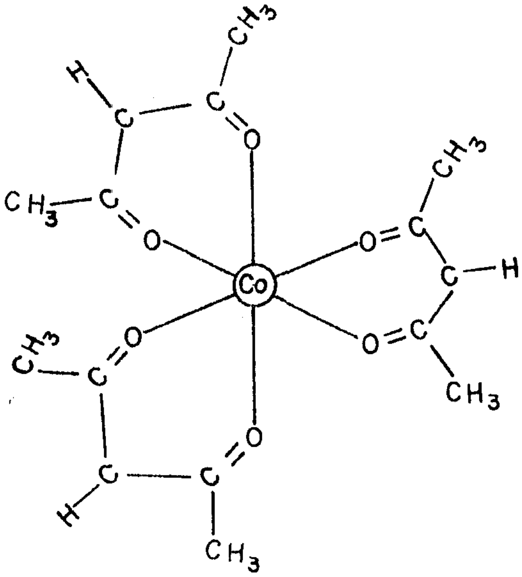


Fig. 1 - Cobolt(III) acetylacetonate complex

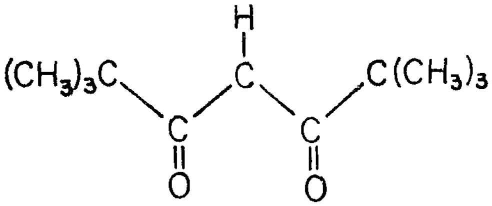
Several studies of vapor-phase He(I) photoelectron spectra of β-diketonate complexes of bivalent (1,2) and trivalent (3-5) transition metals have already appeared, and the spectra observed for these complexes are reasonably well interpreted. These complexes are extremely interesting in that it is theoretically possible for the chelate ring to possess aromaric character if appreciable pi-bonding with the central metal atom is able to take place (6). In this dissertation, a presentation is made of the UPS of several Co(III) β-diketonate complexes in which the ring hydrogen para to the metal has been replaced by a variety of groups. The main thrust of this work was to investigate the influence of these substituents on the ionization potentials of metal localized d-electrons and ligand pi-orbitals with the aim of learning about the extent of metal-to-ligand pi-bonding.

EXPERIMENTAL

$Co(acac)_3$ was prepared (by Harry Brittain (5)) according to the method of Bryant and Fernelius (7). Chlorine and Bromine were substituted onto the chelate rings using N-halo-succinamides (8) and nitration was effected with $Cu(NO_3)_2$ and acetic anhydride (9). Compounds were recrystallized from benzene-heptane until no unreacted $Co(acac)_3$ could be detected in the NMR spectrum.

The photoelectron spectra were measured on a Perkin-Elmer model PS-18 spectrometer, and were calibrated by simultaneus introduction of either argon or xenon into the target chamber. The samples were heated to about 150°C, at which point there was sufficient vapor pressure for the spectra to be measured. The dipivaloylmethane [1] chelate of Co(III) was prepared in the same manner as the acetyl acetone chelate, but was observed to decompose upon sublimation.

[1]



RESULTS

Electrophilic attack on the metal-chelated β-diketone rings results in replacement of the rings' gamma-hydrogens that lie para to the metal. The low energy UPS of $Co(acac)_3$, $Co(acac\text{-}Cl)_3$, $Co(acac\text{-}Br)_3$ and $Co(acac\text{-}NO_2)_3$ are all shown in Fig. 2 . The spectra of $Co(acac)_3$, $Co(acac\text{-}Cl)_3$ and $Co(acac\text{-}Br)_3$ all appear qualitatively similar, except for the appearence of new bands in the 10.5-11.5 eV range for the chlorinated and brominated chelates. Nitration of the chelate ring results in a general shift of all peaks to higher ionization energies, but the spectra still retain the same general pattern of photoelectron peaks. Vertical ionization potentials for all bands are summarized in Table 1.

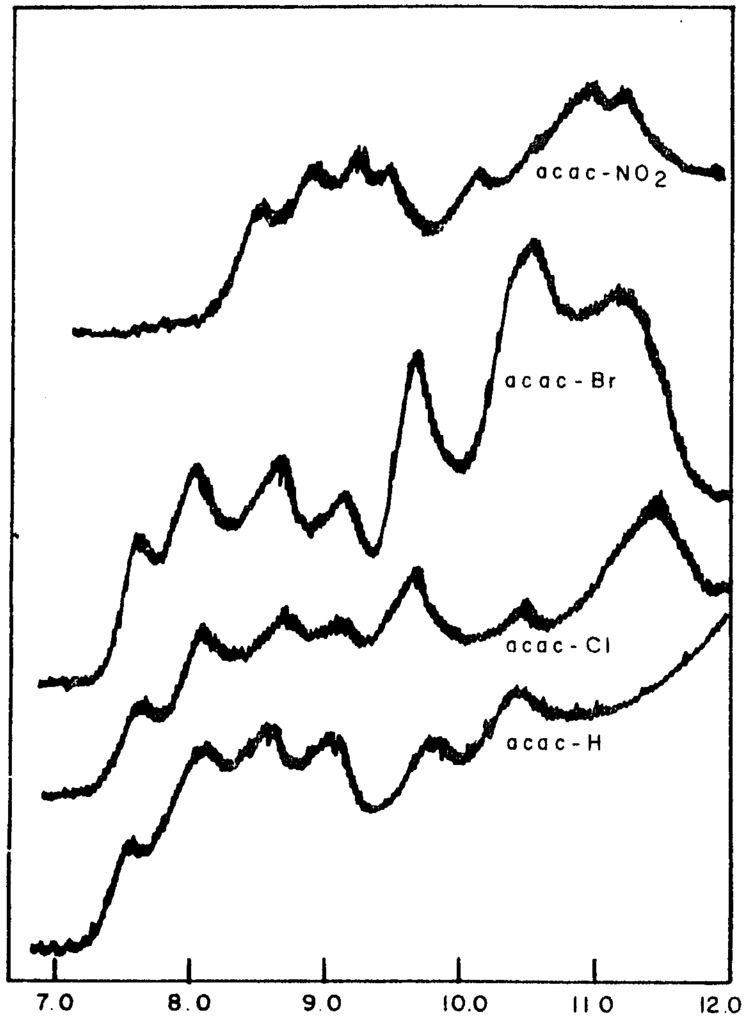


Fig. 2 - Photoelectron spectra of some cobolt(III) acetylacetonate complexes.

TABLE 1

VERTICAL IONIZATION POTENTIALS FOR GAMMA-SUBSTITUTED COBOLT ACETYLACETONATE COMPLEXES

BAND	$Co(acac)_3$	$Co(acac-Cl)_3$	$Co(acac-Br)_3$	$Co(acac-NO_2)_3$
d	7.52	7.59	7.58	8.51
pi	8.09	8.05	8.04	8.86
pi	8.55	8.68	8.67	9.27
n-	8.99	9.11	9.14	9.45
n-	9.54	9.62	9.64	10.16
n+	10.37	10.46	10.50	10.96
n+	----	----	----	----
Halo-LP	----	11.44	10.50	----
Halo-LP	----	----	11.17	----

DISCUSSION

Before attempting to interpret the spectra of these complexes, a brief review will be made of the existing studies on the structure and the spectra of the free, protonated ligands in question.

The prototype ligand, acetylacetone, exists in the vapor phase predominently in the enol form. The six membered ring is thought to be planar, which confers C2v symmetry on the system. The derivatives of acetylacetone can also be assumed to be present as their enol forms in the gas phase.

The pi system of the six membered ring has been shown to be formed from the out-of-plane p-pi orbitals of the three carbon and the two oxygen atoms (see Fig. 3). The two sets

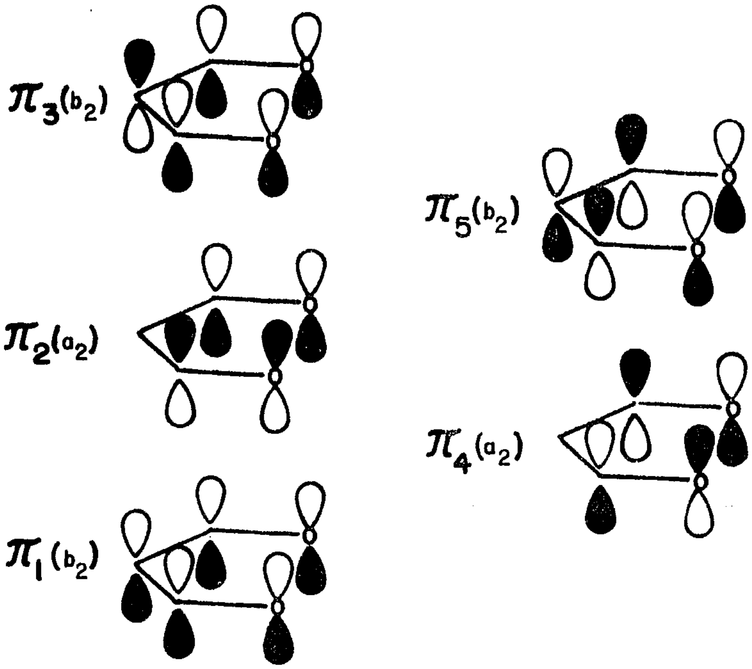


Fig. 3 - The pi-MO's for the enol form.

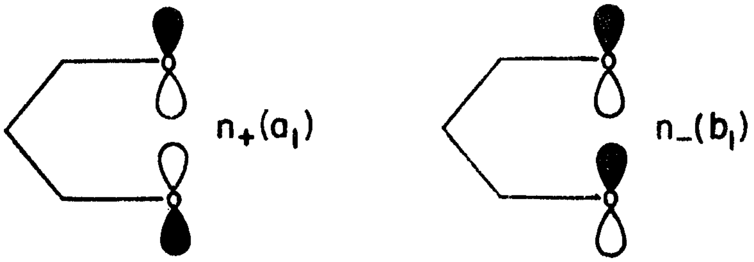


Fig. 4 - Lone pair combinations for the enol form.

of orbitals transform as a2+2b2 and a2+b2 in the C_{2V} point group. According to the simple Huckel model, orbitals are arranged with respect to their energies in the order, pi1<pi2<pi3<pi4<pi5. From energy considerations it is found that pi3 is well separated from pi4, which implies that pi4 will not be of great importance with regard to bonding in metal chelates. The oxygen lone pair orbital on the other hand are shown in Fig. 4, to a first approximation these may be considered as in-plane px orbitals. Of the two, n+(a1) is the one contributing to some bonding with hydrogen in the enol form. The relative energies of the valence orbitals of acetylacetone are estimated from the orbital energies in model carbonyls; Fig. 5 shows a tentative arrangement of the orbitals with respect to their energies. The PE spectra of acetylacetone are generally in support of the ordering in Fig. 5, although the relative ordering of some of these orbitals such as n- and pi3 is still in question, and a reversal in the order given here might occur in some situations.

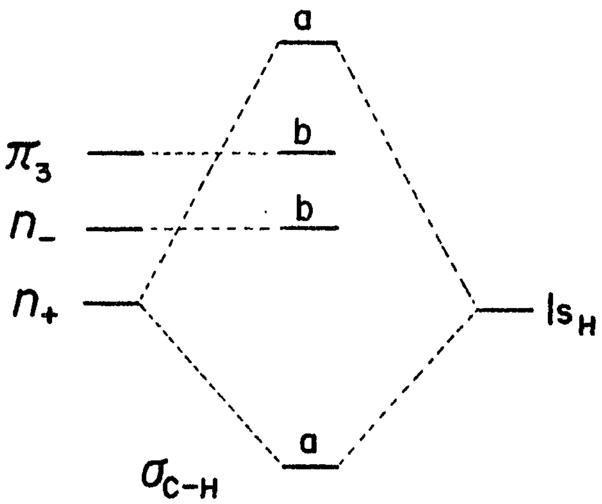


Fig. 5 - MO diagram for the enol form.

The UPS of Co(β-diketone)$_3$ chelates have been interpreted by Evans et al (3). and by Brittain and Disch with slightly differing assignments (2). Both sets of assignments have been based on the assumption that these complexes possess trigonal symmetry (D_3 point group), as do most simple M(acac)$_3$ molecules. The immediate coordination environment of the metal atoms may be described only approximately as an octahedral configuration of the oxygen atoms. Both sets of assignments also agree that the bands of Co(acac)$_3$ found at 8.99 and 9.54 eV are due to ionization from an out-of-phase combination of oxygen non bonding orbitals (n- orbitals) which are split such that e(n-) > a2(n-) because of ligand interactions in the complex. The band at 10.37 eV is due to an in phase combinations of these same orbitals (denoted by n+), which are again split as a result of the same interactions, although the spectrum is not completely resolved in this region. Both interpretations also assign the second band at 8.09 eV to a combination of metal d-electrons and ligand localized pi-orbitals (primarely pi3 orbital). Based upon extrapolated trends in the PE spectra of transition metal tris-chelates, Evans et al. assigned the first band of Co(acac)$_3$ at 7.52 eV to a ligand localized pi-orbital and the third band at 8.55 eV to metal d-electrons. By comparison to several bis chelates, Brittain and Disch concluded that the 7.52 eV band was due to d-electron ionization and that the 8.55 eV band to ionization from the ligand pi-orbital. Owing to the controversy surrounding this issue, a study was initiated of the substituted complexes in the hope of obtaining a definitive assignment . Following the assignments of Brittain and Disch, the leading band at 7.52 eV is ascribed to a metal d-orbital. As will be demonstrated, the substituent effects are in accord with this assignment.

(A) Photoelectron Spectra of $Co(acac)_3$, $Co(acac\text{-}Cl)_3$ and $Co(acac\text{-}Br)_3$

The UPS of $Co(acac)_3$, $Co(acac\text{-}Cl)_3$ and $Co(acac\text{-}Br)_3$ all resemble each other greatly in the 7.0-10.0 eV region, thus enabling the $Co(acac)_3$ assignments to be extended to the halogenated derivatives. A new band is seen in the UPS of $Co(acac\text{-}Cl)_3$ at 11.44 eV, which can be attributed to ionization of chlorine lone pair electrons, and The two new bands that are seen in the spectrum of $Co(acac\text{-}Br)_3$ (10.50 and 11.17 eV) are also assigned to halogen lone pair ionizations. These assignments are reasonable, since Cl lone pair ionizations are seen at 11.3 and 11.7 eV in chlorobenzene, and Br lone pair ionizations are found at 10.6 and 11.2 eV in bromobenzene (10).

It is interesting to note the changes in ionization induced by the substitution of halogen atoms on the chelate ring. It is well known that Cl and Br atoms will withdraw electron density from an aromatic ring inductively, but that they can also donate pi-electron density through a resonance interaction with the pi-system. In Co(acac)$_3$ the two components of the first ligand localized pi-band are split by 0.46 eV, but this gap widens to 0.63 eV in both Co(acac-Cl)$_3$ and Co(acac-Br)$_3$. This increase in splitting must be related to the interaction of the halogen atoms with this pi-orbital. CNDO calculations on model aluminum compounds (2) have shown that the uppermost pi-orbital has almost no electron density present on the central metal, and thus electron density is completely restricted to the ligand. The photoelectron spectra indicate that significant interaction does take place between the gamma-substituent and the ligand pi-system. This finding is not unexpected, since replacement of the gamma-hydrogen on the chelate ring takes place only by an electrophilic attack similar to reactions used on aromatic ring compounds (8,9).

Orbitals not capable of pi-interactions are ionized at higher potentials when an electron withdrawing substituent is introduced onto the chelate ring. This effect has been observed in the bis-chelates and tris-chelates of acetylacetone and hexafluoroacetylacetone (2,4) in which the orbital sequences of various transition metal chelates were preserved upon fluorination, but in which all ionizations were increased by about 2 eV. In this series of compounds, it was observed that the n- and n+ ionizations (which are due to sigma type orbitals) all increased by about 0.1 eV upon halogenation.

The ionization potential of the d-electron band found at 7.52 eV in $Co(acac)_3$ is increased to almost 7.6 eV in the halogenated chelates. This type of behavior resembles that of an orbital incapable of interacting with the ligand pi-system. If strong pi-bonding between the metal and the ligand were to take place, these electrons would be involved, and their ionization potential would be expected to decrease if a substituent capable of electron donation (through resonance) were to be placed on the chelate ring. Since the opposite behavior is, in fact, observed, it is concluded that these metal d-electrons are not involved in strong metal-to-ligand pi-bonding, and that any aromatic character in the chelate ring does not extend to include the metal.

A final remark may be made regarding the difference in assignments made by Evans et al. and Brittain and Disch. To assign the first band to a pi-type ionization instead of a d-orbital ionization would lead to a narrowing of the split between the two components of the split pi-orbital upon halogenation of the chelate ring instead of the observed increase in splitting. CNDO calculations (11) made on gamma-substituted aluminum model compounds also indicate that the splitting between the a2 and E components of the first pi-levels should increase upon halogenation of the chelate ring. Thus it can safely be concluded that the UPS of the Gamma-substituted cobalt chelates support the assignments made by Brittain and Disch.

(b) Photoelectron Spectrum of $Co(acac\text{-}NO_2)_3$

The UPS of the nitrated chelate resembles that of the other chelates somewhat, but exhibits a large increase in ionization potential relative to $Co(acac)_3$. By analogy to the UPS of $Co(acac)_3$ and $Co(hfac)_3$ reported by Evans et al., it can be concluded that no change in orbital sequence takes place upon nitration. INDO calculations (12) made on acetylacetone and its nitro derivative indicate that the only effect of the nitration is the stabilization of all molecular orbitals. Thus the assignments made in Table 1 can be considered valid. The two peaks observed at 10.96 and 11.20 eV can be assigned to the split halves of the n+ band, but an equally probable assignment is that one peak is due to the n+ ionizations and that the other is due to ionization from orbitals localizes on the $-NO_2$ group.

CONCLUSIONS

The examination of the photoelectron spectra of several gamma-substituted Co(III) chelates of acetylacetone has enabled new details to be uncovered regarding the nature of the metal-ligand bond. From the trends observed in our spectra, it can be suggested that:

(1) The substitution of the halogen atoms on the chelate ring extends the ligand pi-system to include the halogen atom, and thus increases the pi-electron density through resonance donation.

(2) All orbitals incapable of pi-interaction are stabilized through electron withdrawal (inductive effect) and are found to ionize at higher potentials relative to the unsubstituted chelate.

(3) Groups that can only serve as electron withdrawers through the inductive effect (such as $-NO_2$ or CF_3) shift the ionizations of all orbitals to higher potentials without altering their sequence.

(4) The central metal does not participate in strong metal to ligand pi-bonding, and, thus, any aromatic character that might be gained is lost. The ligand pi-system is delocalized around the ligand ring, but does not extend to include the central metal atom. These conclusions are supported by measurements of the magnetic anisotropy in acac chelate rings (13), which also indicate that pi-electron delocalization does not extend to include the central metal atom. This in turn supports the $Co(acac)_3$ assignments made by Brittain and Disch, since use of the assignments made by Orchard requires that the metal atom be included in the pi-electron delocalization.

Very recently the assignments made herein have been confirmed by a study of the cross-section variation of the bands (14). In this work He(I) and He(II) photoelectron spectra of $Co(acac)_3$ has been recorded at 150°C. Generally an increase in intensity going from He(I) to He(II) radiation denotes the presence of the metal d-orbitals. Such an increase in the intensity of the first band is observed for $Co(acac)_3$, thus providing evidence in support of assignments in this dissertation vs. the ones by Evans et al.

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