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SPECTROSCOPIC STUDIES OF ORGANOSELENIUM COMPOUNDS—I

THE STRUCTURE OF PHENYLSELENIUM COMPOUNDS

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Abstract—The IR and UV spectra of diphenylselenium, diphenylselenium dichloride and triphenylselenonium chloride have been discussed. The splitting in the 750 cm^{-1} region for the phenyl selenium compounds is suggested to be due to one of the rings being non-equivalent with the other. The intensities of the bands in the 1100 and 1400 cm^{-1} regions have also been used in support of the structure which is suggested to be angular for diphenylselenium and unsymmetrical tetrahedral for diphenylselenium dichloride and unsymmetrical pyramidal for the triphenylselenonium cation. The similarity of the UV spectra of II and III is suggested to be due to the electronic oscillations extending only through two phenyl groups. The non-equivalence of rings may be a result of the coulombic repulsions of the neighbouring phenyl groups or due to an intra-molecular interaction of the anion.

INTRODUCTION

X-ray studies have not been useful in determining the structure of triphenylselenonium chloride because of the predominating influence of the selenium atom.[1] IR and UV spectra are useful in the elucidation of the structure of such compounds particularly regarding the manner of orientation of the rings. The main features of the spectra of the phenylselenium compounds are noted here and are compared with the other phenyl substituted organometallic compounds.

EXPERIMENTAL

Diphenylselenium (I) diphenylselenium dichloride (II) and triphenylselenenonium chloride (III) were prepared by standard methods.[2] IR spectra were recorded on a P.E. 234 spectrophotometer using rock salt optics. UV spectra were recorded on a Beckman DK-2 spectrophotometer and were run in solutions of MeOH. Concentrations were so adjusted that the optical densities at μmax fell in the range of 0·5 to 1·0. The IR absorption bands are listed in Table 1 and the UV absorption maxima in Table 2.

DISCUSSION

The characteristic features of the spectra of the three compounds are the occurrence of bands in the 1600–1300, 1175–1000 and 750–660 cm^{-1} regions.

The 1600–1300 cm^{-1} *region*. The C—C skeletal vibrations absorb in this region and correspond to modes k, l, m, n and o. In compound I the mode l could not be resolved. Mode k and m both are very predominant in I which indicates a charge disturbance in the ring.[3] The interacting species should be the lone pair electrons on the selenium atom which are known to bring about an intense conjugation in this type of molecules. In II and III the k and l modes are resolved, probably as a result of a change in the symmetry of the molecule. The m mode does not absorb as strongly as in I and may be due to a weak conjugative interaction.

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[1] J. D. McCullough and R. E. Marsh, *J. Amer. Chem. Soc.* **72**, 4556 (1950).

[2] H. M. Leicester, *Organic Synthesis* **II**, 240.

[3] A. R. Katritsky, *Quart. Rev.* **13**, 353 (1959).

TABLE 1. VIBRATIONAL FREQUENCIES OF THE PHENYL SELENIUM COMPOUNDS

Mode	Ph_2Se	Ph_2SeCl_2	$Ph_3Se^+Cl^-$
k	1580 s	1575 w	1605 w
l	unresolved	1560 w	1560 vw
m	1470 s	1458 m	1460 m
n	1432 m	1430 s	1430 s
o	1320 w	1322 w	1324 vw
	1298 m	1298 w	1305 w
e	1270 vw	1270 w	1270 w
	1240 vw		
a	1178 w	1175 w	1175 w
c	1152 w	1154 w	1155 w
		1080 w	1100 vw
			1088 vw
d + q	1064 s	1064 w	1064 w
		1056 vw	1050 w
		1048 w	
b	1023 vs	1016 w	1018 w
p	998 s	995 m	992 w
j	984 w	978 w	980 sh
h	962 w	968 w	965 w
i	912 w	918 w	935 vw
g	838 w	835 w	855 vw
			832 vw
f	735 vs	752 s	764 vs
		738 vs	742 vs
			733 vs
v	688 vs	688 m	678 vs
		678 s	
r	666 s	668 m	668 s

TABLE 2. ABSORPTION MAXIMA OF THE PHENYL SELENIUM COMPOUNDS IN THE UV REGION

	λ_{max}	$\log \epsilon$	λ_{max}	$\log \epsilon$
Ph_2Se	255·5	4·020		
	235·0	3·920		
Ph_2SeCl_2	271·5	3·208	238·0	3·250
	265·5	3·315	230·0	3·350
	258·0	3·290		
$Ph_3Se^+Cl^-$	271·0	4·1	238·0	4·060
	265·0	4·168	230·0	4·0995
	256·5	4·140		

In all the three cases and particularly in II and III, mode n absorbs very strongly. This vibration is known to be independent of the nature of the substituent. The high intensity may then be a result of a certain amount of rotation of one of the rings in a manner that makes it out of plane with the other. The X-ray studies on compound II have shown the two rings to be turned so as to make an angle with the plane of the other. Since mode n corresponds to a sort of tilting vibration, the higher intensity possibly implies an unsymmetrical orientation of the rings in both II and III.

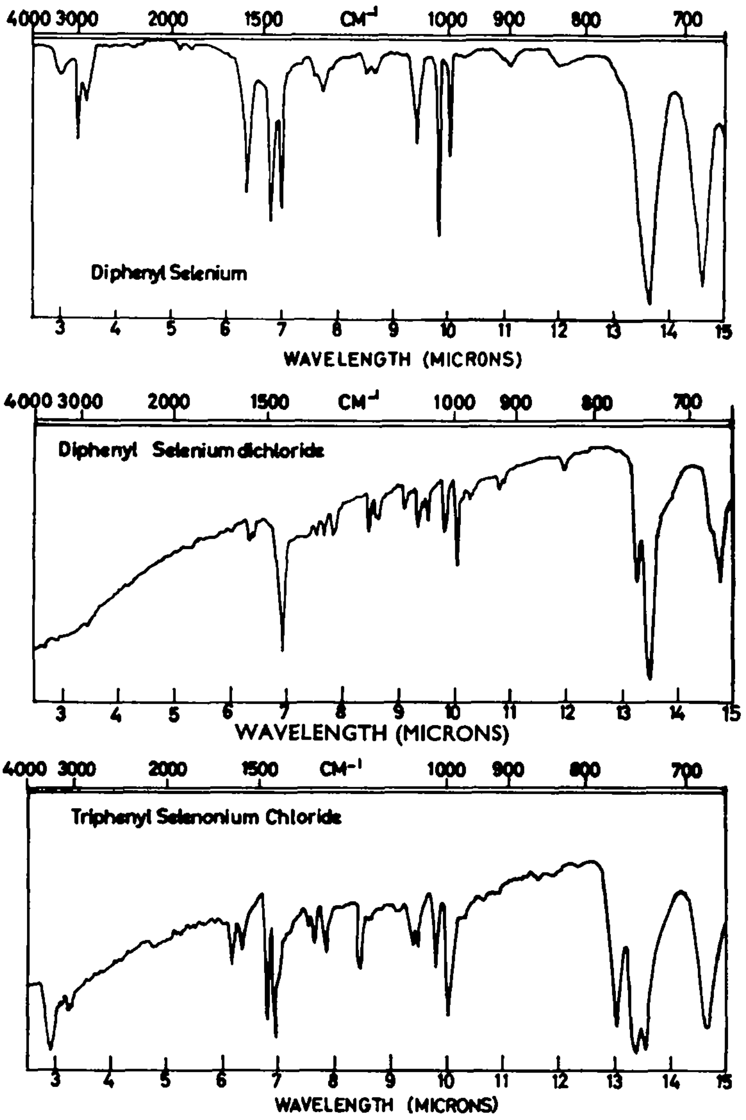

Fig. 1. IR Spectra of Ph_2Se, ph_2SeCl_2 and $Ph_3Se^+Cl^-$.

The 1175–1000 cm^{-1} *region.* The in-plane hydrogen deformation modes occurring in this region also show characteristic changes in the intensity of the bands particularly those due to modes d and b. The substituent sensitive mode q also absorbs here but is most likely coupled with mode d giving a strong absorption. The vibrations d and b correspond to the bending of hydrogen towards the substituent. It appears from a comparison of the spectra of conjugated phenyls that the enhancement in the intensity of these bands is a common feature of their spectra. If however, there is a strain in the structure e.g. if the rings are out of plane with each other, considerable lowering in the intensity of the band would be expected as seen from a comparison of the X-ray and IR studies of II. The weak absorptions at 1064 and 1018 cm^{-1} in the case of III then indicates a lack of conjugative interaction among the rings possibly because of an unsymmetrical distribution of the rings.

The 750–660 cm^{-1} *region.* A strong band at 735 cm^{-1} observed in II is also a characteristic feature of conjugated phenyls. From the structure of diphenyl sulfide whose IR spectrum is similar to that of I, it may be concluded that the two rings make a symmetrical inclination with their common plane.[11] The dipole moment of 1·38D[5] similar to that of diphenyl sulfide also supports this view.

In II a slight amount of splitting occurs and bands at 752 and 738 cm^{-1} are recorded. This may be interpreted in terms of the structure of the compound obtained by the X-ray studies. The out of plane turning of one of the rings would restrict resonance interaction of the lone pair which in this case occupies an equatorial position. This together with a change to lower symmetry would lead to a non-equivalence of the rings and hence splitting of the band would be observed. The unsymmetrical structure is also indicated by the high dipole moment of 3·47D.[6] Since the chlorine atoms occupy apical positions, they would contribute little to the dipole moment and also since the phenyl groups occupy equatorial positions the repulsions due to the lone pair would not shorten the C–Se–C angle as observed for $(p\text{-}BrC_6H_4)_2Se$.[7] The coulombic repulsions would lead to a turning of the rings which would create dissymmetry in the molecule and hence the high moment.

In the selenonium compound three strong bands occur in this region at 764, 742 and 733 cm^{-1}. This compound may then be either propellor shaped or completely unsymmetrical. If it were to have the former structure, the splitting would be into two components, but in the case of an unsymmetrical structure there would be three IR active bands.[8] The orientation of the rings in the selenonium cation is most likely the same as that in the triphenyl-methyl cation which shows similar splitting or as in methyl-triphenylarsonium cation which has an identical band pattern.[9] The variation in intensity and absorption due to the stepwise substitution of the phenyl groups is analogous to that observed for the phenylacetic acids[10] and the reasons assigned for it possibly do follow here. The non-equivalent rings having a higher π electron density would absorb at a lower frequency. The bands at 742 and 733 cm^{-1} may be assigned to the perturbed ring or rings. The marked shift of 22 cm^{-1} of the 764 cm^{-1} band and its lower intensity is possibly due to conjugation and the consequent lowering of the π electron density of the rings. The selenonium cation possibly has an unsymmetrical pyramidal structure in which the three phenyls are differently oriented. It may be similar to that of methyltriphenylarsonium cation with the lone pair replacing the methyl group.

UV spectra. Further support to the structure deduced from the IR spectra is provided by the UV studies. The spectrum of diphenylselenium has a structureless band in the 270 mμ region and is different from that of diphenylselenium dichloride or triphenylselenonium chloride which record fine structure. The spectra of II and

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[4] J. D. McCullough and G. Hamburger, *J. Amer. Chem. Soc.* **64**, 508 (1942).

[5] M. T. Rogers and T. W. Campbell, *J. Amer. Chem. Soc.* **69**, 2039 (1947).

[6] C. P. Smyth, A. J. Grossman and S. R. Ginsbarg, *J. Amer. Chem. Soc.* **62**, 192 (1940).

[7] J. D. McCullough, J. Bryden and R. Marsh, *Structure Reports* **11**, 678 (1948).

[8] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.* 674 (1957).

[9] Sadtlar Standard Spectra No. 205998.

[10] R. D. Kross, V. A. Fassel and M. Margoshes, *J. Amer. Chem. Soc.* **78**, 1332 (1956).

[11] M. A. A. Beg and Samiuzzaman. *Canad. J. Chem.* in press.

III are almost identical but for the intensities of the bands of the latter which are comparable with I. The pattern of absorption in these two cases is comparable with triphenylphosphine and the corresponding phosphonium compounds.[11]

Since the absorption in the 270 mμ region is similar to the low energy transitions in monosubstituted benzenes, it is assigned to π–π^* transitions. A structureless band here suggests a certain amount of charge disturbance in the π electronic structure of the ring similar to that in conjugated systems. The disappearance of fine structure in I is due to the easy dissipation of the energy of the electronically activated system into the vibrationally activated states. This case will depend on the angle between the planes of the rings and the position of the lone pairs. The intense absorption at 255 mμ indicates the angle between the planes of the rings to be conducive to conjugation and as suggested for the sulfur analogue which has a similar spectrum, the rings may be symmetrically inclined with respect to the selenium atom.[12,13]

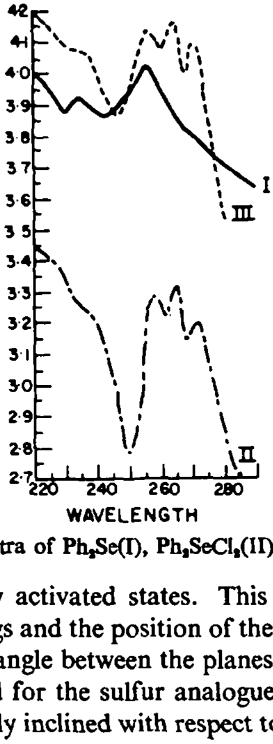

FIG. 2. UV Spectra of Ph_2Se(I), Ph_2SeCl_2(II) and $Ph_3Se^+Cl^-$(III).

With the formation of higher valent selenium compounds, the 4d orbitals start taking part and hence there would be an expected change in the UV spectrum. In the essentially trigonal bipyramidal frame work of the diphenylselenium dichloride, the repulsions due to the lone pair in the equatorial position, the chlorine atoms at the apical positions and the rotation of the ring out of plane with the other as evidenced by the X-ray studies, lead to a slight strain in the structure. Unlike diphenylselenium there would be a hindrance in the dissipation of energy of the activated system leading to fine structure and to a lowering in the intensity of absorption in this region of the spectrum. This suggests that there is no conjugative interaction between the rings which may be treated as monosubstituted benzenes. The occurrence of a band at 258 mμ however, suggests the presence of a partial conjugation which might be through the 4d orbitals.

With the introduction of a third ring a much higher extinction coefficient would have

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[12] H. P. Koch, *J. Chem. Soc.* 387 (1949).

[13] A. Magini and R. Passerini, *J. Chem. Soc.* 1168 (1952).

been expected. Only a slight increase in this value compared with diphenylselenium is noted in the selenonium compound. This suggests a further strain in the structure, the third ring contributing little to the intensity of the band.

The similarity in the pattern of absorption of II and III in the 250–270 mμ region may be due to the partial conjugation between the rings extending through only two rings leaving the third ring almost inequivalent. This was also concluded from the IR studies. It is also likely that one of these rings is intramolecularly bonded to the anion thus making it non-equivalent.

A further support to the non-equivalence of the rings in obtained from the absorption at 240 mμ. Because of their high intensity they are assigned to the n → π transition. In this region also splitting of the bands occurs at 230 and 238 mμ which becomes more pronounced in the spectrum of III. This has been suggested to be due to the non-equivalence of the rings.[14]

An unsymmetrical structure may therefore be concluded for both II and III. As for III the similarity of the IR spectrum with methyltriphenylarsonium compound suggests that the three rings are distributed in a pyramidal framework. The steric hindrance of the *o*-hydrogen atoms coupled with the repulsions from the lone pair would result in a tendency for the rings to be out of plane of the other two.

[14] W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spect.* **5**, 118 (1960).