

THE IR AND UV SPECTRA OF SOME ARYLIODONIUM AND RELATED COMPOUNDS

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The IR and UV spectra of iodobenzene, benzene iododichloride, iodosobenzene, iodoxybenzene, diphenyl iodonium bromide and iodide and bis-*p*-tolyl iodonium bromide and iodide have been recorded. The intensities of the 1570, 1470 and 990 cm^{-1} bands have been correlated with the charge disturbance of the ring π electrons. In the case of *p*-tolyl iodonium compounds the 1590 cm^{-1} band absorbs only weakly which supports our earlier suggestion that this band is related to the interaction of the lone pair electrons with the ring π electrons. The neighbouring group effect is particularly obvious in iodoso and iodoxybenzene. From these studies the iodonium compounds have been shown to have an unsymmetrical orientation of the rings. The UV spectra indicate that the dissipation of the energy of the electronically activated state into vibrationally excited system is slightly hindered, suggesting an unsymmetrical inclination of the rings in the diaryliodonium compounds.

In continuation of our work^{1,2,3} on the correlation of the intensity of the IR spectral bands with the structure, we present here the data on the phenyl and *p*-tolyl iodonium compounds and other related iodo compounds like benzene iododichloride, iodosobenzene and iodoxybenzene. The observations on the iodonium compounds reveal certain interesting results which support the earlier suggestions regarding the orientation of the rings in space and the interaction of the lone pair electrons with the π electrons of the aromatic ring.

The IR spectrum of the diphenyliodonium compound in the far IR region has demonstrated its ionic nature.⁴ Characteristic frequencies⁵ of the iodo compounds and the UV bands⁶ have also been reported. The spectra recorded by us are in close agreement with the earlier studies.

Experimental

All the compounds have been prepared by the reported methods.⁷ Benzene iododichloride was prepared by chlorinating iodobenzene, iodosobenzene by treatment of the dichloride with sodium hydroxide, and iodoxybenzene by the steam distillation of iodosobenzene. Diphenyliodonium iodide was prepared by the alkaline treatment of an equimolar mixture of iodoso and iodoxybenzene. The *p*-tolyl iodonium compounds was prepared by the treatment of toluene with potassium iodate in the presence of acetic acid, acetic anhydride and sulphuric acid. The iodonium bromide was obtained by the metathetic reaction of the bromide of potassium with the corresponding iodonium iodide. The IR spectra were recorded in KBr discs and nujol mulls while the UV spectra were recorded in methanol and formamide solutions. The molar extinction coefficients were calculated by the method given by Flett.⁹

Discussion

As in the other phenyl and *p*-tolyl onium compounds, the main regions of interest are the 1600–1300, 1250–950 cm^{-1} and 850–650 cm^{-1} . The absorption bands are listed in Tables 1 and 2 and are all characteristic of a monosubstituted ring in the case of the phenyl and of the 1,4-substituted ring for the *p*-tolyl compounds. The main difference arises in the intensity of the bands which is particularly important for the correlation of structure.

The 1600–1300 cm^{-1} Region.—Among the phenyl compounds five bands are expected in this region at 1580, 1560, 1470, 1430 and 1320 cm^{-1} which are due to the *k*, *l*, *m n* and *o* modes, respectively. Modes *k* and *l* are found to be degenerate in all the iodo compounds except the iodonium. This must be attributed to the presence of the second phenyl group. A good amount of interaction of the lone pair electrons with the ring π electrons is expected among all the iodo compounds, since 1 to 3 pairs are available with the central atom. The intensities of the 1470 and 1570 cm^{-1} bands have been shown previously to depend on the interaction of this type. Thus the 1470 cm^{-1} band is the most intense in iodobenzene, benzeneiododichloride and diphenyliodonium compounds. The order of decreasing intensity for the first two compounds is 1470 > 1570 > 1430 and for the iodonium compounds it is 1470 > 1440 > 1570 > 1585 > 1310. In the iodoso and iodoxy compounds the order is 1430 > 1570 > 1460 > 1320 except that in iodoxybenzene the 1570 band does not appear.

The intensity of these bands increases in the following order: iodobenzene < iododichloride < iodoso < iodoxy < iodonium iodide < iodonium bromide.

The similarity in the spectral pattern of iodobenzene, benzene iododichloride and the iodonium

compounds suggests that the charge disturbance is of similar type. Lone pairs stimulate conjugation and give rise to various canonical forms. These have already been proposed for the iodonium compounds.⁶ While the high intensity of the iodonium compounds may be attributed to the interaction of the lone pairs with the two rings, the low intensity of iodobenzene and the dichloride must be due to a single ring which does not produce as many canonical forms.

For the iodoso and iodoxy compounds the 1430 cm^{-1} band is the more intense which indicates that the charge disturbance is of a different kind. High intensity of this mode occurs when the tilting motion creates a larger dipole change for which the proximity of the interacting group would be responsible. In the iodoso compounds there are two lone pairs and the lone pair: lone pair repulsions being greater than lone pair: bond pair, the O—I—C plane would be angular. In spite of the electron-withdrawing oxygen, the lone pair of iodine would be able to interact with

the π electrons of the ring. The angular structure would, however, favour the twisting of the ring resulting in the enhanced intensity of the n mode. Two oxygens on the iodine in the iodoxy compounds would arrange themselves away from one another in a tetrahedral framework one of the apices of which is occupied by a lone pair. The two oxygens being more electron-withdrawing, would reduce the electron density on iodine giving it a positive charge, and hence the interaction of the lone pair would not be possible. This accounts for the absence of the 1570 cm^{-1} band. The proximity effect of this oxygen in these compounds has been noted in the case of the *o*-iodoxybenzoic acids.⁵ In the iodoxybenzene spectrum this will lead to the higher intensity of the n mode which we have noted here.

Among the bis(*p*-tolyliodonium) compounds the pattern of absorption is not the same as in the corresponding phosphonium and arsonium compounds, i.e. the 1590 cm^{-1} band is not of higher intensity but is weak as in the *p*-tolylphosphine or

TABLE I.—VIBRATIONAL FREQUENCIES OF THE ARYLIDO COMPOUNDS.

Mode†	I	II	III	IV	V	VI	VII	VIII
<i>k</i>					1570(38)	1585(34)		
	* +							
<i>l</i>	1570(9)(7)	1570(28)	1570(50)		1560(88)	1575(87)		
<i>m</i>	1470(8)(8)	1470(38)	1460(46)	1470(82)	1470(141)	1475(150)	1475(159)	1480(173)
<i>n</i>	1430(8)(5)	1430(27)	1430(70)	1440(119)	1430(95)	1440(125)	1440(138)	1440(101)
Methyl deformation								1385(64)
<i>o</i>	1312(3)		1300(38)	1320(13)	1320(20)	1310(15)	1300(81)	1300(19)
<i>e</i>			1270(25)	1270(15)	1260(25)	1260(29)	1270(90)	1270(50)
							1210(146)	1200(105)
<i>a</i>			1170(29)	1170(24)	1170(33)	1170(24)	1180(123)	1180(110)
<i>c</i>			1150(24)		1155(33)	1155(27)	1115(104)	1110(69)
		1080(10)			1085(20)	1085(6)		
<i>d+q</i>	1055(11)	1058(22)	1062(28)	1060(9)	1060(38)	1060(27)		1115(69)
				1042(67)	1045(30)	1045(22)		
					1040(28)	1040(20)		
<i>b</i>	1010(19)	1020(39)	1010(31)	1010(26)	1010(53)	1012(69)		
<i>p</i>	993(13)	998(38)	995(46)	988(86)	985(113)	988(121)	995(165)	995(184)
<i>h</i>					965(16)	965(52)		
<i>i</i>					908(20)	905(6)		
<i>g</i>					830(12)	830(24)		
<i>f</i>							800(200)	800(253)
							792(253)	790(195)
								780(112)
1— θ stretch				770(301)				
				757(301)				
			740(81)	745(363)				
<i>f</i>	730(41)	730(54)	732(118)	735(472)	740(248)	743(225)		
				729(472)	732(229)	735(208)		
1— θ stretch				713(376)				
<i>v</i>	682(27)	680(27)	688(85)	675(138)	677(133)	675(150)		

* =spectrum taken in chloroform

+ =liquid film

() =E

I =Ph I

II =PhI—Cl₂

III =PhIO

IV =PhIO₂

V =Ph₂I⁺I⁻

VI =Ph₂I⁺Br⁻

VII =*p*-tol₂I⁺I⁻

VIII =*p*-tol₂-I⁺Br⁻

†D.H. Whiffen, J. Chem. Soc., 1350 (1956).

TABLE 2.—UV ABSORPTION MAXIMA OF THE ARYLIO DO COMPOUNDS.

			λ_{\max}	$\log \epsilon$
PhI	257	2.760
			252	2.769
			227	4.002
PhICl ₂	262	2.806
PhIO	262	3.154
PhIO ₂	264	3.241
Ph ₂ I ⁺ I ⁻	270	3.205
			263.5	3.293
			257.5	3.223
			222	4.492
Ph ₂ I ⁺ Br ⁻	271	3.368
			264	3.467
			225	4.094
<i>p</i> -tol I ⁺ I ⁻	286	3.407
			275	3.424
			263	3.696
			235	4.239
			220	4.368
<i>p</i> -tol I ⁺ Br ⁻	275	3.387
			263	3.617
			260	3.680
			235	4.432

arsine. The reason previously assigned to the enhancement of the intensity of this band were the interaction of the lone pair of electrons with the π -electronic system. In the iodonium compounds the lone pairs are available which present a case similar to the phosphin or arsine. The intensity of the band at 1590 in the *p*-tolyliodonium compounds would therefor not be expected to be enhanced.

The *n* mode i.e. the 1430 cm^{-1} band has a highest intensity for the phenyl and *p*-tolyliodonium compounds than for the iodoso or iodoxy benzene. This must be related to the angular structure and the slight turning of one of the rings, out of plane with the other. This structure has been deduced for the diphenyliodonium fluoborate by electron diffraction method⁸ and steric hindrance has been attributed to this type of structure. By analogy with several compounds of similar nature an angular structure with a slight rotation of the rings may be easily assigned to the iodonium compounds.

The 1250–950 cm^{-1} Region.—The second region of interest is the one due to the in-plane hydrogen deformation vibrations. Out of these the ones due to mode *b*, *d* and ring breathing have been found to indicate the presence of conjugative interaction through their high intensity. Thus in the iodonium compound the *b* mode occurring at 1010 cm^{-1} has the highest intensity. It is high in other iodo compounds also but iodoxy benzene is an exception. In the last named compound the ring breathing mode is the highest intensity band. The band which is prominent among the iodonium and the iodoxy compounds but not so much in the others is that due to mode *d* occurring at 1054 in the phenyls and at 1115 in the *p*-tolyls which is due to one of the hydrogens bending towards the substituent and the other away from it. Such a vibration will be facile in twisted ring systems, i.e. those where one of the rings is turned out of plane with respect to the other. The other vibration corresponding to mode *e* should also be active and absorb with a higher intensity than usual and this has been observed in the case of the diphenyl and bis-*p*-tolyl compounds. In iodoxybenzene also these two bands are quite prominent and so is the ring breathing mode, the high intensity of which has been previously attributed to conjugative effect.

The 800–650 cm^{-1} Region.—This region reveals splitting of bands in case of non-equivalence of the rings or the lack of conjugation among the rings. In the diphenyl compounds the splitting into doublets is $\sim 10 \text{ cm}^{-1}$ and in the bis-*p*-tolyl compounds it is 8 cm^{-1} . In case the rings were favourably inclined no splitting would have been expected as in diphenylselenium.¹ It is only when the rings are twisted out of plane that we observe splittings. Keeping in view the structure of diphenyliodonium fluoborate deduced by the electron diffraction method it is possible to suggest that the splitting is a result of unsymmetrical orientation of the rings. It is possible to deduce the angle from the amount of splitting purely on empirical basis, by comparing the structure and spectra of various compounds and on this basis it may be concluded that the rings are inclined to the extent of 15–20°.

Splittings are also noted in the iodoxybenzene spectrum. While the strong bands have been assigned to symmetric and asymmetric I—O stretchings,⁵ the C—H out-of-plane bending deserves to be mentioned. Two bands appear at 730 and 735 cm^{-1} . Strong lattice forces have been noted^{5,9} in the crystal of this compound and hence it is possible that the splittings here are due to lattice interactions. The proximity effect discussed earlier also suggests such interactions and

it is likely that neighbouring group effect results in split bands.

UV Spectra.—The main features of these spectra are: (1) that in most of the compounds a structureless band is observed in the 265 m μ region while the iodonium compounds record shoulders here, and (2) that the intensity of absorption of the various bands increases in the following order: iodobenzene < benzene iododichloride < iodobenzene \leq iodoxybenzene < diphenyl iodonium bromide < diphenyl iodonium iodide < bis-*p*-tolylodonium iodide \leq bis-*p*-tolylodonium bromide.

The 265 m μ region is characteristic of the transitions in the benzene ring. A structureless band has been shown previously to suggest charge disturbance as in conjugated ring systems.^{1,2} For such a charge disturbance to be effective it is necessary that the angle between the planes of the rings and the position of the lone pairs be conducive to the dissipation of the energy of the electronically activated state into the vibrationally activated system. The spectrum of the iodonium compounds is quite similar to that of diphenylselenium except for the shoulders. The intensity of the band is also lower. These observations indicate that there is a slight hindrance in the easy dissipation of the energy into the vibrationally activated state which must be due to the ring being twisted out of plane as deduced from electron diffraction studies.⁸

The increase in the intensity of the band from iodobenzene to the iodonium compounds shows the participation of the various canonical forms mentioned earlier. The position of the band is,

however, shifted and one can easily infer that this is due to the change in the interacting species. In iodoso and iodoxybenzene the position of the band remains the same as in iododichloride but there is a further gain in intensity. Proceeding on these lines, we find that in iodobenzene the number of canonical forms is higher and for iodoxybenzene it is higher still. In the case of iodonium compounds there are two rings and hence the higher intensity is easy to explain. For the *p*-tolylodonium compounds the enhancement may be attributed to the hyperconjugative effect of the methyl group.

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