292. *Absorption Spectra of Substances containing the Carbon–Iodine Bond. Part II.**

By T. M. Dunn and T. Iredale.

The absorption spectra of iodobenzene, the iodonaphthalenes, and 2-iododiphenyl in the near ultra-violet are described. Under suitable experimental conditions a brief, diffuse band system has been found in the vapour of iodobenzene at room temperature, and at 90° K in its solution in frozen light petroleum. The *O–O* bands of iodobenzene in the two states have been indicated. Reasons for the disposition and intensities of the bands of the iodonaphthalenes and of 2-iododiphenyl have been advanced.

In Part I * Iredale, Durie, and Jarvie described the absorption spectra of some compounds containing the C–I bond, in particular iodobenzene and iodoacetic acid. In the vapour state there appeared to be for both these substances a continuum in the 2600-Å region, although it was implied that in the case of iodobenzene not all of the absorption in this region may have been embraced in this phenomenon. This paper describes some experiments carried out to discover if there is any band system, possibly not very strong, which may be obscured by the accompanying continuum.

There is reason to believe that the absorption spectrum of iodobenzene is complex because of the accidental magnitudes of molar extinction coefficients of two different

---

* Part I, *J.*, 1950, 1181.

absorption processes: (i) excitation of π electrons in the ring, analogous to benzene and other halogenobenzenes, (ii) excitation of a non-bonding electron on the iodine. It is difficult to believe, however, that both these processes will be concurrent if there is much conjugation of the iodine with the ring.

An unusual trend is observed when the maximum extinction coefficient ($\varepsilon = 665$) of iodobenzene is compared with the extinction coefficients of the other halogenobenzenes in the same region:

	PhF	PhCl	PhBr
$\varepsilon_{\text{max.}}$ (1)	1650	310	243
$\varepsilon_{\text{max.}}$ (2)	1061	236	200

(1) Conrad-Billroth, *Z. physikal. Chem.*, 1934, *B*, **25**, 139.
(2) American Petroleum Institute Research Project 54, National Bureau of Standards.

There is a progressive decrease of ε with increasing atomic weight of the halogen towards $\varepsilon = 220$ of benzene itself. Since the alkyl iodides have maximum extinction coefficients in the 2600-Å region of the order 400—500 [methyl iodide, 380; ethyl iodide, 460; propyl iodide, 480 (Hillmer and Paersch, *Z. physikal. Chem.*, 1932, *A*, **161**, 46)], it appears likely that the continuum is caused by an alkyl iodide type of absorption superposed on the banded type of absorption characteristic of the other halogenobenzenes. From the trend of the extinction coefficients of these benzene derivatives, iodobenzene would be expected to have for its banded absorption a maximum extinction coefficient $\varepsilon \sim 220$, the same as for benzene itself. This added to the alkyl iodide $\varepsilon = 400$—500 would give a total ε for the two effects of *ca.* 600—700, which is of the order of the observed value, *i.e.*, 665. Some reason must be found for the exceptional behaviour of the iodine atom.

On Sklar's hypothesis (*J. Chem. Physics*, 1939, **7**, 984) that absorption intensity depends upon the extent of migration of electrons into or out of the benzene ring, it would seem that in iodobenzene there is negligible migration. When the halogens are bonded to a benzene ring, there are four non-bonding electrons, two $np\pi_x$ and two $np\pi_z$ (the two-fold axis of rotation being taken as the y axis, and the z axis in the usual sense), and in the case of fluorobenzene where these electrons are $2p\pi_x$ and $2p\pi_z$ we know that there is a strong mesomeric effect tending to cause migration of the π_z electrons into the benzene ring, while the inductive effect more than overcomes this tendency, resulting in the effective dipole moment being away from the ring. This mesomeric migration of charge has been demonstrated theoretically by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39) who showed that, molecular orbitals being used for conjugated systems such as fluorobenzene, the electron density of the electrons on the halogen atom, q_r, is such that $0 \leqslant q_r \leqslant z$. Thus their analysis shows that even though the halogen atom is more electronegative than the carbon atom, it is, in fact, only the magnitude of the electron drift and not its direction which depends upon the nature, *i.e.*, the electronegativity, of the atom, in this case a halogen. Baddeley (*J.*, 1950, 663), from a consideration of available data, suggested that there was a relation between the size of an atom and its mesomeric effect. We have here spectroscopic evidence to support the idea of decreasing mesomeric effect down the halogen series from the small fluorine to the large iodine atom.

The long-wave ultra-violet band of the alkyl halides, and in particular the 2600-Å band of the alkyl iodides [Herzberg and Scheibe's *A* band (*Trans. Faraday Soc.*, 1929, **25**, 716)] has been attributed by Mulliken (*Phys. Review*, 1936, **50**, 1017, 1028; 1937, **51**, 310; *J. Chem. Physics*, 1940, **8**, 234, 382) to the weak perpendicular type $N \longrightarrow Q$ transitions. Price (*ibid.*, 1936, **4**, 539) suggests that the continuum is due to a strong form of predissociation resulting from this transition, rather than that the upper state is a pure repulsion, giving the continuum observed in practice.

This scheme shows that the transition involved is essentially localised on the iodine atom, or at most, since the 6*s* orbital of iodine is very large, it may be localised in the vicinity of the C–I bond, and so has hardly any effect on the molecule as a whole. The same effect is shown in Herzberg and Scheibe's *B*, *C*, and *D* bands (*loc. cit.*) which Mulliken suggests are due to a 5 $p\pi$ non-bonding electron of the iodine excited to a 6 $d\pi$ level, the transition being once more localised on the iodine atom.

Predissociation causes the bond to split with the transfer of one bonding electron to the carbon atom, and the molecule breaks into two neutral parts, one an iodine atom and the other a radical.

Further evidence for the assumption of a purely localised C–I absorption in iodobenzene can be obtained from a consideration of McClure's data (*J. Chem. Physics*, 1949, **17**, 905) on the oscillator strengths of halogenbenzenes :

	PhF	PhCl	PhBr	PhI	PhH
f	0·00816	0·00284	0·00249	0·0134	0·00147

These values have a fair error due to the difficulty of obtaining the correct summation when the bands have much structure, as in the case of all but iodobenzene. Mulliken's approximation (*J. Chem. Physics*, 1939, **7**, 14) $f = 4{\cdot}31 \times 10^{-9} \times \varepsilon_{\max.} \times \Delta\nu$ being used, where $\Delta\nu$ is the " half band width " (this in the case of the alkyl iodides is about 5000 cm.$^{-1}$), $\varepsilon_{\max.}$ has previously been seen to be about 450, and using these values we obtain the electron oscillator strength of the alkyl iodide continuum as 0·0097. This value when added to that for benzene gives an *f* for the combined alkyl iodide and benzene transitions equal to 0·0112, which is still somewhat removed from the experimental value of 0·0134. We have assumed that the extinction coefficient of the iodobenzene band absorption is about the same as for benzene itself; but it is probably greater than that, so the actual combined *f* value will be definitely greater than 0·0112.

Recently, Robertson and Matsen (*J. Amer. Chem. Soc.*, 1950, **72**, 5252) calculated the position and intensity of the halogenobenzene bands by the crude molecular-orbital theory in which allowance has been made for the inductive effect. Their order is $C_6H_5F > C_6H_5Cl > C_6H_5Br$ for the oscillator strengths. Iodobenzene was not considered because of the assumed diffuseness of the absorption. We have seen that iodobenzene falls into line with the other halogenobenzenes if the banded absorption be considered separately from the continuum.

Iodobenzene.—Hitherto we have only observed an absorption continuum, using the strong source of ultra-violet light, a modified form of the Allen hydrogen arc (Dunn, Durie, and Iredale, *Australian J. Sci.*, 1950, **12**, 143), and long exposures with the Hilger 3-metre grating spectrograph. There is some decomposition of the iodobenzene, and a film tends to form on the front window of the absorption cell, in spite of every precaution to prevent this. Possibly this is not the only explanation of the difficulty involved in obtaining discrete absorption bands of the kind found with the other halogenobenzenes. We next tried the absorption in a tube 150 cm. long with the vapour coming from an attached reservoir of the pure liquid kept at temperatures from —10° to room temperature (18°). The source of ultra-violet light was a hydrogen discharge tube of low intensity, of the type 2230 supplied with the Beckman DU spectrophotometer. The spectrograph was the Hilger medium quartz instrument. We also investigated the absorption of a light petroleum solution of iodobenzene, frozen to a solid glass at 90° K in a special apparatus to be described later. In this way we have obtained some diffuse bands, both in the vapour and in the frozen solution. They are degraded to the red. Their wave-lengths, wave-numbers, and separations from the band of longest wave-length are given in the following table :

Iodobenzene bands.

Vapour			Solid		
λ (Å)	ν(cm.$^{-1}$)	$\Delta\nu$	λ (Å)	ν(cm.$^{-1}$)	$\Delta\nu$
2502	39 970 m	3210	2576	38 820 s	2490
2547	39 260 s	2500	2643	37 840 s	1510
2613	38 270 s	1510	2679	37 330 w	1000
2683	37 270 m	510	2714	36 840 m	510
2721	36 760 w	—	2752	36 330 m	—

(s = strong; m = medium; w = weak.)

In benzene it is found that the ε_g^+ vibration has the value 520 cm.$^{-1}$ in the excited state, 606 cm.$^{-1}$ in the ground state. In the halogenobenzenes, this ground state vibration splits into two : ~600 cm.$^{-1}$ of symmetry β_1, and a totally symmetric vibration of lower frequency, α_1 (Sponer, Nordheim, Sklar, and Teller, *J. Chem. Physics*, 1939, **7**, 207) :

	Ground state vibration		Excited state vibration		Ground state vibration		Excited state vibration
	β_1	α_1	β_1		β_1	α_1	β_1
PhF	617	520	517	PhBr	616	317	—
PhCl	615	418	521	PhI	614	268	510

Support for the assignment of 617 and 615 cm.$^{-1}$ in fluoro- and chloro-benzene is given by Wollman (*ibid.*, 1946, **14**, 123) from a comparison with the corresponding bands in benzene, and from a study of the Raman lines (Wittek, *Sitz. Akad. Wiss. Wien*, 1941, 2*B*, **150**, 1; Kohlrausch and Wittek, *ibid.*, p. 75).

The band at 2752 Å (36 330 cm.$^{-1}$) is assumed to be the *0–0* band. The *0–0* band in the vapour, assumed to be 2721 Å (36 760 cm.$^{-1}$), implies a red shift in the solid phase of 430 cm.$^{-1}$. From studies of fluoro- and chloro-benzene, Wollman (*loc. cit.*) concludes that the transition 0—2,β_1 can take place, and that this transition increases in intensity relatively to the 0—1 band intensity as the substituent changes from bromine to chlorine to fluorine. This illustrates the increasing importance of the vibration mechanism in allowing the electronic transition in the order F > Cl > Br > I, and explains the very weak band at 2679 Å ($\Delta\nu = 1000$ cm.$^{-1}$), in the iodobenzene spectrum in the solid phase, which has no counterpart in the vapour.

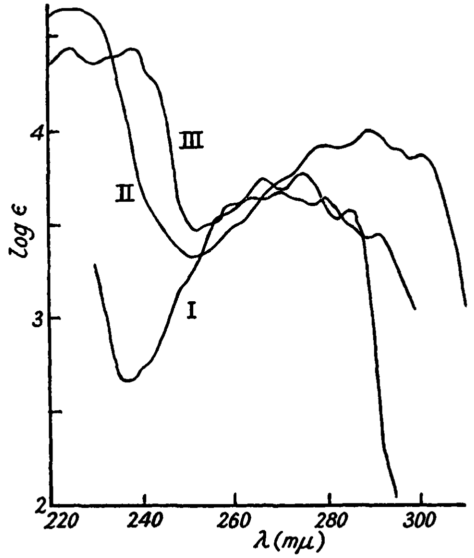


FIG. 1.

(I) *Naphthalene.*
(II) *α-Iodonaphthalene.*
(III) *β-Iodonaphthalene.*
(*All in* n-*heptane.*)

The red shift of the *0–0* band of iodobenzene vapour relatively to benzene is then 1330 cm.$^{-1}$ compared with 1093 and 1037 cm.$^{-1}$ for bromo- and chloro-benzene.

We are unable to confirm Sreeramurty and Rao's finding (*Curr. Sci.*, 1949, **18**, 418) of about 100 bands of iodobenzene in the 2400—2800-Å region. As they gave no experimental details, we are unable to compare their results with ours. We hope to improve experimental conditions and discover more bands, which are doubtless obscured by the continuum.

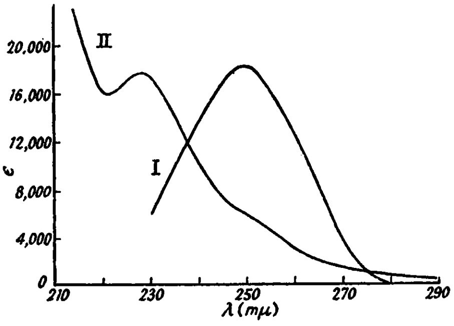
Iodonaphthalenes.—As α- and β-iodonaphthalene have very low vapour pressures at room temperatures, special heating arrangements must be adopted to obtain a reasonable vapour pressure and quantity of absorbing gas in an absorption tube of convenient length. We have worked up to temperatures of 75°, when absorption becomes appreciable. One or two bands have appeared, but the crowding together of so many bands, caused by the greater number of transitions allowed in the naphthalene structure as compared with benzene, and the operation of the Boltzmann factor at the higher temperatures, makes their identification almost impossible. We hope to obtain more satisfactory results with long absorption tubes at lower temperatures.

In heptane solution a banded structure is obtained both for the α- and the β-compound, and the relation of this absorption to that of naphthalene is shown in Fig. 1. The molar extinction coefficients (ε) in the 2600-Å region are of the order 4×10^3, so that the π electron absorption in this case completely swamps the aliphatic C–I ($N \longrightarrow Q$ transition) absorption, where ε ~600.

Of the two absorption bands, the long-wave band of naphthalene may be considered to be due to a transverse polarization through the 1- and 4-positions, and the short-wave band to a longitudinal polarization. In the case of α-iodonaphthalene, the long-wave band has increased in intensity and shifted to the red, whereas for the β-compound, the short-wave band has shifted toward the red, and the long-wave band is almost in the same position as in naphthalene.

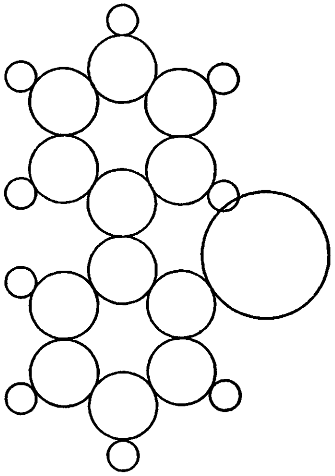
2-Iododiphenyl.—The absorption spectrum of this compound requires special explanation, since it does not follow regularly the expected change upon substitution of iodine in the diphenyl nucleus. The maximum appears to have been shifted to the short-wave side, and there appears to be an overlapped band in the region of 2500 Å (Fig. 2). (The absorption of both diphenyl and iododiphenyl was measured with the Beckman instrument.) Steric effects are of importance in this case. O'Shaughnessy and Rodebush (*J. Amer. Chem. Soc.*, 1940, **62**, 2906) have discussed the cases of 2 : 2′-disubstituted diphenyls, but here we have a case where steric hindrance occurs without a second substituent group. Reference to a scale drawing of the molecule (Fig. 3 : diameter of small circle = 0·62 Å) shows that, even when the effect of bond shortening is neglected, there is considerable overlapping of the hydrogen and iodine orbitals. This undoubtedly leads to a twisting of the molecule out of the planar configuration, resulting in a loss of delocalization energy of the π electron systems. This will lead to a breakdown of the long-wave band of diphenyl, owing to the destruction of the diphenyl symmetry. The spectrum will tend to revert to a composite spectrum of the two mutually unconjugated parts of the molecule. This effect will not be complete, owing to the fact that the angle of twist would not be a complete right angle. This explains the appearance of the band at about 2290 Å, but does not account for the apparently overlapped band. It is suggested that this band is also present in the spectrum of diphenyl, but it is hidden by the band of stronger transition in the same region. It is most likely connected with absorption of light with the electric vector perpendicular to the two-fold axis in diphenyl, and is uncovered when the stronger transition is displaced to shorter wave-lengths, as well as being slightly displaced to the red itself, owing to substitution by iodine in the *o*-position. Platt (*J. Chem. Physics*, 1951,

FIG. 2.



(I) *Diphenyl.*
(II) 2-*Iododiphenyl.* (*Both in* n-*hexane.*)

FIG. 3. *Planar configuration of 2-iododiphenyl.*



19, 101) predicted from a study of the energy levels of molecules iso-π-electronic with diphenyl, such as fluorene, that such a hidden transition should exist. Now Pestemer and Meyer-Pitsch's study of substituted diphenyls (*Monatsh.*, 1937, **70**, 104) also supports this prediction. Their absorption curves for *p*-substituted diphenyls show no trace of a long-wave step, whereas the curves for *m*- and *o*-substituted compounds show such overlapped transitions clearly. The *m*-substitution obviously shifts the transversely polarized band to the red, and leaves the main band almost stationary. In *p*-substituted compounds the strong band still overlaps the band of weaker transition, but in *o*-compounds both steric hindrance and the red shift of the weaker transition cause it to be uncovered.

On account of the high extinction coefficients of these allowed transitions ($\varepsilon > 10^4$), all evidence of a localized, C–I aliphatic absorption has vanished, nor may we expect to find it again, except in compounds like iodobenzene which have an absorption due to a transition of low probability, in the 2600-Å region.

Experimental.—Details of the optical apparatus and methods of measuring the absorptions are given in Part I (*loc. cit.*).

Hexane and heptane were purified by repeated shaking with fuming sulphuric acid, washing, drying, and distilling. They transmitted satisfactorily down to 2200 Å. Light petroleum (b. p. 60—80°) was purified in the same way. The material set to a transparent, glassy solid when quickly frozen with the aid of liquid nitrogen.

Iodobenzene, purified by vacuum distillation, had b. p. 189°/760 mm., α-iodonaphthalene, purified by vacuum distillation, had b. p. 302°, and β-iodonaphthalene, purified by steam-distillation followed by three vacuum sublimations, in which the middle fraction was retained, melted at 53°.

2-Iododiphenyl, purified by steam-distillation, followed by vacuum distillation, had b. p. 110°/0·5 mm. We considered that the substance examined was sufficiently pure when its spectral characteristics did not change any further.

We are indebted to Mr. J. Ferguson for photographing and identifying the iodobenzene bands.

PHYSICOCHEMICAL LABORATORIES, UNIVERSITY OF SYDNEY. [*Received, October 29th*, 1951.]