422. *The Electronic Absorption Spectra of Some Diaryliodonium Salts.*

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The spectrum of the diphenyliodonium cation, Ph_2I^+, is not changed by the presence of anions such as OH^-, F^-, Cl^-, Br^-, I^-, ClO_4^-, ReO_4^-, and SO_4^{2-}. The introduction of a *p*-fluoro- or *p*-methyl group produces only a small bathochromic shift. The absence of fine structure and the high molecular extinction coefficient (which is closer to that of biphenyl than that of diphenylmethane) is interpreted in terms of resonance hybridisation involving the unshared pairs of the iodine atom.

The spectrum of diphenyliodonium iodide and of di-*p*-tolyliodonium iodide can be satisfactorily interpreted by the simple addition of the absorptions due to the components. There is no evidence for any marked charge-transfer effect.

The spectrum of the phenyleneiodonium cation is found to resemble that of fluorene very closely.

THE ease with which iodobenzene, iodine, and benzene are formed by the photochemical decomposition of solutions of diphenyliodonium iodide, $[Ph_2I]^+I^-$, but not of other halides, in chloroform may well be related to the greater deformability of the iodide ion.[1] Indeed the formation of chlorobenzene and iodobenzene in the non-catalysed decomposition of solutions of diphenyliodonium chloride has been viewed as proceeding through the reversible formation and irreversible decomposition of diphenyliodonium–chloride ion-pairs.[2] The analogies between the diaryliodonium cation and the strongly deforming univalent ion Tl^+ have often been commented upon,[3] and it was thought that an examination of the absorption spectra of a series of diaryliodonium salts might be informative.

Specimens of solid diphenyliodonium chloride, bromide, and iodide were prepared by a modification of the procedure of Beringer *et al.*[2] and rigorously purified by recrystallisation from boiling methanol until there was no change in the absorption spectrum of successive fractions. Preparations of identical properties were obtained by the addition of concentrated hydrochloric acid, sodium bromide, or potassium iodide, severally, to concentrated solutions of diphenyliodonium hydroxide or (better) nitrate.

Diphenyliodonium fluoride, prepared from the hydroxide and its equivalent of hydrofluoric acid, is a very soluble, deliquescent solid, m. p. 127—128°. It had previously been prepared by Eméleus and Heal[4] who reported m. p. 85°. Diphenyliodonium perchlorate, m. p. 173—174° (decomp.), was obtained similarly. Samples of diphenyliodonium per-rhenate and tetraphenylborate, of di-*p*-fluorophenyliodonium chloride, and of phenyleneiodonium iodide were available.[1]

A preliminary examination of the electronic absorption spectra of approx. 3×10^{-5}M-aqueous solutions of diphenyliodonium hydroxide, perchlorate, fluoride, chloride, bromide, and per-rhenate (not reproduced) showed no notable differences. In each case there was negligible absorption throughout the visible region, a single well-defined peak at 227·5 mμ ($\varepsilon \cong 1\cdot4$—$1\cdot5 \times 10^4$), a well-defined minimum at 217 mμ, and a slight shoulder at ~265 mμ. The observed small differences between the calculated molecular extinction coefficients for the various salts could well be due to small differences in their purity, for none of the analytical methods available (see p. 2084) permits of a precision much better than $\pm0\cdot2\%$.

To establish unequivocally that the spectrum of the diphenyliodonium cation was not influenced by the presence of hydroxide, perchlorate, fluoride, sulphate, or chloride ions (which are themselves transparent throughout the region in question), a solution of diphenyliodonium hydroxide was prepared from a known weight of pure diphenyliodonium

[1] Irving and Reid, preceding paper.
[2] Beringer, Geering, Kuntz, and Mausner, *J. Phys. Chem.*, 1956, **60**, 141.
[3] Cf. Schwab and Pechlivanidis, *Svensk kem. Tidskr.*, 1947, **59**, 141.
[4] Eméleus and Heal, *J.*, 1946, 1126.

chloride and excess of an anion-exchange resin, Amberlite IRA-400(OH). Equal portions were transferred to standard flasks, made slightly acid with perchloric, hydrofluoric, sulphuric, or hydrochloric acid, and diluted to 100 ml. This ensured that each solution contained exactly the same concentration of diphenyliodonium cation. The absorption spectra of the chloride, fluoride, hydroxide, and sulphate were indistinguishable (Fig. 1, a):
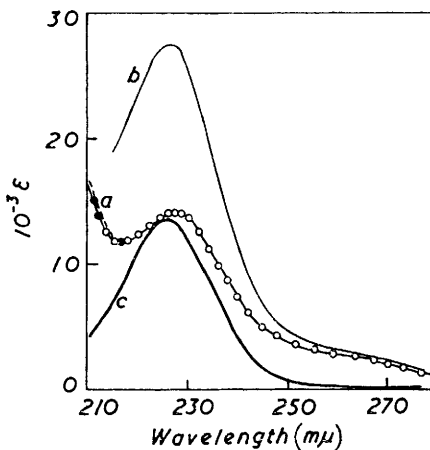
Fig. 1. *Electronic absorption spectra of diphenyliodonium salts and of potassium iodide. (a) Diphenyliodonium hydroxide, fluoride, chloride, bromide, sulphate, and perchlorate. (b) Diphenyliodonium iodide. (c) Potassium iodide.*
The open circles were obtained by subtracting corresponding ordinates of the spectra of the iodide ion (curve c) from those of diphenyliodonium iodide (curve b). The small broken line refers to the chloride.

the spectrum of the perchlorate could be superimposed exactly up to 225 mμ but at shorter wavelengths the absorption appeared to be slightly greater (≯2%) although the positions of maximum and minimum were unchanged.

It thus appears that the absorption due to the ion, Ph_2I^+, is not affected by difficultly deformable ions such as ClO_4^{2-}, F^-, SO_4^{2-}, or even by Cl^-, Br^-, or OH^-. Prue has shown independently that there is no appreciable shift in the ultraviolet absorption spectrum of $(C_6H_5)_2I^+$ with added OH^-. Moreover, the first-order rate constant for the specifically hydroxyl-ion-catalysed depolymerisation of diacetone alcohol actually increases with increasing concentrations of diphenyliodonium hydroxide, thus showing a positive salt effect akin to that of tetramethylammonium hydroxide.[5] There is thus no evidence for the association of hydroxyl and diphenyliodonium ions, a result in marked contrast to the well-established interaction of hydroxyl ions with thallous [6] or dimethylthallous ions.[7]

By using an aqueous solution of diphenyliodonium chloride of known concentration it was shown that the Beer–Lambert law holds rigorously up to a concentration of at least 3.5×10^{-4} mole/l., and the values $(1.43 \pm 0.02) \times 10^4$ and $(1.17 \pm 0.04) \times 10^4$ were found for the molecular extinction coefficients at $\lambda_{max.}$ 227·5 and $\lambda_{min.}$ 217 mμ respectively.

The absorption spectrum of diphenyliodonium iodide (Fig. 1, b) is very similar to that of the other salts in having a shoulder at ∼260 mμ, a maximum at 226·5 and a minimum at 214 mμ. However, the molecular extinction coefficients ($\varepsilon_{max.}$ 2·75 × 10⁴; $\varepsilon_{min.}$ 1·87 × 10⁴) are nearly twice as large because the iodide ion absorbs strongly in nearly the same region ($\varepsilon_{max.}$ 1·35 × 10⁴ at $\lambda_{max.}$ 225·5 mμ; cf. Fig. 1, c). Values calculated for the molecular extinction coefficient of the diphenyliodonium cation (open circles in Fig. 1) by subtracting values found experimentally for $[Ph_2I^+]I^-$ (Fig. 1, b) and I^- (Fig. 1, c) at a series of wavelengths coincide, within the limits of experimental error, with those found by direct measurement on salts of the diphenyliodonium cation and transparent anions (Fig. 1, a). It thus appears that the optical absorptions due to the ions Ph_2I^+ and I^- are additive and that no charge-transfer spectrum is detectable here. The absorption

⁵ Prue, personal communication.
⁶ Bell and Prue, *J.*, 1949, 362.
⁷ Lawrence and Prue, Internat. Conf. Co-ordination Chemistry, *Chem. Soc. Special Publ.* No. 13, 1959, p. 186.

of the nitrate ion (ε 7·0 at $\lambda_{max.}$ 301 mμ) will influence the spectrum of diphenyliodonium nitrate though this has not been analysed in detail. The spectrum of diphenyliodonium per-rhenate was found to be almost indistinguishable from that of the chloride.

Substitution in the phenyl nucleus does not change the character of the spectrum to any great extent. *p*-Fluoro-atoms have a slight bathochromic effect and appear to reduce the intensity of absorption ($\lambda_{max.}$ 229·5 mμ, ε 1·20 × 10^4; $\lambda_{min.}$ 217·5 mμ, ε 0·92 × 10^4). The main absorption band of the di-*p*-tolyliodonium ion is broader than that of the di-phenyliodonium ion and there is a marked bathochromic displacement ($\lambda_{max.}$ 239·5 mμ, ε 1·60 × 10^4; $\lambda_{min.}$ 224·7 mμ, ε 1·18 × 10^4) and the shoulder near 260 mμ is no longer apparent. The same spectrum is given by di-*p*-tolyliodonium perchlorate, chloride, or bromide. However, the spectrum of di-*p*-tolyliodonium iodide presents a broad band centred at 228 mμ ($\lambda_{max.}$ 2·34 × 10^4) and it can be reproduced accurately down to 230 mμ by adding the values appropriate to the ions (*p*-Me·C_6H_4)$_2$I$^+$ and I$^-$. Small divergencies at lower wavelengths are only just outside the limits of experimental error.

EXPERIMENTAL

Diphenyliodonium Chloride.—This was prepared by a modification of published procedures.[1,9] A substantially purer product was obtained (at the expense of some decrease in yield) by replacing ammonium chloride by hydrochloric acid in the last stage. The remaining diphenyliodonium salts in solution were later precipitated by the addition of a solution of potassium iodide. After being washed free from potassium salts, this diphenyliodonium iodide was used as a starting material for the preparation of other salts through the hydroxide or nitrate.

Diphenyliodonium chloride was purified by shaking the finely powdered solid with boiling methanol for a few minutes only, filtering the whole, and rapidly cooling the filtrate. After three such recrystallisations the purest sample (purity > 99·8%) had m. p. 229—230° (Found: Cl, 12·1. Calc. for $C_{12}H_{10}ClI$: Cl, 12·1%).

Diphenyliodonium Nitrate.—Solutions of this salt were prepared by shaking mechanically (24 hr.) in a blackened Winchester quart bottle diphenyliodonium iodide (45 g.), silver nitrate (16·5 g.), and distilled water (360 ml.). After filtration, concentrated hydrochloric acid (30 ml.) was added to the filtrate containing diphenyliodonium nitrate, and the whole placed in a refrigerator overnight. The solution showed a marked tendency to supersaturate but the yield of diphenyliodonium chloride was always 6·0—6·5 g. The remainder of the iodonium cation was recovered by addition of potassium iodide solution in excess.

Diphenyliodonium bromide was prepared by addition of sodium bromide solution to one of diphenyliodonium hydroxide[8] or nitrate. After three crystallisations from hot methanol it formed colourless needles, m. p. 218—219°. Beringer *et al.*[9] report m. p. 207—208° [Found: (C_6H_5)$_2$I$^+$ (by acidimetry, see p. 2082), 76·1; Br, 23·8. Calc. for $C_{12}H_{10}BrI$: (C_6H_5)$_2$I$^+$, 76·3; Br, 23·7%].

Diphenyliodonium Fluoride.—Hydrofluoric acid was added to an aqueous solution of diphenyliodonium hydroxide until the mixture was just acid to litmus. After concentration to small bulk on a water-bath the remaining water was removed by desiccation *in vacuo* over concentrated sulphuric acid. The residual solid recrystallised from redistilled, dry acetone as slightly brown needles, m. p. 127—128° [Found: (C_6H_5)$_2$I$^+$, 89·0. Calc. for $C_{12}H_{10}FI$: (C_6H_5)$_2$I$^+$, 93·1%]. This fluoride is very soluble in water and alcohol, but insoluble in ether. It is very deliquescent and became dark brown in sunlight.

Diphenyliodonium Perchlorate.—A solution of diphenyliodonium hydroxide was neutralised with 2N-perchloric acid; the perchlorate separated at once, but more could be obtained by concentrating the mother-liquors. After two recrystallisations from water it formed long, colourless needles, m. p. 173—174° (decomp.) [Found: (C_6H_5)$_2$I$^+$, 71·5. Calc. for $C_{12}H_{10}O_4ClI$: (C_6H_5)$_2$I$^+$, 72·1%].

Di-*p*-tolyliodonium salts were prepared according to the standard method[9] and recrystallised to constant absorption spectrum from hot methanol.

Absorption Spectra of Diphenyliodonium Salts.—The anion-exchange resin Amberlite IRA-400 was converted into the hydroxide-ion form and washed thoroughly with de-ionised

[8] Meyer and Hartmann, *Ber.*, 1894, **27**, 502.
[9] Beringer, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2705.

water until the washings were neutral. Excess of resin (1 g.), pure diphenyliodonium chloride (0·013 g.), and water (10 ml.) were shaken mechanically (12 hr.) in a stoppered Pyrex tube, covered to prevent direct access of daylight. The resulting solution of diphenyliodonium hydroxide was filtered through sintered glass, and the residual resin washed with boiled-out de-ionised water (220 ml. in all). The filtrate and washings were made up to 250 ml., and 50 ml. aliquot portions were made just acid with approx. 0·001N-hydrofluoric, hydrochloric, sulphuric, or perchloric acid and diluted to 100 ml. In this manner solutions were obtained of concentrations suitable for absorption spectroscopy and containing exactly equal concentrations of the diphenyliodonium cation.

Experiments with a variety of diaryliodonium salts showed that quantitative conversion into the corresponding hydroxide could be achieved by the use of Amberlite IRA-400(OH). Since these hydroxides are strong bases, comparable to tetra-alkylammonium hydroxides,

FIG. 2. *Electronic absorption spectra of iodonium cations and of formally analogous substances. (a) Diphenyliodonium cation in water. (b) Biphenyl in ethanol. (c) Diphenylmethane in ethanol (the ordinate scale has been increased 200-fold). (d) Biphenyleneiodonium cation in water. (e) Fluorene in iso-octane.*[13]
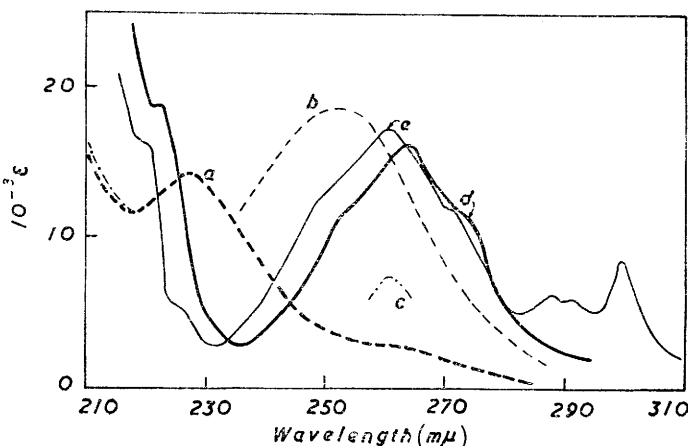
titration with standard acid forms a convenient method for the quantitative determination of the percentage of cation present and supplements the Volhard or other titrimetric methods which are restricted to the analysis of chlorides, bromides, or iodides.

In order to obtain molecular extinction coefficients, pure iodonium salts were weighed on a micro-balance and dissolved in de-ionised water: the absorption spectra were measured with a Unicam S.P. 500 or a Beckman DU Spectrophotometer, calibrated silica cells being used. The absorption spectrum of potassium iodide (Fig. 1, *c*) was obtained from recrystallised " AnalaR " material.

Conformity of Diphenyliodonium Chloride to the Beer–Lambert Law.—A stock solution of diphenyliodonium chloride (0·02688 g./250 ml.) was diluted 2, 5, 10, 12·5, 20, 25, and 40 times, and the optical density measured against distilled water at 217 and 227·5 mμ, calibrated silica cells of length 0·2, 0·5, 1·0, 2·0, and 4·0 cm. being used as appropriate. The measurements were checked with a second stock solution (0·023485 g./250 ml.) prepared from a different sample of diphenyliodonium chloride. Absolutely linear plots of (optical density–cell length in cms.) against concentration (moles/l.) were obtained at 217 and 227·5 mμ with slopes 1·17 $\pm$ 0·04 $\times$ 10^4 and 1·43 $\pm$ 0·02 $\times$ 10^4 respectively. Solutions more concentrated than 3·5 $\times$ 10^{-4}M were not examined.

DISCUSSION

The characteristic peak of the diphenyliodonium ion at 227·5 mμ is clearly due to benzenoid absorption. Benzene itself has one band of high intensity at 198 mμ and another of much lower intensity between 230 and 270 mμ which shows vibrational fine structure with the strongest absorption at 255 mμ ($\varepsilon \cong$ 230).

The absorption spectrum of iodobenzene [10] is similar to that of the diphenyliodonium cation but it is more complex and possesses a pair of overlapping bands of high intensity at 228 mμ (ε 13,300) and 233 mμ (ε 12,500) and a shoulder between 253 and 263 mμ due

[10] American Petroleum Institute Research Project 44, Serial No. 308.

to a number of overlapping bands of much lower intensity (ε 600—700). The general effect of substitution in the benzene nucleus is (*a*) to increase the intensity of absorption; (*b*) to simplify the spectrum by the broadening and overlapping of fine structure bands; (*c*) to displace the principal maximum towards longer wavelengths. If two benzene rings are directly joined, the intensity of absorption far exceeds the value calculated for simple additivity (*e.g.*, biphenyl in ethanol, $\varepsilon_{max.}$ 18,000).[11] If, however, conjugation is prevented by the interposition of a methylene group the increase in absorption is practically additive (*e.g.*, diphenylmethane in ethanol, $\lambda_{max.}$ 262 mμ; ε 190—245 per benzene nucleus).[11]

The intensity of absorption of the diphenyliodonium cation (Fig. 2, *a*) is less than that of biphenyl (Fig. 2, *b*) but much greater than that of diphenylmethane (Fig. 2, *c*) which it might appear to resemble structurally. Now the introduction of hydroxyl, alkoxyl, or amino-groups into benzene causes the fine structure in its spectrum to be replaced by a smoother band with a single maximum showing enhanced absorption. This is due to the participation of the unshared electron pairs of oxygen or nitrogen in the resonating
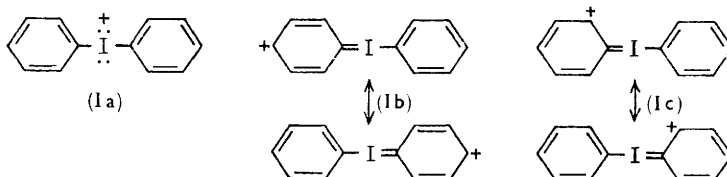
system.[11] It now appears that the unshared electron pairs of the iodine atom play a similar rôle in eliminating the fine structure due to the benzenoid absorption of diphenyliodonium ions. They also permit conjugation between the two phenyl groups. Participation of such canonical forms as (Ia, b, and c) will explain the high intensity of absorption, the absence of fine structure, and the general similarity to the spectrum of biphenyl rather than that of diphenylmethane. Resonance of the type postulated above should favour the coplanarity of the aromatic rings. The examinations of the structure of diphenyliodonium iodide and chloride by *X*-ray methods, apart from establishing their isomorphism, are insufficiently detailed to throw any light on this question.[12]
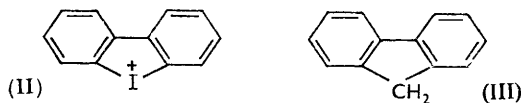
The spectrum of the biphenyleneiodonium cation (II; Fig. 2, *d*) also proved to be unaffected by the nature of the anion. It shows a remarkable similarity to that of fluorene (III; Fig. 2, *e*),[13] closer indeed than that of diphenyliodonium ion to biphenyl. This is to be expected because there is now direct conjugation between the two benzene rings in both (II) and (III) and the geometry of the fused 5- and 6-rings should be very similar.

[11] Gillam and Stern, " Electronic Absorption Spectroscopy," Edward Arnold Ltd., London, 1954, and refs. therein.
[12] Khotsyanova and Struchkov, *Zhur. fiz. Khim.*, 1952, **26**, 644, 669.
[13] American Petroleum Institute Research Project 44, Serial No. 401.