A very persuasive illustration is presented in Fig. 5 of the essential validity of the claim that dielectric constant–temperature variation cannot account for the ΔE^* phenomena observed in mixed solvents. Here the ΔE^* for the solvolysis of *t*-butyl chloride[25c] is plotted against the $(1 - bT)/D$ function. A linear relationship should result if the isodielectric type of analysis is valid. Such a linear relationship is observed (solid line) when the dielectric constant is changed by a total change of solvent from water to methanol to ethanol. However, when the dielectric constant is varied from water to ethanol by changing the composition of the binary mixture, the relationship breaks down completely at both ends of the range. It should be noted, however, that between approximately 0.2 and 0.8 mole fraction of ethanol, the dependence of ΔE^* on the dielectric constant function is very similar to that for the pure solvents.

All of the above facts regarding the dependence of activation energy on dielectric constant or its temperature coefficient argue strongly against dismissing the maximum–minimum behavior of ΔE^* as the result of dielectric constant temperature dependence and strongly in favor of the specific solvation concept.

Conclusions.—The treatment offered in this paper has been restricted to solvolytic reactions for which kinetic data of sufficient accuracy and scope are available. Further substantiation of the essential validity of the specific solvation hypothesis must await more extensive precision measurements, but it is hoped that this treatment will serve as a guide to the choice of critical experiment. A detailed scrutiny of the literature has uncovered many examples of similar behavior in the activation energies of non-solvolytic reactions in mixed solvents,[32–34] many of which give every indication of being amenable to a similar type of treatment. It is hoped to discuss certain of these specific cases in subsequent papers of this series.

It is not the intention of this paper to imply that the observed behavior of the activation energy as a function of binary solvent composition is due solely to specific solvation effects. However, the facts as presented here do appear to constitute strong support for the belief that such a solvent-sorting phenomenon plays an important part in determining the observed activation energy behavior.

Acknowledgments.—The author wishes to acknowledge the helpful comments of Professor J. H. Wolfenden and Dr. A. L. Jacobson, and financial support from the Research Corporation.

[32] E. S. Amis and V. K. LaMer, THIS JOURNAL, **61**, 905 (1939).

[33] C. V. King and J. J. Jacobs, *ibid.*, **66**, 767 (1944).

[34] W. J. Svirbely and A. Schramm, *ibid.*, **60**, 330 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

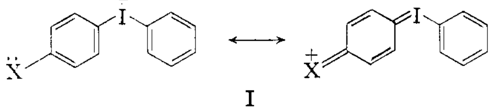
Diaryliodonium Salts. XV. Ultraviolet Absorption Spectra of Salts Bearing Functional Groups[1–3]

BY F. MARSHALL BERINGER[4a] AND IRVING LILLIEN[4b]

RECEIVED JANUARY 16, 1960

Ultraviolet absorption data on alkyl-, halogeno-, hydroxy-, alkoxy-, amino- and nitro-iodobenzenes and diphenyliodonium salts are presented and discussed in terms of the conjugative ability of iodine. It is concluded that in the unsubstituted diphenyliodonium cation, resonance interaction in which the iodine expands its valence shell to accommodate electrons is negligibly small but that such interaction may be made significant in the electronic excited state by the presence of electron-releasing *p*-substituents.

Introduction.—In iodonium salts iodine possesses both a positive charge and a rare-gas configuration. Because of the charge, iodine attracts electrons *via* an inductive or field effect. However, resonance would necessitate valence shell expansion of iodine with acceptance of the electrons into a 5d (or 4f) orbital.



I

Evidence now indicates that some elements below the first row in the periodic table can indeed interact with adjacent unbonded electrons by expansion of their valence shells beyond the octet; this process has been termed d-orbital resonance.[5–7]

The effect of the substituent upon a functional group on a benzene ring has been evaluated by application of the Hammett equation[8,9] to acidity data and by examination and comparison of ultraviolet spectra.[10,11] These methods have been used to demonstrate the ability of sulfur,[12,13] silicon[14] and

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[1] This paper is taken from the dissertation of Irving Lillien, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

[2] For the synthesis of most of the salts bearing functional groups see F. M. Beringer and I. Lillien, THIS JOURNAL, **82**, 725 (1960).

[3] For recent references to the reactions of iodonium salts see F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).

[4] (a) Visiting Associate Professor, Yale University, 1958–1959; (b) Alfred P. Sloan Foundation Research Fellow, 1956–1959.

[5] For a brief survey of d-orbital resonance see: H. B. Henbest, *Ann. Repts. Chem. Soc.*, 137 (1956).

[6] H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954).

[7] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

[8] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[9] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[10] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," Edward Arnold, Ltd., London, England, 1954.

[11] L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

[12] F. G. Bordwell and P. J. Boutan, *ibid.*, **78**, 87 (1956); **79**, 717 (1957); refs. cited in these articles.

germanium[14] to expand their valence shells in conjugation and the inability of nitrogen[15] to do so. The conclusion that a carbanion can be stabilized by resonance interaction with an attached sulfonium or phosphonium group but not with an attached ammonium group has been confirmed by chemical evidence involving rates of deuterium exchange and of addition to unsaturated systems.[16] Evidence from acidities[16] and from ultraviolet spectra[13] suggests that while substituents attached to carbon and sulfur may require planarity for maximum p,d-resonance interaction, deviation from planarity does not greatly decrease this interaction.

Chemical evidence suggests that d-orbital resonance is operative in phosphonium salts[16b,17] and that it is of about the same order of magnitude as that in the sulfonium salts. d-Orbital resonance recently has been invoked for the halogens[18] to explain certain trends in basicities and spectra.[19]

The purpose of this work was to study the ultraviolet absorption spectra of appropriately substituted iodobenzenes and diphenyliodonium salts, to evaluate the electronic interactions involved and to deduce whether in appropriate systems iodine could be significantly involved in d-orbital resonance.

Experimental

Compounds for Study.—Commercial grades of liquid aromatic compounds were purified by distillation. 4-Iodoaniline, 4-iodotoluene and 4-iodochlorobenzene were commercial reagent materials and were recrystallized before use; 2- and 3-iodoanilines were prepared by reduction of the corresponding iodonitrobenzenes.[20] 4-Iodoanisole[21] and 4-iodophenol[22] were prepared as described in the literature. 4,4′-Dimethyl-, 4,4′-dichloro-, 4-methoxy-, 4,4′-dimethoxy-, 2-, 3- and 4-nitrodiphenyliodonium and unsubstituted diphenyliodonium salts were prepared by published procedures.[23,24] The syntheses of 3-methoxy-, 4-benzyloxy-, amino-, nitroamino- and hydroxydiphenyliodonium salts and their derivatives have been described.[2] Samples of 4,4′-dihydroxy- and 4,4′-dinitrodiphenyliodonium salts were kindly furnished by Robert A. Falk.[24,25]

Ultraviolet Absorption Spectra.—All spectra were taken at about 10^{-5} molar concentration in methanol (Fisher spectral reagent) on a Process and Instruments Co. model RS-3 recording spectrophotometer. The slit width was set at 0.6 at 700 mμ.

Tables.—For ease of comparison with present results there are summarized in Table I selected previously reported data on monosubstituted benzenes. Present results on iodobenzenes and diphenyliodonium salts are reported in the following tables: II, substituted iodobenzenes; III, 4- and 4,4′-substituted diphenyliodonium salts; IV, isomeric substituted diphenyliodonium salts; V, substituted phenols.

Usage in the present work concerning terminology and band assignments conforms to that of Doub and Vandenbelt[11] and of Forbes and co-workers[26-28] Different terminology has been used by Burawoy[29] and by Bowden and Braude,[30] among others.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF MONOSUBSTITUTED BENZENES

Subst.	mμ (log ε)	mμ (log ε)
H[a]	203 (3.87)	255 (2.31)
F[b]	204 (3.79)	254 (2.95)
Cl[b]	210 (3.88)	257 (2.33)
Br[b]	210 (3.93)	261 (2.30)
I[c]	207 (3.86) 226 (4.12)	~257 (2.85)
CH_3	211 (3.96)	260 (2.42)
		270[d]
OH[e]	218 (3.78)	271 (3.28)
OCH_3[e]	219 (3.84)	270 (3.23)
		277 (3.18)
NH_2[e]	235 (3.90)	284 (3.23)
O^-[a]	235 (3.97)	287 (3.41)
NO_2[f]	260 (3.93)	

[a] Spectrum reported in water (ref. 11). [b] Spectrum reported in ethanol (ref. 30). [c] The band at 207 mμ is previously unreported; see text. [d] Shoulder fused to shorter wave length (260 mμ) band. [e] Spectrum reported in ethanol (ref. 27). [f] Spectrum reported in ethanol (ref. 26).

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA OF SUBSTITUTED IODOBENZENES

Subst.	A-Band[a] mμ (log ε)	B-Band[a] mμ (log ε)	C-Band[a] mμ (log ε)
2-NO_2[b]		260 (3.54)	310 (3.18)
3-NO_2[b]		260 (3.81)	315 (3.00)
4-NO_2[b]		294 (4.07)	
H	207 (3.86)	226 (4.12)	~257 (2.85)
4-CH_3		228 (4.21)	258 (3.84)
4-Cl	207 (3.96)	235 (4.19)	265 (2.94)
			275 (2.75)
4-OCH_3	209 (3.89)	233 (4.30)	280 (3.15)
4-OH	209 (3.88)	234 (4.32)	285 (3.18)
2-NH_2	213 (4.36)	238 (3.89)	293 (3.42)
3-NH_2	217 (4.31)	243 (3.86)	297 (3.29)
4-NH_2	211 (4.04)	248 (4.22)	298 (3.24)
4-O^-	220 (3.78)	250 (4.46)	~298 (3.38)

[a] This designation corresponds to the usage of Forbes.[26-28] These bands may be nominally identified with the second primary, primary and secondary bands of Vandenbelt,[11] in that order; however, see text and footnote 41. [b] Spectrum in ethanol (ref. 26).

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(13) S. Oae and C. C. Price, THIS JOURNAL, **80**, 3425, 4938 (1958) and refs. cited therein.

(14) (a) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953); (b) R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D. M. Suave, *ibid.*, **78**, 682 (1956); (c) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(15) J. D. Roberts, R. A. Clement and J. A. Drysdale, *ibid.*, **73**, 218 (1951).

(16) (a) W. von E. Doering and K. C. Schreiber, *ibid.*, **77**, 514 (1955); (b) W. von E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 (1955); (c) W. von E. Doering and L. K. Levy, *ibid.*, **77**, 509 (1955).

(17) E. Billmann and K. A. Jensen, *Bull. soc. chim. France*, **3**, 2306 (1936).

(18) V. Baliah and M. Uma, *Naturwiss.*, **45**, 512 (1958).

(19) In the 4-halogenophenols acidities increase in the order Cl < Br < I. In the 4-halogenoanilines basicities decrease in the order Cl > Br > I. There is a shift to higher wave length and intensity of anilines when substituted in the 4-position by Cl, Br or I (see also footnote 39).

(20) A. Bayer, *Ber.*, **38**, 2761 (1905); **40**, 4068 (1907).

(21) F. Reverdin, *ibid.*, **29**, 1000 (1896).

(22) F. B. Dains and F. Eberly, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y.. 1943, p. 355.

(23) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

(24) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, *ibid.*, **81**, 342 (1959).

(25) F. M. Beringer and R. A. Falk, unpublished work.

(26) W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958).

(27) W. F. Forbes, W. A. Mueller, A. S. Ralph and J. R. Templeton, *ibid.*. **35**, 1049 (1957).

(28) See also C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951).

(29) A. Burawoy and J. P. Critchley, *Tetrahedron*, **5**, 340 (1959), and previous papers.

(30) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF 4- AND 4,4'-SUBSTITUTED DIPHENYLIODONIUM SALTS[a]

	4-Monosubstituted		4,4'-Disubstituted	
Subst.	A-Band mμ (log ε)	B-Band mμ (log ε)	A-Band mμ (log ε)	B-Band mμ (log ε)
NO_2[a]	209 (4.05)	251 (4.14)	220 (4.06)	260 (3.83)
H[b]	209 (4.23)	226 (4.19)	209 (4.23)	226 (4.19)
CH_3			209 (4.26)	234 (4.24)
Cl			209 (4.25)	239 (4.28)
CH_3O[b]	210 (4.28)	245 (4.16)	209 (4.32)	252 (4.29)
OH[b]	210 (4.32)	246 (4.12)	211 (4.42)	254 (4.26)
NH_2[a]	211 (3.79)	285 (4.03)	[d]	288 (4.21)
O^-	222 (4.19)[c]	292 (4.21)	218 (4.70)	292 (4.27)

[a] Iodide ion was found to have a maximum at 219 mμ (log ε 4.25) and nitrate ion a maximum at 209 mμ (log ε 4.12) in methanol. Intensities are therefore corrected for this absorption where appropriate; additivity is assumed. [b] Has shoulders at 265 and 275 mμ (log ε 2.8–2.9). [c] Shoulder at 238 mμ (log ε 4.15). [d] Absorption at 218 mμ (log ε 4.23) attributable to iodide ion.

TABLE IV

ULTRAVIOLET ABSORPTION MAXIMA OF ISOMERIC SUBSTITUTED DIPHENYLIODONIUM SALTS[a]

Subst.	A-Band mμ (log ε)	B-Band mμ (log ε)	C-Band mμ (log ε)
3-CH_3O	210 (4.39)	218 (4.38)	298 (3.34)
4-CH_3O	210 (4.28)	245 (4.16)	
2-NO_2[a]	210 (3.94)[b]	260 (3.82)	
3-NO_2[a]	217 (4.05)	248 (4.02)[c]	
4-NO_2[a]	209 (4.05)	251 (4.14)	
4,4'-$(NO_2)_2$	220 (4.06)	260 (3.83)	
2-NH_2[a]	214 (4.40)	222 (4.42)	~323 (3.23)
3-NH_2[a]	211 (4.02)	226 (4.37)	~313 (3.26)
4-NH_2[a]	211 (3.79)	285 (4.03)	
4,4'-$(NH_2)_2$[a]		288 (4.21)	
3-NO_2-4'-NH_2[a]	210 (4.43)	240 (4.20) 286 (4.06)	
4-NO_2-4'-NH_2[a]	210 (4.44)	248 (4.30) 295 (4.12)	

[a] See Table III, footnote *a*. [b] Fused to band at ~224 mμ (log ε 4.24). [c] Fused to band at ~221 mμ (log ε 4.41), which is fused to 217 mμ band.

Discussion

Iodobenzene and the Diphenyliodonium Ion.—A striking similarity exists between the ultraviolet absorption spectrum of iodobenzene (Table II) and that of the diphenyliodonium cation (Table III). Both have similar maxima at 226 mμ. Indeed, it was found that iodide ion absorbed in the same region (Table III, footnote *a; cf.* ref. 13). These results support the concept that iodine acts as a chromophore which is responsible for the absorption maxima in this region.[31–34] The spectrum of iodobenzene thus resembles the superposition of iodide absorption on that of a slightly altered benzene, in that it has maxima at 207 mμ (log ε 3.86)[35] and at 226 mμ (log ε 4.12); there is an additional less intense band at ~257 mμ (log ε 2.85). The intensity of the last band can be relegated to its expected place in the halogenobenzene order by subtraction of alkyl iodide absorption.[31,36] By ascribing the *207 mμ band* to benzenoid absorption such as is found in the other halogenobenzenes from 204–210 mμ (Table I), the ratio $\lambda_{sec}/\lambda_{pri}$ of Doub and Vandenbelt[11] becomes 1.24. This is in good agreement with their values for the other halogenobenzenes (1.25), whereas the assignment of the 226 mμ band produces a rather low value of 1.14.[36a,37]

The molar extinction coefficient of the 209 mμ band of the diphenyliodonium cation (log ε 4.23) is slightly more than double that of the 207 mμ band (log ε 3.86) of iodobenzene, while the 226 mμ band common to both is of about the same intensity. The additivity of absorption ascribable to the benzene ring and the lack of shift in the 226 mμ band in the diphenyliodonium cation is consistent with the picture of benzene rings which are separated by an insulator and not in conjugation. The unsubstituted diphenyliodonium cation thus resembles the cases examined by Jaffé[38] in which the ultraviolet absorption spectra of compounds having simple phenyl groups bonded to a central heteroatom with no unshared electron pairs showed no resonance interaction, each phenyl group making an independent contribution to the molar extinction coefficient.[39,40]

Methoxy- and Hydroxydiphenyliodonium Ions.—If a comparison is made of the B-bands[41] of diphen-

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(31) T. M. Dunn and T. Iredale, *J. Chem. Soc.*, 1592 (1952).

(32) L. Doub and J. M. Vandenbelt, *Anal. Chem.*, **24**, 601 (1952).

(33) E. M. Kosower, R. L. Martin and V. W. Meloche, *J. Chem. Phys.*, **26**, 1353 (1957).

(34) E. M. Kosower, THIS JOURNAL, **80**, 3261 (1958).

(35) Previously unreported.

(36) R. A. Durie, T. Iredale and J. M. S. Jarvie, *J. Chem. Soc.*, 1181 (1950).

(36a) ADDED IN PROOF.—In a private communication, Dr. Forbes has pointed out that this rule is empirical and may break down. However, the alternative viewpoint, which regards the 226 mμ band as due to mesomeric iodine–benzene interaction, begs the question as to why this band, both in wave length and intensity, represents so sudden a break in the halogenobenzene sequence (see Table I).

(37) Both the primary (207 mμ) and secondary (257 mμ) band of iodobenzene are at shorter wave length than those of bromobenzene (Table I), pointing to the ineffectiveness of iodine–aromatic conjugation (ref. 31, 36). However, W. F. Forbes and co-workers already (*cf.* W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 488 (1957)) have noted that bathochromic displacements and intensity increases in the ultraviolet absorption spectra of *p*-substituted benzoic acids (W. F. Forbes and M. B. Sheratte, *ibid.*, 1829 (1955)) were in order of F < Cl < Br < I, leading them to propose a resonance order of I > Br > Cl > F, more important in the electronic excited than the ground state. See also footnote 39, and Table VI.

(38) H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

(39) Burawoy and co-workers have developed an alternative interpretation of electronic spectra based on inductive electron displacements alone; see ref. 29. The present writers prefer the conventional frame of reference, and feel that Burawoy's model leaves much to be explained. It would appear, however, that the spectral behavior of some aryl halides may be explained best in terms of polarizabilities. Such a view has been advanced (A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956)) and strongly supported (W. M. Schubert, J. M. Craven and H. Steadly, THIS JOURNAL, **81**, 2697 (1959)) and does much to resolve the apparent inconsistency between the views of Forbes (ref. 37) and Baliah and Uma (ref. 18), and the accepted order of resonance and inductive effect in the halogens. Further support for the significance of polarizability factors in the halogenobenzenes may be deduced from n.m.r. results (P. L. Corio and B. P. Dailey, THIS JOURNAL, **78**, 304 (1956)).

(40) The failure of an adjacent positive charge to effect the predicted alteration in the spectrum of an aromatic compound recently has been emphasized for arylammonium ions: I. G. Ross and M. L. Tonnett, *J. Chem. Soc.*, 2011 (1959).

(41) Inasmuch as it is felt that the B-band absorption of iodoaromatic and iodonium compounds represents the shift of the 226 mμ absorption of the iodine chromophore by substituents, band B is thus not strictly analogous to Vandenbelt's primary band (see text above), which represents the shift of the absorption due to the benzene chromophore (*i.e.*, 203 mμ, Table I) by substituents. Such a criticism likewise applies to nitroaromatics, where the ~260 mμ absorption may very likely be due to the nitro chromophore. With this reservation in mind, however, interchangeable use of the familiar terminology is convenient.

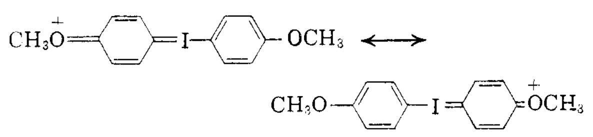
TABLE V

ULTRAVIOLET ABSORPTION MAXIMA OF 4-SUBSTITUTED PHENOLS

	B-Bands[a]			C-Bands[a]		
Subst.	Neutral mμ (log ε)	Base mμ (log ε)	Δλ,[b] mμ	Neutral mμ (log ε)	Base mμ (log ε)	Δλ,[b] mμ
H[c]	218 (3.78)	235 (3.97)	17	271 (3.28)	287 (3.41)	16
4-I	234 (4.32)	250 (4.46)	16	285 (3.18)	~298 (3.38)	~13
$4\text{-}(CH_3)_3\overset{+}{N}$[d]	221 (3.98)	244 (4.15)	23	269 (3.33)	284 (3.60)	15
$4\text{-}(CH_3)_2\overset{+}{S}$[d]	242 (4.03)	269 (4.20)	27	264 (3.66)		
$4\text{-}C_6H_4\overset{+}{I}$	246 (4.12)	292 (4.21)	45			

[a] See footnote *a*, Table II. [b] Difference in mμ between λ_{max} in neutral methanol and that containing an equivalent of sodium hydroxide. [c] Spectrum in ethanol (ref. 27). [d] Spectrum in water (ref. 13).

yliodonium ions *p*-substituted with electron donors (Table III), a bathochromic shift is seen which parallels the order of electron-releasing ability of the substituents. In the simple aromatic compounds (Table II) this trend is less pronounced, and C-bands remain prominent. Fusions in the parent aromatic B-bands are smoothed into single peaks of greater intensity in the iodonium salts, while the C-bands are no longer seen.[42] The wave length increments between the B-bands of the iodoaromatic compounds and the corresponding iodonium cations increase with the electron-releasing power of the substituents, being most prominent for the anilines and phenoxides. The significant increase in λ_{max} in going from the monosubstituted to the disubstituted diphenyliodonium cations (*viz.* 4-methoxy *vs.* 4,4′-dimethoxy) suggests an increase in the length of the conjugated system, *i.e.*



II

These observations lend support to the concept of iodonium participation in conjugation in the excited state. The progress with substitution of iodobenzene's 226 mμ band justifies its assignment as due to iodine excitation modified by substituent interaction.[41]

Further support is given this view by the comparison between 3- and 4-methoxydiphenyliodonium salts (Table IV). The intense band of the 4-methoxy isomer at 245 mμ drops down to 218 mμ in the 3-methoxy compound, the only longer wave length absorption being a weak band at 298 mμ. Conjugation involving iodine in this cation must therefore be absent or minimal, as is expected.

One may compare the large difference (27 mμ) in primary wave length between 3- and 4-methoxydiphenyliodonium cations[43] with the small difference (1 mμ) between 3- and 4-trimethylammoniophenol, in which resonance interaction is considered absent[15] and the difference (27 mμ) between 3- and 4-dimethylsulfoniophenol, in which resonance interaction is considered present.[12,13]

Even more noteworthy are the band shifts for the iodonio-substituted phenols in base. The monophenol undergoes a 46 mμ shift of primary absorption (from 246 to 292 mμ), while the bisphenol shifts 38 mμ (from 254 to 292 mμ).[44] These shifts are more than double the 17 mμ increase in the corresponding band of phenol in base or the 16 mμ increase of 4-iodophenol in base. The difference in B-band wave length between 4-hydroxydiphenyliodonium ion in base and phenol or 4-iodophenol in base (57 and 42 mμ, respectively) is large. This may be a further indication of d-orbital overlap in the substituted diaryliodonium system. One may compare these values with those for the shifts in base of the primary bands of 4-trimethylammoniophenol (23 mμ) and 4-dimethylsulfoniophenol (27 mμ) (Table V).

Aminodiphenyliodonium Ions.—Most interesting to examine is the series of aminodiphenyliodonium cations (Table IV), since the three isomers are available. If the 4-amino isomer is compared with 4-iodoaniline, the 285 mμ band appears to be a bathochromic shift of the 248 mμ band of the iodoaniline, which in turn is identifiable with the 235 mμ band of aniline itself.[45] Thus the conversion of aniline to 4-phenyliodonioaniline causes a displacement of 50 mμ in the aniline B-band. The difference of 37 mμ between 4-iodoaniline and the iodonium cation is greater than the corresponding difference between 4-iodophenol and 4-hydroxydiphenyliodonium cation (12 mμ) which is to be expected from the greater electron-releasing power of the amino group. In contrast, the 4-trimethylammonio group shifts the aniline B-band only 5 mμ, to 240 mμ.[15]

In the 4,4′-diaminodiphenyliodonium cation, the band near 210 mμ is no longer present (Table III). The molecular extinction coefficient of the B-band at 288 mμ is slightly larger than that of the corresponding band for the 4-aminodiphenyliodonium cation at 285 mμ. A visual comparison of the curves for the two compounds supports the inference that this approximately equal shift in intensities on introducing the second amino group is a reinforcement of the B-band at the expense of the A-band. This fact plus the slight red shift (3 mμ) in the B band leads to the view that this effect is roughly additive.

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(42) Forbes has commented that a large mesomeric (resonance) effect results in a low intensity C band; *cf.* ref. 27.

(43) These comparisons of phenols and methoxy compounds are validated by the fact that phenol:anisole (Table I) and 4-iodophenol:4-iodoanisole (Table II) are spectrally almost equivalent pairs. Thus it is not surprising to find that the spectra of 4-hydroxy- and 4-methoxydiphenoliodonium cations are almost identical; the dihydroxy and dimethoxy cations are likewise quite similar.

(44) This may be an example of a "saturation" phenomenon, in which the iodonium atom fully accepts a pair of electrons to form the same monoquinonoid form in either case.

(45) It is a moot question as to whether one relates the displacement in terms of the effect of a substituent on the aniline B-band or on the iodobenzene B-band; see Table VI for the effects of their additivity.

The spectrum of the 3-aminodiphenyliodonium cation (Table IV) indicates the lack of conjugation which is to be expected. The curve resembles that of the unsubstituted salt, with the addition of the C-band at ~313 mμ; the B-band has dropped to 226 mμ, the same as that of the diphenyliodonium cation itself.[46] Thus it appears that amino-aromatic resonance is small or absent in this compound; no trace of the aniline B band (235 mμ) remains, unless it is coincidentally overlapped at 226 mμ. In the diaryliodonium cation, electron-donor substituents which do not interact with the iodine atom apparently show no evidence of aromatic conjugation.

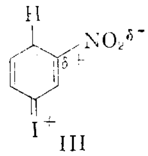
One may compare these results with the only slight difference between 3-trimethylammonioaniline (236 mμ) and 4-trimethylammonioaniline (240 mμ).[15] In the former compound, the B-band is at about the same position as that of aniline (235 mμ) itself.

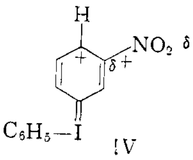
The spectrum of the 2-aminodiphenyliodonium cation (Table IV) is likewise characterized by resemblance to the unsubstituted cation, and by the absence of the aniline B-band. Doub and Vandenbelt[11] and Forbes and co-workers,[47] have pointed out the generality of spectral similarity for *ortho* and *meta* isomers.

Note the advance of the C-band from ~313 mμ in the 3-phenyliodonioaniline to ~323 mμ in the 2-isomer (Table IV); this shift is not seen in the iodoanilines (Table II), where indeed an opposite order prevails. A similar phenomenon is observed in comparing 3- and 4-dimethylsulfoniophenol (283 and 264 mμ) and 3- and 4-trimethylammoniophenol (272 and 269 mμ).[13] These shifts are suggestive of the significance of the inductive effect in relation to the secondary band, a view previously offered by Bowden and Braude[30] and by Robertson and Matsen.[48]

Nitrodiphenyliodonium Ions.—A comparison of the spectra of four nitrodiphenyliodonium salts (Table IV) with those of the corresponding iodonitrobenzenes reveals strong similarities. The nitrobenzene 260 mμ band[41] (Table I) is seen in the iodonitrobenzenes and in the iodonium salts. Only in 4-iodonitrobenzene, where the effects of the substituents are complementary, is a pronounced bathochromic shift observed. In both the 2-nitrodiphenyliodonium cation and 2- and 3-iodonitrobenzene, the nitrobenzene chromophore absorbs at 260 mμ, the same wave length as in nitrobenzene itself. In 2-isomers steric pressure may force the nitro group out of the plane of the benzene ring,[49] diminishing interaction with the system. The spectrum of the 2-nitrodiphenyliodonium cation generally resembles a superposition of the nitrobenzene spectrum on that of the diphenyliodonium cation.

Forbes has pointed out[26] that a *m*-nitro group may displace the B-band either positively or negatively. Thus a *m*-nitro group effects a negative wave length displacement in acetophenone or nitrobenzene but a positive wave length displacement in phenol and anisole. The formation of a negative charge near the *m*-nitro group, as in 3-iodonitrobenzene (III), might account for the bathochromic shift of the 260 mμ band observed. The formation of a positive charge near the nitro group would on this basis produce a hypsochromic shift of this band. Thus the displacement of this band to shorter wave length in the 3-nitrodiphenyliodonium cation may indicate the importance of structure IV in the excited state.


III


IV

In the 4-nitrodiphenyliodonium cation, a similar picture may be used to explain both the displacement of the band to 251 mμ, and the high intensity of this band (log ε 4.14) which may possibly be due to a reduced force constant[50] caused by mutual charge repulsion in the electronic excited state. Thus the nitrodiphenyliodonium cations are primarily examples of the spectral addition of two absorbing systems, nitrobenzene and the diphenyliodonium cation, whose resonance vectors are not additive.

Deviations from Additivity of Absorption Maxima of *p*-Disubstituted Benzenes.—In Table VI are listed deviations from additivity of absorption maxima of a number of *p*-disubstituted benzenes.[51] It is seen empirically that positive deviations are shown by those groups which mutually assist each other electronically, while negative deviations are given by those groups whose electronic effects are similar and therefore opposed.[52] On one

TABLE VI

DEVIATIONS FROM ADDITIVITY IN SHIFTS OF PRIMARY BAND OF *p*-DISUBSTITUTED BENZENES[a,b]

$$\Delta(a,b) = 203 + \lambda(a,b) - \lambda(a) - \lambda(b)$$

	NH_2	I	CH_3	$\overset{+}{N}R_3$	$\overset{+}{S}(CH_3)_2$	$\overset{+}{I}C_6H_5$	$\overset{+}{I}/2$	NO_2
NO_2	80	11	13	−10[c]	−33[d]	−32	−23	−67
CH_3	−1	− 4		1			0	13
Cl	3	− 2		7[c]			2	
CH_3O		− 9				3	10	
OH		− 7	−1	3[e]	7[e]	5	13	42
NH_2		−10	−1	10[f]		27	30	80
O^-		− 8		9[e]	17[e]	34	34	103

[a] An example: $\Delta(NO_2,NH_2) = 203 + \lambda(NO_2,NH_2) - \lambda(NO_2) - \lambda(NH_2) = 203 + 375 - 268 - 230 = 80$ mμ. [b] Deviations were computed from data of Doub and Vandenbelt (ref. 11) and values extracted from previous tables, except where noted. Note that the values used in determining the deviation for a given compound must be derived from spectra in the same solvent. [c] Value from A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956). [d] Value from ref. 12. [e] Value from ref. 13. [f] Value from ref. 15.

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[46] This represents a blue shift of 9 mμ from aniline, or 17 mμ from 3-iodoaniline.

[47] W. F. Forbes, A. S. Ralph and R. Gosine, *Can. J. Chem.*, **36**, 869 (1958).

[48] W. W. Robertson and F. A. Matsen, THIS JOURNAL, **72**, 5238 (1950).

[49] R. J. Francel, *ibid.*, **74**, 1265 (1952).

[50] W. F. Forbes and J. F. Templeton, *Can. J. Chem.*, **36**, 180 (1958).

[51] This treatment makes the reasonable assumption that the electronic vectors of *p*-substituents are approximately spectrally additive in terms of wave length increments.

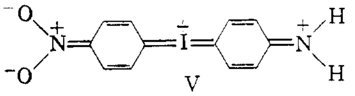
[52] Note that the negative deviations for the *p*-iodo compounds do not support a picture of d-orbital resonance in these cases.

end of the scale are the nitrosubstituted cations with large negative deviations; on the other end is *p*-nitrophenoxide ion, with the very large positive deviation correlatable with resonance interaction. Positive deviations from additivity are observed also for iodonium cations; these grow larger with the electron-releasing abilities of the substituents.

Nitroaminodiphenyliodonium Ions.—With the establishment of a picture of iodonium–substituent interaction, attention is directed to the comparison between 3- and 4-nitro-4′-aminodiphenyliodonium cations (Table IV). Not only are the bands all at longer wave length in the 4-nitro isomer but they are more intense. The 285 mμ band of the 4-aminodiphenyliodonium cation has moved to 295 mμ in the 4-nitro isomer.

The bands at 240 and 248 mμ in the 3- and 4-nitro isomers, respectively, can be identified with the nitro bands at 248 and 251 mμ in the 3- and 4-nitrodiphenyliodonium cations.

These facts point to conjugation between the nitro and amino groups which must be relayed through the iodonium atom; *cf.* structure V.



V

That this through-conjugation is of a relatively low order of magnitude, however, may be deduced from a comparison with 4-nitro-4′-aminobiphenyl, where the much more extensive resonance interaction between the nitro and amino groups gives a band at 380 mμ (log ε 4.20).[53]

The interaction of electronically complementary groups such as nitro and amino when on benzene rings joined directly or through another atom has received previous attention.[54] Spectral studies of 4,4′-disubstituted diphenyl sulfides were construed as demonstrating through-conjugation of substituents.[55] However, by comparison of these with the corresponding 3,4′-disubstituted isomers, Mangini and Passerini[56] were able to show that the essential identity of their spectra precluded an interpretation of conjugation for the 4,4′-disubstituted cases. Mangini has further stated[57,58] that no proof for the expansion of the sulfur valence shell is deducible from the electronic spectra of a number of compounds.

Brode[59] has asserted on spectral grounds that O, S, NH_2 and CH_2 are insulators. However, Lavrushin[60] has interpreted spectral data for diphenylmethane in terms of interaction between the phenyl rings through the bridging methylene group.[61] Litvinenko and co-workers[62] have demonstrated the interaction of substituents on different rings of biphenyl in the ground state by means of kinetic experiments. This group has also recently concluded that such interaction does indeed occur in 4-amino-4′-nitrodiphenyl ethers and sulfides, again on the basis of kinetic evidence.[63]

The present work offers evidence that the iodonium atom also may act as a relayer of electrical effects.

ADDED IN PROOF.—Since the submission of this paper, there has appeared another publication on this topic; see H. Irving, G. P. A. Turner and R. W. Reid, *J. Chem. Soc.*, 2082 (1960).

Acknowledgment.—The generous support of this work by the Alfred P. Sloan Foundation, Inc., is gratefully acknowledged. The authors wish to thank Drs. W. F. Forbes, H. H. Jaffé and E. M. Kosower for reading and commenting on this paper prior to publication.

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(56) A. Mangini and R. Passerini, *Experientia*, **12**, 49 (1956).

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(58) A. Mangini, *J. chim. phys.*, **56**, 240 (1959).

(59) N. Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1945, pp. 218–223.

(60) V. P. Lavrushin, *Proc. Acad. Sci. U.S.S.R.*, **86**, 309 (1952).

(61) For a discussion of the weak electronic coupling between rings in dibenzyl and diphenylmethane evinced in the electronic spectra of their crystals, see R. Coffman and D. S. McLure, *Can. J. Chem.*, **88**, 48 (1958).

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(63) L. M. Litvinenko, R. S. Cheschko and S. V. Tsukerman, *ibid.*, *Chem. Sec.*, **118**, 946 (1958).