870. *The Infrared Absorption Spectra of Diaryliodonium Salts.*

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Some salient features of the infrared absorption spectra of a number of diaryliodonium salts are discussed.

Infrared absorption spectra of a series of diaryliodonium salts[1] in potassium bromide discs have revealed no distinguishing features for this system, according to published observation.[3] The unsubstituted salts differ only little in spectra from iodobenzene, major distinctions being intensification of the C–C stretching, ring breathing, and out-of-plane C–H deformation modes[3] of the latter, occurring, respectively, at 1565 and 1473, 992, and 987, 742, and 736 cm.$^{-1}$ for diphenyliodonium iodide. In the comparison, band shifts, when they occur, are quite small, and to some extent are due to differences in interaction with the potassium bromide matrix.[4]

The 1060 cm.$^{-1}$ frequency of iodobenzene, designated as "substituent-sensitive"[3] and related in a series of substituted benzene derivatives to the electronegativity of the substituent,[5] appears not to vary significantly in the diaryliodonium spectra observed, as shown, for example, by its position in the following diaryliodonium salts: unsubstituted 1064; 4-CO_2Me 1065; 4-NH_2 1063; 4-NO_2 1066 cm.$^{-1}$. This seems to cast some doubt on a simple electronegativity relationship (indeed, the fact that this band thus appears at about the same frequency for tetraphenyl-lead, triphenylstibine, diphenylselenium, iodobenzene, and diphenyliodonium cation with different substituents suggests the probable importance of other factors).

For the aminodiphenyliodonium salts examined (3-NH_2, 4-NH_2, and 4-NH_2-4′-NO_2, as iodides) no observable shifts in N–H stretching frequencies were encountered.[6] However, NH_2 bending frequencies (3-NH_2 1626; 4-NH_2 1632; 4-NH_2-4′-NO_2 1629 cm.$^{-1}$) showed significant deviations from the 1618 cm.$^{-1}$ (solution [7]) band of aniline. While this is partly due to the difference in medium (solid *vs.* solution), it is interesting that for a series of substituted anilines[8] this band varied from 1618 to 1621 cm.$^{-1}$ except only for *p*-nitroaniline, the one compound examined that had a strongly electron-withdrawing substituent. For this, the frequency rose to 1631 cm.$^{-1}$; thus the aminodiphenyliodonium system resembles the latter in magnitude more closely than aniline does. This is reasonably considered as due to the electronegativity of the phenyliodonio-substituent.

Shifts are seen also in the ring stretching and C–N stretching modes compared with those for aniline; however, no trend is apparent within the diaryliodonium group. Notable is the considerably weaker intensity of the C–N stretching band for the 3- (1304 cm.$^{-1}$) than for the 4-amine (1307 cm.$^{-1}$). For this mode, the stretch is an electron-withdrawing process, and $\partial\mu/\partial r$ is in the direction of increasing bond moment; it will be opposed by the electron-withdrawing effect of the phenyliodonio-group. Electron-withdrawal will decrease the ground state C–N bond moment, and thus increase the energy of the stretching transition, reducing the intensity of the absorption.[9] Therefore the above intensity difference may be ascribed to the more effective $-I$ effect of the 3-phenyliodonio-substituent, implying that conjugation between substituents here, which could decrease the C–N bond moment for the 4- but not the 3-amine, is not important to the ground state.[10]

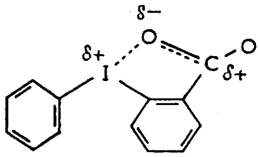
[1] Beringer and Lillien, *J. Amer. Chem. Soc.*, 1960, **82**, 725.
[2] Bell and Morgan, *J.*, 1960, 1209.
[3] Whiffen, *J.*, 1956, 1350.
[4] Baker, *J. Phys. Chem.*, 1957, **61**, 450.
[5] Kross and Fassel, *J. Amer. Chem. Soc.*, 1955, **77**, 5858.
[6] Flett, *Trans. Faraday Soc.*, 1948, **44**, 767.
[7] Evans, *Spectrochim. Acta*, 1960, **16**, 428; Tsuboi, *ibid.*, p. 505.
[8] Califano and Moccia, *Gazzetta*, 1957, **87**, 805.
[9] Brown, *Chem. Rev.*, 1958, **58**, 581.
[10] Beringer and Lillien, *J. Amer. Chem. Soc.*, 1960, **82**, 5141.

The nitrodiphenyliodonium isomers were likewise examined for frequency trends. The NO_2 asymmetric stretching band (1527 cm.$^{-1}$ in nitrobenzene, homogeneous [11]), which has been observed to shift to longer wavelength with electron-donor *para*-substituents in nitrobenzenes,[12, 13] remains at about the same frequency for the 4-NO_2 and 4-NO_2-4′-NH_2 systems. It is at slightly shorter wavelength for 2- and 3-nitrodiphenyliodonium cations (1534 and 1535 cm.$^{-1}$, respectively; about the same as for *o*- and *m*-dinitrobenzene [13]). This should be contrasted with the drastic shift to shorter wavelength (1563 cm.$^{-1}$) for *p*-dinitrobenzene,[13] which indeed may indicate the considerably poorer efficacy of mesomeric electron-withdrawal for the phenyliodonio- than for the nitro-group.

The symmetric NO_2 stretching band (at 1351 cm.$^{-1}$ for nitrobenzene, homogeneous [11]) remains at about the same frequency for all four nitrodiphenyliodonium salts mentioned above, in contrast to those compounds examined by Brown.[12]

The 1482 cm.$^{-1}$ ring stretching band of nitrobenzene, observed to shift to higher frequency with substituents of more negative σ-value,[12] is shifted to lower frequency by the 2-, 3-, and 4-phenyliodonio-substituent (1471, 1473, and 1472 cm.$^{-1}$, respectively), but not by the 4-*p*-aminophenyliodonio-group (1489 cm.$^{-1}$). These shifts are to be expected of the $+\sigma$ phenyliodonio group, whose electronegativity can be dampened by the electron-supplying amino-group.

The spectrum of the 4-carboxydiphenyliodonium cation contains two strong, well-spaced bands in the carbonyl region at 1690 and 1730 cm.$^{-1}$. Since the 4-methoxycarbonyldiphenyliodonium cation has a single strong band at 1725 cm.$^{-1}$, it may be concluded that carbonyl splitting in the acid occurs as a result of hydrogen bonding or electrostatic interaction of the carboxyl group with the potassium bromide matrix [14] in a mixture of monomeric and dimeric acids.[15] In contrast, the 2-carboxydiphenyliodonium spectrum contains one strong band at 1660 cm.$^{-1}$. This shift to longer wavelength coupled with lack of splitting is due to carboxyl–iodine interaction as in (I), which increases carbonyl polarization and prevents dimer formation.



(I)

The very strong tendency of this acid to lose hydrogen halide and form the betaine [1] confirms the importance of this interaction.

In the 4-betaine, as is to be expected by virtue of carboxylate ion formation, the carbonyl stretching frequency is replaced by a new pair of characteristic bands at 1543 and 1360 cm.$^{-1}$ (separation 183), due respectively to asymmetric and symmetric carboxylate stretching.[15] The separation of these bands ($\Delta\nu$) in the benzoate anion has been observed to be dependent on the nature of the cation,[11, 16] varying from 134 for the lithium salt to 173 for the cæsium salt. Although no simple relation has been found between $\Delta\nu$ and cation electronegativity or polarizability, it seems that, since the cæsium and iodonium cations (with the latter bonded to π-electron systems) are isoelectronic, both the similarity in $\Delta\nu$ and the slight difference in magnitude ought to be due to similar but slightly different electronegativities.

The 2-betaine exhibits a poorly resolved doublet at 1613 and 1625 cm.$^{-1}$, and a strong band at 1335 cm.$^{-1}$. The relatively high frequency of the former indicates less ionic character than in the case of the 4-betaine, owing to formation of a relatively covalent I–O bond.

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[11] Green, Kynaston, and Lindsey, *Spectrochim. Acta*, 1961, **17**, 486.

[12] Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

[13] Franck, Hörmann, and Scheibe, *Chem. Ber.*, 1957, **90**, 330.

[14] Farmer, *Spectrochim. Acta*, 1957, **8**, 374—389.

[15] Bellamy, " The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 1958, pp. 161—177.

[16] Stimson, *J. Chem. Phys.*, 1954, **22**, 1942.