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Diaryliodonium Salts. XVI. The Acidities of Carboxy-, Hydroxy- and Ammoniodiphenyliodonium Cations. Electronic Characterization of the Phenyliodonio Group[1]

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To characterize the phenyliodonio group $(C_6H_5\overset{+}{I}-)$ electronically, the apparent acidities of the 2-, 3- and 4-phenyliodoniobenzoic acids, 4-phenyliodoniophenol and the 3- and 4-phenyliodonioanilinium ions have been determined and compared with those of the unsubstituted compounds. Sigma (σ) values for the *m*- and *p*-phenyliodonio groups in the phenol and acids, when compared with those for the trimethylammonio and dimethylsulfonio groups, point to an inductive effect of small magnitude in the ground states. In the substituted anilines, examined in the electronic excited states, the fact that $\sigma_p > \sigma_m$ indicates the ability of the positive iodine to accept electrons conjugatively, presumably by using a vacant 5d-orbital.

The synthesis[3] and ultraviolet absorption spectra[4] of certain functionally substituted diphenyliodonium salts have been described. It was concluded on the basis of spectral evidence[4] that the iodine atom in such cations is able to participate in conjugation with electron-releasing groups in the *p*-position. This paper reports on the acidities of carboxy-, hydroxy- and ammonio-substituted diphenyliodonium cations, measured in an attempt to obtain further evidence concerning the conjugative ability of iodine.

Acetonitrile containing a small amount of water was chosen as a solvent for the titration of the carboxylic acids because of its known ability to dissolve salts and betaines and because of its ability to magnify small differences in acidity. In this medium the phenyliodoniobenzoic acids $(C_6H_5\overset{+}{I}C_6H_4COOH)$ are stronger acids than the nitrobenzoic acids, presumably because of the electrostatic effect of the phenyliodonio group. The apparent pK_a's of substituted benzoic acids are listed in Table I.

TABLE I

APPARENT IONIZATION CONSTANTS OF BENZOIC ACIDS IN ACETONITRILE-WATER (15:1) AT 24°

Substituent[a]	pK_a	Substituent[a]	pK_a
2-Phenyliodonio[b]	3.5 ± 1	3-Iodo	6.45
3-Phenyliodonio[b]	5.55	4-Iodo	6.64
4-Phenyliodonio[b]	4.6[c]	3-Chloro	6.47
4-Trimethylammonio[b]	5.37	4-Chloro	6.60
4-Nitro	5.83	None	6.92
2-Iodo	6.24	4-Methoxy	7.38

[a] All concentrations were of the order of 1-3 millimoles/liter. [b] As the iodide salt. [c] Precipitation of the inner salt occurred; the apparent value is given but would presumably depend on concentration.

The 2-carboxydiphenyliodonium cation (2-phenyliodoniobenzoic acid) gave titration curves appropriate for a strong acid. Using a calibration curve for solutions of sulfuric acid in approximately 15:1 acetonitrile-water, it was found that the pK_a of this 2-isomer lay between 2.5 and 4.5. The fact that this 2-acid is considerably stronger than the 3-acid (pK_a 5.55) is attributable wholly or in part to electrostatic and inductive effects. If, as has been suggested, there is some oxygen-iodine bond formation in the betaine,[5] this would enhance its stability and favor ionization of the acid.

Roberts and co-workers[6] found the order of acid strengths of the trimethylammoniobenzoic acids to be: 3- greater than 4-. Bordwell and Boutan[7] found a similar order for the acid strengths of the dimethylsulfoniobenzoic acids: 3- > 4-. This order indicates the primacy of electrostatic and/or inductive effects in determining the acidities of these cations. In the present study it was not possible to find conditions in which the betaine of the 4-acid did not precipitate, thus giving a low value to the apparent pK_a (4.6), smaller than that of the 3-acid (5.55).

Comparing the σ_m-values obtained from the substituted benzoic acids, one sees that σ_m for the 3-phenyliodonio group (0.85, Table III) is smaller than σ_m for the dimethylsulfonio group (1.00)[7] and σ_m for the trimethylammonio group (1.02).[6] To the extent that pK_a and thus σ_m are determined by electrostatic effects, the smaller values for the phenyliodonio group may be rationalized in terms of the larger size of iodine. Too much emphasis should not be placed on these differences as the measurements were made under different conditions and as the Hammett equation does not rigorously apply to cations.[8]

The titration with base of 4-phenyliodoniophenol in 3:7 ethanol-water gave a pK_a of 8.33 and a σ_p of 0.71 for the 4-phenyliodonio group. This may be compared with a σ_p of 0.70[7] or 0.76[9] for the 4-trimethylammonio group (determined in water) and a σ_p of 1.16[7,9] for the 4-dimethylsulfonio group (determined in water). These data, which establish the conjugative ability of the dimethylsulfonio group, also indicate a small conjugative ability for the phenyliodonio group in the ground state. This conclusion is not in disagreement with that obtained by the interpretation of ultraviolet absorption data[4]: namely, that *in the electronic excited state*

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

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[3] F. M. Beringer and I. Lillien, THIS JOURNAL, **82**, 725 (1960).

[4] F. M. Beringer and I. Lillien, *ibid.*, **82**, 5135 (1960). References to recent articles on d-orbital resonance are given.

[5] H. E. Bachofner, F. M. Beringer and L. Meites, *ibid.*, **80**, 4274 (1958). Other betaines have been prepared from iodonium salts: F. M. Beringer and R. A. Falk, *ibid.*, **81**, 2997 (1959).

[6] J. D. Roberts, R. A. Clement and J. A. Drysdale, *ibid.*, **73**, 2181 (1951).

[7] F. G. Bordwell and P. J. Boutan, *ibid.*, **78**, 87 (1956); **79**, 717 (1957).

[8] J. Hine, *ibid.*, **81**, 1126 (1959); see also: H. H. Jaffé, *ibid.*, **81**, 3020 (1959).

[9] S. Oae and C. C. Price, *ibid.*, **80**, 3425 (1958).

TABLE II

pK_a'S AND VALUES FOR SUBSTITUTED PHENOLS

4-Subst.	Solvent	pK_a	ρ[b]	σ_p	Ref.
N_2^+	Water	3.40	2.113	3.04	11
$(CH_3)_3N^+$	Water	8.21	2.29	0.70, 0.76	7,9
$(CH_3)_2S^+$	Water	7.30	2.29	1.16	7,9
$C_6H_5I^+$	ROH–H_2O[a]	8.33	3.20	0.71	[c]
I	ROH–H_2O[a]	9.66	3.20	.30	12
H	ROH–H_2O[a]	10.61	3.20	.00	10

[a] 3:7 ethanol–water by volume. [b] Rho value used in the calculation of σ_p. [c] Present work.

TABLE III

CONSTANTS FOR THE PHENYLIODONIO GROUP ($C_6H_5I^+$)

Acids	ρ	log K_0	σ_m	σ_p
Benzoic acids[a]	1.61	− 6.92	0.85	[b]
Phenols[c]	3.20[d]	−10.61[d]	[e]	0.71
Anilinium ions[f]	2.73[d]	− 4.56[d]	0.98[g]	1.06[g]

[a] Titration in 15:1 acetonitrile–water. [b] The inner salt precipitated; see Table I. [c] Titration in 3:7 ethanol–water. [d] Ref. 10. [e] Synthesis of 3-hydroxydiphenyliodonium salts has not yet been achieved; see ref. 3. [f] Spectrophotometric comparison with 3-nitroaniline; see ref. 13. [g] Apparent values: see ref. 13.

the phenyliodonio group may have substantial conjugation through the ring with an electron-releasing 4-substituent. Table II summarizes data on the acidities of some 4-substituted phenols. It is seen that the effectiveness of electron-withdrawal by 4-substituents decreases in the order: diazonio[11] > dimethylsulfonio[7,9] > trimethylammonio[6,7,9] ∼ phenyliodonio > iodo[12] > hydrogen.[10]

As the 3- and 4-phenyliodonioanilines proved to be bases too weak for the determination of pK_a's directly from titration curves in water, recourse was had to spectrophotometric comparison[13] (Tables IV and V), with 3-nitroaniline. The results (Table III) show that the 3-amine is a stronger base than the 4-amine: thus, for the phenyliodonio group in this system: σ_m, 0.98; σ_p, 1.06; $\sigma_p - \sigma_m$, 0.08. Since the operation of electrostatic and/or inductive effects should make the 3-isomer the weaker base, it would seem reasonable to invoke conjugative electron-acceptance by the iodine from the 4-amino group to explain its lowered basicity. Such conjugation involving d-orbital resonance in the excited state has already been postulated to explain ultraviolet absorption spectra.[4]

TABLE IV

OPTICAL DENSITIES

Compound[b]	λ, mμ	D of B at λ[a]	D of BH⁺ at λ[d]
3-Aminodiphenyliodonium chloride	225	0.903	0.708
4-Aminodiphenyliodonium chloride	280	.275	.045
3-Nitroaniline[c]	225	.210	.076

[a] In water solution. [b] Concentration of all compounds: 3.32×10^{-5} mole/liter. [c] Reference compound. [d] In 2.5 N sulfuric acid.

TABLE V

DETERMINATION OF pK_a'S

Compound[a]	D at λ[b]	log (C_B/C_{BH^+})	pK_a
3-Nitroaniline	0.115	−0.386	2,62[c]
3-Aminodiphenyliodonium chloride	.844	.363	1.87[d]
4-Aminodiphenyliodonium chloride	.227	.579	1.66[d]

[a] Concentration of all compounds: 3.32×10^{-5} mole/liter. [b] In 0.01 N hydrochloric acid. [c] Value from ref. 10. [d] Apparent pK_a.

Materials for Study.—The synthesis of the iodonium salts used in this work has been reported.[3] The benzoic acids and 3-nitroaniline were commercial products. 4-Trimethylammoniobenzoic acid was prepared as described in the literature.[14]

Experimental.—The carboxylic acids and the phenol were titrated potentiometrically, using a glass electrode and calomel reference electrode, with standard carbonate-free sodium hydroxide solution. The pH meter was standardized against Beckman buffers before each use. Apparent pK_a's were obtained from the titration curves by averaging values in the vicinity of 1/4 to 3/4 neutralization after correction for ionization factors.[15]

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