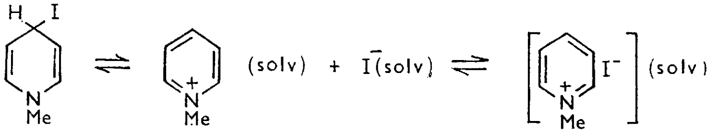
493. *The Electronic Spectra of* N-*Heteroaromatic Systems. Part VIII.* The Charge-transfer Spectra of Quaternary Iodides.*

By S. F. Mason.

The visible and ultraviolet absorption spectra of a number of *N*-heteroaromatic iodide salts have been measured in chloroform solution. Bands other than those given by the corresponding perchlorate in aqueous solution are assigned to electronic transitions from the iodide ion to either the solvent or the cation. The frequency of the lowest-energy charge-transfer band is found to increase as the electron affinity of the *N*-heteroaromatic cation falls, supporting a delocalised rather than a localised model for the excited state resulting from a charge-transfer transition.

It has long been known [1-5] that the salts of a heteroaromatic cation are deeper in colour the more polarisable is the anion, acridine methiodide, for example being red whilst the corresponding chloride is yellow, both in the solid state and in chloroform solution. In 1911 Hantzsch [1] measured the electronic spectra of a number of pyridinium and quinolinium salts, and found, particularly in the case of the iodides, new absorption bands beyond the long-wavelength absorption limit of the heteroaromatic cation. The new absorption bands did not obey Beer's law, the apparent extinction coefficients increasing with the concentration of the salt.[1] With an increase in temperature the bands shifted to longer wavelengths and increased in intensity,[1,2] whilst when the solvent was changed from chloroform to alcohol they showed marked decreases in intensity and large hypsochromic shifts.[1] Hantzsch [3] ascribed the new absorption bands in the spectra of the *N*-heteroaromatic methiodides to a neutral *ortho*- or *para*-quinonoid "chromoisomer" (*e.g.*, I) in equilibrium with the salt (*e.g.*, II), but the effects of temperature and of change of solvent upon the wavelength of the bands suggest [6] that they are due to the transition of an electron from the anion to the cation within an ion pair (*e.g.*, III).



(I) (IIa) (IIb) (III)

The observed intensity changes in the new absorption bands with concentration, temperature, and solvent are consistent with the formulation of the new absorbing species as either a neutral adduct (*e.g.*, I) or an ion pair (*e.g.*, III), but the wavelength positions of the bands in the spectrum of a neutral adduct (*e.g.*, I) should not vary greatly with change of solvent. However, the observed effects of solvent upon the band positions are particularly large; the maximum of the long-wavelength band in the spectrum of 4-methoxycarbonylpyridine ethiodide, for example, shifts from 4489 Å in chloroform to 3311 Å in 7 : 3 ethanol–water solution,[6] representing an increase in the transition energy of 21 kcal./mole due to different interactions between the absorbing species and the solvent. The ground state of a *N*-heteroaromatic methiodide ion pair (*e.g.*, III) is more stabilised by solvation in a polar than in a non-polar solvent, and a charge-transfer electronic transition to a neutral excited state requires a larger transition energy the greater is the

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* Part VII, *J.*, 1960, 1282.

[1] Hantzsch, *Ber.*, 1911, **44**, 1776, 1783.

[2] Hantzsch, *Ber.*, 1919, **52**, 1535 and 1544.

[3] Hantzsch and Burawoy, *Ber.*, 1932, **65**, 1059.

[4] Meisenheimer, *Z. phys. Chem.*, 1921, **97**, 304.

[5] Weitz and Meitzner, *Ber.*, 1931, **64**, 2909.

[6] Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261, 3267.

solvating power of the medium.[6] Similarly, an increase in temperature reduces the solvation of the ion pair, resulting in a decrease in the charge-transfer transition energy.

For the excited state resulting from a charge-transfer electronic transition within a *N*-heteroaromatic methiodide ion pair two models may be envisaged. First, an electron may be transferred from the iodide ion to the lowest unoccupied π-orbital of the *N*-heteroaromatic nucleus, giving a free iodine atom and an aromatic system with an additional π-electron (delocalised model). Secondly, an electron may be transferred from the iodide ion to the *p*-orbital of a particular carbon atom in the *N*-heteroaromatic nucleus (localised model), forming an adduct (*e.g.*, I) in a state of strain, since, by the Franck–Condon principle, the nuclei attached to the localised carbon atom could not attain their equilibrium positions during the transition.

FIG. 1. *The ultraviolet absorption spectra of* (*A*) N-*methylpyridinium and* (*C*) N-*methylpiperidinium iodide in chloroform, and of* (*B*) *pyridinium perchlorate in water.*

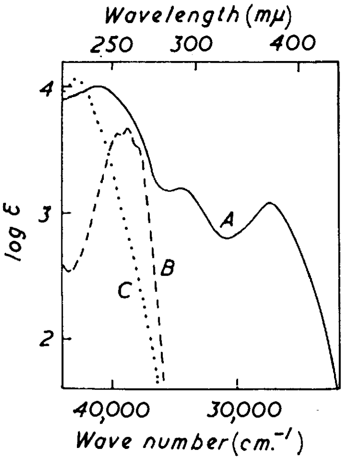
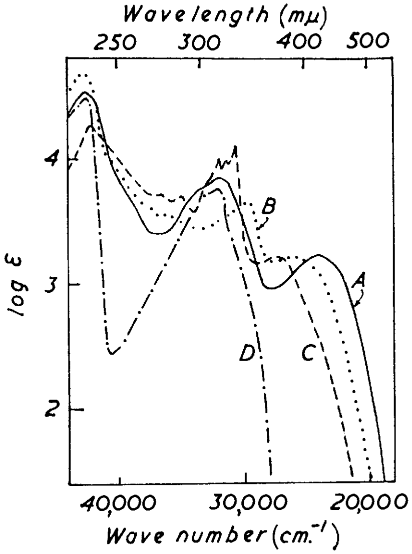


FIG. 2. *The visible and ultraviolet spectra of* (*A*) N-*methylquinolinium,* (*B*) N-*methylisoquinolinium, and* (*C*) *quinolizinium iodide in chloroform, and of* (*D*) *quinolinium perchlorate in water.*



The two models have different consequences. In a series of *N*-heteroaromatic methiodides the charge-transfer transition energy (E_t) is given, according to the delocalised model, by

$$E_t = \text{Constant} - E_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and, according to the localised model, by

$$E_t = \text{Constant} + E_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where E_a, the electron affinity of the *N*-heteroaromatic cation, is the energy of the lowest unoccupied π-orbital of the cation, and E_n is the π-electron localisation energy for nucleophilic attack at a particular carbon atom in the cation.

In order to distinguish between the two models, the visible and the ultraviolet spectra of a number of iodide salts of *N*-heteroaromatic cations in chloroform solution have now been measured, the results being given in Table 1 and Fig. 1—4. Chloroform was chosen as the most suitable solvent, since it is the least polar of the media in which the unsubstituted monoazo-aromatic methiodides are adequately soluble, and a 1 mm. thickness transmits enough ultraviolet radiation for spectroscopic measurement down to *ca.* 230 mμ. Owing to the large hypsochromic and hypochromic effects of polar media on the

TABLE 1. *The wavelengths* ($\lambda_{max.}$) *and the apparent extinction coefficients* (ε) *of the charge-transfer band maxima in the visible and ultraviolet spectra of some* N-*heterocyclic iodides, and the frequency at which the long-wavelength absorption has an extinction coefficient of* 100($\nu_{\epsilon=100}$), *the coefficient* (E) *of the energy* ($E\beta$) *of the lowest unoccupied* π-*electron orbital in the corresponding aromatic hydrocarbon, and the one-electron charge density in that orbital at the position of the nuclear nitrogen atom* (C_r^2). (*Values in italics refer to shoulders.*)

No.	Iodide	$\lambda_{max.}$ (mμ)	ε (l. mole^{-1} cm.$^{-1}$)	$\nu_{\epsilon=100}$ (cm.$^{-1}$)	E	C_r^2
1	*N*-Methylpiperidinium	233	12,000			
2	*N*-Methylpyridinium	367; 284; 243	1250; 1670; 10,500	22,700	1·0	0·333
3	*N*-Methylquinolinium	420; *255*	1700; *6000*	19,500	0·618	0·181
4	*N*-Methylisoquinolinium	380	1650	21,200	0·618	0·069
5	Quinolizinium	362	1600	22,700	0·618	0
6	*N*-Methylphenanthridinium	*~420*	*~2000*	19,800	0·605	0·172
7	*N*-Methylbenzo[*f*]quinolinium	*~420*	*~2000*	20,000	0·605	0·115
8	*N*-Methylbenzo[*h*]quinolinium	*~420*	*~500*	21,400	0·605	0·054
9	Benzo[*c*]quinolizinium	*~420*	*~1500*	20,700	0·605	0·030
10	Benzo[*a*]quinolizinium	*~420*	*~700*	21,700	0·605	0·027
11	Benzo[*b*]quinolizinium	*~450*	*~800*	19,200	0·414	0·008
12	*N*-Methylacridinium	500; 289	1250; 11,700	16,000	0·414	0·193
13	*N*-Methyl-1-azapyrenium	*~470*	*~1000*	18,900	0·445	0·087

FIG. 3. *The visible and ultraviolet absorption spectra of* (*A*) N-*methylacridinium and* (*B*) *benzo*[b]*quinolizinium iodide in chloroform, and of* (*C*) *acridinium perchlorate in* 50% *ethanol–water.*

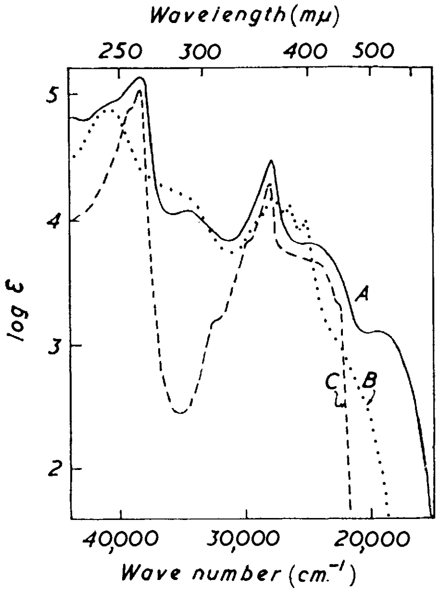
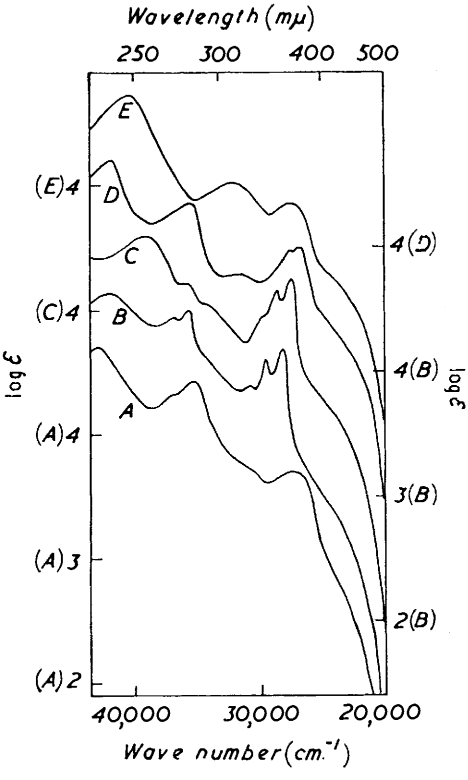


FIG. 4. *The visible and ultraviolet spectra in chloroform solution of* N-*methylbenzo*[h]*quinolinium* (*A*), *benzo*[a]*quinolizinium* (*B*), *benzo*[c]*quinolizinium* (*C*), N-*methylbenzo*[f]*quinolinium* (*D*), *and* N-*methylphenanthridinium iodide* (*E*).



charge-transfer band maxima of *N*-heteroaromatic methiodides,[6] the use of a solvent with a low polarity was found to be essential in the present work, for even in chloroform solution the charge-transfer band of the azaphenanthrene iodide salts appears only as a shoulder on the long-wavelength edge of the absorption due to the cation (Fig. 4), and the observed apparent maximum extinction coefficients of the long-wavelength charge-transfer bands are not large, lying in the range 500—2000 l. mole^{-1} cm.$^{-1}$ (Table 1). The recorded extinction coefficients are apparent only, since Beer's law is not obeyed. An increase in the concentration of the salt produces small hyperchromic and hypsochromic shifts of the charge-transfer bands, due, respectively, to the mass-action effect on the equilibrium between the free ions (*e.g.*, II) and the ion pair (*e.g.*, III), and to the increase in the solvating power of the medium. Accordingly, the recorded measurements (Table 1) were made with salt concentrations in the range 2—5 × 10^{-4}M, over which Beer's law held within 5% and band positions were constant within 1 mμ, the path length being varied to cover the different extinction ranges.

The results (Figs. 1—3) show that the *N*-heteroaromatic iodide salts in chloroform solution have a larger absorption generally than the corresponding perchlorates in aqueous solution over the whole of the observable wavelength range. Not all of the increase in absorption can be ascribed to charge-transfer transitions between the anion and the cation, as saturated ammonium iodides give a high-intensity absorption band near the high-frequency limit of the observable range (Table 1, Fig. 1). A similar band is observed with alkali and quaternary ammonium iodides in water[7] ($\lambda_{\text{max.}}$ 226 mμ; ε 10^4) and in other organic solvents,[6,8] the absorption being due to the transition of an electron from the iodide ion to the solvent.[6-8] Thus only the absorption bands which appear in the spectrum of a *N*-heteroaromatic iodide but not in that of the corresponding perchlorate at a wavelength greater than *ca.* 250 mμ can be assigned to charge-transfer transitions between the iodide ion and the *N*-heteroaromatic cation. This assignment is supported by the observation[9] that the frequency separation (7950 cm.$^{-1}$) between the two longer-wavelength maxima in the spectrum of pyridine methiodide corresponds to that (7600 cm.$^{-1}$) between the $^2P_{3/2}$ and the $^2P_{1/2}$ state of the iodine atom.

The observed energies of the long-wavelength charge-transfer bands in the spectra of the *N*-heteroaromatic iodides support the delocalised model for the excited state resulting from the transition. As some of these bands appear only as shoulders (Fig. 4) the frequency at which the extinction coefficient has the value of 10^2 l. mole^{-1} cm.$^{-1}$ has been taken as a measure of the transition energy (Table 1). Energy values obtained from the frequency at which the extinction coefficient attains one-tenth of its maximum value are not significantly different. These transition energies are related linearly to the electron affinity (E_a) of the *N*-heteroaromatic cation (Fig. 5*A*), as the delocalised model of the excited state requires (eqn. 1), but they do not show the correlation with the nucleophilic

TABLE 2. *The atom localisation energies for nucleophilic attack (E_n) at a carbon atom in a* N*-heteroaromatic system, calculated, with* $\Delta\alpha_N = 0{\cdot}6\beta$, *from the atom localisation energy for the corresponding aromatic hydrocarbon (E_L), and the π-electron charge density (q_r) in the carbanion corresponding to the adduct at the position of the nitrogen atom in the adduct.*

Compound	Position	$E_L\beta^{-1}$	q_r	$E_n\beta^{-1}$
Pyridine	2, 4	2·536	1·333	2·336
Quinoline	2	2·480	1·500	2·180
	4	2·299	1·364	2·081
Isoquinoline	1	2·299	1·364	2·081
	3	2·480	1·125	2·412
Phenanthridine	9	2·299	1·516	1·989
Acridine	5	2·013	1·400	1·773

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[7] Franck and Scheibe, *Z. phys. Chem.*, 1938, **139**, *A*, 22.

[8] Smith and Symons, *Discuss. Faraday Soc.*, 1957, **24**, 206.

[9] Kosower and Skorcz, Handbook of the 4th Meeting on Molecular Spectroscopy, Bologna, **1959**.

atom localisation energies (E_n) of the cations (Table 2) that the localised model predicts (eqn. 2).

When the Hückel method and first-order perturbation theory are used, the effective electron affinity (E_a) of the π-electron system in a *N*-heteroaromatic cation is given by the expression:

$$E_a = \alpha_C - E\beta + C_r^2\Delta\alpha_N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\Delta\alpha_N$ is the increment in the Coulomb integral of nitrogen relative to that of carbon (α_C), $E\beta$ is the energy of the lowest unoccupied orbital in the aromatic hydrocarbon corresponding to the *N*-heteroaromatic cation, E being a calculated coefficient and β an empirical energy representing the carbon–carbon resonance integral, and C_r^2 is the one-electron charge density in that orbital at the position substituted by a nitrogen atom in the cation. Calculated values of E and C_r^2 are given in Table 1. Then eqns. (1) and (3) lead to:

$$E_t = \text{Constant} + E\beta - C_r^2\Delta\alpha_N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so that for a particular value of $\Delta\alpha_N$ in terms of β a linear relation should be observed between the transition energy (E_t) and the calculated values of E and C_r^2 (Table 1), according to the delocalised model for the excited state of the lowest-energy charge-transfer transitions. A linear relation is found (Fig. 5*A*) if $\Delta\alpha_N = \beta$, and the slope of the relation gives these quantities the value of ~15,000 cm.$^{-1}$. The same value of $\Delta\alpha_N$ is obtained from the plot of E_t against C_r^2 for a group of compounds with a common value of E, *e.g.*, the azanaphthalenes or azaphenanthrenes (Table 1).

The π-electron localisation energy for nucleophilic attack at a carbon atom in a *N*-heteroaromatic cation, according to first-order perturbation theory, is given by the expression:

$$E_n = E_L - (q_r - 1)\Delta\alpha_N + \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where E_L is the atom localisation energy, calculated by the Hückel method, for the aromatic hydrocarbon corresponding to the cation, and q_r is the π-electron charge density in the carbanion corresponding to the adduct, formed by nucleophilic attack upon the cation, at the position occupied by the nitrogen atom in the adduct; *e.g.*, the 3-position in the pentadienyl anion in the case of the adduct (I). The nitrogen atom in such adducts (*e.g.*, I) is neutral, and so the appropriate value for $\Delta\alpha_N$, which has been determined experimentally,[10] is 0·6β. Equations (2) and (5) and the calculated values of E_n (Table 2) indicate that the lowest-energy charge-transfer bands of isoquinoline and phenanthridine methiodide should lie at a lower frequency than that for quinoline methiodide, it being assumed that the iodine atom adds to the more reactive of the carbon atoms adjacent to the nitrogen atom in the excited state of the charge-transfer transition, a mode of attack which would be stereochemically favoured by electrostatic interaction in the ground state, or that these bands should lie at the same and at a lower frequency, respectively, than for quinoline methiodide, on the assumption that the iodine atom adds to the 4-position of the quinolinium ion. These consequences of the localised model for the excited state of the charge-transfer transition in the *N*-heteroaromatic iodide salts are not supported by the experimental data (Table 1).

Further evidence for the delocalised model of the excited state resulting from the lowest-energy charge-transfer transition in *N*-heteroaromatic iodides is provided by the electronic spectra of the polymethylpyridine methiodides, measured by Kosower and Skorcz [9] (Table 3). The inductive and hyperconjugative effects of a methyl group attached to a carbon atom raise the energy of the lowest unoccupied π-electron orbital in the pyridinium ion, and thus increase the charge-transfer transition energy in the iodide salt, on the delocalised model for the excited state. First- and second-order perturbation theory indicate [11] that the inductive and hyperconjugative effects of a methyl group upon

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[10] Mason, *J.*, 1958, 674.

[11] Longuet-Higgins and Sowden, *J.*, 1952, 1404.

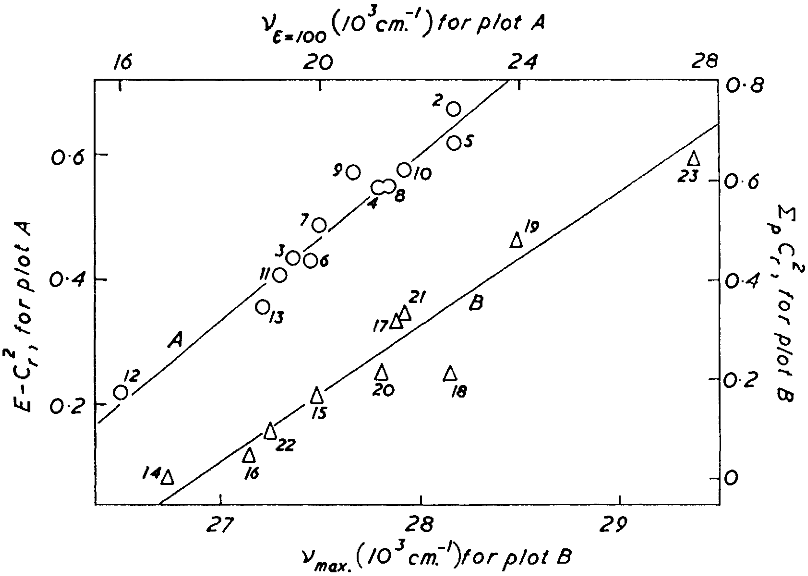
TABLE 3. *The frequency* ($\nu_{max.}$) *and apparent extinction coefficient* (ε) *of the long-wavelength charge-transfer band maxima of the polymethylpyridine methiodides in chloroform solution. The sum of the one-electron charge densities* ($\sum_r C_r^2$) *in the lowest unoccupied* π*-orbital of pyridine at the carbon atoms substituted by methyl groups, calculated with* $\Delta\alpha_N = 0{\cdot}8\beta$.

No.	Pyridinium iodide	ν_{max} (cm.$^{-1}$) [a]	$\varepsilon_{max.}$ (l. mole^{-1} cm.$^{-1}$) [a]	$\sum_r C_r^2$
14	1-Methyl	26,740	1200	0
15	1,2-Dimethyl	27,490	860	0·162
16	1,3-Dimethyl	27,170	1320	0·045
17	1,4-Dimethyl	27,880	1240	0·312
18	1,2,3-Trimethyl	28,160	820	0·207
19	1,2 4-Trimethyl	28,480	940	0·474
20	1,2,5-Trimethyl	27,820	1040	0·207
21	1,2,6-Trimethyl	27,930	440	0·324
22	1,3,5-Trimethyl	27,320	1370	0·090
23	1,2,4,6-Tetramethyl	29,370	480	0·636

[a] Quoted from Kosower and Skorcz, Handbook of the 4th Meeting on Molecular Spectroscopy, Bologna, 1959.

FIG. 5. (*A*) *The relation between the frequency* ($\nu_\varepsilon = 100$) *of the lowest-energy charge-transfer band in the spectra of the polycyclic* N*-heteroaromatic iodide salts and the electron affinity parameter* ($E - C_r^2$) *of the* N*-heteroaromatic cation.* (*The numbers refer to the compounds listed in Table* 1.)

(*B*) *The relation between the frequency* ($\nu_{max.}$) *of the lowest-energy charge-transfer band in the spectra of the polymethylpyridinium iodides and the parameter* ($\sum_r C_r^2$) *governing the inductive and hyperconjugative effects of the methyl groups on the electron affinity of the pyridinium ion.* (*The numbers refer to the compounds listed in Table* 3.)



the charge-transfer transition energy are proportional to the one-electron charge density (C_r^2) in the lowest unoccupied orbital of the pyridinium ion at the position substituted by the methyl group, the effects for polysubstitution being additive. Accordingly the charge-transfer transition energy (E_t) of the polymethylpyridine methiodides is given by

$$E_t = (I + H)\sum_r C_r^2 + \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where I and H are constants representing the intrinsic inductive and the hyperconjugative capacitiy, respectively, of the methyl group in relation to the pyridinium system, the sum being taken over all the carbon atoms, r, substituted by methyl groups.

The calculated one-electron charge densities in the lowest unoccupied orbital of pyridine at the various carbon positions are sensitive (Fig. 6) to the particular value adopted for the

Coulomb integral increment of nitrogen ($\Delta\alpha_N$). Limiting values, obtained experimentally,[10] are 0·6β for a neutral, and 2·5β for a positvely charged nitrogen atom. Within the range $\Delta\alpha_N = 0{\cdot}6$—$1{\cdot}0\beta$ the calculated charge densities give a satisfactory linear relation between E_t and $\sum_r C_r^2$, as required by equation (6), the correlation illustrated (Fig. 5*B*) being obtained from the charge densities calculated with $\Delta\alpha_N = 0{\cdot}8\beta$ (Table 3). The value of $\Delta\alpha_N$ giving charge densities that show the best agreement with equation (6) cannot be closely specified, owing to a possible steric effect of the 2-methyl group on the charge-transfer transition energies. A 2-methyl group lowers the apparent extinction coefficient of the pyridine methiodide charge-transfer band (Table 3), probably by hindering the approach of the iodide ion to the positively charged nitrogen atom in the ion pair.[9] A hypsochromic shift of the band may result in addition, since 1,2,3-trimethylpyridinium iodide, in which the 3-methyl group buttresses the steric effect of that in the 2-position, absorbs at a higher frequency than the 1,2,5-isomer (Table 3). However, such a steric effect is not obvious in the polycyclic compounds with the nitrogen atom in a *peri-*, *meso-*, or bridge-head position, and the hindered molecule, benzo[*h*]quinoline methiodide (IV), whilst absorbing with a low intensity (Table 1), has a charge-transfer transition energy showing satisfactory agreement with equation (4) (Fig. 5*A*).

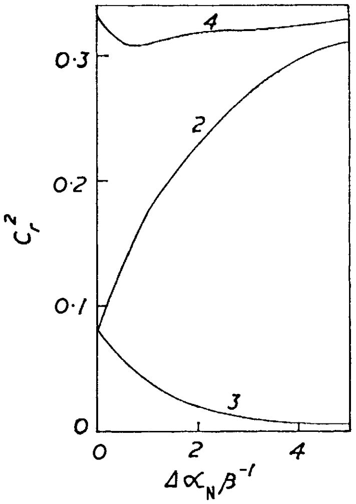
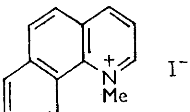


FIG. 6. *The relation between the one-electron charge densities* (C_r^2) *at the* 2-, 3-, *and* 4-*position in the lowest unoccupied* π-*electron orbital of pyridine and the Coulomb integral increment of the nitrogen atom expressed in terms of the carbon–carbon resonance integral* ($\Delta\alpha_N\beta^{-1}$).



(IV)

In the excited state resulting from a charge-transfer transition in a *N*-heteroaromatic iodide the nitrogen atom may retain a partial positive charge, as the electron transferred from the iodide ion is delocalised over the carbon positions in the π-electron system. The particular value ($\Delta\alpha_N = \beta$) of the Coulomb integral increment of the nitrogen atom in the excited state required by equation (4), and the range ($\Delta\alpha_N = 0{\cdot}6$—$1{\cdot}0\beta$) required by equation (6), are thus consistent with the assumptions of the delocalised model for the excited state, lying between the values[10] for a neutral and a positively charged nitrogen atom (0·6β and 2·5β respectively).

EXPERIMENTAL

Materials.—Samples of quinolizinium, and benzo-[*a*]- -[*b*]-, and -[*c*]-quinolizinium salts were kindly provided by Dr. Gurnos Jones.[12] Additional quinolizinium bromide was prepared by the method of Glover and Jones,[12] and benzo[*b*]quinolizinium bromide according to Bradsher and Beavers's directions.[13] The bromides and perchlorates were converted into iodides by double decomposition with potassium iodide in acetone. The remaining compounds were

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[12] Glover and Jones, *J.*, 1958, 3021.

[13] Bradsher and Beavers, *J. Amer. Chem. Soc.*, 1955, **77**, 4812.

prepared from commercial specimens of the parent bases by treatment with methyl iodide in methanol at room temperature, except in the case of benzo[*h*]quinoline, where the reaction mixture was heated in a sealed tube at 100° for 24 hr.

Solvent.—Spectra measured with different batches of " AnalaR " chloroform were not always reproducible, probably owing to a variation in alcohol content. Accordingly, this chloroform was dried by calcium chloride and distilled from phosphoric oxide. 1% by volume of dry ethanol was added as a stabiliser, results with different batches of this solvent being reproducible.

Spectra.—These were measured with a Hilger Uvispek quartz spectrophotometer with a methiodide concentration in the range 2—5 × 10^{-4}M, and cells of 0·1, 1, 4, and 10 cm. fixed path length, and 0·01—1 cm. variable path length.

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