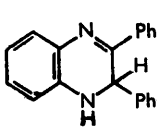
51. *The Effect of Acid on the Electronic Spectra of Organic Molecules containing Conjugated and Unconjugated Nitrogen Atoms.*

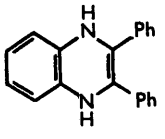
By J. N. Murrell.

The effect of acid on the electronic spectra of organic molecules containing a conjugated and an unconjugated nitrogen atom bears little relationship to the possibility of writing structures in which the positive charge resonates between the two nitrogen atoms. A molecular-orbital theory of the charge-transfer character of the lowest excited states gives a better interpretation of the experimental results.

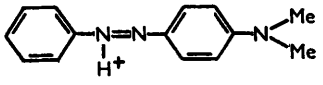
The yellow solution of a dihydro-2 : 3-diphenylquinoxaline instantaneously becomes deep red in the presence of dilute acid.[1] The change is reversed on neutralizing the solution. An explanation of this phenomenon was sought, to decide between the two most likely structures for this compound, (I) and (II).



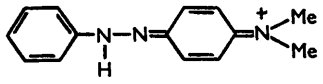
(I)



(II)



(III)

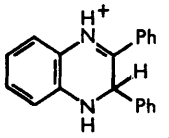


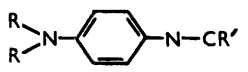
(IV)

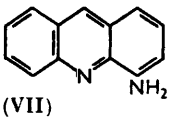
The colour of the free base favours (I), because amino-substituted anils are yellow whereas 9 : 10-dihydrophenazine is colourless. However, if (I) is adopted and assumed to be protonated on the conjugated nitrogen atom, then from conventional valence-bond or resonance ideas there is no reason to expect a large red shift in its absorption spectrum on acidification. Valence-bond theory would associate a red shift with the introduction of new, or lower-energy, resonance structures. For example, *p*-dimethylaminoazobenzene changes from yellow to red on acidification. The protonated form is assumed to be (III) but with a strong contribution from the structure (IV). The red colour is presumably associated with a transition from the ground state (mainly III) to an excited state (mainly IV). Such resonance is possible only when the two nitrogen atoms are separated by an odd number of conjugated atoms. In (I), the two nitrogen atoms are separated by an

[1] Fischer, *Ber.*, 1891, **24**, 719.

even number of conjugated atoms, hence the only low-energy valence structure that can be written is (V).


(V)


(VI)

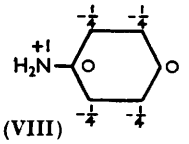

(VII)

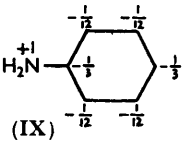
The behaviour of the dihydroquinoxaline is not an isolated case. A yellow-to-red colour change is observed on acidifying [2] *p*-amino-substituted anils of type (VI), and 1-aminoacridine (VII) changes from yellow to blue-black.[3] In neither case can the positive charge " resonate " between the two nitrogen atoms.

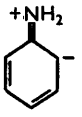
Since the resonance theory appears to fail in these cases, let us consider the molecular-orbital representation. The first absorption bands in amino-aromatic molecules probably have a considerable amount of charge-transfer character, the NH_2 group being a strong electron donor. For example, in aniline there are two low-lying vacant benzene molecular orbitals which can accept an electron from the NH_2 group, one symmetric and one antisymmetric to a rotation of 180° about the C–N axis. The charge densities associated with these two states, relative to the ground state, are depicted in (VIII) and (IX).

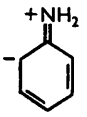
If we could attach a proton to the aromatic ring of the aniline molecule, we would predict that (VIII) would be stabilized if the proton were in the *ortho*- or the *meta*-position but not if it were in the *para*-position, and (IX) would be stabilized four times as much in the *para*-position as in the *ortho* or *meta*.

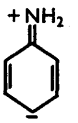
The valence-bond charge-transfer states however will be some combination of the structures (X), (XI), and (XII). The state which is antisymmetric to rotation about the C–N bond will be $\sqrt{\frac{1}{2}}(X - XI)$, and that which is symmetric will be some mixture of


(VIII)


(IX)


(X)


(XI)


(XII)

$\sqrt{\frac{1}{2}}(X + XI)$ and (XII). Thus, the donated charge appears either in the *ortho*- or the *para*-position but not in the *meta*. We should therefore expect no appreciable red shift on attaching a proton to the *meta*-position.

TABLE 1. *Wavelengths of the first two absorption bands of the aminopyridines in neutral (n) and acid (a) solution.*

	Aniline [a]	2-Aminopyridine [b]	3-Aminopyridine [b]	4-Aminopyridine [b]
λ_n (mμ)	288, 235	295, 234	300, 240	270,* 244
λ_a (mμ)	—	300, 227	317, 250	262
$-\Delta\nu$ (cm.$^{-1}$)	—	600, −1300	1800, 1700	~0, 2800

* Shoulder. [a] Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714. [b] Steck and Ewing, *ibid.*, 1948, **70**, 3399.

Calculations show that the lowest excited state of aniline is antisymmetric with respect to the two-fold axis (although the lowest energy charge-transfer configuration is in fact the symmetric one), whilst there is a state of slightly higher energy which is symmetric.[4] Table 1 gives the wavelengths of the first two absorption bands of the amino-pyridines

[2] Moore and Woodbridge, *J. Amer. Chem. Soc.*, 1908, **30**, 1001.
[3] Matsumara, *ibid.*, 1939, **61**, 2247.
[4] Murrell, *Proc. Phys. Soc.*, 1955, *A*, **68**, 969.

in ethanol, and in ethanol with acid added to pH 2: in these circumstances the heterocyclic nitrogen atom will be protonated. The wavelengths of the corresponding bands of aniline are given for comparison; they undergo a blue shift in acid owing to protonation of the amino-group.

For the band of lower energy, there is a red shift of 600 cm.$^{-1}$ and 1800 cm.$^{-1}$ for the 2- and 3-amino-compounds respectively, and for the 4-aminopyridine no shift can be detected as it is obscured by the more intense upper band: however, we probably could have detected a red shift larger than 500 cm.$^{-1}$. The upper band undergoes a red shift of 1700 cm.$^{-1}$ and 2800 cm.$^{-1}$ in the case of the 3- and 4-amino-pyridines respectively, but a blue shift of 1300 cm.$^{-1}$ in the 2-amino-compound. The latter, unexpected from either the molecular-orbital or the valence-bond viewpoint, may be due to second-order energy changes, or to the close proximity of the NH_2 group to the heterocyclic atom. In general, however, we can say from the evidence on 3-aminopyridine that molecular-orbital theory gives a rather better picture of any charge transfer in the excited states of the amino-pyridines than does resonance theory.

The amino *N*-heterocyclic compounds derived from naphthalene provide a more extensive set of data to test resonance theory than is available from the pyridines. Table 2 gives the wavelength of the first absorption band for some amino-quinolines, -*iso*-quinolines, and -quinazolines in neutral and acid solution. In the discussion which follows it is assumed that the molecules are protonated on the heterocyclic nitrogen atoms. For quinazoline I make no attempt to decide whether the proton goes to the 1- or the 3-position; the following arguments hold whichever is the case. R denotes those molecules for which resonance theory would predict a large red shift on acidification.

Table 2 shows that there is little connection between the " resonance " cases and a

TABLE 2. *Wavelengths of the first absorption band of some amino-*N*-heterocyclic compounds of the naphthalene series.*

		λ_n (mμ)	λ_a (mμ)	$-\Delta\nu$ (cm.$^{-1}$)
α-Naphthylamine		322		
4-Aminoquinoline	R	305 + 315 *	305 + 315	0
5-Aminoquinoline	R	345	418	5060
8-Aminoquinoline		338	388	3810
1-Amino*iso*quinoline	R	332 + 300	330 + 280	−180, −2380
4-Amino*iso*quinoline		332	354	1870
5-Amino*iso*quinoline		332	378 + 340	3660 (or 710)
8-Amino*iso*quinoline		345 + 307	417 + 325	5000, 1800
4-Aminoquinazoline	R	323 + 312	324 + 311	100
5-Aminoquinazoline	R	372 + 336 †	462 + 305	5230, −3020
8-Aminoquinazoline		338	415	5490
β-Naphthylamine		340		
2-Aminoquinoline	R	315	308	−720
3-Aminoquinoline		350	372	1690
6-Aminoquinoline		352	383	2300
7-Aminoquinoline	R	352	390	2770
3-Amino*iso*quinoline	R	353	390	2690
6-Amino*iso*quinoline	R	326	352 + 337	2270 (or 1000)
7-Amino*iso*quinoline		349	385	2680
2-Aminoquinazoline	R	352	348 + 339 †	−320 (or −1090)
6-Aminoquinazoline		360	310 *	−4480
7-Aminoquinazoline	R	345	373	2180

* Inflexion. † Shoulder.

Data on aminoquinolines are from ref. *a* of Table 1, and for amino*iso*quinolines and quinazolines from ref. 15.

red shift on acidification. For example, the bands of 2- and 4-aminoquinoline, 1-amino-*iso*quinoline, and 2- and 4-aminoquinazoline are shifted, if anything, slightly towards the blue, whereas 8-aminoquinazoline, a non-resonance case, shows the largest red shift of all.

Let us compare the 5- and 8-amino-compounds. On resonance theory the absorption band of one of these should undergo a large red shift on acidification, and the other should

not be shifted significantly. On molecular-orbital theory, however, the 5- and 8-amino-compounds should be shifted by the same amount, the electron from the amino-group going into an orbital which, by symmetry, gives rise to the same electron density at the two positions. From the Table, the molecular-orbital theory is evidently more satisfactory, although there is some sympathy for the resonance theory for quinoline and *iso*quinoline. The 6- and 7-amino-compounds show a similar behaviour, and support the molecular-orbital theory, although 6-aminoquinazoline is exceptional on either theory; Osborne and Schofield [5] suggest that it is protonated on the amino-group but, as they suggest, the molecule needs further examination.

It has been assumed here that the shifts in the absorption bands which occur on acidification of amino-*N*-heterocyclic compounds can be interpreted by a first-order perturbation theory; that is, that the shifts depend only on the difference in the electron density on the heterocyclic atom between the ground and the excited state. If there is no charge transfer character in the excited state, then the energy changes would have to be interpreted by a second-order perturbation theory.[6] Calculations show that the lowest excited state of aniline has only about 17% of charge-transfer character associated with the structure (VIII). However, since second-order energy changes are usually rather small, the first-order treatment given in this paper will probably still be applicable.

It remains to be said that both molecular-orbital and valence-bond wave functions are only attempts to obtain a first approximation to the true wave function of a molecule. If molecular-orbital theory is extended by configurational interaction, it will take on some of the properties of the valence-bond functions. If the valence-bond functions are extended in a similar way they become more like the molecular-orbital functions. The best functions lie somewhere between the two, but the evidence now presented suggests that any charge-transfer character in the lowest excited states of amino-*N*-heterocyclic compounds is more closely represented by the molecular-orbital than by the valence-bond functions.

DEPARTMENT OF THEORETICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY.

[*Received, July 28th,* 1958.]

[5] Osborne and Schofield, *J.*, 1956, 4191.
[6] Murrell, *J. Mol. Phys.*, 1958, **1**, 384.