*n–π Transitions in Azines.**

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The theory of n–π transitions in azines • is discussed and it is shown that simple molecular-orbital treatments, using the orbitals of the ground state, are not adequate to describe the upper state. A different approach is suggested and the characteristic properties of the n–π transitions are interpreted in terms of it.

IT is now accepted that certain of the longer-wave-length absorption bands in pyridine, pyrazine, etc., are due to n–π transitions in which electrons are transferred from unshared pairs on the nitrogen atoms to π-orbitals of the rings (Platt, *J. Chem. Phys.*, 1951, **19**, 101). In this paper these transitions and the effects of substitution on them are discussed.

The n–π Transitions of Pyridine.—Since the wave functions of the states produced by n–π transitions in pyridine change sign on reflection in the plane of the molecule, they are automatically orthogonal to those of the ground state and of the excited states which are produced from it by π–π' transitions. At first sight, the obvious model for calculations on such states is that of a system of seven electrons in the π-orbitals of a benzene-like ring, perturbed by the positive charge and unpaired electron on the nitrogen atom.

We have used two simple methods to attack this problem, a perturbation calculation and a conventional molecular-orbital treatment. We shall first consider each of these very briefly and show why they are inadequate.

According to simple molecular-orbital theory the two lowest states of the benzene negative ion are obtained by adding an electron to the unfilled orbitals of benzene. The most stable state will be of symmetry class E_{2u} and the other, which cannot be very much

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• The term azine is used in its strictly systematic, generic meaning of an " aromatic " six-membered ring containing one or more nitrogen atoms.

less stable, of class B_{1g}. The orbitals for the added electrons in these states may be written :

$$\psi_{\mathrm{I}} = 2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6$$
$$\psi_{\mathrm{II}} = \phi_2 - \phi_3 + \phi_5 - \phi_6$$
$$\psi_{\mathrm{III}} = \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6$$

where ϕ_i is the $2p_\pi$ function on the *i*'th atom (Eyring, Walter, and Kimball, " Quantum Chemistry," Wiley, New York, 1944). Further excited states arise from the addition of an electron to the excited states of benzene : at first we shall neglect these in order to keep our model as close as possible to the conventional one (Reid, *ibid.*, 1953, **21**, 1906). In pyridine, if the atoms are numbered cyclically from the nitrogen atom, ψ_{I}, ψ_{II}, and ψ_{III} transform as the representations B_1, A_2, and B_1, respectively of the appropriate group C_{2v}.

The valence-state electron affinity of the nitrogen atom when six electrons have been spread evenly over the atoms of the ring corresponds quite closely to the process $sp^3V_4 \longrightarrow sp^4V_3$ and this is given as 12·24 ev. The corresponding value for the neutral carbon atoms is 0·69 ev (Mulliken, *ibid.*, 1934, **2**, 782).

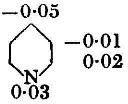
If we regard this difference of electronegativities as acting as a perturbation on the added electron we find that the first-order energy correction to any state is, apart from a constant, approximately equal to $c_1^2\delta$ where c_1 is the coefficient of the unshared electron on the nitrogen atom and $\delta \approx 11{\cdot}5$ ev. The perturbation therefore splits the E_{2u} state of the benzene ion, stabilising the state with wave function ψ_{I} by about 3·5 ev relative to that with wave function ψ_{II}. In second-order theory the wave functions ψ_{I} and ψ_{III} are mixed in such a way as to increase the charge on the nitrogen atom. If the energy separation between them is negligible compared with the perturbation, the resulting orbital has the form :

$$3\phi_1 - 2\phi_2 + \phi_4 - 2\phi_6$$

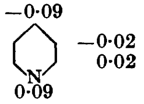
and the second-order perturbation energy is about 2 ev. In fact both the mixing and the perturbation energy would be somewhat smaller as the E_{2u}–B_{1g} separation is not quite negligible.

The treatment suggested above is the best that can be done as long as we restrict ourselves to theories in which we assign the extra electron to an orbital of the benzene ring, without allowing for the reorganisation of the other π-electrons. In view of the magnitude of the perturbation compared with the excitation energy of benzene it is clear this is not satisfactory and that other more highly excited states of the benzene ion should be included in our perturbation calculation. Instead of carrying through such a calculation we shall use conventional molecular-orbital theory, which is largely equivalent to it.

Since, as we shall show, this theory is also unsatisfactory we have not chosen the most plausible parameters. Instead we have considered two extreme cases. We have taken all the resonance integrals β equal, and the coulomb integral for nitrogen as equal to $\alpha + \delta\beta$. Since we are dealing with a seven-electron system in a framework of five unipositive carbon atoms and one dipositive nitrogen atom the value of $\delta\beta$ should be intermediate between the first and the second ionisation potential of nitrogen. We have considered two values of δ,



$\delta = 8$



$\delta = 4$

namely, $\delta = 8$ and $\delta = 4$. The first is probably too large and the second too small. The resulting roots and coefficients are shown in Tables 1 and 2. The coefficients for a system of an isolated nitrogen atom and a pentadienyl chain are included in Table 2 for comparison. The charge distributions derived from these calculations are shown in the annexed diagrams. The obvious fault of these calculations is their lack of self-consistency. The α-values assumed for nitrogen on the basis of electronegativity considerations lead to a final condition of the nitrogen atom very different from that first assumed. The least that is required is a self-consistent method such as that suggested by Mann and Wheland (*ibid.*, 1949, **17**, 264). Such methods, however, are very laborious.

TABLE 1. *π-Electron energies for hypothetical perturbed benzene rings.*

	E_1	E_2	E_3	E_4	E_5	E_6
$\delta = 8$	−8·246	−1·686	−1·000	+0·163	+1·000	+1·769
$\delta = 4$	−4·473	−1·631	−1·000	+0·305	+1·000	+1·799

TABLE 2. *Coefficients for the orbitals of perturbed benzene rings.*

	$\delta = 8$				$\delta = 4$				$\delta = \infty$			
	c_1	c_2	c_3	c_4	c_1	c_2	c_3	c_4	c_1	c_2	c_3	c_4
E_1	0·985	0·121	0·013	0·004	0·945	0·223	0·056	0·025	1·000	0·000	0·000	0·000
E_2	0·086	−0·252	−0·504	−0·598	0·171	−0·203	−0·503	−0·617	0·000	0·287	0·500	0·573
E_3	0·000	0·500	0·500	0·000	0·000	0·500	0·500	0·000	0·000	0·500	0·500	0·000
E_4	+0·253	−0·568	−0·047	+0·576	+0·253	−0·545	−0·087	+0·571	0·000	0·573	0·000	0·573

Although not successful, these calculations suggest a more hopeful approach. Since, as shown in Table 2, the final state of the system is approximately described as a neutral nitrogen atom and pentadienyl radical in its ground state, we start our perturbation calculation from this extreme. We suppose that the upper state of the n–π transitions consists of a nitrogen atom in the rather unusual valence state $sp_xp_y\pi^2$ and a pentadienyl radical, and then allow the π-electron orbitals on the nitrogen atom to interact with those of the terminal atoms of the pentadienyl radical. The final charge distribution and energy are calculated in the usual way.

The appropriate ionisation potential I_{N} of nitrogen is about 12 ev. The electron affinity E_{P} corresponding to the lowest unfilled orbital of pentadienyl is not known. We shall assume a value of 1 ev, but even a large error in this estimate would not affect our qualitative conclusions.

The correct form of the lowest unfilled orbital of the pentadienyl radical is easily found to be $(\phi_2 - \phi_4 + \phi_6)/\sqrt{3}$, and so to a first approximation we may assign the last electrons to an orbital

$$\phi_1 + (\phi_2 - \phi_4 + \phi_6)\,.\,\lambda/\sqrt{3}$$

where, if we neglect overlap,

$$\begin{aligned}\lambda &= \frac{(1/\sqrt{3})\int\phi_1 H(\phi_2 - \phi_4 + \phi_6)\mathrm{d}\tau}{I_{\text{N}} - E_{\text{P}}}\\ &= \frac{(2/\sqrt{3})\int\phi_1 H\phi_2\mathrm{d}\tau}{I_{\text{N}} - E_{\text{P}}}\\ &= 2\beta'_{\text{CN}}/11\sqrt{3}\end{aligned}$$

where β'_{CN} is roughly equal to the usual resonance integral β_{CN} of molecular-orbital theory. Unfortunately the absolute value of this quantity is uncertain, so that our further conclusions are largely qualitative. Assuming a reasonable value of 2 ev for β'_{CN}, we finally find $\lambda = 0{\cdot}21$, *i.e.*, that the charge transferred to the ring is about 0·05 of an electron.

The stabilisation energy

$$\Delta E = (2\beta_{\text{CN}}/\sqrt{3})^2/(I_{\text{N}} - E_{\text{P}})$$

which is about 0·5 ev.

We do not attach any significance to these numerical values. They could be altered by as much as a factor of two by extreme assumptions about the parameters involved. The important conclusion is that delocalisation can cause a considerable stabilisation, without displacing the bulk of the seventh electron from the nitrogen atom.

We must now consider the nature of these states in more detail. There are two unpaired electrons, one in a hybrid σ-orbital on the nitrogen atom, directed away from the ring, and the other in a π-orbital partly on the nitrogen atom but mainly on the pentadienyl chain. The singlet–triplet separation between the two states which arise from this configuration will be roughly equal to $2K_{\sigma\pi}$, where $K_{\sigma\pi}$ is the exchange integral between these two electrons. In view of the uncertainty in λ we cannot estimate this exactly, but rough calculations show that it should be a good deal smaller than that in a π–π′ transition. The actual separation is not known with certainty (Reid, *loc. cit.*).

We conclude that, as has usually been assumed, the first singlet–singlet *n*–π transition of pyridine at just below 2600 Å is formally allowed. The rather low observed intensity of this transition in pyridine and in the diazines (Halverson and Hirt, *ibid.*, 1951, **19**, 711) can readily be understood. The occurrence of the *n*–π transition is associated with a complete reorganisation of the other π-electrons, so that the matrix element of the dipole moment is the product of two terms, one equal to $\int\phi_\sigma r\phi_\pi d\tau$, where ϕ_σ and ϕ_π are the orbitals occupied by the electron which is directly involved, respectively, before and after the transition. The second factor, which is the overlap integral between the initial π-electron distribution and the final distribution of the six other π-electrons, is peculiar to this kind of transition and is responsible for the low intensity. We have evaluated this overlap factor as a sum of products of the overlap integrals between the benzene orbitals and the pentadienyl and the nitrogen orbitals. It is 0·49, thus leading to a decrease in intensity by a factor of four. If we further suppose that the transition is from an sp^2 nitrogen orbital to a π-orbital, then only the *s*-component of the nitrogen orbital makes any contribution to the intensity. We therefore expect a reduction of the intensity from that of a strongly allowed transition by a factor of twelve. This is probably sufficient to account for the low observed intensity.

The energy required to produce the *n*–π transition can be written $E = U_1 + U_2 - U_3$, where U_1 is the energy of excitation of the nitrogen atom from its $s^{1/3}p^{11/3}$ lower valence state to its sp^4 V_3 upper state, U_2 is loss of resonance energy during the transition, and U_3 is the gain in energy due to delocalisation, *i.e.*, the ΔE of the previous discussion. Using reasonable values for U_1 and U_2 we find a value of E of about 7 ev, instead of the observed 4 ev. We believe that the greater part of this discrepancy is due to the reorganisation of the σ-bonds in such a way as to make more use of the nitrogen *s*-orbital.

Substitution Effects.—It is recognised that the most important cause of the red shift of the 2600-Å band of benzene, which occurs on substitution, is the migration of charge into and out of the ring (Sklar, *ibid.*, 1942, **10**, 135). In general the shift gives a measure of the excess of this stabilisation in the upper state over that in the ground state. In the upper state of an *n*–π transition, as we have shown, there is already some negative charge on the carbon atoms. This inhibits further charge transfer from the substituents to the ring and so decreases the amount of stabilisation which can be effected in this way. It follows that substituents which can act as electron donors, but not as acceptors, should produce a blue shift of the *n*–π spectra, since they stabilise the ground state more than the upper state.

Halverson and Hirt's measurements (*loc. cit.*) confirm this prediction. In fact the blue shifts of the *n*–π bands in chloropyrazines mirror the red shifts in the π–π′ band at 2600 Å (cf. their Fig. 10). This suggests strongly that the ratio of the charge stabilisation effects in the upper and the lower states of the π–π′ transitions of the various chloropyrazines is roughly constant. Furthermore the data suggest a value of about 4·5 kcal. for the stabilisation due to charge migration in the ground state of chloropyrazine. On theoretical grounds that in chlorobenzene would be expected to be a little smaller.

Substituents which can act only as electron-acceptors should behave quite differently. They should produce larger stabilisations in the excited state than in the ground state and so should cause a red shift in the *n*–π bands. No spectra of suitable compounds seem to have been reported. The spectra of nitro- and cyano-pyrazines would be very useful in this respect.

The effect of substituents which can act both as donors in the ground state and acceptors in the excited state is not easily predicted. The methyl group, which falls into this class produces a small red shift in the α- and β-picolines and a rather larger blue shift (of 480 cm.$^{-1}$) in γ-picoline (Rush and Sponer, *J. Chem. Phys.*, 1952, **20**, 1847).

It must be noted that simple M.O. theory leads to identical results for the effects of substituents.

The Diazines.—The *n*–π transitions of polyazines can be treated by a generalisation of the theory developed for pyridine. We shall consider pyrazine.

There are clearly two *n*–π transitions in pyrazine corresponding to any one in pyridine. We shall deal with the lowest singlet–singlet transition. From simple symmetry considerations the wave functions for the upper states are of the form :

$$(1/\sqrt{2})(\chi_1 + \chi_2) \text{ and } (1/\sqrt{2})(\chi_1 - \chi_2)$$

where χ_1 and χ_2 correspond to hypothetical states obtained by exciting the first and the second nitrogen atom respectively. Transitions to $(1/\sqrt{2})(\chi_1 + \chi_2)$ are allowed and should have twice the intensity of the pyridine transition. Those to the state $(1/\sqrt{2})(\chi_1 - \chi_2)$ are forbidden.

The effect of the second nitrogen atom on the position of the *n*–π transition is twofold. Acting as an electronegative substituent it should produce a red shift in the 1 : 2- and 1 : 4-compounds. There will also be a much more complicated effect due to the splitting of degeneracy of the states $(1/\sqrt{2})(\chi_1 + \chi_2)$ and $(1/\sqrt{2})(\chi_1 - \chi_2)$ by the non-vanishing matrix-element $\int\chi_1 H\chi_2 d\tau$. There are good reasons for believing that this effect will be very small when the overlap of the unpaired σ-electrons is small. This is so in the 1 : 3- and 1 : 4-compounds but not in pyridazine. Experimentally there is a considerable red shift with respect to pyridine in the *n*–π band of pyrazine and pyridazine but not in that of pyrimidine (Halverson and Hirt, *loc. cit.*).

Discussion.—The treatment suggested above differs from that which is usually given, in rejecting the term diagram scheme. It is suggested that the great change in the nature of the π-bond skeleton accompanying an *n*–π transition completely changes the character of the π-orbitals, so that the orbital classification which is quite adequate for the description of π–π′ transitions is no longer useful. If these conclusions are correct it follows that the intensities and positions of *n*–π transitions cannot be calculated from the same orbitals and level diagrams as are useful in the case of π–π′ transitions.

The principal weakness of this approach is the neglect of σ-polarisation. We have assumed essentially that, in the upper state, the nitrogen atom achieves electrical neutrality at the expense of the π-electron system, without changing the σ-electron system. This cannot be quite correct, but we think that in view of the much greater polarisability of the π-electron system, it is a reasonable approximation.

We think it probable that the general method suggested in the previous section will be applicable to a variety of *n*–π transitions, *e.g.*, in conjugated ketones, nitroso-compounds, azobenzenes, etc. The feasibility of detailed semiempirical calculations along these lines is being investigated at Oxford.

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