

92. *The Electronic Spectra of N-Heteroaromatic Systems.*
Part IX. n → π-Transitions of Polycyclic Azines.*

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The visible and ultraviolet spectra of some polycyclic azines have been measured in hydrocarbon and hydroxylic solvents. The frequencies of the $n \rightarrow \pi$ bands are determined primarily by the energy of the lowest unoccupied orbital in the corresponding aromatic hydrocarbon and the one-electron charge densities in that orbital at the positions occupied by nitrogen atoms, together with ground-state interaction between the lone-pair nitrogen orbitals in the *ortho*-diazines. The intensities of the diazine $n \rightarrow \pi$ bands increase with the sum of the one-electron charge densities at the nitrogen positions in the lowest unoccupied π -orbital.

In the electronic spectrum of a number of *N*-heteroaromatic molecules the long-wavelength absorption is due to the promotion of a lone-pair electron from a nuclear nitrogen atom to a π -orbital of the ring.¹ The frequencies of such $n \rightarrow \pi$ bands in the series of monocyclic azines have been shown^{2,3} to be determined by the energy of the benzene-like

* Part VIII, *J.*, 1960, 2437.

¹ Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.

² Mason, *J.*, 1959, 1240, 1247.

³ Goodman and Harrell, *J. Chem. Phys.*, 1959, **30**, 1131.

lowest unoccupied π -orbital, and in the case of *ortho*-diazines, by ground-state interaction between the two adjacent pairs of non-bonding electrons. In order to examine the generality of these factors, the electronic spectra of some di- and poly-cyclic azines have been measured in cyclohexane and in aqueous or ethanolic solution (Figs. and Table). Most of the present results have been given in a preliminary review,⁴ and subsequent measurements^{5,6} of a number of the compounds studied are in good agreement with the recorded spectra.

Absorptions due to $n \rightarrow \pi$ transitions are detectable in the spectra of only a limited range of polycyclic azines. On annellation, the energies of the highest occupied and the lowest unoccupied π -orbitals of a monocyclic azine are, respectively, raised and lowered to comparable degrees, whilst the non-bonding orbitals remain at the same energy (Fig. 1). Successive annellations shift the $\pi \rightarrow \pi$ bands of the azines to lower frequencies approximately twice as fast as the $n \rightarrow \pi$ bands (*e.g.*, compounds 4, 8, and 19, Table), and the later absorptions, which appear generally as discrete bands in the spectra of the monocyclic azines, are submerged under the stronger $\pi \rightarrow \pi$ absorption of the larger polycyclic compounds.

In marginal cases the presence of $n \rightarrow \pi$ absorption at the long-wavelength edge of the absorption spectrum of an azine may be detected by solvent effects. On changing from a non-polar to a hydroxylic solvent, $\pi \rightarrow \pi$ absorption bands remain stationary or undergo a small shift to the red, whilst $n \rightarrow \pi$ bands generally shift to the blue.⁷ Thus, the presence of $n \rightarrow \pi$ absorption may be inferred if an azine absorbs at longer wavelengths in cyclohexane than in aqueous or ethanolic solution (*e.g.*, quinoline, Fig. 2). Since many of the $n \rightarrow \pi$ bands of the polycyclic azines appear only as shoulders on the long-wavelength edge of the $\pi \rightarrow \pi$ bands (Fig. 2), the frequency at which the extinction coefficient in cyclohexane solution has the value of 20 l. mole⁻¹ cm.⁻¹ has been taken as a measure of the relative $n \rightarrow \pi$ band energies in the series studied (Table).

The introduction of an additional nitrogen atom into the nucleus of an azine, unlike annellation, lowers the energy of both the highest occupied and the lowest unoccupied π -orbital (Fig. 1), and the energies of the lone-pair electrons are relatively unchanged, except in the case of the *ortho*-diazines where interaction between the two adjacent pairs of non-bonding electrons gives rise to two lone-pair molecular orbitals (Fig. 1) separated by an interval^{2,3} of some 12,000 cm.⁻¹. Thus the $\pi \rightarrow \pi$ bands of the azanaphthalenes do not vary greatly in position, but the $n \rightarrow \pi$ bands move progressively to longer wavelengths with increasing aza-substitution, the *ortho*-diazines absorbing at lower frequencies than their isomers (Figs. 2 and 3, Table).

When the effects of annellation and aza-substitution are combined, the relative frequencies of the azine $n \rightarrow \pi$ transitions should be determined mainly by the energies of the lowest unoccupied π -orbital of the heterocycles, with the *ortho*-diazines absorbing generally some 6000 cm.⁻¹ to lower frequencies. First-order perturbation theory gives the absolute frequencies (ν) of the azine $n \rightarrow \pi$ transition energies as

$$\nu = E\beta - \sum_r C_r^2 \Delta\alpha_{N\pi} + \Delta\alpha_{N\sigma}, \quad \dots \dots \dots (1)$$

where $E\beta$ is the energy of the lowest unoccupied π -orbital of the corresponding aromatic hydrocarbon, C_r^2 is the one-electron charge density in that orbital at the position, r , occupied by a nuclear nitrogen atom, and $\Delta\alpha_{N\pi}$ and $\Delta\alpha_{N\sigma}$ are the Coulomb integral increments of the nitrogen atom relative to the carbon atom for π - and σ -electrons respectively.

The variables on the right-hand side of equation (1), namely, E and $\sum_r C_r^2$, may be related to the experimental $n \rightarrow \pi$ transition frequencies ($\nu_{\epsilon=20}$) by assigning a value

⁴ Mason, *Chem. Soc. Special Publ.*, 1955, No. 3, 139.

⁵ Hirt, King, and Cavagnol, *J. Chem. Phys.*, 1956, **25**, 574; Simonetta, Favini, Carra, and Pierpaoli, *Nuovo Cimento*, 1956, **4**, 1364; Osborn and Schofield, *J.*, 1956, 4191; Muller and Dorr, *Z. Elektrochem.*, 1959, **63**, 1150.

⁶ Badger and Walker, *J.*, 1956, 122.

⁷ McConnell, *J. Chem. Phys.*, 1952, **20**, 700.

to $\Delta\alpha_{N\pi}$ in terms of the carbon-carbon resonance integral, β . The value, $\Delta\alpha_{N\pi} = 0.8\beta$, gives the best agreement with equation (1), the experimental frequency ($\nu_{\epsilon=20}$) being linearly related (Fig. 4) to $(E - 0.8\sum_r C_r^2)$. The slope of the relation indicates that $\beta = 19,000 \text{ cm.}^{-1}$, whence $\Delta\alpha_{N\pi} = 15,000 \text{ cm.}^{-1}$, and the intercept gives $\Delta\alpha_{N\sigma} = 20,000 \text{ cm.}^{-1}$. The observed order, $\Delta\alpha_{N\sigma} > \Delta\alpha_{N\pi}$, is expected, as an electron in a sp^2 -orbital of nitrogen has a lower energy than a corresponding p -electron. In the $n \rightarrow \pi$ transition of an azine there is generally a migration of electronic charge from nitrogen to carbon. Owing to the resultant positive charge on the nitrogen atoms, the π -electron Coulomb integral increment, $\Delta\alpha_{N\pi}$, required by equation (1) has a larger value (0.8β) than that of the neutral nitrogen atom⁸ (0.6β).

For $\pi \rightarrow \pi$ transitions in aromatic molecules the empirical spectroscopic carbon-carbon resonance integral has³ a larger value ($23,000 \text{ cm.}^{-1}$) than that found for azine $n \rightarrow \pi$ transitions ($19,000 \text{ cm.}^{-1}$). In an azine $n \rightarrow \pi$ transition the excited lone-pair

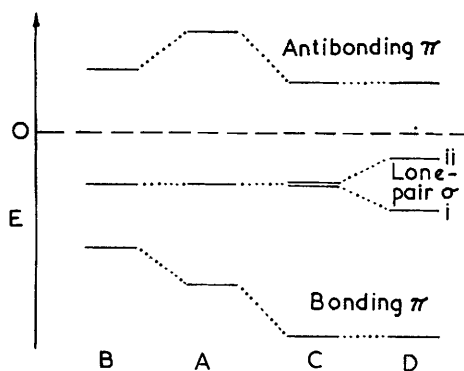


FIG. 1. The relative energies of the highest occupied and the lowest unoccupied π -orbital and the lone-pair orbital in (A) an azine, (B) a corresponding annelated nucleus, and in corresponding diazines with (C) non-adjacent nitrogen atoms and (D) adjacent nitrogen atoms.

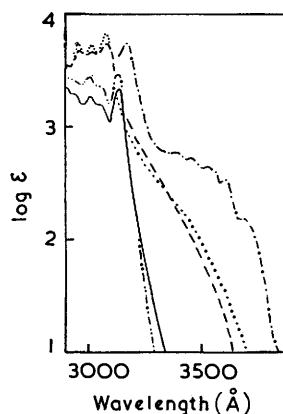


FIG. 2. The electronic spectra of quinoline — in cyclohexane and — — — in aqueous solution, and of — — — 1,8-naphthyridine, · · · 1,5-naphthyridine, and — · — · quinoxaline in cyclohexane solution.

electron moves into a different region of space on promotion, namely, a π -orbital, but in a $\pi \rightarrow \pi$ transition the excited electron continues to move in a similar region of space. The repulsion between the excited electron and the paired electron left in the orbital from which the transition originates is, therefore, greater in a $\pi \rightarrow \pi$ than in a $n \rightarrow \pi$ transition, accounting³ for the relative values of the respective empirical carbon-carbon resonance integrals, β .

Most of the *ortho*-diazines absorb at lower frequencies than required according to equation (1) by the expected increment of $\sim 6000 \text{ cm.}^{-1}$ (Fig. 4), but in the cases of phthalazine (I) and 3,4:5,6-dibenzocinnoline (II) the increments are 3000 and 7500 cm.^{-1} respectively. With the exception of phthalazine, the lowest energy $n \rightarrow \pi$ transition is symmetry allowed in all of the polycyclic azines studied, if the very small interactions between the lone-pair electrons² of non-adjacent nitrogen atoms are neglected. The lowest unoccupied π -orbital in phthalazine (I) has the symmetry B_1 in C_{2v} , and the higher energy lone-pair molecular orbital (Dii, Fig. 1) has the symmetry B_2 . Thus, the lowest energy $n \rightarrow \pi$ transition of phthalazine has the forbidden electronic symmetry of A_2 in C_{2v} , but vibrations of any non-totally symmetric form make this transition weakly

⁸ Mason, J., 1958, 674.

allowed. The observed $n \rightarrow \pi$ band of phthalazine is exceptional (Fig. 3) in consisting of weak extended absorption with no sharp cut-off. The longer-wavelength portion is probably the vibrationally perturbed forbidden lowest energy $n \rightarrow \pi$ absorption, overlaid at shorter wavelengths by the tail of a higher energy allowed $n \rightarrow \pi$ band, due to the promotion of an electron from the higher energy lone-pair molecular orbital to the π -orbital immediately above the lowest occupied. Because of the abnormal $n \rightarrow \pi$ band structure, the frequency, $\nu_{\epsilon=20}$, is not a reliable measure of the $n \rightarrow \pi$ transition energy of phthalazine relative to that of the other azines. Further, in phthalazine it is probable that the 2—3 bond is long, as in naphthalene,⁹ so that the difference between the energies of the lone-pair molecular orbitals (D_i and D_{ii} , Fig. 1) is smaller than in the other *ortho*-diazines.

The structure (II) suggests that the aromatic system of 3,4:5,6-dibenzocinnoline is twisted, owing to steric hindrance between the overlapping C-H groups. In twisted aromatic systems the average value of the resonance integral, β , is reduced,¹⁰ accounting by equation (1) for the abnormally low $n \rightarrow \pi$ transition frequency of (II).

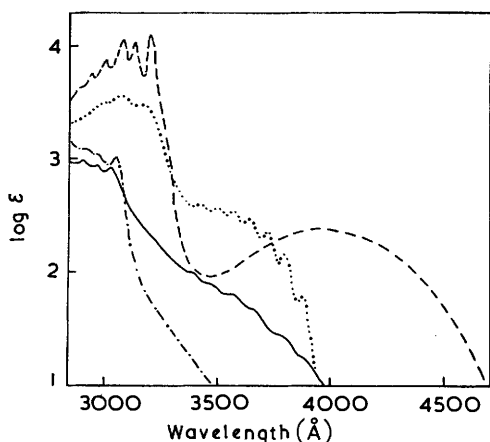


FIG. 3. The electronic spectra of phthalazine — in cyclohexane and - - - in aqueous solution, and of 1,4,6-triazanaphthalene, and - · - · 1,4:5,8-tetraazanaphthalene in cyclohexane solution.

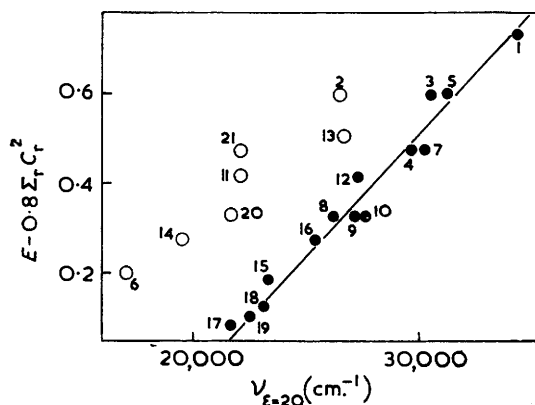


FIG. 4. The relation between the parameter determining the relative energies of the lowest unoccupied π -orbital ($E - 0.8 \sum_i C_i^2$) and the relative $n \rightarrow \pi$ transition frequencies ($\nu_{\epsilon=20}$) of the azines with non-adjacent nitrogen atoms (full circles) and with adjacent nitrogen atoms (open circles). The numbers refer to the compounds listed in the Table.

The present model accounts less satisfactorily for the intensities than for the frequencies of the azine $n \rightarrow \pi$ transitions. The azine $n \rightarrow \pi$ absorption intensity derives its most important contribution from the promotion of electronic charge from the $2s$ component of the lone-pair to the nitrogen $2p_\pi$ -orbital. The moment of this contribution is 0.756 atomic unit, compared with 0.045 and 0.047 for the promotion of electronic charge to the $2p_\pi$ -orbital of an adjacent carbon atom from, respectively, the $2s$ - and the $2p$ -component of the nitrogen lone-pair orbital.¹¹ Using the corresponding aromatic hydrocarbon model, the lowest unoccupied π -orbital of an azine contains a fraction, C_i , of each nitrogen $2p_\pi$ -orbital, so that the sum of the one-electron charge densities, $\sum_i C_i^2$, is the main determinant of the relative intensities of the azine $n \rightarrow \pi$ bands if contributions other than that of the atomic $2s_N \rightarrow 2p_{\pi N}$ transition are neglected. Assuming trigonal hybridisation in all of the azine lone-pair orbitals, and inserting values for universal

⁹ Ahmed and Cruickshank, *Acta Cryst.*, 1952, **5**, 852.

¹⁰ Coulson, "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London, 1958, p. 8.

¹¹ Goodman, *J. Mol. Spectroscopy*, 1961, **6**, 109.

constants in the quantum theory expression for absorption intensities,¹² we obtain extinction coefficients, ϵ , of azine $n \rightarrow \pi$ bands by

$$\epsilon \Delta\nu = 260\nu \sum_r C_r^2 \quad (2)$$

where ν and $\Delta\nu$ are, respectively, the band frequency and half-width in cm^{-1} .

Owing to the general overlapping of $n \rightarrow \pi$ by $\pi \rightarrow \pi$ bands in the spectra of polycyclic azines, the band half-width of the former absorption can be measured only in the cases of cinnoline and 1,2,4-triaza- and 1,4,5,8-tetra-aza-naphthalene, where the values are 4500, 4000, and 4700 cm^{-1} , respectively. For these compounds, equation (2) gives extinction coefficients correct only to within an order of magnitude, a degree of error not unusual in absorption-intensity calculations. However, there is a rough parallelism between the extinction coefficients of the diazine $n \rightarrow \pi$ bands and the parameter, $\sum_r C_r^2$ (Table). The parallelism breaks down in the case of the dicyclic polyaza-compounds where the theoretical extinction coefficients are too large (Table). More detailed

The wavelengths (λ_{max}) and extinction coefficients (ϵ) of the $n \rightarrow \pi$ and the first $\pi \rightarrow \pi$ band in the electronic spectra of some N-heteroaromatic compounds, measured for cyclohexane solutions. The frequency at which the long-wavelength absorption has an extinction coefficient of 20 l. mole⁻¹ cm.⁻¹ ($\nu_{\epsilon=20}$), the coefficient (E) of the energy ($E\beta$) of the lowest unoccupied π -electron orbital in the corresponding aromatic hydrocarbon, and the sum of the one-electron charge densities in that orbital at the positions of the nuclear nitrogen atoms ($\sum_r C_r^2$). Values in italics refer to shoulders.

No.	$\pi \rightarrow \pi$		$n \rightarrow \pi$		$\nu_{\epsilon=20}$	E	$\sum_r C_r^2$	
	λ	ϵ	λ	ϵ				
1	Pyridine ^a	2510	2000	2700	450	34,500	1.000	0.333
2	Pyridazine ^a	2460	1300	3400	315	26,600	1.000	0.500
3	Pyrimidine ^a	2430	2030	2980	326	30,600	1.000	0.500
4	Pyrazine ^a	2600	5600	3280	1040	29,850	1.000	0.667
5	1,3,5-Triazine ^a	2220	150	2720	890	31,500	1.000	0.500
6	1,2,4,5-Tetrazine ^a	2520	2150	5420	829	17,100	1.000	1.000
7	Quinoline	3130	2360	<i>c</i>	<i>c</i>	30,300	0.618	0.181
8	Quinoxaline	3160	5840	3390	631	26,200	0.618	0.362
9	1,5-Naphthyridine	3080	6860	3300	500	27,350	0.618	0.362
10	1,8-Naphthyridine	3080	5780	3300	400	27,700	0.618	0.362
11	Cinnoline	3220	2170	3890	200	22,300	0.618	0.250
12	Quinazoline	3110	2100	3300	200	27,400	0.618	0.250
13	Phthalazine	3030	788	3560	57	25,800	0.618	0.138
14	1,2,4-Triazanaphthalene	2960	3750	4580	400	19,600	0.618	0.431
15	1,4,5-Triazanaphthalene	3080	10,200	3590	364	23,400	0.618	0.543
16	1,4,6-Triazanaphthalene	3080	3760	3500	371	25,500	0.618	0.431
17	1,4,5,8-Tetra-azanaphthalene	3210	16,000	4020	230	21,750	0.618	0.724
18	1,3,5,8-Tetra-azanaphthalene	3010	7490	3870	84	23,200	0.618	0.612
19	Phenazine	3630	15,200	<i>c</i>	<i>c</i>	22,600	0.414	0.387
20	3,4-Benzocinnoline ^b	3615	1150	4040	339	21,900	0.605	0.345
21	3,4,5,6-Dibenzocinnoline ^b	3870	2000	<i>c</i>	<i>c</i>	21,900	0.578	0.114

^a Spectral data quoted from ref. 2. ^b Spectral data quoted from ref. 6. ^c No marked inflexion.

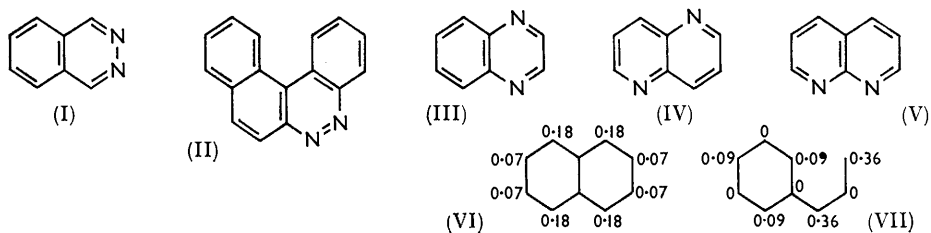
calculations in the monocyclic azine series¹¹ give, similarly, too large a theoretical $n \rightarrow \pi$ absorption intensity for 1,2,4,5-tetrazine.

Even in regard to absorption frequencies, the corresponding aromatic hydrocarbon model accounts only for the salient features, and it does not distinguish between isomeric azines with nitrogen atoms substituted in equivalent positions of a parent nucleus, such as the $\alpha\alpha'$ -diazanaphthalenes, (III), (IV), and (V), which have $n \rightarrow \pi$ absorption frequencies covering a range of 1500 cm^{-1} (Figs. 2 and 4, Table). The different absorption frequencies of these isomers arise mainly from the large electronegativity of the nitrogen atom. In the lowest unoccupied π -orbital of naphthalene the one-electron charge densities (VI) are equal at the α -positions, but the replacement of an α -C-H group by an atom of

¹² Mulliken, *J. Chem. Phys.*, 1939, 7, 14.

larger electronegativity transforms the orbital towards the limiting case of the cinnamoyl cation non-bonding molecular orbital, which has the one-electron charge distribution (VII).

The lowering of the energy of the orbital (VII) upon the replacement of one of the remaining α -C-H groups by a nitrogen atom is proportional to the charge density at the position substituted, accounting for the observed order of $\alpha\alpha'$ -diazanaphthalene $n \rightarrow \pi$ transition frequencies, namely, (V) > (IV) > (III) (Figs. 2 and 4, Table). According to



the cinnamoyl cation model, the lowest unoccupied π -orbital of these diazines is a linear combination of two orbitals with the form (VII), but the mixing energy of the latter does not alter the qualitative order of expected $n \rightarrow \pi$ absorption frequencies derived from the Coulombic perturbation of a single orbital (VII).

Experimental.—Materials. Phthalazine was prepared by the method of Gabriel and Pinkus,¹³ and quinoxaline by that of Hinsberg.¹⁴ 1,4,5,8-Tetra-azanaphthalene was kindly provided by Dr. H. T. Openshaw, cinoline, 1,2,4-triazanaphthalene by Dr. K. Schofield, and the remaining compounds by Professor A. Albert.

Absorption spectra. These were measured with Hilger quartz spectrophotometers for cyclohexane and either aqueous (azanaphthalenes) or ethanol (phenazine) solutions.

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¹³ Gabriel and Pinkus, *Ber.*, 1893, **26**, 2210.

¹⁴ Hinsberg, *Ber.*, 1884, **17**, 318.