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THE ELECTRONIC ABSORPTION AND LUMINESCENCE SPECTRA OF *N*-HETERO-AROMATIC COMPOUNDS AND THEIR DERIVATIVES

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1. GENERAL REMARKS

In recent years considerable progress has been made towards establishing the relationship between the structure and the spectroscopic-luminescent properties of polyatomic organic molecules. This progress is due to the mutual enrichment of theoretical and experimental studies. The work of a large number of experimentalists, using the results of theory, has revealed comparatively simple and general features, which reflect the relationship between spectra and structure and for which theoretical papers have given further qualititative or semi-quantitative explanations based on an examination of successfully chosen approximations and models. The *N*-hetero-aromatic compounds form one class of compound for which important results have been obtained.

N-Heteroaromatic compounds differ formally from aromatic hydrocarbons in that a =CH– group has been replaced by =N– in the aromatic ring. Since the π-system is preserved, it might be expected that the absorption spectra of *N*-heterocyclic compounds would contain bands similar to chose of the hydrocarbon analogues and due to $\pi-\pi^*$ transitions (excitation of an electron from a filled bonding π-orbital of an unoccupied antibonding π^*-orbital). Such bands are in fact observed, although the intensities and positions are slightly different, because of the inductive effect of the N atom and the decreased symmetry of the molecule. In addition to these bands, the spectra of *N*-heterocycles contain other less intense bands due to $n-\pi^*$ transitions (excitation by promotion of an electron of an unshared pair from the non-bonding orbital of the N atom to an antibonding π^*-orbital). The bands due to $n-\pi^*$ transitions are clearly distinguished in the spectrum only when they are the bands with longest wavelength. The assignment of the bands to $\pi-\pi^*$ and $n-\pi^*$ transitions and the classification of the bands of aza-heterocycles and other organic compounds, based on this assignment, were developed in a paper by Kasha[1].

Goodman made a systematic experimental and theoretical study of the electronic spectra of azines, and summarised the results in a review[2], in which he put forward a theory to explain the energies of the transitions, their intensities, and the singlet-triplet splitting. Mason[3-6] made a systematic study of the position and intensities (oscillator strengths) of the π, π^* and n, π^* absorption bands for various *N*-heterocyclic aromatic compounds. Clementi and Kasha[7] examined the problem of spin-orbital coupling in the n, π^*-state of *N*-heterocycles; this was subsequently developed by El-Sayed[8].

The n, π^*- and π, π^*-states show significantly different luminescent properties, which therefore depend on the relative arrangement of the singlet and triplet n, π^*- and π, π^*-levels. For this reason, the luminescent properties of aza-aromatic compounds differ from those of the corresponding hydrocarbon analogues. Aromatic hydrocarbons exhibit fluorescence and phosphorescence, whereas many *N*-heterocycles are non-fluorescent.

If the spectroscopic-luminescent properties of molecules depend on the relative arrangement of the n, π^*- and π, π^*- levels, this arrangement is determined by the structure of the molecules. The similarity in the π, π^*- bands of *N*-heteroaromatic compounds and their hydrocarbon analogues, demonstrated by Zanker[9], makes it possible to transfer the relationships known for the π, π^*-bands of aromatic hydrocarbons to the corresponding *N*-heterocycles.

The empirical relationships between the structure and spectra of aromatic polynuclear condensed hydrocarbons[10] are found to be applicable for the π, π^*-bands of *N*-heterocyclic compounds. These relationships facilitate the examination of the electronic spectra of these compounds. A general feature of triplet-singlet ($T-S_0$) transitions in aromatic hydrocarbons is that they exhibit polarisation perpendicular to the plane of the molecule. Dorr[11,12], who established this characteristic feature, showed that it also applies to the $T-S_0$ transitions of the π, π^* phosphorescence of *N*-heterocyclic compounds. El-Sayed and Brewer[13] showed for various *N*-heterocycles that the n, π^* phosphorescence exhibits polarisation in the plane of the molecule whereas the π, π^* phosphorescence exhibits polarisation perpendicular to the plane of the molecule. Zimmerman and Joop[14] showed that the polarisation of the π, π^*-bands for the absorption and fluorescence of *N*-heterocycles is the same as that for their hydrocarbon analogues.

The presence of an *N*-hetero-atom produces a marked change in the interaction between the molecule and the solvent, compared with the hydrocarbon analogue. This interaction is responsible for the influence of the solvent

on the electronic spectra of N-heterocyclic compounds and sometimes produces a very marked change in the fluorescent properties. This influence has been described by Mataga and coworkers[15-17], Kasha[18,19], and Ermolaev and coworkers[20-22].

2. CHARACTERISTIC FEATURES OF BANDS DUE TO ELECTRONIC $n-\pi^*$ AND $\pi-\pi^*$ TRANSITIONS

Electronic absorption bands may differ in their position, intensity, behaviour in various solvents, and polarisation. In emission, electronic transitions may give fluorescence and phosphorescence bands differing in intensities (quantum yields), polarisation, behaviour in various solvents, lifetimes, or interval between the phosphorescence band and the fluorescence band or long-wave absorption edge when fluorescence is absent (this interval characterises the magnitude of the singlet-triplet splitting). Both absorption and emission electronic bands may also differ in vibrational structure and the degree of structure of the bands.

Kasha[1] was the first to formulate the characteristic empirical criteria of π, π^*- and n, π^*-bands; these were later refined and supplemented[18]. In a review devoted to the spectra of molecules with $n-\pi^*$ transitions (in particular the results of theoretical examination), Sidman[23] also gives a table of the characteristic features of $n-\pi^*$ and $\pi-\pi^*$ transitions.

It should be noted, however, that no one characteristic by itself is unambiguous, and the assignment of experimentally observed bands to a definite type of transition is possible only by examining all their characteristic features. If the molecule contains an electron-donating group of the type -OR, -SR, or $-NR_2$, the unshared pair of the hetero-atom of this group conjugates with the π-electrons, leading to marked changes in the electronic states and transitions[24,25]. We shall refer to these as $\pi, \pi^*(2p_z)$-states, to distinguish them from pure π, π^*-states. As far as luminescent properties are concerned, however, the levels of the π, π^*- and $\pi, \pi^*(2p_z)$-states are similar, so that for the sake of brevity we shall subsequently refer to them as π, π^*-levels.

The distinguishing characteristics of electronic bands of various types are summarised in Table 1.

Platt[26] examined theoretically the problem of the intensity of n, π^*-bands by analysing the local symmetry of the n, π^*-states, and showed that two types of transition are possible: those permitted and those forbidden by local symmetry.

If the n-orbital is a pure p-orbital, the transition is forbidden by local symmetry. If the n-orbital is a hybridised sp^2-orbital, the transition if permitted, and the intensity of the band is determined by the weight of the s-state:

$$\int n(1)\,\hat{M}\,\pi^*(1)\,d\tau \equiv \langle n(1)\,|\,\hat{M}\,|\,\pi^*(1)\rangle$$
$$\langle (s+p)\,|\,\hat{M}\,|\,\pi^*\rangle = \langle s\,|\,\hat{M}\,|\,\pi^*\rangle + \langle p\,|\,\hat{M}\,|\,\pi^*\rangle.$$

Thus the integral of the one-electron transition moment may be vanishingly small, even if the transition is permitted by the general molecular symmetry.

Calculations on the intensities of $n-\pi^*$ transitions were reviewed by Sidman[23] and Goodman[2].

TABLE 1. Characteristic distinguishing features of electronic bands of various types.

π,π^*-bands	$\pi,\pi^*(2p_z)$-bands	n,π^*-bands
Intensity of absorption bands		
Usually of high intensity (if not forbidden by symmetry) $\epsilon \geqslant 10^3$	Intense $\epsilon \geqslant 10^3$	Of low intensity even when transition permitted by symmetry ϵ from 1 to 10^3
Polarisation of absorption bands		
In the plane of the molecule	In the plane	Perpendicular to the plane of the molecule
Influence of polar solvent		
No change or slight displacement of the band, usually towards longer wavelengths	Marked displacement of band, usually towards longer wavelengths	Usually a short-wave displacement, to different extents for different molecules
Behaviour in acid medium		
Slight displacement, if molecule is preserved	Marked transformation	Disappears
Influence of electron-donating (conjugated) substituent		
$\pi,\pi^*(2p_z)$-bands appear in place of the π,π^*-bands. Occasionally some of the π,π^*-bands are preserved, but the band with longest wavelength is a new $\pi,\pi^*(2p_z)$-band		Band displaced towards shorter wavelengths
Fluorescence band		
Adjoins and partly overlaps the long-wave absorption band and is also polarised $\tau = 10^{-8}$–10^{-6} s	Highly sensitive to the nature of the solvent $\tau = 10^{-10}$–10^{-8} s	Either absent or of low intensity $\tau = 10^{-7}$–10^{-5} s
Phosphorescence band		
Long-lived phosphorescence with polarisation perpendicular to the plane of the molecule. Slight displacement in polar solvents $\tau = 0.1$–10 s	Different displacements for different compounds $\tau = 0.1$–10 s	Short-lived phosphorescence, often with high yield $\tau = 10^{-6}$–10^{-2} s
Magnitude of singlet-triplet interval		
Interval large (S^*,T splitting large) and dependent on the geometry of the π-system. For most known hydrocarbons it lies in the range 12 000–5000 cm^{-1}	Interval much smaller than that for the original hydrocarbon. Decrease greater, the stronger the electron-donating power of the substituent.	Interval relatively small (about 2000–3000 cm^{-1}) for molecules with one heteroatom (C=O, C=N, etc.). With several identical groups containing heteroatoms, the picture is complicated by splitting of the states, with removal of the degeneracy.
Sharpness of vibrational structure		
Diffuse vibrational structure for the vapour of most molecules studied. Often much sharper in frozen solutions, both for absorption and more particularly for luminescence.	Bands with diffuse structure predominate, both in the vapour and in solutions.	Exceptionally sharp structure in some instances in absorption and emission for the vapour. Absorption bands diffuse in solutions. Phosphorescence bands often show marked structure at low temperatures. The domination of the progression of an individual frequency is characteristic (for carbonyl compounds).

The difference in the magnitude of the S^*, T splitting for the n, π^*- and π, π^*-levels can also be explained. Examination of the dependence on structure of this splitting for π, π^*-levels in a series of aromatic hydrocarbons showed that its values lie in the range 12 000–4000 cm^{-1}. The magnitude of the S^*, T splitting for n, π^*-levels is always about 2000–3000 cm^{-1}. The magnitude of the S^*, T splitting depends on the magnitude of the two-electron exchange integral (between the orbital from which the electron is excited and the orbital into which it is transferred). For n, π^*-states it is determined by the integral $\langle n\pi^*\,|_G\,|\pi^* n\rangle$. This exchange integral is the energy of repulsion between two n, π^*-electrons and its value is small, since the functions of n- and π^*-orbitals are mutually orthogonal. The value of the integral will increase with increase in the overlap between the n- and π^*-orbitals.

The short-wave displacement of the n, π^* bands in polar solvents is attributed to binding of the n-electrons, leading to a decrease in the energy of the n-orbital. The binding is particularly effective when hydrogen bonds are formed. The binding of the n-electrons in acidic and alkaline media leads to disappearance of the n, π^*-bands.

The efficiency of fluorescence is limited by non-radiative processes. One of these is singlet-triplet conversion. Kasha attributed the luminescent characteristics of n, π^*-states to the high probability of singlet-triplet conversion. Clementi and Kasha[7] confirmed this theoretically by estimating the spin-orbital coupling in aza-heterocycles. Later, El-Sayed[8] showed that the magnitude of the spin-orbital coupling in aza-heterocycles between states with the same type of electronic configuration is of the same order of magnitude:

$$\frac{\langle S_{n\pi^*} | H_{s.o.} | T_{n\pi^*} \rangle}{\langle S_{\pi\pi^*} | H_{s.o.} | T_{\pi\pi^*} \rangle} \sim 1$$

whereas between states with different electronic configuration it is greater by two to three orders of magnitude:

$$\frac{\langle S_{n\pi^*} | H_{s.o.} | T_{\pi\pi^*} \rangle}{\langle S_{\pi\pi^*} | H_{s.o.} | T_{\pi\pi^*} \rangle} \sim 10^2 - 10^3.$$

These results also explain the absence of fluorescence from n,π^*-levels in aromatic compounds, in which the $T_{\pi\pi^*}$-level usually lies between the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels, and also the absence of fluorescence from the $S_{\pi\pi^*}$-level, when the $T_{n\pi^*}$-level lies between this level and the $T_{\pi\pi^*}$-level.

The luminescent properties of molecules with n,π^*-levels should depend on the relative arrangement of the lower single and triplet levels of different character. There are five possible most characteristic mutual arrangements of excited singlet and triplet levels of the π, π^*- and n, π^*-type (Fig. 1). This classification was published earlier[27].

Type I. In molecules of this type the long-wave absorption band is due to an n–π^* transition and has a low intensity. In view of the relatively low probability of $S_{n\pi^*}$–$T_{n\pi^*}$ conversion, it is possible to have n, π^* fluorescence and weak short-lived n, π^* phosphorescence with a short interval (about 2000–3000 cm^{-1}) between the luminescence bands, or absence of luminescence, when non-radiative transitions have a high probability.

Type II. This corresponds to a long-wave absorption band of the n, π^* type, with low intensity. In these molecules there is a high probability of S^*–T conversion, responsible for extinction of the fluorescence. The spectrum shows a band due to short-lived n, π^* phosphorescence ($\tau \sim 10^{-4}$–10^{-2} s) in the frequency range 2000–3000 cm^{-1} below the long-wave absorption edge.

Type III. The lower triplet level is $T_{\pi\pi^*}$, and the lower singlet level $S_{n\pi^*}$. The weak long-wave n, π^* absorption band in these molecules is usually overlapped considerably by the stronger π, π^*-band and appears either as an inflection or as a weak long-wave "tail" (it is therefore difficult to observe experimentally). Fluorescence is also absent, since it is suppressed by $S_{n\pi^*}$–$T_{\pi\pi^*}$ conversion, for which the probability is high. The emission shows only long-lived phosphorescence, due to the $T_{\pi\pi^*}$–S_0 transition ($\tau \simeq 0.1$–10 s). The spectral interval between the long-wave absorption edge and the phosphorescence band will be greater than the first two types. The phosphorescence yield is expected to be lower than that for molecules of type II.

Type IV. This corresponds to a long-wave absorption band of the π, π^*-type, with high intensity. The luminescent properties of molecules of this type are similar to those of molecules of type III. A characteristic feature of these molecules is that direct experimental observation of the n–π^* transitions is difficult. The $T_{n\pi^*}$-level cannot be observed in emission, and the n, π^* absorption band is hidden by more intense bands. Thus the absence of fluorescence provides an important indirect criterion for estimating the energy of the $T_{n\pi^*}$-levels in molecules for which it is expected that this level lies between the $S_{\pi\pi^*}$- and $T_{\pi\pi^*}$-levels.

Since the excitation energy of the n, π^*-state is to a considerable extent localised on the bonds adjoining the hetero-atom, whereas for the π, π^*-state it is delocalised throughout the π-system, the $T_{n\pi^*}$–$T_{\pi\pi^*}$ conversion, according to Ermolaev and Terenin[28], is a process of intramolecular transfer of energy among triplet levels.

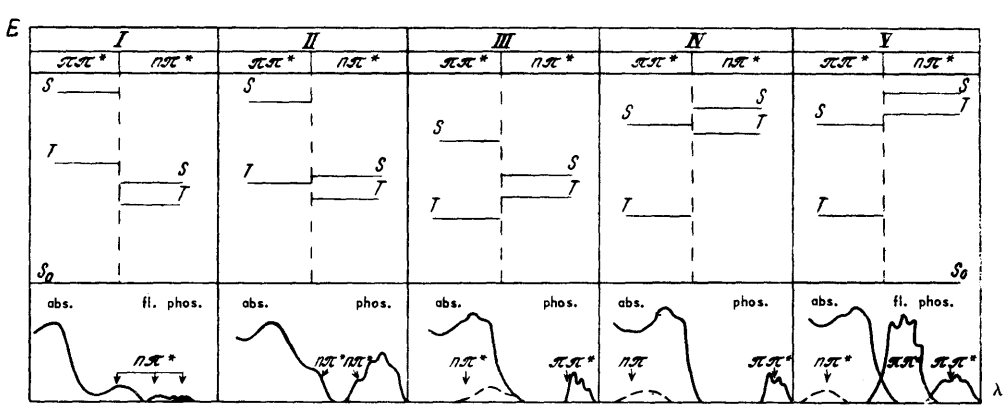


Fig. 1. Various types of arrangement of singlet and triplet π,π^*- and n,π^*-levels and the corresponding qualitative forms of electronic spectra.

Type V. Here the spectroscopic-luminescent properties are similar to those of the corresponding aromatic hydrocarbons. Both fluorescence bands and long-lived phosphorescence bands are observed.

Thus examination of the relative arrangement of the singlet and triplet n, π^*- and π, π^*-levels of molecules containing hetero-atoms and their assignment to one of the above types make it possible to understand the general character of the spectroscopic-luminescent properties of these molecules.

It should be noted, however, that this classification is not absolute, for the influence of various factors in a specific molecule may alter the ratio of the various transition probabilities and hence the luminescent properties.

Let us consider the various structural factors determining the mutual arrangement of the n, π^*- and π, π^*-levels. In systems with one hetero-atom, responsible for the $n-\pi^*$ transition, the energy of the $\pi-\pi^*$ transitions decreases more rapidly with increase in the π-system than the energy of the $n-\pi^*$ transitions. This is illustrated by the levels for the series: pyridine, quinoline, and acridine (Fig. 2). This relationship may provide an additional criterion for distinguishing n, π^*- and π, π^*-bands when the spectra of a series of compounds are compared.

When several identical hetero-atoms determining the n, π^*-levels are present, splitting of the n, π^*-levels takes place, so that the energy of the lower $n-\pi^*$-transition is reduced sharply. The magnitude of the splitting decreases rapidly with increase in the distance between the hetero-atoms. Thus in an aromatic hydrocarbon the replacement of several =CH– groups by an =N– atom leads to appreciable lowering of the $n-\pi^*$ transitions, whereas the $\pi-\pi^*$ transitions change little.

The splitting of the degenerate n, π^*-states in N-heterocycle was examined theoretically by El-Sayed and Robinson[29] on the basis of a localised model, in which it was assumed that the n-electron transferred to the π^*-orbital remains on the N atom, because of the coulombic attraction between this electron and the positive hole produced. El-Bayomi and Kearns[30] showed that the results of calculations based on a delocalised model provide a better explanation of the experimental data than do calculations based on a localised model. Both models predict an increase in splitting with decrease in the distance between the N atoms, and also a difference in the behaviour of the S^* and $T_{n\pi^*}$ states. Thus there should also be a change in the magnitude of the S^*, T interval for the lower n, π^*-levels.

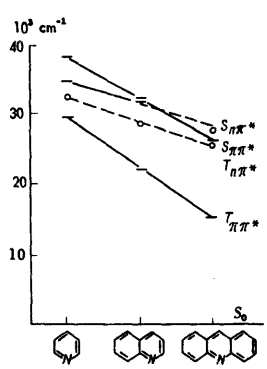


Fig. 2. Relative arrangement of the singlet and triplet π, π^*- and n, π^*-levels in the series: pyridine, quinoline, acridine.

The introduction of electron-donating substituents of the type –OR, –SR, and $-NR_2$ leads to a marked short-wave displacement of the n, π^*-bands (often by 2000–8000 cm^{-1}), whereas the π, π^*-bands are usually displaced towards longer wavelengths.

Finally, certain molecules, for example quinoline[8,18,19], show a change in the relative arrangement of the $S_{\pi\pi^*}$- and $T_{n\pi^*}$-levels under the influence of solvent; this will be illustrated in more detail in Section 3.

3. CONDENSED AROMATIC HETEROCYCLES WITH ONE NITROGEN ATOM

Let us first consider the relationship between structure and the bands due to $n-\pi^*$ and $\pi-\pi^*$ transitions in the series pyridine, quinoline, isoquinoline, acridine, etc., that is, the hetero-analogues of the poly-acene series containing one N atom. The data are given in Table 2.

The n, π^* and π, π^* absorption bands of pyridine (I) were first identified by Kasha[1]. Rush and Sponer[31,50] described the absorption spectrum of pyridine vapour and carried out a vibrational analysis of the structure. In the vapour, the n, π^*-band of pyridine is resolved into a large number of sharp narrow bands with (0, 0)-band at 34 770 cm^{-1}, whereas the π, π^*-band consists of more diffuse bands (ν_{00} = 38 350 cm^{-1}). The intensity of the π, π^*-band ($\epsilon \sim 2000$) is slightly greater than that of the corresponding band of the transition in benzene, where it is forbidden by symmetry. The increase in intensity is related to the decreased symmetry of the pyridine molecule. According to Jaffé and Orchin[51], the fact that the intensity of the band is not as high as might have been expected for an allowed transition indicates that the departure of the distribution of the π-cloud in pyridine from D_{6h} symmetry is slight. Stephenson[52] used the absorption spectra of solutions to estimate the oscillator strengths of the $\pi-\pi^*$ transitions (f = 0.041 in 2,2,4-trimethylpentane) and the $n-\pi^*$ transition (f = 0.003). Kasha first assumed that the low intensity of the $n-\pi^*$ transition is due to the fact that it is forbidden by symmetry, but measurements in the vapour[50] did not confirm this assumption. The low f-value was attributed to the low value of the transition moment integral resulting from the small overlap of the ψ-functions of the ground and excited n, π^*-states[26]. Halverson and Hirt[32] studied the influence of solvents on the absorption spectrum and showed that in polar solvents the n, π^*-band (ν_{00} = 34 000 cm^{-1} in cyclohexane) undergoes short-wave displacement and is overlapped by the π, π^*-band, whose position does not change (ν_{00} = 38 000 cm^{-1}). On going from cyclohexane to alcohol, the displacement is about 2000 cm^{-1}.

The luminescence of pyridine could not be observed, although it might be expected to show phosphorescence of the benzene type[35]. The $T-S_0$ absorption spectrum[35] showed a band at 29 577 cm^{-1}, with frequency close to the frequency of the $T-S_0$ transition for benzene, so that it can reasonably be assigned to the $T_{\pi\pi^*}$-level. Theoretical estimation of the $T_{n\pi^*}$-level predicts a frequency of 32 000–33 000 cm^{-1}.

The absorption spectrum of quinoline (II) is similar to the spectrum of naphthalene (ν_{00} = 31 980 cm^{-1}) for the

TABLE 2. Frequencies of the electronic transitions (cm^{-1}) in *N*-heterocyclic aromatic compounds*.

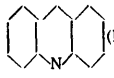
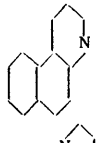
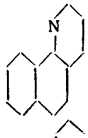
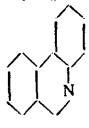
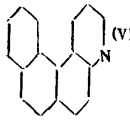
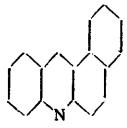
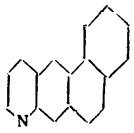
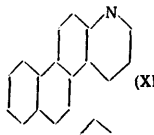
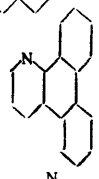
Formula	$\nu S_{\pi\pi^*}$	Refs.	$\nu T_{\pi\pi^*}$	Refs.	$\nu S^*T_{\pi\pi^*}$	$\nu S_{n\pi^*}$	Refs.	$\nu T_{n\pi^*}$	Refs.	$\nu S^*T_{n\pi^*}$
1	2	3	4	5	6	7	8	9	10	11
 (I)	38 350 38 000	31 32	29 577	35	8 800	34 770 34 000 34 000	31 32 2	32000 29 600	35 2	2000 4800
 (II)	32 000	13	21 800	11	10 200	32 000	15			2000—3000
 (III)	31 200	14	21 200	11	10 000					
 (IV)	25 300		15 840	36	9 460					
 (V)	29 000									
 (VI)	28 500	12 33	21 850	11 33	6 750					
 (VII)	28 700	12	22 050	12	6 650					
 (VIII)	25 650	34								
 (IX)	25 650	34								
 (X)	27 400	34								
 (XI)	29 000	34								
 (XII)	26 600	34								
 (XIII)	38 763	33				30 879 30 500 30 875 30 500 30 640	33 32 40 41	26 420 26 553 26 518	45 35 41	4459 3947 4357
 (XIV)	39 000	32				31 000 30 700 30 900	32 42 2	28 332 28 300	46 2	2668 2600
 (XV)	38 750	37				26 656 27 000 26 790	42 2	23 500	2	3290

TABLE 2 (contd.)

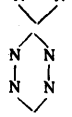
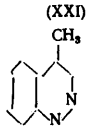
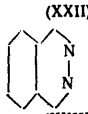
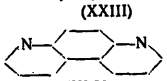
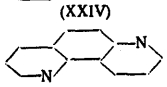
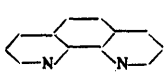
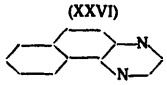
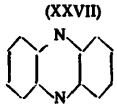
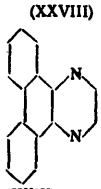
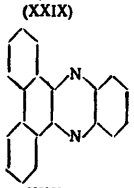
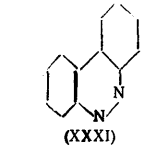
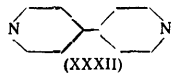
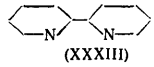
Formula	$\nu S_{\pi\pi^*}$	Refs.	$\nu T_{\pi\pi^*}$	Refs.	$\nu S^*_s T_{\pi\pi^*}$	$\nu S_{n\pi^*}$	Refs.	$\nu T_{n\pi^*}$	Refs.	$\nu S^*_s T_{n\pi^*}$
1	2	3	4	5	6	7	8	9	10	11
 (XVI)	44 000	38				31 000 31 570	38 2	26 400 26 300	47 2	4600 5270
 (XVII)						17 970 18 135 17 800	5 43,44			
 (XVIII)			32 000	12						
 (XIX)	31 630	6,39	21 250	39	10 380	26 670	6			
 (XX)	32 200	39	21 900	39	10 300	27 330	6			
 (XXI)	31 980	39	21 800	39	10 180	25 820	6			
 (XXII)	31 000	39	19 000	39	12 000	23 050	39			
 (XXIII)	33 000	39	23 000	39	10 000	25 820	39			
 (XXIV)	29 800	12	22 200	12	7 600					
 (XXV)	29 700	12	22 150	12	7 550					
 (XXVI)	29 500	12	22 100 22 213	12 48	7 400					
 (XXVII)	27 500	38	21 000	38	6 500					
 (XXVIII)										
 (XXIX)	28 000		23 000		5 000					
 (XXX)	25 400	11	18 400	11	7 000					

TABLE 2 (contd.)

Formula	$\nu S_{\pi\pi^*}$	Refs.	$\nu T_{\pi\pi^*}$	Refs.	$\nu S^*, T_{\pi\pi^*}$	$\nu S_{n\pi^*}$	Refs.	$\nu T_{n\pi^*}$	Refs.	$\nu S^*, T_{n\pi^*}$
1	2	3	4	5	6	7	8	9	10	11
 (XXXI)	28 000 28 800	48a				20 300 22 000	48a	13 500	48a	6 800
 (XXXII)	~34 000	49	24 530	49	9 470					
 (XXXIII)	~33 000	49	23 545	49	9 455					

* Several errors in the formulae have been corrected in the translation (Ed. of Translation).

long-wave π, π^*-band and does not contain a long-wave n, π^*-band. The long-wave absorption bands are classified as ^1L_b (32 000 cm^{-1}) and ^1L (35 000 cm^{-1}) according to Platt, and this is confirmed by polarisation measurements[13]. From the appearance, in the vapour, of exceptionally sharp $n-\pi^*$ absorption lines in the region of 3130 Å against a background of diffuse bands due to the $\pi-\pi^*$ transition, Mataga and coworkers[15] estimated the frequency of the $n-\pi^*$ transition is quinoline as 32 000 cm^{-1}. That this estimate is reasonable is also confirmed by the absence of fluorescence from quinoline in the vapour and hydrocarbon solutions[15-22]; the extinction of the fluorescence can be attributed to the fact that the $T_{n\pi^*}$ level lies slightly below the $S_{\pi\pi^*}$-level for quinoline. The frequency of the $T_{n\pi^*}-S_0$ transition can be estimated as 30 000 cm^{-1}, with the assumption that the magnitude of the S, T splitting of the n, π^*-level of quinoline is about 2000–3000 cm^{-1}, as in pyridine.

The appearance of a fluorescence band, similar to the band given by naphthalene, in polar solvents[15-22] is attributed to a change in the relative positions of the $S_{\pi\pi^*}$- and $T_{n\pi^*}$-levels: under the influence of a polar solvent, particularly when intermolecular hydrogen bonding results, the energy of the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels is raised and they occupy a position above the $S_{\pi\pi^*}$-level of quinoline. Indirect confirmation that such an increase can occur is provided by the N-heterocycles with clearly defined n, π^*-bands, where these bands are displaced towards higher frequencies by 2000–3000 cm^{-1} on going from hydrocarbon solution to alcoholic solution.

Quinoline gives a long-lived phosphorescence band, whose position, structure, and polarisation are similar to those of the phosphorescence band of naphthalene[11]. Dorr and Gropper[11] showed that the phosphorescence spectrum at 90°K in alcohol consists of two series of bands. The frequencies of the main series of bands, with polarisation perpendicular to the plane of the molecule, are given by the formula $\nu = \nu_{00} - n\times1400$ cm^{-1}, where ν_{00} = 21 800 cm^{-1} and n = 0, 1... 4. The beginning of the secondary series is displaced by 500 cm^{-1} towards lower frequencies; this corresponds to the frequency of the asymmetric vibration, which alters by 90° the polarisation of the bands of this series relative to the main series.

The absorption[11], fluorescence, and luminescence spectra of isoquinoline (III) differ only slightly from those of quinoline.

The absorption spectrum of acridine (IV) is similar to that of anthracene. The fluorescence is weak in hydrocarbon solutions at room temperature, but it increases considerably in alcoholic solutions[15-17]. There is no information on the phosphorescence of acridine, but it is reasonable to expect it in the near infrared range, as for anthracene. Evans[36] reported $T-S_0$ absorption of acridine in the region of 15 800 cm^{-1}. The extinction of the fluorescence in hydrocarbons indicates that the $T_{n\pi^*}$-level in acridine is close to the $S_{\pi\pi^*}$ level, although slightly above it.

Spectroscopic data have been used to construct a scheme of triplet and singlet π, π^*- and n, π^*-levels for the series pyridine, quinoline, and acridine (Fig. 2); the change in the frequencies of the $\pi-\pi^*$ transitions in this series with increase in the π-system is the same as that in the polyacene series[10]. On linear ring addition, the frequencies of the $S_{\pi\pi^*}-S_0$ and $T_{\pi\pi^*}-S_0$ transitions decrease by 5000 cm^{-1} per benzene ring, whereas the magnitude of the S^*, T splitting of the π, π^*-level remains about 10 000 cm^{-1} (Table 2). The frequencies of the $n-\pi^*$ transitions decrease at less than half this rate. The decrease in the frequencies of the $n-\pi^*$ transitions is determined by the decrease in the energy of the π^*-orbital and provides evidence in support of the delocalised model of n, π^*-states in aza-heterocycles[30].

Since even in the quinoline molecule the energies of the $S_{\pi\pi^*}$- and $S_{n\pi^*}$-levels coincide and the n, π^*-band does not appear as a long-wave band, the band cannot be a long-wave band in more complex mono-aza-aromatic polycycles.

The absorption spectra of benzo[f]quinoline (V), benzo[h]quinoline (VI), and phenanthridine (VII) are similar to those of phenanthrene[34]. The introduction of the N atom into the phenanthrene ring leads to a slight displacement of the long-wave π, π^*-band and an increase in its intensity, The fluorescence spectrum (ν_{00} = 28 500) and phosphorescence spectrum (ν_{00} = 21 850 cm^{-1}) of benzo[h]quinoline in alcohol at 100°K [12,33] have discrete vibrational structure and are polarised, like the bands due to $S_1^*-S_0$ and $T-S_0$

transitions in phenanthrene. Analogous fluorescence (ν_{00} = 28700 cm^{-1}) and phosphorescence (ν_{00} = 22050 cm^{-1}) spectra were described for phenanthridine[12]. The frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions of the π,π^*-type for mono-aza-phenanthrenes differ from the frequencies for quinoline in approximately the same way as the frequencies of the phenanthrene transitions differ from the frequencies for naphthalene. They are also characterised by a decrease in the magnitude of the S^*, T splitting of the π,π^*-level to 6500–7000 cm^{-1}.

Similarity between the absorption spectra was established for the following pairs[34]: 1′-aza-3,4-benzophenanthrene (VIII)–3,4-benzophenanthrene; 3,4-benzacridine (IX)–1,2-benzanthracene; 5-aza-1,2-benzanthracene (X)–1,2-benzathracene; 3-aza-chrysene (XI)–chrysene; and 1-aza-triphenylene (XII)–triphenylene.

Thus in every instance the changes in the frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions of the π,π^*-type in catacondensed mono-aza-aromatic polycycles are analogous to those in the corresponding aromatic hydrocarbons[10].

From the established dependence of the frequencies of $\pi-\pi^*$ and $n-\pi^*$ transitions on the magnitude of the π-system of mono-aza-aromatic polycyclic compounds, it is not difficult to obtain a general picture of their spectroscopic-luminescent properties. These molecules have a low T-level of the π,π^*-type (beginning with pyridine) so that they can exhibit only long-lived π,π^*-phosphorescence. In the N-hetero-analogue of naphthalene—quinoline—the energies of the $S_{\pi\pi^*}$- and $S_{n\pi^*}$-levels coincide (in the vapour and hydrocarbon solvents) so that in compounds of this series (apart from pyridine) the n,π^*-band cannot appear as a long-wave band. In the acridine molecule, the energies of the $S_{\pi\pi^*}$- and $T_{n\pi^*}$- levels coincide, so that those N-heterocycles (containing one N atom) whose $\pi-\pi^*$ transitions lie at shorter wavelengths than those of acridine will be non-fluorescent, whereas those whose $S_{\pi\pi^*}-S_0$ transitions lie at longer wavelengths will exhibit fluorescence like their hydrocarbon analogues. In acidic media and polar solvents, however, particularly when an intermolecular hydrogen bond is formed with the N atom, fluorescence may appear (be activated) for those molecules in which the $T_{n\pi^*}$-level lies above the $S_{\pi\pi^*}$-level. This is observed for quinoline, azaphenanthrenes, acridine, and benzacridine in alcoholic and other polar solutions.

4. AZABENZENES AND POLYCYCLIC COMPOUNDS WITH TWO OR MORE NITROGEN ATOMS

The introduction of two or more N atoms leads to more marked changes in the spectrum, influencing the positions and intensities of both the n,π^*- and π,π^*-bands. As a result of the interaction of the n,π^*-states of the N atoms, leading to splitting of the n,π^*-levels, the spectrum may show several n,π^*-bands. The interaction of n,π^*-states has been studied in most detail for the diazene series. It was established that the magnitude of the splitting depends to a marked extent on the mutual arrangement of the N atoms, decreasing rapidly with increase in the distance between them.

Azabenzenes

The spectra of diazines differ significantly from the spectra of pyridine and from one another.

Halverson and Hirt[33] found that the absorption spectrum of pyrazine (XIII) vapour consists of a system of sharp bands in the region of 3200 Å and a system of diffuse bands at 2800 Å, and assigned these to $n-\pi^*$ (ν_{00} = 30879) and $\pi-\pi^*$ (ν_{00} = 38763 cm^{-1}) transitions respectively.

The assignment of the bands was confirmed by a study of the behaviour of the absorption bands in various solvents[32]. In particular, a short-wave displacement of the n,π band was observed on going from cyclohexane to alcohol, although the displacement was much smaller ($\Delta\nu \simeq$ 300 cm^{-1}) than that for pyridine.

A detailed analysis of the vibrational structure of the long-wave absorption of the vapour enabled Japanese authors[40] to separate two overlapping systems of bands—a sharp system with a resolved 0–0 band equal to 30875 cm^{-1}, and a more diffuse system with lower intensity in the range 30500 cm^{-1}, assigned to a second $n-\pi^*$ transition, forbidden by symmetry. The behaviour of the absorption bands of pyrazine in various solutions was also described by Shimada[41], who also confirmed the $n-\pi^*$ character of the absorption band with ν_{00} = 30640 cm^{-1} in cyclohexane. Its frequency increases to 31020 cm^{-1} on mono-protonation, and the band disappears in solutions with salt formation[1]. The lower excited singlet level of pyrazine ($S_{n\pi}$) was assumed to be non-fluorescent[35]. Recently, Logan and Ross[53] reported the existence of two emission bands for pyrazine in the vapour and frozen hydrocarbon solutions. In the vapour, the band with shorter wavelength (in the region of 30000 cm^{-1}) adjoins the n,π^* absorption band, and the start of the long-wave band (at about 26500 cm^{-1}) coincides with the start of weak $T_{n\pi^*}-S_0$ absorption[45]. Innes and Giddings[45] obtained the rotational structure of the band due to the $n-\pi^*$ transition. In hydrocarbon solution at 80°K, pyrazine exhibits strong phosphorescence (with ν_{00} = 26420 cm^{-1}) and weak fluorescence with peaks at 29400, 28700, and 28050 cm^{-1}. Goodman and Kasha[35] studied the phosphorescence spectrum in an ether–isopentane–ethanol mixture at 90°K, and found that $\tau \simeq 0.02$ s and that the fluorescence band exhibits polarisation in the plane of the molecule. The influence of substituents, which led to short-wave displacement, confirmed the assignment of the phosphorescent T-level to the n,π^*-type.

Shimada[41] studied the phosphorescence spectrum of pyrazine in various media at 90°K and obtained good resolution of the vibrational structure, particularly in cyclohexane solution (ν_{00} = 26518–26445 cm^{-1}). It may be noted that in alcohol (ν_{00} = 26250) the fluorescence band does not show the characteristic short-wave displacement, indicating that this characteristic is not unambiguous. The $T-S_0$ transition was identified as an $n-\pi^*$ transition[41] from the behaviour of the phosphorescence band in acidic media, in which it undergoes appreciable extinction and is displaced towards higher frequencies, that is, it shows behaviour completely analogous to that of an n,π^* absorption band. Sidman[23] showed theoretically that the lower T-level is an n,π^*-level. The absorption in the region of the $T-S_0$ transition has also been described, with assignment to an 0–0 band equal to 26553 cm^{-1} in isopentane[35] or 26600 cm^{-1} in cyclohexane[37]. It has been shown theoretically[3] that the n,π^*-level lies at 31000 cm^{-1}. The dipole nature of the transition responsible for emission has been examined[54] and it was shown that the transition polarised in the plane of the molecule is symmetry allowed.

The absorption spectrum of pyrimidine (XIV) vapour, described by Uber and Winters[55,56], consists of a system of more than one hundred sharp narrow bands in the range

30 000–38 000 cm^{-1} and a system of broad diffuse bands in the range 39 000–45 000 cm^{-1}. From the behaviour of these bands in various solvents, Halverson and Hirt[32] assigned them to the $n-\pi^*$ transition (ν_{00} = 31 000 cm^{-1} in cyclohexane) and the $\pi-\pi^*$ transition respectively. Shimada[40] confirmed the assignment of the long-wave band to the $n-\pi^*$ transition, demonstrating that it disappears on salt formation.

It has been assumed that pyrimidine does not fluoresce from the n,π^*-state[18,19], but Börresen[57] had reported the observation of n,π^* fluorescence in liquid solution, and Goodman and coworkers[42] have described the n,π^* fluorescence spectrum at 298°K in 2,2,4-trimethylpentane (ν_{00} = 30 700 cm^{-1}) and found that $\tau = 10^{-9}$ s.

The phosphorescence band of pyrimidine—$\tau \simeq 10^{-2}$ s, ν_{00} = 28 332–28 218 cm^{-1} (cyclohexane), ν_{00} = 28 475 cm^{-1} (alcohol)—was studied in detail by Shimada[46], who obtained good resolution of the structure in various solvents. The phosphorescent level was interpreted as an n,π^*-level. In acid media the short-lived phosphorescence band disappears, with the production of weaker phosphorescence with $\tau \simeq 0.1$ s at shorter wavelengths, assigned to emission from the $T_{\pi\pi^*}$-level. The absorption spectrum of pyridazine (XV) vapour also shows two systems of bands—a diffuse system at 2500 Å and a sharp system with a purely electronic band at 26 656 cm^{-1} (3750 Å). According to Hirt[37], the long-wave band starting at 3700 Å in hexane is displaced towards shorter wavelengths by 300 Å in aqueous solution, whereas the second band—the π,π^*-band (2680 Å or 38 750 cm^{-1}) id displaced by only about 50 Å. Halverson and Hirt[32,33] assigned the first band to the $n-\pi^*$ transition, confirming this by observation of a short-wave displacement in polar solvents and under the influence of halogeno-substituents. Although Kasha assumes the existence of a $T-S_0$ transition of the $n-\pi^*$ type with energy 3.08 eV in pyridazine, Shimada[46] was unable to observe any luminescence, even at low temperatures. Goodman and coworkers[42] described the n,π^* fluorescence spectrum of pyridazine (ν_{00} = 27 000 cm^{-1}) in solution at 298°K with $\tau = 2.6 \times 10^{-9}$ s.

The absorption spectra of the vapour and solutions of *sym*-triazine (XVI) have been described[38]. The long-wave system of bands with initial band at 31 000 cm^{-1}, assigned to the $n-\pi^*$ transition on the basis of its behaviour in solutions, the influence of alkyl substituents, and the sharpness in the vapour, is more intense (ϵ = 880 at 36 780 cm^{-1}) than the diffuse system of bands due to the $\pi-\pi^*$ transition, starting at 44 000 cm^{-1} ($\epsilon \sim 150$ at 45 050 cm^{-1}). Paris and Hirt[47] described the phosphorescence spectrum of *sym*-triazine (ν_{00} = 26 400 cm^{-1} and τ = 0.44 s) and detected $T-S_0$ absorption. The $T-S_0$ transition was identified as an $n-\pi^*$ transition.

Mason[5] described the n,π^* absorption spectrum of *sym*-tetrazine (XVII) in the vapour and in cyclohexane solution at room temperature, and also in a mixture of hydrocarbons at 77°K (ν_{00} = 17 970 cm^{-1}). He obtained a resolved vibrational structure, particularly with the vapour (ν_{00} = 18 135 cm^{-1}). Chowdhury and Goodman[43,44] observed the n,π^* fluorescence of tetrazine with ν_{00} = 17 800 cm^{-1} and dimethyl-*sym*-tetrazine with ν_{00} = 17 100 cm^{-1} and $\tau \simeq 10^{-5}$ s. The existence of n,π^* fluorescence, observed for the first time for azines, is related to the absence of a $T_{\pi\pi^*}$-level between the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels, between which there is no direct spin-orbital coupling.

Thus the n,π^*-bands in diazines, triazine, and tetrazine lie at lower frequencies than those in pyridine, whereas their π,π^*-bands are approximately the same. The first theoretical examination of the spectra of azines was made by Orgel[58], who showed that the simple molecular orbital method, used to describe the orbitals of the ground state, is inadequate for a description of the excited states. The changes in the $n-\pi^*$ transitions and to some extent in the $\pi-\pi^*$ transitions were attributed to the electronegativity of the N atoms, leading to a lowering of all the n,π^*- and π,π^*-levels relative to the levels in pyridine. The greater changes in the frequencies of the $n-\pi^*$ transitions were related to the fact that two $n-\pi^*$ transitions are possible in diazines. Although these levels belong to different symmetry classes, there may be approximate degeneracy, because the overlap is small, so that the interaction between the atomic orbitals of the two atoms is small. This degeneracy is removed for excited n,π^*-states. Thus diazines are convenient materials for studying the interaction between excited chromophoric groups in n,π^*-states[29]. Splitting of the n,π^*-levels should lead to the appearance of two n,π^*-bands in the spectra. In accordance with this picture, detailed analysis of the spectra of pyrazine[40] and other diazines established two systems of bands due to $n-\pi^*$ transitions, one symmetry allowed and the other symmetry forbidden, as predicted by theory. The theoretical examination was carried out by Mason[3]. The relationship between the frequencies of the $n-\pi^*$-transitions in the diazone series has not been elucidated completely, however.

Diazanaphthalenes

Although the spectra of quinoline do not show the n,π^*-bands directly, and reveal only the $T_{n\pi^*}$-level in the extinction of the fluorescence, we may expect their appearance in diazanaphthalenes with the displacement of the $n-\pi^*$ transitions to lower frequencies as a result of splitting, as in the diazines. The spectra of the diazanaphthalenes differ significantly from one another. The chief difference is in the position of the n,π^*-bands. As already noted, the extent to which the frequency of the n,π^*-band is lowered increases with decrease in the distance between the N atoms.

The absorption spectra of 1,5-naphthyridine (XVIII) and 1,8-naphthyridine are similar to the spectrum of quinoline, and have n,π^*-bands at shorter wavelengths than the π,π^*-bands[6]. This is readily understood: the N atoms are fairly widely separated, and the effect of splitting is almost absent. 1,5-Naphthyridine apparently does not fluoresce in hydrocarbons but it exhibits fluorescence in alcohol and other polar solvents[12]. The long-lived phosphorescence band (ν_{00} = 22 000 cm^{-1}) is similar to the naphthalene band, but has less structure.

In quinoxaline (XIX), however, the n,π^*-band (26 670 cm^{-1}) appears as a long-wave band[6], and the π,π^*-band (31 630 cm^{-1}) coincides with the naphthalene band, like the prolonged phosphorescence band (21 250 cm^{-1}).

In quinazoline (XX) the n,π^*-band lies at even lower frequencies (27 330 cm^{-1}), and in phthalazine (XXIII) it lies at 25 820 cm^{-1},[6] whereas the π,π^* absorption and phosphorescence bands are similar to those of naphthalene, although the frequencies are slightly higher for phthalazine[39].

The electronic bands due to $\pi-\pi^*$ transitions in all the diazanaphthalenes are similar to the naphthalene bands; in particular, the characteristic magnitude of the S^*,T splitting of the π,π^*-level is preserved. The luminescent properties can be explained on the basis of the theories of

the n, π^*- and π, π^*-states, with allowance for the relative arrangement of their singlet and triplet levels.

Phthalazine has the most symmetrical molecule, and its spectrum is similar to that of naphthalene.

Cinnoline (XXI) gives three strong bands in the range 3100–3200 Å, whereas the other azanaphthalenes do not give bands in this range. The decrease in the energies of the $n-\pi^*$ transitions in diazanaphthalenes as the N atoms approach can be explained by arguments analogous to those for azabenzenes. As a result of this decrease, the long-wave absorption bands in the spectra of diazanaphthalenes are the n, π^*-bands, but the lower T-levels remain the $T_{\pi\pi^*}$-levels.

Diazaphenanthrenes

It is convenient to analyse the spectra of diazaphenanthrenes by comparing them with the spectra of phenanthrene. The absorption, fluorescence, and phosphorescence spectra of p-, m-, and o-phenanthrolines in alcohol solution are similar to the spectra of the original hydrocarbon, as already noted for the monoazaphenanthrenes. Thus the interaction of the n, π^*-states of the N atoms in the phenanthrolines does not produce such a marked decrease in the energy of the $n-\pi^*$ transitions, and they are found to be greater than the energy of the long-wave $\pi-\pi^*$ transition. The differences in the positions of the N atoms lead only to slight spectroscopic changes: the frequencies of the $\pi-\pi^*$ transitions are slightly higher for 4,7-phenanthroline (XXIV) ($S_1^*-S_0 = 29\,800$ cm^{-1}, $T-S_0 = 22\,200$ cm^{-1}) than for the 1,7-isomer (XXV) (29 700 cm^{-1} and 22 150 cm^{-1} respectively) and the 1,10-isomer (XXVI) (29 500 cm^{-1} and 22 100 cm^{-1})[12]. In the molecule of benzoquinoxaline (XXVII) the lower $S_1^*-S_0$ and $T-S_0$ transitions are also the $\pi-\pi^*$ transitions with lower frequencies (27 500 cm^{-1} and 21 000 cm^{-1} respectively in alcohol solution[38]). For diazaphenanthrenes, the magnitude of the S^*, T splitting of the π, π^*-levels remains at about 7500 cm^{-1}, as in phenanthrene; this is a characteristic feature of the geometry of a π-system with bent coupling of the rings[10]. The fluorescence of these compounds in alcoholic solutions is much weaker than that for phenanthrene, and is almost absent in hydrocarbon solvents; this can be attributed to the similarity in the energies of the $T_{n\pi^*}$- and $S_{\pi\pi^*}$-levels in these molecules.

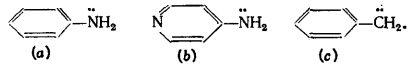
In the molecule of 9,10-diazaphenanthrene (benzocinnoline) (XXXI) with two neighbouring N atoms, the $n-\pi^*$ transitions lie at much longer wavelengths (the n, π^* absorption and fluorescence[48v] have $\nu_{00} = 20\,300$ cm^{-1}, and the n, π^* phosphorescence has $\nu_{00} = 13\,500$ cm^{-1}). Solutions of benzocinnoline give an n, π^* fluorescence band.

Other polycyclic aza-heterocycles whose spectra have been described include phenazine (XXVIII), dibenzoquinoxaline (XXIX), and dibenzo[a, c]phenazine (XXX); in the molecules of these compounds the N atoms are fairly far from one another, and the n, π^*-bands are masked by the π, π^*-bands, so that their spectra are similar to the spectra of the corresponding hydrocarbon analogues.

The spectra of bipyridyls do not show n, π^*-bands, and are similar to the spectra of biphenyl[49].

5. SUBSTITUTED N-HETEROCYCLIC COMPOUNDS

The introduction of substituents leads to various changes in both the absorption spectra and the luminescent properties. A particularly marked influence is shown by electron-donating substituents, which are so-called strong auxochromes. We shall not deal in detail with problems of the interpretation of the influence of substituents, and we refer the reader to the appropriate literature[24,25,59]. We would merely point out that substituents of the type NR_2, OR, and SR produce marked changes in the spectrum as a result of the conjugation of the electrons of the unshared pair with the π-electrons. A common feature of these substituted molecules is that the substituents increase the number of atomic orbitals by one unit and the number of π-electrons by two units. If the N-heterocycle forms an even alternant π-system, its derivative forms an odd alternant system, and this leads to the production of an upper filled π-orbital which is higher than that in the unsubstituted molecule. This is responsible for the appearance of an absorption band with longer wavelength and a decrease in the ionisation potential[59]. This can be illustrated more clearly by comparing the molecules of aniline (a) and aminopyridine (b) with the benzyl anion (c):



(a) (b) (c)

These systems are π-isoelectronic, and the benzyl anion has an upper filled π-orbital of non-bonding character[25].

Thus electron-donating substituents reduce the energy of the lower $\pi-\pi^*$ transitions. Experiment shows, however, that when these substituents are introduced the energy of the $n-\pi^*$ transitions is usually increased, so that these substituents displace the π, π^*- and n, π^*-bands in opposite directions. This characteristic feature of the behaviour of the bands with different character provides an additional criterion for their identification by studying the spectra of a series of substituted molecules.

The short-wave displacement of the n, π^*-bands can be explained qualitatively[39,58], by assuming that the substituents, by acting as electron donors, create a slight negative charge at the C atoms, which hinders the promotion of the n-electron of the N atom to the π^*-orbital. This transition requires even more energy, and the corresponding band lies at shorter wavelengths. A detailed semi-quantitative quantum-mechanical description of this displacement due to electron-donating substituents has not yet been made, however.

Different changes in the energies of the $\pi-\pi^*$ and $n-\pi^*$ transitions due to substituents may lead to changes in the relative positions of the singlet and triplet π, π^*- and n, π^*-levels, and hence in the luminescent properties of the molecules.

Let us examine spectroscopic data on the influence of substituents on the spectra of individual N-heterocyclic compounds.

Stephenson[52] studied the absorption spectra of the three isomers of picoline and 2- and 3-halogeno-substituted pyridines in a hydrocarbon solvent and in alcohol, and showed that in the 2- and 3-picolines, and also in the 3-fluoro, 3-chloro-, and 3-bromo-pyridines the n, π^*-band lies at the same position as that for pyridine, and is displaced in alcohol to higher frequencies by not less than 2000 cm^{-1}. In the spectrum of 4-picoline, the n, π^*-band is found at 35 200 cm^{-1}, but for 2-fluoro-, 2-chloro-, and 2-bromopyridines this band is hidden by the π, π^*-band. The spectra have been used to estimate the oscillator strengths of the $\pi-\pi^*$ and $n-\pi^*$ transitions. Rush and Sponer[50] published

the vibrational absorption spectra of picoline vapours (γ-picoline has $\nu_{n\pi^*} = 35\,165$ cm^{-1} and $\nu_{\pi\pi^*} = 38\,320$ cm^{-1}; for β-picoline the corresponding frequencies are 34 684 cm^{-1} and 37 380 cm^{-1}, and for α-picoline the corresponding frequencies are 34 753 cm^{-1} and 37 620 cm^{-1}). Misra[60] described the absorption spectra of 2-bromo- and 3-bromopyridine in all phase states, and also showed that the $n-\pi^*$ transition is observed for the 3-bromo-isomer ($\nu_{n\pi^*} = 35\,080$ cm^{-1}, $\nu_{\pi\pi^*} = 36\,300$ cm^{-1}) but is not observed for the 2-bromo-isomer; this is due to the inductive effect of the Br atom on the sp^2-electrons of the N atom.

The introduction of substituents of the type OR and NR_2 leads to more marked changes in the spectra; intense π, π^* absorption appears at longer wavelengths, whereas the n, π^*-bands cannot be distinguished. Mason[4] described the absorption spectra of hydroxy- and methoxypyridines in various media, put forward an interpretation of the bands, and discussed problems of tautomerism.

The presence of halogeno-substituents in pyrazine leads to a marked increase in the frequencies of the $n-\pi^*$ transitions. Halverson and Hirt[32] showed that the frequency is increased by 1700 cm^{-1} in 2-chloro-pyrazine and by 3200 cm^{-1} in 2,3-dichloropyrazine, relative to pyrazine. Hirt[37] described the $S_{n\pi^*}-S_0$ (32 068 cm^{-1}) and $T_{n\pi^*}-S_0$ absorption (28 100 cm^{-1}, $\epsilon \sim 0.05$) of pyrazine. The S_1^*, $T-n\pi^*$ splitting is about 4000 cm^{-1}.

Uber and Winters[55] described the absorption spectra of the vapours of dichloro-, trichloro-, and tetrachloropyrimidines, which have a system of bands with low intensity at long wavelengths, together with a more intense second system of bands. Halverson and Hirt[32] described the absorption spectra of chloropyridazine solutions. An n, π^* fluorescence band was observed for 3,6-dichloropyridazine[42]; the frequency of the 0–0 transition for this compound is higher than that for pyridazine, by 1800 cm^{-1}. Trimethyltriazine gives an absorption spectrum[38] with $\nu_{00} = 37\,880$ cm^{-1} for the $n-\pi^*$ transition and $\nu_{00} = 43\,960$ cm^{-1} for the $\pi-\pi^*$ transition, and also bands due to $T-S_0$ absorption and $T-S_0$ emission phosphorescence with $\tau = 0.65$ s), assigned to the $n-\pi^*$ transitions (ν_{00} for the $T_{n\pi^*}-S_0$ transition $\sim 27\,000$ cm^{-1}). Chowdhury and Goodman[44] studied the absorption spectrum and n, π^* fluorescence (with $\nu_{00} = 17\,000$ cm^{-1}) of dimethyltetrazine.

There are some unsystematic data on the spectra of substituted azanaphthalenes. The absorption spectrum of 4-methylquinoline at low temperature[61] and the spectra of dichloroquinazoline and 4-methylcinnoline [(XXII) (Ed. of Translation)][39] have been published.

Kosta and coworkers[62] studied the extinction of the fluorescence of dimethylquinoline solutions by halide, $C_6H_5NH_3^+$, SCN^-, and Cu^{2+} ions. Topolats and coworkers[63] described the extinction of the fluorescence of quinoline derivatives by gallic acid, hydroquinone, resorcinol, phloroglucinol, orcinol, and pyrocatechol. Witwer and Zanker[54] measured the polarisation absorption and fluorescence spectra of mono-and di-aminoacridines at low temperature.

Aromatic N-Oxides

The N-oxides are unique derivatives of aromatic N-heterocycles. Ziolkowsky and Dorr[64] studied the absorption, fluorescence, and phosphorescence spectra, and also the polarisation spectra, of the N-oxides of pyrazine, quinoline, 2-chloroquinoline, isoquinoline, and quinoxaline in various solvents at 90°K, and showed that the electronic absorption and luminescence bands are similar to the bands of the corresponding aromatic hydrocarbons and are very sensitive to change in the solvent; the spectra do not show n, π^*-bands. Thus the attachment of an O atom to the N atom in the hetero-ring leads to a marked change in the state of the n-electrons but has little influence on the π-system.

6. AZOMETHINES AND AZO-COMPOUNDS

A wide range of compounds of practical importance are included among the aromatic azomethines (A) and azo-compounds (B):

Ar—CH=N—Ar′ (A) Ar—N=N—Ar′ (B)

which formally have a π-system isoelectronic with the π-system of the corresponding arylethylenes. If the n-electrons of the N atom are localised on an atomic orbital, two types of transition are possible: $\pi-\pi^*$ and $n-\pi^*$; the π, π^*-bands can be expected to be similar to the bands for the corresponding arylethylenes. This is in fact observed for the molecules of azo-compounds with a planar structure, but is not observed for aromatic azomethines. The sharp difference between the absorption spectrum of benzylideneaniline and the spectrum of stilbene, and also a number of characteristic features of the absorption spectra of benzylideneaniline and its derivatives were attributed by Izmail'skii and Smirnov[65], and later by others[66,67], to the non-coplanar structure of these molecules. The conclusion that the benzylideneaniline molecule is not coplanar was confirmed by the quantum-chemical calculations of Minkin and coworkers[68,69]. The non-planar structure of benzylideneaniline is more stable than the planar structure because of the interaction of the unshared pair of electrons (the n-electrons) of the N atom with the π-electrons of the N-phenyl ring. This complicates the possibility of separating the electron transitions in benzylideneaniline into n, π^*- and π, π^*-types. Nevertheless, its long-wave absorption band has been assigned[66,70] to the $n-\pi^*$ transition.

Conjugation of the n-electrons and simultaneously a p-electron of the nitrogen atom with the π-electrons complicates considerably the interpretation of the spectra of molecules of type (A) with non-planar structure.

Let us consider the simpler case of planar molecules of type (A). The relative energies of the n, π^*-bands in a series of planar molecules (A) can be estimated by selecting a molecule with a shortened π-system. It is known that with increase in size of the π-system, the π, π^*-bands are displaced towards longer wavelengths much more rapidly than the n, π^*-bands, so that by shortening the π-system it is possible to achieve better separation of the π, π^*- and n, π^*-bands. In the absorption spectrum of N-benzylidenebenzylamine $C_6H_5CH{=}N{-}CH_2C_6H_5$, the n, π^*-band does not appear as a long-wave band (the estimated lower boundary $\nu_{n\pi^*} \geqslant 32\,000$ cm^{-1}). Thus the n, π^*-band cannot be the long-wave band in the spectrum of planar models of the molecules of benzylideneaniline $C_6H_5CH{=}N{-}C_6H_5$ and other aryl-substituted compounds with general formula (A), so that their spectra should be similar to the spectra of arylethylenes. This is in fact observed, when a planar structure is forced on molecules of type (A), for example, by enclosing the –CH=N– group in a benzoxazoline

ring. The spectroscopic-luminescent properties of arylbenzoxazoles and arylethylenes have been shown to be similar [65,72,73].

What then is the nature of the absorption spectrum of benzylideneaniline? It extends to much longer wavelengths than the spectrum of stilbene (Fig. 3). This displacement cannot be attributed merely to destruction of the coplanarity of the π-system, which should lead to a short-wave displacement. The benzylideneaniline molecule represents essentially a symbiosis of two molecules: aniline and nonplanar stilbene. Conjugation of the n-electrons with the π-electrons of the N-phenyl ring leads to the production of a system of "aniline" levels, whereas the participation of a p-electron of the N atom in π-conjugation defines a system of "stilbene" levels (Fig. 3). The chief factor [59] responsible for the long-wave displacement of the spectra of aromatic compounds when electron-donating substituents are introduced is the production of higher-lying upper-filled π-orbitals. Thus the long-wave absorption band of benzylideneaniline can be interpreted qualitatively by relating it to the transition of an electron from the upper filled "aniline" π-orbital to the lower vacant "stilbene" π-orbital. Since the electron of the "aniline" orbital is situated chiefly on the N atom and the probability of its transition is determined to a considerable extent by the overlap of the n- and p-orbitals of the N atom, which are mutually orthogonal, it is natural to expect that this transition will have a low probability, and this explains the low intensity of the long-wave band. The bands at shorter wavelengths probably result from the superposition of several transitions. It is reasonable to assume that the range 300–350 nm corresponds to superposition of the "aniline" and "stilbene" bands. Although quantum-chemical calculations have been carried out for the spectra of benzylideneaniline [67-69,74], a more rigorous and detailed theoretical examination of this unique molecule is desirable. The qualitative picture, which makes it possible to understand to some extent the differences between the spectra of benzylideneaniline and stilbene, can be extended to other aromatic azomethines whose spectra have been described [75].

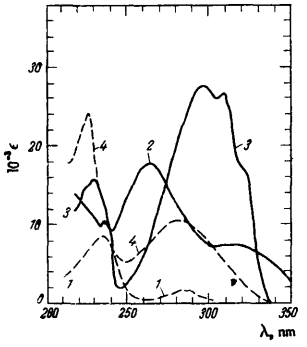


Fig. 3. Absorption spectra of aniline (1), benzylideneaniline (2), *trans*-stilbene (3), and *cis*-stilbene (4).

As expected, the absorption spectra of compounds of the type

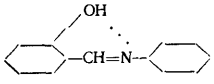
$$C_6H_5CH=N-C_6H_4-X-C_6H_4-CH=N-C_6H_5,$$

whose molecules consist of two benzylideneaniline molecules joined by a bridge X = $-CH_2-$ or $-CH_2-CH_2-$ which does not transmit π-conjugation, are similar to the spectra of benzylideneaniline [76]. The introduction of bridges X formed by –O–, –S–, or –NH– groups, which are electron donors, produces changes in the spectrum which are the same as the changes in the spectrum of benzylideneaniline resulting from the introduction of the substituents OH, SH, or NH_2 into the *para*-position of the aldehyde ring. The absorption spectra of compounds of this series were described by Krasovitskii and Mal'tseva [77]. Increase in the number of benzene rings between the azomethine groups in $C_6H_5CH=N-(C_6H_4)_n-N=CH-C_6H_5$ from $n = 1$ to $n = 3$ does not alter the absorption spectrum [76].

Azomethine compounds of the above types do not show luminescence. The absence of luminescence is apparently due to the non-coplanar structure, which is characterised by an extinguishing effect resulting from the excitation of torsional vibrations.

The introduction of substituents leads to complicated changes in the electronic structure of the molecules, and also influences their degree of non-coplanarity. This complicates the spectra and may alter the luminescent properties of the molecules. The interpretation of the spectra of these derivatives is very difficult. It is clear, however, that the introduction of substituents cannot lead to the appearance of $n-\pi^*$ transitions as long-wave transitions.

With Kozlov, Shigorin, and Puchkov [78-80], we showed that a particularly marked change in spectroscopic-luminescent properties is produced by the introduction of an OH substituent into the *o*-position of the aldehyde ring. *o*-Hydroxybenzylideneaniline (I)

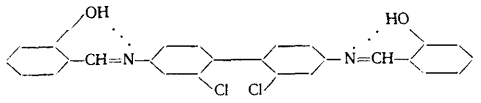


(I)

exhibits bright green fluorescence at 77°K and reversible phototropic properties. The absorption spectrum of *o*-hydroxybenzylideneaniline contains a weak long-wave band, previously assumed to be the n, π^*-band. This band shows an anomalous increase in intensity on going from a non-polar solvent to a polar solvent [81]. Studies of the spectra of *o*-hydroxybenzylideneaniline under various conditions and of the phenomenon of phototropy established [79,80,82] that the long-wave band belongs to another tautomeric form of the *o*-hydroxybenzylideneaniline molecule, whose relative concentration depends on the nature of the solvent and temperature. No explanation has yet been given, however, for the anomalously large Stokes displacement between the long-wave absorption and the fluorescence band [82,83].

The absorption and luminescence spectra of various hydroxyazomethine compounds have been studied [84]. It was shown that doubling of the *o*-hydroxybenzylideneaniline molecule displaces the intense band by about 2500 cm^{-1}, that is, the displacement is not as great as that observed on going from stilbene to bistilbene, and the displacement of the long-wave band (assigned to the other form) is even smaller. A remarkable feature is that the absorption spectrum does not depend on the number of phenyl rings

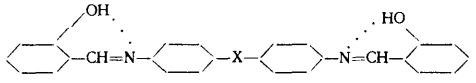
between the N atoms, although there is undoubtedly a conjugation effect, as indicated by the short-wave displacement of the band for (II):



(II)

compared with the molecule which does not contain substituents causing steric hindrance.

It was also shown[77] that the bridge X = –O–, –S–, or –NH– in the molecules (III):



(III)

influences the spectra as an electron-donating substituent, but it does not exhibit the properties of a conjugation transmitter.

Arylazo-Compounds Ar–N=N–Ar′

These have molecules with planar structures. Their intense absorption bands, due to $\pi-\pi^*$ transitions, are similar to the bands of the corresponding arylethylenes[75,85] and the long-wave range (20 000–24 000 cm^{-1}) shows a weak band due to the $n-\pi^*$ transition, which has been most extensively studied for azobenzene. Jaffé and coworkers[70] carried out a detailed study and theoretical examination of the spectra of azobenzene and related compounds. On the basis of the small short-wave displacement in polar solvents and under the influence of substituents, they assigned the long-wave band at 420 nm to an $n-\pi^*$ transition, assuming that it is formed by the superposition of two bands due to $n_a-\pi^*$ and $n_s-\pi^*$ transitions. It should be noted, however, that their method of graphical resolution of the bands has no real basis and can hardly be correct. Dyck and McClure[86] described the structure of the band due to the $\pi-\pi^*$ transition (ν_{00} = 27 662 cm^{-1}), resolved in a mixed azobenzene–bibenzyl crystal at 20°K, using the frequencies 220, 378, and 1342 cm^{-1}. The last frequency was assigned to the stretching vibration of the –N=N– group in the excited π, π^*-state. Hochstrasser and Lower[87] showed that the n, π^*-band exhibits polarisation in the plane of the molecule and that the transition is forbidden by symmetry, in agreement with theoretical calculations of the splitting of the n, π^*-states of the two nitrogen atoms. The magnitude of the splitting was estimated as 8900 cm^{-1}. This estimate agrees with experiment. As noted above, for one N atom the band due to the $n-\pi^*$ transition is expected in the region of 32 000 cm^{-1} (planar benzylideneaniline model) and for azobenzene the $n-\pi^*$ transition lies at about 22 000 cm^{-1}. The molecules of arylazo-compounds may exhibit two configurations: *cis* and *trans*[75,85,86]. The *trans*-configuration is the more stable. The absorption spectra of the *trans*-isomers of various arylazo-compounds Ar–N=N–Ar′ (where Ar = phenyl, α-naphthyl, or β-naphthyl) have been described[85]. The *trans*-isomers may be converted into the *cis*-isomers under the influence of light. The study of the photo-*trans*-*cis*-isomerisation of azo-compounds has been the subject of a number of papers[88]. The spectra of the pure form of *cis*-azobenzene have been isolated and studied[89], and the absorption spectra of the *cis*-isomers of more complex azo-compounds have been described[90,91].

Azo-compounds form one of the most extensive classes of non-fluorescent compound. The absence of fluorescence is apparently due to the high probability of S^*-T conversion from a lower $S_{n\pi^*}$-state into the $T_{\pi\pi^*}$-state, and is also related to the photochemical instability of azo-compounds.

Derivatives of azo-compounds form a large class of organic dyes, so that a large number of their spectra have been studied. Brode and Wyman and coworkers[92–96] studied the absorption spectra of a large number of azo-compounds and azo-dyes in order to establish the relationship between the spectra and chemical structures of the dyes. The phenomenon of phototropy and the *cis*-*trans*-isomerisation of aromatic azo-compounds have been described[92], and the influence of dissolution and temperature on the *cis*-*trans*-isomerisation of the amino-, hydroxy-, alkyl-, and halogeno-derivatives of azobenzene, benzeneazonaphthol, and benzeneazonaphthylamine has been described[51]. The appearance of a new absorption band in the spectrum of azo-dyes as a result of the hydration of the dye molecules when water is added to the organic solvent has been described[94]. The change in the spectra accompanying the interaction of the molecules of binary mixtures of dyes in aqueous solutions[95] and the phenomenon of phototropy in solutions of complex diazo methoxyazo-dyes[96] have also been studied.

A series of papers by Heilbronner, Gerson, Schulze, and coworkers[75,97–106] described the study of the electronic structure and properties of azo-compounds. The ultraviolet absorption spectra of arylazoazulenes have been studied[97,98] and it has been established that the displacement of the band shows a simple dependence on the Hammett constant; the dipole moments of phenylazoazulene derivatives have been studied[99] and the spatial structure of the molecules has been established. The π-electronic structure of phenylazoazulene has been examined theoretically by the MO LCAO method[100], and the energies of transitions and the oscillator strengths have been calculated. A special study has been made[101] of the problem of the influence of a substituent in the benzene ring on the position of the absorption band in the range 16 500–17 000 cm^{-1}, and a study has been made[41] of the bathochromic shifts of the bands accompanying the protonation of the molecules of arylazoazulene derivatives in ethanol–hydrochloric acid systems. Study of the spectra of *trans*- and *cis*-azobenzenes[103] in acid solutions showed that their conjugate acids have different structures; the *cis*-isomer of the acid is gradually converted into the *trans*-form. The spectra and structure of the *p*,*p*′-bis(dimethylamino)azobenzene azonium cation have been studied[105] and the influence of protonation on the spectra of *p*′- and *m*′-derivatives of *p*-dimethylaminoazobenzene[97,98] *p*-dimethylaminophenylazoazulenes[106] has been described.

Robin and Simpson[107] studied the absorption spectra of polyphenyl azo-dyes $C_6H_5-N=N-(C_6H_4-N=N-)_n-C_6H_5$ (n = 0–5); the spectra were interpreted on the basis of a model with transfer of the electronic excitation along the chain of the molecule, the polarisation of the transitions was established, and the $n-\pi^*$ transitions were isolated.

Skulski and Urbanski described the absorption spectra of azo-dyes based on 4-hydroxy- and 4-acetoxyazobenzenes[108], 4-formyl-, 4-nitro-, and 4-(2-nitrovinyl)azobenzenes[109], and acetoxy- and acetylamino-derivatives of 1-phenylazonaphthalene[110]. It has been established[108] that electron-accepting groups in the *o*-position relative to the phenol groups in the dyes $X-C_6H_4-N=N-C_6H_3YOH$ produce a hypsochromic shift of the adsorption band. The absorp-

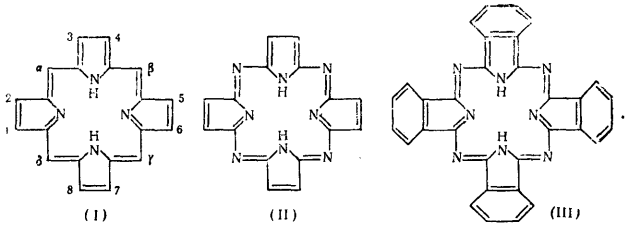
spectra of *o*- and *p*-azo-dyes based on 1-phenylazonaphthalene have also been described[111,112].

Si-Jung and Jaffé[113] studied the transfer of the electronic effects of the $-N=NC_6H_4-$ group in the compounds p-$HO-C_6H_4N=NC_6H_4-X$, where X = OCH_3, CH_3, or Br. Baba[114] studied the influence of intermolecular hydrogen bonding on the absorption spectrum of *p*-hydroxyazobenzene, and showed that the n, π^*-band is displaced towards shorter wavelengths, and the π, π^*-band towards longer wavelengths. It was shown that the displacement of the frequencies is greater for the O–H...N ≤ bond than for the O–H...O < bond.

It is pointed out in Pringsheim's monograph[115] that among more than 700 azo-dyes there is no example of fluorescence in solutions. With Shigorin, Kozlov, and Puchkov[116,117], we investigated structural factors leading to activation of the fluorescence of azo-compounds, and showed that this activation is facilitated by the introduction of an *o*-hydroxy-substituent, which leads to the formation of an intramolecular six-membered quasi-aromatic ring with hydrogen-bonding, and that this ring stabilises the structure of the molecule. The *o*-hydroxyazo-compounds exhibit bright fluorescence in powders and frozen solutions. The substance becomes non-fluorescent when the OH group is methylated. The fluorescent S_1^*-state in the *o*-hydroxyazo-compounds is the π, π^*-state. It is lower because of the decrease in frequency caused by the electron-donating OH substituent, whereas the OH...N interaction removes the degeneracy of the n, π^*-states (the N atoms are not equivalent) and leads to marked displacement of the frequency of the $n-\pi^*$ transition towards higher values.

7. PORPHYRINS AND PHTHALOCYANINES

Without examining in detail the relationship between the spectra and structures of the molecules of porphyrins and phthalocyanines (although this problem deserves attention, despite the existence of a number of reviews[118-120] and theoretical calculations[121-123]) let us examine the extent to which the spectra of these complex systems show general regular features characteristic of heterocyclic compounds. It is of interest to determine the range of the spectrum in which we can expect $n-\pi^*$ transitions for these molecules and to find whether they exhibit luminescence.



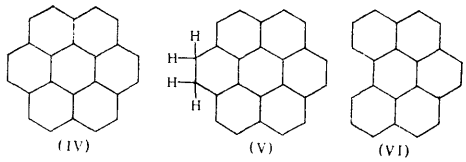
(I) (II) (III)

Porphine (I), the parent compound of the porphyrins, has a lower $S_1^*-S_0$ transition in the region of 6130 Å (16 300 cm^{-1}), active in absorption and fluorescence. Solov'ev, Sevchenko, and coworkers[124] obtained a quasi-line multiplet structure for the fluorescence and absorption bands of porphine in octane at 77°K. There is no information on the phosphorescence of porphine. To understand the relationship between the spectrum and the structure, let us consider the characteristic features of the structure of the porphine molecule. Formally, it is obtained by forming a ring of four pyrrole groups by means of methine bridges. In the process, only two pyrrole rings are preserved; the N atoms of these rings each bring one atomic orbital and two electrons into the π-system. The N atoms of the other two rings each bring one atomic orbital and one electron, and also carry n-electrons, capable of giving $n-\pi^*$ transitions. These could be the lowest frequency transitions, as with the previously examined *N*-heterocycles, only if the entire absorption spectrum lay above 32 000 cm^{-1}. Since the absorption of porphine begins at much lower frequencies, due to the extensive π-system, the $S_{n\pi^*}$- and $T_{n\pi^*}$-levels in molecules of this type will lie above the $S_{\pi\pi^*_n}$-level and will not influence the luminescence of the molecules. The cyclisation of four pyrrole rings to give one large ring should produce properties characteristic of the angular cyclisation of aromatic nuclei. It is convenient to compare the skeletons of porphine and coronene (IV), whose outer perimeters have approximately the same number of π-electrons. As already noted, on angular cyclisation the long-wave bands are α-bands of low intensity (in coronene this band is further forbidden by symmetry). The greater lowering of the frequency of the $S_1^*-S_0$ transition in porphine compared with coronene is due to the presence of the NH group, which produces the strong bathochromic shift of the bands, discussed in Section 5. The angular cyclisation itself does not lead to marked lowering of the frequency of the $\pi-\pi^*$ transition. This is effectively confirmed for porphyrins on going from porphine to tetrabenzoporphyrin, which gives a frequency in the region of 15 200 cm^{-1}, that is, only 1100 cm^{-1} below the $\nu_{S_1^*-S_0}$ frequency of porphine (or only 270 cm^{-1}, calculated for one benzene ring). Shkirman and Solov'ev[125] also obtained a quasi-line structure for the fluorescence and absorption bands of tetrabenzoporphine in octane at 77°K. An important characteristic feature of angular cyclisation is the decrease in the magnitude of the S^*, T splitting, which can also be expected for porphine. Although phosphorescence is not known for porphine, its T-level can be determined from data on metalloporphyrins. The intrdouction of a metal, producing little change in the frequency of the $S_1^*-S_0$ transition, leads to an increase in the relative phosphorescence yield with increased atomic weight of the metal. In various metallomesoporphyrins, the magnitude of the S^*, T splitting is about 3000–3500 cm^{-1},[126] which is even slightly less than that in coronene. It is reasonable to attribute the additional decrease to the electron-donating effect of the NH and N–metal groups. Thus it is also possible, for the complex porphyrin molecules, to distinguish those characteristic features of the spectra which are determined by the topology of their π-electronic structure or the topology of the molecular framework over which the π-electrons are distributed.

This conclusion is further confirmed by examining molecules which are related to porphine but which have a smaller π-system, and this in turn makes it possible to understand various spectroscopic-luminescent characteristics of these molecules.

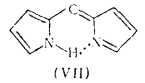
In the molecule of chlorin (which differs from porphine in that it contains a hydrogenated 1–2 bond), the frequency of the $S_1^*-S_0$ transition is displaced towards lower frequencies (ν_{00} = 15 780 cm^{-1})[125]. Rabinowitch tried to attribute this displacement and the increase in the intensity of the long-wave absorption band to the production of a new lower-lying excited level; the band associated with transition to this level is assumed to mask the "porphine" bands of low intensity. It is not at all clear how decrease in the π-system leads to an increase in the number of electron

levels (preservation of the former levels and the production of a new level). Sevchenko and coworkers[124] consider than this explanation is without foundation, but they in turn assume a correlation between the levels of chlorin and porphine. It is not rational, however, to look for such a correlation. When one double bond is eliminated in the coronene ring:



(IV) (V) (VI)

there is also a long-wave displacement of the $\pi-\pi^*$ transition. The spectroscopic properties of dihydrocoronene (V) are similar to those of 1,12-benzoperylene (VI), whose molecule can reasonably be regarded as a doubled phenanthrene molecule[10]. Thus the hydrogenated bond in the chlorin molecule produces the long-wave displacement as a result of the sharp decrease in the circular symmetry, that is, the change in the topology of the π-system. This also explains the difference in the intensity of the band and the absence of phosphorescence. The magnitude of the S^*, T-splitting in 1,12-benzoperylene is approximately double that in coronene. If this also applies on going from porphine to chlorin, the frequency of the $T-S_0$ transition of the latter will lie in the region of 10 000 cm^{-1}. The probability of $T-S_0$ emission in this range would be expected to be very low, because of the strong non-radiative deactivation. This is apparently related to the absence of phosphorescence in metallochlorins[127], although metals such as Cu have a marked ability to increase the phosphorescence yield. Increase in the magnitude of the S^*, T splitting (up to 7000 cm^{-1}) takes place in the molecule of bipyrrole (VII), which is as it were half a porphine molecule:



(VII)

The absorption band for this compound lies in the region of 20 000 cm^{-1}, that is, 3700 cm^{-1} higher than that for porphine. However, the displacement is very slight in relation to the position of the pyrrole band at about 220 nm.

Although bipyrrole exhibits fluorescence, replacement of the methine group by –N= leads to extinction of the fluorescence. The extinction is apparently due to the fact that the π-electrons of the pyrrole ring are conjugated with the n-electrons of the N atom. This leads to breakdown of the planar structure of the π-system, as in benzylideneaniline.

In tetra-azaporphine (II), the =CH– methine bridges are replaced by =N–. This replacement produces almost no displacement of the π, π^*-band (16 350 cm^{-1})[125]. In phthalocyanine (tetrabenzotetra-azoporphine) (III), the frequency is lowered by only 1900 cm^{-1} relative to that for tetra-azaporphine[128].

Evstigneev and coworkers[129-131] and Livingston, and coworkers[132,133] observed "activation" of the fluorescence of chlorophyll: the absence of fluorescence in non-polar solvents and the production of fluorescence when polar solvents were added. The first authors[129-131] attribute this "activation" to breakdown of chlorophyll associates, whereas the second authors[132-135] attribute it, by analogy with quinoline, to a change in the relative position of the $S_{\pi\pi^*}$ and $T_{n\pi^*}$-levels under the influence of the polar solvent. Simple analysis of the structural characteristics of the chlorophyll molecules shows, however, that the $n-\pi^*$ transitions in these molecules cannot be as low as this. In actual fact, as noted for porphine, the energy of the n, π^*-levels in this molecule is much greater than that of the π, π^*-levels. The same is true for tetra-azaporphyrin, since increase in the number of N atoms cannot lower the n, π^*-levels because of their splitting; the latter should be small, because of the relatively short distance between the N atoms. The presence of C=O groups in the chlorophyll molecule may lead to the appearance of n, π^*-bands in the range 27 000–26 000 cm^{-1}, that is, again at higher frequencies than the lower π, π^* transitions of the π-system of the porphine ring. This provides further confirmation of the interpretation given by Evstigneev and coworkers[129-131].

In conclusion it may be noted that the above general features, relating the spectra to the molecular structure, make it possible to obtain an overall picture of the spectroscopic-luminescent properties of a wide range of organic compounds. Many of these regular features require theoretical examination.

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NOTE ADDED IN PROOF

The following reviews appeared after the present paper had been submitted for publication: one by Lower and El-Sayed[136], devoted to the triplet state in intramolecular electronic processes, one by Innes[137] on the spectroscopic properties and geometry of the excited electronic states in azines, and their theoretical interpretation, and a Russian translation[138] of Mason's review on the electronic absorption spectra of heterocyclic compounds.

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