759. *The Electronic Spectra of* N-*Heteroaromatic Systems. Part X.** *Five-membered Ring Systems.*

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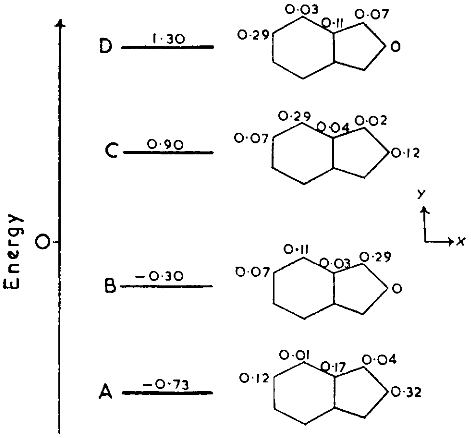
The electronic absorption spectra of the aza-derivatives of indolizine, indole, and 1-methyl-1-pyrindine are analysed in terms of a common energy-level scheme, given by the Hückel theory for the indenyl anion, and first-order perturbation theory. The spectra of the azaindolizines are found to conform more closely than those of the azaindoles to the indenyl anion model, from which it is concluded that π-electron delocalisation is the more extensive in the former series.

As yet, the electronic spectra of heteroaromatic molecules containing five-membered rings have been analysed in less detail than those of the corresponding six-membered ring compounds. The carbocyclic analogues which serve as models for the interpretation of the light-absorption properties of heterocyclic molecules with five-membered rings are non-alternant systems, and they lack the pairing property between bonding and antibonding orbitals and other simplifying features of the alternant hydrocarbons used[1] in the study of heteroaromatic compounds with six-membered rings. However, the single configuration approximation may be employed with more certainty for the treatment of the electronic transitions of five-membered ring compounds, owing to the less frequent occurrence of degenerate configurations, and in the present work the approximation is used to analyse the absorption spectra of the heteroaromatic analogues of the indenyl anion.



The energies, in units of the carbon–carbon resonance integral, and the one-electron charge distributions of the higher occupied (A and B) and the lower unoccupied (C and D) π-orbitals of the indenyl anion.

Early work[2] established that the electronic spectra of pyrrole, furan, thiophen, and cyclopentadiene were similar, consisting of a high-intensity band in the vacuum-ultraviolet followed by a moderate-intensity absorption in the quartz region. From the spectral similarities it was suggested[2] that homocyclic conjugation does not obtain in heteroaromatic molecules with five-membered rings, pyrrole and thiophen, in particular, being essentially cyclic dienes. However, the similarities may indicate, alternatively, that homocyclic conjugation occurs in cyclopentadiene, due either to overlap between the terminal atoms of the diene portion, or to hyperconjugation through the methylene group, so that the chromophore has a quasicyclic character. The energy levels of a cyclic polyene are more widely spaced than those of the corresponding linear polyene, and inter-level transition energies are the larger in the former system. Further, the lowest-energy

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* Part IX, *J.*, 1962, 493.

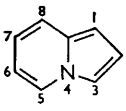
[1] Mason, *J.*, 1962, 493, and previous papers of the present series.

[2] Price and Walsh, *Proc. Roy. Soc.*, 1941, *A*, **179**, 201.

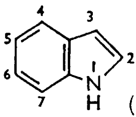
transition of a cyclic polyene is generally forbidden. Experimentally,[3] the lowest-energy absorption band of cyclopentadiene appears at a shorter wavelength and with a smaller intensity than that of cyclohexadiene, in conformity with both of these expectations.

Moreover, the electronic spectra of the condensed benzo-derivatives of the five-membered monocyclic heteroaromatic molecules conform to an indenyl anion model, in which homocyclic conjugation is assumed. The highest occupied π-orbitals of the indenyl anion, A and B, and the lowest unoccupied levels, C and D, have the Hückel energies and one-electron charge distributions indicated in the Figure. The electronic transitions, B$\rightarrow$D and A$\rightarrow$C are x-polarised with moment lengths of 0·30 and 1·20 Å, respectively, whilst the transitions, B$\rightarrow$C and A$\rightarrow$D, are y-polarised with moment lengths of 0·98 and 0·92 Å, respectively. The transitions with the same polarisation direction should mix to some degree, the mixing being limited by the different energies of the excitations, but the transitions with perpendicular moments cannot mix.

In the azaindenes, (I)—(III), the transition energies are changed, the most important perturbation arising from the pyrrole-nitrogen atom. As the pyrrole-nitrogen atom donates two electrons to the π-system of an azaindene, it has a large effective electronegativity and, thus, a large Coulomb-integral increment, $\Delta\alpha$, probably comparable with that of the positively charged nitrogen atom in the pyridinium ion. The pyridine-like nitrogen atoms of the aza-derivatives of indolizine (I), indole (II), and 1-methyl-1-pyrindine (III) have the smaller Coulomb-integral increment of the neutral nitrogen atom in a six-membered aromatic ring system.



(I)



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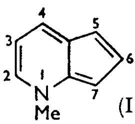

(III)

The replacement of one or more carbon atoms in a conjugated molecule by hetero-atoms changes the energy of each π-orbital in the parent molecule by the quantity, $\sum_r c_r^2 \Delta\alpha_r$, where c_r^2 is the one-electron charge density in the orbital considered at the position of the atom replaced. Thus the pyrrole-nitrogen atom of indolizine (I) lowers the

The electronic absorption spectra of some aza-analogues of the indenyl anion.

Compound	$\lambda_{max.}$ (Å)	ε	Ref.
Indolizine	3465; 2945; 2375	1950; 3600; 32,000	4
1-aza	3100; 2800; 2245	2600; 2600; 26,000	4
2-aza	3440; 2735; 2180	1900; 5240; 29,000	4
3-aza	3005; 2890; 2225	1800; 3300; 36,000	4
7-aza	3720; 2800; 2300	105; 500; 3,000	5
1,2-diaza	3060; 2740; 2130	2200; 4700; 24,000	4
2-methyl-1,3-diaza	2730; 2175	3700; 38,000	4
2,3-diaza	2900; 2700; 2140	2300; 2100; 22,000	4
1,2,3-triaza	2685	4000	4
1-Methyl-1-pyrindine	4560; 3200; 2560	690; 3600; 11,500	6
7-aza	3850; 3090; 2450	980; 8800; 15,700	7
Indole	2880; 2610; 2190	4900; 6300; 25,000	8
2-aza	2960; 2500	3300; 4500	9
3-aza	2770; 2440	4200; 5100	9
4-aza	2920	8300	9
5-aza	2730; 2650	3100; 3900	9
6-aza	2910; 2600; 2180	4500; 3900; 30,000	9
7-aza	2900; 2180	8700; 20,000	7

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[3] Fawcett and Harris, *J.*, 1954, 2673.
[4] Bower, *J.*, 1957, 4510.
[5] Herz and Tocker, *J. Amer. Chem. Soc.*, 1955, **77**, 6355.
[6] Reese, *J. Amer. Chem. Soc.*, 1962, **84**, 3979.
[7] Robison and Robison, *J. Amer. Chem. Soc.*, 1955, **77**, 6554.
[8] Badger and Christie, *J.*, 1956, 3438.
[9] Adler and Albert, *J.*, 1960, 1794.

energy of the oribitals A and D more than that of the orbitals B and C, as the charge density at the bridgehead position in the indenyl anion is the larger in the former orbitals (see Figure). These energy changes reduce the interaction between the single-configuration excitations with *x*-polarisation, which are nearly degenerate in the indenyl anion, owing to the large energy difference between the two transitions. In particular, the orbital changes decrease the energy of the transition B→D, which has the smallest moment length, and it is probable that this excitation is predominantly responsible for the relatively weak long-wavelength absorption band of the indolizines (Table).

The replacement of a C–H group at the 2-position of indolizine (I) by a nitrogen atom should not change the energies of the orbital B and D, since a node passes through the 2-position in these orbitals (Figure). Experimentally, the replacement of a 2-carbon atom by a nitrogen atom in indolizine (I) or its 1- or 3-aza-derivative does not greatly change the position or the intensity of the long-wavelength band (Table). On 1- or 3-aza-substitution in indolizine (I), the energy of orbital B is lowered to a greater degree than that of the orbital D, and it is found that these substitutions produce large blue shifts of the long-wavelength absorption band, the shift being doubled in the 1,3-diaza-derivative (Table). The indenyl anion model requires that 1- and 3-substitution in indolizine (I) should produce the same spectral changes, and, to a good approximation, such an equivalence is observed (Table). The replacement of a carbon by a nitrogen atom at the 7-position of indolizine (I) produces a greater reduction in the energy of the orbital D than in that of the orbital B (Figure), in conformity with the substantial red shift of the long-wavelength absorption band given by 7-azaindolizine (Table).

The shorter wavelength bands of indolizine (I) undergo blue shifts which are larger for 2- than for 1-, 3-, or 7-aza-substitution (Table), suggesting that these bands are due to transitions which originate from the orbital A (Figure). The high-intensity bands in the 2200 Å region are probably due predominantly to the transition A→C, which has the largest transition-moment length, and the bands of intermediate wavelength to a mixture of the *y*-polarised transitions.

The most important single modification of the π-orbitals of the indenyl anion produced by the pyrrole-nitrogen atom of 1-methyl-1-pyrindine (III) is a substantial reduction in the energy of the lowest unoccupied orbital C (Figure). The long-wavelength absorption band of 1-methyl-1-pyrindine (III), if ascribed to the transition B→C, should lie at a lower frequency than the corresponding band of indolizine (I), and in 7-aza-1-methyl-1-pyrindine the band should undergo a large shift to shorter wavelength. Both of these effects are observed (Table).

The pyrrole-nitrogen atom of indole (II), however, produces in the indenyl anion a substantial decrease in the energy of the highest occupied orbital B (Figure). If the band is assigned to the transition B→C, the long-wavelength absorption of indole (II) should lie at a shorter wavelength than that of indolizine (I), and the absorption should shift to longer wavelengths on aza-substitution in the 2-, 4-, or 7-position, and to shorter wavelengths for the corresponding substitution in the 3-position. These effects are observed (Table), but there is a feature of the azaindole spectra which suggests that the indenyl anion model is less applicable to this series.

The symmetry of the indenyl anion indicates that the aza-replacement of a C–H group in the 1-, 4-, or 5-position should produce, respectively, the same spectral changes as a nitrogen atom substituted in the 3-, 6-, or 7-position. However, the spectra of 5- and 6-azaindole are somewhat different (Table), and so too are the spectra of 4- and 7-azaindole in acid solution,[9] where the pyridine-like nitrogen atom is protonated, and the perturbations due to that atom are enhanced.

The different spectral trends observed in the azaindolizine and in the azaindole series may arise from the less complete delocalisation of π-electrons in the latter series of compounds. The localisation of two π-electrons on the nitrogen atom of indole leaves a conjugated residue with the π-electron system of styrene, which has a resonance energy (38 kcal./mole) only 10 kcal./mole less than that of indole.[10] A similar localisation of π-electrons in pyrrole or indolizine would leave the non-aromatic residues of butadiene and octatetraene, respectively, and the reduction of delocalisation energy would be more drastic. The reported resonance energies [10] of pyrrole and butadiene, for example, are 23 and 3 kcal./mole, respectively. The localisation of π-electrons upon the pyrrole-nitrogen atom of the azaindenes studied nullifies the symmetry-determined relations between the absorption spectra of the compounds in the series, and from the degree to which the azaindenes conform to the indenyl anion model it is concluded that π-electron delocalisation is more complete in the indolizine than in the indole series.

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[10] Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955.