137. *The Light Absorption and Resonance Energies of Some Heterocyclic Molecules.*

By Allan Maccoll.

In view of the pronounced red shift of the long wave-length electronic absorption band of the cyclic molecules $[CH]_nN_{6-n}$ as n decreases, the quantum mechanics of these molecules has been investigated to the Förster approximation. If it is assumed that the C–C, C–N, N–N exchange integrals decrease in that order, the observed shifts can be accounted for. The resonance energies of these compounds have also been determined, together with the zeroth order wave functions in those cases in which the two Kekulé forms are non-equivalent.

The observation of the absorption spectra of a number of members of the class $[CH]_nN_{6-n}$ ($n \leqslant 6$), in which the CH groups of the benzene molecule are progressively replaced by the isoelectronic nitrogen atom, has made possible a comparison with quantum-mechanical prediction. The compounds investigated in the gas phase are benzene (Nordheim, Sklar, and Teller, *J. Chem. Physics*, 1939, **7**, 207), pyridine (Sponer, *Rev. Mod. Physics*, 1944, **16**, 244), pyrimidine (Uber, *J. Chem. Physics*, 1941, **9**, 777), and *s*-tetrazine (Koenigsberger and Vogt, *Physikal. Z.*, 1913, **14**, 1269). In solution, 2 : 6-diphenylpyrazine (Tutin and Caton, *J.*, 1910, **97**, 2524) and pyridazine (Evans and Wiselogle, *J. Amer. Chem. Soc.*, 1945, **67**, 79) have been studied. In the case of benzene and pyridine, the long wave-length ultra-violet absorption bands have been analysed, and the respective origins are at 2600 and 2900 A. Pyridine is of interest in that there is a relatively large shift in wave-length (*ca.* 300 A.) on changing from solution in hexane to the gas phase. The data for pyrimidine and *s*-tetrazine have not been analysed, and the absorption maxima are estimated to lie at 3100 and 5200 A., respectively. For 2 : 6-diphenylpyrazine and pyridazine the published absorption curves would suggest that the absorption maxima lie at 3160 and 3380 A. Since the last two substances have been measured in solution, the data are not strictly comparable with those for the former compounds, which were investigated in the gas phase. From the experimental results it may be concluded that the substitution of CH groups in a benzene ring by nitrogen atoms leads to a shift of the long wave-length electronic band towards the red. The effect is most marked when the nitrogen atoms occupy adjacent positions.

The foregoing data suggested an application of the valence-bond method to the series of molecules under consideration. This method was adapted by Pauling (*J. Chem. Physics*, **1933**, **1**, 280) for calculating the ground states of complex molecules, and Sklar (*ibid.*, **1937**, **5**, 669) was the first to utilise it in connection with the excited states. These calculations yield both the resonance energy and the wave-lengths of maximum absorption of the electronic bands. The valence-bond method assumes that in a conjugated system the s, p_x, p_y electrons of each atom taking part in the conjugation hybridise to form a trigonal framework, while the p_z electrons are free to couple in a number of different ways. This gives rise to spin degeneracy, and the required energy levels are the roots of the quantum-mechanical secular equation. For the molecules in question, this can be set up in terms of the five canonical structures and thus will be of the fifth degree. However, as in the case of benzene, group theoretical methods lead to a simplification of the secular equation in those cases where the molecule possesses elements of symmetry other than the plane of the ring. As distinct from benzene, however, three different types of exchange integrals will occur: the C–C integral α, the C–N integral β, and the N–N integral γ, if the usual assumptions of the valence-bond method are made, namely, the neglect of ionic structures and exchange integrals between non-adjacent atoms. Hence, the resonance energy and light absorption of these molecules can be calculated in terms of three empirically determined constants, α, β, γ. Rather than solve the complete secular equation at this stage, recourse will be had to the method used by Förster (*Z. physikal. Chem.*, **1938**, **41**, *B*, 287) in treating a series of polycyclic aromatic hydrocarbons. In this treatment, which is justified by the agreement with experiment, the approximation of only considering Kekulé-type (unexcited) structures was introduced. For the molecules under consideration, the secular equation reduces to a quadratic, which will in turn reduce to two linear factors when the two Kekulé structures are equivalent. The equations for the energy levels resulting from this treatment are given in the Appendix. The difference between the energy of the ground state and its value if only one Kekulé structure is considered is the resonance energy, while the energy difference between the two calculated states corresponds to the long wave-length electronic absorption band.

The constants used in the calculation are: α, 1·97, β, 1·38, and γ, 0·20 v.e. The energy difference for pyridazine and s-tetrazine does not depend very greatly upon γ and so its value cannot be considered to be very accurate. By using these values, the results shown in the table are obtained. The agreement between the observed and calculated absorption maxima is good in view of the approximations involved. The only data with which the calculated resonance energies can be compared are for benzene and pyridine. Wheland ("The Theory of Resonance," Wiley, New York, 1944) gives the value 41 Kcals. for benzene and 43 and 37 Kcals. for pyridine. If the latter value for pyridine is accepted, and it would appear reasonable to do so in view of the hygroscopic nature of pyridine, the agreement is satisfactory.

Calculated and observed wave-lengths of the first absorption bands, and the calculated resonance energies of some heterocyclic molecules.

Molecule.	Wave-length, A. Calc.	Obs.	Resonance energy (Kcals.).	Molecule.	Wave-length, A. Calc.	Obs.	Resonance energy (Kcals.).
Benzene	2600	2600	41	Pyridine	2900	2900	37
	Diazines.				Triazines.		
Pyrimidine	3240	3100	33	*s*-Triazine	3700	—	29
Pyrazine	3240	3160 [a]	33	*vic.*-Triazine	4330	—	25
Pyridazine	3360	3380	22 [b]	*as*-Triazine	3830	—	18 [c]
	Tetrazines.						
s-Tetrazine	5200	5200	20	Pentazine	8650	—	12
as-Tetrazine	5200	—	20				
vic.-Tetrazine	5300	—	10 [c]				

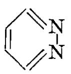
a. This value is for 2 : 6-diphenylpyrazine. *b.* Relative to the structure containing =N—N=. *c.* Relative to the structure containing =CH—CH=.

Evans and Wiselogle (*loc. cit.*) have pointed out the non-equivalence of the Kekulé structures for pyridazine. The same is true of *as*-triazine and *vic.*-tetrazine. It is of interest to calculate the relative importance of the two structures in these cases. The zeroth order (un-normalised) wave functions are:

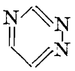
Pyridazine $\psi = \psi_A + 1{\cdot}39\,\psi_B$ *vic.*-Tetrazine $\psi = \psi_A + 1{\cdot}72\,\psi_B$

as-Triazine $\psi = \psi_A + 1{\cdot}47\,\psi_B$

the three more stable structures being (I), (II), and (III), respectively.



(I.)



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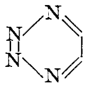

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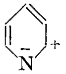
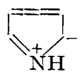


(IV.)

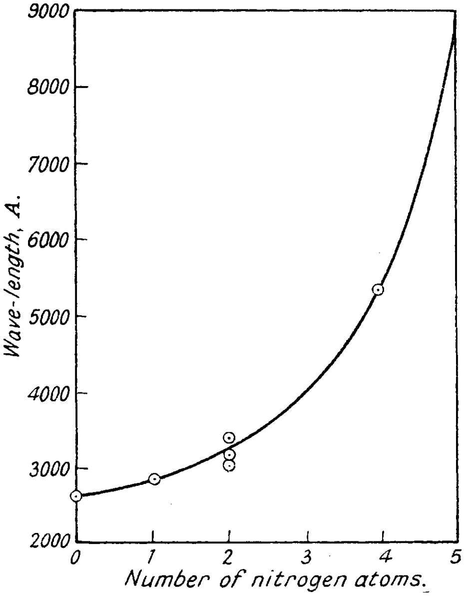


(V.)

Bowen (*Ann. Reports*, **1943**, **40**, 25) has commented upon the way in which N can replace CH in a compound with little effect upon its absorption spectrum. He quotes the case of anthracene and acridine, which have very similar absorption spectra. However, the present calculations would suggest that the similarity in spectra is due rather to the buffering effect of the two fused benzene rings. The effect of the successive replacement of CH groups by nitrogen atoms in a benzene ring is shown in the figure, where the mean wave-length of the first absorption band of the molecules $[CH]_nN_{6-n}$ is plotted against the number of nitrogen atoms.

The neglect of ionic structures in the quantum-mechanical calculation must be more serious in the case of molecules involving C–N bonds than in the case of benzene. Because of the electronegativity of nitrogen, structure (IV), placing a negative charge on a nitrogen atom, would be stabilised. However, as Sklar (*loc. cit.*) has pointed out, ionic structures are highly excited and would be expected only to contribute appreciably to the higher energy states of the molecule. The case of 1 : 3-*cyclo*pentadiene and pyrrole is of interest in this connection. The resonance energy of pyrrole is 24 Kcals., while that of *cyclo*pentadiene is only 3 Kcals. (Wheland, *loc. cit.*). The differences lies in the fact that the nitrogen atom in pyrrole has a lone pair of electrons which can give rise to ionic structures like (V), whereas this possibility is absent in *cyclo*pentadiene. This is presumably responsible for a shift in the wave-length of maximum absorption from 2300 A. for *cyclo*pentadiene to 1800 A. for pyrrole (Price and Walsh, *Proc. Roy. Soc.*, 1941—1942, **179**, *A*, 201). That the ionic structures play a large part in pyrrole is also shown by the high intensity of absorption as compared with pyridine. Whereas in pyrrole the adverse charge distribution is outweighed by the formation of a double bond, in pyridine a desirable charge distribution has to be weighed against the decrease in stability due to the loss of a bond. The evidence is thus not inconsistent with the ground and first states of the pyridine molecule being mainly of a covalent character.

Calculations are proceeding with zeroth order wave functions including the five canonical structures. Preliminary results lead to the conclusion that pyridine on controlled reduction should form 1 : 4-dihydropyridine, while reduction of quinoline should first occur in the ring containing the nitrogen atom, in agreement with experiment. The use of the full canonical set gives rise to a differentiation of the energy levels of pyrimidine and pyrazine, which are equivalent when only the Kekulé-type structures are considered. It is also hoped to extend the treatment now described to other heterocyclic compounds.



Absorption maxima of the molecules $[CH]_nN_{6-n}$. *The smooth curve passes through the calculated points, the experimental points being shown in circles.*

APPENDIX.

The Solution of the Secular Equations.—(a) *The secular equation reduces to two linear factors :*

$$x = 0$$

$$x = -0{\cdot}8(p + q + r).$$

Molecule.	*p*.	*q*.	*r*.	Molecule.	*p*.	*q*.	*r*.
Benzene	1	1	1	*vic.*-Triazine	1	a	b
Pyridine	1	1	a	*s*-Tetrazine *as*-Tetrazine	a	a	b
Pyrimidine Pyrazine	a	a	1	Pentazine	b	b	a
s-Triazine	a	a	a				

(b) *The secular equation is quadratic :*

(i) Pyridazine.

$$15x^2 + (18 + 12a + 6b)x + [6 - 4(a - b)](8a - 2b) - (3 + 2a + b)^2 = 0$$

(ii) *as*-Triazine.

$$15x^2 + (6 + 24a + 6b)x + (4 - 2a + 4b)(- 2 + 10a - 2b) - (1 + 4a + b)^2 = 0$$

(iii) *vic.*-Tetrazine.

$$15x^2 + (6 + 12a + 18b)x + [6b - 4(a - 1)](8a - 2) - (1 + 2a + 3b)^2 = 0$$

where $x = (Q - W)/\alpha$, $a = \beta/\alpha$, $b = \gamma/\alpha$, W being the energy of the molecule and Q the Coulomb integral.

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UNIVERSITY OF SYDNEY, AUSTRALIA.
SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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