[Contribution from the Wm. H. Chandler Chemistry Laboratory, Lehigh University]

COMPARISON OF THE ULTRAVIOLET ABSORPTION SPECTRA OF NAPHTHALENE, PHTHALAZINE, AND CINNOLINE

E. D. AMSTUTZ

Received June 16, 1952

The ultraviolet absorption spectrum of cinnoline (III) has recently been reported (1) and it now becomes possible, using the data of the present paper, to compare the spectrum of napththalene (II) with those of its two *vicinal* diaza derivatives.

Table I lists the main ultraviolet absorption bands for each of the three compounds.

TABLE I

Ultraviolet Absorption Bands

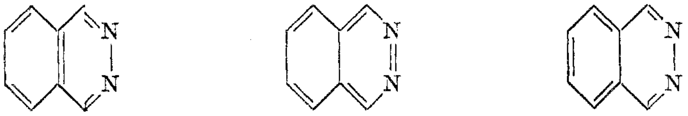
cinnoline[a]		naphthalene[b]		phthalazine[c]	
λ, mμ	log ε	λ, mμ	log ε	λ, mμ	log ε
275.5	3.45	257	3.55	252	3.629
286	3.42	265	3.70	259	3.668
308.5	3.29	275	3.75	267	3.587
317	3.247	283	3.564	290	1.108
322.5	3.318	285	3.568	296.5	1.061
390	2.43				

[a] Solvent used was cyclohexane. [b] Solvent used was isooctane. [c] Solvent used was methylcyclohexane.

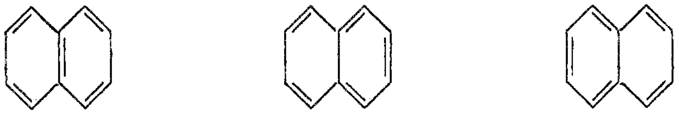
Phthalazine and naphthalene are clearly very similar with the latter showing slightly greater absorbency. It is significant, too, that the strong bands of phthalazine occur at somewhat shorter wavelengths than those of naphthalene. Cinnoline bands on the other hand, are considerably shifted to longer wavelengths and are somewhat weaker than those of naphthalene. Cinnoline also exhibits a group of three fairly strong bands in the 310–320 mμ region at which frequency the other two are transparent.

The hypsochromic shifts of phthalazine bands with respect to naphthalene appear to be similar to those observed (2) in certain open chain or linear analogs. Thus, it has been found that benzalazine absorbs at 301 mμ and 1,4-diphenylbutadiene at 334 mμ in spite of the fact that the isolated imine structure is a stronger chromophore than the isolated ethylenic bond (3). Lewis and Calvin, as well as Ferguson, believe the explanation of this anomaly is to be found in the high potential energy (strain) of the azo linkage present in several of the excited ionic species. Blout, on the other hand argues that the nitrogen atoms of the azine, because of their tendency to acquire negative charges, effectively shorten the length of the excited system in an activated structure. Certainly both of these concepts can be employed to advantage to understand the spectral differences between phthalazine, naphthalene, and cinnoline.

It is considered that the ground states of phthalazine and naphthalene are hybrids of the usual Kekulé types. The ground state of phthalazine may be slightly above that of naphthalene due to the contribution of the higher energy form possessing the —N=N— linkage. Resonance would therefore be somewhat restricted. (Ionic forms may make some relatively slight contribution to the ground state of phthalazine but this may be disregarded.)



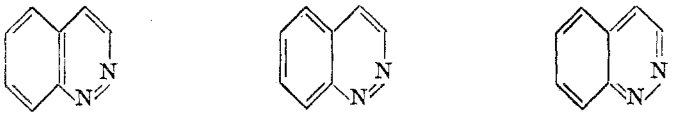
I



II

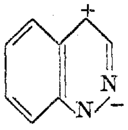
Because nitrogen atoms tend to acquire negative charges in the excited states phthalazine would show a greater tendency to polarize 1–2 than would naphthalene. Thus the length of the excited system in phthalazine would be shorter than in naphthalene and would therefore require the absorption of shorter wavelength (or more energetic) radiation.

The structures which contribute to the cinnoline hybrid are much less stable than those of phthalazine due to the contribution of the quinoidal benzene and pyridazine rings and the azo structure.

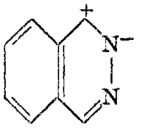


III

The ground state of cinnoline would therefore be expected to be considerably above that of phthalazine. The main excited states for cinnoline (IV) and phthalazine (V) differ also in the ease with which they are produced.



IV



V

The formation of IV would be expected to be accomplished more easily (less energetic radiation) than V because of the larger system involved in the polarization. Thus, the first excited state for cinnoline would be lower than that for phthalazine 1.[1] It is clear that consideration of both ground and excited states leads to the conclusion that cinnoline should absorb at longer wavelengths than phthalazine. If one assumes that the maximum absorption bands represent comparable transitions for cinnoline and phthalazine then the energy difference

---

[1] There are some 43 other excited structures for cinnoline and 39 other ionic structures for phthalazine. Detailed consideration of these does not add appreciably to the understanding of the spectra.

between ground and excited states for cinnoline is about 7 Kcal less than for phthalazine.

It is entirely probable that similar spectral differences will be found among other isomeric *ortho*-diaza hydrocarbon systems. The results here suggest that for polynuclear condensed-ring systems that isomer having the greatest number of Kekulé forms containing nitrogen-nitrogen double bonds will absorb light at the longest wavelengths. For example, 1,2- or 3,4-diazaphenanthrene should absorb closer to the visible than the 2,3-isomer. The extent of the bathochromic shift is proportional to the extent of the incompatibility of the various electronic strains in the molecule and would be a measure of the relative bond orders in the parent hydrocarbon. Examination of the spectra of 4,5- and 5,6-diazaindans would reveal the extent of "bond fixation" in indan and provide additional evidence regarding the Mills-Nixon Effect.

EXPERIMENTAL

Phthalazine was prepared in excellent yield by the condensation of phthalaldehyde with hydrazine hydrate in the usual way. The colorless crystals melted at 89–90°. Gabriel and Pinkus (4) reported m.p. 90–91°.

Spectra were obtained on a Beckman model D U spectrophotometer.

SUMMARY

It has been shown that the U V absorption maxima of cinnoline differ significantly from those of phthalazine. Reasons are given for believing that the maxima displacements are due to differences in both the ground and excited states of the molecules. It is suggested that examination of the spectra of isomeric condensed *ortho*-diaza systems may provide a useful probe for bond multiplicity.

BETHLEHEM, PENNA.

REFERENCES

(1) HEARN, MORTON, AND SIMPSON, *J. Chem. Soc.*, 3318 (1951).

(2) LEWIS AND CALVIN, *Chem. Revs.*, **25**, 273 (1939); FERGUSON AND GOODWIN, *J. Am. Chem. Soc.*, **71**, 633 (1949); BLOUT AND FIELDS, *J. Am. Chem. Soc.*, **70**, 189 (1948).

(3) FERGUSON, *Chem. Revs.*, **43**, 385 (1948).

(4) GABRIEL AND PINKUS, *Ber.*, **26**, 2210 (1893).