[Contribution from the Courtauld Institute of Biochemistry]

Absorption Spectra of Indigoid Dyes

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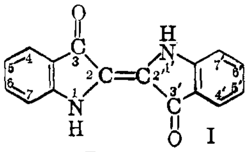
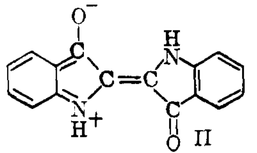
Modification of the absorption spectrum of indigo, produced by substitution in the benzene rings, has been investigated and the results have been discussed in terms of a simple valence bond treatment. The spectrum of indigo shows two main peaks λ_1 (visible) and λ_2 (ultraviolet); the effects of substitution on λ_2 are slight, the changes in λ_1 being of greater significance. Generally, substituents in either the 5- or 6-positions produced equal and opposite effects in λ_1. The effects of substitution in the 7- or 4-positions were found to be unpredictable.

Van Alphen[1,2] and Eistert[3] first suggested indigo to be a resonance hybrid of several canonical forms (I–IV)



I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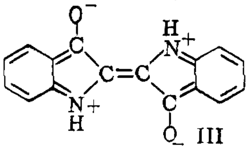
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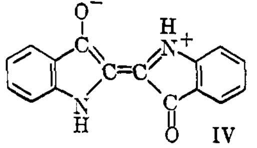
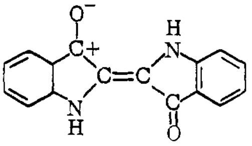

IV

Pauling[4] considered that significant contributions were also made by V and VI.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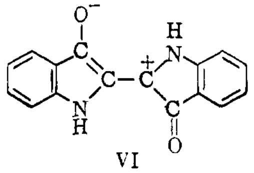

VI

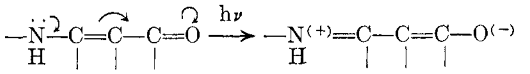
Van Alphen postulated that structures I, II, the mirror image of II, and III were responsible for the intense color of indigo, II being considered to predominate in the monomolecular state in indigo vapor and III to be the main contributor in the crystalline form. That resonance involving relatively unstable structures with separated charges is mainly responsible for the production of color in indigo, is confirmed by the effect of solvent upon the position of absorption maxima. Indigo shows the normal merocyanine effect (Table I), namely it absorbs at lower frequencies with increasing dielectric constant of the medium. This trend toward longer wavelengths, results from the greater stability, hence an increasing contribution, of the ionic structures in the more polar solvents.

TABLE I

Indigo: Variation in Ultraviolet Absorption in Solvents

Solvent	Dielectric constant at 20°	λ_1 mμ
Vapor at 320°	—	546
Xylene	2.4	591
Tetralin	2.8	601
Chloroform	5.0	605
Acetic acid	6.4	616
Aniline	7.3	630
Solid	—	678

The effects of resonance may only be predicted by considering separately the energy changes brought about in the ground and excited states.[5,6] The smaller difference in energies of the ground and excited states the lower is the frequency, or the longer is the wavelength, of the light absorbed. It is not the magnitude of the resonance energy of a substance which determines λ_{max}[7] but whether the resonance stabilizes the excited states more than the ground state.[8] Presumably, Kekulé resonance is mainly responsible for stabilization of the ground state, together with some contribution from structures involving small separation of charge on the carbonyl groups and adjacent carbon atoms *e.g.* V and VI. In the excited state several ionic structures with large separation of charge must be involved. These forms arise by the absorbed light energy causing charge separation by the mechanism.....



$$\underset{H}{-\ddot{N}}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=O \xrightarrow{h\nu} \underset{H}{-N^{(+)}}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-O^{(-)}$$

as in II, III, and IV.

Analogy with other compounds,[1,3] or the study of the effects of substitution, does not provide sufficient evidence to decide which of these structures contributes most to the excited state.

Substituents may affect the energy level of the excited state either by (a) increasing or (b) dimin-

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(1) Van Alphen, *Rec. trav. chim.*, **60**, 138 (1941).

(2) Van Alphen, *Chem. Weekblat.*, **35**, 438 (1938).

(3) Eistert, *Tautomerie and Mesomerie*, Stuttgart (1938), p. 189.

(4) Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939).

(5) Price, *Chem. Revs.*, **41**, 257 (1947).

(6) Walsh, *Trans. Faraday Soc.*, **43**, 158 (1947).

(7) Macoll, *J. Chem. Soc.*, 670 (1946).

(8) Rodebush, *Chem. Revs.*, **41**, 317 (1947).

ishing electron release from the nitrogen atom or electron withdrawal by the carbonyl group. Provided that the substituents have relatively little influence on the ground state it would be expected that (a) would lower the energy of the excited state, thus causing a shift in the absorption maximum to longer wavelengths; the reverse being the case for (b).

Table II contains the main absorption-spectra data for some of the 5,5'-substituted dyes. It can be seen that all the substituents quoted produce bathochromic shifts in λ_1, with the exception of 5,5'-dinitroindigo which produces a marked hypsochromic shift and is in fact quite red. In this molecule structure VII presumably contributes considerably to the resonance in the excited state, diminishing the availability of electrons on the nitrogen atom and reducing their tendency to flow to the carbonyl group. Hence, the energy of the excited state is raised in relation to the ground state and absorption takes place at shorter wavelengths. The reverse is the case for the other substituents quoted in Table II, *e.g.* chloride in the 5-position tends to increase the availability of electrons on the nitrogen atom, their transfer to the carbonyl group being facilitated, causing a smaller energy difference between the excited and ground states and therefore producing a bathochromic shift in λ_1.

TABLE II

Absorption Spectra Data of 5,5'-Substituted Indigoid Dyes in Tetrachlorethane

Substituents	λ_1 mμ	ϵ_1	λ_2 mμ	ϵ_2
None	605	16,580	285	25,500[a]
5,5'-Dinitro	580	—	290	— [9]
5,5'-Dimethyl	620	14,340	295	27,150[10]
5,5'-Difluoro	615	17,820	300	18,500[11]
5,5'-Dichloro	620	17,950	290	35,260[12]
5,5'-Dibromo	620	18,050	290	36,250[13]
5,5'-Diiodo	610	—	295	— [14]
5,5'-Dimethoxy	645	—	305	— [13]

[a] The references in Tables II, III and IV refer to the synthesis of these compounds not to their spectra.

In general, substituents in the 6,6'-positions in indigo produce equal and opposite effects to those in the 5,5'-positions. The shoulder to the λ_2 peak forms a third peak in these compounds at 400 mμ due to the conjugation of the substituent in the 6-position with the carbonyl group as in VIII. The principal spectral data for some 6,6'-substituted dyes are given in Table III.

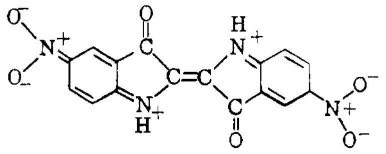
TABLE III

Absorption Spectra Data of Some 6,6'-Substituted Indigos in Tetrachlorethane at 20°

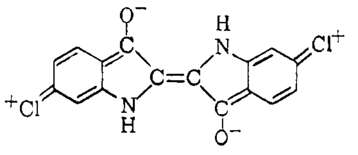
Substituents	λ_1 mμ	ϵ_1	λ_2 mμ	ϵ_2
None	605	16,580	285	25,500[a]
6,6'-Dinitro	635	—	290	— [15]
6,6'-Dimethyl	595	8,750	285	22,000[16]
6,6'-Diiodo	590	19,100	290	— [17]
6,6'-Dibromo	590	17,300	305	29,030[13]
6,6'-Dichloro	590	14,860	305	26,370[18]
6,6'-Difluoro	570	12,920	295	17,020[b]
6,6'-Dimethoxy	570	10,480	282.5	22,110[13]

[a] See footnote *a*, Table II. [b] New compound.

With the exception of 6,6'-dinitroindigo, the substituents in Table III all produce a hypsochromic shift in λ_1. This may be explained by structures such as VIII being the main contributors to the resonances of the excited state. This would discourage the flow of electrons from imino- to carbonyl-groups, thus raising the energy of the excited state in relation to the ground state and thereby causing absorption to occur at shorter wavelengths. The reverse is the case for the 6,6'-dinitro-compound, a bathochromic shift resulting.



VII



VIII

Since similar valence bond structures may be written for the 4,4'-substituted dyes as for the corresponding 6,6'-compounds, a substituent in either the 4- or 6-position would be expected to have the same influence on the absorption spectra, but reference to Table IV shows that this is not the case. It is unlikely that there is a difference in energy between the ground states of the 4,4'- and 6,6'-substituted compounds but in the 4,4'-series there may be an additional *ortho*-inductive effect between the substituent and the carbonyl group. The same lack of agreement occurs between

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(9) Baeyer, *Ber.*, **12**, 1316 (1879).

(10) Meyer, *Ber.*, **16**, 924 (1883).

(11) Roe and Teague, *J. Am. Chem. Soc.*, **71**, 4019 (1949).

(12) Mettler, *Ber.*, **38**, 2809 (1905).

(13) Friedländer, Brückner, and Deutsch, *Ann.*, **388**, 34 (1912).

(14) Borsche, Weuszmann and Fritzsche, *Ber.*, **57**, 1770 (1924).

(15) Schwarz, *Monats.*, **26**, 1261 (1905).

(16) Kuhara and Chicashige, *Am. Chem. J.*, **27**, 1 (1902).

(17) Kalb and Vogel, *Ber.*, **57**, 2105 (1924).

(18) Sachs and Sickel, *Ber.*, **37**, 1861 (1904).

the 5,5′- and 7,7′-substituted compounds, for instead of the bathochromic shifts observed in the 5,5′- series, 7,7′-dichloro-, 7,7′-dibromo-, and 7,7′-diiodoindigo have spectra little different from the unsubstituted compound. It is significant, however, that the strongly electronegative fluoro- and trifluoromethyl-groups *ortho* to the imino-group produce marked hypsochromic shifts.

Although the treatment given above fails to explain the shifts in λ_1 of 4,4′- and 7,7′-substituted indigoid dyes, it finds support in the N,N′-substituted alkyl and acyl compounds. Electron-releasing substituents on the nitrogen atom should produce bathochromic shifts in λ_1, as in fact they do, for N,N′-dibenzyl-, N,N′-dimethyl-, and N,N′-diphenyl-indigo have λ_1 at 660 mμ, 645 mμ, and 630 mμ respectively (indigo 605 mμ). N,N′-Dibenzoyl- and N,N′-diacetyl-indigo (*i.e.* groupings which tend to withdraw electrons from the nitrogen atoms) produce hypsochromic shifts having their absorption maxima at 575 mμ and 545 mμ respectively.

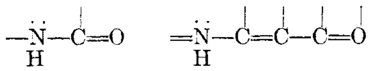
TABLE IV

Absorption Spectra Data for Some 4,4′- and 7,7′-Substituted Indigos in Tetrachloroethane at 20°

Substituents	λ_1 mμ	ϵ_1	λ_2 mμ	ϵ_2
4,4′-Diiodo	620	24,640	297.5	33,140[a, b]
4,4′-Dibromo	610	25,600	292.5	39,330[13]
4,4′-Dichloro	610	25,590	290	39,130[19]
4,4′-Di(trifluoromethyl)	605	8,970	295	16,200[b]
None	605	16,580	285	25,500
7,7′-Diiodo	605	14,220	300	29,370[b]
7,7′-Dibromo	605	20,770	293.5	41,030[13]
7,7′-Dichloro	600	20,550	291	40,020[b]
7,7′-Di(trifluoromethyl)	580	14,470	307.5	22,700[b]
7,7′-Difluoro	560	8,640	275	46,890[11]

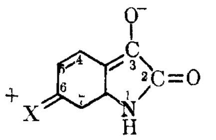
[a] See footnote *a*, Table II. [b] New compound.

These shifts in λ_1 produced by nuclear substitution are general for colored compounds of this class; *e.g.* isatins, indigos, and indirubins, containing either of the following groupings.

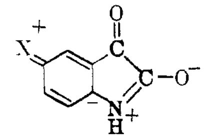


$$-\overset{..}{\underset{H}{N}}-\overset{|}{C}=O \qquad =\overset{..}{\underset{H}{N}}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$$

Mangini and Passerini[20] report three absorption bands (A), (B), and (C) for isatin at 242 mμ, 298 mμ, and 416 mμ respectively, the spectrum being recorded in concentrated sulphuric acid 1: 100,000. Band (A) is attributed by these authors to excitation of the benzene ring, (B) to the carbonyl group and its conjugation with the substituent in the 6-position according to formulae (IX), *cf.* VIII, and a similar but smaller effect due to the 4-substituent. Band (C) was referred to the $-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-$ grouping in conjugation with the 5-, and less distinctly the 7-, substituent according to structure X. This latter band corresponds to the λ_1 band of indigo and is subject to similar shifts in nuclear-substituted isatins as is λ_1 in nuclear-substituted indigoid dyes.



IX



X

For example, 5-methyl-, 5-chloro-, and 5-methoxy-isatin have maxima at 424 mμ, 430 mμ, and 460 mμ respectively (isatin 416 mμ), whereas the corresponding substituents in the 6-position produce hypsochromic shifts having maxima at 416 mμ, 405 mμ, and 404 mμ. A further similarity to the indigo series exists in that discrepancies sometimes occur between the effects produced by 5- or 7- substitution, *e.g.*, 5-chloroisatin has (C) at 430 mμ (a bathochromic shift of 14 mμ) whereas 7-chloroisatin has (C) at 405 mμ (a hypsochromic shift of 11 mμ).

Similar effects are also found in the spectra of substituted thioindigo dyes as shown by some symmetrical dichloro- and dibromo-derivatives.[21] 5,5′-Dichloro- and 5,5′-dibromo-thioindigo have λ_1 at 550 mμ and 559 mμ respectively (thioindigo 546 mμ) and the corresponding 6,6′-compounds both have λ_1 at 541 mμ, the spectra being recorded in tetralin. Contrary to the opinion of Wyman and Brode,[22] hypsochromic shifts in λ_1 are common to all indigoid type dyes containing electron-releasing substituents in the 6-position. This is readily explained by the theory outlined above.

EXPERIMENTAL

The substituted indigoid dyes were prepared from the corresponding diacetylindoxyl compounds by alkaline hydrolysis and air oxidation in the usual way. The synthesis of the indoxyl compounds is to be described elsewhere.

Spectra. Concentrations of about 10 mg. per liter were used, and the spectra were recorded in a Hilger "Uvispek" spectrophotometer using the solvent as reference in 1-cm. matched quartz cells at 20°. For the very sparingly soluble dyes, supersaturated solutions containing 1–2 mg. per liter were prepared and the spectra were recorded at 20° in 4 cm. cells.

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[19] Gindraux, *Helv. Chim. Acta*, **12**, 921 (1929).

[20] Mangini and Passerini, *Boll. sic. fac. Chim. Ind. Bologna.*, **9**, 51 (1951).

[21] Formanek, *Z. angew. Chem.*, **41**, 1133 (1928).

[22] Wyman and Brode, *J. Am. Chem. Soc.*, **73**, 1493 (1951).