Photochromism and Reversible Multiple Internal Transitions in Some spiro*Pyrans at Low Temperatures. Part II.**

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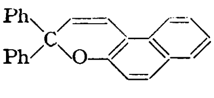
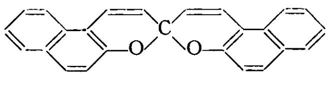
The investigations described in Part I were extended to additional compounds. Under appropriate conditions each photochromic compound gives rise to one or more coloured modifications, all of which spontaneously revert to the original colourless modification at rates depending on the temperature. Thermochromic and photochromic absorption spectra are recorded and compared. Heats of interconversion of coloured and colourless modifications are estimated. In several cases the colour of the dyes formed by ultra-violet irradiation at low temperatures was found to depend reversibly on the temperature of measurement.

It is tentatively suggested that the various coloured modifications in each compound are stereoisomers.

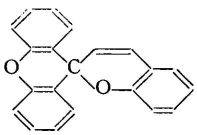
IN PART I of this series * photochromism was reported and discussed for a group of *spiro*-pyrans. The present paper describes an extension of this investigation to several related compounds, namely, those represented by the formulæ (I)—(VIII).



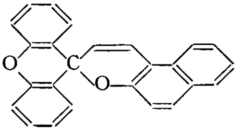
(I)



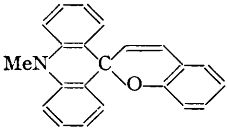
(II)



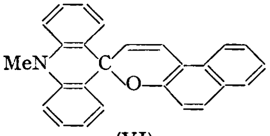
(III)



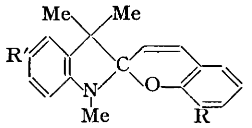
(IV)



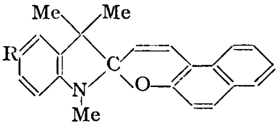
(V)



(VI)



(VII*a*) : R = R′ = H
(VII*b*) : R = R′ = OMe
(VII*c*) : R = H, R′ = OMe
(VII*d*) : R = OMe, R′ = H



(VIII*a*) : R = H
(VIII*b*) : R = OMe

Figs. 1 and 2 show the absorption spectra, at several temperatures, of those among the above compounds which exhibit thermochromism. The increase, with temperature, of the height and area of the curves again indicates a thermal equilibrium between a coloured and a colourless modification, the latter being at a higher energy level.

A comparison of the shape and height of the curves obtained for each compound in various solvents shows that (*a*) polar solvents shift the equilibrium in favour of the dye, and (*b*) in several cases the ratio between the heights of two peaks depends greatly on the solvent. Thus compound (VIII*a*) in dimethyl phthalate has a pronounced peak at 565 mμ and a smaller one at 540 mμ, whereas in diphenyl ether peaks of about equal height are found at 560 and 530 mμ and in decalin there is a shoulder at 555 and a peak at 520 mμ. Compound (VIII*b*) behaves similarly. With other compounds, only shifts towards shorter wavelengths were observed on passing from polar to non-polar solvents : however, these may

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* Part I, *J.*, 1954, 297.

also be due to a change in the ratio between two overlapping peaks. Some compounds show rather broad absorption bands and pronounced shoulders, indicating the co-existence of more than one coloured species [cf. compound (II)]. This assumption is supported by the photochromic absorption spectra described further on.

FIG. 1. *Absorption spectra of thermochromic compounds at several temperatures in dimethyl phthalate* (d.m.p.), *diphenyl ether* (d.p.e.) *or decalin* (d.).

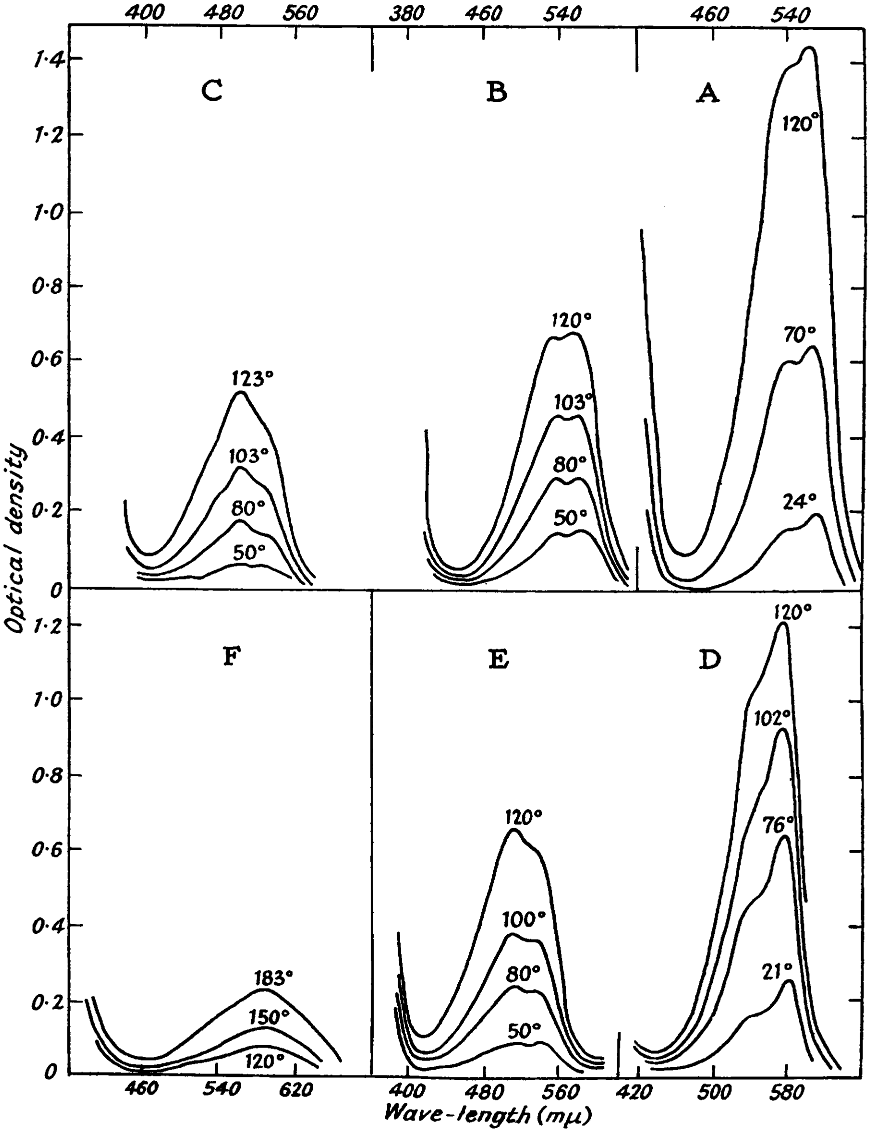


Fig.	Substance	Solvent	Concn. (g./l.)	Fig.	Substance	Solvent	Concn. (g./l.)
1*A*	(VIII*a*)	d.m.p.	1·4	1*D*	(VIII*b*)	d.m.p.	1·0
1*B*	,,	d.p.e.	1·4	1*E*	,,	d.	3·0
1*C*	,,	d.	3·7	1*F*	(VII*c*)	d.m.p.	3·0

Compounds (VII*a* and *b*) are not thermochromic, but heating to about 130° irreversibly converts them into dyes, the absorption spectra of which are somewhat similar to those of the related compound (VIII*b*) (Fig. 2).

The possible overlapping, in the observed absorption spectra, of several bands which may differ with regard to their dependence on temperature, makes it impossible to evaluate exactly the heat of conversion, ΔH, between coloured and colourless modifications from the curves given in Figs. 1 and 2. The values summarized in the following Table should therefore be regarded only as approximations. They were calculated from the rectilinear plots of log (maximal extinction coefficient) against the reciprocal of the absolute temperature.

FIG. 2. *Absorption spectra of thermochromic compounds at several temperatures in dimethyl phthalate* (d.m.p.), *diphenyl ether* (d.p.e.) *or decalin* (d.).

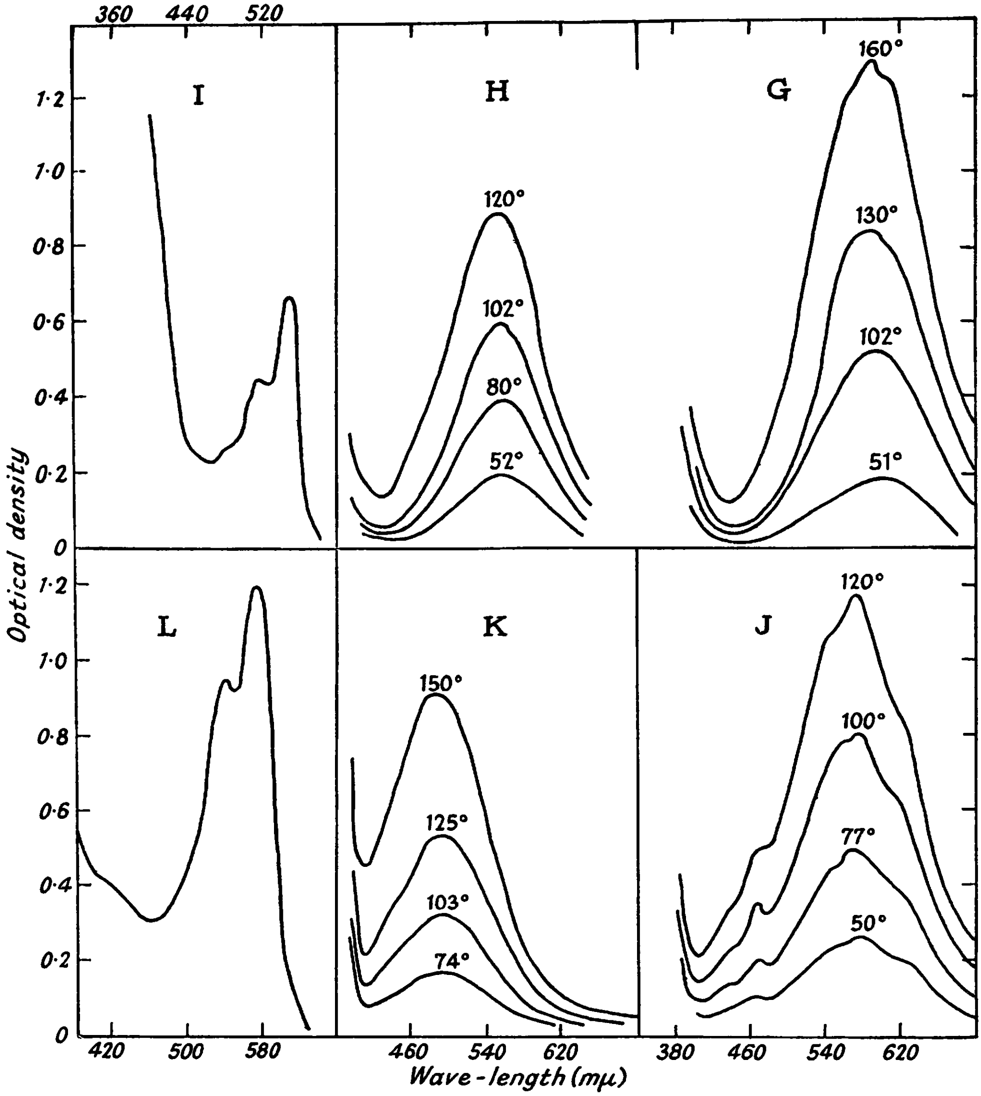


Fig.	Substance	Solvent	Concn. (g./l.)	Fig.	Substance	Solvent	Concn. (g./l.)
2*G*	(VI)	d.m.p.	0·4	2*J*	(II)	d.m.p.	1·2
2*H*	,,	d.	1·0	2*K*	(IV)	,,	3·5
2*I*	(VII*a*)	d.m.p.	3·0	2*L*	(VII*b*)	d.p.e.	1·3

All the compounds examined, except (I), (V), and (VII*a*), exhibit pronounced photochromism, *i.e.*, when their solutions are irradiated with ultra-violet light at low temperatures very intensely coloured dyes are reversibly developed. Figs. 3 and 4 (and their legends)

Compound	Solvent	$\lambda_{max.}$ (mμ)	ΔH (kcal./mole)
(II)	d.m.p.	580	5·3
(IV)	,,	495	6·4
(VI)	,,	590	5·1
(VI)	d.	560	5·5
(VII*c*)	d.m.p.	580	7·0
(VIII*a*)	,,	565	4·9
	d.p.e.	560	5·4
	d.	520	7·2
(VIII*b*)	d.m.p.	575	3·5
	d.	530	7·4

Solvents: d.m.p. = dimethyl phthalate; d.p.e. = diphenyl ether; d. = decalin.

give the absorption curves of the dyes produced under a variety of experimental conditions, as well as details about the luminescence of the dyes, and the spontaneous conversion of the various coloured modifications of each compound into one another. All the dyes, except $(\text{VII}b)_2$ and $(\text{VII}d)_2$, spontaneously revert to their colourless modifications at temperatures around −50°, the rate of this reversion depending on the temperature. With compounds (VII*b* and *d*) this occurs only around 0°.

The following Table indicates the order of magnitude of the molar extinction coefficients ε of the various dyes, the figures being obtained on the assumption that irradiation at low temperatures results in complete transformation into the dye (cf. Part I) [solutions in methyl*cyclo*hexane, but (VII*b* and *d*) in ethanol]:

Compound	(II)	(III)	(IV)	(VI)	(VII*b*)	(VII*c*)	(VII*d*)	(VIII*b*)
10^{-3} ε ...	44	21	115	30	5	23	6	46

Comparison of these values with the apparent ε which may be calculated from the data presented in Figs. 1 and 2 permits the estimation of the percentage of thermal conversion into the respective dyes for the thermochromic compounds.

The results given in Figs. 3 and 4 are in many respects similar to those reported in Part I. The following facts, however, merit special mention.

In several cases only irradiation with the full mercury arc ("full" irradiation) was effective, but in most compounds already the 365 mμ group transmitted by a Wood's filter ("Wood" irradiation) produced the dyes. In (VI), progressive irradiation at −100° results, first, in a single maximum at 560 mμ, and then in an additional band at 690 mμ. At −170° irradiation produces only the latter band.

Compounds (III), (VII*c*), and (VIII*b*) show a new phenomenon. Whereas the spontaneous conversions from one coloured modification into the other (on heating), as described hitherto, are thermally irreversible, the dyes formed from these compounds have absorption spectra depending on the temperature of the solutions. The effect is particularly pronounced with compound (VIII*b*). In solutions of this compound in methyl*cyclo*hexane–*iso*pentane, "Wood" irradiation at −180° produces the dye described by curve 1 for this compound in Fig. 4. Heating to about −135° converts this curve into curve 2, while further heating, to −100°, transforms it into 3. Recooling to −135° again produces 2, which is not changed by further cooling. The transformation $2 \rightleftarrows 3$ is thermally reversible.

This new type of thermochromism is especially interesting in view of somewhat similar effects observed with solutions of several *mero*cyanines structurally related to the above *spiro*pyrans (Hirshberg and Fischer, *J. Chem. Phys.*, 1954, **22**, 572).

Compounds (VII*b* and *d*) exhibit photochromism only when dissolved in alcohol, and not in methyl*cyclo*hexane, possibly because of an interaction between solute and solvent.

Comparison of Figs. 1 and 2 with Figs. 3 and 4 shows that in general those dyes which are formed thermally at elevated temperatures correspond to the dyes which are produced from the same compounds by ultra-violet irradiation at about −100°, or by irradiation at still lower temperatures followed by heating to about −100°.

Some of the maxima at longer wave-lengths in the photochromic absorption curves also appear, at least as shoulders, in the thermochromic spectra. Thus, (II) in Fig. 2 shows a distinct shoulder which corresponds to the maximum at 650 mμ existing in the photochromic curve of this compound (Fig. 3). The low temperatures at which photochromic spectra are

FIG. 3. *Absorption spectra of photochromic compounds under various conditions* (in methyl*cyclo*hexane–*iso*pentane unless otherwise stated).

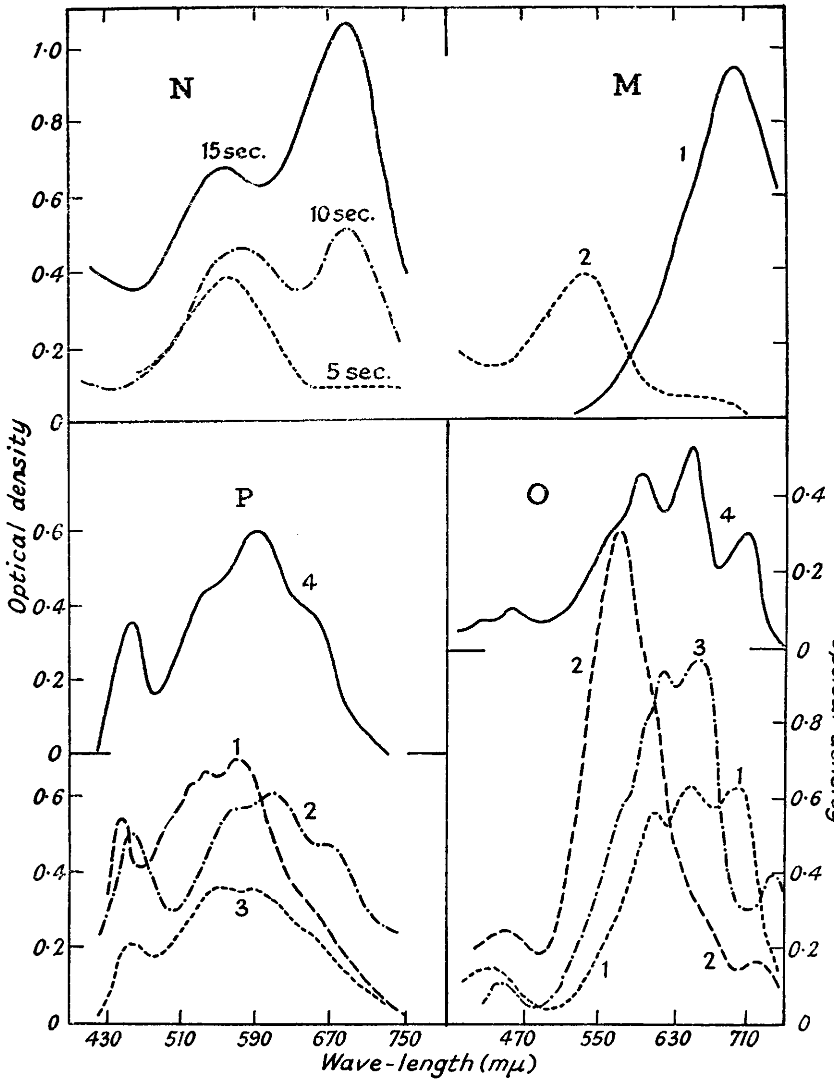


Fig.	Substance	Concn. (mg./l.)	Fig.	Substance	Concn. (mg./l.)
3*M*	(VI)	8	3*O*	(II)	8
3*N*	,,	8	3*P*	(III)	10

3*M* : curve 1, soln. after 2 min.' "Wood" irradiation at −170°; curve 2, soln. 1 heated to −135° and re-cooled (red luminescence).

3*N* : effect of progressive " Wood " irradiation at −100°; solutions were cooled to −170° after each irradiation period.

3*O* : curve 1, after 10 min. " Wood " irradiation at −170°; curve 2, soln. 1 heated to −140° and re-cooled to −170°; curve 3, soln. 2 heated to −100°, not changed when re-cooled to −170°; curve 4, soln. in ethanol–methanol after 5 min.' "Wood" irradiation at −130° (notes eparate scale). Curve 2 is also obtained by " Wood " irradiation at −140°.

3*P* : curve 1, soln. after 1 min.' " full " irradiation at −183°; curve 2, soln. 1 heated to −160° and re-cooled; curve 3, soln. 2 heated to −100°; states 2 and 3 are thermally interconvertible. Curve 4, soln. in ethanol–methanol after 1 min.' " full " irradiation at −160° (note separate scale), not changed when heated to −100°.

taken of course tend to sharpen the maxima, as compared with those measured at high temperatures. The appearance of the shoulder at 650 mμ shows that the energy level of the modification characterized by this band is not considerably higher than the modification possessing its main bands at 580 and 540 mμ.

FIG. 4. *Absorption spectra of photochromic compounds under various conditions* (in methyl*cyclo*-hexane-*iso*pentane unless otherwise stated).

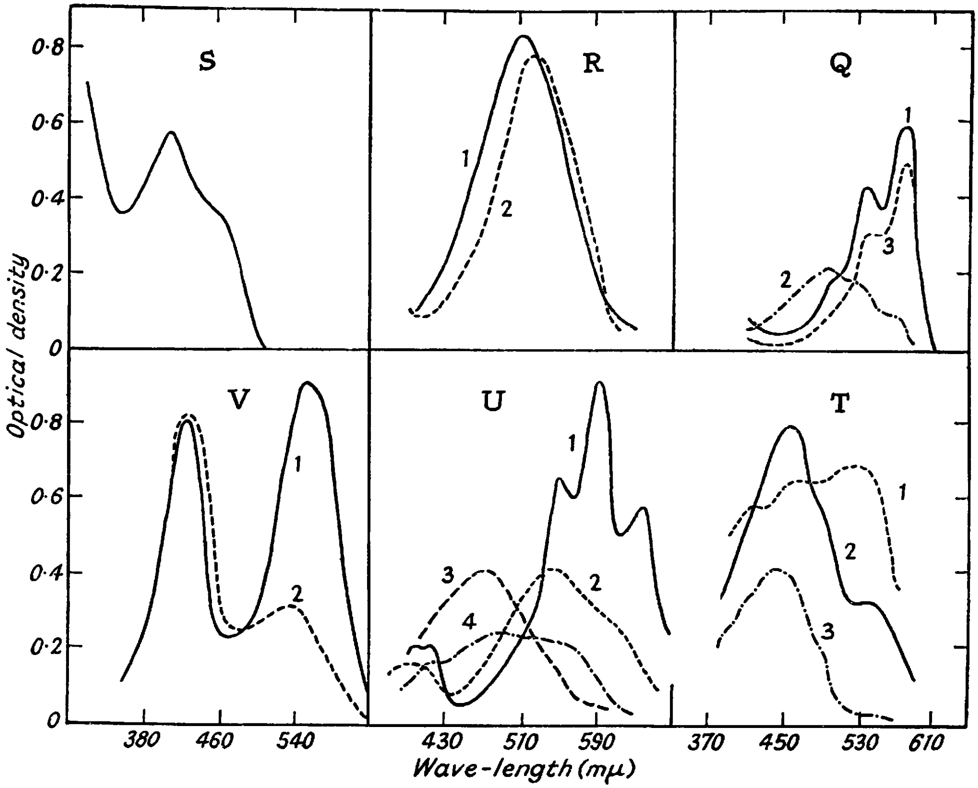


Fig.	Substance	Concn. (mg./l.)	Fig.	Substance	Concn. (mg./l.)	Fig.	Substance	Concn. (mg./l.)
4*Q*	VIII*b*)	10	4*S*	(VII*d*)	20	4*U*	(VII*c*)	15
4*R*	(IV)	1	4*T*	(VII*c*)	10	4*V*	(VII*b*)	80

4*Q* : curve 1, soln. after 15 min.' " Wood " irradiation at −180° (red luminescence); curve 2, soln. 1 heated to −135°, not changed by re-cooling (yellow luminescence); curve 3, soln. 2 heated to −100°; states 2 and 3 are thermally interconvertible.

4*R* : curve 1, soln. after 2 min.' " Wood " irradiation at −181°; curve 2, soln. 1 heated to −115° and re-cooled.

4*S* : soln. in ethanol–methanol after 5 min.' " full " irradiation at −160°. Thermal disappearance of colour starts only at about 0°.

4*T* : curve 1, soln. in ethanol–methanol after 3 min.' " full " irradiation at −150° (red luminescence), not changed when heated to −140°; curve 2, soln. 1 heated to −100° and re-cooled (yellow luminescence); curve 3, soln. 1 after 5 min.' " yellow " irradiation at −140° (yellow luminescence).

4*U* : curve 1, soln. after 10 min.' " full " irradiation at −183° (red luminescence); curve 2, soln. 1 heated to −170° (red luminescence); curve 3, soln. 2 heated to −105° (yellow luminescence); curve 4 soln. 3 heated to −70°; states 3 and 4 are thermally interconvertible.

4*V* : curve 1, soln. in ethanol–methanol after 5 min.' " full " irradiation at −150°; curve 2, soln. 1 heated to −85° and re-cooled.

Disappearance of the photochromic colours under " yellow " irradiation from a carbon arc (cf. Part I) was observed with compounds (VI), (VII*c*), and (VIII*b*). Preferential disappearance of one of two absorption bands is shown in Fig. 4 for compound (VII*c*). With the above compounds, just as with (VIII*a*) described previously, eradication of colour is much faster in alcoholic solutions.

Compound (VII*a*) is neither photochromic nor thermochromic, but shows another reversible effect of ultra-violet irradiation, analogous to photochromism. In solutions of (VII*a*) in methyl*cyclo*hexane–*iso*pentane at −183° no luminescence is excited by the 365 mμ mercury group. Irradiation with the full mercury arc at this temperature results in a strong pink luminescence, which becomes yellow when the solution is heated to about −120° and refrozen, and disappears when the solution is heated to room temperature and refrozen. This compound thus seems to be reversibly converted into a luminescent form, the existence of which does not depend on the rigidity of the solvent.

The behaviour of compound (V) is rather surprising. It differs from the related compounds (III) and (VI) in not being photochromic, and in exhibiting strong luminescence in the unirradiated state.

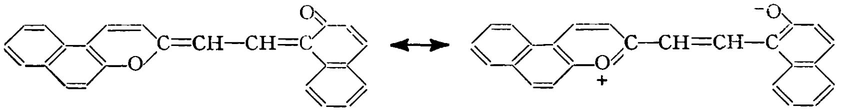
Additional experiments were undertaken to obtain direct evidence for the proposed high polarity of the dye formed on ultra-violet irradiation of compound (VIII*a*) (Fischer and Hirshberg, *J.*, 1952, 4522). Solutions of this compound at a concentration of about 1 g./l. in methyl*cyclo*hexane–decalin were irradiated between −70° and −100°, but without significant increase in the dielectric constant. No visible flocculation occurred under these conditions (cf. Part I), so that some other explanation must be sought for this observation. It should be recalled that under similar conditions solutions of the photochromic xanthylideneanthrone exhibit a pronounced increase in their dielectric constant (Hirshberg and Fischer, *J.*, 1953, 629).

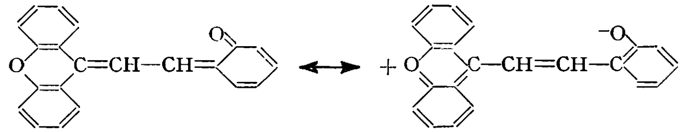
It is hoped to detect the expected effect in more dilute solutions by the application of a new technique suggested by Dr. E. H. Frei of this Institute. According to his method the absorption of polarised light in the respective solutions will be measured, with the latter being placed in a strong electric field.

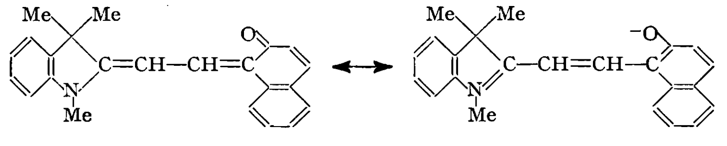
DISCUSSION

The various points raised in the discussion of Part I also apply to the present investigation, and will only be outlined here. In each compound the original spiran and the dyes produced from it at progressively decreasing temperatures represent progressively higher energy levels, a few kilocalories apart from each other and separated by potential barriers of 10—20 kcal. Indirect evidence for the high polarity of the dyes is provided by the difference between solvent effects in polar and non-polar solvents, and by the large molar polarisation observed for related *mero*cyanines (Bergmann, Weizmann, and Fischer, *J. Amer. Chem. Soc.*, 1950, **72**, 5009).

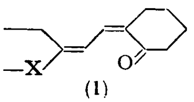
The existence of several dye modifications with each compound may be due to various electronically excited metastable states. Another tentative explanation may be that these dyes are geometrical isomers of the open, *mero*cyanine form postulated for all the coloured modifications (cf. Part I). For example, in analogy with the conclusions reached previously, the dyes corresponding to the compounds (II), (III), and (VIII) may be represented by the annexed formulæ, in which contributions of bipolar mesomers are indicated in each case :

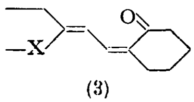

(II)

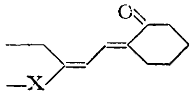

(III)

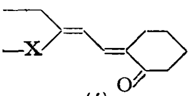

(VIII)

Resonance within these conjugated systems requires a more or less planar structure for the dye molecules, in which *cis–trans*-isomerism may occur both with regard to the central " single " bond and the two adjoining " double " bonds. The " *s* "-*cis*-form is in all cases ruled out for steric reasons. The four possible isomers with respect to the two double bonds are schematically indicated in the formulæ 1—4 for compounds (II) and (VIII) (X stands for oxygen or nitrogen) :

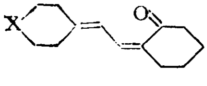

(1)

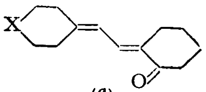

(3)


(2)


(4)

For compound (III) [and the analogous compounds (IV, V, and VI)] configurations 1 and 3, and 2 and 4, are identical, leaving 5 and 6 as the two possible structures :


(5)


(6)

The observed differences between the absorption curves of the postulated isomers are considerably larger than those commonly encountered among geometrical isomers, and may be due to differences in both the distance between the heteroatoms and the contribution of the two main mesomers, among at least some of the isomers of each compound. In accordance with the above reasoning less coloured isomers were found for compounds related to (III) than for those related to (II) and (VII). The low bond order of the two central " double " bonds may explain the easy spontaneous transformations of the isomers.

Coenen and Pestemer in a recent paper (*Z. Elektrochem.*, 1953, **57**, 785) report the isolation of several pairs of *cis–trans*-isomers in somewhat related *mero*cyanines. They found no significant difference between the absorption spectra of the isomers and concluded that the heteroatoms at both ends of the conjugated system do not participate in this conjugation. The present investigation shows that the situation is probably different in the compounds described here.

The existence of stereoisomers in symmetrical cyanine dyes has been assumed by H. Kuhn (*Helv. Chim. Acta*, 1951, **34**, 1308) and supported experimentally by Zechmeister and Pinckard (*Experientia*, 1953, **9**, 16).

EXPERIMENTAL

Solvents.—For work at low temperature a nonpolar solvent mixture of equal parts (by vol.) of methyl*cyclo*hexane and *iso*pentane was used. Both solvents were purified by treatment with sulphuric acid and passage through a column of activated silica gel. A mixture of ethanol and methanol (4 : 1 by vol.) served as a polar solvent at low temperatures. At high temperatures decalin, diphenyl ether, or dimethyl phthalate was used.

Spectrophotometric Technique.—The technique was that described in Part I. Temperature control at high temperatures was further simplified by heating the contents of the Dewar-type absorption cells used throughout, with air passing over a coil of nichrome wire heated electrically. Any desired temperature up to about 180° was rapidly attained and kept constant within 1°.

Dielectric Measurements.—The technique used has been outlined previously (Fischer and Hirshberg, *loc. cit.*). The dielectric cell was immersed in a large unsilvered Dewar vessel filled with methyl*cyclo*hexane. This bath was cooled below the desired temperature by liquid nitrogen introduced at a variable controlled rate into a copper container immersed in the bath. Thermoregulation was achieved with a bimetallic regulator controlling the current in a bare heating coil placed at the bottom of the thermostat.

Materials.—These were prepared according to known methods, viz. : (I), (V), (VI), (VII *a*, *b*, *c*, *d*), (VIII *a*, *b*), Wizinger and Wenning, *Helv. Chim. Acta*, 1940, 23, 247; (II), Dickinson and Heilbron, *J.*, 1927, 14; (III), (IV), Irving, *J.*, 1929, 1093. They had the properties there recorded, except that compound (VII*d*) had m. p. 201° (instead of 122°) in repeated syntheses;

the compound showed the colour reactions described by the above authors; the figure 122° may therefore be a misprint.

The authors are deeply indebted to Prof. Linus Pauling for helpful advice, and to Mr. M. Kaganowitch for the preparation of all the compounds investigated.

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