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

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[Reprint Order No. 4553.]

When solutions of several *spiro*pyrans are irradiated with ultra-violet light at about −100°, coloured modifications are produced. These are spectroscopically identical with those developed on heating ("thermochromism"). From the temperature dependence of the rate of spontaneous disappearance of colour, the critical increment and the frequency factor of the thermal reversion to the colourless modification are estimated for several compounds.

Reversion to the colourless form can also be effected by irradiation of the dye with yellow light.

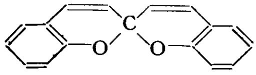
Ultra-violet irradiation at about −170° gives different dyes which pass into those described above at somewhat higher, closely defined temperatures. Several of the compounds give three distinct coloured modifications.

An apparatus is described for spectrophotometric determinations at any temperature between +180° and −180°.

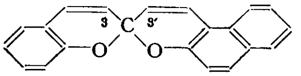
PHOTOCHROMISM has been recorded for compounds related to dianthronylidene (Hirshberg and Fischer, *J.*, 1953, 629) and for two *spiro*pyrans (Fischer and Hirshberg, *J.*, 1952, 4522). The present paper describes results obtained with eight *spiro*pyrans, namely, bis*spiro*-2 : 2′-(5 : 6-benzopyran) (I), 5 : 6-benzopyran-2-*spiro*-2′-β-naphthopyran (II) and its 3- and 3′-methyl derivative, 3 : 3′-dimethylbis*spiro*-2 : 2′-(β-naphthopyran) (III; R = Me) and the corresponding ester (III; R = CO_2Et) and 3 : 3′-trimethylene derivative (IV), and 1 : 3 : 3-trimethylindoline-2-*spiro*-6′-(2′ : 3′-β-naphthopyran) (V).

Compound (II) and its 3-methyl derivative (see Fig. 1), and compound (V), are strongly thermochromic, (IV) shows only slight thermochromism, and the other compounds are not thermochromic. The height and area of the absorption peaks shown in Fig. 1 for the visible range increase with temperature, in accordance with the accepted view that the thermal equilibrium between the colourless and the coloured modification is shifted in favour of the latter at elevated temperatures (Knott, *J.*, 1951, 3038). In polar solvents a much higher proportion of the compound exists in form of the coloured modification (cf. Knott, *loc. cit.*, and Chaudé and Rumpf, *Compt. rend.*, 1951, **233**, 405).

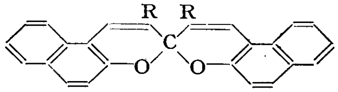
All the compounds except (III; R = Me and CO_2Et) exhibit pronounced photochromism, *i.e.*, when their solutions are irradiated with ultra-violet light at —115°, very intensely coloured dyes are developed. Comparison of Fig. 2, curves *C*, with Fig. 1 shows that, in those compounds which exhibit both thermochromism and photochromism, the respective coloured modifications are apparently spectroscopically identical.



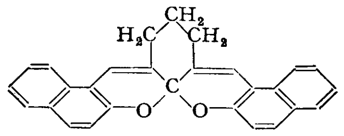
(I)



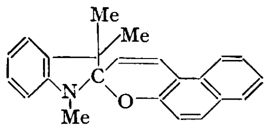
(II)



(III)



(IV)



(V)

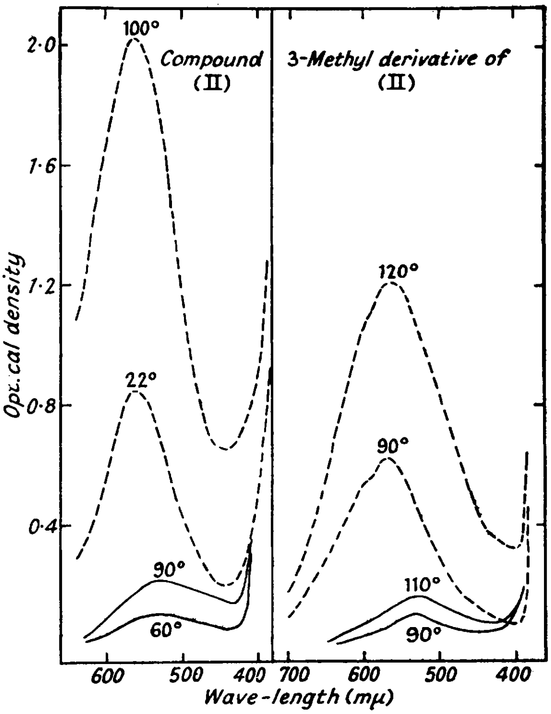


FIG. 1. *Absorption spectra of thermochromic spirans at several temperatures (4-cm. cell, concn. 1 g./l.). Full curves: in xylene. Broken curves: in benzyl alcohol.*

If one assumes that ultra-violet irradiation at —115° causes complete conversion into the coloured modification, values of 10,000—100,000 are obtained for the molar extinction coefficients, ε, as shown in the following Table (solutions in methyl*cyclo*hexane):

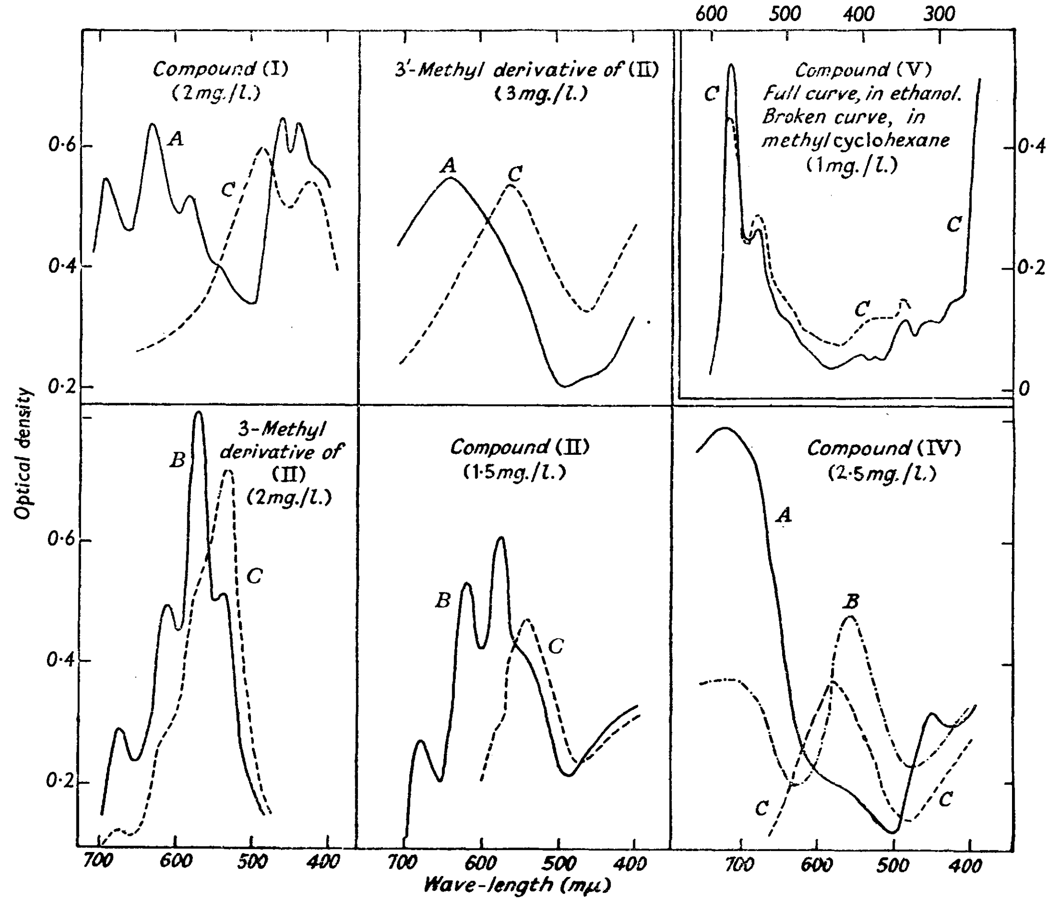
Compound	(I)	(II)	3-Me deriv. of (II)	3'-Me deriv. of (II)	(IV)	(V)
Absorption peak (mμ)	485	540	535	560	580	580
ε at peak	34,000	40,000	49,000	25,000	28,000	67,000

The high values of ε indeed indicate that the above assumption is in the main justified. Furthermore, comparison of the apparent values for ε calculated from the data recorded in Figs. 1 and 2 shows that even at +120° only a very small fraction of the respective compounds exists in form of the coloured modification.

For all of the photochromic compounds except (V), the absorption peaks in the visible region in ethanol solutions are shifted towards longer wave-lengths by 20—40 mμ, compared with solutions in methyl*cyclo*hexane. This is analogous to the solvent effect observed in thermochromism.

When solutions of *spiro*pyrans in methyl*cyclo*hexane at concentrations exceeding about 4 mg./l. are irradiated at —100°, the coloured modifications are sometimes precipitated as minute flakes. It appears that such solutions, in which flocculation has not occurred, are supersaturated, but are stabilised in this state by the low temperatures involved. No precipitation was observed with ethanol solutions, even at much higher concentrations.

FIG. 2. *Absorption spectra after ultra-violet irradiation at —170° (curves A), at —150° (curves B), and at —115° (curves G). (Solutions in methyl*cyclo*hexane, 2-cm. cell.)*



The dependence of absorption on concentration was measured in a broad range of concentrations, with absorption cells of 0·5—20-mm. light path. The results for methyl*cyclo*hexane solutions of (V) at —100°, given in the following Table, show that Beer's law holds up to concentrations of about 50 mg./l. :

Concentration (mg./l.)	5	10	20	40	100
Optical density (0·5-mm. cell)	0·06	0·12	0·25	0·52	1·10

This conclusion involves the assumption that at each concentration low-temperature irradiation results in the same degree of conversion into the coloured form.

All the coloured modifications formed at low temperatures spontaneously revert to the original colourless modifications at rates depending on the temperature. This was investigated with the aid of a special attachment to the spectrophotometer, by means of which absorption measurements could be carried out at closely controlled temperatures as low as −170°. Kinetic measurements were carried out in 2-cm. cells, at correspondingly low concentrations. For compounds (II), the 3-methyl derivative of (II), and (V), the reversion was found to be a first-order reaction. The following Table shows the reaction rates for solutions of (V) in methyl*cyclo*hexane, at −67·5°, at several total concentrations, on the assumption that the concentration of the dye immediately after irradiation is proportional to the total concentration :

Total concn. (mg./l.)	0·4	0·5	1·0	2·0
k (min.$^{-1}$)	0·08	0·08	0·11	0·09

The rates of reversion were measured for each compound at several temperatures, as illustrated by the following data for compound (II) in methyl*cyclo*hexane :

Temp.	−88·8°	−79·5°	−72·7°	−67·6°	−62·8°
k (min.$^{-1}$)	0·0088	0·048	0·132	0·310	0·653

The next Table summarises the values obtained for the critical increment and the frequency factor (E and A in the equation $\ln k = \ln A - E/\boldsymbol{R}T$) from the rectilinear plots of log k against the reciprocal of the absolute temperature.

	(II) in methyl-*cyclo*hexane	3-Methyl deriv. of (II) in methyl*cyclo*hexane	(V) in methyl-*cyclo*hexane	(V) in ethanol
E (kcal./mole)	11·0	13·0	18·5	19·3
log A	9·3	11·3	16·7	16·0

(E and log A are accurate within about 0·5 unit.)

In our previous work (*locc. cit.*), a rather crude method was used for measuring the kinetics of the disappearance of colour. The more accurate, spectrophotometric method described below yields results for E and A which are practically identical with those reported for compounds related to dianthronylidene. For compound (V), however, the figures given above exceed those reported previously by more than the experimental error then assumed.

For solutions of (I), the 3′-methyl derivatives of (II), and (IV) in ethanol and methyl*cyclo*hexane, the plots of log (optical density) against time during spontaneous disappearance of dye always showed very pronounced deviations from linearity. No kinetic results for these compounds could therefore be obtained, possibly because of interference by other coloured modifications which are described below.

In a preliminary note (Hirshberg, Frei, and Fischer, *J.*, 1953, 2184) it was reported that when a solution of the coloured modification of (V), formed as described above, is irradiated with *yellow* light (containing no radiation below 500 mμ) the colour disappears, the original colourless compound being re-formed. Similar effects, though generally less pronounced, have meanwhile been observed with several other compounds, including certain compounds of the dianthronylidene series. It is noteworthy that, whereas colour production by ultra-violet irradiation depends but little on the solvent, colour eradication by yellow light is much faster in ethanol than in methyl*cyclo*hexane. [The *thermal* disappearance of the colour of (V) in ethanol is about 35 times *slower* than in methyl*cyclo*hexane at the same temperature.]

In the experiments described hitherto, the coloured modifications were produced by ultra-violet irradiation at temperatures not below −120° (in a solvent mixture of methyl*cyclo*hexane and light petroleum). When the investigation was extended to temperatures as low as −180°, new phenomena were observed (cf. Hirshberg and Fischer, *J. Chem. Phys.*, 1953, **21**, 1619). Ultra-violet irradiation at −165° (or lower) results in the formation of certain dyes (type A) which, on cautious heating, are converted spontaneously first into a second type of dye (B) and, at a somewhat higher temperature, into a third coloured form (type C) which is spectroscopically identical with the type of dyes described in the preceding sections of this paper. At still higher temperatures the original colourless modification is re-formed.

The temperature ranges in which the three types of dye are stable overlap to a certain extent, making a complete isolation of each type difficult or impossible. A comparatively good separation has been achieved only with compound (IV), which may therefore serve to illustrate the behaviour outlined above (Fig. 2). When a solution of this compound is irradiated at −170° with light from a mercury arc, a green colour develops (curve *A*). If then kept for 5—10 minutes at −150°, the green solution becomes rose (curve *B*, which shows, incidentally, that the green colour has not yet completely disappeared). At −110° the solution rapidly becomes mauve, and at above −50° colour disappears. The whole cycle may be repeated many times, since at −170° irreversible reactions initiated by ultra-violet irradiation are practically suppressed.

Type B was particularly difficult to identify, and could easily have been overlooked were it not for the fact that this type, and only this, shows a bright brick-red luminescence on excitation with the 365-mμ group of a mercury arc (Fig. 3).

The rest of the photochromic compounds, except (V), showed similar behaviour, but separation of the three coloured modifications could be achieved only partially (Fig. 2).

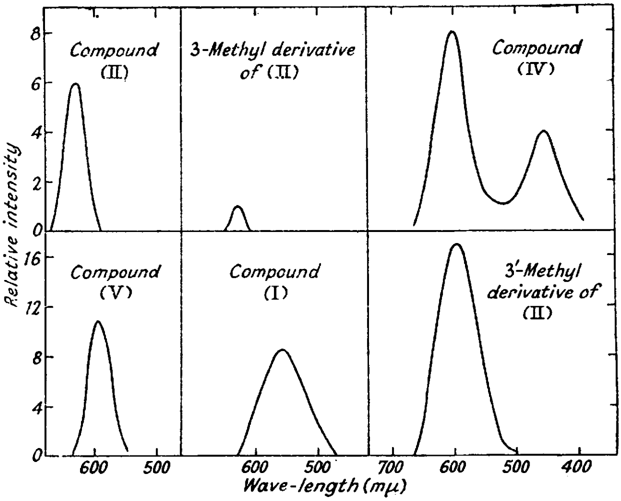


FIG. 3. *Luminescence spectra of modifications B. (Solutions in methyl*cyclo*hexane–light petroleum.)*

In all cases, however, three coloured modifications could be identified, of which only type B exhibited fluorescence. This type is produced at about −150°, either spontaneously from its precursor A, or by ultra-violet irradiation of the colourless form at this temperature. The annexed Table summarises the relevant observations.

*Coloration of solutions in methyl*cyclo*hexane–light petroleum under various conditions.*

Compound	Colour resulting from ultra-violet irradiation at −170° A	 at −150° (also formed spontaneously from A) B	 at −110° (also formed spontaneously from B) C	Luminescence of modification B
(I)	Green	Wine-red	Rose-mauve	Yellow
(II)	Rose	Blue-violet	Rose-mauve	Red
3-Me deriv. of (II) ...	Rose	Blue-violet	Rose-mauve	Red
3'-Me deriv. of (II)...	Blue-green	Rose	Mauve	Orange
(IV)	Green	Rose	Mauve	Brick-red
(V)	Mauve	Mauve	Mauve	Red

The position is different in the case of the spirans containing two hetero-atoms, represented by compound (V). Here irradiation at −170° to −180° produces a light mauve colour which at somewhat higher temperatures becomes deep mauve. Spectrophotometrically, this colour change finds its expression in a slight enhancement of the ratio between the extinction coefficients at 580 and 540 mμ. A strong, red fluorescence is observed in the coloured modification, independent of the temperature at which it had been formed. With the present development of our technique, it has not been possible to rule out the existence of a non-luminescent coloured modification accompanying the luminescent form.

In all the photochromic spirans investigated, the colourless modification shows either no luminescence or only a weak band at about 450 mμ.

The phenomena described in the Table occur at higher temperatures if a solvent mixture of methyl*cyclo*hexane and decalin is used instead of methyl*cyclo*hexane–light petroleum. Thus with a solution of (II) in the decalin mixture, the rose modification is produced by ultra-violet irradiation at —150°, and is converted into the blue one at about —130°. It seems plausible that the higher viscosity of the mixture containing decalin is responsible for this temperature shift. In a solvent mixture of ethanol and methanol similar internal transitions were observed.

In this connection it may be noted that the rate of colour formation by ultra-violet irradiation decreases with increasing rigidity of the medium. Thus coloration at liquid-air temperature is fairly rapid in a solvent mixture of methyl*cyclo*hexane and light petroleum but very slow in a solvent mixture of ethanol and methanol. (Both mixtures form transparent " rigid media " at this temperature.)

DISCUSSION

In general, our tentative conclusions (*locc. cit.*) about the mechanism of the photoconversion of *spiro*pyrans and dianthronylidenes apply also to the compounds described in this investigation. The suggestion that dye C is highly polar (cf., *e.g.*, Knott, *J.*, 1951, 3038) is borne out by the low solubility of the latter in non-polar, as distinct from polar, solvents, and by the fact that in polar solvents the thermal equilibrium is shifted towards the coloured form. The failure to find direct evidence for the proposed high polarity of this dye (Fischer and Hirshberg, *loc. cit.*) may be due to flocculation during the dielectric measurements, which would very greatly reduce the concentration of the dissolved dye. More suitable non-polar solvents, as well as stabilisation of the supersaturated solutions, may eventually make the dielectric measurements more reliable.

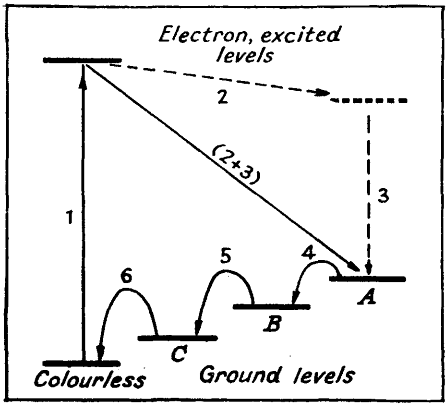


FIG. 4. *Schematic representation of energy levels. Steps* 1, 2, *and* 3 *represent the photoconversion, steps* 4, 5, *and* 6 *represent the spontaneous internal transitions over potential barriers. Thermochromism proceeds by the reverse of step* 6.

It appears that the present experimental conditions do not allow estimation of the activation energies involved in the transitions A ⟶ B, B ⟶ C, both because of the great change in viscosity with temperature in the relevant regions, and because of spectral overlapping of the various modifications.

Direct experimental estimation of the relative energy levels of modifications A and B is also impossible, because these colours do not appear in the thermal equilibrium at elevated temperatures, *i.e.*, in thermochromism. The representation of the energy levels involved, given in Fig. 4, is therefore only schematic.

The lack of thermochromism in some photochromic compounds may be ascribed to an energy difference between the coloured and the colourless form which is so high that *thermal* attainment of detectable concentrations of the coloured form is impossible. In the two compounds exhibiting neither thermochromism nor photochromism, steric interference in the (hypothetical) coloured forms may be so large that these are not sufficiently stable even at liquid air temperature.

EXPERIMENTAL

Solvents.—For work at low temperatures a mixture of methyl*cyclo*hexane and light petroleum was suitable as non-polar solvent. It remains liquid until about −168° and forms a transparent glass of comparatively low rigidity at −175° to −180°. Solutions in this solvent often showed some opacity when cooled, probably because of traces of moisture. They could be cleared by first cooling them to at least −100° and then keeping them for some time at −10° to −20°. On re-cooling, the solutions remained transparent.

A mixture of ethanol and methanol (4 : 1 by vol.) served as a polar solvent at low temperatures. At high temperatures xylene, decalin, or benzyl alcohol was used.

Spectrophotometric Technique.—An attachment to the Beckman model D.U. quartz spectrophotometer was built, permitting the use of Dewar-type cells (Hirshberg and Fischer, *loc. cit.*). Except in kinetic experiments, the low-temperature technique involved production of the desired modification under the appropriate conditions, freezing-in of the state thus attained by introduction of liquid nitrogen into the outer compartment of the cell, and measurement of the absorption. For measurements at high temperatures, the inner compartment of the cell was heated as described in the following paragraph.

Temperature Control.—For work at low temperatures the inner compartment of the cell, containing the solvent or the solution to be measured, was cooled by a variable stream of cold, gaseous nitrogen passing through the outer compartment. The nitrogen was generated by boiling liquid nitrogen, contained in a 50-l. copper Dewar vessel, by means of an immersed electric heater. The cold nitrogen passed from the generator to the absorption cells through two Dewar-type glass tubes, connected by a heated rubber tube, the latter permitting flexibility. By controlling the input of the immersion heater, and thereby the boiling rate of the liquid nitrogen, the temperature of the cell contents could be maintained at any desired level as low as −170°, to within 0·5° or better, as measured by means of a thermocouple immersed in the liquid. For work at −175° to −185°, the outer compartment of the cell was filled with liquid air or liquid nitrogen.

For investigations at high temperatures (up to 180°), similar Dewar-type cells, but having a light path of 4 cm., were used. In these cells the contents of the inner compartment were kept at the desired temperature within 1° by direct thermoregulation of paraffin oil, introduced into the outer compartment together with a thermoswitch and a bare heating element.

Luminescence Spectra.—Solutions were prepared as above, and then photographed as described previously (Hirshberg and Fischer, *loc. cit.*).

Materials.—Bis*spiro*-2 : 2′-(5 : 6-benzopyran) and 1 : 3 : 3-trimethylindoline-2-*spiro*-6′-(2′ : 3′-β-naphthopyran) were prepared according to Bergmann, Weizmann, and Fischer (*J. Amer. Chem. Soc.*, 1950, **72**, 5009). All the other compounds were synthesised according to Dickinson and Heilbron (*J.*, 1927, 1699).

Thermal and Photochemical Decomposition.—When solutions of the thermochromic spirans in decalin or benzyl alcohol were kept at 120°, they slowly decomposed, as shown by an irreversible yellow coloration. This effect was not prevented by keeping the solutions under nitrogen.

Irradiation with the full mercury arc (a Hanovia Type S-100 quartz burner was used) caused a slow decomposition even at −100°. When the short ultra-violet radiation was cut off by means of a Wood's filter, no such decomposition occurred.

The authors are deeply indebted to Mr. M. Kaganowitch for the syntheses of the compounds investigated.

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[*Received, August 5th,* 1953.]