128. *Low-temperature Photochromism and its Relation to Thermochromism.*

By YEHUDA HIRSHBERG and ERNST FISCHER.

When solutions of dianthrone, dixanthylen, xanthylideneanthrone, and their derivatives are irradiated at temperatures between −70° and −150° with light of wave-length not exceeding 450 mμ, reversible formation of coloured modifications takes place (photochromism). Comparison of the visible and near ultra-violet absorption spectra of these coloured modifications with the spectra of the coloured forms obtained reversibly on heating solutions of some of the above compounds (thermochromism) shows that the colours produced by both processes are identical, and that low-temperature irradiation may cause considerable or even complete conversion into the coloured form.

Photochromism is also observed with non-thermochromic derivatives of the above compounds.

From the temperature dependence of the rates of the spontaneous disappearance of colour, the critical increments and frequency factors of the thermal reversion to the colourless modification were estimated.

The dielectric constant of solutions of xanthylideneanthrone in toluene at −78° increased considerably as a result of irradiation.

The relation between photochromism and thermochromism is discussed, and tentative conclusions are drawn with regard to the mechanism of photochromism and the electronic and atomic configuration of the coloured and colourless modifications.

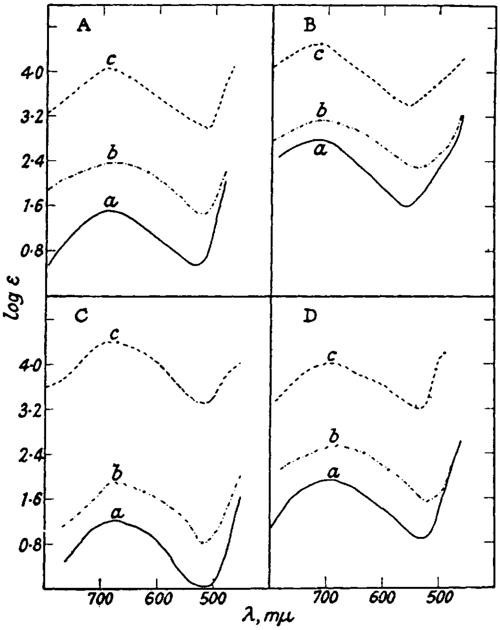
THE reversible formation of colour on heating of solutions of dianthrone (dianthronylidene) (I), dixanthylen (dixanthylidene) (II), xanthylideneanthrone (III), and their derivatives is well-known (for refs. see E. D. Bergmann, "Isomerism and Isomerisation," Interscience Publishers Inc., New York, 1948; Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419). Theilacker, Kortüm, and Friedheim (*Ber.*, 1950, **83**, 508) and Grubb and Kistiakowsky (*loc. cit.*) measured the molar extinction coefficient (ε) of (I) and (II) at several temperatures, and concluded that thermochromism involves transition from a singlet to a diradical triplet state, the reverse transition requiring activation energies below 20 kcal./mole. Theilacker *et al.* also postulated a thermal equilibrium between two interconvertible modifications, and from a plot of log $\varepsilon_{\text{max.}}$ (*i.e.*, the value of ε at the peak of the absorption curve in the visible range) against the reciprocal of the absolute temperature

($1/T$) found that the heats of conversion into the coloured form are 3·5—5 kcal./mole. Assuming that at infinite temperature this conversion is virtually complete, they estimated the $\varepsilon_{\text{max.}}^{\infty}$ of the pure coloured form by extrapolating the above plot to $1/T = 0$.* Values of log $\varepsilon_{\text{max.}}^{\infty} = 3{\cdot}5$ were thus obtained for both compounds. From the ratio $\varepsilon_{\text{max.}}/\varepsilon_{\text{max.}}^{\infty}$ the degree of conversion into the coloured form was calculated for each temperature.

In a preliminary note, Hirshberg (*Compt. rend.*, 1950, **231**, 903) reported that certain derivatives of dianthrone are reversibly converted into coloured modifications by irradiation at low temperatures.† This phenomenon (photochromism) is now described in detail, and its relation to thermochromism elaborated. Similar observations with some spirans have already been reported (*J.*, 1952, 4522).

FIG. 1.

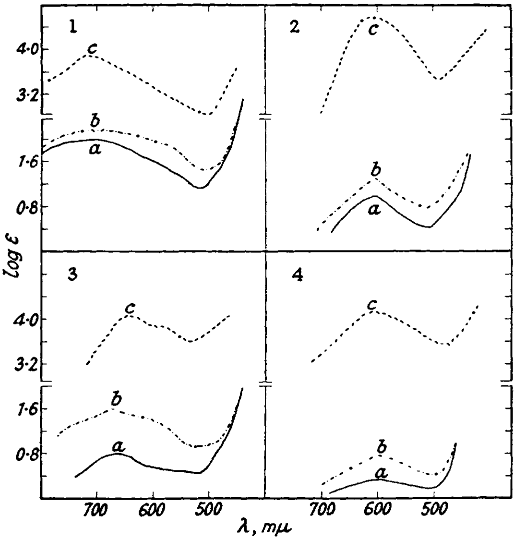
A. 2 : 2′-*Dibromodianthrone.*
B. 2 : 2′-*Dimethoxydianthrone.*
C. *Dianthrone.*
D. 2 : 2′-*Dimethyldianthrone.*



Absorption spectra of thermochromic compounds.
(*a*) *At* 298° K.
(*b*) *At* 418° K.
(*c*) *After low-temperature irradiation.*

FIG. 2.

1. *Xanthylideneanthrone.*
2. 4 : 4′-*Dimethoxydixanthylen.*
3. 3 : 3′-*Dibromodianthrone.*
4. *Dixanthylen.*



Absorption spectra of thermochromic compounds.
1. (*a*) *At* 363° K. (*b*) *At* 408° K.
2. (*a*) *At* 418. (*b*) *At* 458.
3. (*a*) *At* 298. (*b*) *At* 408.
4. (*a*) *At* 363. (*b*) *At* 423.
(*c*) *After low-temperature irradiation.*

Irradiation of solutions of (I), (II), (III), and their derivatives at room temperature generally causes irreversible chemical changes of these substances (Brockmann and Muehlmann, *Ber.*, 1950, **83**, 348; Schoenberg, Ismail, and Asker, *J.*, 1946, 442), but at <*ca.* −70° [or −100° for (I), (II), and some of their derivatives], these irreversible changes are almost completely suppressed, and intense colours are reversibly produced instead. No such effect is observed with the solids or with solutions in rigid glassy media (*e.g.*, methanol–ethanol below −120°), but in solutions in *iso*pentane (m. p. −160·5°) colour is formed even at −150°. The phenomenon thus appears to occur as long as the solution is fluid. No photochromism was observed in any case when the irradiation was carried out with light of wave-length >*ca.* 450 mμ.

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* This extrapolation does not seem to be justified thermodynamically, but appears to give the correct order of magnitude for $\varepsilon_{\text{max.}}$ of the pure coloured form.

† The results there reported for dianthrone were obtained at temperatures which were not sufficiently low, and should be revised in accordance with the present communication.

The absorption spectra of the coloured forms of the above substances are recorded in Figs. 1, 2, and 3 (broken curves). In all cases the solutions were irradiated until there was no further increase in absorption intensity. No appreciable difference in $\varepsilon_{max.}$ was found between solutions in alcohol and in *iso*heptane.

The irradiated solutions lose their colour at rates depending on their temperature, and the production and loss of colour may be repeated indefinitely. The rates of these spontaneous reversion reactions were measured for each compound at several temperatures. The reactions being assumed to be of first order, their critical increments were estimated from the slopes of the graphs of reversion time against $1/T$ (Fig. 4). From the resulting values and the actual rates of reaction, the frequency factors A were evaluated and are listed in Table 1, together with the critical increments, for all the compounds investigated.

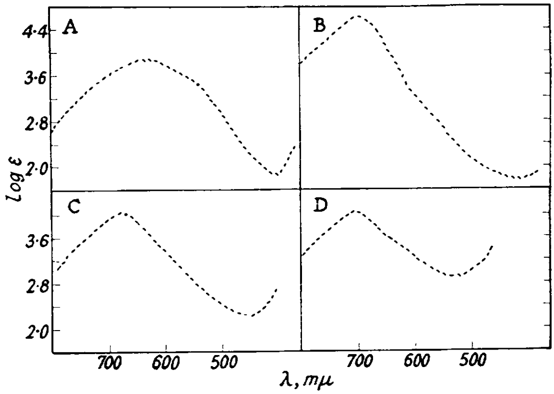


FIG. 3. *Absorption spectra of non-thermochromic compounds, after low-temperature irradiation.*

A. 4 : 4′-*Dimethyldianthrone.*
B. 4 : 4′-*Dimethoxydianthrone.*
C. 4 : 4′-*Dibromodianthrone.*
D. 3 : 4-3′ : 4′-*Dibenzodianthrone.*

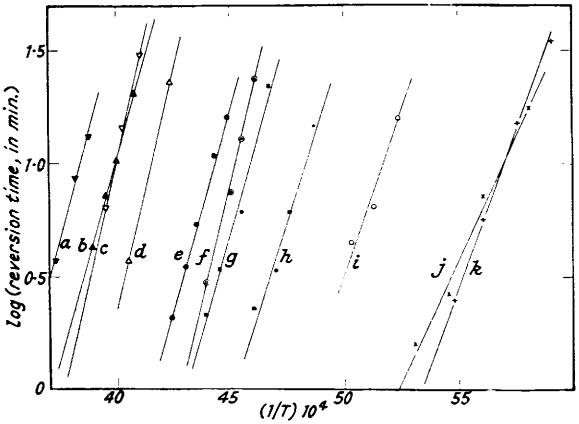
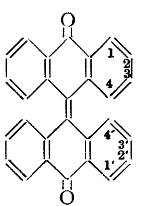


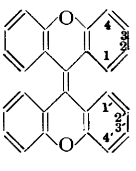
FIG. 4. *Temperature dependence of rate of colour disappearance.*

(*a*) 2 : 2′-*Dimethoxydianthrone.*
(*b*) 2 : 2′-*Dimethyldianthrone.*
(*c*) 2 : 2′-*Dibromodianthrone.*
(*d*) 3 : 3′-*Dibromodianthrone.*
(*e*) 4 : 4′-*Dimethyldianthrone.*
(*f*) *Xanthylideneanthrone.*
(*g*) 3 : 4-3′ : 4′-*Dibenzodianthrone.*
(*h*) 4 : 4′-*Dibromodianthrone.*
(*i*) 4 : 4′-*Dimethoxydianthrone.*
(*j*) 4 : 4′-*Dimethoxydixanthylen.*
(*k*) *Dixanthylen.*

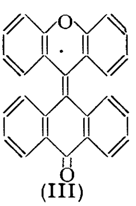
The photochromic substances listed in group (*b*) of Table 1 also show thermochromic behaviour. The absorption spectra of dimethyl phthalate solutions of these substances at room temperature and at higher temperatures are shown in Figs. 1 and 2. By following the method of Theilacker *et al.* (*loc. cit.*), the energy difference ΔH between the coloured



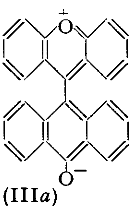
(I)



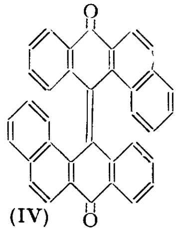
(II)



(III)



(III*a*)



(IV)

and colourless forms, the values of $\varepsilon^{\infty}_{\text{max.}}$ (see p. 631), and the degree of conversion into the coloured form at each temperature were calculated (Tables 1 and 2).

Comparison of the absorption spectra of the thermochromic and photochromic coloured modifications, for the substances exhibiting both phenomena (Figs. 1 and 2), shows that the temperature-dependent band of the thermochromic coloured forms is practically identical with the visible band of the photochromic coloured modification. Moreover, inspection of cols. 4 and 5 of Table 1 shows that the thermochromic $\varepsilon^{\infty}_{\text{max.}}$ and the photochromic $\varepsilon_{\text{max.}}$ are both of an order of magnitude which may be expected by analogy with other dyes. (Values of log $\varepsilon_{\text{max.}}$ exceeding 5 are extremely rare for any type of dye.) It therefore appears plausible that the coloured modifications formed either by heat or by low-temperature irradiation are identical, and that in the latter process conversion into the coloured form takes place to a considerable extent under the conditions described.

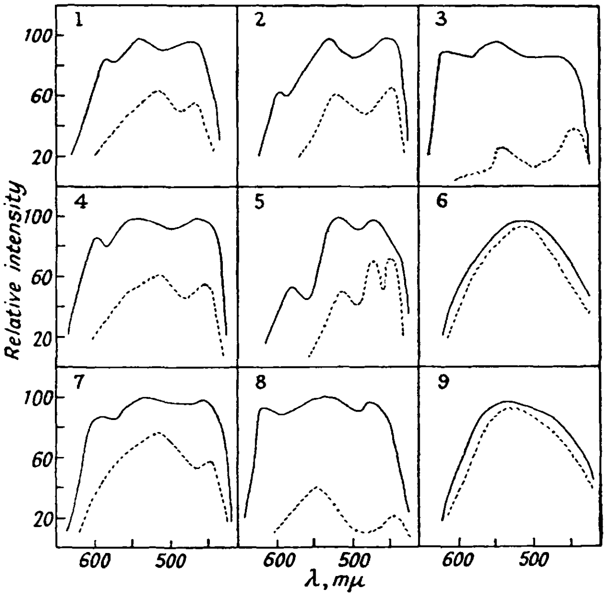


FIG. 5. *Luminescence spectra of colourless (full curves) and coloured (broken curves) modifications.*

(1) 2 : 2′-*Dimethyldianthrone.*
(2) *Xanthylideneanthrone.*
(3) 3 : 4-3′ : 4′-*Dibenzodianthrone.*
(4) 2 : 2′-*Dimethoxydianthrone.*
(5) 4 : 4′-*Dimethyldianthrone.*
(6) *Dixanthylen.*
(7) *Dianthrone.*
(8) 4 : 4′-*Dimethoxydianthrone.*
(9) 4 : 4′-*Dimethoxydixanthylen.*

It is, however, impossible to deduce from the present results whether or not this conversion is complete. (For comparison, the *trans* ⟶ *cis*-photoconversion of azobenzene stops at a photochemical equilibrium of 15—40% of *cis*; Hartley, *J.*, 1938, 633.) The figures

TABLE 1.

Substance	Critical increment (kcal./mole)[a]	log A (sec.$^{-1}$)[a]	log $\varepsilon_{\text{max.}}$ (photochromism)[b]	log $\varepsilon^{\infty}_{\text{max.}}$ (thermochromism)[c]	ΔH, kcal./mole[d]
Group (*a*) :					
4 : 4′-Dimethyldianthrone	16·5	14	3·9	—	—
4 : 4′-Dimethoxydianthrone	11·5	10·5	4·6	—	—
4 : 4′-Dibromodianthrone	15·5	14	4·0	—	—
3 : 4 : 3′ : 4′-Dibenzodianthrone (IV)	20	18	4·0	—	—
Group (*b*) :					
Dianthrone (I)	—	—	4·4	3·7	3·5
2 : 2′-Dimethyldianthrone	16	11·5	4·0	4·0	2·9
2 : 2′-Dibromodianthrone	19	14·5	4·4	4·7	4·1
2 : 2′-Dimethoxydianthrone	16·5	12	4·5	4·0	1·7
3 : 3′-Dibromodianthrone	19	15	4·0	3·7	4·0
Dixanthylen (II)	12·5	13·5	4·2	3·7	5·6
1 : 1′-Dimethoxydixanthylen	12·5	13·5	4·5	4·3	7·2
Xanthylideneanthrone (III)	18·5	16	3·9	4·0	3·5

[a] Accurate within about 2 units. [b] Accurate within about 0·2 unit. [c] It is impossible to assess the error in these values, because of the uncertain extrapolation by which they are obtained (cf. footnote, p. 630). [d] Accurate within about 0·6 unit.

TABLE 2.

Substance	Temp., °K	Conversion % into coloured modification *	Substance	Temp., °K	Conversion % into coloured modification *
Dianthrone (I)	298	0·3	3 : 3′-Dibromodianthrone	298	0·1
	373	1·2		408	0·8
	418	1·6			
			Dixanthylen (II)	363	0·04
2 : 2′-Dimethyldianthrone	298	0·8		408	0·01
	363	2		423	0·13
	418	3			
			4 : 4′-Dimethoxydixanthylen	418	0·04
2 : 2′-Dimethoxydianthrone	298	5		448	0·08
	402	11		458	0·10
	423	13			
			Xanthylideneanthrone (III)	363	1·0
2 : 2′-Dibromodianthrone	298	0·06		408	1·4
	363	0·3			
	418	0·5			

* From $\varepsilon_{\text{max.}}/\varepsilon^{\infty}_{\text{max.}}$, and therefore subject to the uncertainty mentioned in the footnote on p. 632.

presented in col. 4 of Table 1 may therefore be regarded as minimum values for the ε of the pure coloured modifications.

The near ultra-violet parts of the absorption spectra of the coloured and the colourless forms were practically identical, confirming the results of Grubb and Kistiakowsky (*loc. cit.*) and Theilacker *et al.* (*loc. cit.*) with regard to (I) and (II).

It is evident that photochromism makes possible the investigation of the physical properties of the coloured form at concentrations far exceeding those attainable thermally (cf. Table 2), and it is hoped to obtain the coloured modifications from these solutions in solid form and to study them crystallographically.

The following substances showed neither photochromic nor thermochromic behaviour : Anthrone, 4-bromo-, 4-methyl-, and 4-methoxy-anthrone, xanthen, xanthone, diphenylmethylene- and 4-methoxydiphenylmethylene-anthrone, dithioxanthylen, " *NN*′-dimethyldiacridine,"  $[C_6H_4{<}^{NMe}_{C}{>}C_6H_4]_2$.

The total luminescence spectra of the colourless and coloured forms of all the substances showing photochromism were measured in a rigid glassy medium at about −180°. No attempt was made to differentiate between fluorescence and phosphorescence, as defined by Kasha (*Chem. Reviews*, 1947, **41**, 401). No appreciable difference between the two modifications was observed with (II), but with (III) and also with (I) and its derivatives, the luminescence of the coloured modification was weaker and shifted towards shorter wave-lengths (Fig. 5).*

The molar polarisation *P* of the coloured form was investigated for (III), the other photochromic substances not being soluble enough to allow sufficiently accurate measurements of the increment of the dielectric constant of the solutions. The dielectric constants of toluene η_0 and of a toluene solution of (III) before (η_1) and after (η_2) irradiation were measured at −78°. From the observed increments $\eta_1 - \eta_0 = 0{\cdot}0041$ and $\eta_2 - \eta_0 = 0{\cdot}0110 \pm 0{\cdot}0004$, values of *P* of 380 ml. for the colourless form and 890 ml. for the coloured form were calculated (for method of calculation, see Fischer, *J. Chem. Physics*, 1951, **15**, 395). The actual value of P_{coloured} is still higher, because under the experimental conditions illumination could not be carried out until there was no further increase in η. The sum of electronic and atomic polarisation being assumed to be equal for the two modifications, it follows from the above results that the orientation polarisation, and therefore the dipole moment, of the coloured form is considerably larger than that of the colourless species. No significant difference was found between the dielectric constants of fresh solutions of the colourless form and of solutions in which colour had been produced by low-temperature

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* It was shown by Hirshberg *et al.* (*Bull. Soc. chim.*, 1951, **18**, 88) that anthrone and diphenylmethyleneanthrone and their derivatives mentioned in the preceding paragraph exhibit pronounced phosphorescence, whereas the colourless forms of dianthrone, 4 : 4′-disubstituted dianthrones, and xanthylideneanthrone are practically non-phosphorescent. The "low-temperature thermochromism" described in that communication is probably photochromism produced by stray light.

irradiation and then caused to disappear. It thus seems that for (III) high polarisation, like colour, is a reversible effect of low-temperature irradiation.

Discussion.—(a) *Mechanism of photoconversion.* The existence of a threshold wavelength above which no low-temperature photoconversion occurs suggests that this conversion proceeds in the following steps : (1) absorption of ultra-violet light, raising the molecule to an excited electronic level of the colourless form ; (2) transition to an excited electronic level of the coloured form ; (3) transfer to the ground level of the coloured form, and " freezing-in " of this form at the low temperatures involved. The critical increments of 12—20 kcal./mole observed show that in the thermal reversion " coloured → colourless " potential barriers of at least this height have to be passed (the actual activation energies for the complex molecules involved are probably considerably higher). Such potential barriers indicate that the transformation from one modification into the other involves changes in atomic configuration, a conclusion borne out by the absence of photochromism in the solid state or in rigid media. Photochromism should therefore be exhibited by any substance which, in addition to its normal colourless form, can also exist in a coloured form of the type described above. Thermochromism, on the other hand, represents a thermal equilibrium, the position of which depends on the energy difference between the two modifications. It is, therefore, plausible that for compounds such as those listed in group (*a*) of Table 1, which show only photochromism, this energy difference is so large that no observable shift of the equilibrium towards the coloured species occurs within the accessible temperature range. The absence of photochromism with dithioxanthylen and *NN'*-dimethyldiacridine indicates that, contrary to the view expressed by Theilacker *et al.* (*loc. cit.*), coloured modifications of these substances probably do not exist in solution.

FIG. 6. *High-temperature attachment to spectrophotometer.*

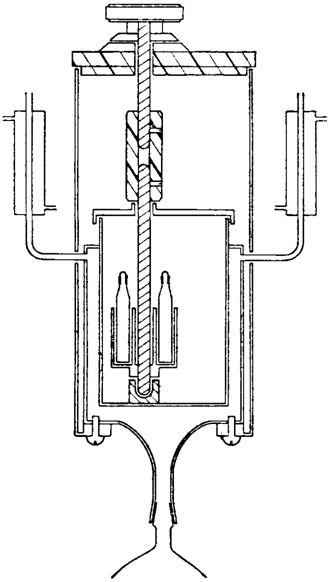
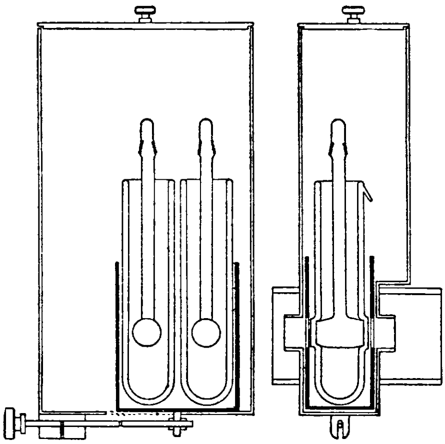


FIG. 7. *Low-temperature attachment to spectrophotometer and Dewar-type cells.*



(b) *Nature of the coloured modification.* As pointed out above, the difference between the energy levels of the ground states of the colourless and coloured forms is only a few kcal./mole. However, no conclusion with regard to configurational similarity between the two modifications can be drawn from this fact, because the resonance energies of the two forms may well differ considerably. The high polarity of the coloured modification of (III) shows that dipolar mesomers, such as (III*a*) suggested by Schoenberg *et al.* (*loc. cit.*), contribute materially to the structure of this modification. The transition from one modification to the other thus appears to involve changes in the electron distribution, as well as in the atomic configuration.

The results described are on the whole not incompatible with Grubb and Kistiakowsky's suggestion (*loc. cit.*) that the coloured modification represents a triplet diradical state.* However, it would be difficult to explain the easy transition between electronic states of dissimilar multiplicity, during irradiation, which one would then have to postulate. Moreover, reactions involving changes in electronic multiplicity should have abnormally low frequency factors, whereas the factors found for the thermal reversion reaction are not smaller than those encountered with common first-order reactions (Laidler, "Chemical Kinetics," McGraw-Hill Book Co. Inc., New York, 1950, p. 108).

In the last analysis only magnetic measurements will make it possible to decide whether or not the coloured modifications described represent an extremely long-lived triplet state of the molecules involved (Kasha, *loc. cit.*). Photochromsism makes such measurements practicable, because of the comparatively high concentrations of the coloured forms attainable.

No final conclusions seem justifiable yet as to the actual nuclear configuration of the two modifications described. However, Grubb and Kistiakowsky's suggestion (*loc. cit.*) about the colourless modification, that " the ground state [of dianthrone] is a singlet, with the double bond in a state of considerable torsion," has recently been shown to be incorrect, at least as far as the solid state is concerned, because the dianthrone molecule is centrosymmetric in the crystal (Harnik, Herbstein, and Schmidt, *Nature*, 1951, **168**, 158). A two-dimensional analysis of the crystal structure of dianthrone has meanwhile led to the suggestion of a centrosymmetric, non-planar model for this molecule (Harnik and Schmidt, forthcoming publication). As to the coloured modification, the fact that it exists also with compounds of group (*a*) in Table 1 suggests that in this modification, too, the two halves of the molecule are not in the same plane. Coplanarity, which would be difficult to attain in compounds of group (*b*), is definitely impossible in compounds of group (*a*), owing to the strong steric interference between the substituents of the 4 : 4'- and 5 : 5'-carbon atoms. (Since the orientation of the two halves of the molecule has not been ascertained, we have numbered all derivatives of dianthrone with the smallest number. Of course, *e.g.*, the 2 : 2'- may really be the 2 : 7'-derivative, and the 4 : 4'- is most probably the 4 : 5'-derivative.)

EXPERIMENTAL

Absorption Spectra.—These were determined by means of a Beckman model D.U. quartz spectrophotometer. Special attachments were made for the measurements at high and at low temperatures. In the high-temperature attachment (Fig. 6) the absorption cells were put into a double-walled container, heated by the vapours of various liquids boiling in an attached Pyrex-glass flask. Silica windows allowed the light to pass through this container. Four silica cells of 1-cm. light path rested in a stand which could revolve in steps of 90°, each step introducing one cell into the light path. The temperature of the solutions could thus be kept constant to within about 5°.

For investigations at low temperatures special Dewar-type cells were designed by Hirshberg and made by the Thermal Syndicate Ltd. for both absorption (Fig. 7) and luminescence (Fig. 8) measurements. For absorption work two cells (containing the solvent and the solution) were placed in the attachment also shown in Fig. 7. The light path in these cells was 2 cm. The external windows of the cells were slightly heated electrically during the measurements in order to keep them clear from fog. The solutions in the cells were kept at the desired low temperature by means of solid carbon dioxide or liquid nitrogen, which were introduced into the Dewar compartment of the cells up to a suitable height.

After photoconversion into the coloured modifications had been effected by irradiation of the cooled cells with a mercury-vapour lamp for the necessary periods (usually 30 seconds were sufficient), the absorption of the solutions was measured.

Luminescence Spectra.—These were photographed with a glass spectrograph on Ilford panchromatic soft gradation plates and evaluated by means of a Leeds and Northrup recording

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* Kasha (*loc. cit.*) has already suggested that the transition triplet ⟶ excited triplet is responsible for the transient colour formation observed with some compounds during phosphorescence, following strong illumination.

microphotometer. In the arrangement used, the surface of the sample, which was activated by the 365-mμ Hg line from a Hanovia 120-watt type S.100 quartz burner, radiated the luminescent light directly to the slit of the spectrograph, thus reducing losses due to absorption. The angle between exciting and luminescent radiation was about 45° (cf. Hirshberg *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 5117). The solutions were cooled by liquid nitrogen introduced into the Dewar compartment of the cell (Fig. 8). Under these conditions the solvent mixture used (ethanol : toluene : ethyl ether, 1 : 1 : 2 by vol.) formed a rigid, non-luminescent glass. For measurements on the coloured modifications, the latter were produced by irradiation of the cells at about −100° before determination of luminescence.

Rate of Thermal Reversion to Colourless Form.—Capillary m. p. tubes of about 1 mm. internal diameter were filled with the solutions to be investigated (generally in *iso*heptane, m. p. −119°) and sealed under nitrogen. They were then irradiated at the respective low temperatures until maximum colour intensity was reached (under the experimental conditions about one minute sufficed). The capillaries were then quickly transferred to a bath at a low temperature kept constant to ±0·25°. There the capillaries were observed against a white background, and the time needed for the disappearance of colour was recorded. The temperatures were chosen so as to give reversion times of 2—30 minutes, and varied between −5° and −105°, according to the substance investigated.

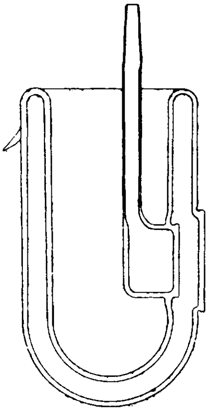

FIG. 8. *Dewar-type cell for measurement of luminescence spectra.*

The limited accuracy aimed at in the present measurements (Table 1) did not warrant the technically difficult introduction of a low-temperature thermostat into the spectrophotometer. The assumption that the colour disappearance is a first-order reaction could therefore not be verified experimentally.

For the calculation of the frequency factor [A in $k = A \exp(-E/\mathbf{R}T)$] it was arbitrarily assumed that the " end-point " of the disappearance of colour in the capillaries corresponds to a reversion of 95% of the solute into the colourless form. (Any assumption between 90 and 99·9% reversion would give the same value of $\log A$, within 0·5 unit, whereas an overall error of 2 units for $\log A$ has been assumed in Table 1.)

For the determination of the frequency threshold of the photo-conversion, the 365, 405, 436, and 546 mμ Hg lines were isolated by suitable filters and used for the irradiation.

Dielectric-constant Increment.—The dielectric constants of the solutions were measured in a slightly modified Sayce–Briscoe cell immersed in a large, unsilvered, silica, Dewar vessel containing alcohol–carbon dioxide snow. The cell could thus be irradiated while in the thermostat. Its contents were mixed during irradiation by applying suction and pressure alternately at one of its two side-tubes.

Materials.—The following substances were prepared according to the references cited: Anthrone (*Org. Synth.*, Coll. Vol. I, New York, 1944, p. 60); xanthone (*ibid.*, p. 552); dianthrone and xanthylideneanthrone (Schoenberg, Ismail, and Asker, *J.*, 1946, 442); dixanthylen (Gurgenjanz and Kostanecki, *Ber.*, 1895, **28**, 2310); xanthen (Heller and Kostanecki, *Ber.*, 1908, **41**, 1324); diphenylmethyleneanthrone (Padova, *Ann. Chim.*, 1910, **19**, 386); *NN*′-dimethyldiacridine (Decker and Peltsch, *J. pr. Chem.*, 1935, **143**, 227). The synthesis of the other substances investigated has been described recently as follows: Anthrone derivatives (4-bromo-, 4-methoxy-, 4-methyl-) and dianthrone derivatives (4 : 4′-dimethyl-, 4 : 4′-dimethoxy-, 4 : 4′-dibromo-, 3 : 3′-dibromo-, 2 : 2′-dimethyl-, 2 : 2′-dimethoxy-, 2 : 2′-dibromo-) by Bergmann and Loewenthal (*Bull. Soc. chim.*, 1952, **19**, 66); 4 : 4′-dimethoxydixanthylen and dithioxanthylen by Bergmann *et al.* (*ibid.*, p. 262); 4-methoxydiphenylmethyleneanthrone by Bergmann *et al.* (*ibid.*, 1951, **18**, 88).

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