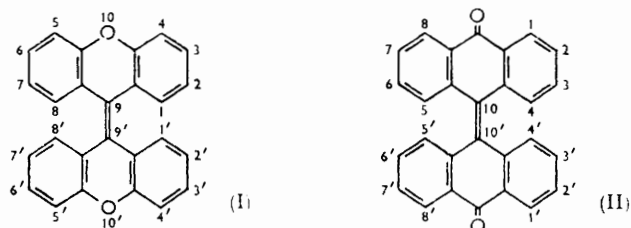


171. Thermochromism and Related Effects in Bixanthenylidenes and Bianthronylidenes. Part II.¹ General Observations.

By J. F. D. MILLS and S. C. NYBURG.

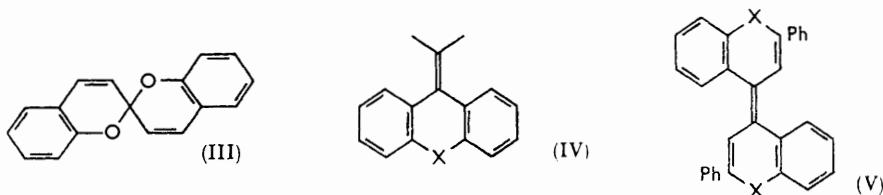
The widely held view that thermochromism and related effects in certain compounds based on 9,9'-bixanthenylidene and bianthronylidene is caused by "conformational twisting" is at variance with the discovery that the molecules in both the yellow and the blue-green crystal modification of the bixanthenylidene have the same untwisted conformations. Some implications and suggestions for further work are discussed.

In the preceding paper¹ we have shown that X-ray crystal structure analysis reveals the identity of the molecular conformation in the blue-green α - and the yellow β -polymorphic modifications of 9,9'-bixanthenylidene (I). Here we survey the present state of the theory of thermochromism and related phenomena and put forward some new considerations arising out of this X-ray analysis. Our aim is to suggest lines of enquiry which need to be pursued if these phenomena are to be better understood.



There are three phenomena to be considered which certain organic systems exhibit: thermochromism, piezochromism, and photochromism, the reversible change in colour brought about by change in temperature and in pressure and by irradiation, respectively.

Systems exhibiting these phenomena have aroused interest primarily because the effects are immediately apparent. A less arbitrary classification in which analogous changes in the ultraviolet region are included would cover more systems and probably add much to our understanding of the effects involved. However, our present information concerns only the visible region.



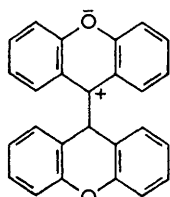
The compounds in question belong primarily to two basic types, those having the molecular skeleton of 9,9'-bixanthenylidene (I), 10,10'-bianthronylidene (II), and the

¹ Part I, *J.*, 1963, 308.

spiropyrans (III). Others showing these effects are those based on structures (IV) and (V).² Possibly the best recent summary is that of Kortüm³ which is primarily concerned with bianthrnylidene and its derivatives but gives some consideration to spiropyrans and bixanthenylidene.

As the temperature of a dimethyl phthalate solution of bixanthenylidene is raised between 70° and 180° the colour changes from yellow to blue-green. The change is due to enhancement of an absorption band at 16,000 cm.⁻¹; the remainder of the absorption spectrum to 40,000 cm.⁻¹ (measured for a decalin solution) appears to be unchanged.⁴ Bianthrnylidene behaves similarly, except that the molar extinction coefficient (ϵ) is ~ 10 times greater at any temperature. The spectral measurements of Hirshberg and Fischer⁵ are substantially the same as those of Theilacker *et al.*, but the former workers do not mention the solvents used and it is known, for bianthrnylidene at least, that ϵ values at 15,000—16,000 cm.⁻¹ are solvent-sensitive.⁶ We believe this solvent-sensitivity to be an important aspect of thermochromic behaviour.

Since the Beer-Lambert law is obeyed thermochromic behaviour is not due to dissociation-association. Theilacker *et al.*⁴ interpret thermochromism to imply the existence of



(VI)

a thermal equilibrium between two forms A and B of the molecule, the form B showing the characteristic absorption at 16,000 cm.⁻¹. They claim support for this view by showing that a plot of $\ln \epsilon$ at 16,000 cm.⁻¹ against $1/\text{Temp.} (^{\circ}\text{K})$ is a straight line. From this they calculate changes in enthalpy, ΔH , of 3.4 ± 0.2 and 4.9 ± 0.1 kcal. mole⁻¹ for bianthrnylidene and bixanthenylidene, respectively. According to Schönberg *et al.*,⁷ form B has a betaine structure such as (VI), but this has not won general acceptance, principally because of the

independence of the thermochromic absorption spectrum on the acidity of the solvent.

Kortüm³ identifies form A with the doubly bent conformation of the molecule which was found in 1954 for bianthrnylidene⁸ and now for bixanthenylidene¹ by X-ray crystal structure analysis, and he attributes to form B a molecule in which the two halves of the molecule preserve coplanarity but are twisted with respect to each other (Fig. 1). This idea has also been put forward by Grubb and Kistiakowsky.⁶ In order for the molecule to change its conformation from A to B, one pair of carbon atoms in the conflicting positions, namely, 1,1' (or 8,8') for bixanthenylidene (I) must pass each other. The steric conflict here is very severe. A scale drawing (Fig. 2) shows that the hydrogen nucleus of H-1 lies only some 0.3 Å in projection from C-1'. Clearly for this hydrogen atom to pass through to the other side of the molecule which, on the X-ray crystal structure evidence is already strained, it must be further strained to an exceptional extent. Our original view was to discount this possibility, but, as stated in Part I, evidence from studies of optical activity made by Theilacker and collaborators⁹ shows that the conflicting carbon atoms can, in solution at least, pass each other. The evidence is based on the spontaneous racemisation of the active isomers of 9,9'-bithioxanthenylidene-4-carboxylic acid. True, the molecular structure of this sulphur analogue of bixanthenylidene will not be quite the same as that of the oxygen compound. The S-C bonds in the heterocyclic ring will be some 0.6 Å longer than their O-C equivalents and this will cause even more conflict at the 1,1'- and 8,8'-positions. Also the sulphur compound is not thermochromic and this direct evidence of racemisation has yet to be obtained for a thermochromic compound. However,

² Cairns-Smith, *J.*, 1961, 182.

³ Kortüm, *Angew. Chem.*, 1958, **70**, 14.

⁴ Theilacker, Kortüm, and Friedheim, *Chem. Ber.*, 1950, **83**, 508.

⁵ Hirshberg and Fischer, *J.*, 1953, 629.

⁶ Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419.

⁷ Schönberg, Ismail, and Asker, *J.*, 1946, 442.

⁸ Harnik and Schmidt, *J.*, 1954, 3295.

⁹ Theilacker, personal communication.

¹⁰ Kortüm and Bayer, personal communication.

although optical isomers of neither bixanthenylidene⁹ nor bianthronylidene derivatives¹⁰ have been separately isolated, their active quinine salts in solution undergo racemisation on addition of concentrated hydrochloric acid. This, together with evidence on the sulphur analogue, seems to show beyond reasonable doubt that the conflicting carbon atoms in all these compounds can pass each other.

To our knowledge these represent some of the most extreme cases of non-bonded atoms overcoming steric repulsion to achieve racemisation. It is tempting to speculate whether it is not the hydrogen atoms which change their allegiance. Woodward and Wasserman¹¹ suggested that biradicals of these molecules might be formed when their solutions are

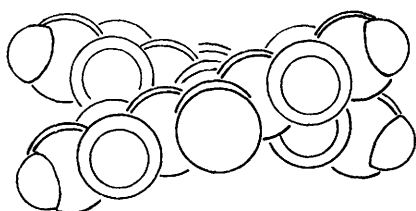


FIG. 1. The twisted conformation (form B) which has been proposed for molecules of types (I) and (II) in their thermochromic state.

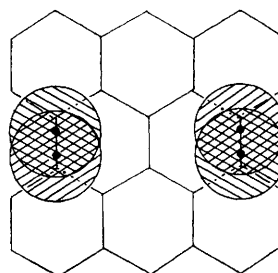
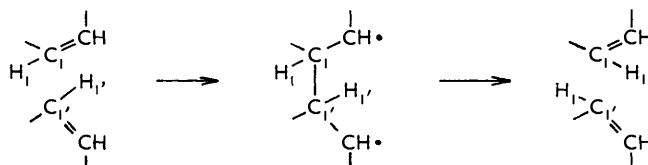


FIG. 2. Scale drawing of molecules of types (I) and (II), showing overlap of hydrogen atoms in conflicting positions.

irradiated with ultraviolet light at low temperatures (see Photochromism, below). It is conceivable that racemisation might proceed through this biradical, presumed unstable at temperatures above those at which photochromism can be produced:



For the established A and the proposed B conformation it is, of course, not known whether when the members of one pair of conflicting carbon atoms pass each other to give form B the members of the other pair do so simultaneously, so that the antimeric A conformation is obtained; and on the present evidence it seems impossible to decide this. However, our crystal structure analysis of the blue form of bixanthenylidene shows that there can be a prominent colour change without a change in conformation and this, we feel, weakens the case for the existence of B conformations. In the rest of this paper we set out other arguments which we think tell, on the whole, against the existence of B (and later C) conformations of these molecules.

Kortüm has attributed the lack of thermochromism in 9,9'-bifluoroenylidene as due to its being already in form B. This he suggested was supported by an unrefined X-ray analysis¹² but refinement¹³ has shown the molecule to have conformation A. Harnik,¹⁴ who supports the twisted-conformation theory, estimates the twisting potential barrier in bianthronylidene to be 28 kcal. mole⁻¹. We cannot say whether this is a realistic estimate but we do not consider Harnik's comparisons with the racemisation of biphenyl

¹⁰ Theilacker, Kortüm, and Elliehausen, *Chem. Ber.*, 1956, **89**, 2306.

¹¹ Woodward and Wasserman, *J. Amer. Chem. Soc.*, 1959, **81**, 5007.

¹² Fenimore, *Acta Cryst.*, 1948, **1**, 295.

¹³ Nyburg, *Acta Cryst.*, 1954, **7**, 779.

¹⁴ Harnik, *J. Chem. Phys.*, 1956, **24**, 297.

derivatives to be relevant; and we disagree with his statement that bithioxanthenyliene is not thermochromic because it is less overcrowded. Matlow¹⁵ has also estimated the barrier to twisting as some 20 kcal. mole⁻¹. Hirshberg and Fischer,⁵ on the other hand, doubt the possibility of twisted conformations.

It seems clear, as other authors have assumed, that where compounds are thermochromic there is a thermally populated state or set of states II of the molecules lying 3–4 kcal. mole⁻¹ above the ground state I [see Fig. 3(b)]. From state II there is a 16,000 cm.⁻¹ transition to an upper state III. As the temperature rises, so state II becomes increasingly populated and ϵ , at 16,000 cm.⁻¹, becomes correspondingly greater. It seems unlikely that state II is merely a new vibrational state and it is generally regarded as a low-lying

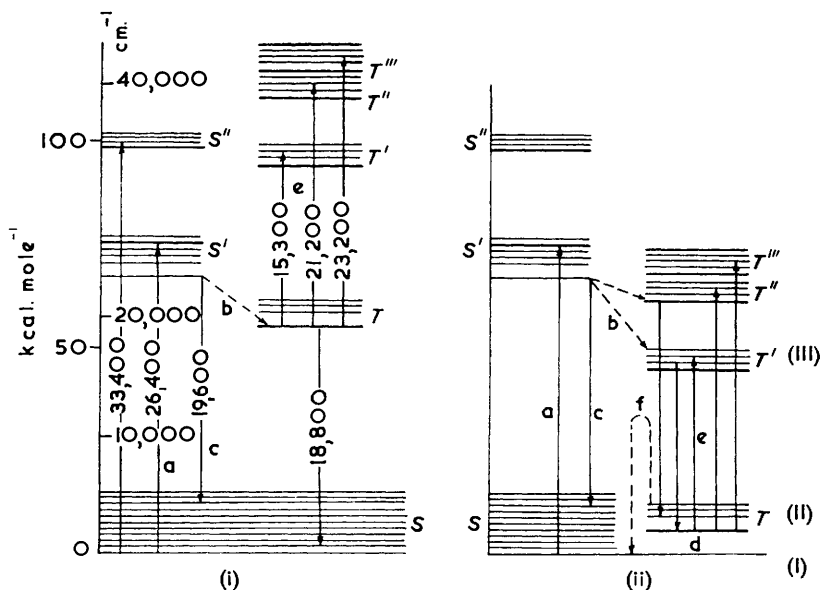


FIG. 3. (i) Scheme proposed by Kortüm *et al.*³² to account for photochromism of 2,4,5',7'-tetramethylbianthrnylidene.

(ii) Scheme of type proposed by Grubb and Kistiakowsky⁶ to account for general type of thermochromic and photochromic behaviour.

- (a) Primary process of irradiation. (b) Radiationless transitions. (c) Fluorescence. (d) This gap can be bridged thermally if small enough. (e) Photochromic bands. (f) Bleaching by irradiation.

triplet, state III being also a triplet. In support of this view is the increasing paramagnetic resonance absorption found in warmed solutions of bianthrnylidene in dimethyl phthalate, decalin, or acetophenone in the range 130–250°¹⁶ and in pyridine.¹⁷ Theilacker *et al.*¹⁸ looked for bulk paramagnetism in warmed thermochromic solutions of methyl 9,9'-bianthrnylidene-3-carboxylate and found none. However, the magnetic balance which they used has a sensitivity some 10³ times less than that obtainable by paramagnetic resonance absorption.⁹ It is possible that the latter method detects the small concentrations of biradicals which might be involved according to the mechanism of racemisation suggested earlier.

The view that thermochromic molecules are in twisted conformation originates from

¹⁵ Matlow, *J. Chem. Phys.*, 1955, **23**, 152.

¹⁶ Nielsen and Fraenkel, *J. Chem. Phys.*, 1953, **21**, 1619.

¹⁷ Wasserman, *J. Amer. Chem. Soc.*, 1959, **81**, 5006.

¹⁸ Theilacker, Kortüm, Elliehausen, and Wilski, *Chem. Ber.*, 1956, **89**, 1578.

the undoubted tendency for many derivatives substituted in the conflicting positions to be non-thermochromic. We believe the reasons for this could be that the increased overcrowding and larger molecular distortions which these substituents bring about raise the low-lying triplet levels so that they are no longer thermally accessible. It is also possible that substituents interfere with the necessary dipolar interaction with the solvent molecules (see below).

It seems that, in the crystals themselves, population of state II again governs the depth of the observed colour. Thus it is observed¹⁹ that crystals of bixanthenylidene at liquid-air temperature are colourless, at 280° are green, and when molten (315°) are so deep blue-green that a 4-mm. layer is almost opaque. The lack of any sudden change in colour suggests that there is no polymorphic transition under these conditions. We find the blue-green α -polymorph obtained by sublimation to be indefinitely stable, contrary to the report by Harnik *et al.*,²⁰ who state that their blue crystals, prepared in an unspecified manner but with unit-cell dimensions identical with those of our blue crystals, "decomposed" to a yellow powder. We have not found an explicit statement that blue crystals of bixanthenylidene, either at elevated temperatures or in the blue polymorphic modification, contain molecules in the twisted conformation although this is implicit in much of the discussion of thermochromism by the authors cited. True, it could be argued that in the blue crystals there is only a minority of twisted molecules, sufficient to impart a blue colour but insufficient to be detected by X-ray diffraction. We have examined the X-ray diffraction photographs for any sign of lattice disorder and have found none; if twisted molecules are present, they are there in very small amounts.

Crystals of bianthronylidene show more diverse effects. They are pale yellow at room temperature,⁷ and at 265° are reported to become, first, light green, and then dark green. After this, the colour change is said to be no longer reversible, the crystals remaining dark green at room temperature and showing a persistent paramagnetic resonance absorption.¹⁶ This permanent deep colouring of the crystals could be due to polymorphism, like that shown by bixanthenylidene on sublimation, and this should be checked by X-ray examination. The colour could be due to the formation of trapped free radicals. However, according to Kortüm^{9a} highly purified and dried crystals do not change colour when heated. Bianthronylidene can also be converted into a green form by sublimation at 10⁻³ mm. on to a surface cooled with liquid nitrogen.²¹ Our blue crystals of bixanthenylidene have been tested for paramagnetic resonance absorption,²² but none was observed; however, this could be because any resonance lines are too broad.

We think it most likely, as we have stressed, that reversible colour changes in thermochromic crystals are due to varying populations of state II, just as in thermochromic solutions. It should be noted that thermochromism is also exhibited when these compounds are adsorbed on solid surfaces. The colour of the adsorbed material at room temperature is not always that shown by the crystals or the solutions. Bianthronylidene shows the same type of reversible spectral behaviour with temperature when adsorbed on powdered magnesium oxide as in solution, apart from a small shift of some 1000 cm.⁻¹ to smaller wave-numbers.²³ Presumably the same mechanism operates.

In passing, we recall that the X-ray temperature factors for yellow and for blue bixanthenylidene crystals are 5.8 and 4.0 Å⁻², respectively. This suggests that increased thermal vibration is not the important feature of state II.

Environmental Effects on the II—III Transition.—There have been insufficient studies of the effect of solvent on the thermochromism of bixanthenylidene or of bianthronylidene solutions for reliable conclusions to be drawn. There seems to be an increase in ϵ with

¹⁹ Schönberg and Schutz, *Ber.*, 1928, **61**, 478.

²⁰ Harnik, Herbstein, Schmidt, and Hirshfeld, *J.*, 1954, 3288.

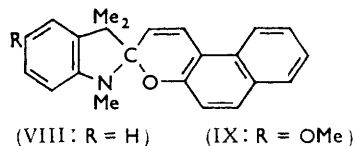
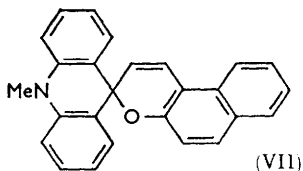
²¹ Wasserman and Davis, *J. Chem. Phys.*, 1959, **30**, 1367.

²² R. Srinivasan, Physics Department, Keele University.

²³ Kortüm, *ref. 3*, Fig. 7.

polarity of the solvent. For bianthrnylidene and its 2,2'-dicarboxylic acid,²⁴ ϵ is greater in acetophenone (2.96 D) than in decalin (0.0 D).⁶ The effect for certain spiropyrans is the same but much better authenticated. Spectral curves show a consistent and marked rise in ϵ with polarity of the solvent.²⁵

Changes in ΔH with solvent do not show a clear trend with bixanthenylidene or bianthrnylidene. For the latter in acetophenone * in the range 25—145° it is 3.1 and in decalin⁶ at 22—145° it is 3.3 (for a smaller range, 25—99°, in acetophenone, it is 3.9), whereas in dimethyl phthalate⁴ it is 3.55. It is difficult to detect a definite trend here. For molecules (VII), (VIII), and (IX) the ΔH values are: ²⁴ in dimethyl phthalate, 5.1, 4.9, 3.5, and in decalin 5.5, 7.2, 7.4, respectively.



Thus the trends seem to indicate that at any given temperature ϵ increases and ΔH over a range of temperature decreases as the polarity of the solvent increases. It is not difficult to see how this might arise. If we assume that for a given population of state II, ϵ is dependent upon the strength of the intermolecular field, then polar solvents giving rise to a larger dipolar electrostatic interactions will, at any given temperature, give enhanced transition moments. However, over a range of temperatures, polar molecules will be subject to Boltzmann-dependent disorientation whereas non-polar solvents will not. Thus, with increasing temperature, in a polar solvent, ϵ will tend to decrease and this will give rise to relatively smaller ΔH values.

It is hardly possible to estimate the intermolecular potential at all points within a large complex molecule in solution. The best that could be hoped for would be to see whether a correlation exists between ϵ at a given temperature in various solvents and the enthalpy of solution at infinite dilution. Apart from experimental difficulties connected with the low solubility of many thermochromic compounds in most solvents, there remains the theoretical difficulty connected with interpreting changes in enthalpy in terms of the mean potential energy between solute and solvent molecules. Such studies might throw light on why certain compounds do not exhibit the thermochromism which might be expected of them. It is possible that, apart from differences in electronic structure which would affect the nature of any low-lying triplet states, steric factors may prevent the necessary electrostatic interaction with solvent molecules.

Solid-state studies give a much better opportunity to examine the effect of intermolecular environment on ϵ . Where there are two or more polymorphic modifications of a thermochromic compound (and these compounds seem to show a marked predilection for polymorphism), estimates of intermolecular fields can be made and a correlation with ϵ looked for. We think this correlation may be the cause of the difference in colour of the α - and the β -polymorph of 9,9'-bixanthenylidene. We have attempted to measure ϵ values of both crystalline forms, but have not overcome the technical difficulties satisfactorily. Until this has been done and the whole question of piezochromism brought to a more satisfactory experimental state (see below) there seems little point in attempting even approximate calculations of expected magnitudes. Such studies of environmental effects should ultimately be capable of explaining the variations in the absorption spectra of thermochromic solids adsorbed on various substrates.

* All enthalpy data are in kcal. mole⁻¹.

²⁴ Or the 2,7'-dicarboxylic acid; in all such cases a distinction is not possible on chemical grounds.

²⁵ Hirshberg and Fischer, *J.*, 1954, 3129.

Piezochromism has received less detailed attention than has thermochromism, and in some cases seems to be an inappropriate name for what would be better described as pressure-induced polymorphism. Thus 4,4'-biflavénylidene crystals (V; X = O) are pale yellow at liquid-air temperature, yellow at room temperature, and ruby-red when molten;¹⁹ when pressed in a mortar the crystals change from yellow to red and then, according to Kortüm,³ gradually revert to yellow after a few days. In any case they can be restored to yellow immediately by treatment with a drop of ether.²⁶ According to Theilacker *et al.*⁴ biflavénylidene does not exhibit thermochromism when warmed in solution, but the spectral absorption curve of solutions is the same as that given by red crystals.³

Crystals of bixanthenylidene and of bianthronylidene are reported to show qualitatively the same colour change when pressed in a mortar as when heated in solution. Bianthronylidene is said²⁰ to revert slowly to its yellow form. Change of colour on grinding has also been reported for certain heterocyclic phenols² and hydroxyalkylamino-hydroxy-*p*-benzoquinones.²⁷ Schönberg and Asker²⁸ give the pressures necessary to bring about changes in colour as about 100 kg. mm.⁻² although we cannot trace any measurements. In fact, we have been unable to find any account of observations made on thermochromic crystals under uniform hydrostatic pressure, all the effects recorded seem to have been obtained by grinding crystals in a mortar or in a ball-mill. This will cause shear in the crystals and may be more efficacious in producing colour changes than uniform pressure. We do not subscribe to Kortüm's view³ that piezochromism arises because of the "less bulky" form of the molecules twisted in form B. Molecular volumes in crystals cannot, in general, be inferred from molecular shapes. We believe that these effects are due both to differing populations of state II in solids at varying temperatures and to changes in ϵ brought about by differences in molecular environment.

Photochromism.—Many thermochromic compounds, when irradiated in suitably low-melting solvents with ultraviolet light (ν 27,4000 cm.⁻¹) at -70° or lower, change markedly in colour. This effect, first noted by Hirshberg,²⁹ reaches a maximum asymptotically with time and is reversible, the colour fading on warming or, in some cases, on irradiation with visible light from an incandescent lamp.³⁰ Electron-bombardment at low temperatures causes the same colour effects.³¹ (No photochromism is observed if the radiation is less energetic than *ca.* 22,000 cm.⁻¹.) Hirshberg and Fischer⁵ later showed that for many bixanthenylidene and bianthronylidene derivatives unsubstituted in the conflicting positions the absorption spectra of the irradiated specimens in the range 12,500—18,200 cm.⁻¹ were the same as the corresponding thermochromic spectra, apart from a markedly larger ϵ throughout. However, according to Kortüm and his co-workers,³² all such unsubstituted derivatives, on irradiation, undergo irreversible dehydrogenation to an extent as much as 45%, even at low temperatures, and this vitiates any comparisons. For the non-thermochromic 2,4,5',7'-tetramethylbianthronylidene, irradiation at low temperatures produces new absorption bands in the visible region, at 15,200, 21,000, and 23,000 cm.⁻¹. The absorption spectrum between 25,000 and 38,000 cm.⁻¹ is substantially altered but warming virtually restores the original spectrum.

Disagreement concerning whether the photochromic bands are the same as those produced thermochromically seems to have been the cause of some acrimony.^{33,34} The fact that prominent photochromic bands are always generated in the 15,000—16,000

²⁶ Schönberg and Asker, *J.*, 1942, 272.

²⁷ König, *Chem. Ber.*, 1959, **92**, 257.

²⁸ Schönberg and Asker, *Chem. Rev.*, 1945, **37**, 1.

²⁹ Hirshberg, *Compt. rend.*, 1950, **231**, 903.

³⁰ Hirshberg, Frei, and Fischer, *J.*, 1953, 2184.

³¹ Hirshberg, *J. Chem. Phys.*, 1957, **27**, 758.

³² Kortüm, Theilacker, and Braun, *Z. phys. Chem. (Frankfurt)*, 1954, **2**, 179.

³³ (a) Hirshberg and Fischer, (b) Kortüm, Theilacker, and Braun, *J. Chem. Phys.*, 1955, **23**, 1723.

³⁴ (a) Hirshberg and Fischer, (b) Kortüm, *Angew. Chem.*, 1958, **70**, 573.

cm.⁻¹ region for these compounds, *i.e.*, in the same position as the prominent thermochromic bands, suggests a common origin. Grubb and Kistiakowsky⁶ and Kortüm *et al.*³² ascribe photochromism to a new molecular form C, in which the two halves of the molecule are twisted even further than in form B, so as to be virtually perpendicular. Wasserman and Davis²¹ believe that the three forms of bianthronylidene obtained by grinding, by sublimation, and photochromically are identical because the kinetics of bleaching in solution are the same in each case. We wonder if this shows any more than that all three forms revert to the colourless form by the same rate-determining step.

For photochromism to be exhibited, the irradiated medium must be fluid. If the lower half of the specimen is frozen by immersion in liquid air, then on irradiation, only the upper half becomes coloured.³² This, Kortüm *et al.* say,³² confirms their view that there is a twisted molecular conformation C which, because of spatial conflict with the immobilised solvent molecules, cannot be obtained by irradiation. Our view is that only in solution are the necessary vibrational distortions of the solute molecules sufficiently pronounced for an electronic transition to be possible.

One set of observations which tells against the twisted-conformation theory, as Woodward and Wasserman¹¹ point out, is that according to Hirshberg and Fischer,⁵ not only are the rates of reconversion after irradiation of compounds having substituents in the conflicting positions in the order MeO > Br > Me,³⁵ but also all these derivatives revert to their colourless forms more quickly than does the unsubstituted parent compound.

Because irradiated solutions show increased molar polarisation Hirshberg and Fischer⁵ favour a betaine-structure for the excited bianthronylidene type of molecule. Woodward and Wasserman,¹¹ maintain, however, that the dependence of rate of reconversion on the nature of the solvent tells against the betaine theory.

The photochromic behaviour of the spiropyrans seems more complicated, the photochromic spectrum depending markedly on the temperature of the irradiated solution. The bleaching behaviour seems also to be more complicated and depends on the acidity of the solution. Bleaching by irradiation with visible light seems to have a complicated dependence also on wavelength. Bleaching of 4,4'-dimethylbianthronylidene is independent of solvent acidity, which suggests caution in comparing the thermochromic and the photochromic behaviour of bixanthenylidenes and bianthronylidenes on the one hand and of spiropyrans on the other. For 4,4'-dimethylbianthronylidene the most effective bleaching radiation lies at about 23,000 cm.⁻¹.

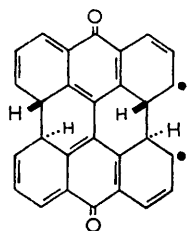
The scheme by Kortüm *et al.*³² to account for the spectroscopic behaviour of the non-thermochromic 2,4,5',7'-tetramethylbianthronylidene is shown in Fig. 3(a). The primary process of irradiation brings about a transition from the singlet ground state to an excited singlet state S'. A set of triplet states is then reached by radiationless transition; from these, upper excited triplet states are reached by absorption of visible light and give rise to photochromism. Kortüm *et al.*^{9a} suspect that thermochromism could be attributed to the presence of a set of singlet states of their B conformation. We favour the alternative type of scheme suggested by Grubb and Kistiakowsky⁶ in which thermochromic and photochromic absorption is due to the same set of triplet states [Fig. 3(b)]. If the compound is thermochromic the lowest-lying triplet state can be reached by thermal excitation; if non-thermochromic this gap, still relatively small, is nevertheless too large to be accessible thermally. Both schemes would account for the decreasing fluorescence (at about 20,000 cm.⁻¹) which irradiated solutions exhibit. This could be due to depopulation of the upper S states in favour of T states. How irradiation with visible light causes bleaching is not clear. We can only conclude, with Hirshberg,³⁶ that this irradiation allows molecules in state II to overcome an energy barrier and return to the ground state. There is support for the view (on either scheme) that photochromism is due to triplet states in the

³⁵ Ref. 5, Fig. 4, e, h, and i.

³⁶ Hirshberg, *J. Amer. Chem. Soc.*, 1956, **78**, 2304.

observation by Kortüm and Littmann³⁷ that photochromic solutions are paramagnetic after irradiation. The fact that Hirshberg and Weissmann³⁸ did not record any electron spin resonance spectrum with photochromically coloured solutions of bianthronylidene derivatives or spiropyrans was possibly due, as they admit, to the breadth of the resonance lines.

Because of the long life of the colour in photochromic solutions at low temperatures, Kortüm³ has suggested that the molecules might better be regarded as being biradicals rather than in triplet states. Woodward and Wasserman¹¹ agree with this view and favour formulations of type (X). We have seen how this radical could represent the intermediate state for racemisation.



To summarise, X-ray crystal analysis of the yellow and of the blue-green polymorph of bixanthenylidene reveals that the molecules have the same conformation, contrary to current views on the cause of thermochromism in this and related compounds. We believe the colour to arise from environment-sensitive triplet-triplet transitions unaccompanied by marked conformational change and believe that this could account for variations with solvent of thermochromic behaviour in solution. The same transitions probably also account for photochromism.

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³⁷ Kortüm and Littmann, *Z. Naturforsch.*, 1957, **12a**, 395.

³⁸ Hirshberg and Weissman, *J. Chem. Phys.*, 1958, **28**, 739.