

THERMOCHROMISM¹

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I. INTRODUCTION

A variety of organic compounds change color when heated and revert to the original color on cooling. This reversible dependence of color on temperature is known as thermochromism.

An important question raised by this kind of definition is: "How great must the color change be to warrant use of the word thermochromism?" There is no doubt in such spectacular cases as bianthrone which goes from a light yellow solid to a green melt, or a spiro-pyran which goes from colorless to deep purple. There are also a number of compounds which undergo a quite noticeable change in shade or intensity over a small temperature range. Whether thermochromism is noticed depends, in the case of solutions, on the solvent chosen since this may limit the concentration or temperature accessible. The visual acuity of the observer may be another factor. For these reasons there is some disagreement in the literature whether some compounds are thermochromic.

A definition in terms of spectral curve properties is difficult because of the variety of behavior shown by the spectra of different thermochromic compounds. Whatever type of dependence of spectra on temperature might be specified as defining thermochromism could also happen outside the visible region so that no color change would be visible.

For the purpose of this review, thermochromism is defined operationally as an easily noticeable reversible color change in the temperature range limited by the boiling point of each liquid compound as the upper temperature, the boiling point of the solvent for solutions, or the melting point for solids. Organic substances which have been noted as thermochromic are included; inorganic compounds are not included.

The mechanism responsible for thermochromism varies with molecular structure. It may be due to an equilibrium between two molecular species, acid-base, keto-enol, lactim-lactam, or between stereoisomers or

(1) Support by National Science Foundation Grant 7307 is gratefully acknowledged.

between crystal structures. It may be due to a simple broadening of a near ultraviolet absorption curve, to ring opening, to thermal achievement of a triplet state configuration, or to the formation of free radicals. The spiro-pyrans, the overcrowded ethylenes and the disulfides have been extensively investigated, while the mechanism for numerous other compound types has not been investigated at all.

The observant reader will note that many of the thermochromic compounds bear more than passing resemblance to well known dyes. Many, if not most, of the compounds are also notably fluorescent, and temperature quenching of fluorescence may be responsible for the apparent thermochromism of some of them. A number of them show piezochromism, photochromism, or dichroism as well.

One use for thermochromic behavior has been suggested: that paint whose color is temperature dependent be used to coat space satellites (*Chem. and Eng. News*, July, 27, 1959, page 43).

Since the numbering of the rings in many compounds is highly individual, the reader of the literature must check names with care. Not only does the numbering vary from author to author, but even from article to article by the same author.

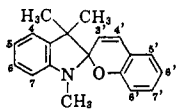
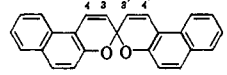
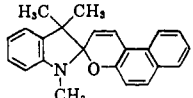
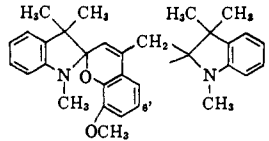
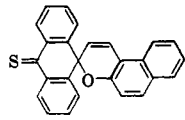
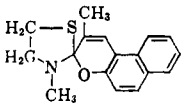
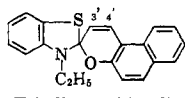
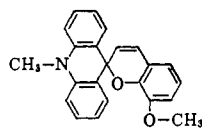
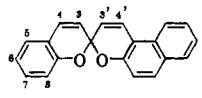
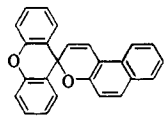
II. THE SPIROPYRANS

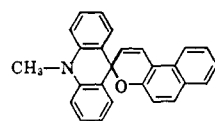
Almost simultaneously in 1926 three reports appeared describing the fact that the colorless compound di- β -naphthospiran gives a blue-violet melt, and that colorless solutions in inert solvents become blue-violet on heating, reverting to the colorless state on cooling (22, 25, 85). Since that time at least sixty thermochromic spiro compounds have been reported. These compounds, their color changes and specific references are recorded in Table I. References containing spectral data are specially noted.

A review of the chemistry of the spiro-pyrans appeared in 1948 (91).

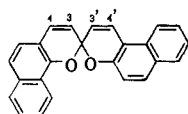
The thermochromic mechanism involves a thermally sensitive equilibrium between the colorless spiro com-

TABLE I
 SPIROPYRANS

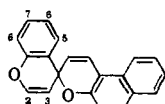
Spiropyran	Color of melt	Color in boiling inert solvent (1) diphenyl ether (2) benzene or xylene (3) anisole	References (s indicates spectra)	Chemical Structure	Color	2 "Colored" in 2	38	
								
N,3,3-Trimethylindolino-benzospiropyran		Violet (in 1)	57 s, ^a 73, ^a 144		Di-β-naphthospiropyran	Blue	Violet in 2 or 3 Purple in 2. Not thermochromic in piperidine	19, 22, 25, 26 44, 51, 57, 66, 91, 99, 100, 105, 113
-3'-methyl-	gives ratio of "colored" to "uncolored" form 11				3-methyl-		Violet in 2 or 3	19, 25, 85, 91, 113
-6'-nitro-	Purple blue	Red soln. in o-chlorophenol blue with heat	9, 45, 73, 74		3-isopropyl- 3-amyl- 3-octyl- 3-phenyl-	Blue	Violet in 2 or 3 Purple in 2 Colorless in 2 Violet in 3	19, 100 27, 91, 113 41, 91 19, 25, 91, 100, 113
-6'-bromo- -7'-nitro- -7'-chloro- -8'-methoxy- -8'-nitro- -6',8'-nitro-	Colorless Orange Purple	Violet in 1	73 9 9		3-benzyl- 3-(β-phenylethyl)- 3,3'-dimethylene-	Deep blue	Blue-violet in 2 Blue-purple in 2 Violet-blue in 3	37, 85, 91 37, 91 19 s, 27, ^{1a} 38, 72, 91, 100, 113
-6',8'-dibromo- -6'-nitro-8'-allyl- -6'-nitro-8'-bromo- -6'-nitro-8'-fluoro- -6'-chloro-8'-nitro- -6'-bromo-8'-nitro- -6'-nitro-8'-methoxy- -6'-methoxy-8'-nitro- -5'-nitro-8'-methoxy-	Blue Purple Purple Purple Purple Purple Dark blue Green Dark green	Blue in 1 Violet in cold 1 Blue in hot 1	74 74 73		3,3'-trimethylene-	Blue	Faint violet in 1	23, ¹ 38, 51, ^{1a} 55, 56 s, 72, 91, 100, 113 ^{2*}
-5-methoxy- -5,8'-dimethoxy-	Violet Intense blue	"Beautiful" in 1 Violet in 1	57, ^b 144 57, ^a 144		N,3,3-trimethylindolino-β-naphthospiropyran	Blue	Pink to intense red in 1. Red-violet	8, 18 s, 19 s, 28 s, 43 s, 44 s, 49, 50 s, 51 s, 56, 57, 60 s, 144
					5-methoxy-	Red-violet	Cold soln. red-violet; more intense hot	49, 50 s, 51 s, 57 s, 144
					β-Naphthothiazanthospiropyran	Deep red	Pink in 1	92
4'-(1,3,3-Trimethyl-2-indolinylmethyl)-8'-methoxy-1,3,3-trimethylindolino-benzospiropyran	Pink		73					
-6'-bromo-8'-methoxy-	Pink		73		3-Methylthiazolidine-β-(3'-methyl)-naphthospiropyran	Yellow at 200°		74
					3-Ethylbenzothiazoline-β-naphthospiropyran-(3'-methyl)-	Purple; remains purple on cooling	Weakly purple in 1	44, 61, 74 74
								
N-Methylacridino-8'-methoxy-benzospiropyran		Violet in 1	144					
					Xantho-β-naphthospiropyran	Deep red	Red in 1 Pink in 2 or 3	38, 44 s, 51 s, 57 s, 69, 113, 114, 144
Benzo-β-naphthospiropyran	Purple	Violet in 2 or 3 Wine red in 2	19, 23, 55, 66, 44, 113, 91		Thiazantho-β-naphthospiropyran	Deep red	Pink in 1	92
3-methyl-	No change purple	Violet in 2 or 3 Wine red in 2	23, 25, 55, 56, 66, 91, 100, 113					
3-isopropyl-	Purple	Purple in 2	91					
3-benzyl-	Purple	Red-purple in 2	91					
3-phenyl-	Purple	Purple in 2	37, 41, 91					
3-(2-phenylethyl)-	Deep	Intense purple in	37, 91					



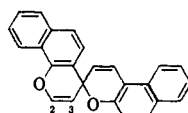
N-Methylacridine- β -naphthospiropyran	Blue	Blue in 2	44 s, 49, 50 s, 51 s, 57 s, 144
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4-Phenyl- α,β -di-(naphthospiropyran)	Deep purple		38, 91
4-phenyl-3-methyl-	Blue		38, 91
4-phenyl-3'-methyl-		Violet in 1	38, 39, 91
4-phenyl-3,3'-dimethyl	Blue	Pale violet in 1	39, 91



Benzo- β -naphthoisospiropyran			
2-Phenyl-3-methylbenzo- β -naphthoisospiropyran	Purple	Purple in 2	91
2-phenyl-3-methyl-7-methoxy-	Purple	Magenta in 2	36, 39, 91
2,3-diphenyl-7-methoxy-	Purple	Pale magenta even at 0°	40, 91



Di- α,β -naphthoisospiropyran			
2-Phenyl-3-methyl- α,β -dinaphthoisospiropyran		"Thermochromic"	39

^a These references state the compound is not thermochromic. ^b Notes as not thermochromic, but after ultraviolet irradiation produces color at low temperature, color changes on warming.

compound and a planar "open form" created by rupture of the bond between the spiro-carbon and the ring oxygen. Much interest has centered on discovering the structure of the colored species, and arguments favoring each specific form are summarized below. Apparently the colored species consists of a large number of resonance forms.

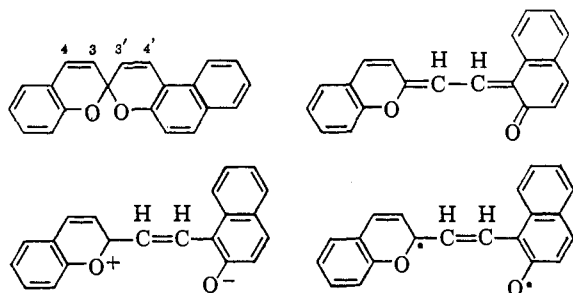


Figure 1.—Benzo- β -naphthoisospiropyran and the structures which have been proposed for the colored modification.

A. STRUCTURAL FEATURES

A number of generalizations can be made about the structural requirements for thermochromism of a

spiropyran: (a) The pyran ring must be at least a naphthopyran (23). Benzopyrans are not usually thermochromic, but they may be, depending on the specific nature of the heterocyclic ring, *i.e.*, indolinobenzospiropyran (144). (b) Substitution on the 3'-carbon prevents thermochromism by making the required planar, open-form sterically impossible (23, 92). The weak thermochromism of 3,3'-dimethylene- and 3,3'-trimethylenedi- β -naphthospiropyran confirm rather than refute the idea, since they do not prevent the required planarity whereas the puckered ring of the 3,3'-tetramethylene compound does, and it is not thermochromic (56, 72, 100). Other 3'-substituted thermochromic compounds are known, particularly the isospiropyran (39). (c) The extent to which a compound is thermochromic is related to the electron release ability of the heterocyclic ring (57, 74, 144). (d) Substitution on either ring enhances thermochromism if it contributes to the positiveness of the spiro-carbon or the heteroatom, or to the negative charge on the pyran ring oxygen (11, 74).

Several investigators have pointed out that a configurational change in the molecule must occur. Koelsch (72) reviewed the evidence up to 1951, and noted that the apparent lack of significant change of dipole moment (66) was not convincing in view of the lack of knowledge of the concentrations involved. He demonstrated that a change in molecular configuration is involved by the sudden chilling of the hot colored solution to -70° , where the color persisted until the solution was allowed to warm to a liquid state. He further noted that if the open, colored form were to be planar, the double bond of the opened ring would have to be *trans* rather than *cis*. Hirshberg and Fischer (56) found that the rate of reversion of the colored form obtained photochemically at low temperature depends inversely on the viscosity of the solvent. They also suggested (57) the possibility that the various colored modifications are more or less planar structures with *cis-trans* isomerism occurring with regard to the central "single" bond and the two adjoining "double" bonds (see Figure 1). Chaude and Masse (10) performed molecular orbital calculations on model spiropyran and found that the double bond which connects the two ring systems in the open form (the 3'-bond) goes from 0.77 in the ground state to 0.56 in the excited state. Replacing the heterocyclic ring oxygen by nitrogen increases the positive charge on that atom from 0.324 to 0.438.

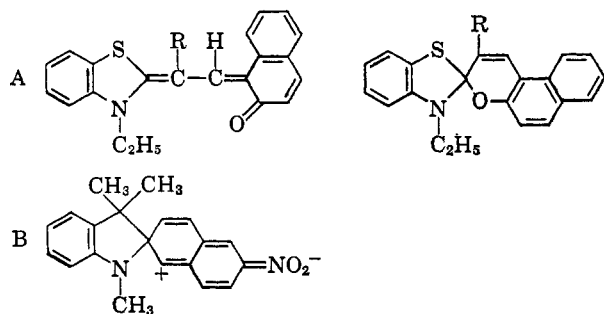
B. STRUCTURE OF THE THERMOCHROMIC FORM

The suggestion that the colored thermochromic form is a quinoid structure was offered by Lowenbein and Katz (85), who ruled out free radical formation, or a dissociation process, on the basis that solutions were stable in air, and gave normal molecular weights. Dickinson and co-workers (22, 23) at first tentatively

ascribed color to a quinoid structure, but then suggested that the colored form might be a "chelate" in which the oxygen of the opened ring forms a bond with the H-atom on the 3'-carbon; this would also explain lack of thermochromism of 3'-substituted compounds. Dilthey and Wizinger (26) pointed out that a strong bathochromic effect is obtained when true quinones are treated with piperidine, whereas there is no such effect on treatment of the spiroopyrans. Bergmann, Weizmann and Fischer (8) compared the dipole moments of the non-thermochromic dibenzospiroopyran (1.2 *D*) with the thermochromic indolino- β -naphthospiroopyran (1.38 *D* at 30° and 1.43 *D* at 90°) and with N-methylquinolino- β -naphthospiroopyran which is deeply colored at room temperature (10.4 *D*). They note that degree of color parallels dipole moment, but that the difference in dipole moment in the range in which the quinolino compound is thermochromic is so small that possibly colored quinoid resonance forms make an appreciable contribution to the colored form.

Evidence favoring polar or ionic resonance structures is convincing. The only negative evidence was the failure of Hukins and LeFevre (66) to find a change in dipole moment over a 30° temperature interval. Schonberg and co-workers (113) attributed this negative result to the small concentration of solute. They offered evidence for polar structures by showing that naphthospiroopyrans are adsorbed on activated alumina as a blue-green adsorbate from the colorless solution (105, 114). Chaudé and Rumpf also concluded that polar structures are important in the colored form (19).

Knott (74) summarized work in this field to 1951 and discussed the effects of substituents as enhancing thermochromism if they contribute to a resonance structure of the open form. He pointed out that 3'-substitution would have less effect in a compound such as A, so that such substitution merely stabilizes the spiran form which is however thermochromic; when R = H, only the open dye is obtained, when R = CH₃, the thermochromic spiran is obtained. He also made nitro-substituted indolinospirobenzopyrans, and suggested their thermochromism might be due to such structures as B. Koelsch and Workman (73) had



begun work along the same lines, and added their results to the literature, concurring with Knott.

Dilthey and Wubken (27) favored the ionic formation theory, and suggested that thermochromism might parallel salt-forming ability of the spiro compounds, and that 3'-substitution operates by reducing the basicity of the molecule. Dickinson and co-workers (24) disagreed, citing the fact that 3'-methylbenzo- β -naphthospiroopyran is not thermochromic, but the 3-methyl compound is, yet both dissolve in glacial acetic acid to give colored solutions of the salts. Hirshberg and Fischer (57) found that polar solvents favor formation of the colored form, and felt that polar structures must contribute strongly to the colored molecule.

Further evidence for polar structures is that electron releasing substituents on the heterocyclic ring favor thermochromic behavior, as does an increase in positiveness of the heterocyclic ring (11, 100).

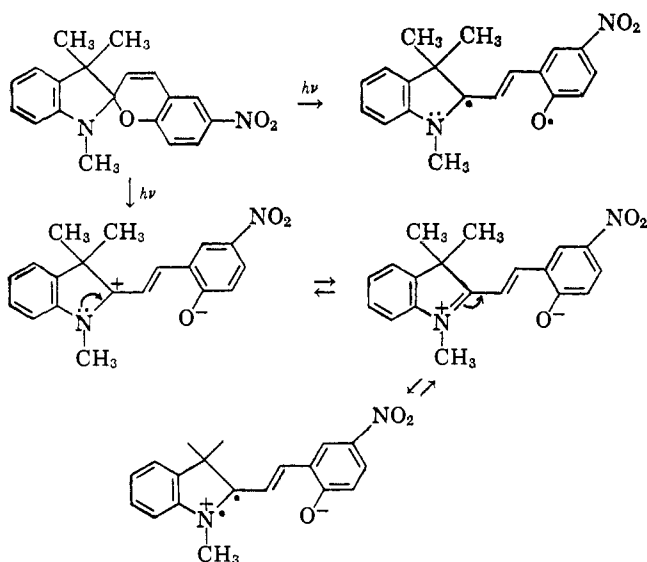
The possibility of free radical formation accounting for the thermochromic color was rejected by Dilthey (25) on the grounds that passage of oxygen or hydrogen through the hot colored solution has no effect on the color; also rejected was the quinoid form, since this seemed equally likely for the nonthermochromic benzospiroopyrans. Lowenbein and Katz (85) rejected the free radical notion for the same reason. Schönberg, Mustafa and Asker (113) brought further evidence; the thermochromic spirans are adsorbed on alumina or silica with formation of color, whereas such a compound as 2,2'-diketo-3,3'-diphenyl-3,3'-dicoumaryl, which does give a blue solution on heating, due to free radical formation, does not give adsorption colors. Hirshberg and Weissman (64) examined the colored form of two naphthospiroopyrans, generated by ultraviolet irradiation, and in no case was electron spin resonance observed. They concluded either that the colored species are not free radicals or that they possess unusually broad resonance lines.

Yet Heller, Fine and Henry (45), working with indolinobenzospiroopyran, substituted in the 6'-position by a nitro group, found weak to medium electron spin resonance absorption of the colored form, indicating formation of free radicals. Their suggested mechanism is shown.

Thus the nature of the colored form may depend on the hetero-atom, and possibly on the substituents.

C. ENERGY OF TRANSFORMATION

There have been several studies of the energy involved in the thermochromic transition. From a plot of log extinction coefficient *vs.* the reciprocal of the temperature Chaudé and Rumpf (19) found values of the heat of transformation for a series of spiroopyrans ranging from 3.1 to 6.9 kcal./mole, the values varying with the solvent; they also estimated that the concentration



of the colored form at 100° is of the order of 10^{-4} mole/liter. Reitz and Kalafawy (99) found a value of 5.8 kcal/mole for di- β -naphthospiropyran, dissolved in phenetole. Chaudé (18) found a value of about 6.6 kcal./mole for the indolinospirans. Heller, Fine and Henry (45) working with 6'-nitro-indolinobenzospiropyran found the rates of conversion of the colored form at 26.5° and 6°; the reversion to the colorless form followed first order kinetics, with rate constants of $7.5 \times 10^{-4} \text{ sec.}^{-1}$ and $4.28 \times 10^{-5} \text{ sec.}^{-1}$. From this they found an activation energy of 23 kcal./mole. Hirshberg and Fischer (56) found that the photochromic form of several spirans, on warming, reverted to the colorless form by first order kinetics, with an activation energy of 11 to 19.3 kcal./mole (see also (20)). Working with merocyanine dyes, Hirshberg (48) found heats of transformation of the order of 2 to 3 kcal./mole.

D. PHOTOCHROMISM

Photochromism is the reversible coloring of compounds on irradiation with ultraviolet light, gamma rays (52) or electrons (51). An excellent review article on the subject appeared in 1961 (14). Some of the photochromic spirans are also thermochromic, and in the cases in which the thermochromic modification can be made by irradiation, it can be obtained in much higher concentration than by thermal means, hence an effective means for studying the thermochromic form is available (42).

Hirshberg and Fischer (56, 57) investigated the relation between photochromism and thermochromism for a series of β -naphthospiropyran and their 3 and 3'-substituted derivatives and found that the thermochromic and the photochromic forms (irradiation at -115°) are apparently spectroscopically identical. They concluded that those compounds which are photochromic but not thermochromic require too much

energy to be formed thermally, and that those compounds which are neither photo- nor thermochromic are so for reasons of steric hindrance. Assuming that the colored form created by irradiation at low temperature is the result of 100% conversion, they calculate that the molar extinction coefficients range from 10,000 to 100,000 in methycyclohexane. Comparison with actual extinction coefficients obtained with the thermochromic solutions shows that there is only a very small degree of thermal conversion even at 120°. They postulated that photoconversion into the colored form involves a transition between excited states of the two modifications, followed by a freezing-in of the colored form (28). It should be noted also that the colored modification obtained by irradiation depends on the temperature; for example, di- β -benzospiropyran is green when irradiated at 103°K., wine red at 123°K. with yellow luminescence, and rose mauve at 163°K. (55, 60).

Hirshberg also studied indolinospirans and N-methylacridinospirans (50) and found their photochromic and thermochromic forms identical. He also noted that the same quantity of ultraviolet light always resulted in the same quantity of the colored molecule, and that the colored form is bleached by visible light proportionately to the amount of visible light. He suggested that this might be used as the first photochemical memory model and could be used to form memory storage in a computer. Berman, Fox and Thompson (9) were also interested in data storage; in their work they found the dependence on substituents of the rate of ring closure showed agreement with the Hammett equation, and that the kinetics of reversion are first order. The difference in spectra before and after irradiation is an increase in $\log \epsilon$ of about 2 units from 4000 to 6000 Å. with no substantial change in shape, while below 4000 Å. there is little change of any kind. Chaudé and Rumpf (20) reported that several indolinobenzospiropyran became colored on ultraviolet irradiation and that the colored solutions were bleached by visible light.

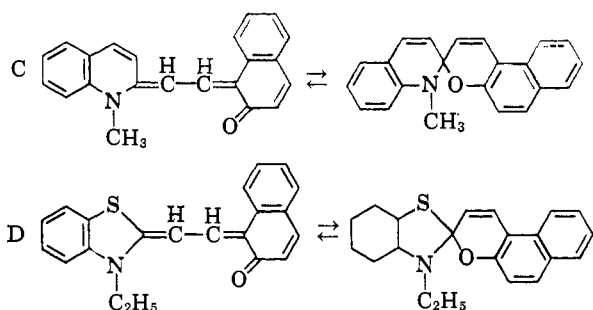
Heller, *et al.*, (45) suggested that since visible light effects photofading of the colored form, it seems possible that ultraviolet radiation absorbed by the colored form might also be effective and that, if this is the case, the photostationary state would have a less colored form than otherwise. This point had been realized also by Hirshberg (44), who spoke of attainment of photo-equilibrium, since at low temperature the thermodynamic equilibrium is almost completely in favor of the spiropyran.

E. SOLVENT EFFECTS

In addition to the various solvent effect noted previously, Hirshberg (44) found that the visible absorption band of spiropyran generally is shifted to longer wave lengths by 200 to 400 Å. in comparing a non-polar solvent with a polar solvent, *i.e.*, methyl-

cyclohexane with ethanol. The more polar solvent also shifts the colorless-colored equilibrium in favor of the colored form; with some compounds the ratio of two peaks changed with the polarity of the solvent, and with others there was only a shift toward shorter wave lengths with increasing solvent polarity, and some compounds showed broad absorption with a pronounced shoulder indicating more than one colored species (57). The same author in a later paper (43) suggested that there might be several interconvertible stereoisomers of the colored modification in solution, the relative concentrations being highly temperature dependent, and that in alcoholic solution one of the isomers might be stabilized by association with the solvent.

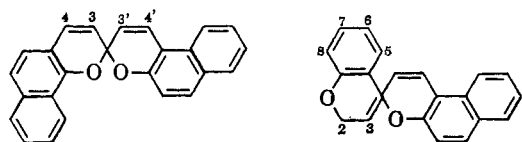
Hirshberg reviewed and interpreted his earlier work (44) and brought out new evidence of similarity in some merocyanine dyes and the thermochromic colored form of some spiropyrans. Dyes C and D in their assumed



closed form have spectra in decalin of striking similarity to those of colorless spiropyrans, and also have similarity in their visible spectra in alcoholic solutions with the photochromic colored spiropyrans. The predominance of the spiropyran form of dye D is particularly striking in decalin solutions, which are actually thermochromic. In alcohol solutions the open form predominates. This solvent effect on the thermal equilibrium between the two forms is similar to that observed with thermochromic spiropyrans. If acid is added to those spiropyrans derived from acridine or indoline, they are converted into salts of the open merocyanine-like form.

F. ISO-SPIROPYRANS

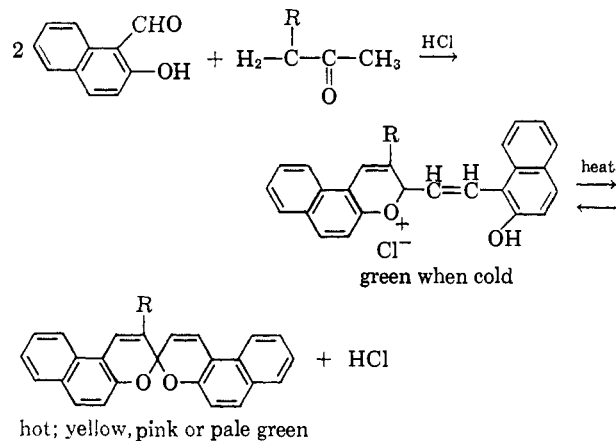
Heilbron and co-workers prepared a number of iso-spiropyrans (36, 39, 40) and reported that they showed thermochromism to an enhanced degree. They also found that 4-phenyl-3'-methyl- α,β -dinaphthospiropyran and the 4-phenyl-3,3'-dimethyl compound are weakly thermochromic.



Di- α,β -naphthoispiropyran Benzo- β -naphthoispiropyran

Heilbron and co-workers synthesized a number of thermochromic spiropyrans (37, 38, 41). They noted that methyl β -phenylethyl ketone condenses with salicylaldehyde in basic solution, then with 2-hydroxy-1-naphthaldehyde to give the non-thermochromic 3'-phenylbenzo- β -naphthospiropyran, while the same condensation in hydrochloric acid gives the corresponding 3-phenyl compound which gives a purple color in boiling xylene. They pointed out that the acid condensation could be used to distinguish methyl ketones.

Sawicki (101) developed a test for methyl ketones which is specific except for a few simple cycloalkyl ketones which also give the test. A methanol solution of the compound to be tested is mixed with a methanol solution of 2-hydroxy-1-naphthaldehyde, then treated with dry hydrogen chloride gas for half a minute. If aliphatic ketones are present the mixture becomes dark blue-green. The mixture is then boiled with *o*-dichlorobenzene to remove all the methanol, and the brilliant green color which fades and almost completely disappears on heating and reappears on cooling indicates the presence of aliphatic ketones containing the acetyl group. The reaction sequence is shown.



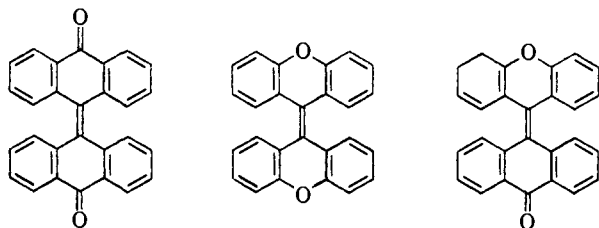
III. THERMOCHROMIC ETHYLENES

A. BIANTHRONE, DIXANTHYLENE AND XANTHYLIDENE-ANTHRONE

It is both convenient and interesting to follow the work on these compounds in chronological order, since this so well illustrates the changing faces of a developing theory. The structure of many of the thermochromic compounds is discussed through reference (139).

Mayer (88, 89) noted in 1909 that bianthrone is lemon yellow and becomes green under pressure, and that warm solutions are green. Padova (138) reported that the colorless bianthrone melts to form green droplets. Schönberg in 1928 (124) found that the faintly yellow dixanthylene is colorless in liquid air, the melt is dark blue-green, and its solution at 282° is deep blue-green and somewhat fluorescent. He conjectured that the thermochromism must be due to the same cause as in the case of bianthrone.

Bergmann and Corte in 1933 (5) noted that color changes on heating had long been known for bianthrone, benzhydrylidene-anthrone, benzhydrylidene-fluorene, dixanthylene, benzalfluorene and benzhydrylidene-xanthene. They suggested the formation of free radicals to account for the color formation, and discounted Padova's suggestion that a dissociation was responsible, based on molecular weight determinations.



Bianthrone Dixanthylene Xanthylideneanthrone

Schönberg, Ismail and Asker (110) argued that the thermochromic compounds derived from anthrone and xanthene have ionic (betaine) resonance forms (see also 90). Proof was offered on three grounds: one, their behavior is similar to that of the spiro compounds, where ionic forms are also postulated; two, some betaines under the influence of light join to form a ring; exactly the same occurs with the diphenylmethylenanthrone; and third, cleavage by thionyl chloride does not occur with true ethylenes, but is explained easily assuming an ionic structure.

In a review article in 1948 (3) Bergmann cited evidence for considering that the thermochromic ethylenes are biradicals in their colored modifications, pointing out that in all these compounds *cis-trans* isomers had not been observed, which would be understandable if the ethylene bond is not a true, rigid double bond, but one twisted enough that biradical formation is easily accomplished.

Theilacker, Kortum and Friedheim in 1950 published the first of a series of articles on thermochromism (136). They measured the spectra of bianthrone and dixanthylene in the temperature range from 76 to 182°. From the fact that the solutions followed Beer's law, dissociation was ruled out. By plotting the equilibrium constant *vs.* the reciprocal of the temperature, they found the heat of transformation from the normal to the colored form to be 3.4 ± 0.2 kcal./mole for bianthrone and 4.9 ± 0.1 kcal./mole for dixanthylene. They found the fraction of bianthrone in the colored state to be 0.014 at 76° and 0.045 at 182°; and for dixanthylene, 0.001 at 99° and 0.004 at 182°. They suggested that the thermochromic form is a triplet state.

Hirshberg (46) reported that solutions of bianthrone and of xanthylideneanthrone change color on irradiation at -60°, and that the original unchanged compounds are recovered on warming. This differs from the photochemical reaction produced at room temperature

which gives helianthrone and naphthodianthrone irreversibly. The non-thermochromic 4,4'-substituted bianthrones were also found to be photochromic.

Bergmann and Fischer (6) measured the dipole moment of bianthrone and found it to be about 1 *D*, which excluded the possibility of the molecule having a symmetrical planar configuration. The same was found for dixanthylene. On this basis they questioned the probability of the ionic structure proposed by Schönberg, Ismail and Asker.

Grubb and Kistiakowsky (30) measured the spectra of bianthrone and its 2,2'-dicarboxyl derivative at temperatures from 25 to 145° in acetophenone and in decalin. Since rapid chilling of the hot thermochromic solution did not "freeze in" the color, they rejected as an explanation of thermochromism the theory that the normal state is non-planar and the colored form planar. The lack of substantial variation in spectra with solvent polarity ruled out any considerable contribution of ionic forms. For these reasons they postulated that the thermochromic state is a diradical triplet state, with the two molecule halves at approximately 90 degree angles to each other, whereas the ground state is a singlet state, with the double bond in a considerable state of torsion. They found that the light absorbing state has an energy content 3.5 kcal./mole higher than the normal state.

Bergmann's suggestion that the thermochromism of bianthrone is due to non-planarity of the normal molecule because of interference between the 4- and 4'-hydrogen atoms, and that raising the temperature stretches the double bond to permit planarity and conjugation, was checked by Hirshberg, Loewenthal and Bergmann (62). They found, as predicted, that 4,4'-dimethyl-, dibromo, and dimethoxy derivatives are non-thermochromic (see also 147).

Hirshberg (47) noted that bianthrone is photochromic while dixanthylene is not, and attributed the photochromic mechanism to the carbonyl group.

Bianthrone and its derivatives, and xanthylideneanthrone change color on cooling, as well as on heating, while the 4,4'-disubstituted bianthrones show only the low temperature thermochromism. All the compounds show fluorescence and phosphorescence in varying degrees in rigid media at low temperatures. Hirshberg, Loewenthal, Bergmann and Pullman (63) suggested as a working hypothesis that a molecule such as bianthrone can assume a planar configuration at elevated temperature, but is not planar at room temperature, while at low temperature the color developed is due to a configuration in which the molecular halves are perpendicular to each other, approaching a biradical state, which would also help explain the low temperature phosphorescence.

Mustafa and Hilmy added to information on the effect of substituents (95). They found that di-1,2-

benzoxanth-9-ylidene is thermochromic, and the 3,4-compound weakly thermochromic.

An attempt was made to interpret the position of the two further ultraviolet bands, based on the assumption that rupture of conjugation by destruction of planarity is much more pronounced in bianthrone than in fluorenylideneanthrone (140).

Seven papers dealing with the thermochromism of bianthrone or dixanthylene appeared in 1953. A series of substituted derivatives of both compounds demonstrated that substitution in the 4,4'-positions renders them non-thermochromic, while substituents on other positions have no such effect (54, 81, 117, 132, 152). Fraenkel and co-workers found the thermochromic form of bianthrone to be paramagnetic in various solutions and in the solid state (147), but that they had no direct evidence to indicate that the paramagnetic form was a triplet state (29, 65, 98) (see also 2).

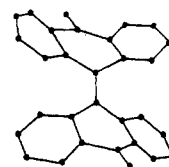
Kortum and co-workers (81) pointed out that the fact that the 4,4'-substituted bianthrone could be made ruled out any possibility that the molecule could be planar, and that 4,4'-substituted bianthrones could not achieve thermochromism by assuming a 90° angle, since substitution would favor such a form, yet prevents thermochromism. They made 1,3,1',3'-tetramethylbianthrone and measured its spectrum at temperatures from 99 to 182.5°, and found the thermochromic band shifted a little toward longer wave lengths compared to the parent compound. They found a heat of transition of about 6.7 kcal./mole. They suggested the thermochromic form might be one in which the molecular halves are in essentially the same plane, but that each half might be slightly folded away from the plane of the central bond, the colored molecule being a triplet state "biradicallette." Experiments with 2,4,2',4'-tetramethylbianthrone indicated that the low temperature photochromic form is due to free radicals, since it absorbs oxygen rapidly. They ruled out ionic forms as responsible for bianthrone thermochromism because the heat of transformation was not sensitive to solvent polarity.

Theilacker (132) mentioned that paramagnetism should be detectable for the colored form of bianthrone, and added that the preparation of an optically active quinine salt of 2-carboxylbianthrone was evidence for the folded form as being the structure of the normal state.

On the other hand, Hirshberg and Fischer (54) found the spectra to be identical for the thermochromic and the photochromic forms of bianthrone, dixanthylene and xanthylideneanthrone. They pointed out that the photochromic change occurs only in liquid solution and not in rigid media, hence that a change in configuration is involved (152). Since the frequency factors for the reversion from the colored form are those commonly encountered for first order reactions, they discount the

triplet state hypothesis, since reactions involving changes in electronic multiplicity should have abnormally low frequency factors (see also (2)). They cited the work of Harnik, Herbstein and Schmidt (32) whose preliminary report on X-ray analysis of bianthrone showed it to have a center of symmetry as was also shown for dixanthylene; therefore the twisted normal state suggested by Grubb and Kistiakowsky could be ruled out.

The report by Harnik and Schmidt (33) in 1954 showed that in bianthrone the central rings are slightly puckered, and while they are in about parallel planes, they are not in the same plane; the benzene rings attached to the central ring are folded slightly and in the opposite direction from their counterparts on the other central ring. The carbonyl oxygens bend slightly away from the folded benzene rings. There is no twisting about the double bond, which is a normal bond.



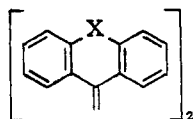
Theilacker, Kortum and Elliehausen (133) measured the magnetic susceptibility of the methyl ester of 2-carboxylbianthrone and found no change with temperature, concluding, in disagreement with Fraenkel, that the thermochromic form is neither a radical nor a "biradicallette."

Kortum, Theilacker and Braun (78) measured the spectra of tetrasubstituted bianthrones in a variety of solvents before and after low temperature ultraviolet irradiation, and concluded that both ground and thermochromic forms were singlet folded states. They found the photochromic and thermochromic forms to be different, and suggested that the photochromic form was the 90 degree twisted radical. All the compounds were luminescent; even the spectrophotometer beam caused appearance of the photochromic form (58, 79).

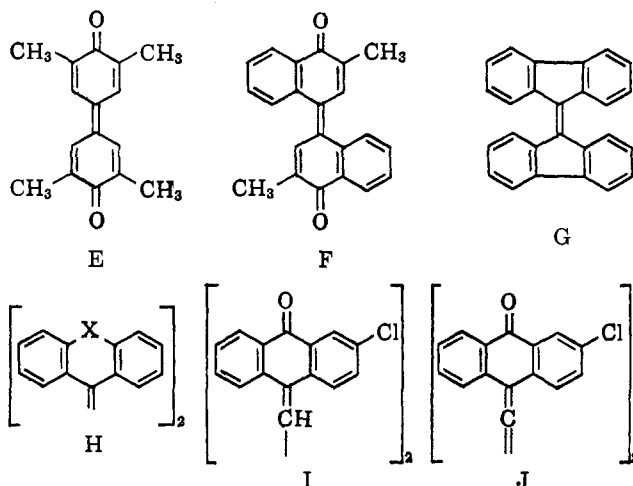
In 1955 Mustafa and Sobhy (97) prepared a series of substituted dixanthylenes, showing them to be strongly thermochromic except when substituted in the positions ortho to the double bond, as in the bianthrones. And Matlow (86) calculated the energies of the ground state, the triplet state for planar configuration, and the triplet state for a perpendicular configuration for bianthrone and for dixanthylene. The results favored the perpendicular triplet state as the excited state responsible for the thermochromism of these compounds.

Kortum and Buck in 1956 (76) found the dipole moments of bianthrone and dixanthylene to be zero. Matsunaga (87) found the diamagnetic susceptibility of bianthrone to decrease with rising temperature, suggesting the occurrence of a paramagnetic state; however, he concluded that the thermochromic effect was due to an irreversible chemical reaction.

Theilacker and co-workers summarized their work to 1956 (135) and from a study of the spectra of a number of compounds enumerated structural criteria to be met for substances such as bianthrone to show thermochromism. The normal or uncolored state must have aromatic halves capable of folding (not possible if the central ring is 5-membered) and the thermochromic form is possible if the valence angle of atom X (see figure) can expand to 120 degrees.



The two forms are thus two steric arrangements of the same molecule (134), "configuration isomers," hence the low heat of transition; the reason for existence of such isomers is the inability of the molecule to be coplanar. To summarize the evidence: compounds E and F cannot have folded halves, and are not thermochromic, the same is true for G because of the five-membered ring; compound H is thermochromic if X is an oxygen atom or carbonyl group, but not thermochromic if X is sulfur; I (80) is not thermochromic since there is free rotation about the central bond, and J, which is forced into planarity, is deeply colored.



Harnik (31) in 1956 demonstrated that there are two possible structures for bianthrone which permit some relief from overcrowding: the previously described structure with folded anthrone-halves, and another structure in which the anthrone halves are planar but twisted 60 degrees with respect to each other. The calculated energy barrier of about 20 kcal./mole is in agreement with earlier estimates (30). This theory is in agreement with the fact that 4,4'-substitution, which would prevent the necessary twisting, prevents thermochromism, and that 4,4'-difluorobianthrone is thermochromic only at a temperature much higher than that needed for bianthrone. The thio-compound, with sulfur

TABLE II
BIANTHRONES AND DIXANTHYLENES

	10,10'-Bianthrone: light yellow at -180° , lemon yellow at 25° , green melt. Cold solution is yellow-green, hot solution is deep green. Piezochromic color is green (2, 5, 6, 30 s, 31, 32, 33, 46, 47, 54 s, 63 s, 65, 78 s, 80 s, 86, 89, 98, 106, 110, 134, 135, 136 s, 138, 140 s, 141, 142, 145)
-2-carboxylic acid	(2)
-3-carboxylic acid	(133, 134)
-3-carboxylic acid methyl ester	(135 s)
2,2'-dimethyl-	(2, 54 s)
2,2'-dibromo-	(54 s)
2,2'-dimethoxy-	(2, 54 s)
-2,2'-dicarboxylic acid	(2, 30 s)
3,3'-dibromo-	(2, 54 s)
4,4'-difluoro-	Thermochromic only at a much higher temperature than bianthrone (31)
1,1',3,3'-tetramethyl-	Deep yellow melt (81 s)
2,3,2',3'-dibenzo-	Cold solution is yellow, hot solution is weakly olive-green (135)
1,2,1',2'-dibenzo-	Cold solution is yellow, hot solution is intense green (135)
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	Dixanthylene: colorless at -180° , bluish-green on heating, deep blue-green melt. Hot solution is deep blue-green (32, 47, 54 s, 106, 110, 124, 136 s).
4,4'-dimethoxy-	(54 s)
1,1'-dichloro-	Very weakly thermochromic (93)
2,2'-dimethyl-	Deep blue-green melt. Hot solution is deep blue-green (93)
2,2'-dibromo-	Cold solution almost colorless, hot is blue-green (97)
3,3'-diphenyl-	Deep blue-green melt (93)
3,3'-dichloro-	Light yellow solid, deep blue-green melt
4,4'-dimethyl-	Cold solution colorless, hot is blue-green (117)
4,4'-dibromo-	Deep blue-green melt. Hot solution is blue-green (93)
4,4'-dichloro-	Cold solution almost colorless, hot is blue-green (97)
2,3,2',3'-tetramethyl-	Almost colorless solid, blue-green melt (117)
2,4,2',4'-tetramethyl-	Cold solution almost colorless, hot is blue-green (97)
di-1,2,1',2'-dibenzo-xanthylene	Yellow green solid, olive-green melt (95). See also (54, 78)
di-3,4,3',4'-dibenzo-xanthylene	Pale yellow solid, green melt, Hot solution is blue-green (95)
10-(9-Xanthylene)-anthrone	Yellow solid, green melt. Hot solution is blue-green. Piezochromic color is green (2, 5, 54 s, 46, 63 s, 107, 110).
Monothiodixanthylene	Colorless solid, yellow melt, deep green at 320° (125)
Bis-thioxanthylene	(47, 80 s, 136 s).

in place of the oxygen in dixanthylene, is not an overcrowded molecule, hence should not be expected to be thermochromic.

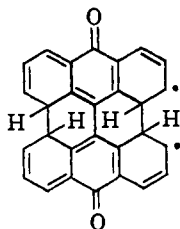
Kortum, Littman and Theilacker in 1957 (77) discarded the theory that the photochromic colored state of bianthrone is in a triplet state, since the lifetime of the photochromic state is 10,000 times longer than that

of normal phosphorescent states. Since the photochromic form is paramagnetic, that leaves only the twisted diradical as a possible structure; lack of photochromism in the solid solution is further confirmation and the solid state itself shows no photochromism, whereas if a triplet state were involved it should be more intense. Kortum, Theilacker and Schreyer (80) demonstrated that bianthrone adsorbed on magnesium oxide showed reversible thermochromism.

Hirshberg (51, 52) found that bianthrone and its derivatives developed color when irradiated at low temperatures with gamma rays or an electron beam.

In 1958 Hirshberg and Weissman (64) examined the photochromic forms of xanthylideneanthrone and substituted bianthrone, and since in no case was electron spin resonance observed, they concluded that the colored species either are not free radicals, or that they possess unusually broad resonance lines (59). Also in 1958, Kortum (75) presented an excellent summary of his work.

In 1959 Wasserman and Davis (142) prepared the green form of bianthrone in three ways: by sublimation onto a cold surface, by grinding in a mortar, and by ultraviolet irradiation at low temperature. The kinetics of the reversion to the normal form was followed for the thermochromic material, the piezochromic material and the photochromic material at -41 and -77° . The rates were the same for all three, showing them to be identical. Wasserman (141) found that pyridine solutions of bianthrone display electron spin resonance absorption which increases with temperature. The five main components of the spectrum possessed relative intensities corresponding to the interaction of an unpaired electron with four equivalent protons. The structure shown was suggested as one resonance form, with each unpaired electron effectively restricted to half of the molecule.



Woodward and Wasserman (145) briefly reviewed the evidence in favor of the form suggested above.

Mustafa, Asker and Sobhy (93) in 1960 prepared a series of substituted dixanthylenes and supported the theory that achievement of planarity in overcrowded molecules is the cause of thermochromic behavior.

B. OTHER ETHYLENES

Diphenylmethylene anthrone (bianthrone minus one carbonyl group), diphenylmethylenexanthene (dixanthylene minus one oxygen) and their derivatives have been extensively investigated (see Table III). Most are

thermochromic and many piezochromic but do not display low temperature photochromism. The diphenylmethyleneanthrone was made in 1906 (137) when dissociation was suggested as the thermochromic mechanism; free radicals were postulated in 1933 (5) and ionic resonance forms later (106, 110). They are discussed as examples of "conformation isomers" of overcrowded molecules in (125). Grubb and Kistiakowsky (30) examined the spectra of diphenylmethyleneanthrone and one derivative at a series of temperatures and concluded that the thermochromism was due simply to a broadening and flattening of the absorption band with no increase in integrated absorption, thus extending the absorption tail into the visible. The lack of change of integrated absorption intensity indicated that there was no temperature dependent equilibrium of any kind.

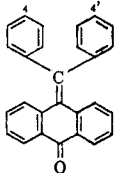
Dimethyldiacridine, bithioxanthylene and diflavylene were demonstrated to be thermochromic when adsorbed on magnesium oxide (80); this article and others (136) reported them not thermochromic in solution, although in 1934 Schönberg (121) mentioned diflavylene derivatives as thermochromic. Diflavylene itself has been investigated extensively (107, 108); thermochromism apparently depends on the solvent chosen. The piezochromic and thermochromic forms apparently are identical (155).

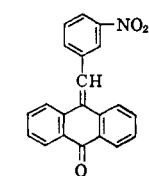
Chromones, their derivatives, and chromone dimers are thermochromic due to a temperature sensitive keto-enol equilibrium (126, 127, 128).

The thermochromism of indanedione-1,3 has been attributed to the general concept of achievement of planarity by overcrowded molecules (116), while that of bindone has been attributed to keto-enol tautomerism (115).

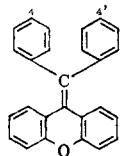
Di-(2-phenyl)-1,3-benzoxaz-4-ylidene and its derivatives are structurally much like diflavylene, and may owe their thermochromism to the same sources as does diflavylene (94). 9-Benzohydrilidene-10-phenyl-9,10-dehydroanthrone is thermochromic, being orange-red when heated (146). Liquid fulvenes, such as dimethylfulvene, are light yellow, fade when cooled, and become dark reddish at the boiling point.

TABLE III
THERMOCHROMIC ETHYLENES

	Diphenylmethyleneanthrone: light yellow at -180° , yellow at 25° , ruby red melt. Hot solution is orange to red. Cold solution varies from yellow to red, depending on solvent (5, 30 s, 46, 84, 106, 110, 120, 137)
4,4'-dimethyl-4-methoxy-	(63 s) Yellow-orange at 25° , yellow-green at -60° (63 s)
4,4'-dimethoxy-	Yellow at 25° , red melt. Hot solution is orange to red. Piezochromic (30 s, 107, 110)



10-*m*-Nitrobenzylidene anthrone: "yellow prisms exhibit pronounced thermochromism." If there is no nitro group it is not thermochromic (68, 125)



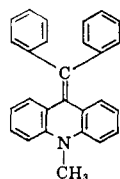
Diphenylmethylenexanthene: colorless at 25°, orange-red melt. Hot solution is orange (5, 10, 120)

4-nitro-
4,4'-dimethyl-
4,4'-dichloro-

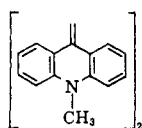
Yellow solid, deep purple melt. Piezochromic color orange-red (109)
Light yellow-green solid, deep orange melt. Cold solution is yellow; hot is orange (109)
Light yellow solid, red-orange melt (109)

2-Phenyl-2-(9-xanthyli-dene)-acetophenone
Bis-thioxanthylene
Diphenylmethyl-thioxantbene

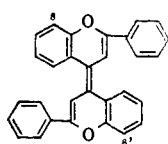
Colorless solid, orange melt (125)
Thermochromic when adsorbed on MgO (80)
Colorless solid, yellow melt (125)



N-Methylacridan: deep red melt (5)



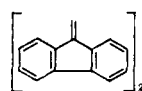
Dimethyldiacridine: thermochromic when adsorbed on MgO (80 s, 136 s)



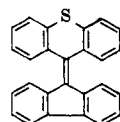
Diflavylene: Yellow solid turns red on heating to deep red melt. Piezochromic color dark red. Not thermochromic in decalin (80, 94, 106, 107, 110, 120, 121, 136)

8,8'-dimethyl-
1,1'-dithio-8,8'-dimethoxy-

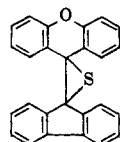
Golden crystals whose hot solution is orange-red. Piezochromic color is deep red (121)
Brown-yellow crystals whose hot solution is orange-red. Piezochromic color is deep red (121)



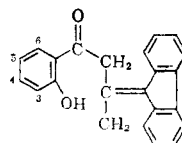
Dibiphenyleneethane: intense red at 25° but colorless at low temperature (3, 4)



10-(9-Fluorenylidene)-thioxanthene; yellow solid gives green melt (125)



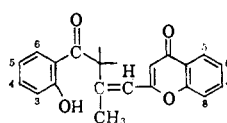
9-(9-Fluorylidene)-xanthene sulfide: this and two methyl derivatives are colorless but give a violet melt (Reversible?) (125)



2-Hydroxy- ω -methyl- ω -fluorenylidene-propiofenone: colorless solid, yellow melt (128)

2-hydroxy- ω -ethyl-
2-hydroxy- ω -phenyl-
2-hydroxy- ω -phenyl- ω -
[2,7-dibromofluorenyli-
dine]-propiofenone
2-hydroxy-5-methyl-
 ω -methyl-
2-hydroxy-5-methyl-
 ω -phenyl-
2-hydroxy-3,4-benzo-
 ω -phenyl
2-hydroxy-3,4-benzo-
 ω -phenyl- ω -[2,7-di-
bromofluorenylidene-]

Light yellow solid, yellow melt (128)
"Thermochromic" (127)
Yellowish solid, red melt (127)
Colorless solid, yellow melt (128)
Yellow solid, red melt (127)
Yellow solid, red melt (127)
Yellowish solid, red melt (127)

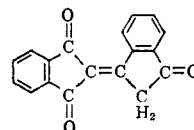


α -(Chromonyl-(2)- β -methyl-(*o*-hydroxyphenacyl)-ethylene: almost colorless solid gives red melt. Red when adsorbed on alumina. Cold solution is red-violet becoming deep red at -70°. Colorless at 80° (126)

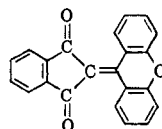
α -(6-Methylchromonyl-2)- β -methyl-(2-hydroxy-5-methylphenacyl)ethylene
 α -(7,8-Benzochromonyl-2)- β -methyl-(2-hydroxy-3:4-benzophenacyl)-ethylene

As above

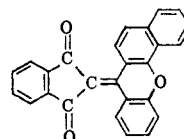
As above



Bindone: solution at -10° is yellow, turns intense yellow with orange tint when heated (115)



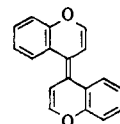
2-(9-Xanthyli-dene)-indandione-1,3: cold solution is violet, hot solution is brownish red with marked fading of color (116)



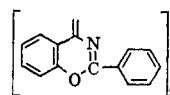
2-[9-(3,4-Benzo)-xanthyli-dene]-indandione-1,3: bronze-red crystals give a red-violet melt. Cold solution deep violet, hot solution brown-red with marked fading of color (116)

o,o'-oxide-tetraphenylethylene

Colorless solid, orange melt. Hot solution is reddish-yellow (120)



Diphenylchromylene: yellow solid. Hot solution is red (120)

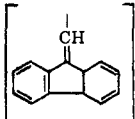
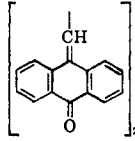
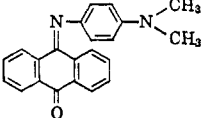
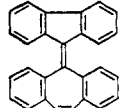


Di-(2-phenyl)-1,3-benzoxaz-4-ylidene: yellow solid, deep red melt. Hot solution is orange red (94)

di-(2-*p*-methylphenyl)-
di-(2-*p*-methoxyphenyl)-

As above

As above

	α,β -Bisdiphenylenebutadiene: orange solid turns red when heated (131)
2,2'- α,β -bisdiphenylenebutadiene	As above
	1,2-Bis-(9,9'-anthronylidene)-ethane: cold solution is yellow, hot solution is orange. Solid is orange at 0° and deep violet at 240° (75, 80, 116, 118)
	Anthraquinone-mono- <i>p</i> -dimethylamino anil cold solution is deep violet, hot solution is violet-red with marked fading of color (116)
	Fluorenylidene-1-dibenzo-2,3,6,7-cycloheptatriene-2,4,6: colorless crystals, red brown melt (163)

IV. SULFUR COMPOUNDS

The thermochromism of a number of sulfur compounds has been investigated, particularly the disulfides. The data are summarized in Table IV. Through 1953 thermochromism was attributed to the formation of free radicals on heating since Beer's law was not followed, although it was also noted that the solutions were stable to heat and to oxygen and molecular weights were normal (7, 70, 96, 104, 111, 122, 123). In 1954 Lecher (83) summarized evidence against this view; free radicals are improbable because of the relatively small number of resonance forms possible; magnetic results reported are not conclusive; splitting of the disulfide bond in reaction is dubious evidence; aryl disulfides show thermochromism in the solid state where a dissociation equilibrium is highly improbable; the claim that Beer's law is not followed are incorrect; and that since these compounds do not act as polymerization initiators even at 90° unless irradiated there can be no radicals present. He theorized that thermochromism may be the precursor of a dissociation occurring at a higher temperature.

Brand and Davidson (13) measured the spectra of thiocarbonyls and disulfides at two temperatures and concluded that the thermal coloring was due to broadening and flattening of a near-ultraviolet absorption band. They confirmed conformance to Beer's law and remarked that the temperature required for thermal fission of disulfides is much greater than that needed for thermochromism.

Davis and Perrin (21) added that kinetic evidence showed that the maximum concentration of free radicals present in disulfides was about 10^{-7} mole per liter,

which would require an extinction coefficient of about 3×10^6 and therefore a narrow intense absorption band, which is not the case. They also concluded that broadening of the absorption band toward the visible was responsible for the visible change in color.

Schönberg, Nickel and Cernik (158) reported that a number of thioesters are thermochromic in solutions and that no causes could be assigned. They also noted diphenyl diselenide as thermochromic.

McClelland and Warren (157) reported the thermochromism of 2,2'-*o,o*-dithiodiphenyl-4,5, dihydroglyoxaline. Marked deviation from Beer's law was noted. The thermochromism was attributed to a reversible dismutation. Lack of reaction with oxygen seemed to rule out free radical formation.

TABLE IV
SULFUR COMPOUNDS

Diphenyl disulfide	Colorless solid, yellow melt (70, 111, 122, 123)
<i>p,p'</i> -Dibromodiphenyl disulfide	Colorless. Hot solution is yellow (70)
β -Dinaphthyl disulfide	Pale yellow, yellow melt. Hot solution is deep yellow (96)
α -Dinaphthyl disulfide	Colorless solid, yellow melt. Hot solution is deep yellow (96)
4,4' - Dicarboethoxy - 1,1'-dinaphthyl disulfide	Colorless solid, yellow melt. Hot solution is deep yellow (96)
8,8'-Dihydroxy-1,1'-dinaphthyl disulfide	Yellow solid, orange melt. Hot solution is yellow-orange (96)
Dibenzoyl-8,8'-dihydroxy-1,1'-dinaphthyl disulfide	Colorless solid, yellow melt. Hot solution is deep yellow (96)
5,5'-Dimethyl-8,8'-dihydroxy-1,1'-dinaphthyl disulfide	Yellow solid, orange melt (96)
Dibenzene sulfonyl - 8,8'-dinaphthyl disulfide	Colorless solid, yellow melt. Hot solution is deep yellow (96)
Bis-(thio- α -naphthyl)-disulfide	Orange solid, orange-red melt "Thermochromic" (13 s, 104, 122, 123)
9,9'-Dianthryl disulfide	Orange solid, orange-red melt. Hot solution is orange-red (96)
Dibenzthiazolyl-2-disulfide	"Thermochromic" (13 s, 21 s, 70 a)
Tetramethylthiuram disulfide	Almost colorless solid, yellow melt (13 s, 21 s, 70 a)
1-Naphthyl phenyl thioketone	Cold solution is blue, hot is blue-green (13 s)
Diphenyl thiocarbonate	Cold solution is blue, hot is blue-green (13 s)
Methyl 1-dithionaphthoate	Cold solution is blue, hot is blue-green (13 s)

V. MISCELLANEOUS COMPOUNDS

Schönberg, Mustafa and Asker (116) put to the test the theory that overcrowded molecules which could achieve a greater degree of planarity by increase in thermal energy might be thermochromic, and reported discovery of thermochromism in eight compounds; rubrene, tetracyclone, acecyclone, 4-triphenyl-1,2-quinone, 2-(9-xanthylidene)-indan-1,3-dione, 2-(9-(3,4-benzo)-xanthylidene)-indan-1,3-dione, anthraquinone-mono-*p*-dimethylaminoanil, and 1,2-bis-(9,9'-anthronylidene)-ethane.

That the nitro group can sometimes confer thermochromism on a compound not otherwise thermochromic was again noted when Bottle and Gilbert (12) reported on 3,5-dinitrosalicylic acid as mildly thermochromic.

The thermochromism of *o*-hydroxy-*p,p',p'',p'''*-tetramethoxytetraphenylsuccinic acid bislactone was established by paramagnetic measurements and molecular weight determinations to be due to free radicals formed by dissociation (143).

Ingold and Marshall (67) found that 9,10-diaryl-anthracenes and their substituted derivatives are colorless or nearly colorless in the solid state, but form colored solutions in xylene, the color of which increases with temperature. For 9,10-di-*p*-anisylanthracene in mesitylene solution, the relative color intensity increased by a factor of ten in going from 20 to 140°.

Sawicki, Stanley and Hauser (103) found that unsubstituted polycyclic *p*-quinones show a reversible thermochromic reaction in reducing media. The compound is dissolved in dimethylformamide, some potassium borohydride is added, and the mixture heated to a vigorous boil. For a positive test a red, violet, blue or green color is obtained at the boiling point, and a pale yellow, orange or pink color on cooling. Also giving positive, but weaker, tests are fluorenone and benzo-fluorenone. Many, but not all, derivatives of anthraquinone give the color reaction. Anthraquinone and its derivatives give red to violet; higher molecular weight polynuclear *p*-quinones give blue colors. 1-Hydroxy-anthraquinone and several heterocyclic *p*-quinones are intense red to violet at room temperature and pale yellow to orange at the boiling point. For the hot color to be green, apparently at least four fused rings are needed. Hauser (34) extended the above test to anthracene and its simple derivatives by using a prior oxidation with chromium trioxide.

Sawicki and Elbert (102) found that compounds containing the fluorenic methylene group, dissolved in dimethylformamide and made alkaline with tetraethylammonium hydroxide are readily oxidized by shaking with air to the fluorenone, and the latter is reduced by potassium borohydride at the boiling point to the highly colored fluorenone anion. On cooling and shaking the less highly colored fluorenone is regenerated. Here the thermochromic mechanism is the temperature dependent equilibrium between fluorenone and the fluorenone anion.

Hauser and Birkofer (35) discovered that *N*-ethylphenazyl radical shows a strong negative thermochromism, with an absorption band at 8000 Å. which vanishes on warming. They noted that inverse thermochromism had previously been noted for Rhodamin 6 G-base (82). 1,1'-Methylenedi-2-hydroxyacridine, the corresponding phenazine, and at least some of their derivatives were found to be thermochromic by Cairns-Smith (15). The thermochromism depends on the crystal structure, and even the state of perfection of the crystals, since the rapidly crystallized materials are not thermochromic. Apparently it is necessary that a mechanism be available for the transfer of a proton from the oxygen

to the nitrogen by an internal rearrangement. The lactam absorbs light at longer wave length than the lactim, and is favored by increase in temperature, with no substantial movement or change in the over-all shape of the molecule required.

Senier and Shepherd (130) prepared 37-arylidene- and naphylideneamines, of which twenty-six were thermochromic. In general the change of color with rise in temperature was from yellow to orange to red. In some cases the color disappeared altogether at -70°. Senier and Clarke (129) prepared twenty-one naphthylideneamines, all of which were more or less thermochromic. The color went from yellow to orange on heating, and in some cases to red.

Brewster and Millam (148) noted in 1933 that over 300 anils ($R-CH=N-R'$) had been reported (159, 160, 161, 162), most of them thermochromic. They added twenty-two such anils, all of them derived from 5-bromosalicylaldehyde.

Though this review does not include inorganic compounds, it is interesting to note some metal organics which have been specifically noted as thermochromic. Hirshberg (53) found that dilute alcoholic solutions of uranyl salts with either diphenylcarbazone or 1,5-diphenylcarbohydrazide are practically colorless, but develop a red color at low temperature. The color is attributed to the formation of colored coordination compounds at the lower temperature. Dilute mixtures of mercuric iodide and diphenylcarbazone behaved similarly.

Bartlett and Seidel (1) prepared monocyclopentadienyltitanium dichloride, a violet solid which forms a light blue solution in acrylonitrile which changes to green at -44°, and to yellow at -78°. The color was believed due to a monomer-dimer equilibrium, with lower temperature favoring the colored dimer.

Schonberg (112) observed that 1,3-diketo-2-phenyl-5-bromoindan crystallizes from non-polar solvents as the almost white ketone, and from polar solvents as a violet-black enol. Dilute solutions of the black modification in ethyl benzoate are orange at -10°, but at the boiling point are light yellowish. Thus the thermochromic mechanism is a keto-enol equilibrium; but curiously the parent compound with no bromine substituent exists only as a colorless solid, and is not thermochromic.

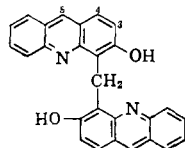
Curtin and Hauser (20a) reported that *p*-methoxy-*p'*-nitrobenzophenone *p*-tolylamine turns from yellow to orange on heating and reverts to its normal state on cooling. Evidence suggested that stereoisomerization rather than change in crystal structure was responsible. Similar behavior was observed for *p*-methoxybenzophenone *p*-tolylamine and for benzo(*p*-ethylbenzoate)-amine.

The thiosemicarbazones of ethylenic ketones of the type $Ar-CH=CRCOME$ are thermochromic, as are the delta-phenylsemicarbazones of $CH_2O_2=C_6H_5-$

CH—COPr (Pr for propyl) and of *p*-iso-Pr-C₆H₄—CH=CH—CO—C₂H₅. The xylene solutions turn yellow on heating (150). Hayashi (151) reports thermochromism for an oxidation product of lophine (2,4,5-triphenylimidazole), with a ΔH value of -5 kcal./mole for the thermochromic coloration. Free radical formation is suggested by electron spin resonance measurements. The compound is strongly photochromic.

TABLE V
MISCELLANEOUS COMPOUNDS

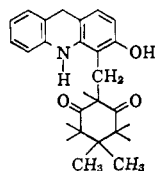
9,10-Di- <i>p</i> -anisylanthracene	This compound and its substituted derivatives are colorless or nearly colorless in the solid state. Xylene solution color intensity increases with increasing temperature by a factor of 10 between 10 and 140° (67)
Rubrene	Orange solid. Hot solution is deep red (116)
Dimethylfulvene	Light yellow at low temperatures, golden yellow at room temperature, red at b.p. (see discussion in Introduction)
3,5-Dinitrosalicylic acid	Cold solution is yellow, turning orange with increasing temperature (12)
Acetylone	Cold solution is blue, hot is violet (116)
Tetracyclone	Cold solution is violet, hot is violet-red with fading. Melt is purple (116)
4-Triphenyl-1,2-quinone	Cold solution orange, hot is brown-green (116)
1,3-Diketo-2-phenyl-5-bromoindan	Orange solution at -10° , pale yellow hot. Melt is red (71, 112, 115)
<i>o</i> -Hydroxy- <i>p,p',p'',o'''</i> -tetramethoxytetraphenylsuccinic acid bislactone	Solution is colorless at 0° , pale blue at 25° . Melt is blue (143)
2,2' - Diketo - 3,3' - diphenyl-3,3'-dicoumaranyl	Cold solution is colorless. Hot solution is blue (113)
2,2' - Diphenylthio - indigo white	Cold solution is colorless. Hot solution is blue-green (113)
N,N'-Dicyclohexyl- <i>p</i> -xylo- <i>p</i> -quinonedimine	Methanol solution is yellow at 25° , red below 0° . Not thermochromic in hydrocarbons. Adsorbs red on silicic acid (17)
9-Diazothiazanthene	Green crystals, red melt (reversible?) (125)



1,1'-Methylenedi-(2-hydroxyacridine): cold solution is yellow, hot solution is red (15)

1,1'-Methylenedi-(2-hydroxy-5-phenylacridine)

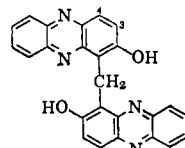
Cold solution is yellow, hot solution is red (15)



1-(4,4-dimethyl-2,6-dioxocyclohexylmethylene)-2-hydroxyacridine: bright red crystals become pale orange at -180° (15)

1-(4,4-Dimethyl-2,6-dioxocyclohexylmethylene)-2-hydroxy-3,4-dimethylacridine

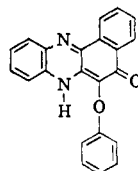
Dark red crystals become bright yellow at -180° (15)



1,1'-Methylenedi-2-(hydroxyphenazine): yellow crystals turn orange above 200° (15)

1,1'-Methylenedi-(2-hydroxy-3,4-dimethylphenazine)

Yellow at 180° . Heating turns it to orange then red and at 280° chocolate brown (15)



Solution at 0° is violet-brown, at 170° is orange, less intense (119). Same is true of *p*-methyl derivative

N-Ethylphenazyl	Inversely thermochromic. A strong absorption band at 8000 \AA . present at -80° disappears on warming (35)
Fluorene and derivatives	(See discussion, Part V) (102)
Polycyclic <i>p</i> -quinones	(See discussion, Part V) (34)
Triphenylchloromethane	Cold solution is colorless, hot solution is yellow (144)
Ditolyl- α -naphthylchloromethane	Hot solution is intense violet (144)
Monocyclopentadienyl-titanium dichloride (1)	Solution is green at -44° , yellow at -78° (1)
Uranyl salts with diphenylcarbazone or with diphenylcarbohydrazide, or mercuric iodide with diphenylcarbazone	Colorless at 25° , red at low temperature (53)

Senier and Shepherd (130) have noted that the compounds listed are thermochromic, after making observations at solid carbon dioxide temperature and at a temperature just below the melting point of each compound.

Salicylidene- <i>m</i> -toluidine	5-Bromosalicylidene- <i>m</i> -toluidine
Salicylidene- <i>m</i> -toluidine	5,5'-Dibromodisalicylidene- <i>p</i> -phenylenediamine
Salicylidene- <i>o</i> -4-xylylidene	
Salicylidene- <i>o</i> -chloraniline	3-Nitrosalicylidene- <i>m</i> -toluidine
Salicylidene- <i>m</i> -chloraniline	5-Nitrosalicylidene- <i>m</i> -toluidine
Salicylidene- <i>p</i> -chloraniline	<i>o</i> -Methoxybenzylidene- <i>p</i> -aminobenzoic acid
Salicylidene- <i>m</i> -aminophenol	2,2'-Dimethoxydibenzylidene- <i>p</i> -phenylenediamine
Salicylidene- <i>p</i> -aminobenzoic acid	
Na, Ca and Ba salts of above	<i>p</i> -Hydroxybenzylidene- <i>m</i> -toluidine
Salicylidene- α -naphthylamine	2-Hydroxy-5-methylbenzylidene- <i>m</i> -toluidine
Salicylidene- β -naphthylamine	2,2'-Dihydroxy-5,5'-dimethyldibenzylidene- <i>p</i> -phenylenediamine
Disalicylidene- <i>p</i> -phenylenediamine	2-Hydroxy- α -naphthylidene- <i>m</i> -toluidine
	2-Hydroxy- α -naphthylidene- β -naphthylamine
	2,2'-Dihydroxy-di- α -naphthylidene- <i>p</i> -phenylenediamine

Senier and Clarke (129) similarly noted the thermochromism of these derivatives of 2-hydroxy- α -naphthylidene compounds (*e.g.*, 2-hydroxy- α -naphthylidene-*o*-chloroaniline)

- <i>m</i> -chloroaniline	- <i>m</i> -bromoaniline	- <i>o</i> -aminophenol
- <i>p</i> -chloroaniline	- <i>p</i> -bromoaniline	- <i>p</i> -aminophenol
- <i>o</i> -bromoaniline	- <i>m</i> -nitroaniline	- <i>m</i> -aminophenol
- <i>o</i> -anisidine	- <i>o</i> -aminobenzoic acid	- <i>o</i> -4-xylylidene
- <i>m</i> -anisidine	- <i>m</i> -aminobenzoic acid	- <i>m</i> -4-xylylidene
		- <i>p</i> -4-xylylidene
- <i>p</i> -anisidine	- <i>p</i> -aminobenzoic acid	- ψ -xylylidene

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