CHROMOGENIC MATERIALS, THERMOCHROMIC

1. Introduction

Thermochromism is the reversible change in the spectral properties of a substance that accompanies heating and cooling. Strictly speaking, the meaning of the word specifies a visible color change; however, thermochromism has come to also include some cases for which the spectral transition is either better observed outside of the visible region or not observed in the visible at all. Primarily, thermochromism occurs in solid or liquid phase, but it also describes a thermally dependent equilibrium between brown nitrogen dioxide [10102-44-0], NO_2, and colorless dinitrogen tetroxide [10544-72-6], N_2O_4, a rare example in the gas phase (1).

Thermochromism could be defined according to J.H. Day in his review (2) as "an easily noticeable reversible color change in the temperature range limited by the boiling point of each liquid, the boiling point of the solvent in the case of solution or the melting point for solids". Other important contributions were published successively (3–5).

There are many materials, especially organic and metal-organic materials, which exhibit true thermochromism, with a variety of sometimes debatable structural transition mechanisms; it is difficult to summarize the whole with any continuity. For this reason, an effort is made to delineate the scope of the field by listing several thermochromic transitions (Table 1). Selected thermochromic material examples are accompanied in each instance by the corresponding transition stimulus for that case. Characteristically sharp transition temperatures, T_t, are indicated where appropriate. At the other extreme are examples of comparatively gradual transitions, associated for example with an equilibrium or a changing bandwidth. The sharpness of the transition is one aspect by which the several mechanisms could be classified. On the other hand, it is useful also to group materials into metal-complex, inorganic, and organic classes. In this way, the variety of thermochromic changes in each of the three material classes can easily be realized.

Thermochromic compounds such as Ag_2HgI_4 and Cu_2HgI_4 have long been known (17). These compounds color reversibly, exhibiting the discontinuous red shift of a charge transfer band edge during heating (18). As for VO_2, the characteristic hysteresis of reflectance in the visible suggests application for infrared image recording (19).

2. Metal Complexes, Spectral Transitions

Crystal field theory, which is simpler to present than the more comprehensive molecular orbital treatment, has been used to describe *d–d* orbital excitations of transition-metal ions and the effect on these excitations of ligand coordination geometry and field strength. Absorption bands in the visible region arise in energy states made nondegenerate by the crystal field. Color changes, such as induced by heating or cooling, are therefore a direct indication of change in the surrounding environment of the metal ion. Crystal field theory, even though it does not include charge-transfer processes, has proven to be qualitatively adequate for the 3*d* orbital transition metals because the 3*d* states are not well shielded from ligand field effects. Crystal field splittings are on the order of 10,000 cm^{-1}. The lanthanide 4*f* orbitals are better shielded and have crystal field splittings only on the order of 100 cm^{-1}. It is not surprising, therefore, that many good examples of thermochromism are to be found in 3*d* transition-metal complexes and other 3*d* metal compounds.

A simple and well-known example, from Table 1, is the case of anhydrous cobalt chloride $CoCl_2$, in alcohol solutions (1,6). At room temperature, Co^{2+} is predominately tetrahedrally coordinated, as dichlorobis(ethanol) cobalt(II), $Co(C_2H_5OH)_2Cl_2$, in the case of ethyl alcohol solution, and is colored blue. The tetrahedral absorption band peaks at about 660 nm. With cooling, this band shrinks in intensity. The solution begins to acquire a pink color indicative of the growing dominance of a weak octahedral coordination band, perhaps assignable to chloropentakis(ethanol) cobalt(II), $[Co(C_2H_5OH)_5Cl]^+$ (1). The temperature-dependent equilibrium in an ethyl alcohol–water solution is a classroom demonstration of a "thermometer" for observations below and above room temperature. By analogy, the proportioning between the blue tetrahedral and pink octahedral coordinations of Co^{2+} is also evident in molten inorganic glasses (7). This is clearly not associated with oxidation to Co^{3+} because the latter is

Table 1. **Some Typical Thermochromic Compounds and Their Transitions**

Thermochromic material	CAS Registry number	Thermochromic transition[a]	T_t^b °C	References
Co^{2+}solutions and glasses		equilibrium shift, two coordinations		1,6,7
$[(C_2H_5)_2NH_2]_2CuCl_4$	[52003-09-5],[52003-08-4]	square planar to tetrahedral	50	8–10
$[(CH_3)_2NH_2]_3CuCl_5$	[52003-06-2]	variation in bandwidth		10
$Cu_4I_4(Py)_4$	[62121-41-9]	fluorescence variations		11
$Al_{2-x}Cr_xO_3$(ruby)	[12174-49-1]	lattice expansion/contraction		1,12,13
VO_2	[12036-21-4]	monoclinic/tetragonal	68	14–16
Cu_2Hgl_4	[13876-85-2]	order/disorder	68	17–19
di-β-naphthospiropyran	[178-10-9]	close/open spiro ring		2
poly(xylylviologendibromide)	[38815-69-9]	hydration/dehydration	100	20
ETCD polydiacetylene[c]	[63809-82-5]	side group rearrangement	∼115	21,22

[a] When applicable, expressed as a change upon heating; various colors have been reported, often qualitatively.

[b] Transition temperatures for sharp transitions.

[c] Urethane-substituted polymer of where $R = (CH_2)_4OCONHCH_2CH_3$.

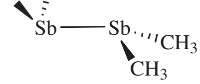
unstable at the high temperatures of glass melting. Cobalt-containing glasses that are pink at room temperature become blue with heating. This color is likely to be retained with rapid quenching. However, if the glass is cooled slowly, equilibrium is more nearly approached in favor of octahedral coordination, although the change from blue may be slow and difficult to detect by the eye in any case. This sort of kinetic problem is a general one that sometimes makes difficult the distinction between processes that are reversible or irreversible.

Other Co^{2+} halide solutions have been reviewed (1), as have equilibria involving complexes and chelates of Cu^{2+} and Ni^{2+} in solutions. Good thermochromism is well known, for example, in aqueous solutions of copper chloride, $CuCl_2$, and it has also been demonstrated in solutions of $Ni(ClO_4)_2$ (23). Good thermochromism is not restricted to transition-metal ions in solution. The example of $[(C_2H_5)_2NH_2]_2CuCl_4$ in Table 1 is solid-state and it has been reported to undergo a particularly pronounced, discontinuous, first-order, reversible, green-to-yellow color transition with heating (8–10). This is associated with a change in coordination geometry for the $CuCl_4^{2-}$ anion. Similar examples abound and many other compounds have been described in depth in an extensive overview about Cu^{2+} and Ni^{2+} salts that show discontinuous thermochromism (9). Various compounds containing *N,N*-diethylethylenediamine (24–28) or the isopropylammonium ion (10,29–31) are included.

The solid-state, transition-metal example in Table 1 of $[(CH_3)_2NH_2]_3CuCl_5$ illustrates another form of thermochromism: the color shifts gradually and continuously because of changes in bandwidth with either heating or cooling (10). It is not unique, as this behavior has been mentioned for the class of compounds $(RNH_3)_2CuCl_4$, where R = alkyl group (10), and also for compounds of the form M(*N,N*-diethylethylenediamine)$_2$(X)$_2$, where $M = Cu^{2+}$ or Ni^{2+} and X is an anion that does not disorder easily (9). With easily disordered anions such as ClO_4^- and BF_4^-, thermochromism occurs discontinuously at a reasonably well-defined T_t.

Halide complexes of Cu^+ with nitrogen base ligands are known to exhibit another form of reversible spectral change known as fluorescence thermochromism. The example of $Cu_4I_4(Py)_4$ from Table 1 is typical and shows red shifting in the visible emission spectrum while the sample is both cooled and irradiated with a 364 nm ultraviolet source (11).

Some organometallic derivatives containing Sb–Sb or Bi–Bi bonds exhibit drastic color changes on melting or dissolution in organic solvents. A representative example is tetramethyl distibane, a compound that is yellow as a liquid and in solution. The crystals of this distribane are bright red at temperatures close to the melting point of 18 °C.



On further cooling a blue shine is observed. At liquid nitrogen temperature the solid becomes yellow again. Similar color changes have been observed for several distribanes dibismuthanes and related compounds. The organic substituents have a strong influence on the development of color. Diarsanes do not show similar phenomena but have been investigated for a better understanding of the thermochromic properties (32).

3. Transitions in Inorganic Compounds

There are not many oxides and sulfides that may be classified as truly thermochromic; again, however, compounds of transition metals dominate. Ruby exhibits a well-known, reversible, ligand-field thermochromism at different temperatures depending on the concentration of Cr^{3+} in the Al_2O_3 lattice (1,12,13). This is a manifestation of change in the ligand field strength as dependent on lattice expansion/contraction. A whole family of oxides is known to undergo reversible, nonmetal-metal, thermoresistive transitions with heating (33–35). The shifts in band structure have frequently been debated. Sometimes these transitions are associated with symmetry changes. VO_2 is one of the best known of these compounds because its transition, which has as much as a five-fold switch in resistivity, occurs close to room temperature with a large, free-carrier, infrared change (14–16). There is also a smaller effect in the visible, as shown for easily grown thin films (16,36). Doping has been found to shift the resistivity transition temperature up and down (37–39), but this does not seem to have any great effect on the spectral range of switching for thin films made in various ways (40). This has discouraged interest in VO_2 films for large-area transparencies. Exploratory work on VO_2 films for optical storage and laser switching applications has also been discussed (41–43).

Another oxide that exhibits a nonmetal–metal transition is V_2O_3. It undergoes a symmetry change at about −123°C (monoclinic/rhombohedral) with as much as a 10^7 fold change in resistivity (44,45). Fe_3O_4 undergoes a small-order symmetry change at about −154°C (46,47). It is orthorhombic below this temperature but a cubic spinel above it. Also, some of the Magnéli phases of vanadium and titanium, of the form $M_nO_{2n}-1$ (M is the metal ion and $n = 3,4,5...$), have been observed to undergo relatively sharp thermal changes, especially as single crystals (33,35). However, except for VO_2, no remarkable spectral switching has been mentioned with any other member in this category of materials.

Four sulfides that also undergo reversible nonmetal–metal transitions are shown in Table 2. In three cases spectral changes are known, although in only

Table 2. **Some Sulfide Compounds with Nonmetal–Metal Transitions**

Compound	CAS Registry number	Thermochromic transition[a]	Approximate T_t, °C	Spectral shift	References
Ag_2S	[21548-73-2]	monoclinic/cubic	178	ir	48–50
NiS(hex)	[16812-54-7]	antiferromagnetic/ paramagnetic	−9	ir	33,51–53
FeS(tet)	[1317-37-9]	tetragonal/hexagonal	157		33,53,54
$Sm_{1-x}Ln_x^{3+}S$[b]		Sm^{2+}/Sm^{3+}	[c]	visible	56,57

[a] Expressed as a change upon heating.

[b] Ln = Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, or Y.

[c] Ln_x^{3+}-dependent.

one case involves the visible region. With the $Sm_{1-x}Ln_x^{3+}S$ series of compounds a dramatic color change occurs at T_t with cooling. It is associated with expansion in the lattice without change in the cubic structure. Qualitatively, the sulfide is black below the transition and metallic yellow above it. This remarkable example derives its behavior from samarium sulfide, SmS, which undergoes a like black-to-yellow color transition when it is rubbed or taken to a relatively low applied pressure of 650 MPa (6400 atm). A large infrared spectral change accompanies the visible change. The high pressure form of SmS has been made stable at room temperature and atmospheric pressure by doping with Ln^{3+}. Doping promotes a shift from Sm^{2+} to Sm^{3+} by 4*f* electron delocalization, so that the sulfide can be switched back and forth below room temperature.

4. Organic and Polymer Compounds

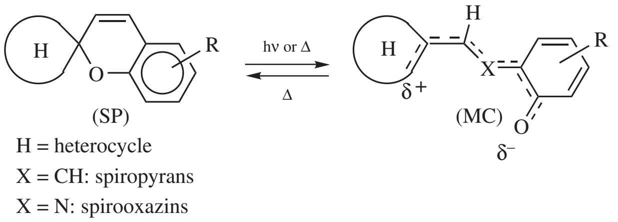
Simple organic molecules tend to be colorless with electronic transitions in ultraviolet light, whereas visible absorption, or color, is usually associated with electronic excitations in extended and conjugated structures. Color is influenced considerably by the extent of conjugation, as well as by the molecular environment imparted by substituents. So, thermochromism arises from critical, thermally induced changes in the existing structure. Thousands of thermochromic organic examples are known (12). Three of these are in Table 1. The di-β-naphthospiropyran example represents a well-known and extensively reviewed family of compounds that develop color at the onset of a thermally induced ring opening (2). Heterolytic bond cleavage in the molecule results in polar or ionic resonance structures, with conjugation, and it is these structural characteristic that have been associated with the appearance of color. The second organic example in Table 1, poly(xylylviologen dibromide) , is conjugated between pyridinium rings. It is characterized by charge-transfer interactions with counterions. The charge-transfer energy levels in the solid state are sensitive to the molecular environment so that thermochromism occurs when the polymer is subjected to hydration/dehydration sequences (20). Similarly, for urethane-substituted ETCD polydiacetylene (Table 1), thermally induced transitions in the conformation of the unsaturated backbone have been associated with restructuring of side-group substituents (21,22). The occurrence is manifested as a change in color.

Certain poly(di-*n*-alkylsilanes) and germanes, when in the solid state in particular, also exhibit large spectral changes that have been associated with side-chain influence on the backbone, but these (the polymer being saturated) occur at uv rather than visible wavelengths (58–60). Poly(di-*n*-hexylsilane) is an example. Initially, crystallization of the *n*-hexyl substituent groups locks the backbone into a configuration that is characterized by a red-shifted absorption band at 374 nm. With heating through about 41°C, there is a reversible relaxation to the higher energy 317 nm band associated with disordering.

The subject of thermochromism in organic and polymer compounds has been reviewed in some depth (2,12,21), and these expansive overviews should be used by readers with deeper and more particular interest in the subject. Many more examples can be found in the reviews that further illustrate the pattern of association between thermochromism and molecular restructuring of one kind or another. The specific assignment of structures is still open to debate in many cases, and there are still not many actual commercial uses for these or any of the other thermally reversible materials discussed herein. Temperature indicators have been mentioned, though perhaps as much or more for irreversible materials.

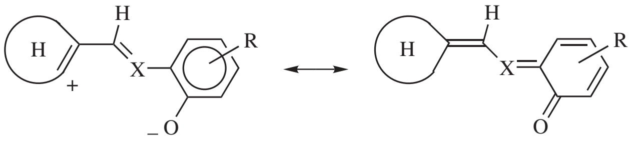
4.1. Spiropyranes and Spirooxazines. The thermochromism of spiropyranes discovered in 1926, has been extensively studied. Nearly every known compound of this class leads to deep color on melting (generally, red, purple, or blue). However heating solutions of spiropyrans also causes coloration. Day (2) in review reports essentially thermochromic spiropyrans of the indoline and spirobipyran series. Bertelson (61) summarized the main spectroscopic and physicochemical data obtained up to 1971. Thermochromic properties of spirooxazines have been reported more recently (62).

The thermochromic mechanism in these classes has been assumed to involve a thermally sensitive equilibrium between the colorless spiroheterocyclic form (SP) and the quasi-planar open merocyanine-like structure (MC) obtained after the breaking of the C=O bond. For both these classes of spiroheterocyclic compounds, it seems certain that the most thermally stable photoinduced-colored form and the species formed thermally are spectroscopically and kinetically indistinguishable (eq. 1).



(1)

Depending on the structure, different stereoisomers of the colored form can be involved, but the most stable corresponds to a E configuration (61,63–67). The electronic distribution of the open form is situated between two resonance forms, its proximity to one form or the other depending on the structure and the medium (eq. 2).



(2)

For example, spiro[indoline-benzopyrans] bearing a 6-NO_2 group should have a zwitterionic tendancy (63), whereas spiro[indoline-naphthopyrans] or spiro[indoline-naphthoxazines] should have a quinoÿdal tendancy (67–73).

During the past decade, new thermochromic spiropyrans have been described, particularly by Russian teams. For example spiropyrans of the 2-oxaindane or azaindanone series with polycondensed chromene fragments exhibiting photo and thermochromic properties, have been synthesized (74,75).

The thermochomic behavior of spiropyrans of the dithiolane series are discussed in Ref. 76. These data confirm that the annellation of the benzopyran moiety favors the thermochromic properties of this class of compounds.

An important contribution (77) concerns the thermochromism of a series of spiropyrans with different types of azaheterocycles, in various solvents such as benzyl alcohol, dimethylphthalate, decalin, toluene and xylene.

Bis spiropyrans have also been studied and could be extended to conjugated bis merocyanines (78).

The mechanism of the thermal of isomeriation has been investigated through theoretical studies using semi-empirical methods (75) and *ab initio* calculations (79) in agreement with some experimental measurements of the activation energy of the ring opening of pyrans, spiropyrans, spirobipyrans or chromenes (80) using nmr spectroscopy.

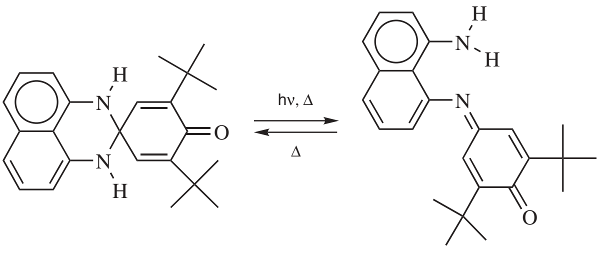
The activation parameters of the isomerization reactions were determined mainly for diversely substituted thermochromic spiro[indoline-benzopyrans] (81–84).

The kinetic and thermodynamic behavior of seven spiro[indoline-oxazines] have been studied (70–72). The investigated molecules exhibit thermochromism in a polar solvent (ethanol), but not in a nonpolar solvent (methylcyclohexane). From thermodynamic data and the kinetic parameters of the bleaching reaction, the rate constants and the activation energy for the thermal breaking of the Cspiro-O bond were obtained. The activation energies of the thermal coloration reaction were found to be in the range 80–120 kJ/mol, and the reaction rates varied over a large interval (10^{-5}–10^{-2} s^{-1}) (72).

Uv-visible spectroscopy is the best method for studying the equilibrium constant *Ke* for the thermochromic equilibrium between the spiroform SP and the merocyanine-like form MC in different solvents ($Ke = [MC]/[SP] = k_f/k_b$). The parameters ΔH°, ΔG°, ΔS° and *Ke* were determined (5).

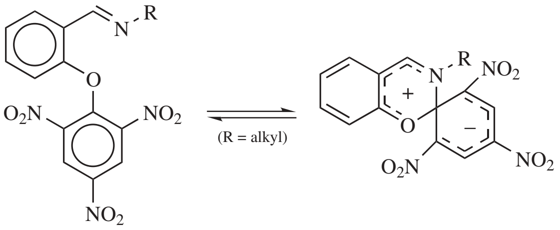
4.2. [2*H*]Chromenes (Benzo- or Naphthopyrans). 2-Phenylamino-2*H*-pyran (85) and benzo- or heteroannellated 2*H*-pyrans (77) have been reported to exhibit thermochromic behavior in solution. Di-β-naphthospiropyran have been investigated (2).

4.3. Other Spiroheterocyclic Compounds. A series of novel photo- and thermochromic perimidine spirocyclohexadienones whose mechanism involved a ring-chain tautomerism with recently developed (eq. 3) (86).



(3)

Interesting zwitterionic spirocyclic compounds (87) such as 2,4,6-trinitroaryl derivatives of *o*-hydroxyaldehydes and the corresponding imines show a negative thermochromism. Indeed in this case the colored spirocyclic form is more stable than the open colorless form even in an apolar solvent (eq. 4).

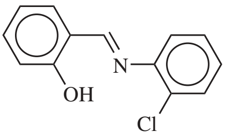


(4)

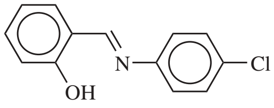
4.4. Schiff Bases and Related Nitrogen-containing Compounds.

The Schiff bases of salicylaldehydes with arylamines, aminopyridines and aryl- or thienylalkylamines show thermochromism and photochromism in the solid state due to hydrogen transfer (88). At the beginning of the century, Senier and Shepheard (89) observed that many of the colored crystalline salicylideneanilines were thermochromic. In most cases, the color changed, upon heating, from yellow to orange or red.

With this in mind, extensive investigations were carried out by Cohen and Schmidt (90,91) who found that photochromism and thermochromism were mutually exclusive properties of this series of compounds and suggested that this phenomenon is related to the crystal structure of the compounds and not to the chemical nature of the ring substituents. For instance, salicylidene-2-chloroaniline (**1**) is photochromic whereas salicylidene-4-chloroaniline (**2**) is thermochromic.

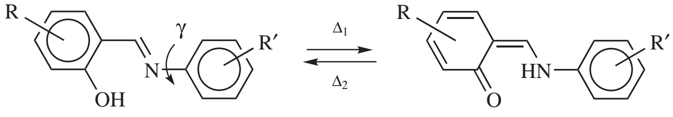


(**1**)



(**2**)

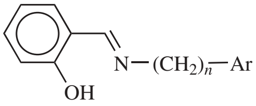
The presence of the ortho-hydroxy group is essential for the observation of both types of chromisms, and the mechanism involves intramolecular hydrogen transfer via a six membered-ring transition state, producing enol-keto tautomeric species, with the spectra of the keto forms showing a bathochromic shift (eq. 5).



(5)

Thermochromism is restricted to planar molecules and is attributed to a shift of the tautomeric equilibrium toward the “NH” form absorbing at longer wavelengths. For a nonplanar molecule, much energy is required for hydrogen transfer in the ground state and the transfer occurs only in photochemically excited states. A subsequent *Z* to *E* isomerization leads to the photo *trans-keto* configuration (90,92).

Structural variations have been determined for many Schifft bases having an *o*-hydroxy group in order to investigate the problem of planarity, stack packing in the crystal and correlation with the thermochromic behavior (**3**) (5).



(**3**)

$n = 1, 2$
Ar = phenyl, pyridyl, thienyl

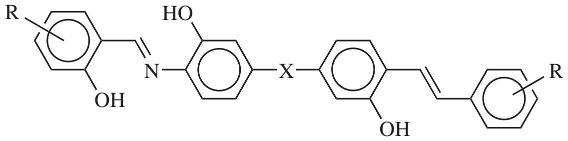
From semiempirical calculations by the CNDO/2 method, the relative energy of photo- and thermochromic salicylidenearylamines can be calculated (93).

Intensive investigations have been conducted to elucidate the nature of the mechanism of thermochromism of salicylidene Schiff bases.

Different techniques or methods suitable for the study of the tautomeric equilibrium between the enol form and the (*Z*)-keto form have been used, including X-ray diffraction, ^{1}H and ^{13}C nmr, infrared (ir) and Raman spectroscopy and theoretical calculations.

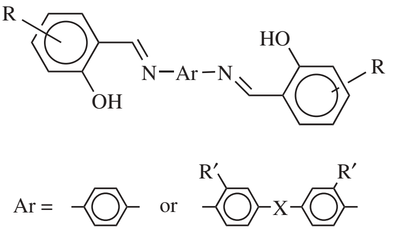
The temperature dependence of the ^{14}N NQR frequencies has been measured (94) for a series of seven thermochromic salicylideneanilines or salicylidene benzylamines and one photochromic compound. The energy difference (ΔE) between the two forms varies from 56 meV to 104 meV depending on the structure and the substitution. ΔE is larger for nonplanar photochromic compounds than for planar thermochromic ones. In the latter case, there is an equilibrium between the enol and (*Z*)-keto isomers, while for photochromic compound, at 300 K, only the enol form exists.

Thermochromic *N*-bis(salicylidene) diamines (**4**) and thermochromic *N,N′*-bis(salicylidene)diamines (**5**) (95,96) have been also synthesized and their physico-chemical behavior studied.



$X = CH_2, SO_2$

(**4**)



with R′ = H, CH_3 and X = —, CH_2, O

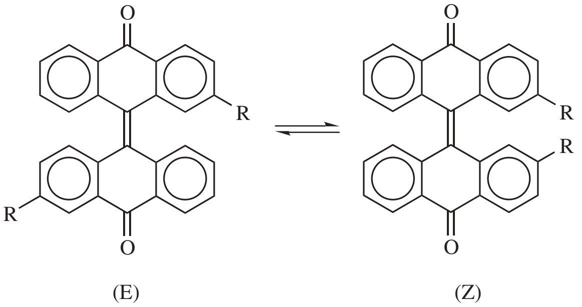
(**5**)

4.5. Bianthrones and Other Overcrowded Ethenes.

Bianthrones and related bianthrylidene systems undergo a reversible color change induced by light (photochromism), temperature (thermochromism) or pressure (piezochromism).

Since the original description of thermochromism of bianthrones at the beginning of the century, this phenomenom has evoked considerable interest and has been the subject of numerous reviews, the most recent was published in 1988 (97).

The thermochromism of bianthrone in solution has been shown to result from a thermal equilibrium between two distinct and interconvertible isomeric species A → B. Species A exists at room temperature as a yellow form ($\lambda_{max} \cong 380$ nm); upon heating of solutions of A, a significant fraction is converted to the green B form ($\lambda_{max} \cong 680$ nm), whose enthalpy is 12.5 kJ mol^{-1} greater than that of the A form (eq. 6) (98).



(6)

In the A form, the severe repulsion between the two anthrone moieties is avoided by the adoption of a folded conformation (Fig. 1). This feature has been confirmed by X-ray crystallographic investigations and dynamic nmr studies (98,99). Among the various proposed structures for the thermoinduced B species (supposedly identical to the photochromic species (97)) the twisted conformation has gathered a variety of experimental and theoretical support (100,101).

The experimental value of the activation energy for the A → B transformation is close to 84 kJ mol^{-1} (97,98).

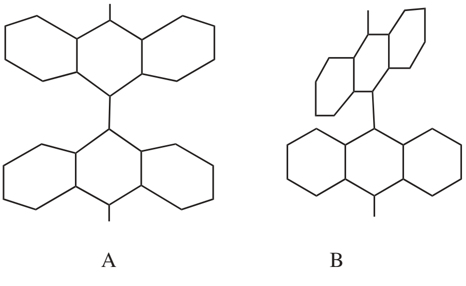
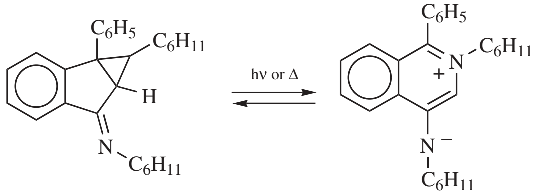


Fig. 1. Representation of the folded A form and of the twisted B form of bianthrone (5).

The thermochromism is prevented by bulky substituents at the 1,1′- and 8,8′-positions. In these cases, potential barriers that must be surmounted on the thermal path leading to the B form are too high, and the B form is therefore unobservable.

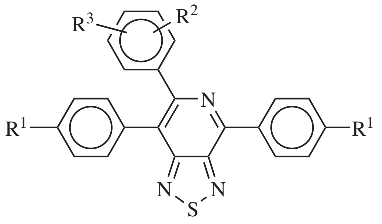
Besides bianthrone derivatives, other sterically overcrowded alkenes (101) have generated considerable interest owing to their intriguing thermochromic (and photochromic) properties (97,102), such as dixanthenylidenes, bithioxanthylidenes, 9,9′-fluorenylidene anthrones, 9-diphenylmethyleneanthrones, xanthylideneanthrones, and [2-(thioxanthen-9-ylidene) indane-1,3-dione (103).

4.6. Miscellaneous Compounds. Some indano[1,2-b]aziridines are reported to exhibit thermo-(and photo-)chromism, eq. 7 is an example (103,105).



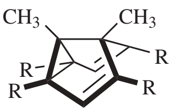
(7)

A reversible color change of 4,6,7-tri(alkoxy-substituted phenyl)-1,2,5-thiadiazolo[3,4-c]pyridines is observed in the solid state (**6**) (106).

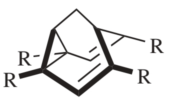


(**6**)

The polysubstituted semibullvalene (**7**) and barbaralane (**8**) skelettons exhibit thermochromism in solution and in solid state (107–109).



(**7**)



(**8**)

Thermochromism of hindered amino-substituted cyclohexadiones due to C–N bond cleavage has been described by Russian authors (Fig. 2) (110,111).

In the case of Mannich bases exhibiting thermo-(and photo-)chromism the proposed mechanism is quite similar (112,113).

A solution of pyridinium *N*-phenoxide betaine in ethanol is blue-violet (λ_{max} = 568 nm) at +78°C and red-colored (λ_{max} = 513 nm) at −78°C. This corresponds to a hypsochromic shift of the charge transfer band of the betaine by −55 nm with decreasing temperature ($\Delta T = 156°C$). This temperature

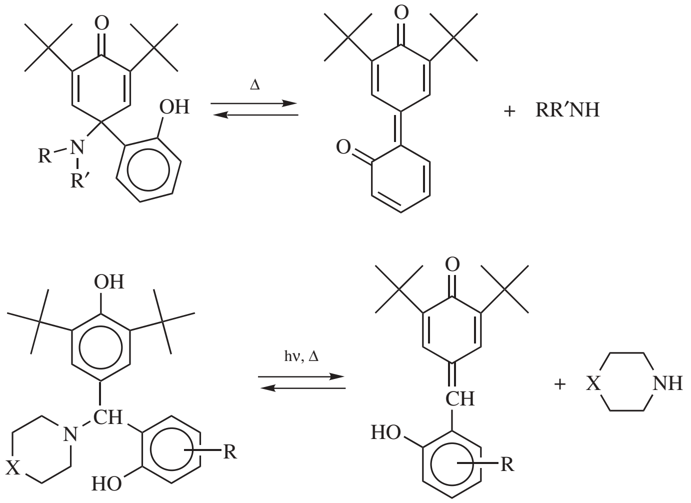
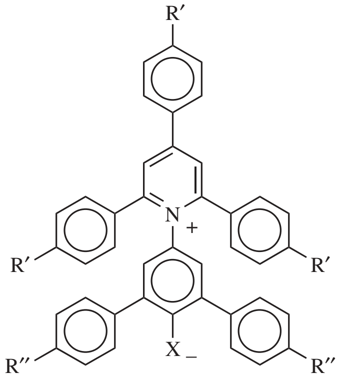


Fig. 2. Thermochromism of hindered amino-substituted cyclohexadiones. X = O, CH_2; R = benzo, Cl, Br.

dependent behavior of the betaine represents a new type of thermochromism ("negative thermo-solvatochromism"). It is obviously caused by the increased differential stabilization of the dipolar electronic betaine ground state, relative to its less polar excited state, with decreasing solution temperature (**9**) (114).



$R^1 = R^2 = H, X = O$

(**9**)

5. Uses

The optical properties of thermochromic coatings are strongly temperature dependent. In recent years, it has been shown that some transition metal oxide and related compounds undergo an abrupt reversible transition from a metallic to a semiconductor state with decreasing temperature (115). The material showing maximum promise is vanadium dioxide, VO_2, with a transition temperature at 68°C (116), ie, in a convenient range for technical applications (117).

Films of vanadium oxide were produced by reactive RF magnetron sputtering. For the major technological applications, the undoped VO_2 has a high transition temperature. Addition of a dopant such as tungsten or molybdenum lowers the transition temperature.

It has been reported (118) that in the tungsten-doped VO_2 films, the transition temperature decreases linearly with the concentration of tungsten in the film ($-23°C$ per at % of W). For example, one can reach a transition temperature of 0°C with 3% of W in a $V_{1-x}\ W_xO_2$ mixed oxide.

Commercialy, only two types of thermochromic systems have been successfully applied to textiles: the liquid crystal type and the molecular rearrangement type. Both depend on microencapsulation involving polymer binders for their success. At present more research needs to be carried out with respect to the formulation, encapsulation, and application of thermochromomic systems (119).

Thermochromic coatings that reduce the transmission of solar energy as the temperature rises can prevent overheating and find application in the thermal control of building and housing sectors, satellites, and spatial equipment (116).

The scientific and technological challenges of large-area electrochromic and thermochromic devices are great, involving improvements such as low cost, high uniformity, high rate and large area thin-film deposition techniques (DC and RF sputtering, chemical vapor deposition [CVD, plasma-enhanced CVD and dip-coating]). Sputtering techniques are particularly interesting. The remaining problems of uniformity of the films and reproducibility are expected to be solved by accurately monitoring the substrate temperature and the partial pressure of oxygen in reactive sputtering (115).

Very few new thermochromic molecular systems have been reported during the past 15 years.

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