# Photochromism and thermochromism of Schiff bases in the solid state: structural aspects

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This *tutorial review* describes in a brief historical perspective the most important organic compounds that exhibit photochromism in the crystalline state since its discovery in 1867 up to now and considers in detail Schiff bases of salicylaldehyde with amines (anils). The latter comprise a chemical system undergoing hydrogen-atom tautomerism between enol and keto forms and show the phenomena of solid state photochromism and thermochromism. The system has been investigated extensively. Thus it has been shown that the photochromic property is a characteristic of the molecules but their chromobehaviour is influenced by the crystal structure of the compounds. Anils, apart from their fundamental interest, have potential for various applications.

## 1 Introduction

Photochromism is defined as the reversible photocolouration of a single chemical species between two states having distinguishably different absorption spectra, which is brought about by the action of electromagnetic radiation in at least one direction. Photochromism poses the same problems as other photochemical reactions *i.e.* the system generally represents a photoequilibrium and the photoproduct does not appear as a separate phase. However, it is distinguishable from general photochemical reactions by a characteristic feature: reversibility. Therefore, irreversible reactions are not discussed in this article. Most photochromic systems are based on unimolecular reactions, although bimolecular reversible processes are not excluded.

In Fig. 1 the starting compound **A**, under electromagnetic radiation, gives product **B**. The reverse (back) reaction **B** to **A** can occur thermally ($\Delta$) or photochemically.

The typical pattern for the absorbance prior, during and after irradiation of the photochromic molecule at a fixed wavelength is shown in Fig. 2.
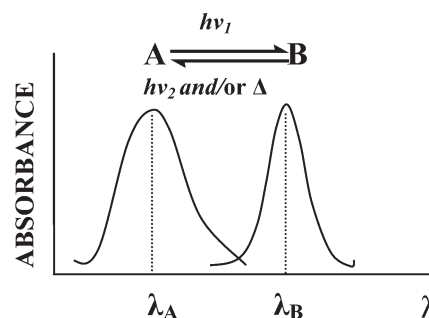


**Fig. 1** Reversible photocolouration of compound **A**.

Photochromic systems can be classified in several groups:

1. Photoreversible systems, in which the initial form **A** absorbs at a shorter wavelength than **B** (Fig. 1). These are further distinguished according to the back reaction of the coloured form **B**: (a) it undergoes a light induced reaction to form **A**, (b) it reverts thermally to **A** and (c) it goes back to **A** both thermally and photochemically.

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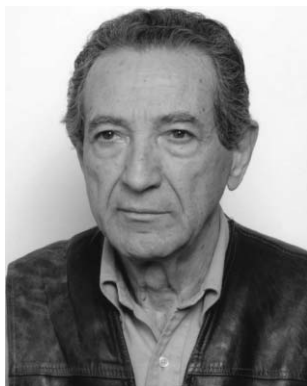
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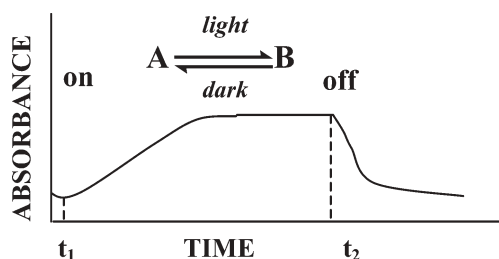
**Irene M. Mavridis**

Fig. 2 Typical analysis curve of absorbance *versus* time for the described photochemical system.

2. Reversible photochromic system, in which form **A** absorbs at longer wavelengths than form **B** ($\lambda_B < \lambda_A$).

3. Multireversible photochromic systems, in which more than one chromophore is present. In this case it is not always clear if one or more chromophores are active.

Photochromism has received considerable attention ever since its discovery in 1867 by Fritsche,[1] who observed that orange tetracene underwent a reversible photoreaction to a colourless material, and this continues to be a very active field of research due to its actual and potential applications, as well as for its paramount importance in biological phenomena. The sub-field of the photochromism of crystalline organic compounds is relatively narrow[2] but its scope has been increasing recently because of its technological potential. In the following sections, we give a representative and historical review of the subject, which may serve as a guide for further exploration of the field.

## 2 Photochromic solid organic compounds

Marckwald (1899)[3a] reported that of the two known $\alpha$ and $\beta$ isomers of tetrachloroketodihydronaphthalene, the $\beta$ isomer (**1**) changed its colour reversibly under irradiation. He used the term *phototropy* to describe this change but the term was already used by botanists to indicate the alignment of plants towards a light source.
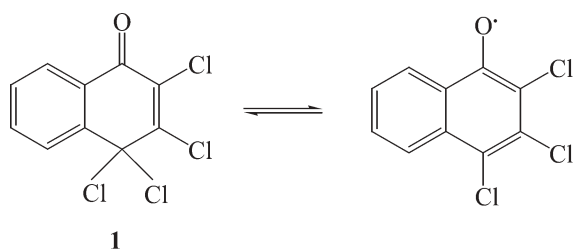


The structure of the $\beta$ isomer was confirmed by Hoppe and Rauch in 1960.[3a]

Stobbe (1904)[3a] extensively investigated the photochromism of fulgides (**2**). These are derivatives of dimethylenesuccinic anhydrides and at least one of the substituents, $\alpha$, $\alpha'$, $\delta$, $\delta'$ must be aromatic, so that the fulgide behaves as a 1,3,5-hexatriene, the aromatic bond serving as one double bond of the triene. According to the mechanism,[4] there is a structural interconversion between the colourless but flexible *E*-form and the photostationary state (generated upon UV irradiation) composed of the coloured and rigid *C*-form, as the main component, and the *E*-and *Z*-forms.

Fulgides were first regarded as candidates for materials in photon-mode optical recording media. Recent interest, however, has moved to their application in photoswitchable functional materials, including the photoswitching of liquid crystalline states, photoregulation of the binding of proteins with carbohydrates and photoswitching of the emission of fluorescence.
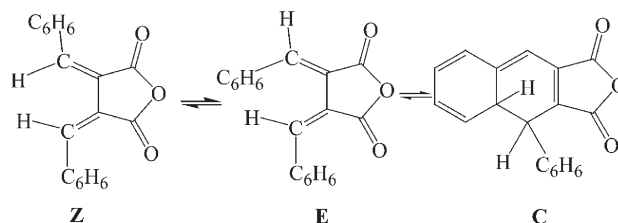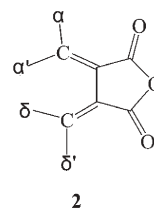




Senier *et al.* (1909, 1912)[5] observed the reversible solid state photocolouration of *N*-salicylideneanilines (**3**) and noted that the various ring substituted compounds were polymorphic, of which only a few were photochromic. Both observations revealed the effect of the structure on photochromism. Cohen, Hirshberg and Schmidt (1959–1964)[3a,5] showed that the presence of an *ortho*-hydroxy group is a structural requirement for the photochromism of these compounds and proposed the H-transfer mechanism for the crystalline *N*-salicylideneanilines.
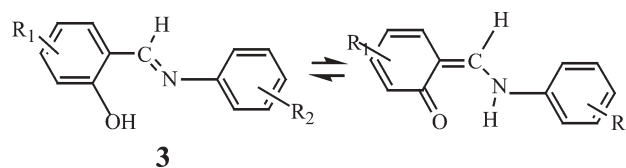


Weitz and Scheffer (1921)[3a] described the photochemical interconversion of white 2,3-diphenylindenone 4-oxide (**4**) and its red valence tautomer, 1,3-diphenyl-2-benzopyrilium 4-oxide (**5**). The photochemistry of this system was studied by Ulman *et al.* (1962–1967)[3a] and later by Gegiou *et al.*[6] who extended the investigation in the crystalline state.
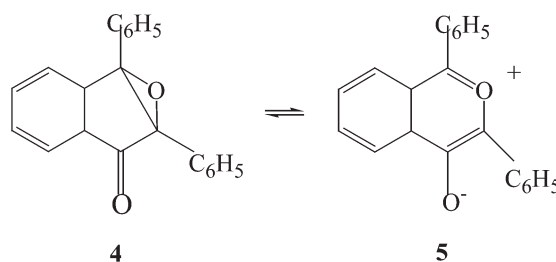


Chichibabin *et al.* (1925)[1] studied one of the most intriguing photochemical reactions known for over 70 years, the photoinduced and thermally activated H-transfer between the colorless CH (**6**) and the blue NH (**7**) forms of crystalline 2-(2′-4′-dinitrobenzyl)pyridine (DNBP). Recently (2002) Ohashi *et al.*[7] reported the structure of the blue NH isomer (**7**) produced by a two-photon excitation in a single crystal of DNBP.

Cycloadditions [2+2] have been shown to lead to
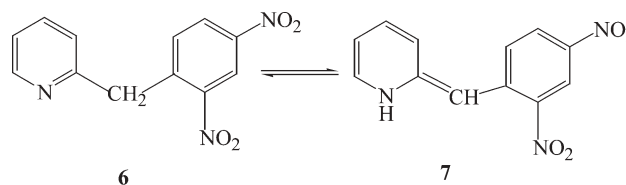
photochromism. Golden (1961)[1] investigated the structure, properties and reaction of anthracenophene (**8**) and reported that upon exposure to sunlight it becomes colourless (**9**), while it returns to its orange colour in the dark. The mode of formation of the photoisomer suggests a mechanism related to the intermolecular formation of dimers from anthracene and its 9-substituted derivatives upon irradiation, as reported earlier by Calas and Lalande.[1]



**8**          **9**



**10**          **11**
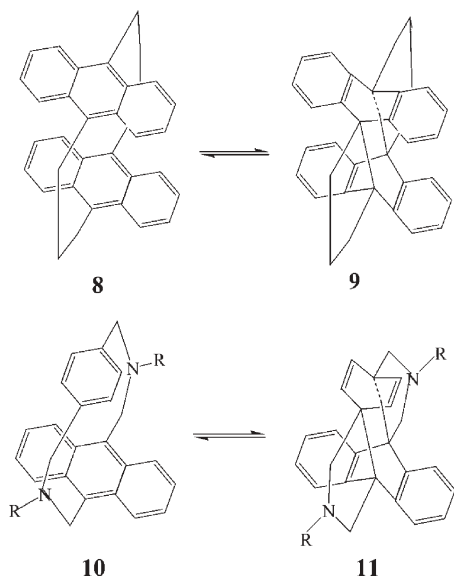
Later, Usui *et al.* (1984)[1] showed a related and interesting case, that of the photochromism of paracyclo(9,10)anthracenophanes (**10**), in which benzene and anthracene rings undergo photoreversible intramolecular cycloaddition (**11**) both in solution and in the solid state. The system has attractive features *i.e.* convenient wavelength range, large differences in absorption spectra between reactants and photoproducts and thermal stability at room temperature of the latter. Hesse and Hünig (1985)[8] described another system (**12**) undergoing a [2+2] photodimerisation in a single crystal, which subsequently returns thermally to the pure single crystal of the monomer. It is thus possible to switch between monomer (**12**) and dimer (**13**) without loss of crystal quality. Later, Novak *et al.* (1993),[9] through the crystallographic study of the single-crystal-to-single-crystal photodimerisation, showed that it is possible to use the above system in order to store and read holograms repeatedly using a He–Ne laser and subsequently to delete them thermally.



**12**          **13**
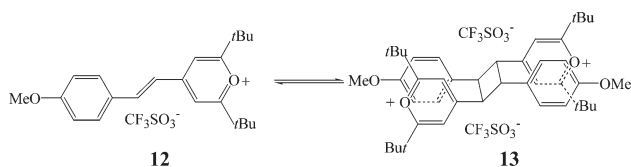
Heine *et al.* (1967) and Trozzolo *et al.* (1970) described[1] the photochromism of bicyclic aziridines (**14**). Upon irradiation ($\lambda < 450$ nm) at 77 K, the compounds investigated develop an intense blue colour, which can be erased by exposure to light in the visible region ($\lambda > 550$ nm) or by heat. The stability of the coloured species is strongly influenced by both electronic and steric changes in the structure of the aziridines.

Dürr *et al.* (1979–1989)[1] extensively studied 1,5-electrocyclisation, a type of intramolecular cycloaddition. Among the compounds studied, the spiro[1,8*a*]di-hydroindolizines (DHI) (**15**) proved to be a very efficient class of photochromic



**14**
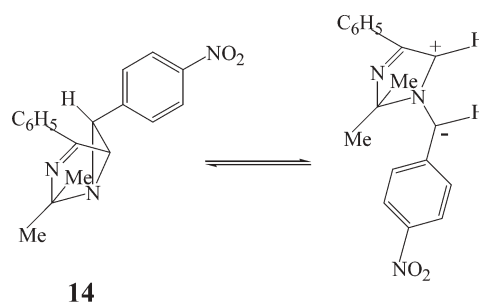
compounds. Irradiation of DHI with long wavelength UV or visible light reversibly affords a coloured betaine (**16**).



**15**          **16**
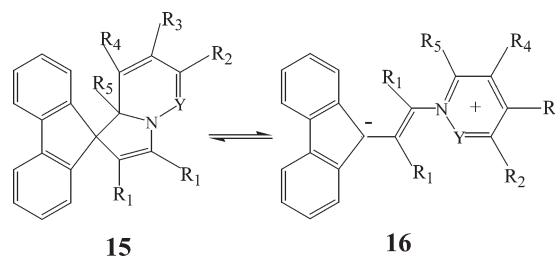
It should be noted that photochromism in these compounds is observed in solution. However, when both R1 groups are cyano groups, the compounds are photochromic in the crystalline state as well. Moreover, if the compound is adsorbed onto $SiO_2$, the photochromic behaviour persists and the spectrum compares well with that of the crystalline state.

Benard and Yu (2000)[10] reported the first case of a spiropyran derivative undergoing photochromism not only in solution but in the crystalline state. *N*-methylation of spirooxazine yields a yellow crystalline solid (**17**) that upon cleavage of the C(spiro)–O bond is transformed to the green open form (**18**). The usually less stable open form reverts back to the spirooxazine both photochemically and thermally.



**17**          **18**
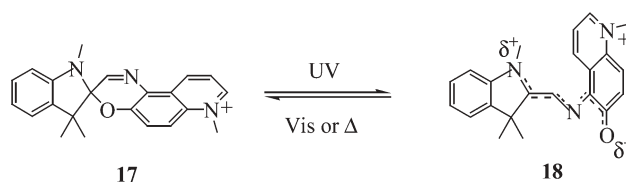
It is claimed that the large stabilisation of the zwitterionic open form brought about by *N*-methylation is an important factor for photochromic behaviour. The nature of the anion might also play an indirect role in the above behaviour resulting in more free volume of the photoactive species, thus presenting the possibility of fine-tuning the properties by changing the anion. Later, a related case was reported,[11] that of 1′-(*n*-propyl)-3,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indone] (**19**).



**19**          **20**
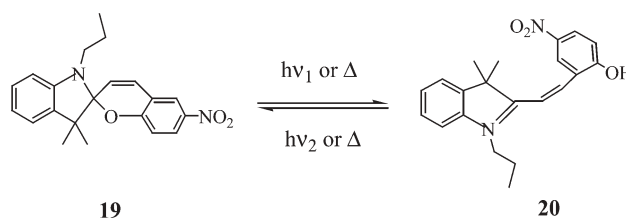
Based on UV–visible and IR spectra, it was proved that the red-purple coloured species is the open merocyanine form (**20**). In darkness, the IR and visible bands decay homogeneously, an indication of a back-process involving thermally activated ring

closure. Interestingly, the decay curves of the visible band could be fitted only to biexponential decay, suggesting the presence of two independent decaying merocyanine species. Crystal structure determination of **19** indicates two crystallographically independent molecules in the crystal. Although the molecules have the same geometry, they are found in a different environment (different nearest neighbors). Therefore, two non-equivalent molecules of **19** yield two structurally different merocyanine species in the crystal lattice and exhibit different thermal reactivity for cyclisation reactions.

Diarylethenes belong to another class of promising photochromic compounds that receive attention due to their thermal stability and excellent fatigue-resistant properties. Irie *et al.* (1995)[12] have found that 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene (**21**) undergoes a reversible photochromic reaction in a single crystal during which a ring closure takes place. Both the open-ring (colourless) and the photogenerated red isomer (**22**) were thermally stable even at 100 °C and the colouration/decolouration cycles could be repeated more than $10^4$ times without destruction of the crystals. The quantum yields of the photocyclisation reactions are 100% and the conversion rates close to 10%.[13]
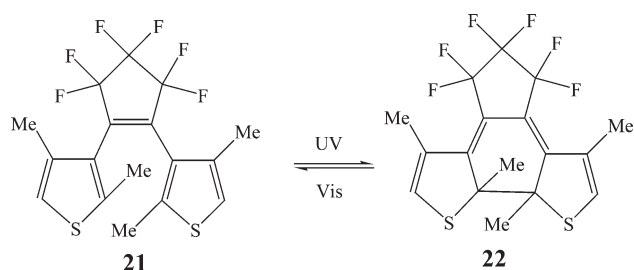
It has also been shown[14] that different derivatives of the above diarylethenes exhibit photochromism in the glass state, where the open forms as well as the photocyclised products form amorphous films.

## 3 Anils: the pioneering period

As mentioned already, Schiff bases of salicylaldehyde derivatives with aniline derivatives (anils) (**3**) were first studied by Senier and Shepheard (1909),[5] who observed that only a few of the compounds were photochromic. The term *photochromism* was coined later (1950) by Hirshberg[1] and it comprises the Greek words φως = light and χρωμα = colour. Cohen and Schmidt *et al.* (1959–1964)[5] undertook a more systematic study of crystalline anils and confirmed that many compounds are dimorphic and occasionally the two forms differ in colour (yellow or orange-red). They noted also (a) the importance of the *ortho*-hydroxy group in order to observe the photochromic phenomenon (Scheme 1), (b) the exhibition of photochromism
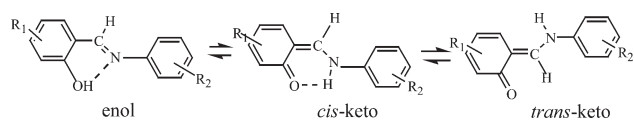
Scheme 1 Reversible thermochromic and photochromic processes in anils.

within a temperature range (working range) and finally (c) the related phenomenon of thermochromism: upon heating, the anils that are not photochromic in the crystalline state develop a spectrum closely resembling the spectrum of the coloured photochromic solid.

On the basis of three dimensional X-ray structures, crystalline anils were classified as thermochromic or photochromic

and these properties were found to be mutually exclusive. In thermochromic crystals, the molecules are essentially planar exhibiting intermolecular π···π interactions ("close-packed structures"), as shown in Fig. 3, with short inter-planar
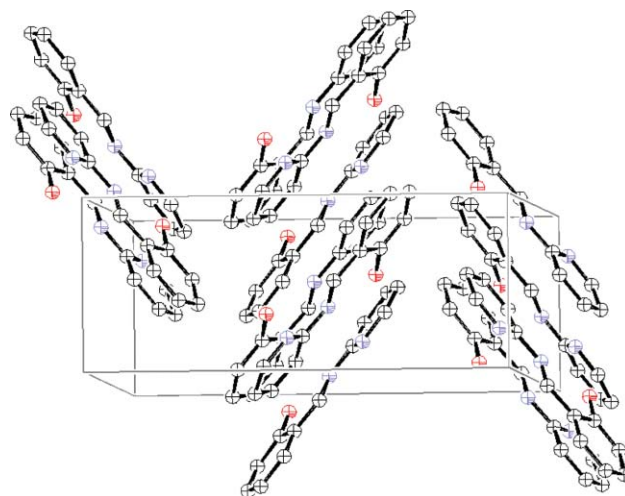
**Fig. 3** Example of a "close-packed structure": *N*-salicylidene-2-aminopyridine (*b* axis is horizontal, *a* is vertical).

distances (3.5 Å) and the salicylaldimine group is locked by an intramolecular H-bond (Scheme 1). In photochromic crystals, only the latter moiety is planar and it exhibits the intramolecular H-bond, whereas the aniline ring is rotated by about 50° with respect to this plane, thus precluding close contacts in the crystal lattice (Fig. 4).
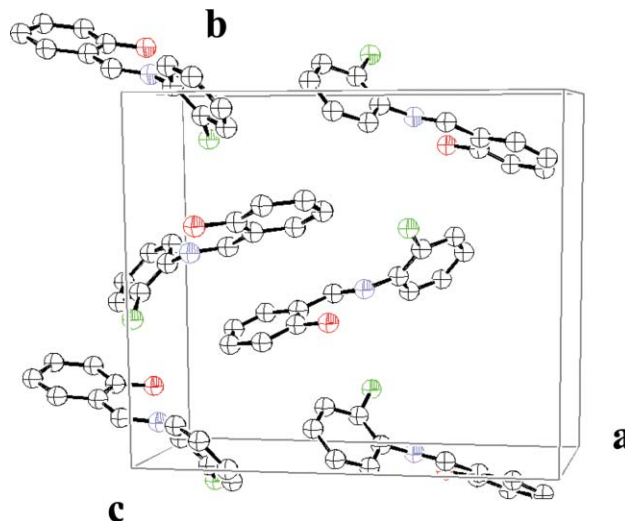
**Fig. 4** Example of "open structure" packing: *N*-salicylidene-2-chloroaniline (*a* axis is horizontal, *b* is vertical).

Further, in order to interpret the phenomena of thermochromism and photochromism, Cohen, Schmidt and co-workers proposed an intramoleculer H-transfer mechanism as shown in Scheme 1; there is a temperature-sensitive equilibrium between the enol tautomer and the *cis*-keto tautomer, which absorbs at longer wavelengths. The H-transfer can occur either in the ground or the excited electronic state. In the planar molecules, the basicity of the imine N-atom is higher because its lone pair does not overlap with the aniline ring, in contrast to the non-planar molecules, where the aniline ring is rotated with respect to the bridge and such overlap exists. Therefore, the OH···N hydrogen bond is stronger in the

ground state of the planar molecules. By raising the temperature, the population of the *cis*-keto form in the thermochromic crystals increases resulting in deepening of their colour. In the photochromic crystals, due to their non-planar conformation, the energy required for the H-transfer is very high in the ground state and no absorption attributable to the *cis*-keto form is observed. H-Transfer can occur, however, in the excited state, where subsequent rupture of the intramolecular H-bond and isomerisation to the *trans*-keto form results, permissible by the crystal packing, which does not have close contacts ("open structure", Fig. 4). Scheme 1 explains the mutually exclusive character of both phenomena and suggests that there is interplay between the molecular structure and the crystal packing. The above results stimulated the exploration of this reaction in the solid-state and the search for the structure of the photoproduct. The last goal proved not to be an easy task, since the system is described by equilibrium between the species, the photoproduct not appearing as a separate phase. In the course of the above studies it was realised that all anils are photochromic in rigid glasses, irrespective of their behaviour in the crystalline state, thus triggering solution studies. The latter process is very fast and requires flash photolysis techniques, by which it was possible to detect a transient species with an absorption spectrum similar to the photoproduct in solid solutions.[5]

Weller (1956)[3a] had proposed proton transfer across H-bonds in the excited state of a related system, salicylic acid and its methyl ester (**23**). These show an abnormally large Stokes shift (14 kcal mol$^{-1}$) of fluorescence emission (the displacement to longer wavelengths of the fluorescence band relative to the absorption band) as compared to the corresponding *ortho*-methoxy compounds, for which the fluorescence band is a mirror image of the absorption band. It was concluded that the hydroxy-molecules must have a mechanism for energy transfer in the excited state provided by the proton transfer across the OH···O hydrogen bond. It was calculated from the spectra that the required energy in the ground state is 13 kcal mol$^{-1}$ and in the excited state ∼1 kcal mol$^{-1}$. In the thermochromic anils there is a similarly large Stokes shift of fluorescence (∼14 kcal mol$^{-1}$) to longer wavelengths (530 nm). In fact, the low temperature (LT) fluorescence band is related to the thermochromic high temperature (HT) absorption band by a mirror plane. The fluorescence spectra of the thermochromic anils change markedly with temperature. The light emitted at LT is strong green-yellow, whereas at HT it is yellow and the intensity drops. Fig. 5 shows the spectral changes with temperature of crystalline thermochromic *N*-(5-chlorosalicylidene)aniline.[5]

**23**
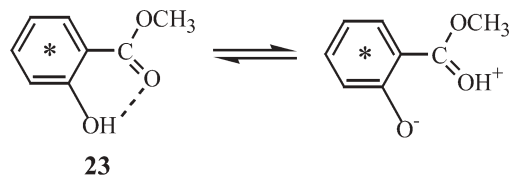
Cohen, Flavian and Schmidt[3b] (Fig. 5) have shown that the differences in the ground state energy forms (Scheme 1: enol = yellow, *cis*-keto = orange-red) of the thermochromic anils are small, *i.e.* 1.76 kcal mol$^{-1}$ for *N*-(5-chlorosalicylidene)aniline. Thus the larger displacement of the fluorescence band is attributed to the excited state proton transfer across the OH···N hydrogen bond (Scheme 2) by analogy with the methyl ester of salicylic acid (**23**). The drop in fluorescence with the rise in temperature is an additional indication for proton transfer in the excited state.

The photochromic crystalline anils do not fluoresce above the minimum temperature of the range, within which
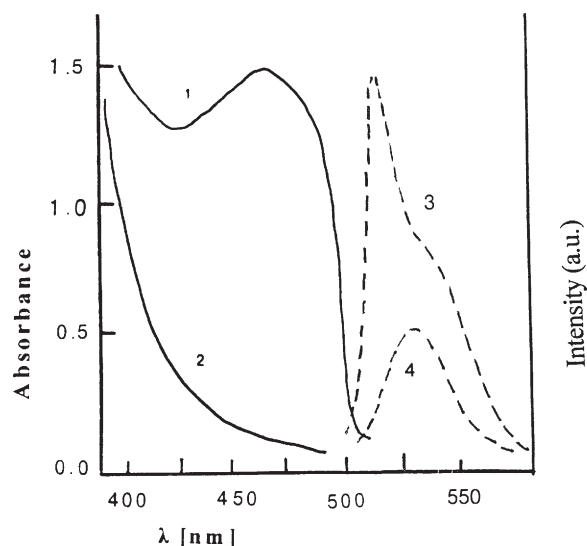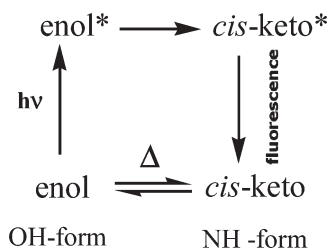


**Fig. 5** Thermochromic solid *N*-(5-chlorosalicylidene)aniline: absorption spectra at 297 K (1) and 120 K (2). Fluorescence spectra at 90 K (3) and 297 K (4) (irradiation with light of 365 nm). From M. D. Cohen, G. M. J. Schmidt and S. Flavian, *J. Chem. Soc.*, 1964, 2041.[3b]



**Scheme 2** Proton transfer in thermochromic crystals.

photocolouration is induced. When the temperature drops below this minimum, the photo-colour disappears and fluorescence emission (very similar to that of the thermochromic crystals) emerges. The hypothesis of an excited quinoid structure of the photochromic anils upon irradiation is supported by the latter and by the following two additional phenomena: (a) the photo-colour is preserved upon cooling and (b) reversal of the photo-coloured species by irradiation at the maximum of the absorption band (∼450 nm) or thermally in the dark (activation energy ∼20–25 kcal mol$^{-1}$). In addition, stabilisation of the quinoid structure by *cis*-to-*trans* isomerisation as indicated in Scheme 1 is supported by the fact that the decay rate of the photoproduct is unaffected by deuteration of the OH group, a fact indicating that the rate determining step of this reaction corresponds to *trans*-to-*cis* rather than keto-to-enol conversion.

## 4 Structural aspects of photochromism

In order to strengthen their proposition shown in Scheme 1, Schmidt and Leiserowitz *et al.* (1964)[5] undertook X-ray crystal structure determinations of the strongly thermochromic *N*-(5-chlorosalicylidene)aniline (**24**) at room temperature (RT) and at LT (∼90 K) and the strongly photochromic *N*-salicylidene-2-chloroaniline (**25**) before and after irradiation hoping to detect structural changes before and after the appearance of colour in the compounds. However, the attempt was inconclusive, because of the low thermal population of the red (quinoid) species at RT (estimated at ∼5%) in the case of **24** and the low depth of penetration (∼10$^{-4}$ cm) of the inducing light for **25**. The packing of the above compounds confirmed the general trend: thermochromic = "close-packed structure",

photochromic = "open structure". Subsequently, the structure determinations of thermochromic salicylideneazine (**26**)[15] (close plane-to plane stacking of 3.4 Å) and *N*-salicylideneaniline (**27**)[16] (non-planar molecules with an angle of 49° between the phenyl moieties and no π···π interactions) also followed this trend.

**24**

**25**

**26**

**27**
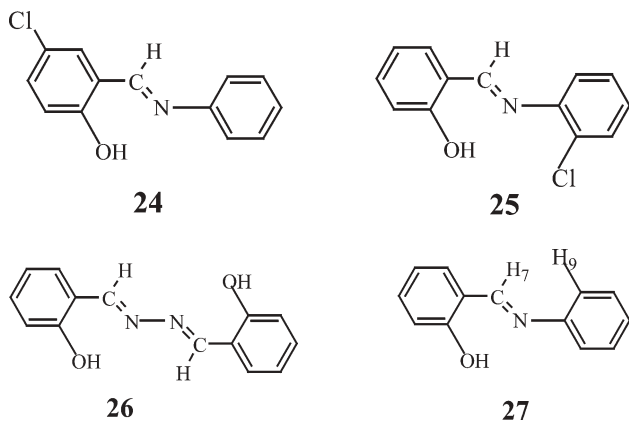
Mavridis *et al.*[17] tested the assumption that planar molecules with "close-packed structures" do not exhibit photochromism. Structure determination of four out of a large number of derivatives of *N*-salicylidene-2-aminopyridine (**28**), which are all thermochromic, showed that they are essentially planar. Thermochromism of these compounds was interpreted as due to an enol–keto tautomerism (Scheme 1), as in *N*-salicylideneanilines. In addition, they exhibit fluorescence that mirrors roughly the absorption band of the *cis*-keto isomer as in the *N*-salicylideneanilines (Fig. 5). Planarity of the derivatives of **28** is attributed to (a) the orientation of the pyridine ring: the hetero N-atom is *cis* with respect to the $H_7$, and (b) the strong intramolecular H-bond, which locks the salicylaldimine group in the plane. In these planar molecules there is no strain between the hetero N-atom and $H_7$ (distance N···$H_7$ is 2.5 Å), in contrast with the planar *N*-salicylideneanilines (**27**), in which hydrogen atoms $H_9$ and $H_7$ come very close and an intermolecular distance $H_9$···$H_7$ of 2.0 Å is achieved by a lot of deformation in bond distances and angles around these atoms plus a slight rotation of the aniline ring. The latter relieves the strain but results in a less planar molecule.

**28**

$R_1=R_2=H$
$R_1=5$-Br, $R_2=H$
$R_1=3$-MeO, $R_2=3$Me
$R_1=5$-MeO, $R_2=5$-Cl
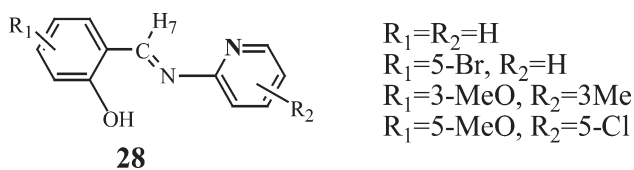
To test the importance of the heterocyclic N-atom in the *ortho* position with respect to the C–N bridge for the planarity and consequently for thermochromism, the same researchers investigated derivatives of *N*-salicylidene-3-aminopyridine (**29**), which are weakly thermochromic.[18] The crystal structures of two of these compounds revealed that the $H_7$···$H_9$ distance is 2.0 Å as in *N*-salicylideneanilines and the orientation of the hetero N-atom with respect to the bridge is not preserved, in contrast to the *N*-salicylidene-2-aminopyridines. The compounds are not very planar (the dihedral angle between the aniline ring and the salicylaldimine plane is ~15°), thus explaining the weak thermochromism. However the crystal packing is still very dense to permit any possible *cis*-to-*trans* isomerisation (and thus photochromic behaviour). Derivatives of *N*-salicylidene-4-aminopyridines had stability problems and they could not be crystallised, however the derivatives that were

examined showed either thermochromic or photochromic behaviour.

**29**

$R_1=R_2=H$
$R_1=5$-MeO
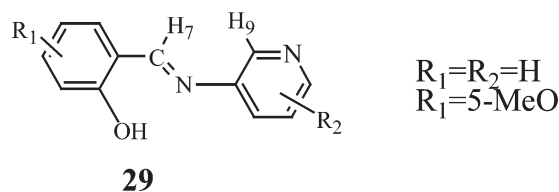
The anils of aminopyridines present a good example of crystal engineering defined as the molecular design that induces a specific crystal structure. Insertion of a nitrogen atom into position 2 of the aniline results in only a thermochromic compound as is the case of *N*-salicylidene-2-aminopyridines. On the other hand, Kawato *et al.*[19] have also tested the influence of the molecular structure on the crystal packing and subsequently on photochromism and thermochromism. *N*-(3,5-Di-*tert*-butylsalicylidene)aniline (**30**) is photochromic with substantially more stable photoproduct compared to *N*-salicylideneaniline (**27**), a fact attributed to an increase in the free space in the crystal packing due to the bulky *tert*-butyl groups.

**30**

$R_1$=H, $R_2$=*tert*-butyl
$R_1$=*tert*-butyl, $R_2$=*tert*-butyl
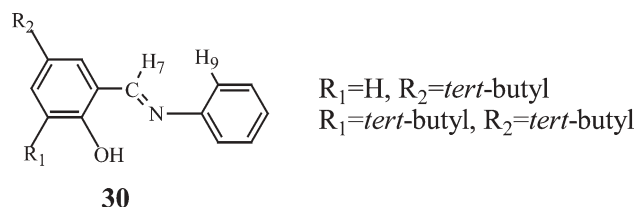
In a number of compounds investigated later,[18] derivatives of *N*-salicylidenebenzylamines (**31**) and *N*-salicylidene-2-thienylmethylamines (**32**), the imine N-atom is insulated from the aromatic end group by a methylene. The compounds display either thermochromic or photochromic properties, except for one which is simultaneously thermochromic and photochromic, in contrast to all compounds studied so far
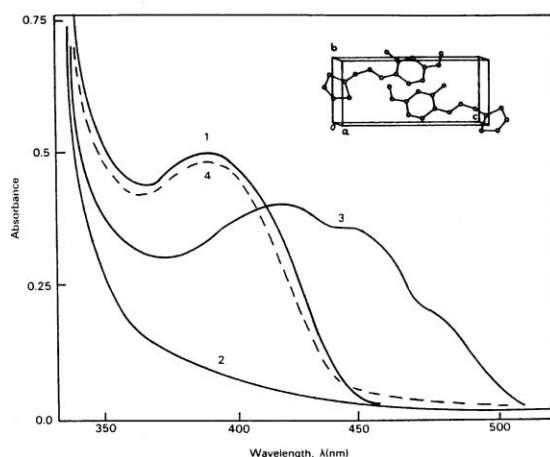


**Fig. 6** Thermochromism and photochromism of a thin polycrystalline film of *N*-(4-methoxysalicylidene)-2-thienymethylamine. Absorption spectra at 298 K (1); 77 K (2); at 77 K after irradiation for 20 min with light of 365 nm (3) and after staying in the dark overnight at 298 K (4). The insert shows the molecular packing as viewed along the *a* axis.

(Fig. 6). The salicylaldimine part of the latter molecule is planar but the whole molecule is not and its molecular packing differs from the characteristic packing of planar molecules, in contrast to the thermochromic anils studied so far.[20]

R₁ with H₇... 

$R_1$ ... $H_7$

**31**

$R_1$ ... $H_7$

**32**

$R_1$=H Photochromic
$R_1$=5-Br Photochromic
$R_1$=5-MeO Photochromic
$R_1$=3-MeO Photochromic
$R_1$=3,5-di-Br Thermochromic
$R_1$=3,5-di-Cl Thermochromic
$R_1$=4-MeO Photo/thermochromic
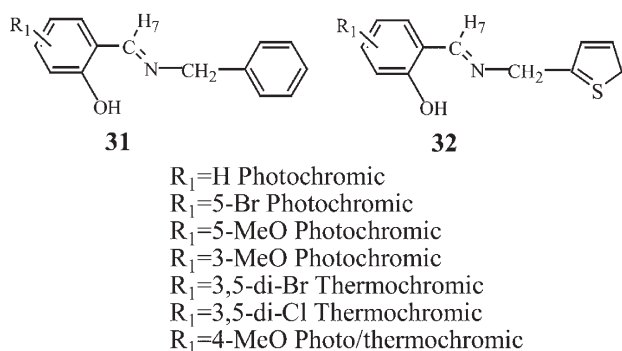
The above results indicate that molecular planarity is not a necessary factor for thermochromism, whereas it is detrimental to photochromism. What is crucial to thermochromism is the electron density on the imine N-atom. In the case of anils **31** and **32** this density is not decreased in the non-planar molecule because the aromatic group has been isolated. It follows therefore, that anils of aliphatic amines should exhibit thermochromism irrespective of molecular packing and they may exhibit photochromism simultaneously, if the molecular packing permits the *cis*-to-*trans* keto isomerisation for the formation of the photoproduct. The latter statement has indeed been verified in the cases of *N*-salicylidenemethylamine (**33**)[21] and *N*-salicylidene-2-propylamine(**34**)[22] that are photo/thermochromic simultaneously and several dianils of 1,2-diaminecyclohexane (**35–38**).[23] All the latter compounds are thermochromic and **35** and **37** additionally exhibit photochromism. Crystal structure determinations of **36** and **38** show very clearly that *cis*-to-*trans* keto isomerisation of the photoproduct is impossible due to the very dense packing (Fig. 7), thus explaining the absence of photochromism.[23] On

the other hand, the packing of **35** and **37** is quite open and permits photochromism.

**33**

$H_7$ ... $N$—$CH_3$ ... OH

**34**

$H_7$ ... $CH_3$ ... $N$—$C$—$H$ ... $CH_3$ ... OH

**35** R=H
**36** R=3,5-di-Cl
**37** R=3,5-di-*t*-butyl
**38** Naph
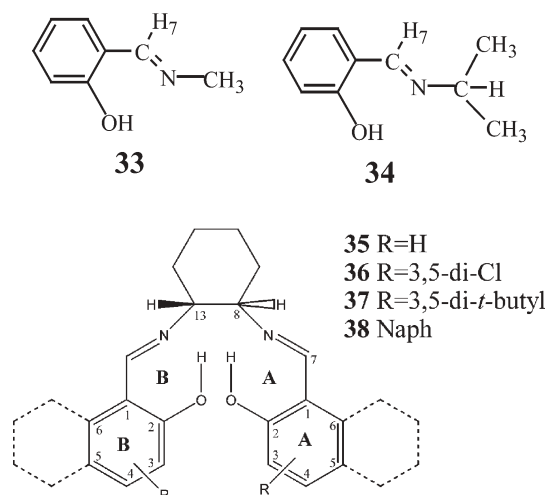
## 5 The mechanism of the photochromic process

Higelin and Sixl[24] examined the reaction mechanism of photochromic *N*-salicylideneanilines using dibenzyl and stilbene host crystals and rigid glasses. *N*-Salicylideneaniline exhibits photochromism down to 10 K in dibenzyl and to 180 K in stilbene host crystals. The LT emission spectra confirmed observations mentioned earlier. Thus large shifts between absorption and emission have been attributed to the intramolecular H-transfer (OH···N to O···HN) following photoexcitation of the enol species, whereas absence of a Stokes shift in the LT emission spectra of the photoproduct indicated disruption of the OH···N or O···HN H-bond. The latter suggest a *trans*-keto form of the photoproduct structure, in agreement with a previous assignment. Fig. 8 summarises the essential pathways of the forward and backward reactions as deduced from the above experiments in the crystal matrices and previous ones in dilute solutions and rigid glasses.

The extremely shifted and structured Stokes emission is a result of the transitions of the intermediates QA*→ QA (high-energy) and the QB*→ QB (low-energy, broad). No stabilisation of the proton at the nitrogen atom results in very short lifetime of QA and QB after de-excitation and the proton returns to the original oxygen atom. The fact that in the final stable photoproduct, QC, proton return from the N-atom to the O-atom is strongly hindered shows that stabilisation of the NH configuration takes place immediately after the initial proton transfer. The emission characteristics of the species show that the QA state has a chemical structure related to QC, which, having no intramolecular H-bond, is postulated to be the *trans*-keto form. Therefore, upon excitation of the enol *E*-form and the proton transfer, the H-bond is cleaved by a distortion of the *cis*-quinoid configuration in the excited QA state. QA* is suggested to have a structure between QB* and QC* and may decay into QB or QC thus being a precursor of both. It has been also suggested that a QB*→QC* reaction is excluded. This study confirmed the previous interpretations of Cohen and Schmidt in that the *cis*-keto form is the product of the thermochromic process and the *trans*-keto form the photoproduct.

Sekikawa, Kobayashi and Inabe[25] investigated the effect of the aromatic rings' substituent groups on the proton transfer of three thermochromic *N*-salicylideneanilines in the crystalline state by femtosecond time-resolved fluorescent spectroscopy. It was concluded that the lifetime of the excited enol is less than a few picoseconds and its decay rate almost corresponds to the proton transfer rate. LT experiments at 77 K showed that the
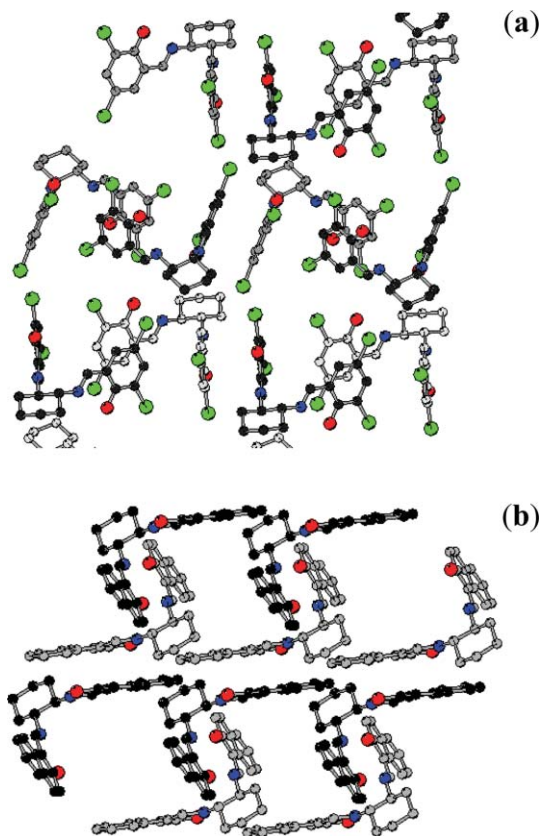
**Fig. 7** Packing diagrams of the thermochromic compounds *trans-N,N'*-bis(3,5-dichlorosalicylidene)-1,2-cyclohexanediamine (a) and *trans-N,N'*-bis(2-hydroxynaphthylmethylene)-1,2-cyclohexanediamine (b).
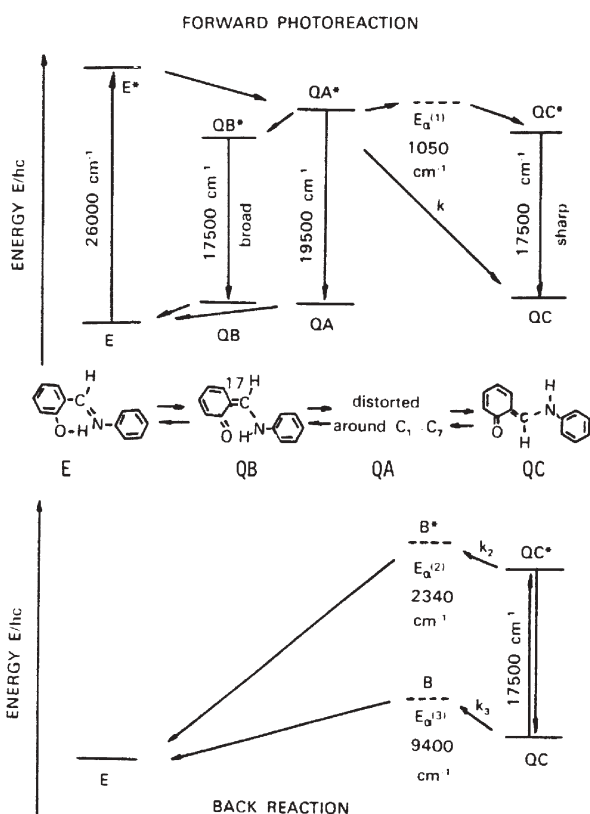
**Fig. 8** Energy level scheme of the forward and backward reactions of *N*-salicylideneaniline in dibenzyl host crystals. (Reproduced with permission from ref. 24. Copyright 1983 Elsevier.)

latter was not much different from the one at RT, contrary to an expected inverse exponential behaviour according to the thermal activation mechanism. Therefore, it was suggested that quantum mechanical proton tunnelling through a barrier is taking place. This hypothesis was supported by the reduction of the proton transfer rate by deuteration, but it is in contrast to previous results on gas or liquid phase systems that suggested a barrierless potential.[26] The end conclusion of the study was that the proton transfer rate changes drastically by substitution and decreases with the energy separation between the excited enol ($E_e$*) and keto ($K_k$*) forms (Scheme 3). This is
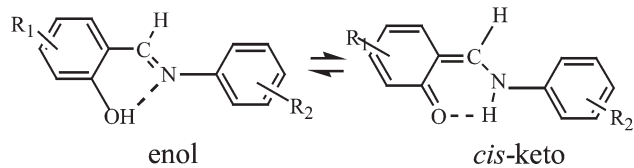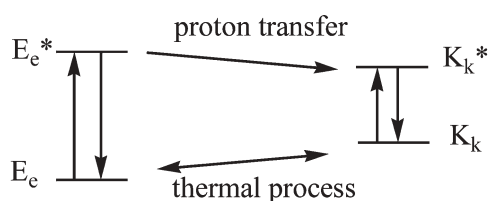


**Scheme 3** Energy diagram and constitutional formulas of thermochromic *N*-salicylideneanilines.

attributed to different barrier heights of the proton potential in the excited state. Thus substituents weakening the O–H bond or enhancing the proton accepting property of the N-atom favour thermochromism.

## 6 Hunting for keto forms

The necessity to demonstrate the existence of *cis*- and *trans*-keto forms and the required isomerisation of the former to the latter have spurred many crystal structure determinations of anils by X-ray crystallography and other supplementary techniques. Initially these studies did not detected any structures in the keto form,[5] but the situation has changed. Inabe *et al.*[27] found that in the structures of the photochromic compounds *N*-(2-hydroxy-1-naphthylmethylene)-1-pyren-amine (**39**) and *N*,*N*-bis(2-hydroxy-1-naphthylmethylene)-1,4-phenylenediamine (**40**), there exist equal populations of enol and keto forms in equilibrium. The stabilisation is attributed to the π-electron delocalisation effect that stabilises the NH form. The structural results are in agreement with the frequency and band shape of the OH and NH stretching mode absorptions in the IR spectra and the energy separation between the OH and NH-forms as determined from the spin–lattice relaxation rates of the proton NMR.
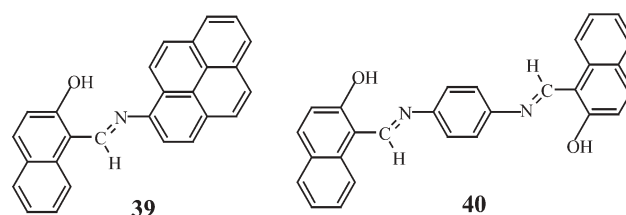


The first observation of a change in the crystal structure of a compound was achieved by the X-ray diffraction of *N*-(5-chlorosalicylidene)-4-hydroxyaniline.[28] At a given temperature the structure is a superposition of the enol and keto forms, whose population varies with the temperature along with the bond lengths and angles. The latter are the weighted average of the corresponding lengths and angles of the OH and NH forms (Fig. 9). It was determined that at 90 K, *ca.* 90% of the
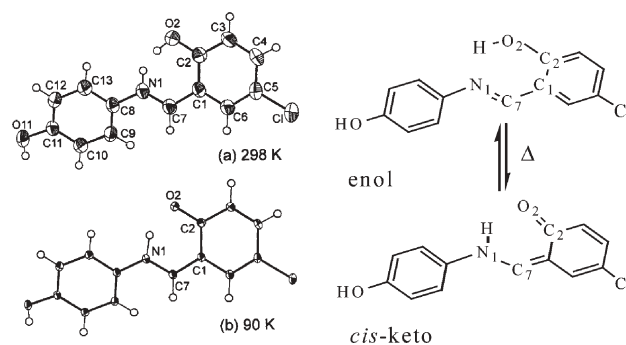


**Fig. 9** Perspective views of *N*-(5-chlorosalicylidene)-4-hydroxyaniline with an atom numbering scheme: at 298 K (a) and at 90 K (b). (Reproduced with permission from ref. 28. Copyright 1998 American Chemical Society.)

compound exists in its NH form and as the temperature increases this percentage decreases. Compared to that which has been discussed up to now, this compound exhibits a *negative* thermochromism. The molecular packing reveals that the OH group at the 4-position of the aniline ring stabilizes the *cis*-keto form.

On the other hand, Harada *et al.*[29] later succeeded in observing crystallographically the structural changes accompanying the reversible phototransformation of *N*-(3,5-di-*tert*-butylsalicylidene)-3-nitroaniline, a photochromic Schiff base (Fig. 10). Initially, the molecule exists as the enol form in the crystal. The photoreaction has been induced by two-photon irradiation at 730 nm, where the compound does not have any absorption band, in order to achieve sufficient penetration of
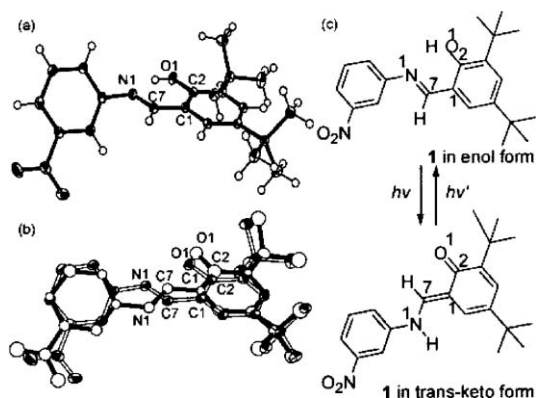
**Fig. 10** Molecular structure of *N*-(3,5-di-*tert*-butylsalicylidene)-3-nitroaniline before light irradiation (pale yellow crystal) (a). Disordered structure after laser irradiation (red crystals) (b) (the bonds of the enol and *trans*-keto forms are shown by open and filled lines). The chemical structures of the original enol form and the photoinduced *trans*-keto form (c). (Reproduced with permission from ref. 29. Copyright 1998 American Chemical Society.)

the radiation into the crystal and produce enough of the photoproduct. The latter has been proven to be the same as the one produced by the normal excitation at 365 nm with a high-pressure mercury lamp. In the study it was possible to obtain an irradiated dark-red crystal of sufficiently good quality and determine the crystal structure. In this case also the structure is a superposition of two forms: the original enol and the photoproduct, which has been proven to be the *trans*-keto form (Fig. 10). Subsequently, the coloured crystal was bleached to a yellow one by white light irradiation. X-Ray crystal structure determination of the bleached crystal proved that the original enol form had been acquired. Thus for the first time the *trans*-keto form of the photoproduct has been proven. The authors moreover, propose another mechanism for the *cis*-to-*trans* keto transformation, instead of the normal rotation of the amine part of the molecule that requires a huge empty volume in the crystal. This is based on the observed structural changes and involves a concerted movement of the bridge atoms and the aromatic rings resembling the pedal motion of a bicycle (Fig. 10). Albeit this movement requires less space than the rotation initially proposed, it also demands free space in the photochromic crystals.[23]

## 7 Conclusion and outlook

Photochromism, exhibited by a variety of widely different crystalline organic compounds, is presented in a brief historical perspective. The basic processes in crystalline photochromic systems comprise hydrogen transfer, dimerisation, cyclisation, ring opening, valence tautomerisations and isomerisation. Crystalline Schiff bases of salicylaldehyde (anils) undergo photochromism or the related phenomenon of thermochromism initiated by an intramolecular hydrogen transfer from the *ortho*-hydroxy group to the nitrogen atom of the imine in the ground (thermochromism) or the excited (photochromism) electronic state, *via* a six-membered ring transition state, producing keto species with bathochromically shifted spectra. The phenomenon of photochromism involves structural changes (*cis*-to-*trans* isomerisation) stabilizing the photoproduct, which imposes specific spatial requirements on the crystal packing. In the case of thermochromism the role of the molecular structure and the crystal packing is important in so far as it affects the electron density on the nitrogen atom of the imine moiety. The mechanism of this apparently simple reaction presents still a number of intriguing problems especially for processes in the excited state, as for example

the decay mechanism of the excited enol form. However, new techniques employed in the studies have already made a difference. Thus femtosecond fluorescent studies have contributed to the clarification of the mechanism and two-photon excitation has increased the low photocolouration efficiency, therefore rendering the quantum yields more appropriate for applications.

Several attempts have been reported which explore the suitability of anils as functional materials. A representative example is derivatives of **41**, which combine charge transport and proton transfer properties, proposed by Inabe[30] for a novel type of molecular electronic device. In molecular conductors such as **41**, electron carriers move under a periodic potential, which can be modulated by the proton transfer. If the coupling between the two properties is sufficiently strong, memory or switching functions can be obtained. Thus by controlling the strength of the coupling, the proposed system gives various types of charge conduction, which might be utilized in versatile electronic devices. *N*-Salicylideneanilines have also been the focus of non-linear optical (NLO) studies for potential applications such as data storage, information processing, telecommunications and optical switching.[31] Along this line Nakatani and Delaire[32] studied molecules exhibiting both NLO properties and photochromism, since the latter could modulate the former owing to the switching between molecular species. Thus *N*-salicylidene-4-bromoaniline, a known photochromic anil[5] crystallising in a non-centrosymmetric space group (a prerequisite for NLO properties), shows a totally reversible second harmonic generation change correlated to the change of the two molecular species of the reversible photochromic reaction. Although the system has not yet been optimized, it is considered as capable of competing with inorganic crystals for reversible photoswitching applications. Related studies have been extended to other non-centrosymmetric photochromic crystals of anils[33] in order to generate materials for data storage and optoelectronic switching.



**41**
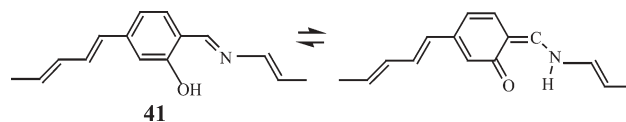
Because photochromism arises from geometrical isomerisation, colouration is sensitive to the surrounding environment. This gives enormous flexibility for the development of photochromic compounds with designed properties. Some reported cases are: 2,4-dihydroxy-*N*-octadecylbenzylidene-amine, an amphiphilic molecule, which can be assembled into monolayer and multilayer films,[34] highly ordered and densely packed structures that exhibit photochromism upon irradiation with 365 nm light. On the other hand, inclusion complexes of the abundant class of thermochromic anils in various matrices such as cyclodextrins, deoxycholic acids and mesoporous silica have produced materials showing photochromic behaviour.[35] The modulation of the properties of anils due to environmental effects, combined with their easy synthesis gives an enormous field of molecular design in order to produce compounds with a wide palette of properties. These will combine photochromic and thermochromic behaviour with others such as non-linear optical or charge transfer properties in order to generate applications. Detailed knowledge of the photoactivity of the compounds and their structure is very important in order to achieve the above goals.

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