Journal of Photochemistry and Photobiology
A: Chemistry 86 (1995) 241–246

Thermochromism and photochromism of N-salicylidenebenzylamines and N-salicylidene-2-aminomethylpyridine

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Received 16 June 1994; accepted 2 August 1994

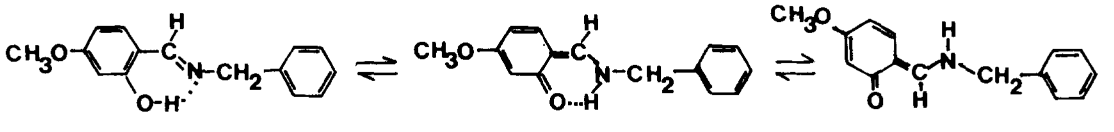
Abstract

N-salicylidenebenzylamine (II), N-salicylidene-2-phenylethylamine (III), their mono- and di-substituted derivatives, N-salicylidene-2-aminomethylpyridine (XIV) and N-salicylidene-2-aminoethyl- pyridine (XV) were investigated for their thermochromic and photochromic properties in the solid state and in solution, in the temperature range 298 K–77 K. II, III, XV, some of the monosubstituted derivatives of II and all the monosubstituted derivatives of III studied presented both properties, i.e they were both thermochromic and photochromic. The di-substituted derivatives were, practically, photochemically inactive. All the compounds investigated and found to be thermochromic, presented negative thermochromism in non-polar solvents and some in polar solvents also. Negative thermochromism in non-polar solvents was due to aggregation as it was mainly shown by the concentration dependence on the electronic spectra. The same also seemed true in polar proton donating solvents but the picture was diversified by solubility.

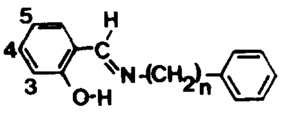
Keywords: Thermochromism; Photochromism

1. Introduction

Thermochromism and photochromism have been found to be mutually exclusive properties in N-salicylideneanilines and substitution not to have any effect on these properties [1]. In the thermochromic crystal structure, the molecules are essentially planar but in the photochromic form, the aniline ring is twisted about the exocyclic N–C bond. In the planar molecular structure the lone pair of the nitrogen does not overlap with the π electrons of the aniline ring whereas in the 'twisted' structure such overlap is possible; consequently, thermochromism is mainly controlled by the basicity of the nitrogen atom. However, N-(4-methoxysalicylidene)-benzylamine (IV) has been found to be both thermochromic (T) and photochromic (P) [2]:



In this work the following N-salicylidenebenzylamines (II, IV–VIII) and N-salicylidene-2-phenylethylamines (III, IX–XII), as well as N-salicylidene-2-aminomethylpyridine (XIV), and N-salicylidene-2-aminoethylpyridine (XV) have been investigated in solution and in the solid state in the temperature range 298 K–77 K:



I:	n=0	VII:	3-Br, 5-Br-II
II:	n=1	VIII:	3-Cl, 5-Cl-II
III:	n=2	IX:	5-CH_3O-III
IV:	4-CH_3O-II	X:	5-Br-III
V:	5-CH_3O-II	XI:	3-Br, 5-Br-III
VI:	5-Br-II	XII:	3-Cl, 5-Cl-III

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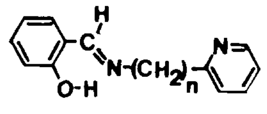
1010-6030/95/$09.50
SSDI 1010-6030(94)03943-7



XIII: n=0
XIV: n=1
XV: n=2

Negative thermochromism has been observed in the Schiff bases [2,3], but it has not been investigated. The study of negative thermochromism has been performed in non polar and polar solvents.

2. Experimental details

2.1. Materials

The compounds were synthesized by direct condensation of the appropriate salicylaldehyde with the appropriate amine or aminopyridine in ethanol, followed by repeated recrystallization from the same solvent. IR, melting points and elemental analysis were utilized to establish the purity of the compounds [2].

2.2. Spectra

The compounds were screened, in powder polycrystalline form, for photochromic and thermochromic properties. For more quantitative experiments thin polycrystalline films were used. These films were prepared from the melt between two optical quartz plates under pressure and their quality was examined under a polarizing microscope. To measure their optical spectra at various temperatures, a quartz Dewar vessel with quartz windows was used.

The rigid-state experiments were conducted in MCH/IP (methylcyclohexane: isopentane, 3:1), EPA (ether: isopentane: ethanol, 1:5:5), E/M (ethanol: methanol, 2:1) and in polymerized methyl methacrylate (PMMA). In these rigid media, the fading of the photocolour was not appreciable during the measurement of the spectrum; therefore, all the spectra were obtained satisfactorily. No correction was made to the spectra for contraction of the solution on cooling.

The absorption spectra were recorded with a Cary-17 or Varian Techtron 635 spectrophotometer. Steady-state photochemical experiments employed a 200 W high pressure Hg lamp with Corning glass filters.

3. Results and discussion

3.1. Absorption spectra

The long wavelength band maxima of the Schiff bases studied in MCH and methanol are presented in Table 1. The maxima undergo a blue shift as the methylene groups are inserted between the C=N bond and the aromatic ring adjacent to the nitrogen, because of the isolation of the aniline ring from the conjugated π system of the rest of the molecule. At the same time, the resonance of the nitrogen lone pair with the π system of the aniline ring is decreased or interrupted by the insertion of the second methylene group. The maximum of the long-wavelength band of XIII is red shifted by 5 nm compared with that of I. This shift probably shows that XIII is more planar than I in solution as well. XIII is planar [4] whilst I is nonplanar [1] in the solid state.

Table 1
Thermochromic and photochromic properties of Schiff bases

No	Long wavelength (max., nm)		Rigid glass			Solid state
	MCH	M	MCH	EPA	E/M	
I	345	338(432)[a]	P[b]	p	P	P[1]
II	322	316(400)	N[c],P	P	P	T[d],P
III	318	313(400)	N	P	N,P	T,P
IV	314	310(380)	N	N	N	T,P
V	340	–	P	P	P	P
VI	334	328(415)	P	P	P	P
VII	340	334(425)	N	N	–	T
VIII	340	333(423)	N	N	–	T
IX	343	338(430)	N,P	P	P	T,P
X	326	322(410)	N	P	N,P	T,P
XI	335	334(425)	N	N	N	–
XII	335	333(423)	N	N	N	–
XIII	350	–	P	P	P	T[5]
XIV	320	–	P	P	P	P
XV	311	307(400)	N,P	–	–	T,P

[a] Wavelengths in parentheses, additional band at longer wavelengths.
[b] Photochromic.
[c] Negatively thermochromic.
[d] Thermochromic.

The spectra of the 5-Br and 5-OCH_3 substituted N-salicylidene-benzylamines (VI and V, respectively) and N-salicylidene-2-phenylethylamines (X and IX, respectively) indicate an increase in stability compared with the unsubstituted molecules. In contrast, the -OCH_3 substituent at the 4-position brings about a blue shift to the maximum of the long-wavelength band.

The absorption spectra of the thin polycrystalline films, except in the cases of I, V, VI and XIV, contain an additional band at longer wavelengths (Fig. 1). In the case of XIII, this band at 475 nm has been attributed to the cis-quinoid form (thermochromic form) [5].

3.2. Thermochromism and photochromism

3.2.1. Rigid glasses

Generally, the Schiff bases are photochromic in rigid glasses irrespective of how they appear in the solid

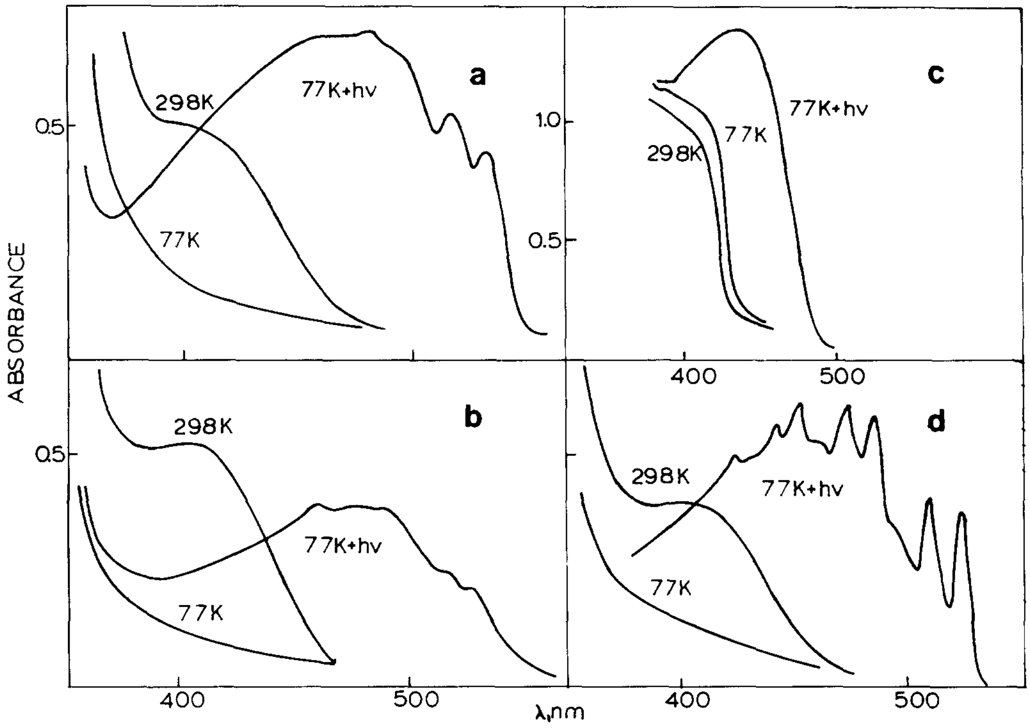


Fig. 1. Absorption spectra of thin polycrystalline films: a, N-salicylidenebenzylamine (II); b, N-salicylidene-2-phenylethylamine (III); c, N-salicylidene-2-aminomethylpyridine (XIV); d, N-salicylidene-2-aminoethylpyridine (XV).

state. On the contrary, the compounds II–IV, VII–XII and XV investigated in MCH/IP at 77 K show negative thermochromism (Table 1); when negative thermochromism is strong, photochromism is weak or non existent; consequently, the negatively thermochromic form (or forms) cannot be transformed to the trans-quinoid form, photochemically. In EPA rigid glasses, all the compounds are photochromic, except IV and the di-substituted halogen derivatives VII, VIII, XI and XII which present strong negative thermochromism and, practically, are not photochromic. The compounds III, IV and X–XII show negative thermochromism in E/M rigid glasses as well.

The Schiff bases investigated in PMMA glass solutions are photochromic. The absorption spectra of the di-substituted halogen derivatives VII, VIII, XI and XII in PMMA at 298 K contain an additional band at about 430 nm, which decreases partly at 77 K and the compounds are photochromic at low temperatures (Fig. 2). This has previously been observed in glass solutions of VII and VIII in PMMA of 0.6% w/w and 1% w/w, respectively (thickness of the samples 0.2 mm) whilst it has not been observed in glass solutions in PMMA of 10^{-4} M (thickness of the samples, 0.5 cm and 1 cm, respectively) [2].

Consequently, the additional band seems to be due to intermolecular interaction products, because of the high concentrations used. It is interesting that an additional band around 430 nm is also present in the thin polycrystalline films of the same compounds.

3.2.2. Thin polycrystalline films

The compounds II–XII, XIV and XV have also been investigated in thin polycrystalline films and the results are presented in Table 1. The compounds II–IV, IX, X and XV have been found to be both thermochromic and photochromic.

The probability of intramolecular proton transfer in the ground state (thermochromy) depends on the basicity of the nitrogen atom, the acidity of the *ortho*-OH, the planarity of the semi-aromatic ring with the hydrogen bond and the energy of the π electrons in the system. The lone pair of the nitrogen atom does not overlap with the π system of the aniline ring in the planar molecules of N-salicylidene-anilines; consequently, the nitrogen atom is more basic compared with the non-planar molecules, where the overlap is possible. This results in the formation of the cis-quinoid thermochromic form in the ground state. The insertion of the methylene group between the bond C=N and the ring adjacent to the nitrogen in benzylamines decreases the resonance of the lone pair of the nitrogen with the π system and, thus, the basicity of the nitrogen increases in the ground state. Consequently, N-salicylidenebenzylamine (II) (maximum of the long-wavelength band in MCH 322 nm, Table 1) appears thermochromic though non-planar. N-(5-bromosalicylidene)-benzylamine (VI) and N-(5-methoxysalicylidene)-benzylamine (V) (maxima of the long-wavelength bands in MCH 334 nm and 340 nm, respectively) are not thermochromic, because of the stabilization of the

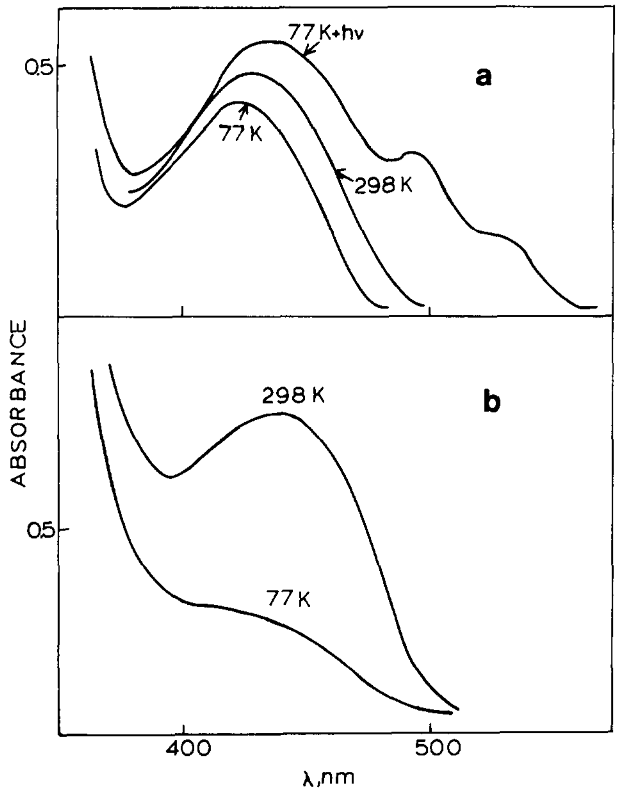


Fig. 2. Absorption spectra of N-(3,5-dichlorosalicylidene)-benzylamine (VIII): a, in PMMA, 1% w/w, irradiation with 365 nm light; b, thin polycrystalline film.

conjugation system by the substitution, while the opposite happens when the substitution takes place at the 4-position in the compound IV (maximum of long-wavelength band in MCH 314 nm); IV has been found thermochromic and photochromic.

The basicity of the nitrogen atom increases even more in N-salicylidene-2-phenylethylamines as the overlap of the lone pair is practically interrupted, by the insertion of the second methylene group so as to cover the stabilization brought about by the substitution of bromo- and methoxy- groups at the 5-position; thus, III, IX and X are thermochromic. The absorption spectra of the di-substituted halogen derivatives of N-salicylidenebenzylamine (II) and N-salicylidene-2-phenylethylamine (III) in the solid state contain an additional band at ca. 430 nm, which disappears partly on cooling in the cases of VII and VIII. The spectra of the concentrated solutions of these compounds in PMMA also contain an additional band in the same region which behaves in a similar manner (Fig. 2). Furthermore, their solutions in polar and non-polar solvents are strongly negatively thermochromic.

These properties indicate intermolecular interactions which practically render the molecules light inactive. However, it cannot be excluded that VII and VIII are also thermochromic.

N-salicylidene-2-aminopyridine (XIII) is planar and thermochromic [5]. N-salicylidene-2-aminomethylpyridine (XIV) is non-planar and photochromic. The insertion of the second methylene group between the bond C=N and the pyridine ring in N-salicylidene-2-aminoethylpyridine (XV) increases the basicity of the bridge nitrogen sufficiently so as to take place the proton transfer in the ground state and the molecule is both thermochromic and photochromic.

Concerning photochromism in the solid state, the photoreaction is possible provided the crystal structure is sufficiently 'open' in order for the cis-to-trans photoisomerization to take place.

3.2.3. Negative thermochromism

The following compounds have been found negatively thermochromic: II–IV, VII–XII and XV (Table 1). The absorption spectra of III in MCH/IP are presented in Fig. 3, where the concentration dependence is clear. The negatively thermochromic absorption band appears in the same region as the additional band at longer wavelengths in proton donating solvents at 298 K (Table 1). This band has been attributed to the cis-quinoid form [6], although the assignment has been questioned [7].

The concentration effect and the way of cooling on the absorption spectra of the negatively thermochromic solutions have been studied. Strong deviation from

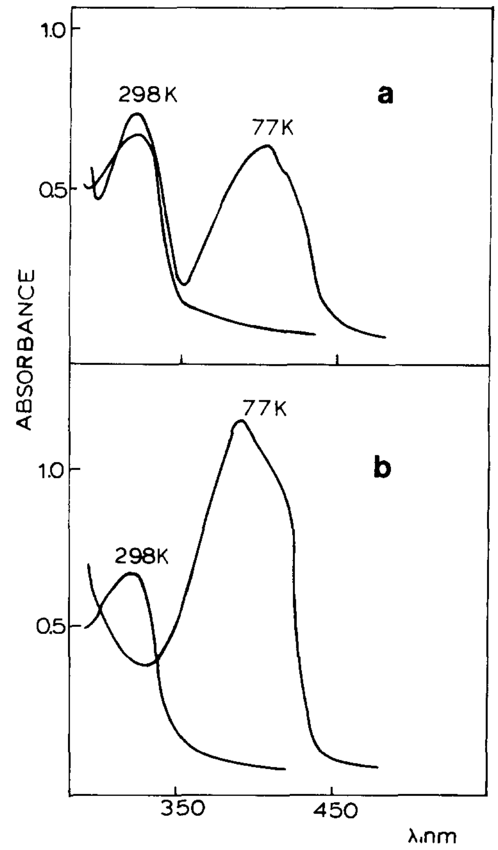


Fig. 3. Absorption spectra of N-salicylidene-2-phenylethylamine (III) in MCH/IP: a, 10^{-3} M in a 1 mm cell; b, 10^{-4} M in a 10 mm cell.

Beer's law is observed when the concentration or the way of cooling (rapid or gradual) is changed; the spectra of IV in MCH/IP and EPA of 10^{-3} M and 10^{-4} M, recorded in 1 mm and 10 mm cells, respectively, are compared in Fig. 4. The spectra of IX in MCH/IP and E/M, rapid and gradual cooling, are also compared in Fig. 5. Formation of aggregates is obvious in MCH/IP in both cases; characteristic also is the low intensity band recorded at 77 K after gradual cooling (precipitation) in the solution of the higher concentration. On the contrary, there is no evidence of aggregation in EPA or E/M.

The aggregates are probably packed edge-to-edge as expected in H-bonded dimers or oligomers since transition(s) to the lower energy state(s) is allowed. Formation of aggregates has been observed in the Schiff bases when the nitrogen of the bridge is sufficiently basic and the molecules are thermochromic. Actually, all the thermochromic N-salicylidenebenzylamines, N-salicylidene-2-phenylethylamines, N-salicylidene-2-aminomethylpyridine and N-salicylidene-2-aminoethylpyridine studied are negatively thermochromic in solution.

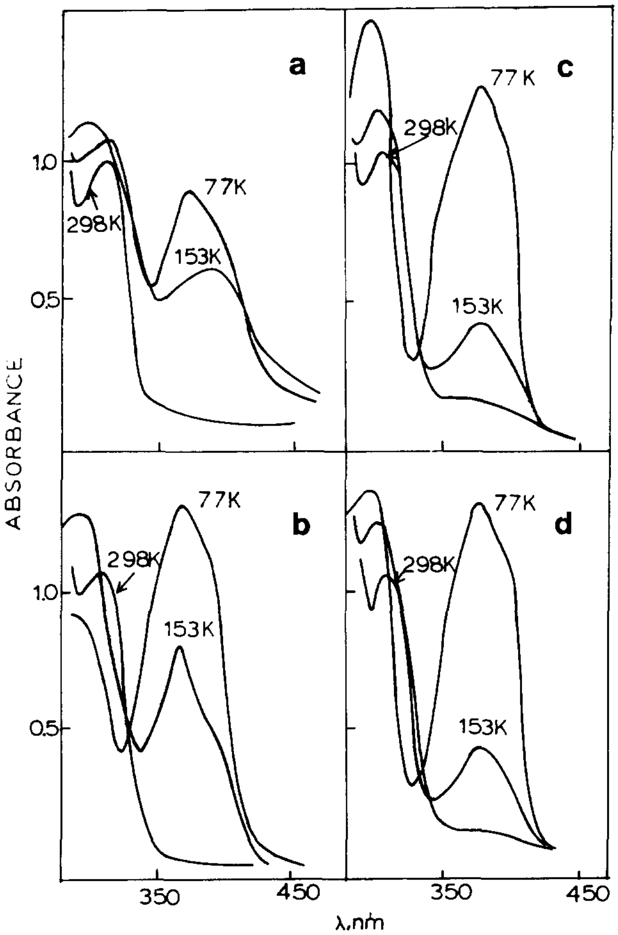


Fig. 4. Absorption spectra of N-(4-methoxysalicylidene)-benzylamine (IV): a, in MCH/IP, 10^{-3} M, in a 1 mm cell; b, in MCH/IP, 10^{-4} M, in a 10 mm cell; c, in EPA, 10^{-3} M, in a 1 mm cell; d, in EPA, 10^{-4} M, in a 10 mm cell.

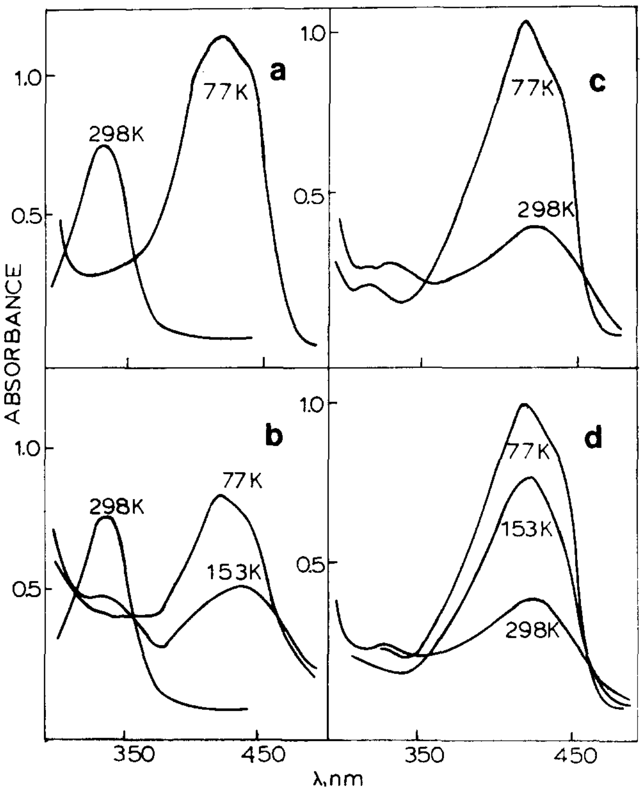


Fig. 5. Absorption spectra of N-(3,5-dibromosalicylidene)-2-phenylethylamine (IX): a, in MCH/IP, rapid cooling; b, in MCH/IP, gradual cooling; c, in E/M, rapid cooling; d, in E/M, gradual cooling.

The absence of evidence for aggregation in polar solvents is an indication that solubility interferes with aggregation.

The following indications exist, concerning the nature of the negatively thermochromic product(s), which is probably formed from the cis-quinoid form: 1. The negatively thermochromic absorption band is located in the same area as the additional absorption band of these compounds in proton donating solvents at 298 K, which has been attributed to the cis-quinoid form. In the same area the thermochromic absorption band in the solid state has also been observed. 2. All the compounds studied (except XIII) and found thermochromic in the solid state are negatively thermochromic in rigid glasses. 3. Negative thermochromism has also been observed in *ortho*-hydroxy azo-compounds in non-polar solvents and it has been attributed to dimers or oligomers of the hydrazonic form [8].

4. Conclusions

In N-salicylidenebenzylamines, the favourable condition of planarity for thermochromism is removed by the insertion of the methylene group between the imine nitrogen and the aniline ring, but at the same time the basicity of the nitrogen atom increases compared to the non-planar N-salicylideneanilines, because of the reduction of the lone pair resonance with the π system of the aniline ring. Thus, N-salicylidenebenzylamine is non-planar, but thermochromic. The effect of the substitution on the salicylaldehyde ring which stabilizes the conjugated system is suspensive to thermochromism, e.g. N-(5-bromosalicylidene)-benzylamine (VI) and N-(5-methoxysalicylidene)-benzylamine (V) are not thermochromic; on the contrary, N-(4-methoxysalicylidene)-benzylamine (IV) is thermochromic. In N-salicylidene-2-phenylethylamines, the basicity of the imine nitrogen increases even more by the insertion of the second methylene group and substitution cannot act suspensively, e.g. N-(5-bromosalicylidene)-2-phenylethylamine (X) and N-(5-methoxysalicylidene)-2-phenylethylamine (IX) are both thermochromic.

The photoproduct (trans-quinoid form) is formed provided the crystal structure is 'open', i.e. there is enough space for the photoisomerization to take place. Therefore, all the compounds studied, except the disubstituted halogen derivatives, have been found photochromic.

The negative thermochromism of the compounds studied in non polar solvents is due to aggregation (dimers and oligomers probably of the cis-quinoid form); in alcoholic solvents there is evidence that the phenomenon is the same, but the behaviour is changed by the interference of solubility.

Suggestion

We would like to propose cryochromism to replace the term negative thermochromism, since the property is in this way expressed by one word and more precisely.

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