

Photochemistry of Anils in NaY Zeolite

Isabel Casades,^[a] Mercedes Álvaro,^[a] Hermenegildo García,^{*[a]} and Manoj Narayana Pillai^[a]*Dedicated to Prof. W. Adam on the occasion of his 65th birthday***Keywords:** Zeolites / Raman spectroscopy / Photochemistry / Photochromism

A series of anils (**1–6**) have been incorporated in NaY zeolites and the resulting samples characterised spectroscopically. Raman spectral analysis showed that anils exist in the zeolite microcavities predominantly in a zwitterionic form. In agreement, diffuse reflectance UV/Vis spectra showed the presence of a significant concentration of the zwitterionic form, characterised by an absorption band around 400 nm. A sharp contrast is drawn between their photochemistry in solution or in the crystalline form with that in NaY zeolites. Thus, steady state irradiation at 400 nm led to persistent changes in the diffuse reflectance UV/Vis spectra with decrease of the reflectance of the band at 400 nm and the appearance of a new absorption band at longer wavelengths. No photochromism is observed and this is attributed to the isomerization

of the zwitterionic form to other stereoisomers, possibly by rotation about C–C or C–N bonds with partial double bond character. This photochemical isomerization has not been reported so far. Even though the hydrogen bonding ability and polarity of NaY zeolite has been reported to be similar to that of polyfluorinated alcohols, based on the enolisation equilibrium of anils, the photochemical behaviour of these compounds incorporated within NaY is different to that reported in polyfluorinated alcohols. Specifically, no excited-state proton transfer or proton catalysed re-enolization of the zwitterionic form is observed with anils in NaY.

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Introduction

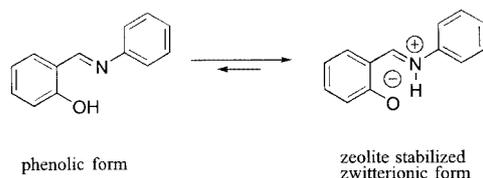
The interest in photochromic materials has grown recently because of their potential use for photonic applications.^[1–8] Photochromism is the reversible photochemical switching of one form to another with a visible change in the colour. Among the molecules that are described in the literature as photochromic, salicylideneanilines (anils) have received much attention.^[8–16] Here, the enol-zwitterionic (keto) tautomerism is identified as the photochemical pathway responsible for showing photochromism.^[9,11–13] This reaction has been investigated in detail by previous groups who have established the different intermediates involved in the process (including *cis/trans* stereoisomers) and, thus, a detailed mechanistic pathways for the overall reaction.^[17–21] According to these studies photoirradiation brings about reversible colour changes when they are in the crystalline form, in rigid glasses or in films. In solution laser flash photolysis has established that the photochemical reaction mechanism remains the same as in solid or heterogeneous media. However, the very fast re-enolization reaction occurring on the millisecond time

scale does not permit the observation of any visual changes in the absorption spectrum.^[17,18] Zeolites have found to be a convenient medium for the alteration and control of the photochemical reactions of adsorbed guest molecules.^[22–27] Therefore, it is of interest to determine how the highly polar, restricted environments of zeolite microcavities affect the photochemistry of anils. Here we report the phototransformations taking place in salicylideneanilines and their derivatives when encapsulated in NaY zeolite. No photochromism has been observed, although an unprecedented photochemical isomerization of partial C–C and C–N double bonds was seen.

Zeolites are microporous aluminosilicates made up of [SiO₄]^{4–} and [AlO₄]^{5–} tetrahedra. These are arranged in a three dimensional array, which gives the zeolite its open framework structure.^[28–31] This framework geometry of zeolites consists of pores of different sizes within the molecular dimension range. For example, zeolite NaY has a spherical cavity of diameter 13 Å with four tetrahedrally arranged pore openings of 7.4 Å. This makes it suitable as a host for several molecules of adequate dimensions and they can be incorporated by means of direct adsorption or by a “ship-in-a-bottle” synthesis.^[32–34] A “ship-in-a-bottle” synthesis was first used to encapsulate large metallic complexes within the supercages of zeolite Y.^[35] Its role as a rigid matrix for several chemical and photochemical reactions has been established through numerous studies.^[22,23]

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Here, we have taken advantage of the property of zeolites as hosts, restricting the mobility of guest molecules inside these microcavities. These host-guest assemblies have allowed us to observe otherwise impossible photochemical behaviour of salicylideneaniline in solutions at room temperature.^[13] In zeolites at low loading, guest molecules are considered as isolated molecules surrounded by the lattice and, therefore, the adsorbed guest molecules lack the strict well-structured ordering found in the crystal state. We are interested in knowing whether or not anils exhibit photochromism in zeolites. Related work on the photochromism of spiropyrans inside the Y zeolite has recently been published by us.^[34] Dutta and co-workers reported the use of salicylideneanilines as probe molecules for studying the hydrogen bonding ability of Y zeolites in 1991 but they did not address the photochemical behaviour of anils in zeolites.^[36] According to these authors salicylideneaniline exists in the zeolite in equilibrium between the benzenoid or enol form and the zwitterionic form (Scheme 1). In their study they concluded that the solvent-like nature of the zeolite cavity is like trifluoroethanol, trifluoro-2-propanol and hexafluoro-2-propanol solutions. Surprisingly, however, these authors did not pay attention to how the special characteristics of the zeolite cavities influence the known photochromism of anils.



Scheme 1

Herein we report a photoinduced transformation of anils incorporated into NaY zeolites, leading to visual colour changes that persist for more than a week. Therefore, anils are devoid of photochromism when adsorbed in NaY. Table 1 shows the structures of the salicylideneaniline derivatives studied in this work.

Results and Discussion

Raman Spectra and Diffuse Reflectance Spectra of Anils in Zeolite

In agreement with the previous study by Turbville and Dutta, the Raman spectra of all the anils included in the NaY zeolite exhibit remarkable differences compared to those in their crystalline form.^[19] Thus, the Raman spectra of salicylideneanilines in the crystalline form are characterised by strong bands around 1620, 1575 and 1490 cm^{-1} due to the vibrations of C=N, HOCCN and C–O bonds, respectively.^[19] In addition, there is a sharp band at 1600 cm^{-1} which is assigned to the ring mode. While the latter band was found to be unaffected by inclusion in zeolites,

Table 1. Structure and absorption maxima (λ_{max}) of compounds 1–6 in methanol and when incorporated in NaY zeolite

Compound	Structure	λ_{max} , nm		
		Methanol	NaY	
1		338	327	403
2		346	341	403
3		420 ^[a]	383	430
4		351	339	395
5		369	358	429
6		373	353	440

^[a] The zwitterionic form predominates

all the other bands either disappeared or shifted to new positions upon inclusion in NaY. For example, in the case of compound **2**, the bands at 1572 cm^{-1} and 1460 cm^{-1} disappeared and new bands at 1523 cm^{-1} , due to C=NH⁺, and 1367 cm^{-1} , due to a C–O[−] vibrational mode, are observed. Also, the band at 1621 cm^{-1} was shifted to 1641 cm^{-1} which has been previously assigned to a C=NH⁺ stretching vibration. Figure 1 shows our own recording of the Raman spectrum of compound **2** in the crystalline form compared to when it is included in the zeolite NaY. All these spectroscopic observations are in agreement with Dutta's proposal in the sense that the zwitterionic form of the anil predominates upon inclusion of the phenolic form within NaY. In addition, the broad base of the bands at 1641 and 1600 cm^{-1} suggests the presence of a minor percentage of the phenolic form of the salicylideneaniline. This fact was further confirmed from the diffuse reflectance UV/Vis spectra of the samples in zeolite.

The absorption spectra of anils in various solvents and in the solid state have been studied thoroughly.^[13] They exhibit a single absorption band at about 350 nm that is char-

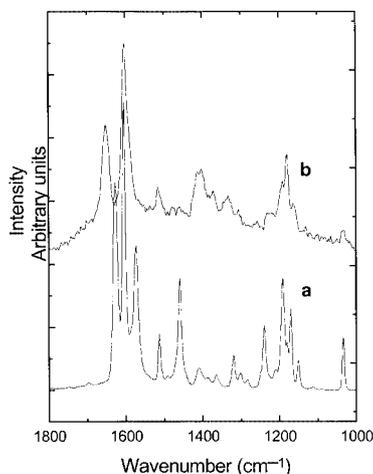


Figure 1. Raman spectra of anil **2** in the crystalline form (a) and in NaY zeolite (b)

acteristic of the phenolic form. In contrast to solution or to the crystalline state, all the zeolite samples were either yellow or orange in appearance after incorporation of anils and their respective diffuse reflectance are characterised by two bands, one at 350 nm and the other around 400–450 nm. The relative intensity of the reflectance spectra of the longer wavelength band was found to depend on the type of substituent present. The absorption maximum of the band around 350 nm is unaffected by the nature of the substituents on the aromatic rings. Based on the UV/Vis absorption spectra of anils in solution and literature precedence we attribute the band at 350 nm to the phenolic form and the long wavelength band to the zwitterionic form (Scheme 1).^[19] Typical diffuse reflectance spectra of compounds **1** and **2** incorporated in NaY compared to the absorption spectra in methanol are shown in Figure 2 in which the Kubelka–Munk function of the reflectance has been plotted against the wavelength.^[37] Table 1 summarizes the absorption maxima of the anils measured in methanol and when included in NaY. It is worth noting that the maximum observed for the zwitterionic form of anils **1–6** is

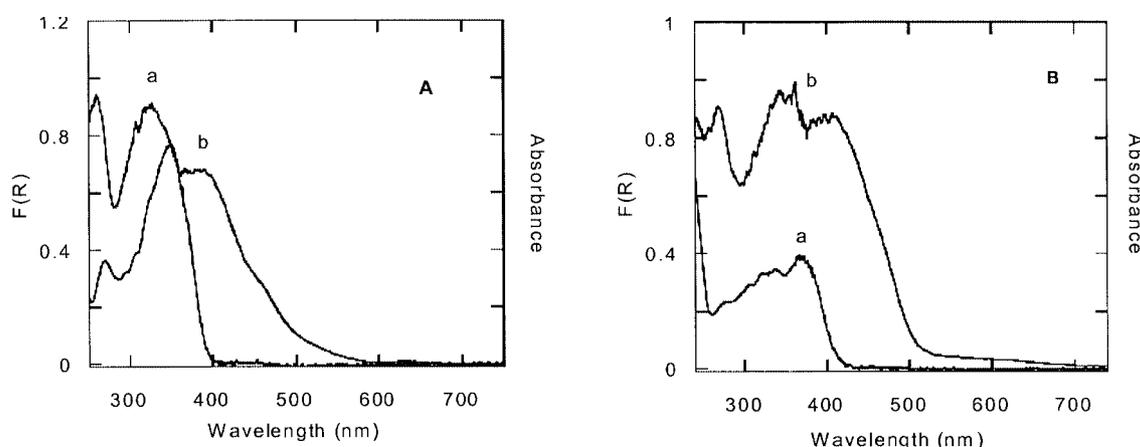


Figure 2. UV/Vis absorption spectra of anil **1** (A) and anil **2** (B) in methanolic solution (a, 10^{-4} M plotted with optical density on right axis) and in NaY zeolite powder (b, plotted as the Kubelka–Munk function of the reflectance on left axis)

slightly blue-shifted relative to the absorption maxima reported earlier.^[19] This could be due to the difference in the polarity and Si/Al ratio of the zeolite used, since it has been reported that these parameters can induce solvatochromic shifts in the absorption spectrum of anils.^[36]

Depending on the aromatic substitution, anils can exhibit both photochromism and thermochromism in the crystalline state but not in solution.^[13] In order to see any effect of temperature on the UV/Vis spectra, we recorded the reflectance spectra for all the anils at various temperatures. However, they did not show any temperature effect on cooling to 77 K or on heating to 100 °C, except for compound **2**, which showed an irreversible colour change upon heating to 100 °C. Anils incorporated within NaY exhibit a very weak emission compared to that in methanol and in both cases the emission maximum is observed around 540 nm. This weak emission is attributed to the low percentage of the phenolic form.

Photochemical Isomerizations of Salicylideneanilines in Zeolites

Steady-state irradiations of all anils included within NaY were carried out in order to assess their photochromic behaviour in zeolites. Irradiations of the zeolite powders were carried out using the 200 W output of a high-pressure mercury lamp with a 400 nm band-pass filter. Contrary to what is observed in solution, photolysis of the NaY powders containing anils leads to persistent changes in the diffuse reflectance UV/Vis spectra of the solids recorded at different time intervals (Figure 3 and Figure 4). Thus, these spectra showed bleaching of the band at 400 nm with a concomitant increase in the absorbance in 500–600 nm region. The final spectra after irradiation were found to be stationary on keeping in the dark for several days. Our attempts to reverse the process by selective irradiation at the newly formed band were unsuccessful.

The photochemical behaviour of anils observed upon inclusion in NaY is unprecedented in solution or in any other media. Generally, anils exhibit photo- or thermochromism only in the crystalline state, but not in solution. Even

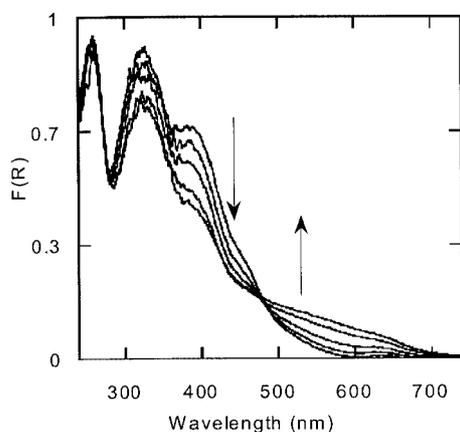


Figure 3. Change in diffuse reflectance UV/Vis spectra [plotted as the Kubelka–Munk function $F(R)$] of anil **1** with time upon irradiation with 400 nm light

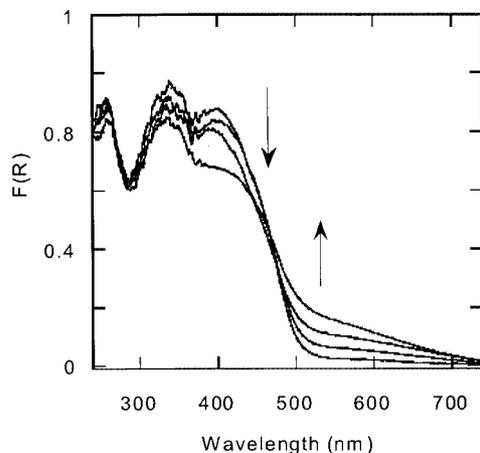


Figure 4. Change in diffuse reflectance UV/Vis spectra [plotted as the Kubelka–Munk function $F(R)$] of anil **2** with time upon irradiation with 400 nm light

though it has been established by time-resolved techniques that the rearrangements responsible for the chromism also occur in solution, the lifetime of the isomers involved is much too short to produce visible colour changes. Anil molecules when they are incorporated within the cavities of NaY lack the structural ordering found in the crystal lattice of the solid state. The structure of the species responsible for the chromism and the nature of the processes involved have been thoroughly studied in other media. With the help of steady-state and time-resolved absorption spectroscopy it has been established that the photochromism arises from an excited state intramolecular proton transfer followed by a *cis-trans* isomerization.^[17,18,20] This has been further confirmed by resonance Raman and X-ray crystallographic studies.^[19,38,39] The same pathways are reported for these molecules in nonpolar solvents and in non-hydrogen bonding solvents. In these cases it was not possible to observe

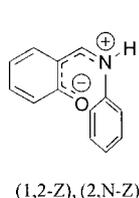
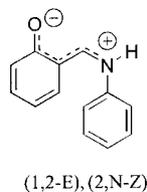
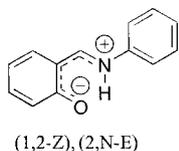
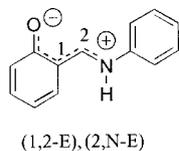
the *anti*-iminium form because of the very short lifetime (μs) of this species. In hydrogen bonding solvents such as methanol and ethanol this reverse reaction is catalysed by the solvent. Based on the Raman spectra of anils on Y zeolites Dutta and co-workers have proposed that the zeolites can be considered to be on a par with trifluoroethanol and hexafluoroethanol, and therefore, based on this, one could draw in principle an analogy between the observed chemistry in these solvents and that observed in zeolites.^[19] Becker et al. have studied the chemistry of salicylideneaniline in trifluoroethanol in detail.^[17,18] According to them, in strong hydrogen-bonding solvents salicylideneaniline exists as a solute-solvent intermolecular hydrogen-bonded complex with an absorption maximum around 420 nm. Later, that band was assigned to a zwitterionic species. Importantly, in spite of the very special characteristics of these fluorinated alcohols no visible transformation such as that shown in Figure 3 and 4 was ever observed upon irradiation. Therefore, the behaviour observed in NaY is anomalous, new and it contrasts sharply with that of fluorinated alcohols. Clearly, the photochemistry of anils on NaY cannot be explained by Scheme 1 (phenolic and *anti* zwitterionic forms at $\lambda_{\text{max}} \approx 350$ and ≈ 400 nm, respectively), although it does explain the photochromism in solution. The results shown in Figure 3 and 4 clearly emphasise the ability of zeolites to act as a medium for the stabilization of highly polar elusive species and to alter the solution photochemistry.

Taking into consideration that anils exist predominantly in the zwitterionic form in NaY zeolite, any photochemistry will arise mainly from the direct excitation of this species. In this regard, the situation is analogous to that described in trifluoroethanol, where the *anti* zwitterionic form also predominates, but where the process shown in Scheme 1 operates. It is worth mentioning at this point that there is no effect of oxygen on the photochemistry of anil **1** as evident from the laser flash photolysis studies in this solvent.^[17,18]

Therefore, a reasonable explanation that can reconcile all the observations of the photochemistry of anils adsorbed on NaY with the pathways reported in other media is that upon light absorption the only photoprocess undergone by the zwitterionic form is an *anti-syn* isomerization through the C–C and C–N bonds with partial double bond character. This rationalization is supported by the following facts: i) our studies on the steady-state irradiation and product isolation by continuous extraction gave only anils back (no stable products formed); ii) such stereoisomers have been detected earlier in the photochromism of anils in solution by time-resolved spectroscopy, but they were assumed not to play any role in the photochromism;^[17,18,20] iii) the parent *N*-phenylimine of benzaldehyde adsorbed on NaY only undergoes *syn/anti* isomerisation upon irradiation as was reported in solution for anils and other carbon-nitrogen double bond-containing molecules;^[40,41] iv) stereoisomers of the related zwitterionic merocyanine form of spiropyrans have also been reported: depending on the nature of the solvent used at least four isomers have

been identified (see Structure 1) by transient Raman spectroscopy;^[42,43] and

v) the occurrence of *cis/trans* isomerization is compatible with the observation of only minor changes in the absorption wavelength seen in the steady-state diffuse reflectance UV/Vis spectra recorded after the irradiation in NaY.



By time-resolved spectroscopy in solution it has been found that the *Z/E* isomerization of the zwitterionic form gives rise to an isomer whose transient absorption appears at the long wavelength edge of the *anti* isomer.^[17,18,20] We believe that in NaY zeolite the more stable configuration of the zwitterionic form upon irradiation undergoes a *Z/E* isomerization through the bonds that have partial double-bond order, giving a stationary distribution among the possible configurations. Analogous *Z/E* isomerizations through partial C=C double bonds leading also to indefinitely persistent colouration changes have been previously reported by us for α,ω -diphenylallylic carbocations incorporated in mordenite and ZSM-5.^[44] As far as we know, the observation of this type of photoisomerization in the anil zwitterionic form has not been considered previously.

In aprotic solvents the re-enolization reaction is a diffusion-controlled second order process involving two zwitterionic molecules collapsing to the phenolic form.^[17,18,20] The way that the zwitterionic form reverts to the phenolic form is different in protic solvents such as polyfluorinated alcohols for which this reaction is a double proton transfer catalysed by the solvent molecules. This implication of the solvent is deduced from the pseudo-unimolecular kinetics for the decay of the photochromic transient observed in the laser flash photolysis experiments.^[17,18,20] For anils incorporated within NaY the situation is different since the chromism occurs by interconversion between *syn/anti* conformers; the phenolic form plays no significant role in the visual changes.

The role of NaY as a medium in this process is twofold, firstly stabilizing the zwitterionic form, which is the species that undergoes changes upon irradiation and secondly slowing down the reverse thermal *syn/anti* isomerization by restricting the molecular mobility and not acting as acid medium. This second effect derives from the essential neut-

ral character of the NaY zeolite with only a residual presence of silanol groups, that contrasts with the known proton-donor ability of polyfluorinated alcohols.

Conclusion

In summary, upon incorporation of a series of anils in NaY the zwitterionic form becomes predominant with respect to the phenolic form. Photolysis of these powders gives rise to a persistent colour change due to the *syn/anti* photochemical isomerization of C–C and C–N bonds with partial double bond order. In spite of the extensive studies dealing with the photochromism of anils this situation has not been observed in any other medium. Thus our report constitutes an additional example of the ability of zeolites to control and modify molecular properties of organic guest molecules.

Experimental Section

General: The salicylideneanilines were prepared by condensation of equimolar amounts of salicylaldehydes and anilines according to the reported procedures and were purified by recrystallization from methanol.^[13,19] The structures of all the compounds were analysed by elemental analysis, FT-IR, GC-MS and ¹H and ¹³C NMR spectroscopy. They were included in dehydrated NaY zeolites (Union Carbide SK-40) by direct adsorption from a 0.01 M dichloromethane solution containing the substituted salicylideneaniline, followed by washing several times with fresh CH₂Cl₂ aliquots to remove molecules adsorbed on the external surface. All the samples were degassed under vacuum and kept under a nitrogen atmosphere. The zeolite samples were analysed by combustion chemical analysis using a Fisons EA 1108 CHNS combustion chemical analyser, and by thermogravimetry and differential scanning calorimetry by using a Netzsch STA 409 thermobalance under a stream of air and with kaolin as standard. The amount of anils loaded was calculated to be 3% by weight. The diffuse reflectance UV/Vis spectra were recorded using a Shimadzu Model UV 2101 PC spectrophotometer fitted with a Praying Mantis accessory for solid samples, with BaSO₄ as the standard. FT Raman spectra were obtained on a BioRad Model II FT Raman Spectrophotometer with a Nd:YAG laser as the excitation source and a liquid nitrogen cooled detector. The power of the laser at the sample was 100 mW and the spectral resolution was 4 cm⁻¹. The photochemical isomerizations were carried out by irradiating the zeolite powders using the 200 W output of a high pressure mercury lamp with a 400 nm band pass filter.

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