Articles

Polymorphism in *N*-Salicylideneaniline Reconsidered

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ABSTRACT: The aromatic Schiff base *N*-salicylideneaniline (SA) represents the aristotype of a whole family of chromic derivatives. SA forms two photochromic polymorphs, α_1 and α_2, both of which feature non-coplanar phenyl rings. Since many details of its reversible photoreactivity are still unexplained, we report the structure of a planar, thermochromic polymorph, named β, and propose a new model for the structure of the α_1-polymorph. Finally, we discuss structure−property relations between the polymorphs and the β to α_1 phase transition.

Introduction

Design and synthesis of organic compounds with targeted physical properties are currently being developed. SAs have been classified according to their photochromic or thermochromic properties[1−4] and are of particular interest to chemists and physicists, owing to their reversible photoreactivity in the solid state. Indeed, success in obtaining and, more importantly, controlling such tailor-made ground and excited-state properties can lead to future applications in such fields as nonlinear optics, organic superconductors, optical sensors, control and measurement of radiation intensity, optical computers, and display systems.[5−9] The solid state behavior is, however, virtually impossible to understand without a detailed knowledge of the shapes and packing arrangements of molecules in crystals.

SAs are a typical class of photochromic materials featuring both excited-state intramolecular proton transfer of the hydroxyl proton, e.g., by photoexcitation with UV light, and cis−trans isomerization to form an orange-red colored photoproduct from the colorless enol form. Because of this electronic redistribution, a subsequent geometrical rearrangement occurs in the excited state; different proportions of the cis-keto and trans-keto forms (with respect to the C1−C7 bond) were found by various authors.[10−12] These proportions furthermore seem to depend on the sample history (equilibrium between enol and cis-keto form in the ground state) and crystal quality (all glassy systems are photochromic). The colored species can be reversibly bleached either by irradiation with visible light or by heating the crystals. The photochromic reaction of SA has been extensively studied with various spectroscopic methods.[13]

SA is particularly interesting because it crystallizes in two photochromic forms,[3] α_1 (Destro et al.)[14] and α_2 (Arod et al.)[15] as well as a thermochromic polymorph, β.[16,17] It is generally accepted that the stable form of the SA molecule is an enol form with an intramolecular hydrogen bond between the hydroxyl proton and the nitrogen atom. It was only recently
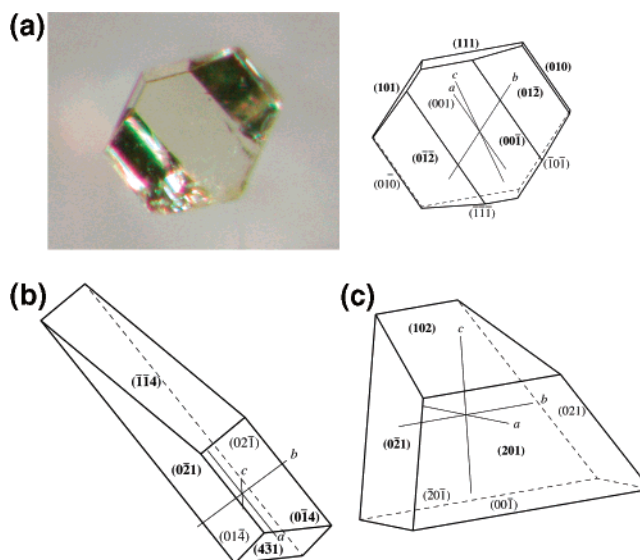

Figure 1. (a) Growth morphology of a α_1-polymorph crystal (can reach several mm). (b, c) Growth morphologies of β-polymorph crystals.

demonstrated[18] that the ground state is colorless instead of pale yellow as believed until now. In 1964, Cohen et al.[3] showed that the presence of an *ortho*-hydroxy group is a structural requirement for the photochromism of these compounds.

In this paper we report the structure of the planar β-polymorph (**1**) and its crystallization and morphology. We also discuss its phase transition to the nonplanar α_1-polymorph (**2**) by means of the differential scanning calorimetry and X-ray diffraction. We also revisit the disordered structure of the α_1-polymorph. Finally, we present the preliminary structures of two ethyl-4-(2-hydroxybenzylideneamino)benzoate (ESA) structures.

Experimental Section

Synthesis, Crystal Growth, and Morphology. It seems a Sisyphean task to crystallize any of the SA polymorphs alone, be this by evaporation or from the melt. Indeed, from most solvents, at least two

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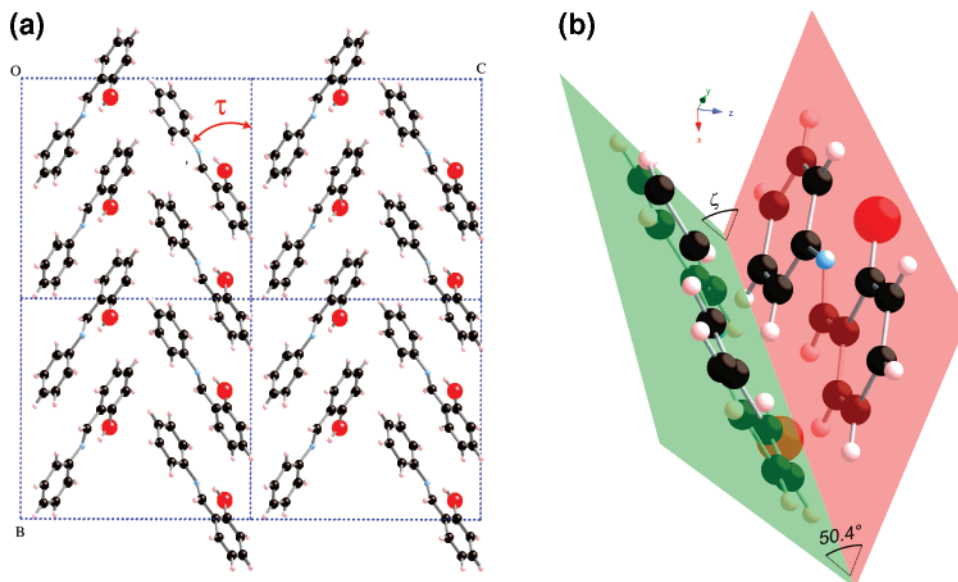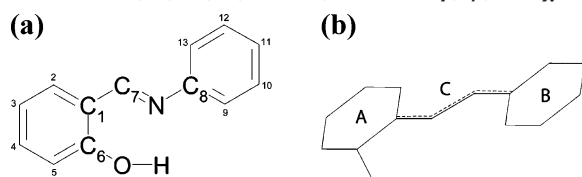† École Polytechnique Fédérale de Lausanne.
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(a)

(b)

Figure 2. (a) Molecular packing of the β-polymorph. The angle τ corresponds to the angle between the molecular normal and the *b*-axis. (b) Angle ζ corresponding to the angle between the normals of two adjacent molecules along the *b*-axis.

Scheme 1. (a) Enol Form of SA and (b) Angles between Planes (A,B), (A,C), and (B,C) Called φ, ψ, and χ

(a)

(b)

polymorphs crystallize concomitantly.[17,19] We have mainly used two methods: (i) slow evaporation from high boiling petroleum ether (hbPE); (ii) sublimation of the crude material with Arend's apparatus,[20] in air and under vacuum (Shen et al.[11]). Both methods afforded the α_1- and β-polymorphs of SA together. The α_1-polymorph usually grows as transparent, pale-yellow needles, but Shen et al.'s method[11] yielded bulky, particularly neat specimens (see Figure 1a) that were invariably multiply twinned. The bright yellow β-SA crystals develop various habiti. From hbPE, we found two different morphologies, namely slender [100] joists sideways bounded by {02$\bar{1}$} and {014} pseudopinacoids, an incomplete {1$\bar{1}$4} pyramid, and a cut face (see Figure 1b) and bulky (201) plates decorated by a {02$\bar{1}$} dome, an incomplete {102} dome, and a (001) pedion (see Figure 1c). The measured crystal was of the second type (Figure 1c).

A capricious crystallization behavior is noteworthy: when recrystallizing SA in ethanol, we did not obtain the α_1-polymorph of SA in contrast to Andes and Manikowski's[17] (1968). In fact, our crystals were shown, by diffraction, to be salicylaldehyde azine (SAz) of which there exist four virtually identical structures[21–24] in the CCDC (noteworthy in Arcovito et al.[21] that has a much higher melting point (220 °C) than ours (51 °C)).

Differential Scanning Calorimetry (DSC). Measurements were performed on a Mettler-Toledo DSC823^e (temperature range, −93 to 523 K; aluminum crucible with pierced lid; sample mass, 3.3–7.57 mg; air atmosphere; heating/cooling rate, 5/10 K min^{-1}).

UV/Vis Spectroscopy. The absorption spectra of the three polymorphs were measured with a xenon lamp on the spectrometer described below. The focusing of the xenon beam required crystals of a minimum size of 50×50 μm. A mercury lamp, an interference filter, and two fiber optic guides were used for the irradiation of the samples. The spectrograph (DK240, CVI) was equipped with two different gratings, one more adapted to the UV region (1200 grooves/mm, blaze wavelength 300 nm) and the other optimized for the visible region (300 grooves/mm, blaze wavelength 500 nm). The first-order signal was projected onto a liquid-nitrogen-cooled CCD. The wavelength axis was calibrated for both gratings with a Hg "pen-ray" lamp (Oriel). As expected, we observed no changes in the absorption spectrum of the β-polymorph during irradiation in contrast to the spectra obtained with the α-polymorphs.

X-ray Diffraction. At 293 K, powder diagrams of **2** were collected on (i) a PANalytical X'PERT Pro MPD diffractometer using the hybrid monochromator (λ(Cu Kα_1) = 1.5406 Å) from 3 to 93° in steps of 0.017° and (ii) on the high-resolution powder diffractometer of SNBL/ESRF (λ = 0.6992 Å) from 2 to 37° in steps of 0.004°. The sample was ground and lightly packed into a 0.5 mm borosilicate capillary for case i and into a 1.5 mm capillary for case ii. Cell constants were refined using the XND program[25] for case i and the JANA2000 program[26] for case ii. Single crystal measurements (see Table 1) were carried out, at T = 120 K (using an Oxford Cryostream), on the KUMA−KM6 at ESRF/SNBL for **1** and **2** and on a Stoe IPDS II for the study of the $\beta \rightarrow \alpha_1$ phase transition. The data were processed with the help of the CRYSALIS software,[27] and the structure of **1** was solved and refined using the WinGX[28] package.

The measured specimen of **2** was twinned but contained a very dominant individual (in fact, in the triclinic system, reflection overlap is minimal and so the relatively nice R_{int} factor of 0.0408 is hardly surprising). Structure solution with SHELXS immediately revealed the inherent disorder of the structure, i.e., of the C−N group and the O atom (as apparent in Figure 6) that persisted throughout an anisotropic refinement to R_1 0.095. At this stage, atoms C1, C2, C6, C8, C9, and C13 had adopted rather elongated ADP ellipsoids with the long axes perpendicular to the radius vectors from the center of gravity (see Supporting Information). These suggested two fully disordered molecules for the final refinement with the help of the CRYSTALS[29] suite. Since parameters were highly correlated, the geometry had to be confirmed by means of restraints (see Supporting Information). From these data (see Table 1) a model featuring two disordered SA molecules with 0.460(9)/0.540(9) occupations could be successfully refined (see Figure 6). Only the C7, N, and O atoms were refined anisotropically.

Results and Discussion

Crystal Structure of the β-Phase, 1. This polymorph, named β in agreement with Cohen's classification,[3] had already been mentioned by Ebara in 1961,[16] who had also witnessed the β-to-α transition. According to the bonds susceptible to tautomerism (self-isomerization), the β phase is in its enol form. We observed 1.422(3), 1.466(3), 1.364(3), and 1.294(3) Å for the C1−C6, C1−C7, C6−O, and C7−N bonds (see Supporting Information). The C6−O bond in this enol−imino tautomer is comparable to those in phenols (1.362(15) Å),[30] and the C7−N bond, to those in imines (1.279(8) Å).[30] Lindeman et al.[31,32] suggested that *N*-salicylidene-4-chloroaniline (planar) and *N*-salicylidene-4-bromoaniline (nonplanar) differ mainly by their conformations, whereas the other geometrical parameters were close to each other. Indeed, we observed that distances and

Table 1. Crystallographic Information

param	β-polymorph (**1**)	α_1-polymorph (**2**)		α_2-polymorph[15]
cryst system	orthorhombic	triclinic	triclinic	orthorhombic
cryst size (mm)	0.05 × 0.08 × 0.14	0.01 × 0.05 × 0.55	powder	0.18 × 0.14 × 0.06
temp (K)	120(2)	120(2)	293(2)	120(2)
wavelength	0.7500	0.7256	CuKα1	MoKα1
a (Å)	5.7941(5)	5.9183(15)	5.9459(5)	6.0750(11)
b (Å)	13.0175(14)	7.1869(16)	7.0969(9)	11.6306(15)
c (Å)	13.6171(15)	14.295(3)	14.329(3)	14.484(2)
α (deg)	90	85.130(19)	84.95(1)	90
β (deg)	90	78.03(2)	77.835(3)	90
γ (deg)	90	65.80(2)	65.33(2)	90
space group	$Pbc2_1$	$P1$	$P1$	$P2_12_12_1$
cell vol (Å³)	1027.07(18)	542.5(2)	537.1(2)	1023.37(3)
calcd density (g/cm³)	1.275	1.207		1.280
Z	4	2	2	4
data/restraints/params	2002/1/140	1542/137/266		1237/0/140
R_1 (%)	4.26	6.07		4.1
wR_2 (%)	10.18	6.34 (wR)		9.5

Table 2. Selected Hydrogen Bonds

param	α_2[15] (120 K)	α_2[15] (293 K)	α_1[14] (293 K)	α_1 (disordered)	β (120 K)
N···O	2.615(3)	2.610(3)	2.598(8)	2.627(9)−2.649(11)	2.639(3)
N···H	1.74(4)	1.74(4)		1.79(7)−1.82(7)	1.79(4)

angles of **1** are similar to those found in the nonplanar α_2-polymorph.[15] The molecule is quite planar with a φ angle (Scheme 1) of 2.27(15)°, but χ (=6.93(27)°) is larger than ψ (=4.77(26)°).

It appeared interesting to study (CrystalMaker)[33] other near-planar (φ < 10°) SA derivatives found in the CCDC database.[34] For a long time, planar compounds have been claimed to be thermochromic and nonplanar photochromic and further that these two properties were exclusive.[3,10,35] More recently, Hadjoudis and Mavridis[35] have extended Cohen et al.'s[3] idea by stating that the truly decisive feature is the electron density on the imine nitrogen atom, but Fujiwara et al.[18] maintained that all SAs are thermochromic in the solid-state and some also photochromic, depending on their nonplanarity.

It is known[35] that flat molecules pack as "closed structures" in which the molecules stack along the shortest axis (stacking distance 3.3−3.5 Å) and in which there exist π···π interactions. Indeed, all the structures studied follow this rule, but **1** and some of the other structures studied do not present any intermolecular π···π interactions, be this between two aromatic rings or between one aromatic ring and the imine C(−H)=N group. In the plane perpendicular to the shortest axis, quite different

molecular dispositions may exist but the long molecular axes are all parallel. This is not the case for **1** (Figure 2), which adopts a herringbone packing pattern allowing several edge-to-face C−H···π interactions. Only four other structures present a similar arrangement, *N*-(5-chlorosalicylidene)aniline,[36,37] *N*-(3-hydroxyphenyl)-5-methoxysalicylaldimine,[38] 2-chloro-4-nitro-*N*-(5-bromosalicylidene)aniline (YAGFAN),[39] and *N*-(3,5-dichlorosalicylidene)-4-dimethylaminoaniline (YICPAB),[40] among which the last two[39,40] display angles (molecular normal/*b*-axis = τ) similar to that of **1**. Moreover, we noted that the molecular planes of two adjacent stacks (along *b*-axis in **1**) are not parallel but subtend an angle of approximately 50° between their normals (ζ). In the two other structures similar to **1**, the stacks are parallel. In summary, we emphasize that the β-polymorph represents a novel packing type for planar structures for this family of compounds.

At this stage, we suggest that this angle ζ allows the planar molecules to change their conformation to obtain the α_1-
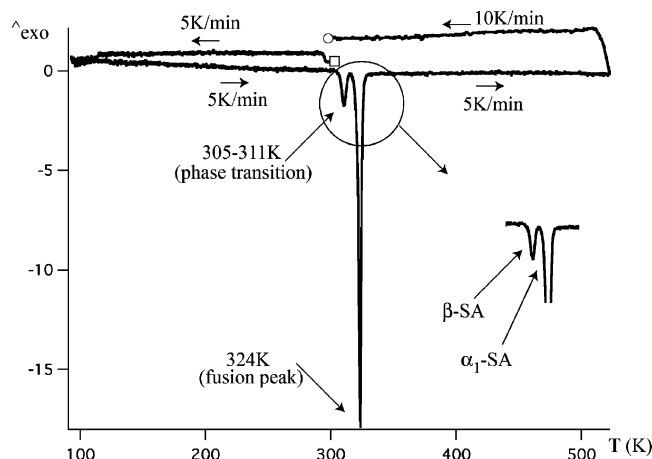

Figure 3. DSC curve of **1**. The small maximum preceding the fusion peak corresponds to the $\beta \rightarrow \alpha_1$ phase transition. The arrows indicate the direction of the experiment, and the square and the circle correspond respectively to the beginning and the end of the measurement.
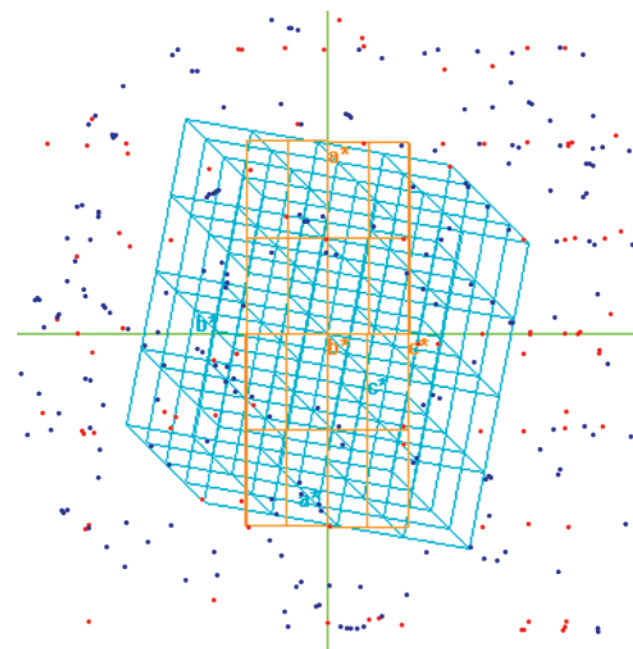

Figure 4. Diffraction spots and the corresponding dual cells of the β- and α_1-polymorphs at 309 K.
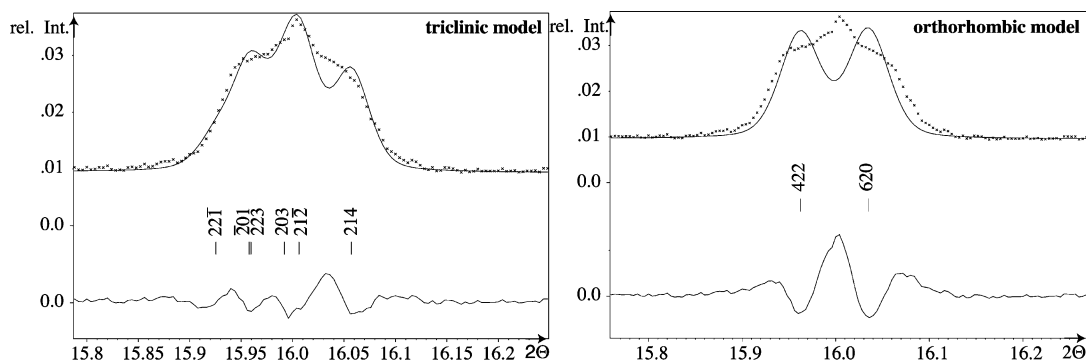
Figure 5. Comparison of two models (full lines) for a selected region of the SNBL powder diagram (dotted lines) of **2**. The vertical markers correspond to the powder lines as calculated with JANA.[26]

polymorph in which we find again this 50° angle but inside the molecule, which provides a tempting explanation for the ability of the β-polymorph to transform toward the nonplanar α_1-polymorph. An intramolecular O−H···N hydrogen bond occurs between the O and N atoms [2.639(3) Å]. Contrary to the claim of Hadjoudis and Mavridis,[35] the O−H···N bond seems to be stronger in the α_2 polymorph than in the β one (see Table 2).

In his study, Ebara[16] states that (i) the β-polymorph is red, (ii) its color gradually changes to yellow upon heating near 306 K and that the change abruptly completes at 308 K accompanied by the appearance of many cracks in the crystals, and (iii) that the red color slowly reappears upon cooling. Our DSC studies of the different polymorphs reveal that both α-polymorphs display simple melting curves ($T_m \approx 321$ K for α_1 and 322 K for α_2) but a phase transition (see Figure 3) around 310 K in the case of the β polymorph just below the final melting at 324 K.

To learn more about the β-to-α_1 transition, we undertook a study of the temperature dependence of the diffraction pattern of the β phase by raising the temperature in steps of 2° and collecting partial set of intensities at each temperature. Seeing that a transition took place at around 310 K, we heated another crystal to 309 K at 14 K h^{-1} and exposed eight images. These revealed the coexistence of the diffraction patterns of the β and α_1 forms (see Figure 4). Thus, this transition is of first order and the relation between the two cells is $a_\alpha \approx a_\beta$, $b_\alpha \approx a_\beta - c_\beta$, $c_\alpha \approx 2a_\beta + b_\beta$. Unfortunately, after another 0.5 h at 309 K, the crystals began to crack and soon after did not diffract anymore. The β-to-α_1 transition appears to be kinetically controlled and reconstructive. Indeed, preliminary synchrotron measurements suggest that, at 300 K, almost 30% had already transformed to the α_1 phase. Therefore, it might be hope that waiting longer at a lower temperature might produce a completer transition without destroying the crystals, but this latter point is more than doubtful.

Crystal Structure of the Disordered α_1-Phase Revisited, 2. Destro et al.'s[14] orthorhombic structure of the α_1-polymorph (1978) appears questionable because of rather unusual bond distances about the 2-fold axis. We believe that their disordered model is due to the superposition (see Supporting Information) of several triclinic domains which we have identified, to higher or lesser degree, in all diffraction patterns of our α_1 samples and which contradict the orthorhombic symmetry. Figure 5 illustrates the deficiency of the orthorhombic model, which therefore does not provide the best possible description. Indeed our two powder diagrams can be fully explained by the triclinic cell in Table 1. We endeavor in this section to offer a more satisfactory model of this polymorph.

Geometrical problems in the original study[14] could be overcome in our model. Indeed, distances and angles of the four half-molecules in the disordered α_1-polymorph (see Supporting Information) adopt more reasonable values. The distances of
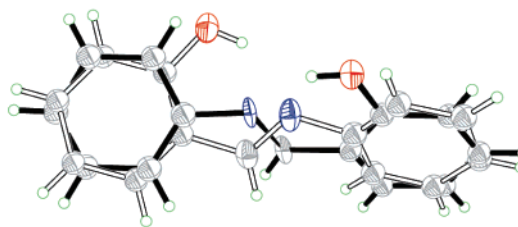

Figure 6. XP[30] view of the disordered α_1 molecules.

the C1−C6, C1−C7, C6−O, and C7−N bonds, namely 1.417-(5)−1.422(8), 1.488(8)−1.494(8), 1.348(5)−1.361(8), and 1.281-(1)−1.291(5) confirm that the α_1-polymorph is in its enol form. The C1−C7 and C8−N distances are longer (even before restraining them) than in the α_2- and β-polymorphs, while the other distances are in the same range.

Harada et al.[41,42] and Harada and Ogawa[43,44] have also found disordered conformations in crystals of azobenzenes, (E)-stilbenes, and in some N-benzylideneanilines. They conjecture that upon docking, a molecule can adopt one of two orientations related by an approximate twofold rotation about the long molecular axis. This disorder is likened to the motion of a bicycle pedal: the benzene rings acting as the pedals. The same motion was also reported to be a key process in the photochromism of SAs and the photodimerization of *trans*-cinnamides in the crystalline state.[12,45,46] Our growth disorder (see Figure 6) is clearly different and cannot be explained by such a pedal model; it is similar to Destro et al.'s[14] and is also found in some other N-benzylideneanilines.[47]

The molecules in this phase are nonplanar. Our refinement (49.26(2)° $\leq \varphi \leq$ 50.34(2)°) confirms Destro's value of $\varphi = 49°$ (Scheme 1). Like in the α_2-polymorph, the main contribution to φ stems from the χ angle lying between 41.14(2) and 43.94-(3)°. The packings of the α_1 and β-polymorphs are indeed quite similar but clearly different from that of the α_2-polymorph[15] (see Figures 2 and 8), which is, as expected, relatively open. It is worth stressing this point, since it was categorically stated[3,10,35,48] that the structure of nonplanar polymorphs is relatively open and planar polymorphs have closed structures. Since the packing of the α_1-polymorph is closer to that of the planar β-polymorph, we conclude that the previous statement needs amendment and that some other polymorphs, with different chromic behavior, related by a phase transition, should be investigated. For example, there are two compounds already observed by Cohen
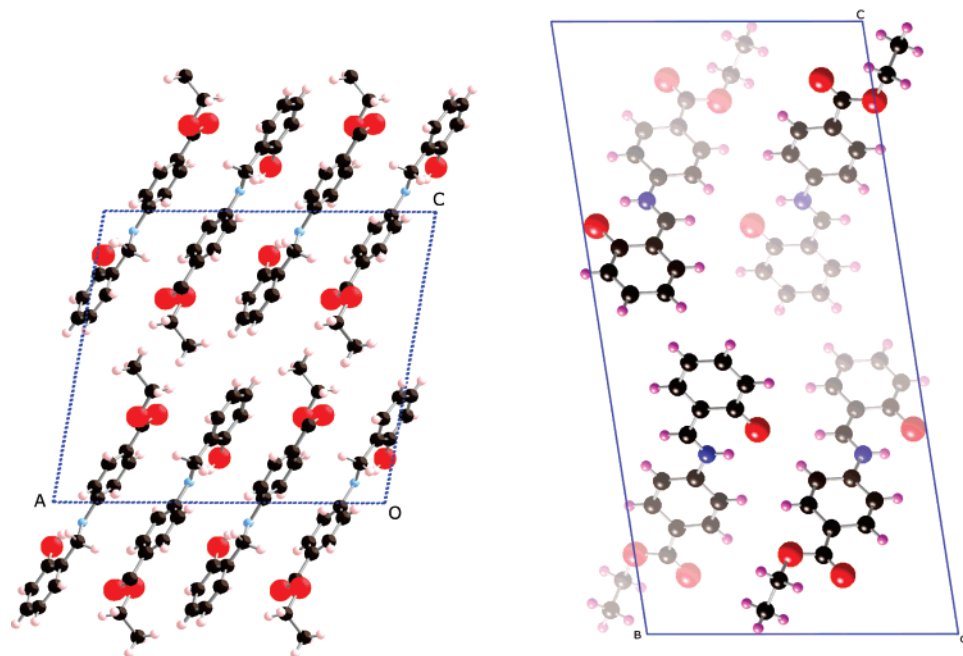
Figure 7. Molecular packing of the α (left) and of the β (right) polymorphs of ESA.
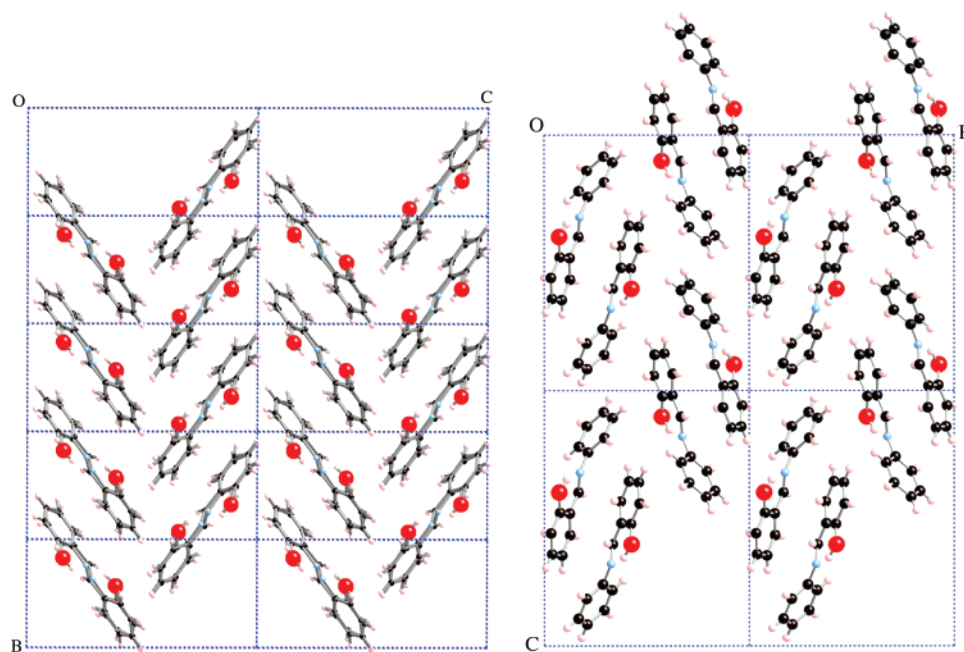

Figure 8. Molecular packing of the α_1 (left) and α_2 (right) polymorphs of SA.

et al. in 1964[3] presenting such properties, for which the structures have still not been solved (*N*-(5-methylsalicylidene)-aniline and ESA. In this context, we present the preliminary structures of the α- and β-polymorphs of the latter compound (see Figure 7 and the Supporting Information). The two polymorphs are different from the corresponding polymorphs of SA, but the O−H···N hydrogen bond agrees with Hadjoudis et al.'s conjecture.[35] The intramolecular O−H···N hydrogen bond in the β-polymorph is, as expected, stronger (1.77 versus 1.79 Å) than in the α-polymorph.

Moreover, it can be assumed that the packing of **2** is identical with the packing of YAGFAN and YICPAB[39,40] mentioned in the discussion of the β-packing, since two adjacent stacks are parallel to each other, in contrast to the β-polymorph.

Diffuse scattering, indicative of correlated micro- or nano-domains, was neither present in the reconstructed layers of **2** nor present in those of the α_2 and **1** polymorphs. Our next goal is to study the α_1-polymorph obtained via the transformation from the ordered β-phase, hoping that the order of the latter phase would persevere during the phase transformation, thus yielding an α_1-polymorph devoid of the growth disorder that hindered the deduction of truly accurate geometric parameters for the α_1 phase.

Conclusion

Our choice of SA turned out to be fortuitous for several reasons. We have been able to weave the recently determined

structure of the α_2 form,[15] an improved structure of the α_1 form, and the novel, planar β form into a coherent picture of the three polymorphs and their interrelation. Finding selective crystallization procedures for the respective polymorphs will be a major challenge, since their lattice energies are very similar indeed. It is only for **1** that a rather promising solvent has made its apparition: namely acetone from which **1** seems to crystallize quite easily and solely. From most other solvents, at least two polymorphs crystallize concomitantly, not to mention the cases in which the solvent incrusts itself into the molecule. Another promising lead seems to be methanol for the α_2-polymorph except that occasionally, under not yet understood conditions, the azine compound is produced. The nucleation of perfectly ordered crystals such as the α_2- and β-polymorphs, next to the highly disordered α_1-polymorph, must crucially depend on very minor differences of not yet identified factors. This nucleation ambiguity is well reflected in the very different habiti in which the same form may crystallize. The interrelation of the β and α_1 cells might eventually provide a clue regarding the nucleation behavior of the α_1 phase. But we will not be able to advance without understanding the structure of SA solutions in as many solvents as possible.

The molecular structure of the planar β-polymorph is in contrast to that of the α forms, in which the aniline ring is rotated about the N—C8 bond by $\sim 50°$, but their crystal packings are quite similar indeed. It therefore appears that it is a subtle interplay of packing and molecular conformation that determines the thermo- or photochromic character confirming Bregman et al.'s[49] hypotheses. With respect to Fujiwara et al. and Hadjoudis and Mavridis' hypotheses,[18,35] we conjecture that color, transition behavior, and reversibility depend on quite a few rather subtle parameters (defects, impurities, grain boundaries, internal stress, etc.) which unfortunately have not been fully identified so far (Ebara's color and reversibility are different from ours). It seems that we have to conclude that the packing is not sufficient to explain the chromic properties of the compounds but that planarity or nonplanarity play an essential role.

The entropy of the β-to-α_1 transition being rather small, it may be hoped that said transition is not as reconstructive as we though at the beginning, not withstanding the fact the crystals suffer considerably in this transition.

Another noteworthy observation is the negative expansion along the *b*-axis of **2** between room temperature and liquid-nitrogen temperature.

Supporting Information Available: X-ray crystallographic information in CIF format for **1** and **2**, a table of selected bond distances and angles, ORTEP plots, cell relations and domains, structural information, and a detailed list of restraints (PDF). This material is available free of charge via the Internet at http://pubs.acs.org. X-ray files have also been deposited under the CCDC Nos. 607915 and 610192, respectively.

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