

Thermal analysis of a polymorphic azo dye derived from 2-amino-5-nitrothiazole

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Abstract

An azo dye, derived from 2-amino-5-nitrothiazole and a substituted N,N-dimethyl aniline, was studied by various techniques. Two sets of proton signals were obtained by NMR in CDCl₃ solution, suggesting that two polymorphs coexist, however only one set of signals is observed in DMSO solution. Differential scanning calorimetry and thermogravimetric analysis were used to confirm the existence of two forms. The events registered during thermal treatment of a sample were assigned to a glass transition, recrystallization and fusion of crystalline compounds. Hot-stage microscopy was used to obtain images of the dye samples at various stages of the heating program and these observations support the interpretation of the calorimetric results.

Keywords: Azo dye; Polymorphism; NMR; DSC; Hot-stage microscopy

1. Introduction

Heterocycles are extensively used in disperse dye chemistry [1, 2] in textile and non-textile applications such as in reprographics, functional dye and non-linear optical systems, photodynamic therapy and lasers.

When the synthesis of dyes of this type, **1** and **2**, was accomplished [3], it was found that certain examples of dyes, in particular compound **1** (R=Et) showed two sets of proton resonances in deuteriochloroform solutions. These two independent proton resonances suggested the presence of two forms (two conformers, **A** and **B**) of (**1**) (Fig. 1). The compound mentioned was subjected to further NMR characterization and theoretical calculations were also carried out [4].

A molecule capable of forming more than one crystalline structure is said to display polymorphism. Different polymorphs have different arrangements of atoms within the unit cell and naturally this can have a profound effect on the physical and chemical properties of

the substance. Polymorphism is a complex phenomenon, previously described in detail by Bernstein [5,6]. Polymorphism has also been observed in dyes and pigments and several examples are described in the literature [7]. The characterization of polymorphs by NMR has been reported by Chippendale [8] and Lyčka [9].

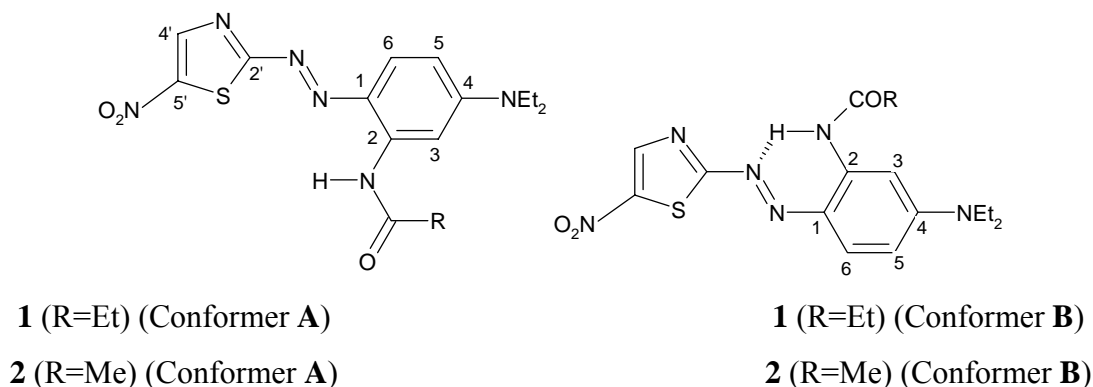


Fig. 1. Structures of compounds **1** and **2**

In our previous study of compound **1**, thermodynamic data indicated that the B form is favoured by DMSO solvation, probably due to the formation of intermolecular hydrogen bonding and also to the higher viscosity of this solvent [4].

In view of the possible existence of polymorphs of dye **2**, further characterization was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The complementary technique of hot-stage microscopy was also applied to support our interpretation of calorimetric results.

Hot-stage microscopy (HSM) provides a qualitative method for screening substances for polymorphism. It is complementary to DSC because phase changes may be observed in HSM that are barely detectable by DSC. Thermal analysis provides quantitative information regarding the energies involved in phase changes.

2. Experimental

2.1. NMR

^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were determined at 75.4 MHz both on a Varian Unity Plus Spectrometer. Double resonance, Heteronuclear Multiple Quantum Coherence (HMQC) and Heteronuclear Multiple Bond Correlation (HMBC) experiments were carried out for complete assignment of proton and carbon signals in the NMR spectra.

2.1.1 *N*-[5-Diethylamino-2-[(5'-nitrothiazol-2'-yl)diazenyl]phenyl]-acetamide (**2**) [4]

^1H NMR (DMSO- d_6) δ (ppm): 1.25 (t, $J=7.5$ Hz, 6H, 2xCH₃), 2.22 (s, 3H, CH₃), 3.61 (q, $J=7.2$ Hz, 4H, 2xCH₂), 6.83 (dd, $J=2.7$ and 9.8 Hz, 1H, H-4), 7.75 (d, $J=9.6$ Hz, H-6), 7.90 (d, $J=2.7$ Hz, H-3), 8.68 (s, 1H, H-4'), 10.28 (br s, 1H, NH). ^{13}C NMR (DMSO- d_6) δ (ppm): 12.39 (CH₃), 24.58 (CH₃), 45.36 (CH₂), 100.79 (C-6), 110.90 (C-4), 129.15 (C-3), 132.01 (C-2), 141.36 (C-1), 144.01 (C5'), 144.88 (C-4'), 155.63 (C-5), 169.10 (C=O), 181.15 (C-2').

^1H NMR CDCl₃) δ (ppm): 1.34 (t, $J=7.5$ Hz, 4xCH₃, A and B), 2.31 and 2.34 (2 x s, 2 x CH₃, A and B), 3.60 (q, $J=7.5$ Hz, 4H, 2xCH₂, A and B), 6.54 (dd, $J=2.4$ and 9.9 Hz, H-5, A), 6.63 (dd, $J=2.7$ and 9.9 Hz, H-5, B), 7.58 (d, $J=9.3$ Hz, H-6, B), 8.00 (d, $J=9.6$ Hz, H-6, A), 8.07 (d, $J=2.1$ Hz, H-3, A), 8.31 (d, $J=2.7$ Hz, H-3, B), 8.54 (s, H-4', B), 8.58 (s, H-4', A), 9.03 (br s, NH, A), 12.6 (br s, NH, B).

2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were performed on a Mettler DSC 821e, calibrated with indium to ensure the accuracy of the calorimetric scale. The weighed sample (0.5–1.5 mg) was characterized in a sealed 40 μL aluminium cans with perforated lids and subjected to thermal analysis under a flowing argon atmosphere (35 mL min⁻¹). Analysis was carried out under a variety of experimental conditions using an identical empty sample pan as reference.

Selected samples were heated from room temperature to 225 °C at a rate of 10 °C min⁻¹. These samples were subsequently cooled to -60 °C temperature at a rate of 5 °C min⁻¹. A second heating program, between -60 °C and 225 °C at a rate of 10 °C min⁻¹ was then applied. Other samples were subjected to different heating and cooling rates in order to identify optimum conditions.

2.3. Thermogravimetric studies (TG)

Samples for thermogravimetric characterization were located in open platinum crucibles and analyzed using a Rheometric Scientific TG1000 thermobalance operating under a flowing argon atmosphere (28 mL min⁻¹). A heating rate of 10 °C min⁻¹ was used and all samples were studied between 30 and 400 °C.

2.4. Hot stage microscopy studies

The dried dye particles were mounted between a glass slide and a cover slip, placed on a Mettler FP 82 hot stage and observed with a polarized light Olympus BH2 microscope equipped with a digital camera. The calibration of the temperature scale was carried out in accordance with the manufacturer's instructions.

The samples were heated to complete melting at a rate of 10 °C min⁻¹, fast cooled at about 40 °C min⁻¹ down to room temperature and re-heated again at 10 °C min⁻¹.

3. Results and discussion

3.1. NMR spectra

The NMR spectra for the dye **2** were obtained in DMSO-d₆ and in CDCl₃, but the low solubility of the compound in chloroform prevented the acquisition of the ¹³C spectrum in this solvent.

The spectrum in CDCl₃ displays two sets of signals, as shown in fig. 2b and described in the experimental part. The assignment was based on a similar example (fig.1, compound 1) where the proton and carbon resonances of each conformer were attributed by HMBC and HMQC, starting from the NH signals and assuming that the highest chemical shift corresponds to the NH involved in a hydrogen bond forming a six membered ring [4]. All the signals for our compound parallel those observed for compound **1** which would be expected from their structural similarity. The spectral data are consistent with the coexistence of both conformers where conformer B was associated with the most acidic NH signal at 12.6 ppm and for conformer A, the NH resonance shows at 9.03 ppm.

The ¹H NMR spectrum acquired in DMSO-d₆, either at room temperature, 50 or 70 °C, displayed only one set of signals. At room temperature very broad signals are observed for NH, 9.60 ppm, H-3, 7.85 ppm, and H-6, 7.75 ppm. When temperature is increased to 70 °C the H-3 and H-6 doublets become sharp, 7.90 and 7.75 ppm, respectively. The NH signal shifts from 9.60 ppm at room temperature to 10.10 and 10.28 at 50 ° and 70 °C, respectively and sharpens slightly. The appearance and the chemical shifts of H-4', H-5 and of the aliphatic protons do not change with temperature. These observations may be consistent with exchange between the two conformers. (Fig. 2b).

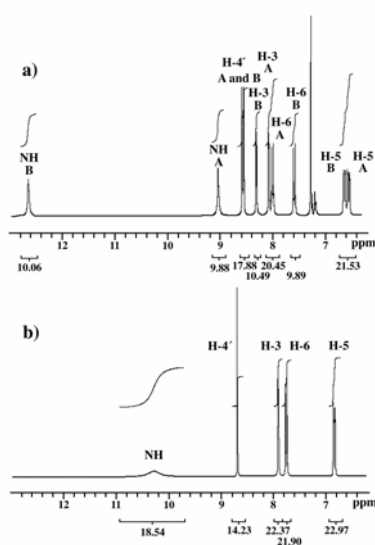


Fig. 2. ¹H NMR spectra in CDCl₃ (a), RT and in DMSO b), 70 °C)

3.2. Thermal analysis

The thermal behaviour of solid samples was studied during heating cycles using thermogravimetry and differential scanning calorimetry. The results of the thermogravimetric study are illustrated in Fig. 3 and confirm that the material suffers thermal degradation at temperatures above about 240 °C. This value for onset of degradation is obtained from the point of intersection of the extrapolated pre-weight-loss baseline with the tangent to the curve produced by the decomposition reaction. The maximum error associated with this process is estimated as about 5 °C. Observations using both DSC and thermogravimetric techniques are consistent with a minimum thermal stability of 240±5 °C for dye **2**. The DSC curves of **2** were obtained using the heating programs described in the experimental section and a typical example is shown in Fig. 4. This figure illustrates the results obtained by heating from room temperature to 225 °C. A sample of the dye **2**, as prepared, subjected to a heating rate of 10 °C min⁻¹, was observed to undergo fusion at an extrapolated onset temperature of 204.6±0.1 °C. The enthalpy of melting was $\Delta_{\text{fus}}H = -164.0 \pm 0.1$ mJ or $\Delta_{\text{fus}}H = -35.7 \pm 0.1$ J mol⁻¹. Other samples of the same dye, subjected to different heating rates, showed similar thermal behaviour confirming the reproducibility of results and the expected dependence of onset temperature on heating rate. The first heating cycle confirms that the sample as prepared adopts the structure of the more stable form. This sample was subsequently cooled to -60 °C, at a cooling rate of 5 °C min⁻¹, and no phase transitions were observed. The results for the second heating cycle, at a rate of 10 °C min⁻¹ (Fig. 5), confirmed the presence of a low intensity endothermic event at 54.2±0.1 °C, a broad exothermic peak with an onset of 111.5±0.1 °C and an endothermic peak with an onset of 183.6±0.1 °C ($\Delta_{\text{fus}}H = -29.9 \pm 0.1$ J mol⁻¹). These results suggest that fast cooling of the dye melt leads to the formation of a metastable amorphous solid as confirmed by hot-stage microscopy (Fig. 6c). On heating this solid undergoes a weakly discernible glass transition followed by crystallization. The thermal events recorded during analysis [10] were therefore assigned to a glass transition (54.2±0.1 °C), recrystallization (111.5±0.1 °C) and fusion (183.6±0.1 °C). These observations are consistent with NMR measurements and with a previous publication which describes the results obtained with another azo dye [4]. Although melting points of polymorphs can be very close [5, 11], in this case the melting point of the metastable polymorph lies significantly below that of the thermodynamically stable form.

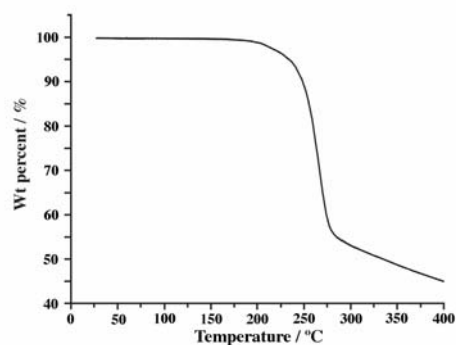


Fig. 3. Thermogravimetry curve for dye **2**

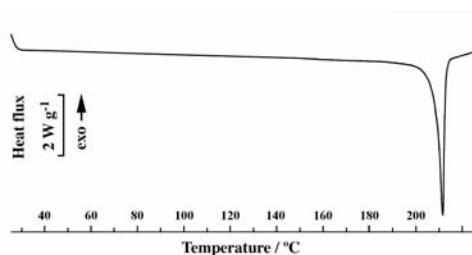


Fig. 4. DSC heating run for dye **2** at 10 °C min⁻¹

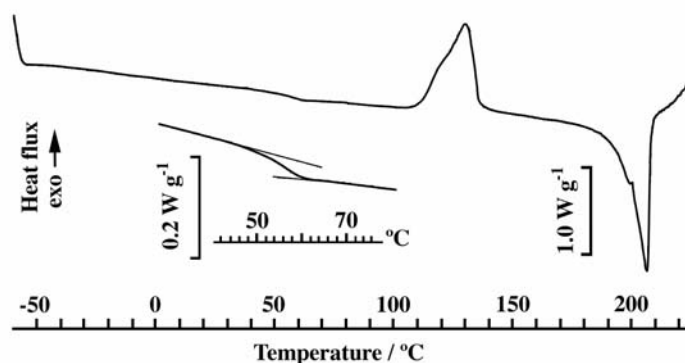


Fig.5. Second DSC heating run for dye **2**, starting from an undercooled melt.

3.3. Microscopical analysis

Hot-stage microscopy was used to obtain images of the dye samples at various stages of the heating program. The dye particles, as prepared, have an acicular form (Fig. 6a) that remains unchanged up to the melting temperature at about 208 °C (fig. 6b). Fast-cooling of the melt did not crystallize the material (Fig. 6c), however, during the second heating the material recrystallized at about 145 °C forming highly birefringent acicular crystals (Fig. 6d), radiating outwards from the original droplet. The recrystallized material melted at approximately the same temperature as that observed in the first heating program.

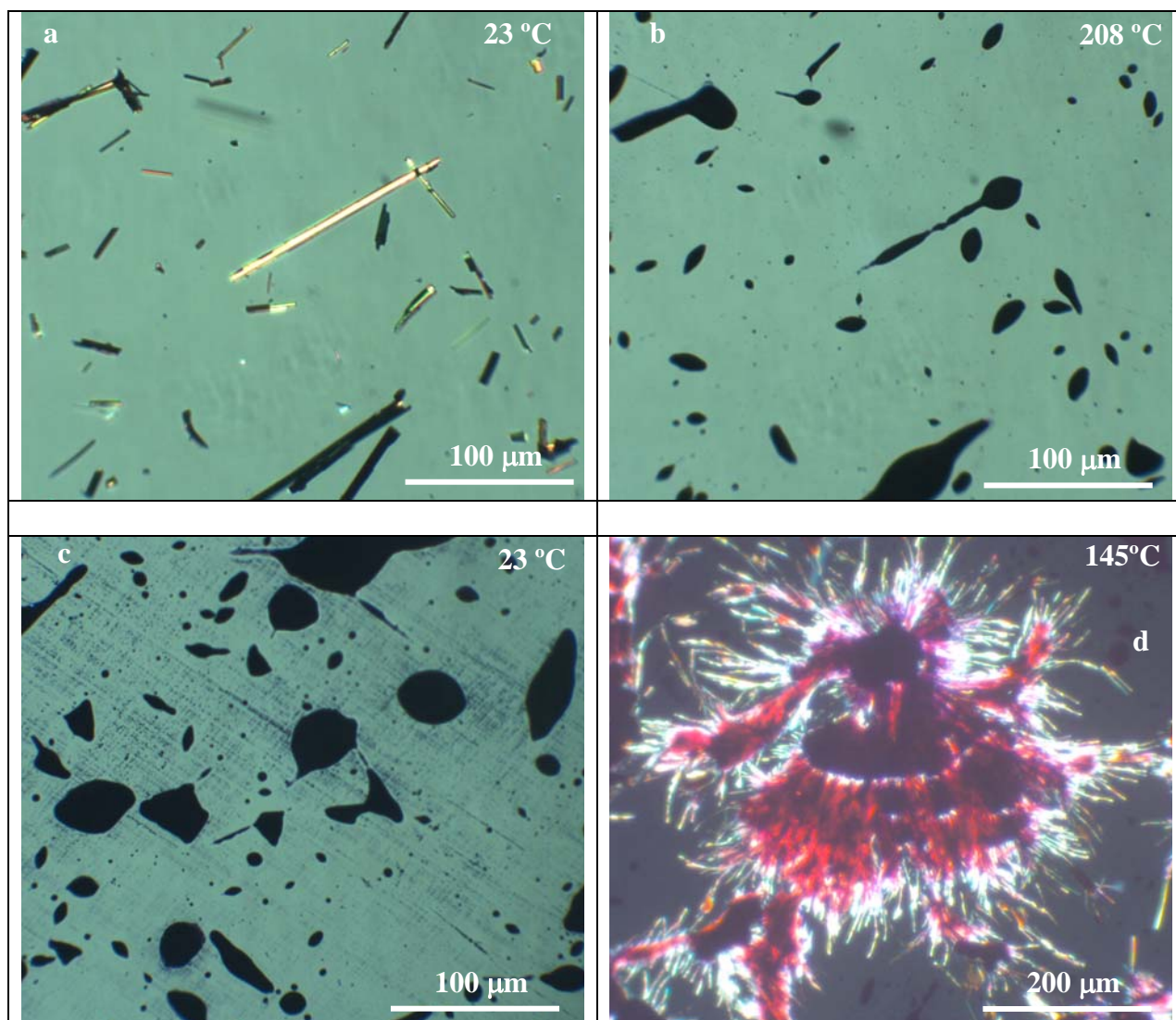


Fig. 6 Photomicrographs of the dye 2. a- Dye 2 as prepared; b-Melt; c-Fast-cooled; d- Recrystallized from the melt.

4. Conclusions

Thermal analysis has been used to further characterize a polymorphic system of an azo dye after preliminary studies by ^1H NMR identified an anomalous behaviour. The information obtained from the melting curves of the organic dye compounds by DSC show two polymorphs with quite close melting points. The existence of two different crystalline forms was also confirmed visually by hot-stage microscopy.

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