

# Theoretical and NMR structural characterisation of a polymorphic azo dye

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## Abstract

Proton and carbon-13 NMR studies in solution and carbon-13 CP-MAS NMR in the solid state of a polymorphic azo dye derived from 2-amino-5-nitrothiazole were performed and the results are discussed and compared with theoretical data from quantum chemical calculations. The polymorphism of this compound has conformational character, two conformers coexist in CDCl<sub>3</sub> solution and in solid state, as shown by NMR. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Azo dye; Polymorphism; NMR; <sup>13</sup>C CP-MAS NMR; PM3; B3LYP

## 1. Introduction

Heterocycles are extensively used in disperse dye chemistry either for textile or non-textile uses. Non-textile applications of heterocyclic dyes include their use in reprography, functional dye and non-linear optical systems, photodynamic therapy and lasers [1].

Azo dyes containing heterocyclic rings lead to brighter and often deeper shades than their carboxylic analogues [2] and they are still very important for applications such as disperse dyes for polyester fibres [3].

When the synthesis of this type of dye was accomplished [4], it was found that some of them, namely compound (1) (Fig. 1) showed two sets of proton resonances in deuteriochloroform solutions, even after repeated purification. These two independent proton resonances seem to indicate the presence of two forms (two conformers, A and B) of (1). The presence of both forms is not due either to hindered rotation about the amide bond, or a *cis-trans* isomerization since the latter would need higher energy. Chippendale et al. described polymorphism for Disperse Red 278 (2) (Fig. 1),

which presents broad carbon resonances for C-2 and C-6, in CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub>, due to slow exchange between two conformers [5]. Lyčka published an excellent review on the NMR of azo dyes [6], where cases of polymorphism and the characterisation of the corresponding polymorphs by NMR were discussed.

## 2. Experimental

<sup>1</sup>H NMR spectra were recorded on a Varian Unity Plus and on a Bruker Avance 300 with operating frequencies of respectively, 299.94 and 300.13 MHz for <sup>1</sup>H and 75.42 and 75.47 MHz for <sup>13</sup>C. Chemical shifts ( $\delta$ ) are reported in ppm, coupling constants ( $J$ ) are in hertz and the internal standard was TMS. <sup>13</sup>C Assignments were made with the aid of 2D gHSQC and gHMBC (delays for one bond and long-range  $J$  C/H couplings were optimised for 145 and 7 Hz, respectively) experiments. HSQC spectra give <sup>1</sup>J<sub>C/H</sub> correlations while HMBC spectra allowed the establishment of connectivities between coupled proton and carbons two to three bonds away from each other. <sup>13</sup>C CP-MAS NMR spectra were recorded at 100.62 MHz on a Bruker Avance 400 spectrometer with the following conditions: 5 s of

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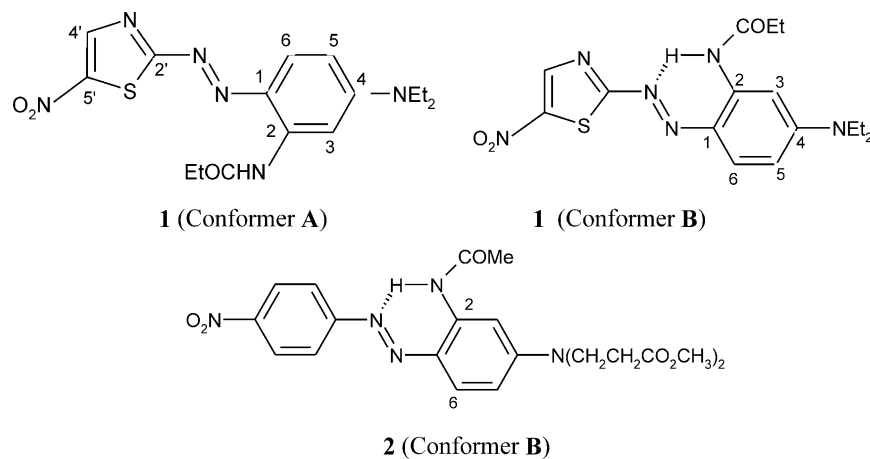


Fig. 1. Structures of compounds **1** and **2**.

recycle delay, 1.5 ms of time contact, 90° pulse of 5  $\mu$ s and AQ of 33.8 ms. In the dipolar dephasing experiment a contact time of 50  $\mu$ s was used.

### 3. Quantum chemical calculations

The structures were firstly optimized using the semi-empirical PM3 method, based on the AMPAC 6.56PC software [7]. The structures were then refined using a DFT method (B3LYP/6-31G\*\*), aiming a better description of the electronic structure [8]. The Berny analytical gradient was used in this optimisation. The requested convergence limit on RMS density matrix was  $1 \times 10^{-8}$  and the threshold values for the maximum force and the maximum displacement were 0.000450 and 0.001800 a.u., respectively. The results were viewed using Gaussview (03W) [9]. From the refined structures, the geometric and thermodynamic parameters for both forms, for the isolated (AMPAC) and solvated (Hyperchem) [10] molecule (chloroform, dimethylsulfoxide, methanol), and for transition state (TS), only for the isolated molecule, were calculated using PM3 method. The conversion between the A and B forms was obtained by the rotation of the C(14)–C(12)–N(11)–N(8) dihedral angle (Fig. 2, Inset), using the PM3 method and the facilities of AMPAC. The DFP/BFGS optimizer was used in these calculations. The solvated molecules (in chloroform, methanol and dimethylsulfoxide) were modeled using the facilities of Hyperchem 5.11 (UHF calculation, gradient 0.1000 kcal/Å mol, Polak-Ribiere optimisation algorithm). The simulations using solvent molecules involved at least 14 solvent molecules distributed in the neighborhood of one molecule, with the minimal distance of 2.3 Å. From  $\Delta^0 H_f$  and  $\Delta S$  (reaction entropy) furnished in the output of AMPAC,  $\Delta^0 G_f$  and  $\Delta^{\#} G^0$  ( $A \leftrightarrow B$  conversion) could be estimated.  $\Delta^0 S_f$  could be estimated from the expression,

$$\Delta^0 S_f = \Delta S - \sum \Delta S_{\text{elements}}$$

in which  $\Delta S_{\text{elements}}$  were obtained from  $S_{\text{element}}^0$  data [11]. Particularly,  $\Delta S$  was estimated from thermodynamic calculation using AMPAC with the combination of the keywords PM3 PRECISE FORCE GRAD THERMO and ROT=1.

The activation energy rate constant and the A-factor from Arrhenius equation, were estimated from thermodynamic and kinetic equations based on transition state theory [12],

$$E_a = \Delta^{\#} H^0 + 2RT$$

$$k_r = \frac{k_B T}{hc_0} \exp(-\Delta^{\#} G^0/RT)$$

$$A = \frac{k_B T \exp(2)}{hc_0} \exp(\Delta^{\#} S^0/R)$$

For solvated species,  $\Delta^0 G_r$  was estimated considering that both species possess the same  $\Delta^0 S_f$  value ( $\Delta^0 G_r = \Delta(\Delta^0 H_f)$ ).

### 4. Results and Discussion

Fig. 2 presents the structure of both conformers, and their charge distribution,

The results from optimisation show that both species are almost planar, due to a significant electron delocalisation between the diethylamino and the nitro group, mainly for B conformer. The conversion from A to B implies in a magnification of this effect, principally in the region in which the intramolecular hydrogen bond occurs (Fig. 2). This results in a more polar species. In fact, the dipole moment calculated for B (10.90 Debye) is slightly higher than the value obtained for A (10.55 Debye).

In the conversion from A to B, significant changes are observed in the charge over the atoms. The analysis of these variations indicates that the  $A \rightarrow B$  conversion induces a considerable displacement of the electronic density towards the region in which the intramolecular hydrogen bonding occurs.

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