



Crystal structures, solvatochromisms and DFT computations of three disperse azo dyes having the same azobenzene skeleton



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ABSTRACT

Three disperse azo dyes having the same 4-nitrobenzene/azo/4-aminobenzene skeleton but different color have been structurally and spectrally characterized and compared in this paper. X-ray single-crystal diffraction analysis of compound **3** reveals that it has a planar molecular conformation between the azo and the nitrobenzene units. However, severely twisted aminoazobenzene structures in compounds **1** and **2** are observed because of the steric hindrance effect of *ortho* chloro and bromo groups. Electronic spectra of **1–3** are closely related to their molecular structures, which demonstrate that the presence of different substituted groups and the spatial crowding effect in the aminoazobenzene backbone leads to the significant alterations of bathochromic and hypochromic shifts. In addition, theoretic computational studies as well as solvatochromisms for three azo dyes have been included.

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1. Introduction

Over the past few decades, azobenzene based dyes have been extensively studied in the field of material chemistry as well as dye industry [1–4]. In particular, disperse azo dyes have shown a lot of fascinating advantages [5,6], such as excellent photophysical properties, high sublimation and light fastness for meeting end-use applications. However, one of the most important scientific problems is how to bridge the gap between chemical structures and properties [7]. Recently, it is noted that some theoretical and experimental studies [8–11] have been carried out to reveal the structure–performance relationship of these commercially available disperse dyes, where some single-crystal structures are involved to provide model dye compounds for theoretical studies.

In our previous work, several disperse azo dyes and Schiff bases having the same D– π –A skeleton have been investigated from syntheses to structures to spectroscopic properties [12]. As an extensive study in this area, we have selected some commercially

available disperse monoazo dyes with twisted and untwisted D– π –A charge transfer chromophores (Scheme 1) for further investigating the structure–performance relationship. We report herein their single-crystal structures and the comparisons on their UV–Vis spectra and related DFT computational results. So this work is suggested to provide some useful information on the design, electronic spectra and applications for the extension of this family of well-known azo dyes having the 4-nitrobenzene/azo/4-aminobenzene skeleton.

2. Experimental section

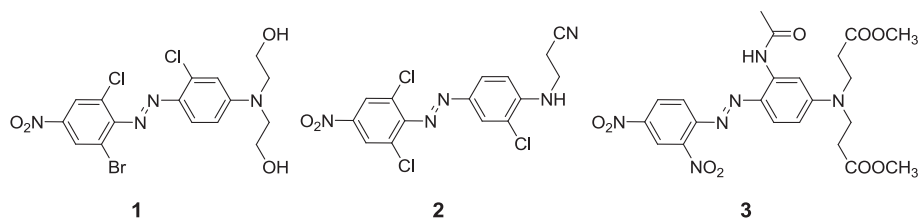
2.1. Materials and measurements

Disperse azo dyes **1–3** were purchased from the commercial sources and purified before used. A typical purification process is listed as follows: the commercially available dye sample was dissolved in hot DMF and filtered to remove the inorganic impurities. The filtrate was condensed via a rotary evaporator and the residue was dried in a vacuum. Acceptable single crystals of **1–3** suitable for the X–ray diffraction measurement were grown by slow evaporation from a mixture of acetonitrile and acetone ($v/v = 1:1$) in air at room temperature after several weeks. All other reagents and

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Scheme 1. Chemical structures of three disperse azo dyes **1–3** having the same azobenzene skeleton.

solvents were of analytical grade and used without further purification. UV–Vis spectra were recorded with a Shimadzu UV–3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm at room temperature.

2.2. X-ray data collection and solution

Single-crystal samples of **1–3** were glue-covered and mounted on glass fibers for data collection on a Bruker SMART 1K CCD area detector at 291(2) K using graphite mono-chromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The collected data were reduced by using the program SAINT [13] and empirical absorption corrections were done by SADABS [14] program. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences by using XPREP. The structures were solved by direct method and refined by least-squares method. All non-hydrogen atoms were refined on F^2 by full-matrix least-squares procedure using anisotropic displacement parameters, while hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times of the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. In the case of **3**, the two oxygen atoms (O8 and O9) of *ortho* nitro group in 2,4-dinitroaniline moiety are found disorderedly over two positions with the site occupancy factors of 0.531(7):0.469(7). All calculations were carried out on a PC computer with the SHELXTL PC program package [15] and the molecular graphics were drawn by using XSELL, XP and ChemDraw softwares. Details of the data collection and refinement results for compounds **1–3** are listed in Table 1, while selected bond distances and bond angles are given in Table S1. In addition, intermolecular hydrogen-bonding parameters are tabulated in Table S2.

2.3. Computational details

All calculations were carried out with Gaussian09 programs [16]. The geometries of **1–3** were fully optimized and calculated by the B3LYP method and 6-31G* basis set without any symmetry constraints and the single-crystal structures of dyes **1–3** were used as the starting geometries.

3. Results and discussion

3.1. Structural descriptions of **1**, **2** and **3**

The molecular structures of azo dyes **1**, **2** and **3** with atom-numbering scheme are shown in Figs. 1–3. The bond lengths of azo unit (N=N) in **1–3** are in the range of 1.223(5)–1.314(11) \AA , and those for their neighboring N–C bonds lengths vary from 1.369(4)–1.444(6) \AA , respectively, exhibiting typical double-bond and π -conjugated single-bond character. Different from the conventional planar azobenzene compounds, dye **1** presents a twisted azobenzene structures because of the steric hindrance effect between the chlorine and bromine atoms at the 2 and 6 positions of phenyl

ring A and the azo unit. It is worthwhile to mention that an intramolecular C–H \cdots N hydrogen bond is found between one azo nitrogen atom (N2) and one phenyl hydrogen atom (H12) with the H \cdots A distance of 2.467(11) \AA in **1**. Thus, a five-membered C₂N₂H hydrogen-bonded ring is formed, which can keep the local planarity between the azo and ring B units. Similar to dye **1**, dye **2** also presents a twisted azobenzene structure due to the presence of dichloro groups in ring A, and an intramolecular C–H \cdots N hydrogen bond is found between one azo nitrogen atom (N2) and one phenyl hydrogen atom (H8) with the H \cdots A distance of 2.490(5) \AA , forming. However, double intramolecular N–H \cdots N and C–H \cdots N hydrogen bonding interactions are found with the H \cdots A distances of 2.016(4) and 2.436(4) \AA . Thus, fused five-membered C₂N₂H hydrogen bonded rings are formed in this case, which will promote the planar conformation for the whole molecule. In addition, the two *N*-substituted hydroxyethyl groups are found to point to the same side of aminobenzene ring B in dye **1**. In contrast, the two *N*-substituted methyl propionate groups in dye **3** are found to point toward different sides of aminobenzene ring B.

The large torsion angles for C3–C4–N2–N3 (131.1(9) $^\circ$), C5–C4–N2–N3 (52.1(9) $^\circ$) and N2–N3–C7–C8 (176.7(9) $^\circ$) in dye **1** also manifest the nonplanarity of the chromophore skeleton. Furthermore, the dihedral angle θ between the benzene rings A and B is 46.8(8) $^\circ$ and the distance d of C11 \cdots N3 is 2.980(12) \AA in **1**. The torsion angles for C3–C4–N2–N3 (107.0(5) $^\circ$), C5–C4–N2–N3 (82.4(5) $^\circ$) and N2–N3–C7–C12 (179.6(5) $^\circ$) exhibit more twisted character between the benzene rings A and B. Different from dye **1**, the d value in dye **2** is 3.266(5) \AA for C12 \cdots N3 and the θ value is 79.9(3) $^\circ$, indicative of the distortion order of **2** > **1**. Accordingly, the length of C11 \cdots N3 is 3.539(5) \AA in **2**, which is shorter than that of Br1 \cdots N3 (3.886(9) \AA) in **1**. The discrepancy of torsion angles in **1** and **2** is suggested to arise from the alteration of *N*-substituted tails which will influence their packing fashions.

The dihedral angle θ between the two benzene rings A and B in dye **3** is only 5.4(3) $^\circ$, indicating the essentially coplanar character. The two oxygen atoms (O8 and O9) of *ortho* nitro group in 2,4-dinitroaniline moiety are found disorderedly over two positions with the site occupancy factors of 0.531(7):0.469(7), in order to minimize the steric hindrance from neighboring acetylamino group fixed by above-mentioned intramolecular N–H \cdots N hydrogen bond. It should be mentioned that the observation of disorder of nitro group is uncommon especially in the aminoazobenzene based azo dyes. It is also noted that the two parameters depend on each other, which are intuitionistic and can be applied to this family of twisted azobenzene based dyes.

As shown in Fig. S1, no obvious π – π stacking interactions can be found in the crystal packing of dye **1**. Different from **1**, a head-to-tail dimeric packing manner is found in the crystal packing of **2** as displayed in Fig. S2, where strong π – π stacking interactions are observed between adjacent nitrobenzene rings from contiguous molecules with the centroid-to-centroid separation of 3.481(5) \AA . In addition, intermolecular hydrogen bonding interactions are not found in **2** in part because of the steric hindrance effect of *N*-substituted cyanoethyl group.

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