



Characterization of non-genotoxic diarylides using experimental and molecular orbital methods



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ABSTRACT

The synthesis of colorants from non-genotoxic benzidine analogs such as 3,3'-dipropoxybenzidine and 2,2'-dimethyl-5,5'-dipropoxybenzidine led to diarylides having atypical physical and chemical properties. For instance, the products obtained from coupling these diamines with acetoacetanilide and acetoacet-*p*-chloroanilide produced diarylides behaving more like dyes than pigments and thus had significantly lower photostability. In addition, unlike the well-known and widely used commercial diarylide pigments (e.g. CI Pigment Yellow 12) the present compounds had solubility, albeit low, in CHCl₃ and CH₂Cl₂. To account for these observations, the diarylides in our study were characterized using single crystal X-ray crystallography whereupon it was found that they possess varying levels of twist about the biphenyl moiety, impacting the way they pack in the crystal state. The visible spectra for the diarylides were measured in the solid state and in solution, and a 12 nm higher λ_{max} was observed in the solid state for the diarylide derived from 3,3'-dipropoxybenzidine and acetoacetanilide. To account for this λ_{max} change, molecular conformations were probed by 2D dynamic VT-NMR (25–60 °C) in solution using homonuclear 2D-NMR (COSY, COSY-LR, and ROESY), which revealed a single conformation with a torsion angle (θ) across the biphenyl linkage of 56° in solution. The correlation of these results with λ_{max} values for this system is presented.

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1. Introduction

Diarylide pigments range in color from greenish-yellow to reddish-yellow and they are known to exhibit twice the color strength of the corresponding monoarylide pigments [1]. Commercial interest in these colorants led to a number of key studies designed to define their structural nature. Christie and Standring used UV/visible spectroscopy and PPP MO calculations to extend their previous work on monoarylide pigments [2] to the characterization of diarylide pigment structures. They reported good agreement between ϵ_{max} values and the calculated oscillator strengths, spectroscopic evidence for the bis-ketohydrazone form, and the effect of rotation about the biphenyl link in C.I. Pigment Yellow 12 (PY12) on the predicted spectroscopic properties [3]. During the subsequent decade, Barrow and co-workers reported the X-ray crystal structures of five diarylide yellow pigments (PY12,

PY13, PY14, PY63, and PY83), confirming that the associated molecules exist in the bis-ketohydrazone form and showing that they are not planar, do not have intermolecular H-bonding but do have intramolecular H-bonding. It was also found that the molecules pack together in inclined stacks [4–6]. This work was followed by an important study involving a determination of the crystal structures of PY12, PY13, PY14 and PY83 from X-ray powder data using lattice energy minimizations and subsequent Rietveld refinements [7]. PY12 crystallized in a herringbone arrangement with twisted biphenyl fragments. PY13 and PY14 formed a layered structure of planar molecules. PY83 showed a herringbone structure with planar molecules. According to quantum mechanics (QM) calculations, the twisting of the biphenyl fragment results in a lower color strength of the pigments. The experimentally observed lower color strength of PY12 in comparison with that of PY13 and PY83 was explained as a pure packing effect.

Altogether, the above-mentioned studies indicate that increasing the torsion angle (θ) across the biphenyl linkage produced a hypsochromic shift, changed the hybridization and basicity of the *N*-atoms attached to the biphenyl moiety, and impacted

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intermolecular interactions, crystal packing and photostability. It is also known that close packing of molecules in organic pigments is highly desirable for properties such as photostability, wherein the energy of absorbed UV light can be dissipated *via* a nondestructive mechanism, and that the torsion angle across the biphenyl linkage can play a significant role in achieving the desired molecular arrangement [8]. Also, one would anticipate that changes in the λ_{\max} of an organic pigment upon transition from the solid state to solution occur as molecules adopt different geometries and/or conformations.

As part of a study aimed at developing non-genotoxic alternatives to benzidine and its congeners, benzidine analogs containing bulky alkoxy groups were synthesized and used to make a variety of interesting azo dyes and pigments. It was shown that coplanarity in certain non-mutagenic diarylide yellow pigments plays a significant role in determining their performance properties, including λ_{\max} , color strength, and photostability [9–14]. In this regard, diarylides **1** (2,2'-[(3,3'-dipropoxy-1-biphenyl-4,4'-diyl)dihydrazin-1-yl-2-ylidene]bis[N-(phenyl)-3-oxobutyramide]) and **2** (2,2'-[(2,2'-dimethyl-5,5'-dipropoxy-1-biphenyl-4,4'-diyl)-dihydrazin-1-yl-2-ylidene]bis[N-(*p*-chlorophenyl)-3-oxobutyramide]) (cf. Fig. 1) were prepared by diazotization of 3,3'-dipropoxybenzidine and 2,2'-dimethyl-3,3'-dipropoxybenzidine, followed by coupling with the corresponding acetoacetanilides, as previously reported [9,10]. These diarylides had significantly higher solubility in organic solvents and lower lightfastness than the commercial prototypes, making a study of their molecular structures of interest.

In this paper, we report results from studying the molecular features of non-mutagenic derivative diarylides **1** and **2** in solution and the solid state. Of special interest was how changes in the torsion angle across the biphenyl moiety affect crystal packing and the properties of these pigments, especially spectral changes associated with diarylide **1** and the inferior photostability of diarylide **2**.

2. Experimental

2.1. Geometry optimizations

Structures were built with the aid of a graphical editor interface using either the CAChe or Cerius2 editor. Formal charges and partial charges were assigned whenever appropriate. A process in the editor interface, in CAChe called “Beautification” and in Cerius2 “Clean”, was used to provide a starting structure with standard bond lengths, bond angles, and correct configuration of each atom in the structure. Lone pairs of electrons and hydrogen atoms were added where appropriate. To obtain the most precise final structure, they were built in CAChe, saved as .pdb (Protein data bank) files, and transferred to Cerius2 prior to running DMol₃.

In the case of PISYSTEM, the structure to be modeled was edited in the canvas. Then, the two-dimensional geometry optimization process called “idealize” was performed to provide a realistic structure before running PPP SCF CI calculations. However, if the

structure under study was twisted significantly, a more correct starting geometry was obtained by manually incorporating the appropriate torsion angles.

In some cases, manual adjustments of dihedral angles were necessary, before running molecular mechanics (MM) or quantum mechanics (QM) calculations in order to generate more accurate starting structures (e.g., rotamers, isomers, and structures containing intramolecular H-bonds) [15], thereby facilitating the determination of low-energy minima.

2.1.1. Classical molecular mechanics

After editing the structure to be modeled, a force field was chosen to run MM. MM2 [15] forcefields and a conjugate gradient minimizer were used.

2.1.2. Geometry optimizations using DMol₃

Structures were generated as car files using Cerius2 on a Sonoma Supercomputer and transferred to an IBMSP supercomputer. Local (JMW) [16–18] and the double numerical plus polarization (DNP) basis set with restricted Hartree Fock (RHF), were performed in DMol₃ using 8 processors and 4 GB of RAM on an IBMSP supercomputer.

2.1.3. Semi-empirical molecular orbital (SEMO) methods

The semi-empirical AM1 (Austin Model 1) model implemented in MOPAC in CAChe was used to perform self-consistent field (SCF) calculations using an RHF method. AM1 was used to locate lowest energy equilibrium geometries [15]. The eigenvector (product of molecular coefficients and molecular functions) was used to iteratively reduce the SCF energy in MOPAC calculations until no further changes were produced. The following special MOPAC settings and key words were used in order to produce more accurate calculations:

Search options:

- Precise: Enhances all optimizations, electronic and geometric, by a factor of normally 100.
- XYZ: Uses Cartesian coordinates in the optimization to make the calculations more accurate.
- Minimize gradient: EF (eigenvector following minimizer)
- Minimized geometry: EF (Allows explicit definition of the optimizer)
- HESS = 1: Generates a matrix consisting of the derivative of the atomic coordinate displacement with respect to SCF energy before beginning the first optimization cycle (makes EF optimization more efficient)
- GNORM = 0.1: Continue geometry optimization until the conjugate gradient fall below 0.1
- Input file geometry:
 - Internal coordinates
 - Maintain orientation
- SCF options:
 - Converger the default setting was used

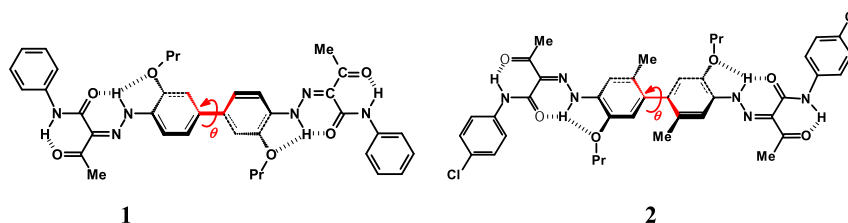


Fig. 1. Molecular structures of diarylides **1** (left) and **2** (right).

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