



# The influence of fluorination on the structure and properties of azo pigments



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## ABSTRACT

The synthesis and single crystal X-ray structures of two fluorinated azo pigments and their non-fluorinated analogues derived from N-acetoacetanilide and N,N'-(1,4-phenylene) bis-(acetoacetamide) as coupling components were described. These two kinds of pigments existed in the ketohydrazone and bisketohydrazone tautomeric form with intramolecular hydrogen bondings respectively. Fluorination had a profound influence on the structure of molecules and crystals and consequently altered the morphology and pigmentary performance. The results demonstrated that the solvent resistance was improved upon fluorination due to enhanced intermolecular interactions and efficient  $\pi$ -packing of molecules. However, in both cases fluorination gave rise to pigments with poorer stability to heat and light.

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## 1. Introduction

Fluorine is the most electronegative non-metallic element widely distributed in nature. As a result of the negative inductive effect, a fluorinated organic compound exhibits different  $\pi$ -cloud compared to that of its nonfluorinated analogue and thereby the structure of molecules and crystals is changed [1]. The special electronic character of fluorine allows it to act as a hydrogen bond acceptor, which is of particular interest to the study of organic compounds [2,3]. The C–F bond is very robust and is thought to enhance thermal stability, which is important in terms of heat-resisting materials [4,5]. Furthermore, due to the similar Van der Waals radii of fluorine to that of hydrogen (1.35 Å and 1.20 Å, respectively), there is no gross distortion of geometry upon fluorination which is essential in biocompatibility.

Fluorination has a significant effect on the crystal structure and technical performance of organic pigments which are used in

microcrystalline form. However, due to the limited solubility of organic pigments in solvent, it is difficult to obtain suitable crystals for X-ray single crystal diffraction. Previous work on crystal engineering of organic pigment using fluorine has suggested that fluorination modifies the crystal packing of the molecules [6–8]. For example, CuPc and CuF<sub>16</sub>Pc adopt significantly different stacking patterns, the former possesses one-dimensional  $\pi$ – $\pi$  stacking similar to alpha type metal phthalocyanine, whereas the latter takes a herringbone-type stacking and subsequently the electron mobility is improved. The other cases include fluorinated perylene bisimide (PBI) dyes and quinacridone derivatives. Nonfluorinated PBI adopts a slipped stack arrangement while the difluoro-substituted PBI takes a typical “herringbone” structure and also owns higher mobility. All of these changes may originate from intermolecular interactions involving fluorine.

However, systematic study on the crystal structure and properties of fluorinated azo pigments and their nonfluorinated analogues is rare. In order to clarify the influence of fluorine substitution on the structure and properties of azo pigments, two fluorinated pigments and their nonfluorinated analogues derived from N-acetoacetanilide and N,N'-(1,4-phenylene)bis-(acetoacetamide) as coupling components have been synthesized and their crystal structures described, both of which is shown in Fig. 1.

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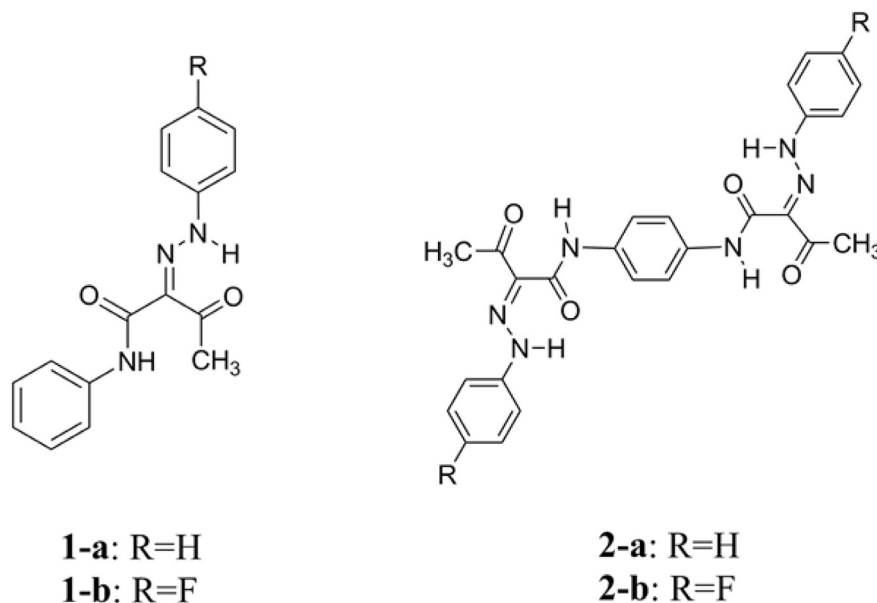


Fig. 1. Molecular structure of as-synthesized compounds.

A comparison of the pigmentary properties in relation to crystal structures provides some clues for molecular design of organic pigments in future.

## 2. Experimental section

### 2.1. Materials and methods

All chemicals used were of analytical reagent (Aladdin or Sigma products). All the measurements were carried out at room temperature (298 K) except the single crystal X-ray diffraction (113 (2) K).

The infrared spectrum were obtained as KBr disks on a Thermo Nicolet 380 spectrometer. The UV–vis spectra were recorded in the range of 200–600 nm on a Thermo Spectronic spectrometer using 1 cm matched quartz cells. All MS data were collected using a microTOF-Q II mass spectrometer (Bruker Daltonic Inc.). NMR spectra were obtained on a Bruker AVANCE III 400 NMR spectrometer with CDCl<sub>3</sub> as solvent. Thermogravimetric analysis was carried out on a Mettler TGA/DSC thermal analyzer at a heating rate of 10 °C/min under a flowing nitrogen atmosphere. Scanning electron microscope (SEM) were collected on a Rigaku XtaLab P200 diffractometer. Light fastness testing was carried out on a Solar Simulator PL-X500C (Xe-lamp, 400–1100 nm). The particle size measurement was taken on a Delsa Nano S particle size analyzer.

### 2.2. Synthesis

#### 2.2.1. Synthesis and characterization of 3-oxo-N-phenyl-2-(phenyldiazenyl)butanamide (**1-a**) and 2-((4-fluorophenyl)diazenyl)-3-oxo-N-phenylbutanamide (**1-b**)

Aniline (4.66 g, 0.05 mol) was stirred with concentrated hydrochloric acid (12.4 mL) in water (24 mL). A solution of sodium nitrite (3.62 g, 0.0525 mol) in water (8.5 mL) was added with stirring over 30 min keeping the temperature below 5 °C and held it for 30 min. The pH was then adjusted to 6 by addition of sodium acetate anhydrous. The presence of excess sodium nitrite was indicated using starch/KI paper. Before the coupling, a few drops of aqueous urea solution were added to destroy excess nitrous acid. The reaction mixture was filtrated, and washed with water to

provide a yellow filtrate. The diazonium liquor was then added to the suspension of N-acetoacetanilide (9.30 g, 0.0525 mol) in water with mechanical agitation over 30 min and maintained for 1 h at room temperature. The terminal was detected using H-acid test. The slurry was heated at 70 °C for 1 h, then filtered and washed salt free with water. The residue was dried under vacuum at 60 °C to obtain a greenish yellow solid (3.2 g, 93.6%). Crystals **1-a** suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution of the complex at room temperature. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3446 (amide I, N–H bond), 1662 (ketone, C=O stretch), 1523 (amide II, N–H bond); ES-MS: calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> M<sup>+</sup> 282.1237, found 282.1260; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  14.82 (d, *J* = 47.4 Hz, 1H), 11.49 (s, 1H), 7.64 (t, *J* = 10.2 Hz, 2H), 7.50–7.33 (m, 6H), 7.25–7.14 (m, 2H), 2.61 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.50 (s), 163.06 (s), 141.73 (s), 137.20 (s), 129.64 (s), 129.05 (s), 126.09 (s), 125.40 (s), 124.80 (s), 120.94 (s), 115.90 (s), 26.12 (s).

Compound **1-b** was obtained as a bright yellow solid (14.4 g, 96.3%) according to Section 2.2.1. Crystals **1-b** suitable for X-ray analysis were obtained by slow evaporation of a mixed petroleum ether/chloroform (1:3) solution of the complex at room temperature. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3444 (amide I, N–H bond), 1660 (ketone, C=O stretch), 1516 (amide II, N–H bond); ES-MS: calcd for C<sub>16</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>F M<sup>+</sup> 300.1161, found 300.1143; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  14.81 (s, 1H), 11.47 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.39 (dd, *J* = 10.5, 5.1 Hz, 4H), 7.15 (dt, *J* = 17.1, 8.0 Hz, 3H), 2.59 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.34 (s), 163.09 (s), 138.07 (s), 137.11 (s), 129.05 (s), 126.08 (s), 124.86 (s), 120.94 (s), 117.22 (d, *J* = 8.1 Hz), 116.62 (s), 116.39 (s), 26.07 (s); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  116.76 (s).

#### 2.2.2. Synthesis and characterization of N,N'-(1,4-phenylene)bis(3-oxo-2-(phenyldiazenyl)butanamide) (**2-a**) and N,N'-(1,4-phenylene)bis(2-((4-fluorophenyl)diazenyl)-3-oxobutanamide) (**2-b**)

Aniline (3.73 g, 0.04 mol) was stirred with concentrated hydrochloric acid (9.9 mL) in water (19 mL). A solution of sodium nitrite (2.90 g, 0.042 mol) in water (6.8 mL) was added with stirring over 30 min keeping the temperature below 5 °C with ice cooling for 30 min. The pH was then adjusted to 6 by addition of sodium acetate anhydrous. The presence of a nitrous acid excess of sodium

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