



# Synthesis and X-ray analysis of a perfluoroalkyl-substituted azobenzene dye



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## ABSTRACT

A search for colorants capable of reducing the surface energy of synthetic fibers as well as adding color led to the synthesis and characterization of the repellency behavior of dyes such as 4-*N,N*-diethylamino-4'-tridecafluorohexylazobenzene. Unexpectedly high surface energy values and a low fluorine content on fiber surfaces then led to an interest in determining the crystal structure of this new dye. Accordingly, a single crystal was grown from acetone solution, and its structure was established using X-ray diffraction analysis. Interestingly, it was found that the azobenzene skeleton is appreciably nonplanar, having an N2–N1–C1–C2 torsion angle of 30.6°, despite the absence of substituents *ortho* to the azo bond. Further, the structure is characterized by head-to-tail molecular stacking and the *N*-ethyl groups in the molecule are positioned above the aminobenzene plane on the same side. It is likely that this combination of factors contribute to the observed surface properties of the target dye.

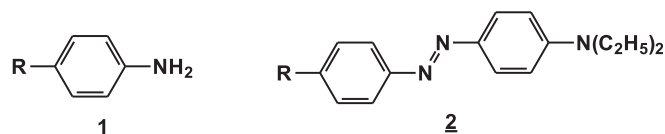
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## 1. Introduction

Our long-standing interest in arylazo compounds stems from the fact that they comprise the dominant class of synthetic colorants, are relatively easy to make, are widely used when color is sought, and their aromatic amine precursors remain of considerable interest in environmental studies. In addition, their method of synthesis opens the door to a myriad of colorants that are customized to fit specific applications. For instance, azo compounds derived from judiciously selected donor and acceptor groups can be used in non-linear optics and optical data storage [1,2]. From such studies, it is known that the optical properties obtained depend not only on the spectroscopic properties of the constituent molecules, but also on their crystallographic properties [3–5].

As part of a study aimed at designing synthetic dyes that simultaneously convey color and reduce the surface energy of natural and synthetic fibers, type **1** arylamines were used to synthesize azo dyes such as **2**. Following their application to synthetic fibers, it was found that the resultant surface energy was

surprisingly higher than expected and ESCA (Electron Spectroscopy for Chemical Analysis) experiments showed a low fluorine level on the fiber surface – despite the presence of a built-in perfluorohexyl chain. Since it was known from prior studies that dye conformations in the crystalline state influence technical performance [6] and that several recent studies have benefited from the characterization of monoazo compounds using single crystal X-ray analysis [7–12], the structural characteristics of dye **2b** were assessed using this method. While the results did not provide an unequivocal explanation for the observed surface energy properties of dye **2b**, the resultant structure was quite interesting and seemed worthwhile to report. With these points in mind, we describe here the synthesis and first crystal structure of a perfluoroalkyl-substituted azobenzene dye, namely 4-*N,N*-diethylamino-4'-tridecafluorohexylazobenzene (**2b**).



a. R = C<sub>4</sub>F<sub>9</sub>; b. R = C<sub>6</sub>F<sub>13</sub>

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## 2. Experimental

### 2.1. General

All chemicals used in this study were purchased from either Aldrich Chemical Company or Fisher Scientific Company. Thin layer chromatography (TLC) was conducted using Whatman 250  $\mu\text{m}$  silica gel 60A plates. Mass spectral data were generated using a Jeol HX110 double-focusing mass spectrometer, employing FAB(+) or ESI(+) as the ionization method, and  $^1\text{H}$  NMR spectra were recorded on a General Electric Omega 300 MHz spectrometer using  $\text{CDCl}_3$  as the solvent.

### 2.2. Synthesis of arylamines **1a–1b**

A mixture of nonafluorobutyl iodide (9.80 g, 27.8 mmol), 4-iodoaniline (5.59 g, 25 mmol), and copper bronze (5.34 g, 83.3 mmol) in DMSO (50 mL) was stirred at 120 °C for 10 h. The inorganic salts were removed by filtration, and the filtrate was diluted with  $\text{H}_2\text{O}$  (100 mL) and diethyl ether (100 mL). After stirring for 5 min, the organic layer was collected and washed five times with  $\text{H}_2\text{O}$  (100 mL) to remove DMSO and nonafluorobutyl iodide, and evaporated under reduced pressure. The mixture was distilled to give **1a** (bp 108–111 °C, 28 in Hg) as a pale yellow liquid (4.55 g, 59%). TLC:  $R_f = 0.59$  (hexane:EtOAc/1:1). EI-MS  $m/z$  (rel. int.): 311 ( $\text{M}^+$ , 31), 295 (54), 142 (100).

A mixture of 4-tridecafluorohexyl iodide (12.38 g, 27.8 mmol), 4-iodoaniline (5.59 g, 25 mmol), and copper bronze (5.34 g, 83.3 mmol) in DMSO (50 mL) was stirred at 120 °C for 10 h. Inorganic salts were removed by filtration, and the filtrate was diluted with  $\text{H}_2\text{O}$  (100 mL) and diethyl ether (100 mL). After stirring for 5 min, the organic layer was collected and washed five times with  $\text{H}_2\text{O}$  (100 mL) to remove DMSO and 4-tridecafluorohexyl iodide, and evaporated under reduced pressure. The crude product was distilled to give **1b** (bp 110–114 °C, 28 in Hg) as a pale yellow liquid (4.95 g, 48%) [13]. TLC:  $R_f = 0.64$  (hexane:EtOAc/1:1). FAB-MS (positive ion)  $m/z$  (rel. int.): 412 ( $\text{M} + \text{H}$ , 73), 411 ( $\text{M}^+$ , 100).

Both perfluoroalkyl-substituted arylamines were used without further characterization.

### 2.3. Synthesis of dyes **2a–2b**

To a stirred suspension of compound **1a** (3.11 g, 10 mmol) in 2 M HCl (15 mL) at 0–5 °C,  $\text{NaNO}_2$  (0.71 g, 10.2 mmol) in  $\text{H}_2\text{O}$  (3 mL) was slowly added. The diazotization step was continued for 30 min and excess  $\text{HNO}_2$  was destroyed by the addition of solid sulfamic acid. The resultant diazonium salt solution was added dropwise to *N,N*-diethylaniline (1.53 g, 10.2 mmol) dissolved in HOAc (25 mL), at a rate such that the temperature remained below 5 °C. The pH of the coupling reaction was maintained near pH 5 by the addition of solid  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ . The coupling step was continued for 3 h and the mixture produced was stirred overnight. The precipitate was collected by filtration, washed with  $\text{H}_2\text{O}$ , and air dried to give **2a** as an orange solid (3.49 g, 74%).  $\lambda_{\text{max}}/\epsilon_{\text{max}}$  (EtOH) = 444 nm/22,300  $\text{L mol}^{-1} \text{cm}^{-1}$ ; TLC:  $R_f = 0.82$  (hexane:EtOAc/1:1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.21–1.26 (t, 6H,  $J = 4.0$ ),  $\delta$  3.43–3.50 (q, 4H,  $J = 4.0$ ),  $\delta$  6.71–6.74 (d, 2H,  $J = 7.5$ ),  $\delta$  7.52–7.68 (d, 2H,  $J = 7.5$ ),  $\delta$  7.86–7.92 (dd, 4H,  $J = 8.4$ ). FAB-MS (positive ion)  $m/z$  (rel. int.): 472 ( $\text{M} + \text{H}$ , 78), 471 ( $\text{M}^+$ , 100), 470 (36).

To a stirred suspension of compound **1b** (4.11 g, 10 mmol) in 2 M HCl (15 mL) at 0–5 °C,  $\text{NaNO}_2$  (0.71 g, 10.2 mmol) in  $\text{H}_2\text{O}$  (3 mL) was slowly added. The diazotization step was continued for 30 min and excess  $\text{HNO}_2$  was destroyed by adding solid sulfamic acid. The resultant diazonium salt solution was added drop wise to *N,N*-diethylaniline (1.53 g, 10.2 mmol) dissolved in HOAc (25 mL), at a

rate such that the temperature remained below 5 °C. The pH of the coupling reaction was maintained near pH 5 by the addition of solid  $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ . The coupling step was continued for 3 h and the mixture was stirred overnight (14 h). The precipitate was collected by filtration, washed with  $\text{H}_2\text{O}$ , and air dried to give **2b** as a reddish orange solid (3.71 g, 65%).  $\lambda_{\text{max}}/\epsilon_{\text{max}}$  (EtOH) = 444 nm/23,500  $\text{L mol}^{-1} \text{cm}^{-1}$ ; TLC:  $R_f = 0.79$  (hexane:EtOAc/1:1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.21–1.26 (t, 6H,  $J = 4.0$  Hz),  $\delta$  3.43–3.50 (q, 4H,  $J = 4.1$  Hz),  $\delta$  6.71–6.74 (d, 2H,  $J = 7.54$  Hz),  $\delta$  7.65–7.69 (d, 2H,  $J = 7.53$  Hz),  $\delta$  7.86–7.92 (dd, 4H,  $J = 8.39$  Hz); FAB-MS (positive ion)  $m/z$  (rel. int.): 572 ( $\text{M} + \text{H}$ , 76), 571 ( $\text{M}^+$ , 100); ESI-MS (+),  $\text{C}_{22}\text{H}_{19}\text{F}_{13}\text{N}_3$  [ $\text{M} + \text{H}$ ] $^+$ : calcd. 572.1371, obsd. 572.1365.

### 2.4. X-ray analysis

X-ray quality crystals of dye **2b** were grown by slow evaporation of an acetone solution at room temperature. The selected crystal was mounted on a nylon loop using a small amount of Paratone N oil, and X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer at 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 4145 reflections with  $5.24^\circ < 2\theta < 42.22^\circ$ . The data collection strategy involved the use of a number of  $\omega$  and  $\phi$  scans to collect data up to  $42.32^\circ$  ( $2\theta$ ) and the frame integration was performed using SAINT [14]. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS [15].

The structure was solved by direct methods using the SIR92 program [16]. All non-hydrogen atoms were obtained from the initial solution and the hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on  $F^2$ . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the XL program from SHELXTL [17], graphic plots were produced using the NRCVAX crystallographic program suite. Crystallographic data are summarized in Table 1. These data have been deposited with the Cambridge Crystallographic Data Centre and was assigned CCDC 1057216.

### 2.5. Electron density calculations

Electron density calculations were conducted using PiSystems version 6.3, Copyright 2002–2013 Neutronix Software. This software allows the semi-empirical quantum-theoretical calculation of the  $\pi$  system of organic molecules. Values obtained from calculating electron-density alterations correspond to increase (decrease) of the negative charge at a specific atom. The values obtained have the unit number of electrons and the algebraic sum of these numbers over all  $\pi$  atoms is zero. Further, these values show the difference in the  $\pi$ -electron densities (=charge orders) between the ground and the electronically excited state at each atom of the  $\pi$  system, i.e. the shift of the electrons in the  $\pi$  system when it is electronically excited.

## 3. Results and discussion

### 3.1. Dye synthesis

The synthesis of monoazo dyes having a perfluoroalkyl chain in the diazo component is illustrated in Fig. 1. In step 1, 4-(nonafluorobutyl)aniline and 4-(tridecafluorohexyl)aniline were prepared by the reaction of 4-iodoaniline with the corresponding perfluoroalkyl iodides (RI) in the presence of copper bronze [18]. Diazotization of 4-(perfluoroalkyl)anilines (**1**) followed by coupling

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