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Synthesis and Characterization of Photoactive Methyl 4-Bromo-3-((2,6-Difluorophenyl)diazenyl) Benzoate

Eric D. Sylvester¹ · Jason B. Benedict²

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Abstract

The synthesis and structure of a novel ortho-fluoroazobenzene, methyl 4-bromo-3-((2,6-difluorophenyl)diazenyl) benzoate is described. The title molecule crystallizes in the centrocemetric space group P-1 with two rotomer molecules of the title compound in the asymmetric unit. The position of ortho-fluoro azo rings differ between the two rotomers with one molecule having a rotation angle of 4.4° and the other molecule having a rotation angle of 76.9° with respect to the methyl 4-bromobenzoate. Due to the tight packing the pure molecule was not seen to be photoactive. However, in solution the absorption bands in the visible region show a separation of about 20 nm as expected for o-fluoroazobenzene. A comparison to related and previously published co-crystals of substituted azobenzenes are presented.

Graphic Abstract

The structure of a novel ortho-fluoroazobenzene, methyl 4-bromo-3-((2,6-difluorophenyl)diazenyl) benzoate reveals the presence of two crystallographically unique rotomers in the lattice, and although the molecule is photoactive in solution, the close-packed lattice appears to inhibit photo-induced structural reorganization in the crystalline state.



 $\textbf{Keywords} \ Crystal \ structure \cdot Photochrome \cdot Ortho-fluoroazobenzene \cdot Azobenzene \cdot Twisted-confirmation$

Jason B. Benedict jbb6@buffalo.edu

Introduction

Photochromic solid-state materials are appealing for a wide variety of applications including separations, advanced sensors, drug delivery, data storage and molecular switches through external control [1–7]. It has been shown that photomechanical molecular crystals can undergo various

¹ 730 Natural Sciences Complex, Buffalo 14260-3000, USA

² 771 Natural Sciences Complex, Buffalo 14260-3000, USA

mechanical motions, including twisting, bending and even jumping, using light as the reaction mechanism, thus, converting photochemical energy to mechanical energy [8–10]. The development of novel photoactive molecules that may be incorporated into a variety of solid-state materials is crucial for the advancement of next generation light responsive smart materials [11].

The integration of azobenzenes into photoswitchable materials has been of investigated due their desirable photoactive properties. This class of photoswitch often exhibits extremely fast trans to cis isomerization, on the order of picoseconds [12], with overall excellent resistance to fatigue [13, 14]. However, unsubstituted azobenzene based molecules generally exhibit a thermal back reaction from cis to *trans* without the use of light at room temperature [15-17]. The inability to perform as a bi-stable photoswitch and the pronounced overlap of the cis/trans excitation bands in the visible region often results in a mixture of both isomers when the materials are irradiated. Because of this, materials which contain azobenzenes tend to be studied under constant irradiation of ultraviolet light to maximize the concentration of cis isomer present. The need for constant UV irradiation diminishes the potential utility of these photoswitches, especially in biological systems [18, 19]. However, recently it has been found that the chemical functionalization of the phenyl ring attached to the azo group, namely ortho-fluoro substitution, can greatly increase the stability of the cis form of azobenzenes and increase the spectral separation of the isomers as well [20].

It has been shown that ortho-fluoroazobenzenes, like 2,6-difluoroazobenzene, can be stable in the *cis* form for up to two years in the absence of light at room temperature [21]. Ortho-fluoroazobenzenes also have the advantageous property of separation of the *cis* and *trans* absorbance bands in the visible light region [21]. This means that the material is photoswitchable using only visible light eliminating the need for the more hazardous UV light altogether.

These improved properties of o-fluoroazobenzenes relative to standard azobenzenes has previously been explained using molecular orbital theory [21]. For azobenzenes, the interaction with the lone pair orbitals on the N atoms from the azo functional group determine the overall *n* (HOMO) orbital level [22]. The trans isomer has lone pair orbitals that interact along the N-N sigma bond greatly reducing the energy of the *n* orbital level; whereas, the repulsion of the lone pair orbitals from the azo functional group of the cis isomer results in a higher energy HOMO [23]. Also, the decrease of π -electron delocalization from the large dihedral angles of the C-N = N-C bonds only found in the *cis* isomer results in a larger net separation between the π and π^* energies causing an increased π^* orbital and a lower π orbital [24, 25]. Therefore, the small increase of the *n* orbital level in the cis form compared to the trans isomer is counteracted be the small increase of the π^* orbital; thus the change of relative energies between the *cis* and *trans* forms of azobenzenes are similar.

The difference in the excitation energy of the *cis* isomer relative to the *trans* isomer will cause a separation of the absorbance bands of both the *cis/trans* isomers in the visible light region. The addition of electron withdrawing ortho-fluoro functional groups should lower the *n*-electron density of the cis isomer, causing a decrease in the overall repulsion of the lone pair orbitals. This should lower the HOMO relative energy resulting in a larger *n* to π^* excitation energy for the cis isomer.

With these properties in mind, a novel bromine-functionalized ortho-fluoroazobenzene photoswitch, methyl 4-bromo-3-((2,6-difluorophenyl)diazenyl) benzoate (1) (Scheme 1), was synthesized and determined to be photoactive. Furthermore, 1 exhibited the spectral separation characteristic of o-fluoroazobenzenes, and possessed functional groups suitable for creating light-responsive halogen-bonded crystalline solids [26, 27]. Halogen-bonded co-crystals have been used to monitor temperature effects on molecular pedal motion of molecular solids [28]. Additionally, 1 may be useful as an intermediate compound for additional ortho-fluoroazobenzene photoswitches as the ester is readily converted to the carboxylic acid to create hydrogen bonded materials and the halogen may be used to perform coupling reactions. Here we present the synthesis and characterization of 1 which includes a detailed analysis of unique structural features found in the neat crystalline solid.

Experimental Details

Synthetic Procedure

All chemicals were obtained commercially from Sigma-Aldrich and Combi-Blocks, and used as received.



Scheme 1 Synthetic route of 1

1,3-Difluoro-2-Nitrosobenzene

The synthetic procedure was performed using previously reported methods [21]. First, 2,6-difluoroaniline was reacted to form 1,3-difluoro-2-nitrosobenzene by partially dissolving 4.76 g of Oxone (0.0155 mol, 2 eq) in 10 mL of DI water in a flask with a solution of 1 g of 2,6-difluoroaniline (0.0078 mol, 1 eq) in 10 mL DCM. The flask was allowed to react in open air at room temperature for 6 h, stirring vigorously to create emulsions between the organic phase and aqueous phase. Next, the organic DCM layer was separated from the aqueous layer, and the aqueous layer was extracted further using 20 mL of DCM, three times. The combined DCM extracts were then washed 3 times using 10 mL of DI water. The organic solvent was then removed using rotary evaporation resulting in a brown crude solid of 1,3-difluoro-2-nitrosobenzene, 1.086 g (98%).

¹H NMR (CDCl₃, 400 MHz) δ 8.24(s, 1H), 7.66(dd, 2H), 7.53(t, 1H), 7.44(t, 2H).

Methyl 4-Bromo-3-((2,6-Difluorophenyl)diazenyl) Benzoate (1)

To form 1, 1.30 g of methyl 3-amino-4-bromobenzoate (0.0057 mol, 1 eq) was mixed with 0.81 g of 1,3-difluoro-2-nitrosobenzene (0.0057 mol, 1 eq) in 20 mL of glacial acetic acid. The reaction was heated to 80 °C for 3 days to form a dark purple viscus solution. The solution was neutralized with saturated sodium bicarbonate and extracted with ethyl acetate and purified by column chromatography using 30% ethyl acetate in hexanes. The resulting 1 was an orange/red solid, 1.25 g (62%). Then, 20 mg of 1 was dissolved in 5 ml of ethyl acetate and was allowed to evaporate uncovered resulting in orange plate crystals suitable for single crystal structure determination.

¹H NMR (CDCl₃, 400 MHz) δ 8.25(s, 1H), 8.02(d, 1H), 7.85(d, 1H), 7.39(m, 1H), 7.08(dd, 2H), 3.95(s, 4H).

X-ray Diffraction

X-ray diffraction data were collected on a Bruker SMART APEX2 CCD diffractometer installed at a rotating anode source (MoK α radiation, $\lambda = 0.71073$ Å), and equipped with an Oxford Cryosystems (Cryostream700) nitrogen gas-flow apparatus. The data were collected by the rotation method with a 0.5° frame-width (ω scan). Using Olex2 [29], the structure was solved with the XS structure solution program [30] using Direct Methods and refined with the olex2.refine refinement package [31].

UV-Vis Spectroscopy

All UV–*vis* absorption spectra were recorded in absolute darkness to prevent any room lights from interfering in the photochemical reactions. The samples were irradiated with a Thorlabs 365 nm LED (4.1 mW) and Thorlabs 405 nm LED (4.1 mW). The UV–*vis* spectra were collected using a Perkin Elmer Lambda 35 dual beam UV–*vis* spectrometer.

¹H NMR Spectroscopy

Nuclear magnetic resonance spectra were recorded on a Varian Inova-400 MHz NMR spectrometer. For the NMR light studies, the spectra were obtained within 5 min of irradiation.

Results and Discussion

Structural Commentary

1 crystallizes in the centrosymmetric space group *P*-1 with two crystallographically independent molecules in the asymmetric unit (Fig. 1). The two molecules are easily distinguished from one another as one molecule is nearly planar, 1_{\parallel} , while the other exhibits a pronounced rotation about the N_4 - C_{21} bond, 1_{\perp} . To our knowledge, this is the first reported pure azobenzene crystal structure that contains both planar and nearly perpendicular rotational isomers within the same lattice. Crystal data, data collection and structure refinement details are summarized in Table 1.

In order to quantify the twist present for both molecules, the angle between the surface normal vectors of the mean planes for the two phenyl rings was determined using Olex2 [29]. For 1_{\parallel} , the angle was determined to be 4.4(1)°. In the case of 1_{\perp} , the two rings were nearly perpendicular with an angle between the two surface normal vectors of 76.9(1) ° (Fig. 2).

While planar or nearly planar azobenzene structures are common in the literature, using the CCDC database [32], only a few neat twisted azobenzenes have been previously reported in the literature [33–36]. For example, in the structure of dichloroazobenzene (Ref code: XOT-CAM, Fig. 3), the twist angle was reported to be 74.9(5) [36] which is nearly identical to 1_{\perp} . The crystal structure of XOTCAM does not contain the co-planar rotamer of the dichloroazobenzene.

Supramolecular Features

In the structure of **1**, extended sheets of 1_{\parallel} held together by $\pi_{\dots}\pi$ stacking, interact with adjacent 1_{\perp} molecules through C–Br_{...}Br–C halogen bonds forming a 3-dimentional lattice

Fig. 1 Asymmetric unit of 1 showing the numbering scheme. The hydrogen atoms were removed for clarity. Atom colors: fluorine (green), bromine (maroon), oxygen (red), nitrogen (blue), and carbon (grey) (Color figure online)



 Table 1 Data collection and structure refinement details for 1

Empirical formula	$C_{56}H_{36}Br_4F_8N_8O_8$
Formula weight	1420.56
Temperature (K)	90
Crystal system	triclinic
Space group	P-1
a (Å)	7.6992 (11)
b (Å)	11.5425 (18)
<i>c</i> (Å)	15.642 (2)
α (°)	83.709 (5)
β (°)	85.431 (5)
γ (°)	77.561 (5)
Volume (Å ³)	1347.0 (4)
Z	1
ρ_{calc} (g/cm ³)	1.751
$\mu (mm^{-1})$	3.08
F(000)	703.6
Crystal size (mm ³)	$0.1 \times 0.02 \times 0.01$
Radiation	Mo Ka ($\lambda = 0.71073$)
2Θ range for data collection (°)	2.62 to 56.32
Index ranges	$ -10 \le h \le 10, -15 \le k \le 15, -20 \le 1 \le 20 $
Reflections collected	28,109
Independent reflections	6593 [R _{int} =0.0774, R _{sigma} =0.0761]
Data/restraints/parameters	6593/0/381
Goodness-of-fit on F ²	1.032
Final R indexes $[I \ge 2\sigma (I)]$	R1 = 0.0450, wR2 = 0.0879
Final R indexes [all data]	R1 = 0.0802, wR2 = 0.1001
Largest diff. peak/hole (e $Å^{-3}$)	0.89/- 0.93

(Fig. 4). The molecule 1_{\perp} forms 1-D chains with complementary molecules of 1_{\perp} through $\pi_{...}\pi$ interactions of the twisted azobenzene ring of 1_{\perp} (Fig. 5). Halogen bonding is categorized based on whether the halogens are less than the sum of the van der Waals radii, the angle between the bonding halogens where, $\angle X_1 \cdots X_2 - C_2 = \theta_1$ and $\angle C_1 - X_1 \cdots X_2 = \theta_2$ (X = halogen atom) [37, 38]. Type I halogen bonding is defined as, $0^{\circ} \leq |\theta_1 - \theta_2| \leq 15^{\circ}$, type II halogen bonding is defined as a quasi type I/type II halogen bond [37, 38]. Since the halogens for 1_{\parallel} and 1_{\perp} are within halogen bonding distance (Br_{1...}Br₂=3.630 Å), the halogen bonding angles were found to be $\angle C_{15}$ -Br_{2...}Br₁=169° and, $\angle C_1$ -Br_{1...}Br₂=97°, thus the halogen bond is described as type II.

Database Survey

A search of the Cambridge Structural Database (version 5.41 updated through August 2020) using orthro-fluoroazobenzene returned 77 hits when the protons were not specified. Similar molecules containing halogen-halogen interactions between halogen substituted azobenzenes have been reported, e.g. AZ07 (Fig. 6a) [39]. The structure of AZ07 pack using C–Br... π interactions, π ... π stacking of the aromatic rings, and more notable type II halogen bonding C–Br...Br–C, forming a herringbone shaped pattern. What gives rise to the distinctive herringbone shape is the type II halogen bond (Br₁...Br₁=3.526 Å, \angle C₁–Br₁...Br₁=169°).



Fig.4 Diagram illustrating **a** the halogen bonding network of **1** viewed down [100] and **b** extended sheets interactions of 1_{\parallel} molecules viewed down [010]; 1_{\perp} interactions were omitted for clarity. Atom

colors: fluorine (yellow), bromine (brown), oxygen (red), nitrogen (blue), carbon (grey), and hydrogen (white) (Color figure online)

The compound AZ07 has similar halogen contacts as the $1_{\perp}/1_{\parallel}$ reported (Fig. 6b). The contacts of 1_{\parallel} with 1_{\perp} molecules are C-Br...Br-C type II halogen bonds (Br₁...Br₂ = 3.630 Å, $\angle C_{15}$ -Br₂...Br₁ = 169°, $\angle C_1$ -Br₁...Br₂ = 97°). However, **1** is unique due to the nonplanar nature of 1_{\perp} , causing the overall structure to have 3-dimensionality not found in the extended sheets of the planar AZ07.

Photoisomerization

The photochromism of **1** in solution was monitored using UV-vis absorption spectroscopy. The following three spectra of a 23 μ M solution of **1** in MeOH were obtained after dissolving the compound, irradiating the solution with 365 nm light for 1 h, and finally after irradiating the solution with 405 nm light for 1 h (Fig. 7). As expected for



Fig. 5 Diagram illustrating the $\pi_{..}\pi$ interactions of 1_{\perp} molecules viewed down [001]; 1_{\parallel} interactions were omitted for clarity. Atom colors: fluorine (yellow), bromine (brown), oxygen (red), nitrogen (blue), carbon (grey), and hydrogen (white) (Color figure online)

o-fluoroazobenzenes, the absorption maxima of the *cis* and *trans* isomers in the visible region show a separation of about 20 nm.

The photoisomerization was also monitored using ¹H-NMR spectroscopy. Two ¹H-NMR spectra were obtained after irradiating the sample using the same irradiation conditions mentioned above (Fig. 7). Although both spectra collected showed the presence of both cis and trans isomers, the bulk solution after irradiation with 405 nm light for 1 h indicated the majority of the mixture was the trans isomer (Fig. 8a). This can be seen by comparing the signals at 3.95 ppm (**a**), 7.08 ppm (**b**), 7.39 ppm (**c**) and, 7.85 ppm (**d**) with the signals of the *cis* isomer at 3.82 ppm (\mathbf{a}'), 6.83 ppm $(\mathbf{b'})$, 7.12 ppm $(\mathbf{c'})$, and 7.75 ppm $(\mathbf{d'})$. After irradiating the sample with 365 nm of light for 1 h, the increase in the concentration of the cis isomer was observed (Fig. 8b). The integrated intensities of the peaks located at 3.95 ppm (a) and 3.82 ppm (a'), representing the methyl ester for the trans and cis isomers, respectively were then used to calculated relative fractions of the two isomers in the solutions. The methyl ester peaks were selected due to them being well isolated and readily determined for both isomers. The spectrum collected after irradiating the sample using 405 nm of light for 1 h indicated that the solution contained 90% *trans* isomer and 10% *cis*. After irradiating the sample for 1 h using 365 nm of light, the relative concentration of the *cis* isomer increased resulting in a solution containing a 70% to 30% ratio of *trans* and *cis* isomers, respectively.

To assess the degree to which the pure molecular crystal was photochromic, the crystal of **1** which contains only the *trans* isomer was irradiated with 365 nm of light for a period of 1 h. A second crystal structure was then obtained after irradiation. Unfortunately, although somewhat expected, there was no change in the diffraction pattern after irradiation. Subsequent analysis revealed no new regions of electron density in the solved structure.



Fig. 7 UV–*vis* spectra of a 23 μ M solution of **1** in MeOH (triangle, red line), after irradiating with 365 nm for 1 h (square, blue line) and, 405 nm for 1 h (circle, green line); inset is an expansion of the visible absorption region (Color figure online)



Fig. 6 Crystal structure highlighting the halogen interactions of a AZ07 [39] and b 1. Atom colors: fluorine (green), bromine (maroon), oxygen (red), nitrogen (blue), carbon (grey), and hydrogen (white) (Color figure online)

Fig. 8 ¹H-NMR (400 MHz, CDCl₃) spectrum of collected **1** after **a** 1 h of irradiation using 405 nm light and **b** after 1 h of irradiation using 365 nm light



As is often the case for azobenzene-based systems, the tight crystal packing prevent any large structural changes needed for isomerization [40, 41] Using a probe radius of 1.2 Å and approximate grid spacing of 0.7 Å in Mercury, resulted in zero calculated residual void space within the crystal lattice 1 (Fig. 9). This is consistent with previously reported non-photochromic neat azobenzene crystals which exhibit tightly packed crystalline lattices.

Conclusion

The successful synthesis and characterization of a novel bromine-functionalized ortho-fluoroazobenzene photoswitch will be of interest to researchers seeking to design light-responsive halogen-bonded materials. The crystal structure of **1** confirms the chemical structure of the



Fig.9 Space filling model of **1** highlighting the tight packing. Atom colors: fluorine (yellow), bromine (brown), oxygen (red), nitrogen (blue), carbon (grey), and hydrogen (white) (Color figure online)

molecule and contains two distinct rotamers of the *trans* isomer. Unfortunately, as with many azobenzenes, this one included, the pure molecular crystals do not exhibit photoisomerization. Although the crystal of **1** is not photoactive, the synthesized molecule in solution exhibits the same band separation in the visible light region between the *cis* and *trans* isomers expected with *o*-fluoroazobenzenes. As photoisomerization was observed in solution, it seems entirely possible that multi-component crystals containing **1** could likewise exhibit photoactivity. Therefore **1** may be useful as an intermediate for the design of future ortho-fluoroazobenzene photoswitches or as a building block for photo-responsive halogen-bonded materials.

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