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Crystal Structure of 2-Trifluoromethyl-4′-dimethylaminoazobenzene

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Crystals of 2-trifluoromethyl-4′-dimethylaminoazobenzene (2-TFMDAB) are orthorhombic, space group *Pbca* with a = 15.625(4), b = 23.028(6), c = 7.685(2)Å, and Z = 8. The structure was solved by direct methods (SIR88) and refined to a final R value of 0.049 for 2536 reflections ($I>0.80\sigma(I)$). 2-TFMDAB has a *trans* geometry about the azo linkage. The bond lengths and angles are similar to those of other azobenzene compounds. The abnormal UV-vis absorption spectrum in an acidic solution can be explained by the existence of the bulky and electronegative CF_3 group at the 2-position, which prevents protonation at the Nβ atom of the azo group in an acidic solution.

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4′-Dimethylaminoazobenzene dyes are used as acid-base indicators because of a discernible color change upon a change of the pH. Typically, an aqueous solution of this dye group is colored yellow at neutral-to-alkaline pH, and turns orange-red when the pH is lowered to below the color-change interval. This color change has been ascribed to a structure change from the neutral azo form (I) to the protonated azo form (IIa), which has a resonance structure of the quinoid form (IIb), as shown in Fig. 1.[1] In acidic solution, the protonated azo form (II) is in equilibrium with the colorless ammonium form (III). The chemical species (I), (II) and (III) are associated with absorptions at around 460, 500 and 320 nm, respectively, in the UV-vis absorption spectra. We have investigated the resonance Raman spectra of aqueous solutions of 4′-dimethylaminoazobenzene dyes, and characterized the Raman bands which originated from molecular species (I), (II) and (III).[2-4] During the course of a study on the complex formation of azo dyes with peptides, we prepared 2-trifluoromethyl-4′-dimethylaminoazobenzene (2-TFMDAB). Unlike other 4′-dimethylaminoazobenzene dyes, this compound exhibits a color change from yellow to colorless upon going from neutral to acidic pH. In this work, we undertook the X-ray analysis of 2-TFMDAB in order to examine the structural features that

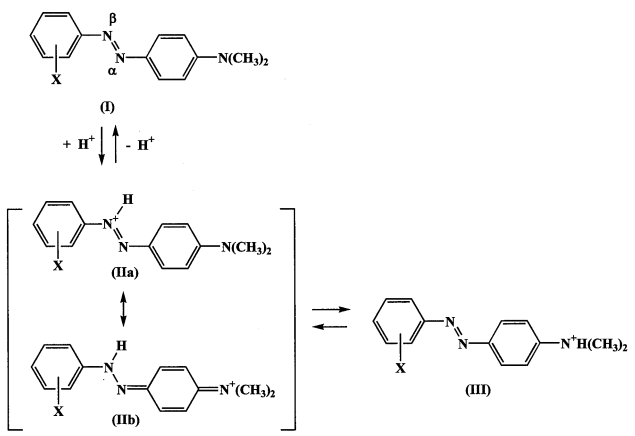

Fig. 1 Protonation equilibrium of 4′-dimethylazobenzene dye. The substituent X is 4-SO_3^- for methyl orange, 2-COOH for methyl red and 2-CF3 for 2-TFMDAB.

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Table 1 Crystal and experimental data

Formula: $C_{15}H_{14}N_3F_3$
Formula weight: 293.29
Crystal color, habit: orange-red, plates
Crystal size: 0.20 × 0.13 × 0.03 mm
Crystal system: orthorhombic
Space group: *P bca* Z = 8
Radiation: Mo K_α(0.71069 Å)
T = 123 K
$2\theta_{max}$ = 55.0°
F(0 0 0) = 1216.00
a = 15.625(4)Å
b = 23.028(6)Å
c = 7.685(2)Å
V = 2765(1)Å^3
D_{calc} = 1.409 g/cm^3
μ= 1.14 cm^{-1}
R, Rw = 0.049, 0.070
No. observations = 2536 ($I>0.80\sigma(I)$)
No. variables = 246
Goodness of fit = 0.98
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.33 eÅ^{-3}
$(\Delta\rho)_{min}$ = –0.36 eÅ^{-3}
Measurement: Quantum CCD/Rigaku AFC-7
Program system: teXsan
Structure determination: direct method (SIR88)
Refinement: full-matrix least-squares

Table 2 Positional parameters of non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
F(1)	0.2506(1)	0.26046(9)	0.5985(3)	2.74(5)
F(2)	0.1623(1)	0.20898(9)	0.7428(3)	2.76(5)
F(3)	0.2183(2)	0.1755(1)	0.5090(3)	3.65(6)
N(1)	0.2259(2)	0.0956(1)	0.8096(4)	1.76(6)
N(2)	0.2307(2)	0.0440(1)	0.8677(4)	1.65(6)
N(3)	-0.0609(2)	-0.0957(1)	0.8298(4)	2.00(6)
C(1)	0.2352(2)	0.2064(2)	0.6526(5)	2.00(7)
C(2)	0.3087(2)	0.1822(1)	0.7540(5)	1.69(7)
C(3)	0.3838(2)	0.2149(2)	0.7707(5)	1.99(8)
C(4)	0.4511(2)	0.1944(2)	0.8700(5)	2.09(8)
C(5)	0.4442(2)	0.1416(2)	0.9544(5)	2.06(8)
C(6)	0.3715(2)	0.1084(2)	0.9392(5)	1.91(8)
C(7)	0.3036(2)	0.1277(2)	0.8361(5)	1.73(7)
C(8)	0.1561(2)	0.0107(1)	0.8460(4)	1.59(7)
C(9)	0.1569(2)	-0.0446(2)	0.9221(5)	1.79(7)
C(10)	0.0856(2)	-0.0801(2)	0.9161(5)	1.81(7)
C(11)	0.0105(2)	-0.0618(1)	0.8340(4)	1.61(7)
C(12)	0.0106(2)	-0.0063(2)	0.7539(5)	1.85(7)
C(13)	0.0816(2)	0.0290(1)	0.7612(5)	1.79(7)
C(14)	-0.0606(3)	-0.1522(2)	0.9101(7)	2.85(10)
C(15)	-0.1385(3)	-0.0761(2)	0.7425(6)	2.21(8)

$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Table 3 Selected bond lengths (Å), bond angles (˚) and torsion angles (˚)

Atom	Atom	Distance	Atom	Atom	Distance
F(1)	C(1)	1.334(4)	F(2)	C(1)	1.335(4)
F(3)	C(1)	1.339(4)	N(1)	N(2)	1.271(4)
N(1)	C(7)	1.437(4)	N(2)	C(8)	1.406(4)
N(3)	C(11)	1.362(4)	N(3)	C(14)	1.440(5)
N(3)	C(15)	1.457(5)	C(1)	C(2)	1.495(5)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N(2)	N(1)	C(7)	112.4(3)	N(1)	N(2)	C(8)	114.7(3)
C(11)	N(3)	C(14)	120.3(3)	C(11)	N(3)	C(15)	120.9(3)
C(14)	N(3)	C(15)	118.7(3)	F(1)	C(1)	F(2)	105.9(3)
F(1)	C(1)	F(3)	105.9(3)	F(1)	C(1)	C(2)	111.9(3)
F(2)	C(1)	F(3)	106.5(3)	F(2)	C(1)	C(2)	113.6(3)
F(3)	C(1)	C(2)	112.5(3)	C(1)	C(2)	C(3)	119.4(3)
C(1)	C(2)	C(7)	121.5(3)	N(1)	C(7)	C(2)	116.4(3)
N(1)	C(7)	C(6)	123.9(3)	N(2)	C(8)	C(9)	116.0(3)
N(2)	C(8)	C(13)	125.6(3)	N(3)	C(11)	C(10)	121.7(3)
N(3)	C(11)	C(12)	120.5(3)				

Atom	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Atom	Angle
N(1)	N(2)	C(8)	C(9)	-174.6(3)	N(1)	N(2)	C(8)	C(13)	3.0(5)
N(1)	C(7)	C(2)	C(1)	3.1(5)	N(1)	C(7)	C(2)	C(3)	-178.1(3)
N(1)	C(7)	C(6)	C(5)	178.7(3)	N(2)	N(1)	C(7)	C(2)	171.1(3)
N(2)	N(1)	C(7)	C(6)	-10.1(5)	N(2)	C(8)	C(9)	C(10)	177.0(3)
N(2)	C(8)	C(13)	C(12)	-177.1(3)	N(3)	C(11)	C(10)	C(9)	-178.6(3)
N(3)	C(11)	C(12)	C(13)	178.3(3)	C(1)	C(2)	C(3)	C(4)	177.2(3)
C(1)	C(2)	C(7)	C(6)	-175.7(3)	C(7)	N(1)	N(2)	C(8)	179.6(3)
C(10)	C(11)	N(3)	C(14)	-0.3(5)	C(10)	C(11)	N(3)	C(15)	-179.5(3)
C(12)	C(11)	N(3)	C(14)	179.5(4)	C(12)	C(11)	N(3)	C(15)	0.3(5)

Estimated standard deviations in the least-significant fugure are given in parentheses.

account for the abnormal color change.

2-TFMDAB was prepared by the diazotization of 2-aminobenzotrifluoride with sodium nitrite, followed by coupling with *N*-dimethylaniline. The crude product was purified through recrystallization from an ethanol solution. Orange-red plate crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of an aqueous ethanol solution at room temperature (m.p. 105 – 106˚C).

All of the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were determined from a difference Fourier map and were refined isotropically. The crystal and experimental data are listed in Table 1. The final

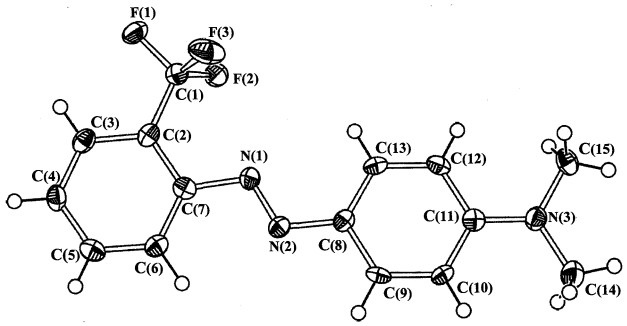

Fig. 2 Molecular structure of 2-TFMDAB with the atom numbering. Thermal ellipsoids of the non-hydrogen atoms are scaled to enclose 50% probability. The spheres of the hydrogen atoms are drawn in an arbitrary scale.

fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 2. Selected bond distances, bond angles and torsion angles are listed in Table 3.

The title compound has a *trans* geometry about the azo linkage. The bond lengths and angles are similar to those of other azobenzene compounds.[5-8] The N=N and the C–N bond lengths [N(1)–N(2) 1.271(4)Å, N(1)–C(7) 1.437(4)Å and N(2)–C(8) 1.406(4)Å] are in the normal range of azobenzene compounds. The N(1)··F(2) and the N(1)··F(3) distances of 2.841(3)Å and 2.956(3)Å are slightly shorter than the sum of the respective van der Waals radii [1.55 Å for the N atom and 1.47 Å for the F atom].[9] The two phenyl rings are almost co-planar; the dihedral angle between the planes defined by the two aromatic rings is 5.5(1)˚. This molecule adopts a conformation in which N(2) is oriented *anti* with respect to carbon C(2). The corresponding *syn* conformation would lead to a considerable repulsion between the CF_3 group and the electron pair on N(2), and no doubt a non-planar molecule would result.

An aqueous methanol solution (20%) of 2-TFMDAB gives a λ_{max} at 440 nm (ε_{max}, 21900) and 1 M hydrochloric acid solution shows a λ_{max} at 317 nm (ε_{max}, 19970) with a minor peak at 480 nm (ε, 1560). The present X-ray result shows that 2-TFMDAB has a normal *trans*-azobenzene structure. The abnormal UV-vis absorption spectrum in an acidic solution can be reduced to the existence of the bulky and electronegative CF_3 group at the 2-position, which prevents protonation at the Nβ atom of the azo group in an acidic solution, and eventually leads to the formation of a colorless species (III).

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