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X-ray Structure Analysis Online

Crystal Structure of 4-*N*,*N*-Dimethylamino-2,3,5,6-tetrafluorobenzonitrile

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Crystal structure of 4-*N*,*N*-dimethylamino-2,3,5,6-tetrafluorobenzonitrile (4F-DMABN) has been determined by X-ray diffraction. This compound crystallizes in the monoclinic system, space group $P2_1/c$, with unit cell parameters: a = 4.373(2)Å, b = 10.654(6)Å, c = 20.05(1)Å, β = 92.92(2)˚, Z = 4, V = 933.2(9)Å^3. The crystal structure was solved by direct methods and refined by full-matrix least squares to final values of R = 0.082 and Rw = 0.089 with 1129 reflections (I>1.20σ(I)). The dimethylamino group is out of the aromatic ring plane. The dihedral angle between the least-squares planes of the aromatic ring and the dimethylamino group is 32.73(5)˚. The aromatic ring has a significant quinoid nature.

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The photophysical behavior of 4-*N*,*N*-dimethylamino-benzonitrile (DMABN) in the excited singlet state has been extensively studied since the discovery of an unusual dual fluorescence by Lippert.[1] The molecular and crystal structures of DMABN and related species have been determined by a few research groups.[2–4] We have been interested in the photophysical properties of polyfluorinated analogs of DMABN. In this work, an X-ray structural analysis of 4-*N*,*N*-dimethylamino-2,3,5,6-tetrafluorobenzonitrile (4F-DMABN) was carried out in order to understand the effect of fluorine substitution to the phenyl group on the ground-state molecular structure.

The title compound was prepared in the following manner: a dimethyl sulfoxide solution (10 ml) containing pentafluorobenzonitrile (3.5 ml, 28.5 mmol), dimethylamine hydrochloride (0.50 g, 0.6 mmol), 18-crown-6 (0.16 g, 0.6 mmol) and anhydrous potassium carbonate (3.31 g, 23.9 mmol) was heated at 40˚C for 5.5 h. The reaction mixture was cooled and 100 ml of water was added. The organic layer was extracted with chloroform and dried with anhydrous sodium sulfate. The crude product was obtained by evaporation of the solvent and purified by recrystallization from an ethyl acetate/hexane solution (0.92 g, 70%). ^{1}H-NMR ($CDCl_3$): d 3.7 (6H). The melting point of the compound agreed with the value reported in the literature.[5]

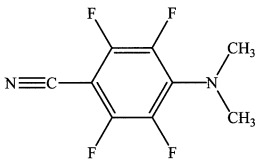

Fig. 1 Chemical structure of 4F-DMABN.

A colorless plate crystal of the title compound having approximate dimensions of 0.50 × 0.20 × 0.10 mm was mounted on a glass fiber. Data collections were performed at 116 K with graphite-monochromated Mo K_α radiation (λ = 0.71069 Å) on a Rigaku/MSC Mercury CCD diffractometer. The data were corrected for Lorentz and polarization effects. The structure

Table 1 Crystal and experimental data

Formula: $C_9H_6N_2F_4$
Formula weight: 218.15
Crystal color, habit: colorless, plates
Crystal size: 0.50 × 0.20 × 0.10 mm
Crystal system: monoclinic
a = 4.373(2)Å
b = 10.654(6)Å β = 92.92(2)˚
c = 20.05(1)Å
V = 933.2(9)Å^3
Space group: $P2_1/c$ Z = 4
D_{calc} = 1.553 g/cm^3
F(0 0 0) = 440.00
μ(Mo K_α) = 1.51 cm^{-1}
T = 116 K
$2\theta_{max}$ = 54.9˚ with Mo K_α (0.71069 Å)
No. observations = 1129 (I>1.20σ(I))
No. variables = 136
R, Rw = 0.082, 0.089
Goodness of fit = 1.63
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.31 eÅ^{-3}
$(\Delta\rho)_{min}$= –0.29 eÅ^{-3}
Diffractometer: Rigaku/MSC Mercury CCD
Program system: teXsan
Structure determination: direct method (SIR92)
Refinement: full-matrix least-squares

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Table 2 Positional parameters of non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
F(1)	1.6646(3)	0.4427(1)	0.27086(7)	2.66(3)
F(2)	1.5085(3)	0.4265(1)	0.14148(7)	2.74(3)
F(3)	0.8015(3)	0.1003(1)	0.18985(7)	2.56(3)
F(4)	0.9724(3)	0.1176(1)	0.31805(7)	2.62(3)
N(1)	1.4913(6)	0.3017(3)	0.4234(1)	4.26(5)
N(2)	1.0683(5)	0.2490(2)	0.09234(9)	2.69(4)
C(1)	1.4169(6)	0.2936(2)	0.3676(1)	2.97(4)
C(2)	1.3242(5)	0.2809(2)	0.2986(1)	2.27(4)
C(3)	1.4437(5)	0.3606(2)	0.2504(1)	2.06(4)
C(4)	1.3627(5)	0.3516(2)	0.1834(1)	2.16(4)
C(5)	1.1441(5)	0.2622(2)	0.1582(1)	2.12(4)
C(6)	1.0214(5)	0.1842(2)	0.2082(1)	2.10(4)
C(7)	1.1099(5)	0.1935(2)	0.2741(1)	2.11(4)
C(8)	1.0566(7)	0.3559(2)	0.0461(1)	3.08(5)
C(9)	0.9904(7)	0.1278(2)	0.0624(1)	3.22(5)

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

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

F(1)	C(3)	1.351(3)	F(2)	C(4)	1.343(3)		
F(3)	C(6)	1.350(3)	F(4)	C(7)	1.359(3)		
N(1)	C(1)	1.153(4)	N(2)	C(5)	1.352(4)		
N(2)	C(8)	1.469(4)	N(2)	C(9)	1.457(4)		
C(1)	C(2)	1.429(4)	C(2)	C(3)	1.408(4)		
C(2)	C(7)	1.393(4)	C(3)	C(4)	1.376(4)		
C(4)	C(5)	1.424(4)	C(5)	C(6)	1.427(4)		
C(6)	C(7)	1.362(4)					
C(5)	N(2)	C(8)	122.4(2)	C(5)	N(2)	C(9)	122.3(2)
C(8)	N(2)	C(9)	115.3(2)	N(1)	C(1)	C(2)	178.8(4)
C(1)	C(2)	C(3)	120.7(3)	C(1)	C(2)	C(7)	124.0(3)
N(2)	C(5)	C(4)	122.9(2)	N(2)	C(5)	C(6)	122.9(3)
N(2)	C(5)	C(4)	C(3)	-177.8(2)	N(2)	C(5)	C(6)	C(7)	176.6(3)
C(1)	C(2)	C(3)	C(4)	179.7(3)	C(1)	C(2)	C(7)	C(6)	179.0(3)
C(4)	C(5)	N(2)	C(8)	-34.5(4)	C(4)	C(5)	N(2)	C(9)	145.9(3)
C(6)	C(5)	N(2)	C(8)	148.1(3)	C(6)	C(5)	N(2)	C(9)	-31.4(5)

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

was solved by direct methods using SIR92. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All hydrogen atoms were located by a geometrical calculation and were not refined. All calculations were performed using the teXsan crystallographic software package.

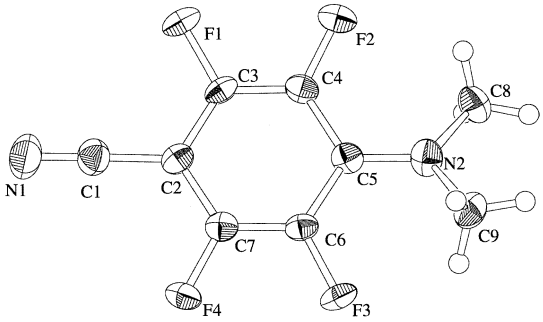

Fig. 2 Moleculer structure of 4F-DMABN with the atom numbering. Thermal ellipsoids of the non-hydrogen atoms are scaled to enclose 50% probability. The spheres of the hydrogen atoms are drawn in an arbitrary scale.

Table 1 gives the crystal data and experimental conditions. Figure 2 is an ORTEP diagram of the molecule with the atomic-labeling scheme. The final positional parameters are given in Table 2, and selected bond lengths, bond angles and torsion angles are listed in Table 3.

The bond lengths and angles are normal and comparable with those of other DMABN derivatives.[3,4] The C≡N group is in the plane of the aromatic ring within 0.002(5)Å for the N(1) and –0.003(4)Å for the C(1) atom. On the other hand, the dimethylamino group is not coplanar with the aromatic ring. The dihedral angle between the least-squares planes of the aromatic ring and the dimethylamino group is 32.73(5)˚. The C(3)–C(4) and C(6)–C(7) bonds [1.376(4) and 1.362(4)Å, respectively] are clearly shorter than the C(2)–C(3), C(4)–C(5), C(5)–C(6) and C(2)–C(7) bonds [1.408(4), 1.424(4), 1.427(4) and 1.393(4)Å, respectively]. This finding indicates that the aromatic ring has a significant quinoid nature.

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