Crystal structure of 4-methyl-*N*-(4,5-diazafluorenylidene)benzenamine monohydrate, $C_{18}H_{13}N_3 \cdot H_2O$

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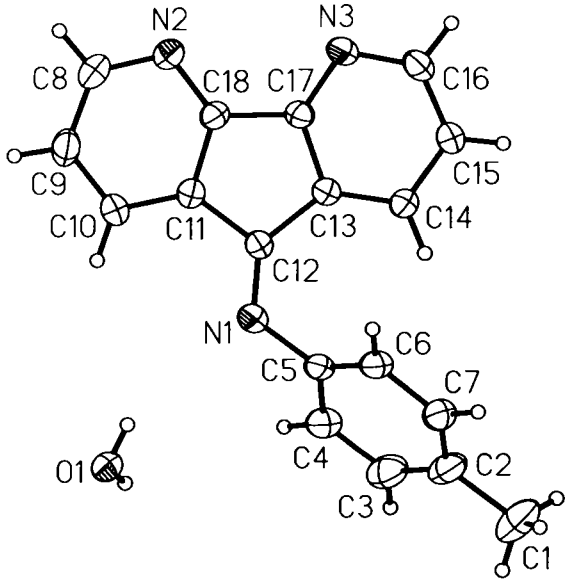

Abstract

$C_{18}H_{15}N_3O$, triclinic, $P\bar{1}$ (no. 2), a = 7.624(2) Å, b = 8.626(2) Å, c = 11.086(2) Å, α = 77.68(3)°, β = 86.66(3)°, γ = 86.49(3)°, V = 710.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.088, $wR_{ref}(F^2)$ = 0.156, T = 293 K.

Source of material

4-Methyl-*N*-(4,5-diazafluorenylidene)benzenamine monohydrate (0.289 g, 1.000 mmol) was dissolved in 20.0 ml solution of water and methanol (1:1, *v*/*v*). The solution was kept at room temperature for two weeks, and pale yellow crystals suitable for single-crystal X-ray analysis were afforded.

Experimental details

The H atoms attached to C atoms were included at calculated positions and treated as riding atoms, with C—H distances constrained to 0.93 Å – 0.96 Å and with U_{iso}(H) = 1.2U_{eq}(C). The water H1WA and H1WB atoms were found in a Fourier difference map and then treated as riding atoms, with O—H distances of 0.85 Å and with U_{iso}(H) = 1.5U_{eq}(O1). The large R values are caused by the poor quality of the used crystal chosen as the best from a series of syntheses.

Discussion

The asymmetric unit consists of one 4-methyl-*N*-(4,5-diazafluorenylidene)benzenamine molecule and one lattice water molecule. C1, N1 and the benzene ring are almost in one plane. In the 4,5-diazafluorenylidene unit, the rings A and B are nearly coplanar with a dihedral angle of 0.7(2)°. The 4,5-diazafluorenylidene unit and benzene ring have a dihedral angle of 65.1(1)°. Hydrogen-bonding and π-π stacking interactions are the most remarkable structural features in the title structure. In the [100] direction, the organic main molecules are aligned in such a way that neighboring 4,5-diazafluorenylidene planes face in anti-parallel fashion with interplanar distances of 3.44 Å and 3.47 Å, indicating significant π-π stacking interactions. The lattice water molecule donates one hydrogen atom to the N2 atom to form O–H···N hydrogen bonds (d(O1···N1) = 3.087 Å, ∠O1–H···N1 = 169°), and accepts hydrogen atoms from C6 and C8 groups of two neighboring organic molecules to result intermolecular C–H···O hydrogen bonds (d(O1···C6) = 3.090 Å, ∠O1···H–C6 = 121°; d(O1···C8) = 3.425 Å, ∠O1···H–C8 = 156°). The atom N1 also forms weak C–H···N hydrogen bonds with C16 group (d(N1···C16) = 3.495 Å, ∠N1···H–C16 = 161°). Because of the extensive hydrogen bonding interactions, the lattice water molecules and the 1D chains of main molecules are assembled into 3D framework. The bond distances and angles are comparable with corresponding values of related fluorenylidene compounds $4[C_{13}H_8N(C_6H_5)] \cdot C_6H_6$ [1], $C_{20}H_{15}NO$ [2], $C_{21}H_{17}N$ [3].

Table 1. Data collection and handling.

Crystal:	pale yellow needle, size 0.05 × 0.08 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.87 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX II CCD, ω/φ
$2\theta_{max}$:	51.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2574, 2574
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1879
$N(param)_{refined}$:	201
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.1151	0.6859	0.6185	0.118
H(1B)	2*i*	–0.0623	0.6327	0.5793	0.118
H(1C)	2*i*	–0.0439	0.8098	0.5884	0.118
H(3)	2*i*	–0.1249	0.9068	0.3666	0.090
H(4)	2*i*	–0.0273	0.9633	0.1629	0.078
H(6)	2*i*	0.4020	0.6782	0.2464	0.071
H(7)	2*i*	0.3070	0.6243	0.4513	0.073
H(8)	2*i*	0.5658	0.7755	–0.4366	0.072
H(9)	2*i*	0.5545	1.0094	–0.3668	0.074
H(10)	2*i*	0.4273	1.0201	–0.1731	0.066
H(14)	2*i*	0.1267	0.5109	0.1877	0.055
H(15)	2*i*	0.1038	0.2474	0.1692	0.059
H(16)	2*i*	0.2162	0.1673	–0.0024	0.064
H(1WA)	2*i*	0.2594	0.3569	0.5683	0.077
H(1WB)	2*i*	0.3551	0.4332	0.6429	0.077

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.0167(7)	0.7178(8)	0.5670(4)	0.094(4)	0.047(5)	0.055(3)	−0.026(3)	0.018(2)	−0.028(3)
C(2)	2*i*	0.0812(6)	0.7571(5)	0.4333(4)	0.072(3)	0.087(3)	0.054(2)	−0.024(2)	0.018(2)	−0.032(2)
C(3)	2*i*	−0.0188(6)	0.8602(6)	0.3429(4)	0.070(3)	0.089(3)	0.069(3)	−0.002(2)	0.016(2)	−0.029(2)
C(4)	2*i*	0.0384(6)	0.8926(5)	0.2206(4)	0.077(3)	0.059(2)	0.062(2)	−0.005(2)	0.010(2)	−0.023(2)
C(5)	2*i*	0.1938(5)	0.8203(4)	0.1828(3)	0.071(2)	0.039(2)	0.051(2)	−0.013(2)	0.015(2)	−0.018(1)
C(6)	2*i*	0.2949(5)	0.7230(4)	0.2703(3)	0.073(3)	0.051(2)	0.056(2)	−0.008(2)	0.015(2)	−0.022(2)
C(7)	2*i*	0.2379(5)	0.6914(5)	0.3937(3)	0.074(3)	0.059(2)	0.053(2)	−0.015(2)	0.007(2)	−0.017(2)
N(1)	2*i*	0.2532(4)	0.8587(3)	0.0573(3)	0.075(2)	0.040(2)	0.056(2)	−0.008(1)	0.013(2)	−0.013(1)
C(8)	2*i*	0.5152(5)	0.7762(5)	−0.3583(3)	0.066(2)	0.072(3)	0.040(2)	−0.005(2)	0.004(2)	−0.008(2)
C(9)	2*i*	0.5081(5)	0.9193(5)	−0.3167(3)	0.071(3)	0.060(2)	0.048(2)	−0.014(2)	0.003(2)	0.003(2)
C(10)	2*i*	0.4328(5)	0.9265(4)	−0.2024(3)	0.070(2)	0.039(2)	0.053(2)	−0.009(2)	0.005(2)	−0.006(1)
C(11)	2*i*	0.3658(4)	0.7888(4)	−0.1329(3)	0.049(2)	0.044(2)	0.041(2)	−0.003(1)	0.002(1)	−0.006(1)
C(12)	2*i*	0.2839(4)	0.7521(4)	−0.0063(3)	0.049(2)	0.037(2)	0.044(2)	−0.003(1)	0.003(1)	−0.008(1)
C(13)	2*i*	0.2493(4)	0.5797(3)	0.0184(3)	0.042(2)	0.038(2)	0.041(2)	−0.002(1)	−0.001(1)	−0.009(1)
C(14)	2*i*	0.1697(4)	0.4768(4)	0.1170(3)	0.051(2)	0.045(2)	0.041(2)	−0.007(1)	0.004(1)	−0.010(1)
C(15)	2*i*	0.1570(4)	0.3202(4)	0.1056(3)	0.056(2)	0.040(2)	0.050(2)	−0.008(1)	0.002(2)	−0.006(1)
C(16)	2*i*	0.2230(5)	0.2737(4)	0.0007(3)	0.063(2)	0.036(2)	0.063(2)	−0.007(1)	−0.002(2)	−0.011(1)
C(17)	2*i*	0.3071(4)	0.5193(3)	−0.0860(3)	0.041(2)	0.038(2)	0.044(2)	0.000(1)	−0.001(1)	−0.011(1)
C(18)	2*i*	0.3817(4)	0.6503(4)	−0.1812(3)	0.043(2)	0.046(2)	0.039(2)	0.000(1)	0.000(1)	−0.010(1)
N(2)	2*i*	0.4532(4)	0.6401(3)	−0.2916(3)	0.057(2)	0.054(2)	0.043(2)	−0.001(1)	0.004(1)	−0.011(1)
N(3)	2*i*	0.2973(4)	0.3704(3)	−0.0985(3)	0.059(2)	0.039(2)	0.056(2)	−0.004(1)	0.003(1)	−0.015(1)
O(1)	2*i*	0.336(2)	0.348(2)	0.621(1)	0.060(2)	0.040(2)	0.057(2)	−0.004(1)	0.003(1)	−0.014(1)

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