Crystal structure of bis(4-dimethylaminopyridinium)methane dichloride bis(acetonitrile) solvate, $C_{19}H_{28}Cl_2N_6$

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Received November 1, 1996, CSD-No. 402688

$C_{19}H_{28}Cl_2N_6$, orthorhombic,
 $P2_12_12_1$ (No. 19), $a = 10.544(2)$ Å,
 $b = 11.620(2)$ Å, $c = 18.298(4)$ Å,
 $V = 2241.9$ Å³, $Z = 4$, $R(F) = 0.056$, $R_w(F^2) = 0.114$.

Source of material: 4-Dimethylaminopyridine (3.00 g, 24 mmol) was heated in methylene chloride at 323 K for 2 hours. After cooling to ambient temperature a colorless precipitate was obtained and extracted twice with 5 ml water. Ethanol (20 ml) was added to the water layer followed by an azeotropic distillation. The residue was treated with 5 ml abs. ethanol. All volatiles were removed in vacuo (10^{-3} mm). The yield was 2.77 g (70%, mp 543 K).

The compound crystallizes with two acetonitrile molecules per formula unit (not shown in the figure). All nitrogen atoms have almost trigonal planar geometry. The planes through N1, C12, C13 and N4, C14, C15 show a 8.3° and 12.7° deviation, respectively to the corresponding ring attached. Both pyridinium moieties exhibit a substantial quinoidal character (see ref. 1) as seen from the C2–C3 (133.6 pm) and C4–C5 (135.6 pm) distances being significantly shorter than C1–C2 (143.8 pm) and C1–C5 (141.4 pm). The bond length C1–N(1) (132.9 pm) is found to be between a single and double bond (147 pm and 127 pm, respectively) (see ref. 2).

Table 1. Parameters used for the X-ray data collection

Crystal:	colorless, prismatic, size 0.3 x 0.5 x 0.6 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	3.05 cm ⁻¹
Diffractometer:	Siemens P4
Scan mode:	$2\theta/\omega$
$T_{\text{measurement}}$:	173 K
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{unique}}$:	3494
Criterion for I_o :	$I_o > 2 \sigma(I_o)$
$N(\text{param})_{\text{refined}}$:	250
Programs:	SHELXS-86, SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{iso}
H(12A)	4a	-0.1115(7)	0.469(3)	0.1278(5)	0.049
H(12B)	4a	-0.002(2)	0.512(2)	0.1815(8)	0.049
H(12C)	4a	-0.015(2)	0.378(1)	0.163(1)	0.049
H(13A)	4a	0.102(3)	0.630(1)	0.1159(8)	0.051
H(13B)	4a	0.075(2)	0.623(1)	0.030(1)	0.051
H(13C)	4a	0.2073(8)	0.5784(5)	0.062(2)	0.051
H(2A)	4a	0.1980(6)	0.4764(5)	-0.0396(3)	0.040
H(3A)	4a	0.2157(6)	0.3351(5)	-0.1242(3)	0.042
H(4A)	4a	-0.0199(6)	0.1308(5)	-0.0161(2)	0.042
H(5A)	4a	-0.0441(6)	0.2668(5)	0.0731(3)	0.039
H(6A)	4a	0.1169(5)	0.0557(5)	-0.1091(3)	0.041
H(6B)	4a	0.2036(5)	0.1419(5)	-0.1557(3)	0.041
H(7A)	4a	0.1098(6)	0.2554(5)	-0.2519(2)	0.039
H(8A)	4a	-0.0445(5)	0.2696(5)	-0.3410(3)	0.037
H(10A)	4a	-0.2451(6)	0.0202(5)	-0.2351(3)	0.042
H(11A)	4a	-0.0901(6)	0.0126(5)	-0.1484(3)	0.042
H(14A)	4a	-0.272(4)	0.3280(6)	-0.3773(4)	0.049
H(14B)	4a	-0.325(2)	0.240(2)	-0.437(1)	0.049
H(14C)	4a	-0.175(1)	0.253(2)	-0.425(1)	0.049
H(15A)	4a	-0.425(2)	0.092(2)	-0.3858(4)	0.046
H(15B)	4a	-0.440(1)	0.140(2)	-0.304(1)	0.046
H(15C)	4a	-0.3675(6)	0.021(1)	-0.318(2)	0.046
H(17A)	4a	-0.296(3)	0.258(1)	-0.166(2)	0.104
H(17B)	4a	-0.420(1)	0.337(3)	-0.176(2)	0.104
H(17C)	4a	-0.321(4)	0.366(2)	-0.1127(5)	0.104
H(19A)	4a	-0.194(2)	0.714(1)	-0.080(2)	0.064
H(19B)	4a	-0.341(2)	0.678(2)	-0.075(2)	0.064
H(19C)	4a	-0.255(4)	0.630(1)	-0.1399(3)	0.064

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cl(1)	4a	0.1402(1)	0.7000(1)	0.26287(7)	0.0308(8)	0.0430(8)	0.0343(7)	0.0031(9)	-0.0050(8)	-0.0040(8)
Cl(2)	4a	-0.4656(2)	0.1050(1)	-0.53438(7)	0.0343(8)	0.0420(8)	0.0284(6)	-0.0004(9)	-0.0020(8)	-0.0046(8)
N(1)	4a	0.0618(4)	0.4701(4)	0.0809(2)	0.019(3)	0.043(3)	0.026(2)	-0.005(3)	0.007(2)	-0.004(2)
C(12)	4a	-0.0238(6)	0.4563(5)	0.1436(3)	0.037(4)	0.046(4)	0.038(3)	-0.005(4)	0.007(4)	-0.007(3)
C(13)	4a	0.1161(6)	0.5850(5)	0.0714(3)	0.042(4)	0.044(4)	0.041(3)	-0.009(4)	0.012(4)	-0.007(3)
C(1)	4a	0.0728(5)	0.3900(5)	0.0295(3)	0.021(3)	0.036(3)	0.029(3)	0.005(3)	-0.001(3)	-0.003(3)
C(2)	4a	0.1527(6)	0.4064(5)	-0.0334(3)	0.030(3)	0.034(3)	0.036(3)	-0.006(4)	0.007(3)	-0.006(3)
C(3)	4a	0.1627(6)	0.3224(5)	-0.0830(3)	0.028(4)	0.050(4)	0.027(3)	-0.004(4)	0.006(3)	-0.001(3)
N(2)	4a	0.1016(4)	0.2206(4)	-0.0778(2)	0.025(3)	0.032(3)	0.024(2)	0.000(3)	-0.002(2)	-0.002(2)
C(4)	4a	0.0245(6)	0.2016(5)	-0.0199(2)	0.041(4)	0.039(3)	0.025(3)	-0.001(4)	-0.001(3)	0.007(3)
C(5)	4a	0.0099(6)	0.2826(5)	0.0328(3)	0.035(4)	0.040(3)	0.023(2)	0.001(3)	0.006(3)	0.000(3)
C(6)	4a	0.1192(5)	0.1323(5)	-0.1328(3)	0.029(3)	0.045(4)	0.028(3)	0.006(4)	-0.008(3)	0.000(3)
N(3)	4a	0.0201(4)	0.1379(4)	-0.1899(2)	0.018(2)	0.036(3)	0.035(3)	0.001(3)	-0.005(3)	0.004(2)
C(7)	4a	0.0350(6)	0.2103(5)	-0.2481(2)	0.031(3)	0.040(3)	0.028(3)	0.002(4)	0.004(3)	0.005(3)
C(8)	4a	-0.0563(5)	0.2187(5)	-0.3010(3)	0.025(3)	0.039(3)	0.028(3)	-0.001(3)	-0.006(3)	0.004(3)
C(9)	4a	-0.1691(5)	0.1512(5)	-0.2963(3)	0.026(3)	0.035(3)	0.027(3)	0.004(3)	0.003(3)	-0.001(3)
C(10)	4a	-0.1751(6)	0.0714(5)	-0.2382(3)	0.031(3)	0.043(4)	0.031(3)	-0.007(3)	-0.007(3)	0.010(3)
C(11)	4a	-0.0831(6)	0.0666(5)	-0.1871(3)	0.036(4)	0.033(3)	0.035(3)	-0.001(4)	0.002(3)	0.005(3)
N(4)	4a	-0.2625(5)	0.1620(4)	-0.3455(2)	0.026(3)	0.038(3)	0.026(2)	-0.011(3)	-0.007(2)	0.005(2)
C(14)	4a	-0.2583(6)	0.2533(5)	-0.4008(3)	0.043(4)	0.054(4)	0.026(3)	0.001(4)	-0.009(3)	0.009(3)
C(15)	4a	-0.3841(5)	0.0984(5)	-0.3379(3)	0.028(3)	0.053(4)	0.033(3)	-0.012(4)	-0.003(3)	0.011(3)
N(5)	4a	-0.2080(7)	0.4651(5)	-0.2533(3)	0.093(6)	0.076(5)	0.061(4)	-0.023(5)	0.006(5)	0.010(4)
C(16)	4a	-0.2606(8)	0.4105(6)	-0.2125(4)	0.062(5)	0.057(5)	0.044(4)	-0.006(5)	0.003(4)	0.007(4)
C(17)	4a	-0.3301(8)	0.3369(7)	-0.1627(4)	0.087(7)	0.111(7)	0.061(4)	-0.030(7)	0.014(5)	0.000(5)
N(6)	4a	-0.2005(7)	0.4725(6)	-0.0100(4)	0.069(5)	0.076(5)	0.114(6)	0.014(5)	-0.032(5)	0.002(5)
C(18)	4a	-0.2224(7)	0.5538(7)	-0.0444(4)	0.042(5)	0.051(4)	0.071(5)	-0.001(5)	-0.007(5)	-0.010(4)
C(19)	4a	-0.2558(7)	0.6517(5)	-0.0882(3)	0.067(5)	0.048(4)	0.045(4)	-0.005(5)	-0.012(4)	0.000(4)

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for financial support.

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