Synthesis and Crystal Structure of 1-2 Diphenyl ethylenediammonium Chloride

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The salt 1-2 diphenyl ethylenediammonium chloride crystallizes at room temperature in the monoclinic system with polar space group $P2_1$; the unit-cell dimensions are: $a = 8.720(2)$, $b = 6.243(2)$, $c = 13.972(5)$ Å, $\beta = 106.67(3)^\circ$ with $Z = 2$. The structure consists of $[C_{14}H_{18}N_2]^{2+}$ cations and isolated chlorine anions. These entities are linked together through N-H...Cl hydrogen bonds, forming a three-dimensional network.

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The research of organic polar crystals is very interesting for quadratic non-linear optical phenomena, which is presently oriented to organic aromatic cations containing π -electrons systems asymmetricized by electron donor and/or accepted substituents.¹⁻³ Research has also been devoted to ionic host-matrices that may increase the packing cohesion built up through ionic, hydrogen bonding and van der Waals interactions. Taking these considerations into account, we report on the chemical preparation and the crystal structure of 1-2 diphenyl ethylenediammonium chloride.

Crystals were obtained by dissolving in a concentrated HCl (36%) solution of $C_{14}H_{18}N_2$ (molar ratio 1/2). The reaction occurred according to the following scheme: $C_{14}H_{18}N_2 + 2HCl$ in the presence of water. The resulting solution was then kept at room temperature. After several days of evaporation, parallelepipedic monocrystals appeared in the solution.

A single-crystal study was performed by using an Enraf-Nonius Kappa CCD diffractometer. The main crystal data and a summary of the parameters related to intensity data collection and structure refinement are reported in Table 1. The final atomic coordinates are given in Table 2. The crystal structure was solved by a direct method using the SHELXL 97 program, which revealed the positions of all non-hydrogen atoms, and refined by a full matrix least-squares refinement. After introducing thermal-displacement parameters for the non-hydrogen atoms, the hydrogen atoms were localized and

optimized to restraint positions. Their thermal displacement contributions were isotropically introduced into the calculation and fixed. Corrections were applied for Lorentz and polarization effects and for absorptions. The final anisotropic full-matrix least squares resulted in a convergence of the R factor at 0.0419, $R_w = 0.1123$, and incorporating the weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.33P]$, where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$.

The atomic arrangement of the complex is depicted in Fig. 2. The structure of the title compound consists of 1-2 diphenyl ethylenediammonium cations and isolated chlorine anions. The

Table 1 Crystal and experimental data

Compound	$C_{14}H_{18}N_2Cl_2$
Formula weight	570.41
Space group	$P2_1$
Temperature	298 K
Cell constants	
a	8.720(2) Å
b	6.243(2) Å
c	13.972(5) Å
β	106.67(3)°
Cell volume	724.67(3) Å ³
Formula units/unit cell	2
D_{calc}	1.300 g cm ⁻³
Diffractometer/scan	Enraf-Nonius Kappa CCD
Radiation, graphite monochromator	Ag K_α ($\lambda = 0.56087$ Å)
Max, crystal dimensions, mm	0.12 × 0.08 × 0.09
μ_{calc}	0.23 mm ⁻¹
Unique reflections	2581
$2\theta_{\text{max}}$	40°
No of parameters	163
Goodness-of-fit	1.088
Absorption correction	numerical
R	0.0419
$(\Delta\rho)_{\text{max}}$	0.303 e/Å ³
$(\Delta\rho)_{\text{min}}$	-0.404 e/Å ³
Refinement	full matrix
Computer programs	SHELXL 97
CCDC	679638

Fig. 1 Chemical structure of $C_{14}H_{18}N_2Cl_2$.

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Table 2 Atomic coordinates and temperature factors for $C_{14}H_{18}N_2Cl_2$

Atom	x	y	z	U_{eq}
Cl1	0.81191(8)	-0.85832(17)	0.49866(5)	0.0370(2)
Cl2	0.36054(8)	-0.86417(16)	0.37827(5)	0.0356(2)
N1	0.8161(3)	-0.3680(6)	0.45530(16)	0.0310(5)
N2	0.4599(3)	-0.3631(6)	0.38800(17)	0.0321(5)
C1	0.7215(4)	-0.314(5)	0.3502(2)	0.0275(7)
C2	0.8204(3)	-0.3732(7)	0.28103(19)	0.0306(6)
C3	0.8537(5)	-0.2126(8)	0.2198(3)	0.0534(11)
C4	0.9512(6)	-0.2630(9)	0.1598(4)	0.0567(15)
C5	1.0167(5)	-0.4620(9)	0.1623(3)	0.0564(12)
C6	0.98835(4)	-0.6177(8)	0.2224(3)	0.0480(10)
C7	0.8848(4)	-0.5734(6)	0.2817(3)	0.0393(8)
C8	0.5613(3)	-0.4342(5)	0.3229(2)	0.0279(7)
C9	0.4701(3)	-0.4013(5)	0.2138(2)	0.0288(8)
C10	0.4560(4)	-0.5685(7)	0.1474(3)	0.0409(9)
C11	0.3769(5)	-0.5401(8)	0.0470(3)	0.0480(10)
C12	0.3128(4)	-0.3448(10)	0.0129(2)	0.0499(10)
C13	0.3239(5)	-0.1778(7)	0.0779(3)	0.0468(10)
C14	0.4038(4)	-0.2044(7)	0.1788(3)	0.0394(8)

Fig. 2 Projection of the $C_{14}H_{18}N_2Cl_2$ structure in the plane (a, c).

most stable conical forms of 1-2 diphenyl ethylenediammonium cations indicate that the N1 and N2 atoms are protonated. In this compound, the cation, present as a dication, $[C_{14}H_{18}N_2]^{2+}$, has a cis configuration. Table 3 reports on the principal geometrical features of the $[C_{14}H_{18}N_2]^{2+}$ cations. The aliphatic bond lengths of C-N and C-C are in the range of 1.501(4) –

Table 3 Selected bond distances (Å) and angles (°)

N1 – C1	1.501(4)	N1 – C1 – C2	108.4(2)
C1 – C2	1.515(4)	N1 – C1 – C8	109.8(2)
C1 – C8	1.534(4)	C2 – C1 – C8	111.5(3)
N2 – C8	1.506(4)	C3 – C2 – C1	118.1(4)
C8 – C9	1.517(4)	C7 – C2 – C1	121.7(3)
		N2 – C8 – C9	109.7(2)
		N2 – C8 – C1	110.9(3)
		C9 – C8 – C1	111.2(2)
		C10 – C9 – C8	119.6(3)
		C14 – C9 – C8	121.3(3)

Table 4 Hydrogen bonds for $C_{14}H_{18}N_2Cl_2$

	N-H (Å)	H...Cl (Å)	N...Cl (Å)	N-H...Cl (°)
N1-H1A...Cl1 ^a	0.960	2.328	3.121	139.51
N1-H1B...Cl1	0.960	2.210	3.123	158.43
N1-H1C...Cl2 ^b	0.960	2.224	3.136	158.35
N2-H2A...Cl2 ^a	0.960	2.647	3.238	120.22
N2-H2A...Cl1 ^b	0.960	2.735	3.206	110.89
N2-H2B...Cl2 ^c	0.960	2.278	3.226	169.22
N2-H2C...Cl2 ^b	0.960	2.254	3.191	165.01

a : $-x+2, y+0.5, -z+1$; b : $-x+2, y+0.5, -z+1$; c : $-x+2, y+0.5, -z+1$

1.506(4) Å and 1.515(4) – 1.534(4) Å, respectively. The aromatic C-C bond length varies from 1.364(7) to 1.401(6) Å, which is in agreement with that found in related compounds.^{3,4} All of the hydrogen bonded to the nitrogen atoms participate in the formation of N-H...Cl hydrogen bonding with distances of between 2.210 to 2.735 Å (Table 4). Comparing their geometrical parameters of the sum of the van der Waals radii of the hydrogen and acceptor atoms,⁵ they can be considered to be strong. The hydrogen bonds (N-H...Cl) give rise to a three-dimensional network in the structure, which adds stability to this compound.

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