Kina Muller, Eric C. Hosten and Richard Betz*

The crystal structure of *N*-(2-chloroethyl)-*N,N*-diethylammonium chloride, $C_6H_{15}Cl_2N$

<https://doi.org/10.1515/ncrs-2020-0562>

Received November 1, 2020; accepted December 4, 2020;

published online February 12, 2021

Abstract

$C_6H_{15}Cl_2N$, triclinic, $P\bar{1}$ (no. 2), $a = 6.9579(4)$ Å, $b = 8.1852(5)$ Å, $c = 8.7912(5)$ Å, $\alpha = 66.606(2)^\circ$, $\beta = 86.105(3)^\circ$, $\gamma = 89.834(2)^\circ$, $V = 458.30(5)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0226$, $wR_{ref}(F^2) = 0.0599$, $T = 200$ K.

CCDC no.: 2048021

The molecular structure is shown in the Figure. Table 1 contains crystallographic data, and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Merck Schuchardt). Crystals suitable for the diffraction study were taken directly from the provided product.

*Corresponding author: Richard Betz, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa, E-mail: Richard.Betz@mandela.ac.za. <https://orcid.org/0000-0002-5730-2152>

Kina Muller and Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa. <https://orcid.org/0000-0003-4173-2550> (E.C. Hosten)

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.58 \times 0.57 \times 0.31$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.64 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7662, 2255, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2129
$N(\text{param})_{\text{refined}}$:	89
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{eq}(C)$.

The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [3]), with $U(H)$ set to $1.5U_{eq}(C)$.

The nitrogen-bound H atom was located on a difference Fourier map and refined freely.

Comment

The effect of size and steric pretense of large ions on chemical and spectroscopic properties of compounds have been a focus of research for many decades [7–12]. In continuation of our interest in metrical features of large cations [13–15], the structure of the title compound has been determined. The latter has only been reported once in connection with an anionic platinum coordination compound [16].

The structure solution shows the presence of the chloride salt of a triethylammonium derivative. One of the ethyl chains bonded to the pnictogen atom features a chlorine atom as terminal substituent. N–C bond lengths

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Cl1	0.35047 (5)	0.88692 (4)	−0.32071 (3)	0.04592 (11)
N1	0.23092 (11)	0.67604 (10)	0.17716 (9)	0.02131 (16)
H71	0.1014 (19)	0.6751 (16)	0.1737 (15)	0.031 (3)*
C11	0.31705 (13)	0.79164 (13)	0.00694 (11)	0.02602 (19)
H11A	0.457391	0.772328	0.000870	0.031*
H11B	0.298160	0.918254	−0.013008	0.031*
C12	0.22682 (15)	0.75177 (14)	−0.12677 (12)	0.0307 (2)
H12A	0.088198	0.779483	−0.128003	0.037*
H12B	0.239353	0.624190	−0.105621	0.037*
C21	0.27873 (15)	0.75203 (14)	0.30097 (12)	0.0299 (2)
H21A	0.418458	0.781351	0.287736	0.036*
H21B	0.248800	0.661343	0.414932	0.036*
C22	0.16680 (17)	0.91766 (14)	0.27850 (14)	0.0357 (2)
H22A	0.210644	1.013723	0.172519	0.054*
H22B	0.188062	0.954029	0.369771	0.054*
H22C	0.029131	0.892594	0.278639	0.054*
C31	0.29449 (15)	0.48656 (12)	0.22950 (13)	0.0299 (2)
H31A	0.431760	0.480535	0.253941	0.036*
H31B	0.283287	0.448836	0.136436	0.036*
C32	0.17640 (18)	0.35942 (14)	0.38105 (14)	0.0386 (2)
H32A	0.200600	0.386264	0.477330	0.058*
H32B	0.212892	0.236850	0.402767	0.058*
H32C	0.039207	0.372770	0.361223	0.058*
Cl2	0.79351 (3)	0.68042 (3)	0.14921 (3)	0.03337 (9)

span a range of 1.5003(11)–1.5067(12) Å with the shortest bond realized to the halogenated alkyl chain. These values are in good agreement with the most common values reported for this type of bond in other alkylamines whose metrical parameters – determined on the basis of diffraction studies performed on single crystals – have been deposited with the Cambridge Structural Database [17]. The non-hydrogen atoms of the halogenated side chain are almost co-planar with the central atom as the least-squares plane defined by these very atoms shows a maximum deviation of only 0.027(1) Å for the nitrogen-bonded carbon atom. The least-squares planes as defined by the non-hydrogen atoms of the respective side chains enclose angles of 81.02(12)°, 77.91(12)° and 76.11(13)°.

In the crystal, classical hydrogen bonds of the N–H...Cl type are observed next to C–H...Cl contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii. These contacts are established by one hydrogen atom each on both methylene groups of the halogenated alkyl chain. In terms of graph-set analysis [18, 19], the descriptor

for these contacts is *DDD* at the unitary level. In total, the entities of the title compound are connected to chains along the crystallographic *a* axis.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The corresponding author thanks the National Research Foundation for financial support.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *APEX2*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Bruker. *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
3. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, *A64*, 112–122.
4. Farrugia L. J. *WinGX and ORTEP for Windows: an update*. *J. Appl. Crystallogr.* 2012, *45*, 849–854.
5. Macrae C. F., Bruno I. J., Chisholm J. A., Edgington P. R., McCabe P., Pidcock E., Rodriguez-Monge L., Taylor R., van de Streek J., Wood P. A. *Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures*. *J. Appl. Crystallogr.* 2008, *41*, 466–470.
6. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.
7. Enokida J. S., Hu W., Fang H., Morgan B. F., Beyer F. L., Winter H. H., Coughlin E. B. Modifying the structure and dynamics of ionomers through counterion sterics. *Macromolecules* 2020, *53*, 1767–1776.
8. Oh S. G., Shah D. O. Effect of counterions on the interfacial tension and emulsion droplet size in the oil/water/dodecyl sulfate system. *J. Phys. Chem.* 1993, *97*, 284–286.
9. Piotrowski P., Miller J. R. Counterion effects in intramolecular charge transfer in radical anions. *J. Phys. Chem.* 1993, *97*, 13052–13060.
10. Mathias M. F., Haas O. Effect of counterion type on charge transport at redox polymer-modified electrodes. *J. Phys. Chem.* 1993, *97*, 9217–9225.
11. Minguiraba A., Vamhindi B. S. D. R., Koyambo-Konzapa S. J., Nsangou M. Effects of counterions and solvents on the geometrical and vibrational features of dinucleoside-monophosphate (dNMP): case of 3',5'-dideoxycytidine-monophosphate (dDCMP). *J. Mol. Model.* 2020, *26*, Article #99.
12. Roof L. C., Kolis J. W. New developments in the coordination chemistry of inorganic selenide and telluride ligands. *Chem. Rev.* 1993, *93*, 1037–1080.
13. Hosten E. C., Betz R. Redetermination of the crystal structure of benzyltriethylammoniumchloride monohydrate at 200 K – localization of hydrogen atoms, C₁₃H₂₄ClNO. *Z. Kristallogr. NCS* 2015, *230*, 21–22.

14. Abrahams A., van Brecht B., Betz R. Bis(pyridin-2-ylmethyl) ammonium nitrate. *Acta Crystallogr.* 2013, *E69*, o661.
15. Betz R., Gerber T., Hosten E., Siddaraju B. P., Yathirajan H. S. Opi Pramol dihydrochloride. *Acta Crystallogr.* 2011, *E67*, o2994–o2995.
16. de Renzi A., di Blasio B., Panunzi A., Pedone C., Vitagliano A. «not accessible». *Gazz. Chim. Ital.* 1976, *106*, 709–«not accessible».
17. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
18. Bernstein J., Davis R. E., Shimoni L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 1555–1573.
19. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, *B46*, 256–262.