Marius Maritz, Eric C. Hosten and Richard Betz*

Crystal structure of benzylthiouronium chloride, $C_8H_{11}ClN_2S$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.51 \times 0.45 \times 0.29$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.56 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} :	16553, 2398, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2077
$N(\text{param})_{\text{refined}}$:	125
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

<https://doi.org/10.1515/ncrs-2020-0429>

Received August 30, 2020; accepted September 22, 2020;
published online October 5, 2020

Abstract

$C_8H_{11}ClN_2S$, orthorhombic, *Pbca* (no. 61), $a = 11.3126(6)$ Å, $b = 8.3567(4)$ Å, $c = 20.4130(11)$ Å, $V = 1929.76(17)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0240$, $wR_{\text{ref}}(F^2) = 0.0680$, $T = 200$ K.

CCDC no.: 2033285

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 (Hopkin & Williams Ltd.). 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>

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.55112 (3)	0.39898 (4)	0.404030 (15)	0.02740 (9)
N1	0.41950 (10)	0.66140 (14)	0.42571 (6)	0.0283 (2)
H711	0.4078 (14)	0.753 (2)	0.4414 (8)	0.036 (4)*
H712	0.3581 (14)	0.606 (2)	0.4219 (8)	0.036 (4)*
N2	0.61698 (10)	0.67443 (14)	0.45016 (6)	0.0310 (2)
H721	0.6812 (16)	0.627 (2)	0.4586 (9)	0.047 (5)*
H722	0.6070 (14)	0.766 (2)	0.4670 (8)	0.043 (5)*
C1	0.52448 (11)	0.59542 (14)	0.42863 (6)	0.0235 (2)
C2	0.41370 (11)	0.33877 (14)	0.36493 (6)	0.0274 (2)
H2A	0.4126	0.2206	0.3613	0.033*
H2B	0.3470	0.3706	0.3935	0.033*
C3	0.39410 (10)	0.40884 (14)	0.29786 (6)	0.0241 (2)
C4	0.47472 (11)	0.38159 (14)	0.24754 (6)	0.0281 (3)
H4	0.5446	0.3219	0.2559	0.034*
C5	0.45361 (12)	0.44104 (16)	0.18535 (6)	0.0331 (3)
H5	0.5089	0.4216	0.1512	0.040*
C6	0.35232 (13)	0.52865 (17)	0.17262 (7)	0.0372 (3)
H6	0.3380	0.5687	0.1298	0.045*
C7	0.27218 (12)	0.55783 (19)	0.22206 (7)	0.0397 (3)
H7	0.2029	0.6186	0.2134	0.048*
C8	0.29289 (11)	0.49806 (16)	0.28464 (7)	0.0326 (3)
H8	0.2375	0.5183	0.3186	0.039*
Cl1	0.66773 (3)	0.50164 (3)	0.027813 (16)	0.02983 (9)

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for methylene groups) and were included in the

refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

All nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

Comment

The effect of size and steric presence of large ions on chemical and spectroscopic properties of compounds have been a focus of research for many decades. Among the many effects that can be attributed to the spatial requirements of counterions have been the glass transition temperature in ionomers [7], surfactant modifying properties [8], the charge transfer in radical ions [9] and polymer-modified electrodes [10] as well as the structural and vibrational spectroscopic behaviour of DNA building blocks [11]. The benefit of choosing the adequate size of counterions to crystallize ionic compounds has been confirmed and reviewed several times [12]. Thiuronium derivatives are especially interesting in this context as they constitute a compound class that has been known for many decades. Their ease of synthesis in connection with their ready crystallizability – especially as picrates – has played a major role in the identification of alkyl halides [13]. However, due to the size of the picrate anion the metrical parameters of the pertaining thiuronium cations might not be free from crystal-packing-induced distortions. To eliminate this potential biased view, the crystal structure of the title compound was determined to account for this factor by opting for chloride as a much smaller anion.

The structure solution shows the presence of the benzylthiuronium cation with chloride as the counterion. The two sulphur-carbon bond lengths differ markedly from one another with values of 1.7430(12) Å and 1.8186(13) Å with the shorter bond formed towards the thiourea motif. The formal C=S double bond is longer than the most-commonly reported values for the pertaining bond in other thiuronium derivatives whose metrical parameters have been deposited with the Cambridge Structural Database [14]. The least squares planes as defined by the non-hydrogen atoms of the aromatic moiety and the thiourea moiety enclose an angle of 82.04(4)°.

In the crystal structure, all nitrogen-bonded hydrogen atoms act as donors in classical N–H···Cl hydrogen bonds. Furthermore, one of the hydrogen atoms of the methylene group gives rise to C–H···Cl contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. In terms of graph-set

analysis, [15, 16], the descriptor for these contacts is DDDDD at the unary level. In total, these interactions connect the entities present in the crystal structure to double layers perpendicular to the crystallographic c axis. π Stacking is not a prominent stabilizing feature of the structure as the shortest intercentroid distance was measured at 5.0240(8) Å.

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

Research funding: R. Betz thanks the NRF for financial support.

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

References

1. Bruker. *APEX2* and *SAINT*. 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. Piotrowiak 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. b, 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. Becker H. G. O., Beckert R., Domschke G., Fanghänel E., Habicher W. D., Metz P., Pavel D., Schwetlick K. *Organikum – Organisch-chemisches Grundpraktikum*, 21st ed.; Wiley-VCH: Weinheim, 2001.
14. Allen F. H. The Cambridge structural database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
15. Bernstein J., Davis R. E., Shimon L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. *Angew Chem. Int. Ed. Engl.* 1995, *34*, 1555–1573.
16. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, *B46*, 256–262.