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1-Benzylsulfanyl-2-(benzylsulfanylmethyl)-propanaminium chloride

Daniel J. Cline, Joel P. Schnieder, Colin Thorpe and Glenn P. A. Yap*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

Correspondence e-mail: gpyap@udel.edu

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.127
Data-to-parameter ratio = 21.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title quaternary ammonium salt, $C_{18}H_{24}NS_2^+\cdot Cl^-$, was reported several decades ago, but its structure was not determined at the time. The crystal structure displays extensive hydrogen bonding, linking cations and anions into infinite chains. There are two cations and two anions in the asymmetric unit.

Comment

The title compound, (I), is an intermediate in the synthesis of 4-aminomethyl-1,2-dithiolane hydrochloride, (II), originally synthesized for the study of Demjanov rearrangements (Bergson, 1962) and later studied as a radioprotective drug (Li *et al.*, 1981). We are generating a series of dithiol-containing probe molecules by coupling the amine functionality in (II) to several fluorescent (or fluorescence-quenching) compounds using isothiocyanate, sulfonyl chloride or succinimidyl ester chemistry.

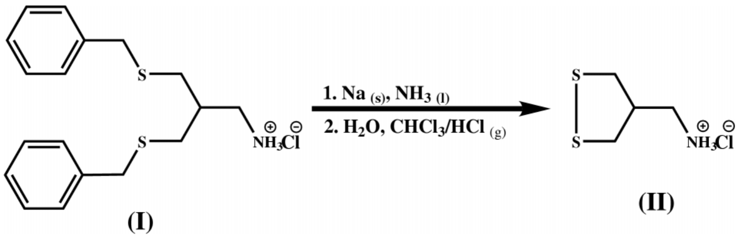

Fig. 1 shows one of the two symmetry-unique and geometrically similar ion pairs in the asymmetric unit of (I). The two symmetry-unique ion pairs aggregate as an oligomer along with two ion pairs generated by a twofold rotation around the c axis. Each oligomer is connected by hydrogen bonding to others generated by translation along the c axis, forming an infinite chain polymer, as shown in Fig. 2. In both symmetry-independent NH_3 groups, two of the three H atoms are hydrogen bonded to chloride counter-ions and the third H atom is engaged in a bifurcated hydrogen bond to the chloride ion and, intramolecularly, to an S atom.

Experimental

The title compound was prepared from 1,3-dibromoisobutyric acid as described by Bergson (1962). This compound was crystallized from dry diethyl ether and recrystallized from acetone at room temperature to afford yellow spars after 24 h. Sample quality was assessed by polarized microscopy. The crystals selected for data collection displayed even and sharp extinction and did not have reentrant angles, consistent with untwinned crystals. A single crystal was attached to a glass fiber using Paratone oil for subsequent crystallographic investigation at 120 K.

Crystal data

$C_{18}H_{24}NS_2^{+}\cdot Cl^{-}$
$M_r = 353.95$
Orthorhombic, $P2_12_12$
$a = 16.396\ (4)$ Å
$b = 31.633\ (8)$ Å
$c = 7.1438\ (19)$ Å
$V = 3705.1\ (17)$ Å^3
$Z = 8$
$D_x = 1.269$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1007 reflections
$\theta = 3.2$–$27.8°$
$\mu = 0.43$ mm^{-1}
$T = 120\ (2)$ K
Needle, yellow
$0.36 \times 0.04 \times 0.04$ mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.861$, $T_{\max} = 0.983$
41652 measured reflections
8603 independent reflections
8297 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 28.3°$
$h = -20 \rightarrow 21$
$k = -40 \rightarrow 41$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.127$
$S = 1.05$
8603 reflections
400 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 1.3761P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), 3633 Friedel pairs
Flack parameter = 0.55 (6)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···Cl2$^{\rm i}$	0.91	2.24	3.126 (2)	163
N1—H1C···S1	0.91	2.59	3.216 (2)	126
N1—H1C···Cl2$^{\rm ii}$	0.91	2.66	3.242 (2)	122
N1—H1D···Cl1	0.91	2.29	3.195 (3)	174
N2—H2B···Cl1$^{\rm iii}$	0.91	2.25	3.123 (2)	161
N2—H2C···Cl2	0.91	2.30	3.207 (3)	174
N2—H2D···S4	0.91	2.62	3.238 (2)	126
N2—H2D···Cl1$^{\rm iv}$	0.91	2.70	3.190 (2)	114

Symmetry codes: (i) $1-x, 1-y, z-1$; (ii) $1+x, y, z-1$; (iii) $1-x, 1-y, z$; (iv) $x-1, y, z$.

Although the structure could be solved in *Pccn*, the resulting solution involves rejection of 3090 data, 1658 systematic absence violations, a final $R = 0.173$, $wR2 = 0.579$ and an average C—C bond precision of 0.014 Å. Additionally, the mean value of $E^2 - 1$, 0.789, suggests a non-centrosymmetric space group and there are no correlation matrix elements larger than 0.5 in the the least-squares refinement of the model in the space group $P2_12_12$. Preliminary data collected from four different crystals, one of which was investigated at ambient temperature with the crystal mounted with epoxy cement, indicate the same non-centrosymmetric space group with similar systematic absence violations if the centrosymmetric space group is assumed. Two symmetry-unique but chemically equivalent ion pairs were located in the asymmetric unit. The nitrogen-bonded H atoms were located in a difference density map, and the NH_3 groups were allowed to rotate freely during refinement using a riding model (N—H = 0.91 Å), with displacement parameters $U_{\rm iso}(H) = 1.5U_{\rm eq}(N)$. The remaining H atoms were placed in calculated positions (C— H = 0.95–0.99 Å) and refined using a riding model, with displacement parameters $U_{\rm iso}(H) = 1.2U_{\rm eq}$ of the carrier atom. The Flack (1983) parameter indicates probable inversion twinning of the structure

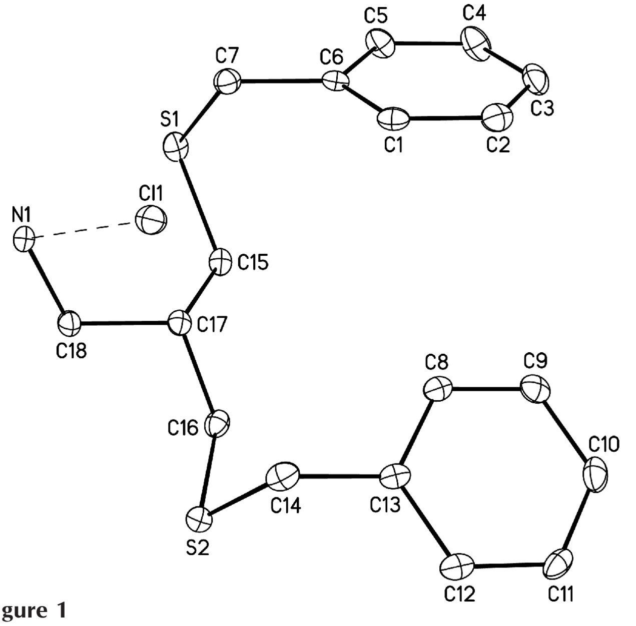

Figure 1
The molecular structure and labeling scheme for (I), showing 30% probability ellipsoids for one of the two symmetry-unique ion pairs. H atoms have been omitted.

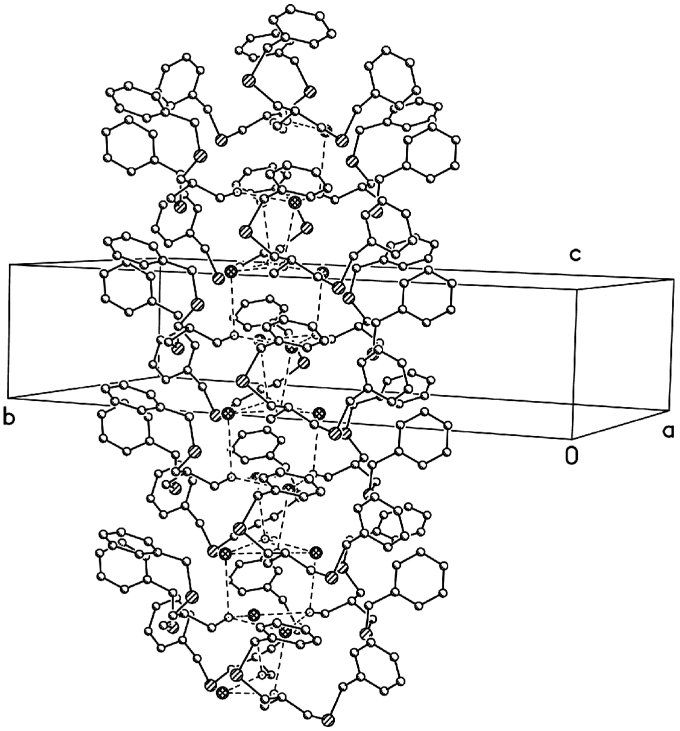

Figure 2
Packing diagram viewed approximately along the *a* axis of the crystal. Hydrogen atoms have been omitted. Dashed lines indicate hydrogen bonds.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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