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Benzyltripropylammonium bromide: a structure in polar space group $P4_2bc$

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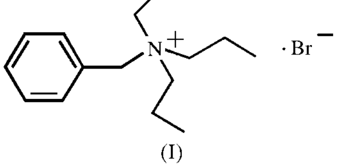
Crystals of the title compound, $C_{16}H_{28}N^+\cdot Br^-$, were grown from solution in a mixture of acetone and propan-2-ol by slow evaporation. The structure was solved in the polar space group $P4_2bc$ with five moieties in the asymmetric unit, namely two benzyltripropylammonium cations in general positions, and two Br^- anions in special Wyckoff positions (4*a*2.. and 4*b*2..) and one in a general position. The structure consists of two kinds of molecular columns parallel to **c**, built of cations connected through C—H$\cdots\pi$ hydrogen bonds and stabilized by weak C—H$\cdots$Br interactions.

Comment

Quaternary alkylammonium cations are the subject of widespread interest because they are able to change the nature of the surface of clay minerals, such as montmorillonite or bentonite, from hydrophilic to hydrophobic. The surfaces of the resultant organoclays can then adsorb organic pollutants which have low solubility in water (Lee *et al.*, 1989; Lo *et al.*, 1997; Polubesova *et al.*, 1997). Recently, the cation of the title compound was investigated for its sorption properties on montmorillonite (Lorenc, 2001) and was found to have a significantly lower ability than the benzyltrimethylammonium ion used as a reference cation.



(I)

The crystal structure analysis of selected quaternary alkylammonium salts was undertaken to find the relationship between the geometry of the alkyl chains and the packing properties of the ammonium cations. The other important question we wished to address was how a possible mutual arrangement of the cations could influence their sorption behaviour, either on a montmorillonite or on a bentonite. Here, the tetragonal polar structure of crystals of benzyltripropylammonium bromide, (I), is reported.

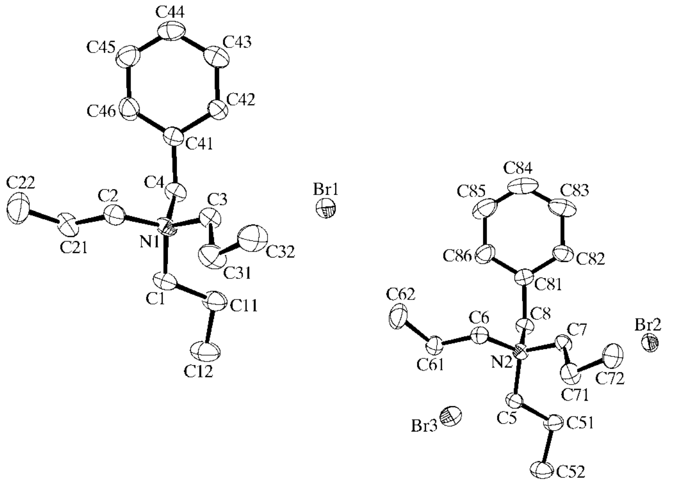


Figure 1
The asymmetric part of the unit cell of (I), showing the conformation of the two independent BTPA cations containing atom N1 (left) and atom N2 (right), and the atom-numbering schemes. H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

The asymmetric part of the unit cell of (I) contains five distinct moieties: two symmetrically independent benzyltripropyloammonium (BTPA) cations, *A* and *B*, and three Br^- anions. The bond lengths and angles of these symmetry-independent molecules are quite similar (Table 1) and the normal probability plot analysis (Abrahams & Keve, 1971; International Tables for X-ray Crystallography, 1974, Vol. IV, pp. 293–309) shows that the differences are of a statistical rather than systematic nature. The correlation coefficient

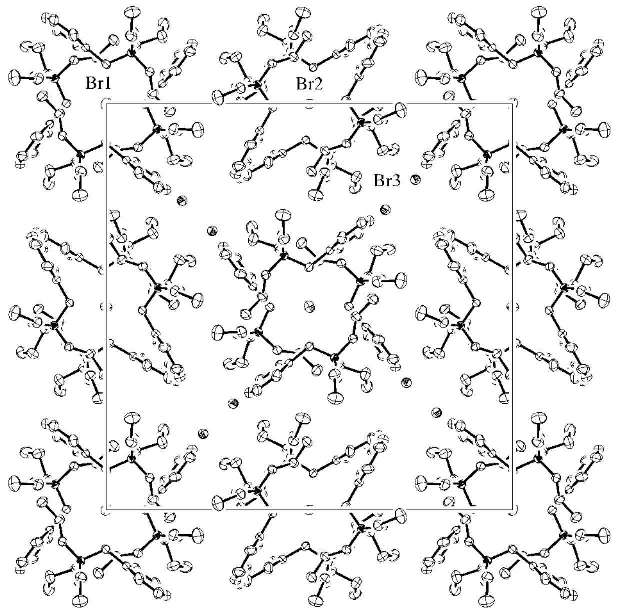


Figure 2
Projection of the structure of (I) on to the *ab* plane. A cross-section of two types of channels at $0,0,z$ and $0,\frac{1}{2},z$ can be distinguished.

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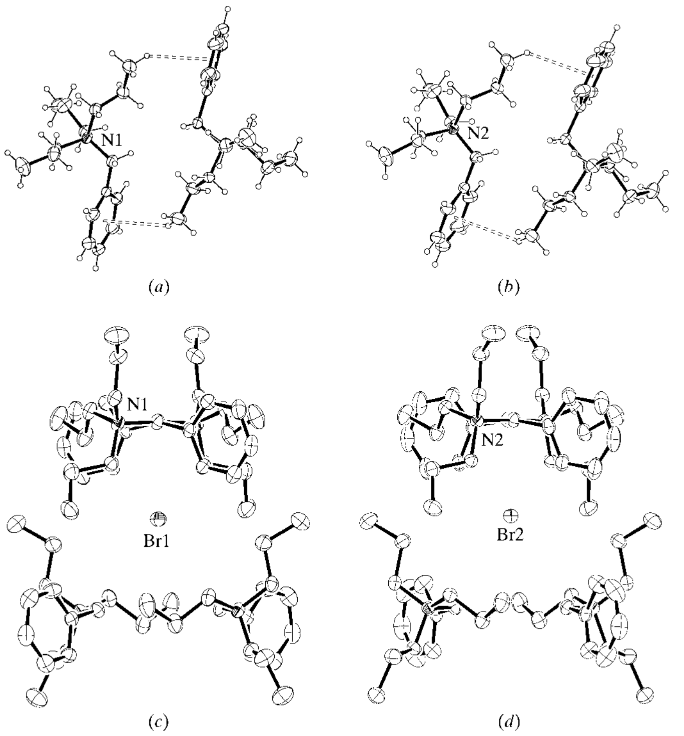

Figure 3
C—H$\cdots\pi$ interactions of type III (Malone *et al.*, 1997) in the dimers formed by (*a*) cation *A* (θ = 78.4° and d = 0.62 Å) and (*b*) cation *B* (θ = 84.8° and d = 0.28 Å), viewed along [001]. Two types of kerbs at (*c*) 0,0,*z* (4*a*2..) and (*d*) 0,$\frac{1}{2}$,*z* (4*b*2..) are shown along [100].

between experimental and theoretical distributions is 0.9962 for bond lengths and 0.9903 for bond angles.

The conformation of the BTPA cations in the crystalline state is shown in Fig. 1. Each cation has a synclinal (*gauche*) conformation of two propyl chains relative to the benzyl moiety, defined by the C4(benzyl)—N1—C1—C11 and C4(benzyl)—N1—C2—C21 torsion angles for cation *A*, and by C8(benzyl)—N2—C5—C51 and C8(benzyl)—N2—C6—C61 for cation *B*, with an antiperiplanar conformation for the third propyl substituent in each case (Table 1). All propyl chains have a zigzag-like conformation, with N*x*—C*x*—C*x*1—C*x*2 torsion angles close to −180°.

The packing in the structure of (I) is shown in Fig. 2. The ammonium cations form a framework enclosing two types of molecular columns running along the [001] direction, one at Wyckoff positions 0,0,*z* (4*a*2..) and the second at 0,$\frac{1}{2}$,*z* (4*b*2..). The column at 0,0,*z* (of 4_2 symmetry) is built up of translationally repeated kerbs, each containing four BTPA cations of type *A*, arranged into two dimers rotated relative to each other by 90°. The cations included in these dimers are interconnected by C—H$\cdots\pi$ interactions (Fig. 3*a*). Such a kerb is stabilized by Coulombic interactions with the Br1 counter-ion (Fig. 3*c*). The second molecular column, at 0,$\frac{1}{2}$,*z*, is also of twofold symmetry but results from crossing two *c*-glide planes. Here, the dimers are formed of type *B* cations symmetrically independent of the first type but stabilized according to a similar scheme (*i.e.* C—H$\cdots\pi$ interactions and Coulombic interactions with the Br2 anion; Figs. 3*b* and 3*d*). Both columns are joined together into a tetragonal structure *via* interactions with the Br3 anions in general positions. The geometry of the short C—H$\cdots$Br contacts and weak C—H$\cdots\pi$ hydrogen bonds is given in Table 2.

In conclusion, the three propyl-chain substituents of (I), with their specific conformations relative to the benzyl moiety, could sterically hinder the hypothetical direct interaction of N^+ cations with the negatively charged surface of a single montmorillonite silicate layer when adsorbed on to the surface of grains or intercalated between silicate layers. The structure of the montmorillonite, with a typical chemical composition $M_x(Al_{4x}Mg_{4x})Si_8O_{20}(OH)_2$, consists of layers, each composed of an alumina or magnesia octahedral sheet sandwiched between silica tetrahedra. The thickness of such a layer is about 1 nm and the interlayer space contains water molecules and simple cations of sodium, potassium or calcium. The montmorillonite has high cation exchange capacity (CEC) and quaternary alkylammonium cations can easily replace the simple cations, finally forming so called organomontmorillonite belonging to organoclay materials. Such steric hindrance could be the reason for the much worse sorption properties of BTPA cations on montmorillonite clay than those of the benzyltrimethylammonium cations used as reference (Lorenc, 2001). Additionally, the tendency of BTPA to form molecular columns through hydrophobic interactions between the cations hampers its intercalation between montmorillonite silicate layers.

Experimental

The title salt was obtained using the procedure described by Lorenc (2001) and was recrystallized from a mixture of acetone and propan-2-ol.

Crystal data

$C_{16}H_{28}BrN$
M_r = 314.31
Tetragonal, $P4_2bc$
a = 22.4411 (4) Å
c = 13.3749 (2) Å
V = 6735.6 (2) Å^3
Z = 16
D_x = 1.240 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 7799 reflections
θ = 1.0–27.5°
μ = 2.43 mm^{-1}
T = 293 (2) K
Prism, colourless
0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (*HKL DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.582, $T_{\max}$ = 0.642

14 346 measured reflections
7591 independent reflections
5740 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\max}$ = 27.5°
$h = -29 \rightarrow 29$
$k = -20 \rightarrow 20$
$l = -17 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.076
S = 1.05
7591 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 1.9763P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.29 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.006 (8)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.523 (4)	N2—C5	1.512 (3)
N1—C2	1.521 (4)	N2—C6	1.518 (3)
N1—C3	1.521 (4)	N2—C7	1.527 (3)
N1—C4	1.535 (4)	N2—C8	1.534 (3)
C1—C11	1.519 (5)	C5—C51	1.517 (4)
C11—C12	1.511 (5)	C51—C52	1.508 (4)
C2—C21	1.504 (4)	C6—C61	1.509 (4)
C21—C22	1.515 (5)	C61—C62	1.521 (5)
C3—C31	1.522 (5)	C7—C71	1.519 (4)
C31—C32	1.496 (5)	C71—C72	1.509 (4)
C1—N1—C2	108.6 (2)	C5—N2—C6	108.8 (2)
C1—N1—C3	112.0 (2)	C5—N2—C7	111.6 (2)
C2—N1—C3	108.5 (2)	C6—N2—C7	108.2 (2)
C1—N1—C4	107.9 (2)	C5—N2—C8	108.7 (2)
C2—N1—C4	111.6 (2)	C6—N2—C8	111.2 (2)
C3—N1—C4	108.2 (2)	C7—N2—C8	108.4 (2)
N1—C1—C11	115.9 (2)	N2—C5—C51	115.7 (2)
C12—C11—C1	108.8 (3)	C52—C51—C5	109.4 (3)
C21—C2—N1	115.9 (3)	C61—C6—N2	116.4 (3)
C2—C21—C22	109.0 (3)	C6—C61—C62	109.1 (3)
C31—C3—N1	115.7 (2)	C71—C7—N2	116.2 (2)
C32—C31—C3	110.5 (3)	C72—C71—C7	108.9 (3)
C41—C4—N1	115.5 (2)	C81—C8—N2	115.3 (2)
C42—C41—C46	117.6 (3)	C82—C81—C86	118.5 (3)
C2—N1—C1—C11	−171.5 (3)	C6—N2—C5—C51	−174.2 (2)
C3—N1—C1—C11	−51.7 (4)	C7—N2—C5—C51	−54.9 (3)
C4—N1—C1—C11	67.3 (4)	C8—N2—C5—C51	64.6 (3)
N1—C1—C11—C12	−175.5 (3)	N2—C5—C51—C52	−178.2 (3)
C1—N1—C2—C21	−53.7 (4)	C5—N2—C6—C61	−51.9 (4)
C3—N1—C2—C21	−175.7 (3)	C7—N2—C6—C61	−173.2 (3)
C4—N1—C2—C21	65.1 (4)	C8—N2—C6—C61	67.8 (3)
N1—C2—C21—C22	−176.9 (3)	N2—C6—C61—C62	−164.7 (3)
C1—N1—C3—C31	−52.9 (4)	C5—N2—C7—C71	−49.4 (3)
C2—N1—C3—C31	67.0 (4)	C6—N2—C7—C71	70.2 (3)
C4—N1—C3—C31	−171.7 (3)	C8—N2—C7—C71	−169.1 (3)
N1—C3—C31—C32	−169.4 (3)	N2—C7—C71—C72	−171.7 (3)

Table 2
Geometry of short C—H···Br contacts and weak C—H···π hydrogen bonds (Å, °).

*Cg*1 is the centroid of the C41–C46 benzene ring and *Cg*2 the centroid of the C81–C86 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H42···Br1^{i}	0.97	2.96	3.888 (3)	161
C4—H41···Br1	0.97	3.19	4.106 (3)	157
C8—H81···Br2	0.97	3.06	3.982 (3)	159
C8—H82···Br2^{ii}	0.97	2.88	3.837 (3)	169
C61—H612···Br2^{ii}	0.97	3.15	4.006 (4)	148
C7—H71···Br2	0.97	3.18	4.108 (3)	161
C82—H821···Br2	0.93	3.20	4.003 (4)	146
C6—H61···Br3	0.97	2.87	3.762 (3)	153
C71—H711···Br3	0.97	3.05	3.941 (3)	153
C1—H11···Br3^{i}	0.97	3.04	3.964 (3)	160
C43—H431···Br3^{iii}	0.93	3.02	3.905 (4)	160
C2—H21···Br3^{i}	0.97	3.08	3.886 (3)	142
C31—H311···Br3^{i}	0.97	3.21	3.953 (4)	134
C12—H121···*Cg*1^{iii}	0.96	3.07	3.791 (15)	133
C52—H521···*Cg*2^{iv}	0.96	3.06	3.735 (15)	128

Symmetry codes: (i) $1-y, x-1, \frac{1}{2}+z$; (ii) $\frac{1}{2}+y, x-\frac{1}{2}, \frac{1}{2}+z$; (iii) $2-x, -y, z$; (iv) $1-x, -y, z$.

The space group $P4_2bc$ was assigned from the systematic absences observed in the diffraction pattern: *hkl* – no systematic absences, 0*kl* $k = 2n+1$ (*h*0*l* $h = 2n+1$), *hhl* $l = 2n+1$, 00*l* $l = 2n+1$, and *h*00 $h = 2n+1$ (0*k*0 $k = 2n+1$). Among 352 space-group extinctions only a few reflections could be considered as observed (7 reflections of type 0*kl* and 3 reflections of type *hhl*), with intensities in the range 4–7$\sigma(I)$. The systematic absences are identical for space groups $P4_2bc$ and $P4_2/mbc$. Nevertheless, all tests [mean Abs(E^2−1) of *SHELXS*97 (Sheldrick, 1997), as well as Abs(*E*) distribution and the *N*(*z*) test of *maXus* (Mackay *et al.*, 2000)] clearly indicated that the intensity distribution is non-centrosymmetric. Examination of the structure with *PLATON* (Spek, 2003*a*,*b*) detected no obvious extra crystallographic symmetry. The absolute structure was established by the anomalous dispersion effect of the Br atoms in diffraction measurements on the crystal (3569 Bijvoet pairs) and is described by a Flack parameter of −0.006 (8) (Flack, 1983; Flack & Bernardinelli, 1999, 2000). More than half of the total number of H-atom positions were observed in a difference Fourier map. Nevertheless, in the refinement procedure, all H atoms were included from geometrical constraints in a riding model (C—H = 0.93–0.97 Å) and were refined with isotropic displacement factors of $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1174). Services for accessing these data are described at the back of the journal.

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