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(Carboxymethyl)dimethyloctylammonium Bromide

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Abstract

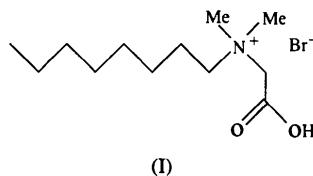
The title compound, C₁₂H₂₆NO₂⁺·Br⁻, forms monolayers and crystallizes in a head-to-tail arrangement stabilized by Br⁻···H—O hydrogen bonds and Br⁻···N⁺ contacts.

Comment

Surface-active carboxybetaines have a wide field of applications, particularly in cosmetic formulations. The adsorption ability of a carboxybetaine is important in determining its surface-active properties.

Alkylbetaines can exist in aqueous solution in zwitterionic and protonated forms depending on the pH. The homologous hydrobromides can be purified easily, in contrast to the corresponding betaines. The series of *N*-*n*-alkyl-*N,N*-dimethylammonio acetic acid hydrobromides of the formula R—N⁺(CH₃)₂—CH₂—COOH Br⁻ are good candidates for adsorption studies in aqueous solutions as they show good solubility up to an alkyl-chain length of 18 C atoms. The interest in analogies between the three-dimensional crystal structures and the two-dimensional monolayers formed by these compounds results from comparable intermolecular interactions in the layer planes.

The zigzag octyl chain in the title compound, (I), is nearly planar. The atoms C2 to C8 have a maximum deviation from the least-squares plane of 0.05 (4) Å. C1, N1 and C31 deviate from the plane by 0.41 (4), 0.49 (4) and 0.46 (5) Å, respectively. O1, O2, C31 and C32 are coplanar with a maximum deviation of 0.006 (2) Å. The conformation of the head region of the title molecule is comparable with that of the B form of octadecanoic acid, the atoms C31, C32, N1 and C1 in the former corresponding to the atoms C1 to C4 in the latter (Kaneko, Sakashita, Kobayashi, Kitagawa, Matsuura & Suzuki, 1994). The average C—C bond distance in the octyl chain is 1.511 Å. The C—C bond distances are alternately short and long, the average of the short distances being 1.498 (4) Å and the average of the long distances being 1.520 (4) Å.



The molecules form monolayers parallel to the (001) plane and are packed in a head-to-tail arrangement. All planes defined by the alkyl chains are parallel to each other. In the polar region, each Br⁻ ion is coordinated by three N atoms at distances of 4.211 (3), 4.260 (3) and 4.535 (3) Å (see Fig. 2). Shorter contacts are prevented by the steric hindrance afforded by the four C atoms bonded to each N atom [compare, for example, with the results of Okuyama, Mizuguchi, Xu & Shimomura (1989) or Taga, Machida, Kimura, Hayashi, Umemura & Takenaka (1986)]. One of the three Br⁻···N contacts connects two different monolayers; the other two are intralayer contacts. This threefold coordination may be the reason why the N atom has the smallest displacement parameter of all of the atoms in the molecule. One intralayer hydrogen bond, Br⁻···H2—O2, with a Br⁻···O distance of 3.121 (3) Å, is formed.

All C···C distances between neighbouring alkyl chains are longer than 4 Å. There are six C···C contacts below 4.2 Å. The displacement parameters of the

C atoms increase from C1 to C8 by a factor of two. The terminal chain C atom, C8, is close to the polar group of the neighbouring molecule, C8...O1 being 3.701 (6) Å.

The triclinic subcell has the cell constants $a_s = 4.578$, $b_s = 5.497$, $c_s = 2.519$ Å, $\alpha_s = 60.45$, $\beta_s = 109.00$, $\gamma_s = 95.95^\circ$ (compare with Abrahamsson, Dahlén, Löfgren & Pascher, 1978). The area per alkyl chain is 25.02 Å² ($\frac{1}{2}absin\gamma$). The direction of the chain axis is about [101] and the angle between the polar plane and the chain axis is 51.5°. The packing of the title compound is different from the packing in betaine hydrobromide (Clastre, 1964).

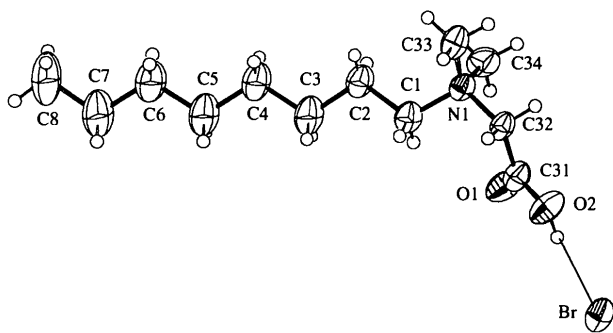


Fig. 1. PLATON (Spek, 1990) drawing of the asymmetric unit. Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms are represented by spheres of arbitrary size. The hydrogen bond is represented by a thin line.

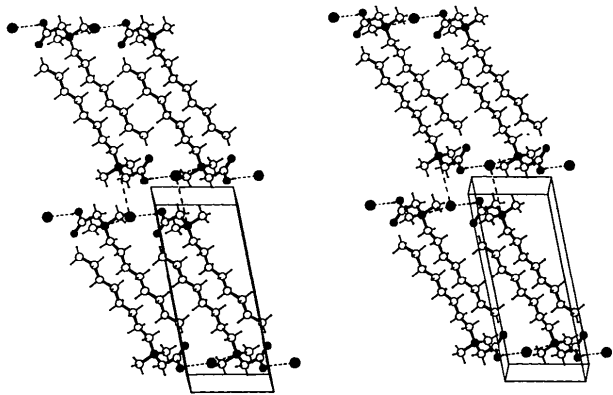


Fig. 2. SCHAKAL92 (Keller, 1992) drawing of the molecular packing viewed along the direction [010]. The Br⁻...N contacts and the hydrogen bonds are represented by dotted lines.

Experimental

Equimolar quantities of *N,N*-dimethylglycine butyl ester and octyl bromide were refluxed for 7 h in dry methanol. After addition of methanolic KOH, the product was hydrolyzed by refluxing for 1 h. Aqueous hydrobromic acid (48%) was added until the solution became acidic and the surplus inorganic salt was removed by filtration. The title compound precipitated, was filtered off and was dried using P₄O₁₀ under vacuum. The

product was purified by repeated recrystallizations from dry acetone containing small amounts of methanol. The synthesis of *N-n*-alkyl-*N,N*-dimethylammonio acetic acid bromides is described in detail elsewhere (Wüstneck, Kriwanek, Herbst, Wasow & Haage, 1992).

Crystal data

C₁₂H₂₆NO₂⁺.Br⁻

$M_r = 296.25$

Triclinic

$P\bar{1}$

$a = 6.771$ (4) Å

$b = 7.516$ (2) Å

$c = 15.765$ (4) Å

$\alpha = 85.19$ (2)°

$\beta = 80.00$ (2)°

$\gamma = 79.52$ (4)°

$V = 775.8$ (6) Å³

$Z = 2$

$D_x = 1.268$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 25 reflections

$\theta = 12.9$ – 18.4°

$\mu = 2.612$ mm⁻¹

$T = 293$ (2) K

Plate

0.65 × 0.35 × 0.16 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

2 θ/ω scans

Absorption correction: none

2808 measured reflections

2703 independent reflections

2419 observed reflections

[$I > \sigma(I)$]

$R_{int} = 0.0114$

$\theta_{max} = 24.97^\circ$

$h = -7 \rightarrow 8$

$k = -8 \rightarrow 8$

$l = 0 \rightarrow 18$

2 standard reflections

frequency: 60 min

intensity decay: 4.6%

Refinement

Refinement on F

$R = 0.039$

$wR = 0.045$

$S = 1.604$

2585 reflections

149 parameters

$w = 1/\sigma^2(F_o)$

where $\sigma(F_o^2) = [\sigma^2(I) + (pF_o^2)^2]$ and $p = 0.04$

$(\Delta/\sigma)_{max} = 0.10$

$\Delta\rho_{max} = 0.77$ e Å⁻³

$\Delta\rho_{min} = -3.0$ e Å⁻³

Extinction correction:

Zachariasen (1967)

Extinction coefficient:

3.85×10^{-7}

Atomic scattering factors

from *International Tables*

for *Crystallography* (1974,

Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Br	0.68084 (4)	0.20429 (4)	0.13647 (2)	0.0559 (1)
O1	0.9626 (3)	0.5955 (3)	0.18893 (16)	0.0713 (8)
O2	1.0703 (3)	0.3832 (3)	0.09279 (15)	0.0680 (7)
N1	1.3469 (3)	0.7346 (3)	0.13254 (14)	0.0424 (6)
C1	1.3757 (5)	0.6704 (4)	0.22440 (19)	0.0512 (8)
C2	1.4787 (5)	0.7887 (4)	0.2702 (2)	0.0564 (9)
C3	1.5064 (5)	0.7057 (5)	0.3584 (2)	0.0679 (10)
C4	1.6486 (5)	0.7932 (5)	0.4006 (2)	0.0689 (11)
C5	1.6795 (6)	0.7133 (5)	0.4884 (2)	0.0760 (11)
C6	1.8331 (6)	0.7908 (5)	0.5276 (2)	0.0780 (11)
C7	1.8626 (7)	0.7163 (6)	0.6164 (2)	0.0905 (16)
C8	2.0214 (7)	0.7950 (7)	0.6515 (3)	0.1097 (16)
C31	1.0854 (4)	0.5264 (4)	0.13213 (19)	0.0488 (8)
C32	1.2816 (4)	0.5882 (3)	0.09133 (19)	0.0439 (7)
C33	1.5476 (4)	0.7636 (4)	0.07965 (19)	0.0543 (8)
C34	1.1964 (5)	0.9091 (4)	0.1301 (2)	0.0636 (10)

Table 2. Selected geometric parameters (Å, °)

O1—C31	1.194 (4)	C2—C3	1.503 (5)
O2—C31	1.314 (4)	C3—C4	1.526 (5)
N1—C1	1.521 (4)	C4—C5	1.495 (5)
N1—C32	1.492 (3)	C5—C6	1.519 (6)
N1—C33	1.508 (4)	C6—C7	1.496 (5)
N1—C34	1.510 (4)	C7—C8	1.518 (7)
C1—C2	1.519 (5)	C31—C32	1.507 (4)
C1—N1—C32	108.9 (2)	N1—C1—C2	115.7 (2)
C1—N1—C33	110.0 (2)	C1—C2—C3	110.2 (3)
C1—N1—C34	111.7 (2)	O1—C31—O2	125.5 (3)
C32—N1—C33	105.8 (2)	O1—C31—C32	126.8 (3)
C32—N1—C34	111.3 (2)	O2—C31—C32	107.7 (2)
C33—N1—C34	108.9 (2)	N1—C32—C31	117.8 (2)
C32—N1—C1—C2	169.3 (2)	O1—C31—C32—N1	9.1 (4)
C1—N1—C32—C31	60.3 (3)	O2—C31—C32—N1	-172.1 (2)
N1—C1—C2—C3	-177.4 (3)		

H2 was found by difference Fourier synthesis and all other H-atom positions were calculated assuming tetrahedral or staggered tetrahedral geometry and a C—H bond length of 0.95 Å. Isotropic displacement parameters for H atoms were calculated by multiplying the displacement parameter of the bonding partners by 1.3. The position of H2 was refined; all other H-atom parameters were fixed.

Data collection: CAD-4 diffractometer software (Enraf-Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *PLATON92* (Spek, 1990), *SCHAKAL92* (Keller, 1992). Software used to prepare material for publication: *PLATON92*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and contact distances, have been deposited with the IUCr (Reference: SE1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Carboxymethyl)dimethyldodecylammonium Bromide

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Abstract

The title compound, C₁₅H₃₂NO₂⁺.Br⁻, crystallizes to form layers with interdigitating hydrocarbon chains stabilized by Br⁻···H—O hydrogen bonds and Br⁻···N⁺ contacts.

Comment

In a systematic study, analogies between the crystal structures and the self-assembling properties of the homologous *N-n*-alkylcarboxybetaines have been investigated. It is of special interest whether there are similarities between layers within the crystal structures of the amphiphilic homologues and the adsorption monolayers they form.

This is the second publication in a series describing the crystal structures of surface-active carboxybetaines. The aim is to find relationships between alkyl-chain length and molecular packing in the crystal. The questions to be addressed are whether there is an even-odd effect, *i.e.* whether the crystal structures of compounds with an even number of alkyl C atoms are different from the crystal structures of those with an odd number (Müller-Fahnow, Hilgenfeld, Hesse, Saenger & Pfannenmüller, 1988), and how long or how short the alkyl chain should be for the molecules to form a layered structure. In the first publication of this series the structure of the octyl betaine was presented (Rudert, Schulz, Reck, Vollhardt & Kriwanek, 1995).

The zigzag undecyl chain in the title compound, (I), is nearly planar. The atoms C2 to C11 have a maximum deviation from the least-squares plane of 0.08 (5) Å. C1, N1 and C31 deviate from the plane by 0.48 (5), 0.56 (5) and 0.90 (5) Å, respectively. The same kind of deviation of C1 from the plane was observed for the octyl betaine.