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N-*n*-Alkyl *N*,*N*-dimethylammonioacetic acid bromides: the first complete series of crystal and molecular structure determinations of an amphiphilic compound with alkyl chain lengths *n* = 1,..., 16

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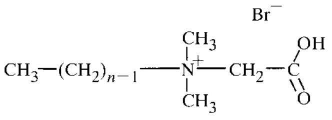
The molecular and crystal structures of 16 *N*-*n*-alkyl *N*,*N*-dimethylammonioacetic acid bromides with chain lengths between n = 1 and n = 16 have been determined. All compounds from n = 5 to n = 16 form bilayers with interdigitated chains. The even-numbered chains display the chain packing type M_2^{II}. The chain packing of the odd-numbered chain compounds is less regular. The head groups of all compounds are connected *via* electrostatic $N^+\cdots Br^-$ interactions, and by $OH\cdots Br^-$ hydrogen bonds. The compounds with short chains are packed in different ways. Their molecular conformation depends on the crystal packing.

1. Introduction

Monolayers of amphiphilic substances tend to form ordered structures at the air–water interface. The current interest in the structural analogies of three-dimensional crystals of amphiphiles and their two-dimensional mono- or bilayers at interfaces is due to the comparable intermolecular interaction with the layer planes in both systems. With the introduction of synchrotron X-ray diffraction, a new technique is available to obtain direct information on the lattice structure of Langmuir monolayers which form condensed monolayer phases. It is however difficult or impossible to use this technique for the direct determination of the structure of amphiphilic adsorption layers where the substance is dissolved in water. Studies of the crystal structure of these amphiphiles may be helpful as the amphiphilic molecules normally form two-dimensional planes in crystals which may be similar to ordered monolayer structures at the air–water interface.



$$CH_3-(CH_2)_{n-1}-\overset{CH_3}{\underset{CH_3}{\overset{|+}{N}}}-CH_2-C\begin{matrix}OH\\ \\ O\end{matrix}\quad Br^-$$

In a systematic study, we focused on analogies between the crystal structures and the self-aggregating properties of the homologous *N*-*n*-alkyl *N*,*N*-dimethylammonioacetic acid bromides.

We have now completed a series of structure determinations of *N*-alkyl betaine hydrobromides. We were especially interested in the relationship between chain length on the one hand and crystal and molecular structure on the other.

The crystal structures of five of the compounds have already been published [n = 1 (Clastre, 1964), 2, 4 (Rudert *et al.*, 1996), 8, 11 (Rudert *et al.*, 1995*a*,*b*)]. The structure of betaine hydrobromide (n = 1) has been redetermined by us with higher precision. Of the remaining compounds those with n = 3, 7, 14, 16 have R values below average and will be discussed in detail.

In this article the compounds will be named as (1), (2),..., (16), depending on the alkyl chain length.

2. Synthesis and preparation of crystals

The title compounds were synthesized according to the following general procedure: equimolar quantities of *N,N*-dimethylglycine butyl ester (0.1 mol) and the corresponding alkyl bromides (0.1 mol) were mixed, and after adding 25 ml of methanol refluxed for 7 h. After cooling the mixture to ambient temperature concentrated methanolic KOH was added until it became alkaline. The batch was allowed to stand overnight, inorganic salt (KBr) was removed by filtration, and the solution was acidified with concentrated hydrobromic acid (~20 ml). The resulting precipitate of hydrobromide (in case of the short-chain hydrobromides the solution must be evaporated to half its volume) was filtrated, washed with acetone and dried over P_2O_5 under vacuum. Microanalytically pure products were obtained by recrystallization from dry acetone (100 ml) containing small amounts of methanol (for the long-chain hydrobromides somewhat more methanol was needed).

Single crystals were grown by evaporating an acetone solution. Compounds (3) and (5) tend to include crystal water, therefore, especially dry acetone had to be used for them.

3. Structure determination and refinement

Measurements were carried out on a CAD-4 diffractometer (Enraf–Nonius, 1977) using in most cases Mo $K\alpha$ radiation [(6) and (10): Cu $K\alpha$ radiation]. The temperature of the measurements was normally ~298 K. For (3) a temperature of 223 K was used because of an apparent instability of the crystal. Data reduction was carried out using *MolEN* (Fair, 1990). In most cases the structures were solved by direct methods, and in some cases by assuming a bromide ion at the same position as in a homologue. Missing atoms were found by difference Fourier synthesis. The positions of those H atoms which could not be found in the difference Fourier map were calculated. In those cases where the hydroxyl-H atoms could not be located the torsion angle C32—C31—O2—H2 with closest Br···H distance was chosen. All non-H atoms were refined anisotropically. H atoms were refined riding on their bonding partners. Absorption corrections were carried out using the method of Walker & Stuart (1983).

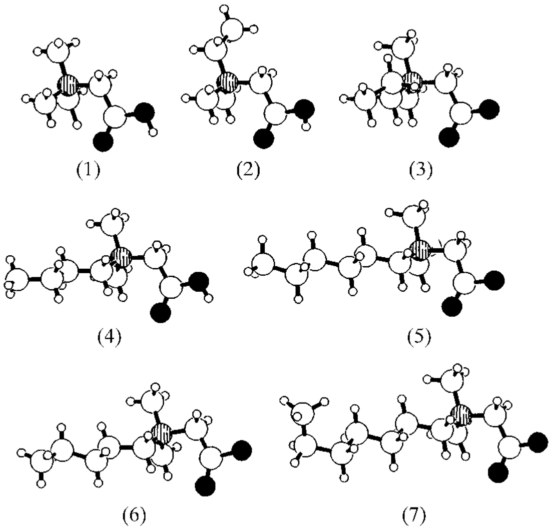


Figure 1
Molecular structures of (1)–(7). Drawn using *SCHAKAL*92 (Keller, 1992).

Experimental details are listed in Table 1,[1] atomic coordinates in Table 2, selected bonds and angles in Table 3, and selected torsion angles in Table 4.

4. Discussion

4.1. Molecular structure

The head group conformation is virtually the same in all compounds. The carbonyl O1 atom is near to the positively charged N1 atom, the distance between both atoms lying between 2.8 and 3.0 Å. In all the compounds the C32, C31, O1 and O2 atoms are coplanar with very small deviations. N1 deviates significantly from this plane. The main differences between the molecular structures of the compounds are the position and direction of the hydrocarbon chain relative to the head group (Fig. 1). With the exception of (2) the first chain carbon atom is in a *gauche* position relative to the head group fragment N—C—COOH. The second chain carbon atom is in a *gauche* position in (2) and (3) and in a *trans* position in all other compounds. All compounds from (4) to (16) have regular *all-trans* hydrocarbon chains, with the exception of (7), whose last chain carbon atom is in a *gauche* position. There is always a small deviation of the first chain carbon atom from the chain plane. Because of the weak van der Waals interactions between the hydrocarbon chains, the thermal motion increases from the beginning to the end of the chains. The displacement parameters of the odd-numbered long chains [(7), (9), (11), (13) and (15)] are much larger than those of the even-numbered ones. In an unpublished structure determination of one of the title compounds at low temperature carried out by the authors the displacement parameters were even higher, so they may be partly due to disorder.

4.2. Crystal structure

With respect to their crystal packings the compounds can be divided into two groups: Compounds (1)–(4), which form three-dimensional nets, and (5)–(16), which form bilayers. Typical examples are shown in Figs. 2 and 4. The most important interactions between the head groups is *via* the Br^-

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ0007). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details (Niggli reduced cell).

	(1)	(2)	(3)	(4)
Chemical formula	$C_5H_{12}NO_2{}^+.Br^-$	$C_6H_{14}NO_2{}^+.Br^-$	$C_7H_{16}NO_2{}^+.Br^-$	$C_8H_{18}NO_2{}^+.Br^-$
Chemical formula weight	198.07	212.09	226.12	240.15
a (Å)	7.613 (1)	12.113 (6)	6.793 (3)	11.110 (7)
b (Å)	9.236 (3)	7.282 (2)	13.85 (1)	13.428 (5)
c (Å)	11.853 (4)	10.925 (3)	11.420 (5)	15.038 (5)
α (°)	90	90	90	90
β (°)	98.08 (2)	107.35 (3)	102.71 (4)	90
γ (°)	90	90	90	90
V (Å^3)	825.1 (4)	919.84	1048 (1)	2243 (2)
D_x (Mg m^{-3})	1.594	1.53	1.433	1.42
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
μ (mm^{-1})	4.92	4.376	3.882	3.596
Temperature (K)	298 (2)	294 (2)	223 (2)	294 (2)
Crystal size (mm)	0.45 × 0.23 × 0.15	0.46 × 0.22 × 0.14	0.38 × 0.20 × 0.22	0.70 × 0.60 × 0.28
Crystal colour	Colourless	Colourless	Colourless	Colourless
2θ range (°)	2.7–25	2.5–25	2.3–22	2.5–25
No. of measured reflections	1551	812	1533	2244
No. of observed reflections	1219	797	1090	2052
$R[F^2>2\sigma(F^2)]$	0.0258	0.032	0.038	0.053
$wR(F^2)$	0.0832	0.034 [$wR(F_o)$]	0.100	0.052 [$wR(F_o)$]

	(5)	(6)	(7)	(8)
Chemical formula	$C_9H_{20}NO_2{}^+\cdot Br^-$	$C_{10}H_{22}NO_2{}^+\cdot Br^-$	$C_{11}H_{24}NO_2{}^+\cdot Br^-$	$C_{12}H_{26}NO_2{}^+\cdot Br^-$
Chemical formula weight	254.17	268.20	282.23	296.25
a (Å)	6.771 (3)	6.739 (6)	6.872 (2)	6.771 (4)
b (Å)	7.599 (2)	7.525 (2)	7.519 (1)	7.516 (2)
c (Å)	12.273 (5)	13.67 (2)	14.107 (1)	15.765 (4)
α (°)	94.17 (3)	85.61 (6)	85.59 (1)	85.19 (2)
β (°)	92.04 (3)	86.18 (9)	87.20 (2)	80.00 (2)
γ (°)	98.83 (3)	79.81 (4)	81.44 (2)	79.52 (4)
V (Å^3)	621.6 (4)	679.3 (12)	718.2 (2)	775.8 (6)
D_x (Mg m^{-3})	1.358	1.311	1.305	1.268
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	1.54178	0.71069	0.71069
μ (mm^{-1})	3.282	3.973	2.79	2.61
Temperature (K)	298 (2)	298 (2)	296 (2)	293 (2)
Crystal size (mm)	0.66 × 0.14 × 0.055	0.40 × 0.15 × 0.07	0.35 × 0.24 × 0.05	0.65 × 0.35 × 0.16
Crystal colour	Colourless	Colourless	Colourless	Colourless
2θ range (°)	1.7–20	3.2–54	1.5–25	2.6–25
No. of measured reflections	672	1422	2623	2703
No. of observed reflections	331	1297	1558	2419
$R[F^2>2\sigma(F^2)]$	0.0953	0.3871	0.066	0.039
$wR(F^2)$	0.2239	0.7018	0.069 [$wR(F_o)$]	0.045

	(9)	(10)	(11)	(12)
Chemical formula	$C_{13}H_{28}NO_2{}^+\cdot Br^-$	$C_{14}H_{30}NO_2{}^+\cdot Br^-$	$C_{15}H_{32}NO_2{}^+\cdot Br^-$	$C_{16}H_{34}NO_2{}^+\cdot Br^-$
Chemical formula weight	310.28	324.3	338.34	352.36
a (Å)	6.816 (2)	6.755 (2)	6.791 (3)	6.777 (2)
b (Å)	7.572 (2)	7.493 (2)	7.554 (4)	7.452 (3)
c (Å)	16.526 (3)	17.571 (6)	18.304 (7)	19.325 (5)
α (°)	84.89 (1)	91.15 (2)	89.89 (7)	92.34 (3)
β (°)	81.95 (2)	97.41 (2)	84.06 (4)	91.84 (2)
γ (°)	81.42 (2)	100.73 (2)	81.94 (8)	101.21 (3)
V (Å^3)	833.0 (5)	865.6 (4)	924.7 (9)	955.7 (5)
D_x (Mg m^{-3})	1.237	1.244	1.22	1.224
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	1.54178	0.71069	0.71069
μ (mm^{-1})	2.46	3.20	2.20	2.15
Temperature (K)	293 (2)	298 (2)	294 (2)	298 (2)
Crystal size (mm)	0.46 × 0.32 × 0.03	0.57 × 0.29 × 0.10	0.65 × 0.38 × 0.20	0.6 × 0.55 × 0.15
Crystal colour	Colourless	Colourless	Colourless	Colourless
2θ range (°)	2–25	2.5–70	2.5–25	2–25
No. of measured reflections	–	3392	3233	3456
No. of observed reflections	1654	2901	2926	2803
R	0.086	0.097	0.060	0.153
wR	–	0.301	0.055[$wR(F_o)$]	0.374

Table 1 (continued)

	(13)	(14)	(15)	(16)
Chemical formula	$C_{17}H_{36}NO_2{}^+\cdot Br^-$	$C_{18}H_{38}NO_2{}^+\cdot Br^-$	$C_{19}H_{40}NO_2{}^+\cdot Br^-$	$C_{20}H_{42}NO_2{}^+\cdot Br^-$
Chemical formula weight	366.39	380.41	394.44	408.46
a (Å)	6.804 (3)	6.778 (4)	6.834 (6)	6.762 (3)
b (Å)	7.546 (4)	7.484 (1)	7.531 (6)	7.466 (2)
c (Å)	20.037 (7)	21.348 (5)	21.87 (2)	23.40 (2)
α (°)	90.18 (3)	87.34 (2)	90.18 (8)	86.90 (5)
β (°)	89.68 (3)	86.96 (3)	94.58 (9)	83.14 (5)
γ (°)	97.87 (4)	79.04 (3)	97.79 (8)	78.87 (3)
V (Å^3)	1019.0 (5)	1061.0 (5)	1111.5 (17)	1150 (1)
D_x (Mg m^{-3})	1.194	1.191	1.178	1.180
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
μ (mm^{-1})	2.02	1.92	1.86	1.78
Temperature (K)	298 (2)	296 (2)	298 (2)	296 (2)
Crystal size (mm)	0.7 × 0.4 × 0.36	0.78 × 0.70 × 0.26	0.33 × 0.30 × 0.03	0.38 × 0.16 × 0.05
Crystal colour	Colourless	Colourless	Colourless	Colourless
2θ range (°)	2–25	1.5–25	1.9–23	1.0–20
No. of measured reflections	2079	3706	3027	2368
No. of observed reflections	1732	3345	987	1849
R	0.055	0.034	0.152	0.039
wR	0.149	0.101	0.252	0.103

ions. Normally there are three $Br^-\cdots N$ contacts for each Br^- ion. A prototype of this kind of interaction is tetramethylammonium bromide (Cheban *et al.*, 1987; Evans & Hughes, 1990), where each N atom is tetrahedrally surrounded by four Br^- ions. In the title compounds the fourth contact position is blocked by the carboxy group, therefore, only three $Br^-\cdots N$ contacts per Br^- ion exist. Only in (4) are there four contacts for one of the Br^- ions, but the coordination symmetry deviates very much from tetrahedral symmetry. In the layered structures one $Br^-\cdots N$ contact connects different bilayers, the other two are intralayer contacts. In all title compounds there are short hydrogen bonds $Br^-\cdots HO$. The $Br^-\cdots O$ distances lie between 3.075 (7) and 3.139 (3) Å.

The compounds (1)–(4) form three-dimensional nets which are dominated by $Br^-\cdots N$ interactions and $Br^-\cdots HO$ hydrogen bonds (see, for example, Fig. 2). They have three

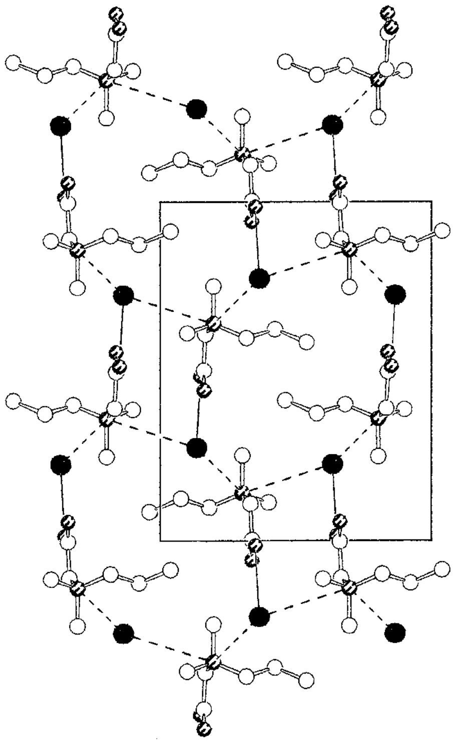


Figure 2
Molecular packing of (3) viewed in the direction of *a*. Filled circles are Br, shaded circles are N and O, and open circles are C. H atoms were omitted for the sake of clarity. Dotted lines are N⋯Br contacts, thin lines are hydrogen bonds. Drawn using *SCHAKAL*92 (Keller, 1992).

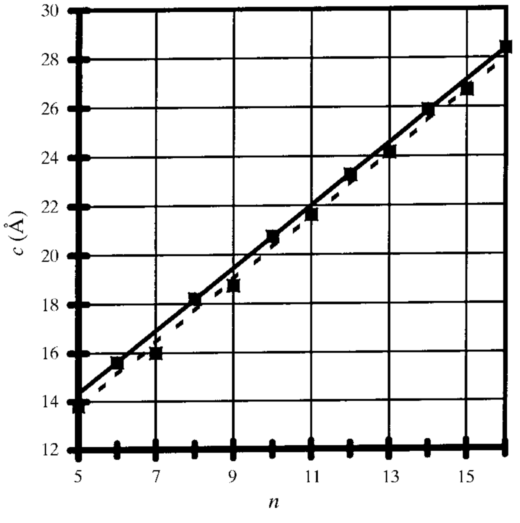


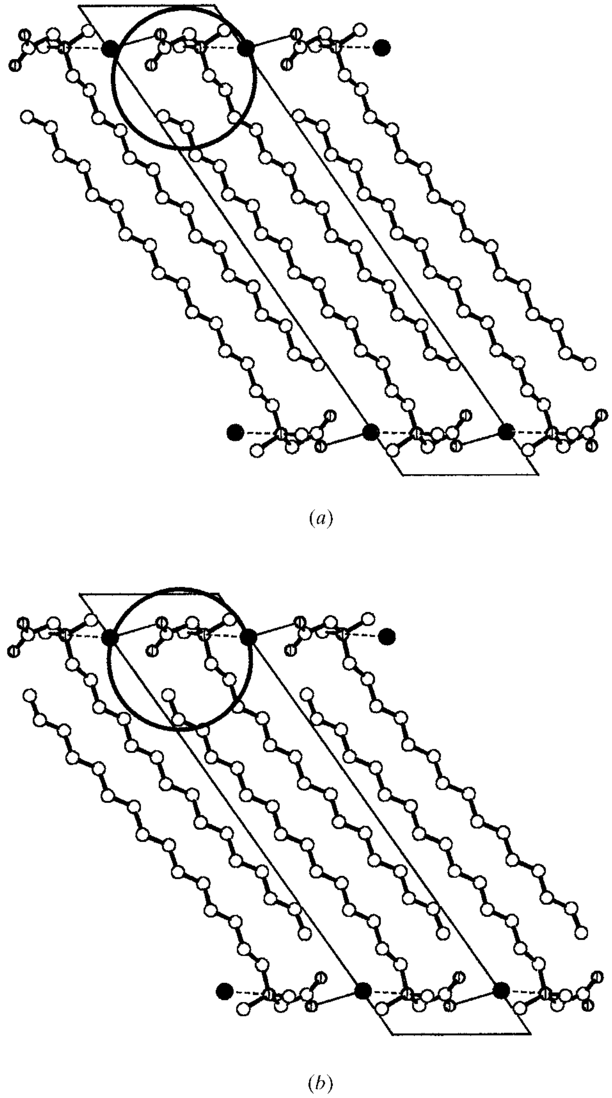
Figure 3
Cell constant *c* in dependence of the chain length *n*. The solid line is a least-squares fit to the *c* of the even-numbered chain compounds, the dotted line is fitted to the *c* of (5), (11), (13) and (15).

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2), all related to the Niggli reduced cell as in Table 1.

$$U_{\rm eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(3)				
Br	0.24162 (7)	0.22588 (4)	0.63472 (5)	0.0455 (3)
O1	0.2053 (5)	−0.0585 (2)	0.3364 (4)	0.0526 (10)
O2	−0.1040 (5)	−0.0108 (3)	0.3493 (3)	0.0466 (10)
N1	0.3145 (5)	0.1403 (3)	0.3030 (3)	0.0317 (9)
C31	0.0824 (7)	0.0030 (4)	0.3388 (4)	0.0347 (11)
C32	0.1177 (7)	0.1100 (4)	0.3309 (5)	0.0341 (11)
C33	0.3116 (10)	0.2481 (4)	0.2977 (6)	0.0449 (13)
C34	0.4905 (8)	0.1106 (5)	0.4011 (5)	0.0410 (12)
C1	0.3490 (8)	0.0987 (4)	0.1857 (4)	0.0411 (12)
C2	0.1964 (12)	0.1247 (6)	0.0759 (6)	0.074 (2)
C3	0.2509 (16)	0.0806 (8)	−0.0342 (7)	0.088 (3)
(7)				
Br1	−1.7934 (1)	−0.7946 (1)	−0.84966 (6)	0.0689 (3)
O1	−1.4910 (7)	−0.3989 (7)	−0.7987 (4)	0.082 (1)
O2	−1.4111 (8)	−0.6213 (7)	−0.8969 (4)	0.079 (1)
N1	−1.1174 (8)	−0.2699 (7)	−0.8546 (4)	0.057 (1)
C31	−1.384 (1)	−0.4734 (9)	−0.8567 (6)	0.062 (3)
C32	−1.195 (1)	−0.4170 (9)	−0.8990 (5)	0.056 (1)
C33	−0.927 (1)	−0.246 (1)	−0.9076 (6)	0.068 (3)
C34	−1.257 (1)	−0.097 (1)	−0.8648 (7)	0.080 (3)
C1	−1.077 (1)	−0.331 (1)	−0.7488 (5)	0.067 (3)
C2	−0.953 (1)	−0.221 (1)	−0.7007 (5)	0.070 (3)
C3	−0.943 (1)	−0.287 (1)	−0.5952 (6)	0.080 (3)
C4	−0.796 (1)	−0.203 (1)	−0.5418 (7)	0.087 (3)
C5	−0.796 (1)	−0.264 (1)	−0.4355 (7)	0.098 (4)
C6	−0.644 (2)	−0.185 (2)	−0.3779 (8)	0.117 (4)
C7	−0.441 (2)	−0.273 (2)	−0.405 (1)	0.149 (5)
(14)				
Br	0.22069 (3)	0.20898 (3)	0.09980 (1)	0.05183 (14)
O1	0.5159 (3)	0.6035 (3)	0.13844 (12)	0.0694 (6)
O2	0.5964 (4)	0.3865 (3)	0.06816 (12)	0.0653 (6)
C31	0.6223 (4)	0.5317 (3)	0.09655 (13)	0.0463 (5)
C32	0.8064 (4)	0.5914 (3)	0.06615 (13)	0.0428 (5)
C33	1.0687 (4)	0.7669 (4)	0.05772 (14)	0.0508 (6)
C34	0.7317 (5)	0.9166 (4)	0.0942 (2)	0.0605 (7)
N1	0.8822 (3)	0.7403 (2)	0.09673 (9)	0.0399 (4)
C1	0.9384 (4)	0.6793 (3)	0.16364 (12)	0.0460 (5)
C2	1.0551 (5)	0.7983 (4)	0.19573 (13)	0.0519 (6)
C3	1.1102 (5)	0.7170 (5)	0.26046 (14)	0.0582 (7)
C4	1.2680 (5)	0.8031 (5)	0.28924 (15)	0.0612 (7)
C5	1.3262 (5)	0.7230 (5)	0.35395 (14)	0.0627 (7)
C6	1.4969 (5)	0.7968 (5)	0.3803 (2)	0.0645 (7)
C7	1.5562 (5)	0.7169 (5)	0.44505 (15)	0.0645 (8)
C8	1.7291 (5)	0.7871 (5)	0.47081 (15)	0.0637 (7)
C9	1.7872 (5)	0.7093 (5)	0.53600 (14)	0.0628 (7)
C10	1.9601 (5)	0.7794 (5)	0.5619 (2)	0.0643 (8)
C11	2.0160 (5)	0.7042 (5)	0.62733 (14)	0.0628 (7)
C12	2.1876 (5)	0.7762 (5)	0.65333 (15)	0.0643 (7)
C13	2.2417 (7)	0.7068 (6)	0.7190 (2)	0.0770 (9)
C14	2.4139 (8)	0.7808 (8)	0.7437 (2)	0.0936 (13)
(16)				
Br	0.19972 (7)	0.20940 (6)	0.09149 (2)	0.0554 (3)
O1	0.4865 (6)	0.6048 (5)	0.1267 (2)	0.0708 (10)
O2	0.5812 (6)	0.3865 (5)	0.0621 (2)	0.0672 (10)
C31	0.6001 (7)	0.5320 (7)	0.0887 (2)	0.0487 (13)
C32	0.7919 (6)	0.5918 (6)	0.0607 (2)	0.0440 (12)
C33	1.0550 (7)	0.7675 (7)	0.0528 (2)	0.0513 (13)
C34	0.7109 (8)	0.9162 (6)	0.0870 (2)	0.0622 (14)
N1	0.8615 (5)	0.7411 (5)	0.0887 (2)	0.0412 (9)
C1	0.9035 (7)	0.6800 (6)	0.1497 (2)	0.0477 (12)
C2	1.0117 (7)	0.7994 (7)	0.1798 (2)	0.0528 (13)
C3	1.0537 (8)	0.7190 (7)	0.2387 (2)	0.0611 (14)
C4	1.2039 (8)	0.8058 (7)	0.2652 (2)	0.0612 (14)
C5	1.2501 (8)	0.7275 (7)	0.3241 (2)	0.0617 (14)
C6	1.4149 (8)	0.7989 (8)	0.3489 (2)	0.0651 (15)
C7	1.4605 (8)	0.7217 (8)	0.4081 (2)	0.068 (2)
C8	1.6278 (8)	0.7916 (8)	0.4316 (2)	0.0659 (15)
C9	1.6718 (8)	0.7142 (8)	0.4909 (2)	0.0655 (15)
C10	1.8401 (8)	0.7831 (7)	0.5143 (2)	0.0650 (15)
C11	1.8846 (8)	0.7068 (8)	0.5737 (2)	0.0659 (15)
C12	2.0521 (8)	0.7765 (8)	0.5979 (2)	0.0662 (15)
C13	2.0942 (8)	0.7014 (8)	0.6575 (2)	0.067 (2)
C14	2.2612 (8)	0.7729 (8)	0.6812 (2)	0.068 (2)
C15	2.3015 (10)	0.7027 (9)	0.7416 (2)	0.081 (2)
C16	2.4677 (10)	0.7772 (10)	0.7644 (3)	0.097 (2)

different space groups (regarding $P2_1/c$ and $P2_1/n$ as equivalent, Table 5). Compounds (5)–(16) have all space group $P\overline{1}$. Their cell constant c is linearly dependent on the chain length (Table 5, Fig. 3).



(*a*)

(*b*)

Figure 4
Molecular packing of (*a*) (16) and (*b*) (15) viewed in the direction of **b**. The circles mark the region of close contact between a head group and a chain methyl group. For further explanations see Fig. 2.

Table 3
Selected bond distances and angles (Å, °) .

The reciprocal of the standard deviation was used as weight.

	(3)	(7)	(14)	(16)	Weighted average of all compounds
O1—C31	1.197 (6)	1.190 (9)	1.199 (3)	1.185 (6)	1.194 (2)
O2—C31	1.311 (6)	1.33 (1)	1.313 (3)	1.315 (6)	1.318 (4)
C31—C32	1.508 (7)	1.51 (1)	1.509 (4)	1.516 (7)	1.509 (3)
N1—C32	1.501 (6)	1.488 (9)	1.501 (3)	1.499 (5)	1.495 (3)
N1—C33	1.494 (7)	1.502 (9)	1.516 (3)	1.508 (6)	1.504 (3)
N1—C34	1.505 (6)	1.499 (9)	1.507 (3)	1.496 (6)	1.504 (3)
N1—C1	1.523 (6)	1.554 (9)	1.525 (3)	1.519 (6)	1.532 (6)
C1—C2	1.485 (9)	1.50 (1)	1.507 (4)	1.505 (6)	–
C2—C3	1.52 (1)	1.54 (1)	1.519 (4)	1.510 (7)	–
C3—C4	–	1.53 (1)	1.518 (4)	1.511 (7)	–
C4—C5	–	1.53 (1)	1.521 (4)	1.512 (7)	–
C5—C6	–	1.57 (2)	1.517 (4)	1.509 (7)	–
C6—C7	–	1.49 (2)	1.523 (4)	1.514 (7)	–
C7—C8	–	–	1.510 (4)	1.505 (7)	–
C8—C9	–	–	1.525 (4)	1.514 (7)	–
C9—C10	–	–	1.511 (4)	1.505 (7)	–
C10—C11	–	–	1.522 (4)	1.515 (7)	–
C11—C12	–	–	1.512 (4)	1.512 (7)	–
C12—C13	–	–	1.512 (4)	1.513 (7)	–
C13—C14	–	–	1.511 (6)	1.511 (7)	–
C14—C15	–	–	–	1.518 (7)	–
C15—C16	–	–	–	1.508 (8)	–
C1—N1—C32	113.4 (4)	108.5 (5)	109.6 (2)	109.3 (3)	109.4 (4)
C1—N1—C33	110.2 (4)	109.7 (5)	109.8 (2)	110.2 (3)	109.8 (3)
C1—N1—C34	107.5 (4)	112.2 (6)	112.4 (2)	112.1 (3)	111.8 (6)
C32—N1—C33	106.5 (4)	106.2 (5)	105.3 (2)	105.3 (3)	106.2 (4)
C32—N1—C34	111.4 (4)	111.0 (5)	111.3 (2)	111.3 (3)	111.0 (3)
C33—N1—C34	107.8 (4)	109.0 (5)	108.2 (2)	108.5 (4)	108.3 (3)
O1—C31—O2	126.3 (4)	125.8 (7)	125.5 (2)	126.4 (5)	125.6 (2)
O1—C31—C32	125.2 (4)	126.7 (7)	126.9 (2)	126.4 (5)	126.6 (3)
O2—C31—C32	108.5 (4)	107.5 (6)	107.6 (2)	107.2 (5)	107.9 (3)
N1—C32—C31	116.6 (4)	117.3 (6)	117.0 (2)	117.3 (4)	117.2 (4)
N1—C1—C2	116.0 (4)	115.0 (6)	115.4 (2)	115.7 (4)	–
C1—C2—C3	110.5 (6)	108.4 (7)	110.0 (2)	110.5 (4)	–
C2—C3—C4	–	113.1 (7)	112.8 (3)	112.9 (4)	–
C3—C4—C5	–	112.4 (8)	113.7 (3)	114.2 (4)	–
C4—C5—C6	–	114.3 (9)	113.7 (3)	115.1 (4)	–
C5—C6—C7	–	108 (1)	114.0 (3)	115.2 (4)	–

4.3. Chain packing

Compounds (5)–(16) form bilayers with interdigitated tails. Their chains are all packed with parallel chain axes and parallel chain zigzag planes. All of the chain axes are parallel to the (010) crystal plane. Segerman (1965) found 10 simple packing types for hydrocarbon chains, eight of them having parallel chain planes. In his classification the chains are assumed to be infinitely long to form a three-dimensional crystal with an asymmetric unit consisting of CH_2 having the cell constant c_s in the chain direction, and a_s and b_s in the other directions. Two other useful parameters are the area per chain (projection of the unit cell constants a_s, b_s, γ_s onto a plane perpendicular to the chain axes) and the area per head group (area of the bilayer divided by the number of head groups). In our case the area per chain is $(1/2)\cdot a_s\cdot b_s\cdot\sin\gamma_s$ or $a_s\cdot b_s\cdot\sin\gamma_s$ (assuming $\alpha_s = \beta_s = 90°$), the area per head group is $(1/2)\cdot a\cdot b\cdot\sin\gamma$. These areas can be compared with the results from monolayer studies. The experimentally found chain packings deviate more or less from the simple packing types because of interactions between chain ends and/or head groups. A review article by Abrahamsson *et al.* (1978) reported the experimental confirmation of six simple packing types, four having parallel chain planes. The packing of the title compounds is different from these six experimentally found ones. We will now describe the packing types in detail.

4.3.1. Type *A* [(6), (8), (10), (12), (14) and (16)]. There are infinite rows of nearly coplanar chains with an approximate chain–chain distance of $b_s \simeq 4.78$ Å (Fig. 5*a*). The chains in this row are related by a simple translation perpendicular to the chain axes. Adjacent rows are related by another translation perpendicular to the chain axes and a 180° rotation around the chain axes. The distance between adjacent chains in this other direction, $a_s/2$, is about 4.25 Å. The angle between both translations, γ_s, is about 109°. This is the rarely found packing type M_2^{II} described by Segerman (1965).

The distances between the terminal C atom and the doubly bonded O atom of the next layer are between 3.70 and 4.14 Å (Fig. 4*a*, Table 6). The area per chain is about 19.3 Å^2, the average area per head group (parallel to the head group plane) is 24.76 Å^2.

4.3.2. Type *B* [(11), (13) and (15)]. The odd-numbered chain compounds cannot adopt packing type *A*, because it would lead to a distance between the terminal C atom and the doubly bonded O atom of the next layer, O1, shorter than 2.5 Å. The repulsion between those two atoms forces the chains to adopt a less symmetric packing. As in type *A*, type *B* can be described by two translations, a_s and b_s, with $a_s \simeq 4.81$, $b_s \simeq 4.30$ Å and $\gamma_s \simeq 110°$ for the chain axes (Fig. 5*b*). However, the zigzag planes are not parallel to one of those translations. Adjacent rows of chains are related by the translation a_s and a 180° rotation around the chain axes for every second row. The distances between the terminal C atom and O1 are between 3.40 and 3.47 Å (Fig. 4*b*, Table 6). The chain packing may be described as a hybrid of the types M_1 and M_2 (Segerman, 1965). The area per chain is about 19.3 Å^2, and the average area per head group is 25.46 Å^2. Regarding the cell constants (Table 5), (5) seems to belong to type *B* also. However, the low precision of the structure determination did

Table 4
Selected torsion angles (°).

The reciprocal of the standard deviation was used as weight.

					wt av. of (5)–(16)	
	(3)	(7)	(14)	(16)	*n* = odd	*n* = even
C32—N1—C1—C2	59.7 (7)	165.4 (6)	168.2 (2)	168.9 (4)	164.4 (9)	168.8 (2)
C33—N1—C1—C2	−59.5 (7)	49.9 (8)	53.1 (3)	53.6 (5)	50 (1)	53.1 (5)
C34—N1—C1—C2	−176.5 (6)	−71.5 (8)	−67.4 (3)	−67.3 (5)	−71.8 (10)	−67.48 (15)
C1—N1—C32—C31	57.6 (5)	60.1 (7)	60.3 (3)	60.3 (5)	62.1 (7)	60.2 (3)
N1—C32—C31—O1	7.7 (7)	9.7 (11)	9.0 (4)	9.1 (7)	10.4 (4)	9.2 (9)
N1—C32—C31—O2	−172.6 (4)	−171.0 (6)	−171.9 (2)	−172.1 (4)	−171.1 (3)	−171.8 (6)
C4 —C5—C6 —C7	–	−72 (1)	–	–	–	–
C31—C32—N1—C33	178.9 (4)	178.0 (6)	178.3 (2)	178.6 (4)	179.2 (4)	178.6 (4)
C31—C32—N1—C34	−63.8 (5)	−63.6 (8)	−64.7 (3)	−64.0 (5)	−63.5 (6)	−64 (1)

Table 5
Cell constants (Å, °), volumes (Å^3) and space groups of all compounds.

For (5)–(16) a unit cell with *c* parallel to the chain axis was chosen instead of the Niggli reduced cell.

	a	b	c	α	β	γ	V	Space group
(1)	7.613 (1)	9.236 (3)	11.853 (4)	90	98.08 (2)	90	825.1 (4)	$P2_1/c$
(2)	12.108 (7)	7.277 (3)	10.835 (9)	90	107.58 (5)	90	910 (2)	Cc
(3)	6.867 (1)	13.837 (3)	11.460 (3)	90	101.78 (2)	90	1066.0 (4)	$P2_1/n$
(4)	11.110 (7)	13.428 (5)	15.038 (5)	90	90	90	2243 (2)	$P2_12_12_1$
(5)	6.771 (3)	7.599 (2)	13.804 (6)	81.96 (3)	62.69 (3)	81.17 (3)	621.6 (4)	$P\overline{1}$
(6)	6.736 (7)	7.526 (2)	15.62 (1)	81.72 (5)	60.44 (8)	79.86 (4)	677 (1)	$P\overline{1}$
(7)	6.872 (2)	7.519 (1)	15.991 (3)	82.42 (3)	61.78 (1)	81.44 (2)	718.2 (5)	$P\overline{1}$
(8)	6.771 (4)	7.516 (3)	18.206 (4)	81.94 (2)	58.51 (2)	79.52 (4)	775.8 (5)	$P\overline{1}$
(9)	6.816 (2)	7.572 (2)	18.738 (4)	82.37 (1)	60.84 (2)	81.42 (2)	833.0 (5)	$P\overline{1}$
(10)	6.755 (2)	7.493 (2)	20.737 (6)	82.05 (2)	57.17 (2)	79.27 (2)	865.6 (4)	$P\overline{1}$
(11)	6.791 (2)	7.554 (3)	21.636 (5)	85.04 (3)	57.30 (2)	81.94 (3)	924.7 (5)	$P\overline{1}$
(12)	6.777 (2)	7.452 (3)	23.245 (6)	81.53 (3)	56.19 (2)	78.79 (3)	955.7(5)	$P\overline{1}$
(13)	6.804 (3)	7.546 (4)	24.158 (9)	85.73 (3)	56.04 (3)	82.13 (4)	1019.0 (5)	$P\overline{1}$
(14)	6.778 (4)	7.484 (1)	25.888 (9)	82.08 (2)	55.43 (3)	79.04 (3)	1061.0 (5)	$P\overline{1}$
(15)	6.834 (6)	7.531 (6)	26.70 (3)	86.17 (8)	54.74 (7)	82.21 (8)	1112 (2)	$P\overline{1}$
(16)	6.762 (3)	7.466 (2)	28.39 (2)	82.15 (4)	54.92 (4)	78.87 (3)	1150 (1)	$P\overline{1}$

Table 6
Intermolecular distances (Å).

The reciprocal of the standard deviation was used as the weight. The symmetry operations are related to the Niggli reduced cell (Table 1).

					wt av. of (6)–(16)	
	(3)	(7)	(14)	(16)	*n* = (11), (13), (15)	*n* = even
O2···Br	3.139 (5)$^{\mathrm{i}}$	3.124 (6)	3.119 (3)	3.110 (5)	3.104 (10)	3.116 (2)
N1···Br	4.102 (5)	4.229 (5)$^{\mathrm{iv}}$	4.195 (3)$^{\mathrm{iv}}$	4.185 (6)$^{\mathrm{iv}}$	4.238 (6)	4.22 (2)
N1···Br	4.355 (5)$^{\mathrm{ii}}$	4.490 (6)$^{\mathrm{v}}$	4.541 (3)$^{\mathrm{v}}$	4.536 (6)$^{\mathrm{v}}$	4.450 (2)	4.539 (4)
N1···Br	4.242 (5)$^{\mathrm{iii}}$	4.227 (6)$^{\mathrm{iv}}$	4.280 (3)$^{\mathrm{viii}}$	4.277 (6)$^{\mathrm{viii}}$	4.261 (3)	4.269 (5)
$\mathrm{C_{end}}$†···O1	–	3.875 (15)$^{\mathrm{vi}}$	3.709 (5)$^{\mathrm{ix}}$	3.72 (1)$^{\mathrm{ix}}$	3.48 (3)	3.71 (2)
$\mathrm{C_{end}}$···C33	–	5.7811 (15)$^{\mathrm{vii}}$	5.997 (7)$^{\mathrm{x}}$	5.97 (1)$^{\mathrm{x}}$	5.845 (14)	5.97 (4)
$\mathrm{C_{end}}$···C34	–	4.140 (16)^{l}	4.211 (6)^{m}	4.21 (1)^{m}	4.119 (12)	4.185 (9)

Symmetry operation applied to the second atom: (i) $-x, -y, 1-z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iv) $1+x, y, z$; (v) $1+x, y, z$; (vi) $2-x, 1-y, 1-z$; (vii) $2-x, -y, 1-z$; (viii) $1-x, 1-y, -z$; (ix) $3-x, 1-y, 1-z$. † $\mathrm{C_{end}}$ is the last C atom in the alkyl chain except for (7), where $\mathrm{C_{end}}$ is the last but one C atom.

not allow a reliable least-squares line fit to a chain as short as in this compound.

4.3.3. Type C [(7)]. Hybrid of M_2 and M_2^{II} – a_s = 4.96, b_s = 4.62 Å. A close C···O contact is avoided by the *gauche* position of the terminal C atom. Therefore, the area per chain is as large as 22.5 Å^2, but thermal motion is not exceptionally high. The area per head group is 25.54 Å^2.

4.3.4. Type D (9). The packing of the chain axes can be described by two translations of a pair of chains, $a_s \simeq 4.89$, $b_s \simeq 4.56$ and $\gamma_s \simeq 104°$. The zigzag planes are nearly parallel to the

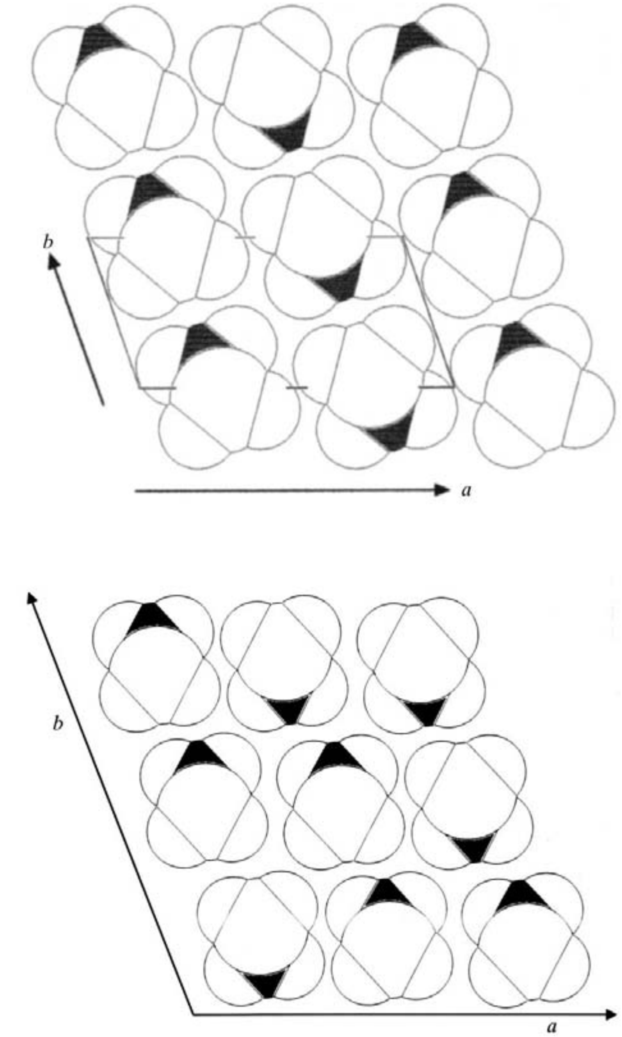


Figure 5
Packing types (*a*) *A* and (*b*) *B* (schematically), viewed along the chain axes. Only two C atoms and four H atoms of each chain are shown. Black C atoms are beneath and white C atoms are above the plane of the paper.

a translation. The neighbouring chains along the *b* translation are rotated relative to each other around the chain axes by 180°. The packing type is a hybrid of $\mathrm{O}^{2\perp}$ and $\mathrm{O}^{2\parallel}$. The distance between the terminal C atom and the doubly bonded O atom of the next layer is only 2.77 Å. The area per chain is about 21.6 Å^2. Therefore, the displacement parameters of the chain are higher than those of all other compounds in this article. The area per head group is 25.52 Å^2.

5. Conclusions

This first series of single-crystal structure determinations of amphiphilic compounds with chain lengths between $n = 1$ and $n = 16$ gave us an opportunity to investigate the influence of a single structural parameter (*i.e.* the chain length) on the crystal packing. As expected, very different crystal structures were found for the short-chain compounds. Rules were discovered for the packing of the even-numbered and some of the odd-numbered long-chain compounds. The deviation of (7) and (9) from these rules is surprising.

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