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Structure of Dodecyldimethylpropylammonium Bromide Hemihydrate

By Tooru Taga and Katsunosuke Machida

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, *Japan*

and Noriyuki Kimura, Soichi Hayashi, Junzo Umemura and Tohru Takenaka

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, *Japan*

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Abstract. $C_{17}H_{38}N^+.Br^-.\frac{1}{2}H_2O$, $M_r = 345{\cdot}4$, triclinic, $P\bar{1}$, $a = 8{\cdot}362\,(2)$, $b = 9{\cdot}161\,(2)$, $c = 27{\cdot}457\,(2)$ Å, $\alpha = 76{\cdot}68\,(2)$, $\beta = 82{\cdot}90\,(2)$, $\gamma = 85{\cdot}90\,(2)°$, $V = 2029\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}13$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}14$ mm^{-1}, $F(000) = 748$, $T = 295$ K, $R = 0{\cdot}067$ for 4506 observed reflections. The molecules are packed in a bilayer parallel to the (001) plane. The zigzag dodecyl chain is not strictly extended, and the curved chains are arranged in a deformed orthorhombic packing at the central region of the bilayer. The ammonium group is surrounded by four or five Br ions in a distorted trigonal bipyramidal arrangement. Each Br ion accepts one hydrogen bond from the water molecule.

Introduction. This work is part of our continuous studies on the crystal properties and molecular packing of alkylammonium halides with various alkyl chain lengths. Both the hemihydrate and the monohydrate of dodecyldimethylpropylammonium bromide crystallize from the solution containing ethyl acetate and water at room temperature, but the hemihydrate form was obtained from the solution containing a small amount of water. The crystal structure of the monohydrate was determined previously (Taga, Machida, Kimura, Hayashi, Umemura & Takenaka, 1986), and the present paper deals with the structure determination of the hemihydrate so that it may be compared with that of the monohydrate structure.

Experimental. Colourless transparent plate-like crystal, 0·15 × 0·2 × 0·2 mm; Rigaku AFC-5RU diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from 18 reflections with $22{\cdot}0 < 2\theta < 34{\cdot}8°$; three standard reflections measured every 56 reflections, no significant change in intensities; 6045 observed reflections within the range $2\theta < 55°$ ($0 \le h \le 10$, $-11 \le k \le 11$, $-32 \le l \le 32$); 4506 unique reflections with $F_o > 3\sigma(F)$ used for structure determination; 3601 unobserved, $R_{\rm int} = 0{\cdot}017$. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); refined by full-matrix least squares; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(F) + (0{\cdot}023F)^2]^{-1}$; non-H atoms anisotropic; H atoms from difference map, isotropic; $R = 0{\cdot}067$, $wR = 0{\cdot}076$, $S = 1{\cdot}98$; $(\Delta/\sigma)_{\max} = 0{\cdot}50$; max. residual electron density 0·59 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on a FACOM

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Table 1. *Atomic parameters and equivalent isotropic thermal parameters for non-*H *atoms in dodecyldimethylpropylammonium bromide hemihydrate*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Br(1)	0·88294 (9)	0·22013 (8)	0·15342 (3)	5·55 (2)
Br(2)	0·54358 (9)	0·25594 (8)	0·89728 (3)	5·82 (3)
O(*W*)	0·7828 (8)	0·5389 (6)	0·0724 (2)	4·4 (4)
N(1)	0·3488 (6)	0·2507 (5)	0·0639 (2)	4·4 (3)
C(1)	0·3393 (8)	0·1814 (6)	0·1202 (2)	4·5 (4)
C(2)	0·4043 (8)	0·2756 (7)	0·1515 (2)	4·7 (4)
C(3)	0·3857 (9)	0·1940 (8)	0·2059 (2)	6·2 (5)
C(4)	0·4211 (10)	0·2862 (8)	0·2419 (2)	6·2 (5)
C(5)	0·4009 (11)	0·2028 (8)	0·2966 (3)	7·3 (6)
C(6)	0·4028 (10)	0·2965 (8)	0·3344 (3)	6·9 (5)
C(7)	0·3857 (11)	0·2104 (8)	0·3877 (3)	7·2 (6)
C(8)	0·3787 (10)	0·2973 (8)	0·4284 (3)	7·0 (5)
C(9)	0·3656 (10)	0·2085 (8)	0·4815 (2)	6·8 (5)
C(10)	0·3616 (10)	0·2908 (8)	0·5225 (3)	6·6 (5)
C(11)	0·3500 (12)	0·1988 (9)	0·5746 (3)	8·3 (6)
C(12)	0·3484 (12)	0·2770 (11)	0·6173 (3)	9·4 (8)
C(13)	0·5194 (7)	0·2799 (7)	0·0390 (2)	4·3 (4)
C(14)	0·6360 (8)	0·1437 (7)	0·0467 (3)	5·7 (5)
C(15)	0·7964 (8)	0·1828 (9)	0·0163 (3)	6·1 (5)
C(16)	0·2707 (8)	0·1469 (7)	0·0392 (3)	5·5 (5)
C(17)	0·2520 (8)	0·3984 (7)	0·0541 (2)	5·2 (4)
N(1′)	1·0342 (6)	0·2703 (5)	0·8300 (2)	4·6 (4)
C(1′)	0·9417 (8)	0·1960 (7)	0·7988 (2)	5·0 (4)
C(2′)	0·9224 (9)	0·2890 (7)	0·7466 (3)	5·9 (5)
C(3′)	0·8911 (8)	0·1937 (8)	0·7099 (3)	5·6 (5)
C(4′)	0·8621 (9)	0·2858 (8)	0·6595 (3)	6·0 (5)
C(5′)	0·8531 (10)	0·1983 (8)	0·6197 (3)	6·6 (5)
C(6′)	0·8460 (10)	0·2897 (8)	0·5670 (3)	6·6 (5)
C(7′)	0·8569 (10)	0·2018 (8)	0·5263 (3)	6·9 (5)
C(8′)	0·8581 (10)	0·2926 (8)	0·4740 (3)	6·7 (5)
C(9′)	0·8722 (11)	0·2027 (9)	0·4336 (3)	7·5 (6)
C(10′)	0·8785 (10)	0·2912 (8)	0·3801 (3)	7·3 (7)
C(11′)	0·8924 (12)	0·1971 (9)	0·3407 (3)	8·3 (6)
C(12′)	0·9014 (14)	0·2848 (11)	0·2901 (3)	10·8 (9)
C(13′)	1·2014 (8)	0·3132 (8)	0·8057 (2)	5·4 (4)
C(14′)	1·3022 (9)	0·1911 (9)	0·7875 (3)	7·5 (6)
C(15′)	1·4609 (10)	0·2549 (11)	0·7596 (3)	9·0 (7)
C(16′)	1·0434 (9)	0·1647 (8)	0·8803 (2)	6·2 (5)
C(17′)	0·9442 (9)	0·4117 (7)	0·8392 (3)	6·3 (6)

M382 in the Data Processing Center of Kyoto University, using *KPPXRAY* programs (Taga, Higashi & Iizuka, 1985).

Discussion. The final atomic parameters are listed in Table 1.* Bond distances and angles are listed in Table 2. Fig. 1 depicts two crystallographically independent molecules. The dodecyl and propyl chains of both molecules have an extended *trans*-zigzag form. A noticeable feature of these molecules is that the dodecyl chain curves out of the *trans*-zigzag plane, as was observed in cholesteryl laurate (Sawzik & Craven, 1980). The dodecyl chain of molecule *B* bends towards the side of the propyl group, while that of molecule *A* bends to the opposite side. The average C—C and C—N bond distances are 1·502 (12) and 1·517 (5) Å for molecule *A* and 1·502 (25) and 1·508 (6) Å for molecule *B*. These bond distances are consistent with the corresponding distances 1·510 and 1·516 Å in the monohydrate crystal. The average C—C—C bond angle is 115 (3)° for both molecules. So, although the chain bending of molecule *A* differs from that of molecule *B*, there are no significant differences in the bond distances and angles of the two molecules. The difference in the chain bending between the two independent molecules is mainly due to variation of the torsion angles about the *trans*-zigzag C—C bonds [178·9 (5)–191·5 (6)° for *A* and 172·0 (5)–187·9 (5)° for *B*].

The molecules are packed in a bilayer parallel to the (001) crystal plane (Fig. 2). The long chain is approximately parallel to the *c* axis which forms a tilt angle of 75·5° with the *ab* plane, and the layer thickness is about 26·5 Å. This layer structure is quite

Table 2. *Bond lengths* (Å) *and valence angles* (°) *in dodecyldimethylpropylammonium bromide hemihydrate*

N(1)—C(1)	1·524 (7)	N(1)—C(13)	1·518 (7)
N(1)—C(16)	1·512 (10)	N(1)—C(17)	1·513 (8)
C(1)—C(2)	1·518 (10)	C(2)—C(3)	1·503 (7)
C(3)—C(4)	1·507 (10)	C(4)—C(5)	1·515 (9)
C(5)—C(6)	1·494 (12)	C(6)—C(7)	1·489 (10)
C(7)—C(8)	1·508 (12)	C(8)—C(9)	1·492 (9)
C(9)—C(10)	1·488 (11)	C(10)—C(11)	1·479 (10)
C(11)—C(12)	1·507 (14)	C(13)—C(14)	1·519 (9)
C(14)—C(15)	1·509 (9)	N(1′)—C(1′)	1·518 (9)
N(1′)—C(13′)	1·510 (8)	N(1′)—C(16′)	1·500 (7)
N(1′)—C(17′)	1·507 (8)	C(1′)—C(2′)	1·510 (9)
C(2′)—C(3′)	1·533 (12)	C(3′)—C(4′)	1·484 (10)
C(4′)—C(5′)	1·508 (12)	C(5′)—C(6′)	1·501 (10)
C(6′)—C(7′)	1·511 (12)	C(7′)—C(8′)	1·484 (10)
C(8′)—C(9′)	1·516 (13)	C(9′)—C(10′)	1·502 (11)
C(10′)—C(11′)	1·520 (13)	C(11′)—C(12′)	1·432 (11)
C(13′)—C(14′)	1·493 (11)	C(14′)—C(15′)	1·531 (11)

C(1)—N(1)—C(13)	113·8 (5)	C(1)—N(1)—C(16)	108·1 (4)
C(1)—N(1)—C(17)	110·6 (4)	C(13)—N(1)—C(16)	110·1 (5)
C(13)—N(1)—C(17)	107·6 (4)	C(16)—N(1)—C(17)	106·4 (5)
N(1)—C(1)—C(2)	115·2 (4)	C(1)—C(2)—C(3)	109·1 (5)
C(2)—C(3)—C(4)	114·2 (6)	C(3)—C(4)—C(5)	113·6 (6)
C(4)—C(5)—C(6)	115·8 (6)	C(5)—C(6)—C(7)	114·3 (6)
C(6)—C(7)—C(8)	117·8 (6)	C(7)—C(8)—C(9)	116·9 (6)
C(8)—C(9)—C(10)	118·2 (6)	C(9)—C(10)—C(11)	116·6 (6)
C(10)—C(11)—C(12)	118·5 (7)	N(1)—C(13)—C(14)	114·8 (5)
C(13)—C(14)—C(15)	109·9 (5)	C(1′)—N(1′)—C(13′)	113·8 (5)
C(1′)—N(1′)—C(16′)	107·9 (5)	C(1′)—N(1′)—C(17′)	110·2 (5)
C(13′)—N(1′)—C(16′)	110·2 (5)	C(13′)—N(1′)—C(17′)	107·2 (5)
C(16′)—N(1′)—C(17′)	107·3 (5)	N(1′)—C(1′)—C(2′)	114·3 (5)
C(1′)—C(2′)—C(3′)	112·7 (5)	C(2′)—C(3′)—C(4′)	112·7 (6)
C(3′)—C(4′)—C(5′)	115·2 (6)	C(4′)—C(5′)—C(6′)	116·0 (6)
C(5′)—C(6′)—C(7′)	115·9 (6)	C(6′)—C(7′)—C(8′)	115·8 (6)
C(7′)—C(8′)—C(9′)	115·1 (6)	C(8′)—C(9′)—C(10′)	116·5 (7)
C(9′)—C(10′)—C(11′)	114·9 (6)	C(10′)—C(11′)—C(12′)	113·5 (7)
N(1′)—C(13′)—C(14′)	115·0 (6)	C(13′)—C(14′)—C(15′)	109·0 (7)

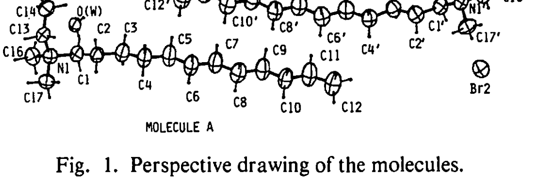

Fig. 1. Perspective drawing of the molecules.

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* Lists of atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms and srtucture factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43776 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

different from that of the monohydrate with thickness 17·1 Å. This difference is caused by the absence of a water molecule in the ionic region of the hemihydrate bilayer. The one water molecule links the two Br ions with Br···H—O hydrogen bonds, while in the monohydrate form the two water molecules bridge the two Br ions. The Br···O distances of 3·361 (5) and 3·332 (5) Å are comparable with those of the monohydrate, but the Br···O···Br angle of 119·4 (5)° is larger than 108·0 (1)° of the monohydrate. The Br ions are arranged in a distorted trigonal bipyramidal form about the ammonium group; N(1) is surrounded by five Br ions with N···Br distances 4·332 (5)–5·318 (5) Å, while N(1′) is surrounded by four Br ions with N···Br distances 4·284 (5)–4·899 (6) Å [one Br ion missing at one apex of the trigonal bipyramid about the central N(1′) atom]. Such ionic interactions between the Br ions and the terminal groups of long-chain molecules probably have a large influence on the chain packing. The long hydrocarbon chains are efficiently packed at the central region of the bilayer, while they are loosely packed at the boundary region. The comparatively regular-packing portions of the hydrocarbon chains at the central region are arranged in an approximate orthorhombic packing $O^{\parallel}$ ($B22_12$) (Abrahamsson, Dahlén, Löfgren & Pascher, 1978) with the dimensions $a_s = 8\cdot36$, $b_s = 8\cdot93$ and $c_s = 2\cdot54$ Å (c_s corresponds to the translation in the chain direction and the a_s axis is parallel to the a axis); the cell dimensions are comparable with those of (–)-2-ethyl-2-methylicosanoic acid, the first molecule found with $O^{\parallel}$ packing (von Sydow, 1958). According to Segerman (1965), the $O^{\parallel}$ packing has a slightly higher attractive van der Waals energy in comparison with the other types of packings. There are no short C···C intermolecular contacts less than 4·0 Å between adjacent dodecyl chains, and the shortest C···C contact between dodecyl and propyl chains is 3·74 (1) Å at C(3′)···C(15′) $(-1+x,+y,+z)$. Thus the chain packing in this bilayer structure is loose, and is different from that of the monohydrate in which the fully extended dodecyl chains are tightly packed in the $T^{\parallel}$ arrangement.

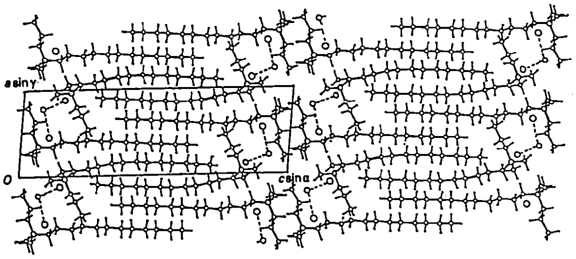

Fig. 2. Packing diagram projected along the *b* axis.

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Structure of 17α-Ethynylestra-1,3,5(10)-trien-3,17β-diol Hemihydrate (Ethynyl Estradiol)

BY V. J. VAN GEERESTEIN

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Transitorium 3, *Padualaan* 8,
3508 *TB Utrecht, The Netherlands*

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Abstract. $C_{20}H_{24}O_2.\frac{1}{2}H_2O$, $M_r = 305\cdot42$, monoclinic, $C2$, $a = 20\cdot99$ (1), $b = 6\cdot647$ (7), $c = 12\cdot124$ (2) Å, $\beta = 90\cdot51°$, $V = 1692$ (2) Å^3, $Z = 4$, $D_x = 1\cdot199$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0\cdot7$ cm^{-1}, $F(000) = 660$, room temperature, $R = 0\cdot053$ for 1491 unique reflections with $I \geq 2\cdot5\sigma(I)$. The molecular conformation is similar to the conformations found for estradiol. In the crystal, bilayers are formed of

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