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Di-*n*-octadecylammonium Bromide

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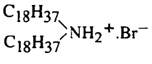
Abstract

The title compound, $C_{36}H_{76}N^+.Br^-$, has two diad-related n-C_{18} methylene chains bonded to a central quaternary N atom which lies on the diad axis. The N atom and first three C atoms on each side of it form a coplanar zigzag. At the third C atoms, the chains bend sharply so that the backbones of the two parts of each chain subtend an angle of 129°. The chains continue outwards as coplanar zigzags.

Comment

The present analysis was undertaken in order to establish how, in the title compound, (I), the normal requirement for long methylene chains to be linear zigzags might be compromised by the presence of a bulky bromide ion presumed to lie close to the quaternary N atom.



$$\begin{matrix} C_{18}H_{37} \diagdown \\ C_{18}H_{37} \diagup \end{matrix} NH_2{}^+.Br^-$$

(I)

As a result of the high residual due to the intensity data containing substantial errors (as evidenced by poor internal consistency), this analysis cannot be expected to yield accurate atomic coordinates.

The crystal and molecular structure is illustrated in Figs. 1 and 2. The Br^- ion and N atom both lie in the plane $y = 0$. In other crystal structures, considerable variation is found in nominally single N—C bond lengths (1.47–1.53 Å). The N—C length of 1.50 (2) Å found here agrees well with the three values of 1.541, 1.512 and 1.508 Å found in a trimethylammonium derivative (Bardi, Piazzesi & Del Pra, 1983). The C—N—C bond angle of 111.0 (18)° agrees with those found generally [109.0–114.6°]. Although the C—C bond-length range of 1.45 (4)–1.66 (4) Å is clearly unacceptable, the average of all 17 independent C—C lengths is 1.54 Å, in excellent accord with that generally found in long-chain alkane compounds. The observed N···Br distance of 3.27 (1) Å compares well with that found in other structures.

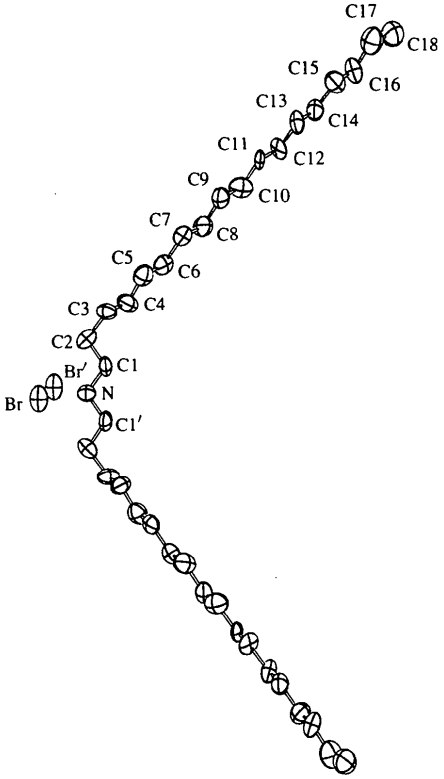


Fig. 1. An *ORTEP* diagram (Johnson, 1965) showing ellipsoids at the 50% probability level. Primed atoms are at ($-x$, $-y$, z) from their unprimed equivalents.

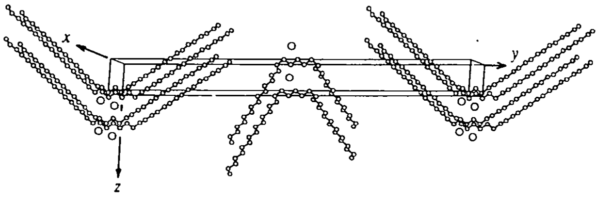


Fig. 2. A packing diagram in near projection along **x** showing the conformation of the title molecules.

The first three C atoms of each C_{18} chain bonded to the ammonium N atom lie on a zigzag whose backbone is parallel to the y axis. Between atoms C3 and C4 there is a sharp bend in the chain which then continues as a linear zigzag to its termination. The angle between the backbones of the two parts of the chain is 129°. The conformation of the chain in the bent region is easily described. If one looks along the line joining atoms C1 and C3, then, if there were no bend, atom C4 would be in line with C2. The actual position occupied by C4 corresponds to the bond C3—C4 being rotated about C2—C3 so that the dihedral angle between planes C1—C2—C3 and C2—C3—C4 is 112°. The reason all these four atoms are not coplanar is due presumably to conflict between the H atoms on C1 and C4. The distance between H1*A* and H4*B* is only 2.21 (1) Å compared with the usual lower limit of 2.4 Å. This overcrowding could account for the fact that the C2—C3 and C3—C4 bond lengths are both longer than normal with values of 1.59 (3) and 1.66 (4) Å, respectively. Whether

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or not the effect is genuine must await a more accurate structure analysis on a compound containing a similar bent alkane-chain conformation.

The nature of the chain packing will be discussed elsewhere.

Experimental

The title compound was prepared by treatment of di-*n*-octadecylamine (Exxon Chemical Technology) with hydrogen bromide. Regardless of the solvent used, the material crystallized as extremely thin fragile plates. Slow evaporation from a toluene/chloroform solution gave the best results, but in no case did the crystals yield diffraction data of good quality.

Crystal data

$C_{36}H_{76}N^+.Br^-$
$M_r = 602.7$
Orthorhombic
$P2_12_12$
$a = 5.392\ (2)$ Å
$b = 67.18\ (8)$ Å
$c = 5.374\ (3)$ Å
$V = 1947\ (3)$ Å^3
$Z = 2$
$D_x = 1.03$ Mg m^{-3}
$D_m \simeq 1.00$ Mg m^{-3}
D_m measured by flotation in water

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 15 reflections
$\theta = 21\text{–}27°$
$\mu = 1.56$ mm^{-1}
$T = 288$ K
Very thin plate
$0.80 \times 0.70 \times 0.01$ mm
Colourless

Data collection

Picker automated four-circle diffractometer
$\theta\text{–}2\theta$ scans
Absorption correction: none
989 measured reflections
989 independent reflections
867 observed reflections $[I > 2.5\sigma(I)]$

$\theta_{\max} = 45°$
$h = 0 \rightarrow 4$
$k = 0 \rightarrow 60$
$l = 0 \rightarrow 4$
1 standard reflection monitored every 100 reflections intensity variation: ±12%

Refinement

Refinement on F
$R = 0.109$
$wR = 0.114$
$S = 8.22$
989 reflections
175 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.015$

$\Delta\rho_{\max} = 1.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.84$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 0.047
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\text{eq}} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{iso}
Br	1/2	0	0.4214 (7)	7.1 (2)
N	0	0	0.074 (4)	4.7 (13)
C1	0.003 (6)	−0.0184 (3)	−0.084 (4)	5.4 (14)
C2	−0.020 (6)	−0.0371 (3)	0.074 (4)	6.1 (13)
C3	−0.033 (5)	−0.0560 (3)	−0.102 (5)	5.6 (15)
C4	0.237 (5)	−0.0596 (3)	−0.244 (5)	6.6 (15)
C5	0.206 (5)	−0.0786 (4)	−0.385 (5)	6.8 (16)
C6	0.434 (4)	−0.0839 (3)	−0.530 (5)	5.8 (14)
C7	0.409 (4)	−0.1036 (4)	−0.700 (5)	5.3 (14)
C8	0.639 (6)	−0.1082 (3)	−0.844 (6)	7.8 (18)
C9	0.595 (5)	−0.1277 (4)	−1.004 (5)	7.1 (17)
C10	0.835 (5)	−0.1329 (4)	−1.145 (6)	7.8 (17)
C11	0.795 (5)	−0.1519 (4)	−1.314 (4)	5.7 (14)
C12	1.030 (5)	−0.1576 (3)	−1.446 (5)	6.0 (15)
C13	0.967 (6)	−0.1759 (3)	−1.613 (4)	5.9 (14)
C14	1.210 (5)	−0.1822 (4)	−1.737 (5)	6.4 (15)
C15	1.187 (5)	−0.2015 (4)	−1.911 (6)	7.6 (17)
C16	1.412 (5)	−0.2072 (4)	−2.041 (5)	7.2 (17)
C17	1.383 (6)	−0.2270 (7)	−2.198 (7)	9 (2)
C18	1.603 (8)	−0.2299 (6)	−2.344 (7)	11 (2)

Table 2. *Selected geometric parameters (Å, °)*

N—C1	1.50 (2)	C9—C10	1.54 (4)
C1—C2	1.52 (3)	C10—C11	1.58 (4)
C2—C3	1.59 (3)	C11—C12	1.50 (4)
C3—C4	1.66 (4)	C12—C13	1.56 (3)
C4—C5	1.49 (4)	C13—C14	1.53 (4)
C5—C6	1.50 (4)	C14—C15	1.60 (4)
C6—C7	1.61 (4)	C15—C16	1.45 (4)
C7—C8	1.49 (4)	C16—C17	1.58 (5)
C8—C9	1.58 (4)	C17—C18	1.43 (5)
C1—N—C1$^{\text{i}}$	111.0 (18)	C8—C9—C10	109 (2)
N—C1—C2	111.2 (17)	C9—C10—C11	111 (2)
C1—C2—C3	109.2 (18)	C10—C11—C12	111 (2)
C2—C3—C4	111 (2)	C11—C12—C13	107 (2)
C3—C4—C5	105 (2)	C12—C13—C14	106 (2)
C4—C5—C6	112 (2)	C13—C14—C15	114 (2)
C5—C6—C7	115.2 (19)	C14—C15—C16	116 (2)
C6—C7—C8	114 (2)	C15—C16—C17	114 (2)
C7—C8—C9	109 (2)	C16—C17—C18	108 (3)

Symmetry codes: (i) $-x, -y, z$.

Oscillation and Weissenberg photographs of the crystal chosen for analysis showed the X-ray intensity data to be of rather poor quality. The crystal clearly belonged to the orthorhombic system, but there were too few $h0l$ reflections for the space group to be immediately assignable; $0k0$ were absent for k odd.

Considerable problems were encountered in the diffractometer alignment procedure. Although some reflections had smooth 2θ intensity profiles, others were multiply undulating. Indexing was difficult, reflections with k indices differing by one unit lying close together in r space. Automated alignment (Grant & Gabe, 1974) was carried out several times on two sets of eight Laue symmetry-related reflections. It was noted during these alignments that the agreement between Friedel-related intensities was nearly always poor. The internal residuals were also poor. Thus, using the square roots of the raw scaled intensities, the internal residual for $0kl$ *versus* $0\bar{k}l$ was 0.14 and for hkl *versus* $\bar{h}\bar{k}l$ was 0.13. All $h0l$ reflections had poor intensity profiles and it could not be established with any confidence whether they showed any systematic absences; the structure solution and refinement used only those reflections from the hkl octant. Initially, the space group could be any of the four $PX2_1X$ space groups, where X is either 2 or 2_1. Using *SOLVER* (*NRCVAX*; Gabe, Le Page, Charland, Lee & White, 1989), E maps of all four possible space groups were examined but none were chemically interpretable. Moreover, although there are only two Br^- ions per cell whatever the space group (unless there is disorder), no clear Br—Br vectors appeared on the Patterson function.

It was noted that the resolution of close-lying reflections was improved by the partial closure of the vertical diffractometer after-slits. A new data collection over four octants was carried out under these conditions but there appeared to be no obvious solution for any of the four possible space groups.

Packing considerations led ultimately to the structure being solved. The molecules cannot be both simultaneously linear, parallel to **y** and packed end-to-end, as this would require a **b** repeat of *ca* 100 Å. Thus, the alkane chains, if linear or nearly linear, must make an angle of about 40° with the y axis. Moreover, as seen in **y** projection, the chains cannot lie parallel to the x or z axes because those in adjacent cells would conflict. Thus, in this projection, the alkane chains must make substantial angles with both the x and z axes. With such chain orientation, the **b** spacing of 67 Å could be more readily explained. To overcome uncertainty in the space group, the data were indexed as belonging to the monoclinic space group $P2_1$. The E map corresponding to the highest figure of merit was promising. It showed, in addition to two prominent peaks for Br separated by **b**/2, both isolated atoms and short isolated lengths of zigzag chains, each of three or four atoms (37 peaks in all). Guided by the above packing considerations, it was found that when suitably translated parallel to **x** and/or **z** into neighbouring cells, 26 of these peaks became part (with many gaps) of just two zigzag chains; the remaining peaks proved spurious. Refinement by least squares and ΔF maps proceeded slowly to reveal the whole structure (36 C atoms in each of two molecules per cell) in space group $P2_1$. It immediately gave the missing symmetry elements, showing the true space group to be unambiguously $P2_12_12$ (No. 18). In this space group, the Br^- ion and N atom are in special positions $(0,\frac{1}{2},z_{\rm Br})$ and $(0,0,z_{\rm N})$. Only 18 of the 36 C atoms found in $P2_1$ are independent in the true space group as the molecule possesses a diad axis.

After making the necessary change in the origin of the coordinates, the requisite atomic positions obtained from the $P2_1$ structure were refined in $P2_12_12$. The Br^-, N and C atomic positions were obtained by anisotropic least-squares refinement. H-atom positions were allocated to calculated positions using C—H and N—H distances of 1.08 Å, with isotropic displacement parameters. Intensity data were also refined for secondary extinction. The high residuals and poor goodness-of-fit can be traced to the large values of $R_{\rm int}$ referred to above. These, in turn, certainly result from the poor quality of the crystal. Absorption corrections were applied to the intensity data, but these resulted in higher residuals, possibly due to uncertainty in the true thickness of the very thin crystal plate used.

A four-circle diffractometer system (Grant & Gabe, 1974) was used for data collection and cell refinement, and *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) was used for all calculations. Molecular graphics were obtained using *ORTEP* (Johnson, 1965).

The sample of the title compound was kindly prepared by Dr A. W. Parkins.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-(4-*n*-Heptylbenzoyloxy)benzoic Acid

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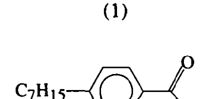
Abstract

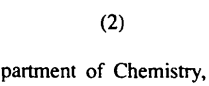
In the title compound, $C_{21}H_{24}O_4$, the molecules exist as hydrogen-bonded dimers. The hydrogen bonds occur pairwise, involve the carboxylic acid groups and are of the form C═O···HO—C. The O···O distances are 2.53 (1) and 2.59 (1) Å.

Comment

The asymmetric unit of the title compound, (1), contains two independent molecules, which exhibit both similarities with and differences from molecules of 4-*n*-heptylbenzoic acid, (2), a simpler analogue of (1). The similarities (Fig. 1) include the extended all-*trans* con-



(1)



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