

Fig. 2. Crystal structure in the *ab* projection.

The stacking arrangement and direct intermolecular contacts of the diacetylene rods, which are characteristic for reactive (in particular polymerizable) diacetylenes in the solid state, are absent [the shortest distances between diacetylene groups are C(2)···C(3) ($x, y + \frac{1}{2}, z - \frac{1}{2}$), 4.553 (7) Å, and C(2)···C(4) ($x, y + \frac{1}{2}, z - \frac{1}{2}$), 4.453 (7) Å].

The packing of the molecules in the crystal is apparently governed primarily by the hydrogen bonds mentioned above and by short intermolecular contacts between the molecular chains, which prevent further mutual approach of the diacetylene rods. The observed peculiarities of the molecular packing are consistent with the observed inertness of the title compound to solid-state polymerization.

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Acta Cryst. (1986). **C42**, 608–610

Structure of Dodecyldimethylpropylammonium Bromide Monohydrate

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(Received 21 October 1985; accepted 3 December 1985)

Abstract. [C₁₇H₃₈N]Br·H₂O, *M_r* = 354.4, triclinic, *P* $\bar{1}$, *a* = 8.234 (1), *b* = 8.502 (1), *c* = 17.494 (1) Å, α = 84.96 (1), β = 78.41 (1), γ = 61.24 (1)°, *V* = 1051.7 (2) Å³, *Z* = 2, *D_x* = 1.12 Mg m⁻³, λ (Cu *K*α) = 1.54178 Å, μ = 2.64 mm⁻¹, *F*(000) = 384, *T* = 295 K, *R* = 0.046 for 3119 reflections. The long hydrocarbon chains are fully extended in a zigzag form, and have an antiparallel arrangement in a triclinic subcell. The Br ions exist near the N atoms of the hydrocarbon chains. The two Br ions and two water molecules form a large divalent anionic group, held together by Br···O hydrogen bonds.

Introduction. As part of an investigation on the crystal properties and molecular packing of alkylammonium

halides with various lengths of alkyl chains, the crystal structure of the title compound was determined. Dodecyldimethylpropylammonium bromide crystallizes in several different hydrate forms. In the present study of the monohydrate form, the role of the water molecules in the crystal structure was of particular interest.

Experimental. Crystal grown from ethyl acetate solution, needle-shaped transparent prism, 0.15 × 0.2 × 0.3 mm. Rigaku AFC-5RU diffractometer, graphite-monochromated Cu *K*α radiation; lattice parameters from 20 reflections with 18 < θ < 26°; three standard reflections measured every 56 reflections, no significant change in intensities; 3210 unique

Table 1. Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Br(1)	0.68143 (5)	0.33297 (4)	0.61936 (2)	6.58 (3)
C(1)	0.7751 (4)	0.8430 (4)	0.6862 (1)	4.6 (2)
C(2)	0.6188 (4)	0.7941 (4)	0.6940 (1)	4.7 (2)
C(3)	0.5017 (4)	0.8359 (4)	0.7760 (1)	4.7 (2)
C(4)	0.3374 (4)	0.7978 (4)	0.7837 (2)	5.0 (2)
C(5)	0.2268 (4)	0.8186 (4)	0.8666 (1)	5.3 (2)
C(6)	0.0672 (4)	0.7743 (4)	0.8736 (2)	5.4 (2)
C(7)	-0.0427 (4)	0.7928 (5)	0.9564 (2)	5.6 (3)
C(8)	-0.2002 (4)	0.7443 (5)	0.9650 (2)	5.7 (2)
C(9)	-0.3090 (4)	0.7630 (5)	1.0482 (2)	5.7 (3)
C(10)	-0.4651 (4)	0.7147 (5)	1.0572 (2)	5.8 (2)
C(11)	-0.5739 (5)	0.7362 (5)	1.1399 (2)	6.6 (3)
C(12)	-0.7331 (6)	0.6879 (7)	1.1487 (2)	7.9 (4)
C(13)	1.0203 (4)	0.5631 (4)	0.6100 (2)	5.2 (2)
C(14)	1.1018 (5)	0.4676 (6)	0.6804 (2)	7.5 (3)
C(15)	1.1863 (6)	0.2678 (6)	0.6697 (3)	9.0 (4)
C(16)	1.0702 (5)	0.8272 (5)	0.6141 (2)	6.4 (3)
C(17)	0.8415 (4)	0.8395 (4)	0.5422 (2)	5.4 (2)
N(1)	0.9266 (3)	0.7667 (3)	0.6140 (1)	4.5 (2)
O(1)	0.5250 (4)	0.7114 (4)	0.5183 (2)	8.0 (3)

reflections ($-8 \leq h \leq 8$, $-9 \leq k \leq 0$, $-16 \leq l \leq 18$) with $2\theta < 120^\circ$, 3119 with $F_o > 3\sigma(F_o)$ used for further calculations. Structure solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$ minimized; $w = [\sigma^2(F) + (0.023F)^2]^{-1}$; H atoms from difference map, isotropic, other atoms anisotropic; $R = 0.046$, $wR = 0.069$, $S = 1.67$; $(\Delta/\sigma)_{\max} = 0.13$; max. residual electron density $\pm 0.7 \text{ e \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on a FACOM M382 in the Data Processing Center of Kyoto University, using *KPPXRAY* programs (Taga, Higashi & Iizuka, 1985).

Discussion. The final atomic parameters are given in Table 1.* A perspective view of the molecule and the numbering scheme are shown in Fig. 1. Bond distances and angles are listed in Table 2. The average C—C bond distance is 1.516 (8) Å and the average C—C—C bond angle is 113 (1)°. These agree well with the values observed in other long-chain structures; e.g. 1.519 Å and 113° for cetrimonium bromide (Grochowski, 1981). The average C—N bond distance is 1.510 (9) Å, in good agreement with the values of 1.50 Å for hexamethylenhexamethyldiammonium dibromide (Lonsdale, Milledge & Pant, 1965) and 1.54 Å for hexadecyltrimethylammonium ICl_2 (Bandoli, Clemente & Nicolini, 1978). The zigzag dodecyl chain is roughly

* Lists of atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42697 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and bond angles (°)

C(1)—C(2)	1.511 (6)	C(1)—N(1)	1.518 (3)
C(2)—C(3)	1.522 (3)	C(3)—C(4)	1.515 (6)
C(4)—C(5)	1.524 (4)	C(5)—C(6)	1.512 (6)
C(6)—C(7)	1.523 (5)	C(7)—C(8)	1.517 (6)
C(8)—C(9)	1.525 (5)	C(9)—C(10)	1.504 (6)
C(10)—C(11)	1.516 (5)	C(11)—C(12)	1.529 (8)
C(13)—C(14)	1.503 (5)	C(13)—N(1)	1.520 (4)
C(14)—C(15)	1.507 (7)	C(16)—N(1)	1.500 (6)
C(17)—N(1)	1.501 (4)		
C(2)—C(1)—N(1)	114.7 (2)	C(1)—C(2)—C(3)	110.8 (3)
C(2)—C(3)—C(4)	111.6 (3)	C(3)—C(4)—C(5)	114.0 (3)
C(4)—C(5)—C(6)	113.2 (3)	C(5)—C(6)—C(7)	113.6 (3)
C(6)—C(7)—C(8)	114.4 (3)	C(7)—C(8)—C(9)	113.9 (3)
C(8)—C(9)—C(10)	114.2 (3)	C(9)—C(10)—C(11)	113.7 (4)
C(10)—C(11)—C(12)	113.5 (4)	C(14)—C(13)—N(1)	115.3 (3)
C(13)—C(14)—C(15)	109.9 (4)	C(1)—N(1)—C(13)	112.3 (2)
C(1)—N(1)—C(16)	108.5 (2)	C(1)—N(1)—C(17)	109.7 (2)
C(13)—N(1)—C(16)	110.3 (2)	C(13)—N(1)—C(17)	108.1 (2)
C(16)—N(1)—C(17)	107.8 (2)		

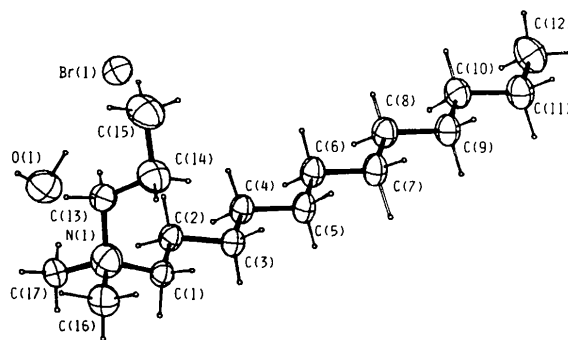


Fig. 1. Perspective view of the molecule with the atomic numbering scheme.

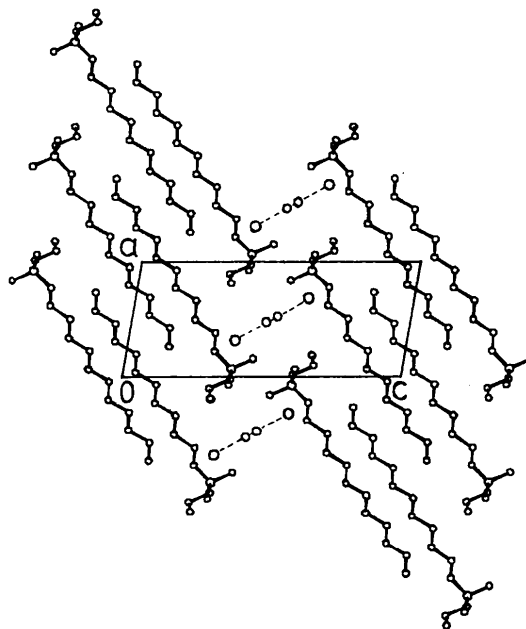


Fig. 2. View of the structure along b.

planar with a maximum deviation of 0.11 (6) Å from the least-squares plane, and the N(1) and C(16) atoms deviate from the plane by 0.53 (7) and 0.46 (7) Å, respectively. The C(13), C(14) and C(15) atoms of the propyl group, and the N(1) and C(17) atoms are planar within 0.05 Å. The two zigzag chains cross at the N(1) atom with a dihedral angle of 98.4 (5)°.

The molecular packing is illustrated in Fig. 2. The long hydrocarbon chains have an antiparallel arrangement forming a layer parallel to the (001) plane. The direction of the long-chain axis is approximately parallel to $[\bar{3}01]$. The chain packing may be expressed by a triclinic subcell with dimensions $a_s = 2.535$ (2), $b_s = 4.20$ (1), $c_s = 4.88$ (1) Å, $\alpha_s = 75.4$ (1), $\beta_s = 88.0$ (1), $\gamma_s = 63.2$ (1)°. These values are comparable with those of the triclinic subcells observed in other crystals (Abrahamsson, Dahlén, Löfgren & Pascher, 1978), and they agree well with $a_s = 2.54$, $b_s = 4.30$, $c_s = 4.45$ Å, $\alpha_s = 78$, $\beta_s = 90$, $\gamma_s = 72.5$ ° given for ideal packing of infinite hydrocarbon chains (Kitaigorodsky, 1973). The Br ions and water molecules are located between the hydrocarbon layers, held together by hydrogen bonds. The two Br ions and two water molecules form an isolated anionic group with a square shape. The Br...O hydrogen-bond distances are 3.326 (3) and 3.354 (4) Å, and the O...Br...O and Br...O...Br angles are 72.0 (1) and 108.0 (1)°. These values are in good agreement with those of a similar

group found in decamethylenehexamethyldiammonium dibromide monohydrate (Lonsdale, Milledge & Pant, 1965). The plane normal of the anionic group is parallel to $(\bar{2}03)$, and makes an angle of 28 (2)° with the long-chain axis. The anionic group is surrounded by ammonium groups with shortest Br...N distance 4.526 (5) Å and shortest O...N distance 4.221 (5) Å.

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Acta Cryst. (1986). **C42**, 610–615

Structure–Reactivity Correlations of Aromatic Nitro Compounds: Structures of 1-*tert*-Butyl-3,5-dimethyl-2,4,6-trinitrobenzene (I) and 1-*tert*-Butyl-3,4,5-trimethyl-2,6-dinitrobenzene (II)

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(Received 28 August 1985; accepted 26 November 1985)

Abstract. (I): $C_{12}H_{15}N_3O_6$, $M_r = 297.28$, monoclinic, $P2_1/a$, $a = 9.226$ (1), $b = 11.104$ (1), $c = 14.622$ (1) Å, $\beta = 107.79$ (1)°, $V = 1426.3$ (2) Å³, $Z = 4$, $D_m = 1.365$ (floatation in KI), $D_x = 1.384$ g cm⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.7107 \text{ Å}) = 0.72$ cm⁻¹, $F(000) = 624.0$, $T = 293$ K, $R = 5.0\%$ for 1591 significant reflections. (II): $C_{13}H_{18}N_2O_4$, $M_r = 266.30$, monoclinic, $P2_1/n$, $a = 9.610$ (1), $b = 14.619$ (1), $c = 11.006$ (1) Å, $\beta = 115.43$ (1)°, $V = 1396.3$ (1) Å³, $Z = 4$, $D_m = 1.243$

(floatation in KI), $D_x = 1.267$ g cm⁻³, $\mu(\text{Cu } K\alpha, \lambda = 1.5418 \text{ Å}) = 6.99$ cm⁻¹, $F(000) = 568.0$, $T = 293$ K, $R = 5.9\%$ for 1869 significant reflections. Both (I) and (II) crystallize in a common conformation for the *tert*-butyl group and the two *ortho* nitro groups, where the latter are almost perpendicular to the plane of the benzene ring. The solid-state photoreactivity of these compounds, in which the O of the nitro group intramolecularly abstracts an H from the *tert*-butyl