

O...N distances reflect a substantial attractive interaction with a large negative charge on O and a positive charge on N giving rise to a Coulombic attraction between the atoms.

The carboxyl groups form H-bonded dimers across centers of symmetry. The intermolecular distances in these dimers are O(2)...O(1) (at $-x, -1-y, 1-z$) of 2.684 (2) Å, and H...O(1) of 1.71 (3) Å. There are no other significant nonbonded contacts.

The only other structure with the CH₃-C(NO₂)₂- fragment which has come to the notice of the authors at the time of reporting this structure is 2-chloro-5,5-dinitro-3-aza-4-oxa-2-hexene [(II) (Grigor'eva *et al.*, 1975)] at $R = 0.15$. The present investigation gives a more precise geometry of this molecular fragment, although basically it is very similar to that in (II). The six tetrahedral angles at C(4) have a range of 103.7 (2) to 117.5 (2)° with an average of 109.3 (2)°. In (II) C(3) is replaced by an O atom, and only two angles at C(4) differ significantly, C(3)-C(4)-C(5) 117.5 (2) and C(3)-C(4)-N(2) 105.4 (2)°, the corresponding angles in (II) being 109 and 112°. The other four tetrahedral angles are nearly equal in the two structures. The nitro group N(1)-O(3)-O(4) makes a small angle of 10.2° with the plane of C(3), C(4), N(1); the other nitro group N(2), O(5), O(6) makes an angle of 15.9° with the plane of N(1)-C(4)-N(2). The corresponding angles in (II) are 5 and 9°. A comparison of the eight non-H atoms of the common fragment CH₃-

C(NO₂)₂- in structures (I) and (II) with Nyburg's (1974) molecule-fitting program gave an r.m.s. deviation of 0.138 Å.

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Hexadecyltrimethylammonium Bromide

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Abstract. [N(CH₃)₃(C₁₆H₃₃)]Br, $M_r = 364.5$, monoclinic, $P2_1/c$, $a = 5.638$ (1), $b = 7.260$ (2), $c = 52.072$ (7) Å, $\beta = 93.78$ (1)°, $V = 2128.8$ (8) Å³, $Z = 4$, $D_m = 1.14$ (2), $D_x = 1.14$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 2.80$ mm⁻¹, $F(000) = 792$, $T = 298$ K, $R = 0.07$, and $wR = 0.07$, for 2205 observed reflections with $I \geq 2\sigma(I)$. The methylenic groups of the hexadecyltrimethylammonium cation are in a fully extended conformation. The bromide ions are embedded within pockets, giving rise to van der Waals

contacts, less than 4 Å, with six methyl and two methylenic groups and to Coulombic interactions with the trimethylammonium polar heads. No water molecules were detected. The cations have an anti-parallel arrangement within a bilayer. The chain axis forms a tilt angle of 65° with the plane containing the nitrogens of the polar heads.

Introduction. Hexadecyltrimethylammonium bromide (CTAB) is one of the most studied cationic surfactants

which is used in many fields such as, for example, micellar catalysis, medicine and detergency. This surfactant forms micellar aggregates in aqueous solution which are responsible for its peculiar physico-chemical properties. Of course, a knowledge of the structure of the micellar aggregate is essential for the understanding of its behaviour. Unfortunately, the problem of the micellar structure is still an open question. Therefore, we have undertaken a research programme with the aim of acquiring structural models of micelles by studying suitable crystal phases and, hence, of checking the validity of these models in aqueous solution mainly by spectroscopic, diffractometric and calorimetric techniques. The crystal structure of CTAB has been briefly and incompletely reported without atomic coordinates or drawings of the molecular packing (Grochowski, 1981). For this reason we decided to solve the crystal structure to obtain information on the packing of the alkyl chains and on the coordination of the bromide ions and of the polar heads.

Experimental. $[N(CH_3)_3(C_{16}H_{33})]Br$, Fluka purum, purified by crystallization in absolute ethanol/diethyl ether, kindly supplied by Dr G. Cerichelli. Plate-shaped colourless crystals obtained from aqueous solution, melting point 492–493 K, used for measuring density by flotation in benzene/carbon tetrachloride mixture. The observed density agrees with the above formula, without water of crystallization. A crystal, dimensions $0.4 \times 0.6 \times 0.08$ mm, was mounted on an automated Siemens AED diffractometer on-line to a General Automation 220 computer. Cell constants determined from least-squares refinement (independently from orientation matrix calculation) based on 24 reflections within 2θ range 31.8 – 107.8° ; Ni-filtered $Cu K\alpha$ radiation, θ – 2θ step scan and diffraction profile analysis (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979); standard reflection 002 selected for orientation control and measured every 50 reflections remained essentially constant throughout the run; 2205 independent reflections, out of 4365 collected up to $2\theta = 140^\circ$, having $I \geq 2\sigma(I)$ ($-6 \leq h \leq 6$, $0 \leq k \leq 8$, $0 \leq l \leq 62$) used in crystallographic calculations; Lorentz and polarization (but no absorption) corrections applied.

A Patterson synthesis gave a solution leading to a good refinement. A difference Fourier map showed only two hydrogen atoms [bonded respectively to C(1) and C(2)] with acceptable distances and angles, while the others were generated at their expected positions. Positional coordinates and anisotropic thermal parameters were refined by full-matrix least squares for non-H atoms; function minimized $\sum w(|F_o| - k|F_c|)$; the hydrogens had fixed positional coordinates and $U(H) = U_{iso}$ of parent atom. The final difference Fourier map showed some low peaks near the Br^- ion, max. and min. values 1.70 and $-1.48 e \text{ \AA}^{-3}$. Cal-

culations were performed using *SHELX76* (Sheldrick, 1976) with a weighting scheme $w = 1.0$ in the first stages of refinement and $w = 1.00/[\sigma^2(F) + 0.015173F^2]$ in the final stages; for torsion angles and other geometric calculations a program by Caruthers & Spagna (1975) was used; scattering factors were taken from *International Tables for X-ray Crystallography* (1974); anomalous dispersion for Br was used. Final reliability values were $R = 0.07_5$, $wR = 0.07_4$, $S = 0.52$, refinement with max. $\Delta/\sigma = 0.10$. The rather high R value may be due to the absorption effect, owing to the laminar shape of the crystal.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for the non-H atoms of CTAB with their e.s.d.'s in parentheses

U_{eq} is defined as $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	U_{eq}
Br	-8696 (1)	2485 (1)	5361.7 (1)	56.8 (3)
N	-5091 (6)	2500 (7)	4604 (1)	37 (2)
C(1)	-6549 (9)	776 (7)	4584 (1)	48 (2)
C(2)	-6681 (9)	4126 (7)	4580 (1)	48 (2)
C(3)	-3753 (8)	2555 (8)	4865 (1)	50 (2)
C(4)	-3240 (7)	2508 (8)	4409 (1)	41 (2)
C(5)	-4160 (9)	2207 (7)	4129 (1)	48 (2)
C(6)	-2183 (10)	2764 (9)	3959 (1)	57 (2)
C(7)	-2650 (9)	2269 (8)	3674 (1)	51 (2)
C(8)	-778 (10)	2984 (7)	3506 (1)	49 (2)
C(9)	-1001 (10)	2313 (8)	3231 (1)	54 (2)
C(10)	858 (10)	3095 (8)	3063 (1)	50 (2)
C(11)	740 (10)	2287 (8)	2790 (1)	52 (2)
C(12)	2583 (10)	3105 (8)	2623 (1)	53 (2)
C(13)	2470 (9)	2319 (8)	2351 (1)	53 (2)
C(14)	4293 (10)	3118 (8)	2182 (1)	49 (2)
C(15)	4197 (10)	2311 (8)	1911 (1)	52 (2)
C(16)	6012 (10)	3110 (8)	1741 (1)	54 (2)
C(17)	5871 (10)	2298 (8)	1471 (1)	56 (2)
C(18)	7700 (11)	3117 (9)	1299 (1)	65 (3)
C(19)	7523 (14)	2231 (9)	1030 (1)	92 (3)

Table 2. Bond distances (\AA) and angles ($^\circ$) for non-H atoms, with their e.s.d.'s in parentheses

N–C(1)	1.497 (7)	C(1)–N–C(2)	109.5 (4)
N–C(2)	1.483 (7)	C(1)–N–C(3)	108.9 (4)
N–C(3)	1.511 (7)	C(2)–N–C(3)	108.6 (4)
N–C(4)	1.503 (7)	C(1)–N–C(4)	111.0 (4)
C(4)–C(5)	1.531 (7)	C(2)–N–C(4)	112.5 (4)
C(5)–C(6)	1.523 (8)	C(3)–N–C(4)	106.3 (4)
C(6)–C(7)	1.533 (7)	N–C(4)–C(5)	115.9 (4)
C(7)–C(8)	1.507 (8)	C(4)–C(5)–C(6)	107.5 (4)
C(8)–C(9)	1.510 (7)	C(5)–C(6)–C(7)	114.5 (5)
C(9)–C(10)	1.519 (8)	C(6)–C(7)–C(8)	113.5 (5)
C(10)–C(11)	1.535 (8)	C(7)–C(8)–C(9)	114.9 (5)
C(11)–C(12)	1.519 (8)	C(8)–C(9)–C(10)	114.1 (5)
C(12)–C(13)	1.524 (8)	C(9)–C(10)–C(11)	113.6 (5)
C(13)–C(14)	1.512 (8)	C(10)–C(11)–C(12)	113.0 (5)
C(14)–C(15)	1.526 (8)	C(11)–C(12)–C(13)	113.4 (5)
C(15)–C(16)	1.512 (8)	C(12)–C(13)–C(14)	114.1 (5)
C(16)–C(17)	1.522 (8)	C(13)–C(14)–C(15)	114.0 (5)
C(17)–C(18)	1.530 (8)	C(14)–C(15)–C(16)	114.2 (5)
C(18)–C(19)	1.539 (8)	C(15)–C(16)–C(17)	113.3 (5)
		C(16)–C(17)–C(18)	113.2 (5)
		C(17)–C(18)–C(19)	111.4 (5)

Discussion. Atomic parameters are given in Table 1,* bond distances and angles in Table 2. The atomic numbering is shown in Fig. 1.

The hexadecyltrimethylammonium cation has normal geometry with average values $C-C = 1.523$ (8), $C-N = 1.499$ (6) Å, $C-C-C = 113.2$ (5) and $C-N-C = 109.5$ (4)°. The carbon atoms $C(5)-C(19)$ are nearly planar, within 0.198 (7) Å, while $C(4)$ lies about 0.5 Å out of the mean plane.

The alkyl chain is in a nearly fully extended conformation and its long axis is approximately parallel to the ac plane and forms a tilt angle of 65° with the ab plane. Its torsion angles are 180° with good approximation for the group of atoms $C(9)-C(19)$, whereas the deviation from 180° increases on approaching the nitrogen atom. The molecular packing, shown in Fig. 2, is controlled by Coulombic and van der Waals interactions which cause the formation of bilayers. The cation moieties are arranged in antiparallel fashion giving rise to a pronounced interdigitation within the bilayer, which presents a low charge density on its polar surfaces, owing to the large bulkiness of the $N(CH_3)_3$ groups. Many contacts within the range $3.7 \text{--} 4.2$ Å involving the methyl groups $C(1)$, $C(2)$, $C(3)$ and $C(19)$ and other $C \cdots C$ contacts of about 4.1 Å among methylenic groups stabilize the bilayer. The strongest van der Waals interactions involve the Br^- ions which act as cement between adjacent bilayers, helped in this action by the $C(1)$, $C(2)$ and $C(3)$ methyl groups. The nearest neighbours of Br^- within the range $3.6 \text{--} 4.0$ Å are six methyl and two methylenic groups (see Fig. 3). The coordination with $C(1^{iv})$, $C(1^v)$, $C(2^{ii})$ and $C(2^{iii})$ is nearly square planar, Br^- being 0.29 Å out of the plane defined by the four methyl groups. Moreover, Br^- is roughly tetrahedrally surrounded by two other methyl [$C(3)$ and $C(3^i)$] and two methylenic [$C(4^{ii})$ and $C(4^v)$] groups. The Coulombic interactions of the bromide ion occur mainly with the polar heads containing N^i , N^{ii} and N^v , the shortest distance $Br^- \cdots N$ being 4.2 Å. This value is much higher than that of 3.3 Å observed in the crystal structure of *n*-dodecylammonium bromide (Lundén, 1974), and obviously

* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42996 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

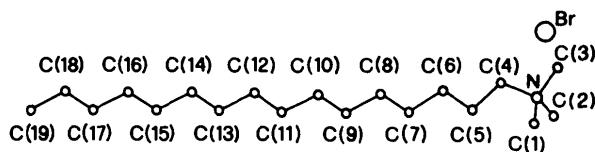


Fig. 1. Atomic numbering of CTAB.

can be accounted for by the hindrance of the methyl groups for the approach of Br^- to N. The arrangement of the ionic groups on each surface gives rise to a rectangular network, with a and b edges, producing weak attractive interactions. In conclusion, the arrangement of the bromide ions suggests an unusual model which will be checked in the study of the aqueous solutions.

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Fig. 2. ORTEP (Johnson, 1965) stereoscopic view of molecular packing. Crossed circles are methyl groups.

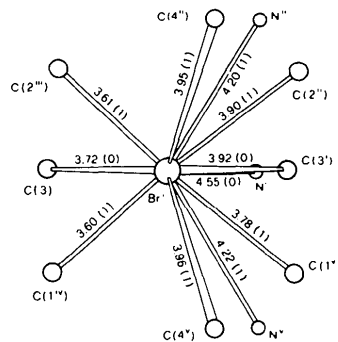


Fig. 3. The shortest van der Waals and Coulombic interactions of the Br^- ion (Å). The atoms are projected on to the ab plane. The roman-numeral superscripts refer to the following symmetry operations: (i) $1+x, y, z$; (ii) $\bar{x}, 1-y, 1-z$; (iii) $-1-x, 1-y, 1-z$; (iv) $-1-x, \bar{y}, 1-z$; (v) $\bar{x}, \bar{y}, 1-z$.

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Structure of Harman, 1-Methyl-9H-pyrido[3,4-*b*]indole

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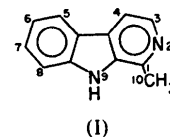
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Abstract. C₁₂H₁₀N₂, *M_r* = 182.23, orthorhombic, *P*2₁2₁2₁, *a* = 9.540 (4), *b* = 13.378 (7), *c* = 15.525 (7) Å, *V* = 1981.4 (1.6) Å³, *Z* = 8, *D_x* = 1.230 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 5.93 cm⁻¹, *F*(000) = 768, *T* = 295 K, *R* = 0.055 for 1169 *I*s 3σ above background. There are two molecules in the asymmetric unit, without any significant differences in bond lengths and angles. The average out-of-plane distances for the 13 ring atoms in the two molecules are 0.022 and 0.029 Å respectively. Each molecule is hydrogen-bonded to two others to form continuous spiral chains through the structure.

Introduction. The hallucinogenic plants and their constituents have been reviewed (Marderosian, 1967). The major botanical sources investigated constitute one or more members of the families Leguminosae, Malpighiaceae, Zygophyllaceae, Gramineae, and Convolvulaceae. In these surveys, the indolic bases *N,N*-dimethyltryptamine, 5-methoxy-*N*-methyltryptamine, 5-methoxy-*N,N*-dimethyltryptamine, bufotenine, harmine, harmaline, harmalol, harman, lysergic acid amides, psilocin and psilocybin were reported as the pharmacologically active constituents of the plants.

A few species of the family Zygophyllaceae, *viz* *Peganum*, *Tribulus* and *Zygophyllum*, were reported to

contain harmine-type alkaloids (Borkowski, 1959; Borkowski & Lutomski, 1960; Ivanov, Nikolov & Tonev, 1965; Ikram & Hug, 1966). The main alkaloids isolated from *Peganum harmala* are harmine and harmaline (Brimblecombe & Pinder, 1975). Ethanol extracts of *Peganum* were reported to show a broad spectrum of antimicrobial activity. Moreover, examination of each alkaloid of this group separately showed that only harmine, harman and harmalol had antimicrobial activity (Al Shamma, Drake, Flynn, Mitscher, Park, Rao, Simpson, Swayze, Veysoglu & Wu, 1981). Harman also has been identified in cigarette smoke (Poindexter & Carpenter, 1962). The crystal and molecular structure of harman (I), the major alkaloid isolated from *Fagonia cretica* L. (Zygophyllaceae) (Ahmed, Rizk, Hammouda & Abdel-Gawad, 1969), is reported.



Experimental. Isolated from wild-plant aerial parts of *Fagonia cretica* L., Egypt; prismatic crystals grown