

longer than the S—S bond length in compounds having an *N*-aryl grouping, and the S—N bond length of 1.791 (2) Å is significantly shorter. The S—S bond in the title compound is 0.4 Å longer than that of an accepted single-bond length of 2.10 Å (Hordvik, 1970), but 0.70 Å shorter than the shortest distance found in a crystal between two non-bonded S atoms of 3.20 Å (Lozac'h, 1971). The sum of the S—S and S—N bond lengths is 4.287 (3) Å, approximately 10% greater than the sum of typical two-centre, two-electron covalent S—S and S—N bond lengths (3.85 Å), and is thus similar to that found in analogous molecules (Hansen, 1977).

The N—S—S bond angle, 173.4 (1)°, is very close to that found in analogous structures [see 1(*a*), 1(*b*), and 1(*c*)]. The length of the bond from the central S atom to the central C atom, S(2)—C(3), is 1.741 (2) Å. This is in the range found for the other three analogues, 1.740 (6)–1.752 (7) Å (Leung & Nyburg, 1971, 1972; Borel *et al.*, 1978). The S(1)—C(1) bond length is 1.713 (2) Å, which is significantly shorter than that of S(2)—C(3), indicating multiple-bond character for the S(1)—C(1) bond in contrast to the single bond of S(2)—C(3). Again this is typical of these types of molecule.

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Structure of Benzyldimethyl(phenyl)ammonium Chloride Monohydrate

BY S. CHAUDHURI AND T. BANERJEE

Saha Institute of Nuclear Physics, Sector I, Block 'AF' Bidhannagar, Calcutta-700 064, India

M. K. DEB PURKAYASTHA

Karimganj College, Karimganj 788 710, India

K. P. SEN SARMA

Jadavpur University, Calcutta-700 032, India

AND G. BOCELLI

Centro di Studio per la Strutturistica Diffattometrica CNR, Viale delle Scienze, 43100 Parma, Italy

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Abstract. C₁₅H₁₈N⁺.Cl[−].H₂O, *M_r* = 265.7, monoclinic, *C*2/*c*, *a* = 14.115 (8), *b* = 12.704 (8), *c* = 16.866 (8) Å, β = 108.83 (3)°, *V* = 2862 (3) Å³, *Z* = 8, *D_m* = 1.24, *D_x* = 1.23 Mg m^{−3}, $\lambda(\text{Cu } K\alpha)$ = 1.5418 Å, μ = 2.13 mm^{−1}, *F*(000) = 1136, *T* = 298 K, final *R* = 0.054 for 1947 'observed' reflections. The conformation of the N⁺—C—C—C part of the molecule is similar to the conformation of the active part of

acetylcholine and its structural analogues. The Cl[−] ions and the water molecules form hydrogen-bonded chains. The packing of the cations is determined mainly by Coulombic and van der Waals forces.

Introduction. Benzyldimethyl(phenyl)ammonium chloride was synthesized by the method of Michler & Gradmann (1877) and characterized by UV, IR and

NMR spectroscopy (Deb Purkayastha & Sen Sarma, 1985). This quaternary ammonium compound undergoes non-Faradaic electrolysis in weak aqueous solutions and has some structural similarity with the neurotransmitter acetylcholine chloride (Herdklotz & Sass, 1970) and some of its structural analogues (Jellinek, 1957; Chothia & Pauling, 1978). Crystal-structure analyses of some of the neurotransmitters have shown that the $N^+-C-C-O$ moiety, which is the active part of this group of compounds, exists in the *gauche* form, rather than the *trans* form expected from steric considerations (Sundaralingam, 1968). The present work was undertaken to study the conformational similarity of this compound with acetylcholine and its structural analogues.

Experimental. Pale-blue irregular crystals from isoamyl alcohol, density by flotation (benzene–bromoform mixture), crystal size $0.25 \times 0.32 \times 0.37$ mm, Siemens AED diffractometer, Ni-filtered $Cu K\alpha$ radiation, accurate cell parameters from least-squares fit of setting angles for 20 reflections ($13 \leq \theta \leq 44^\circ$) using the routine *CTDIF* (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979), $C2/c$ or Cc (systematic absences: hkl , $h+k$ odd; $h0l$, l odd), former confirmed by E statistics and successful refinement, 5410 reflections ($-10 \leq h \leq 16$, $-15 \leq k \leq 11$, $-19 \leq l \leq 20$, $2 \leq \theta \leq 70^\circ$) measured, one standard reflection monitored every 50 reflections, correction for L_p and statistical fluctuation (Belletti *et al.*, 1979), absorption ignored, merged to 2720 unique reflections ($R_{int} = 0.026$), direct methods with *SHELX76* (Sheldrick, 1976), structure solved in Cc ; 394 E 's ≥ 1.4 used; origin, enantiomorph-defining and four multisolution reflections chosen manually; all non-H atoms located from best E map, centre of inversion located between corresponding atoms of the two molecules in the 'asymmetric unit', subsequent full-matrix refinement using *SHELX76* in space group $C2/c$ with 1947 'observed' reflections [$I \geq 2.5\sigma(I)$], non-H atoms anisotropic and H atoms (located from ΔF synthesis) isotropic; $R = 0.054$, $wR = 0.061$, $S = 1.21$, $w = 1/[\sigma^2(|F_o|) + 0.0093|F_o|^2]$, reflections 200, 223 and 204 omitted in the last cycles of refinement because of extinction; scattering factors of *SHELX76* used; $(\Delta/\sigma)_{max} < 0.05$; $\Delta\rho$ in final ΔF synthesis in the range -0.22 to 0.27 e \AA^{-3} .

Discussion. The atomic parameters are listed in Table 1.* Fig. 1 shows a projection of the cation. Bond

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms and details of weighted least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43880 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances, bond angles and some selected torsion angles are listed in Table 2.

The N^+-C bond distances agree well with those found in other similar structures (Chothia & Pauling, 1978; Bardi, Piazzesi, Del Pra & Villa, 1983; Craven &

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

For non-H atoms $U_{eq} = 1/6\pi^2 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$				
	x	y	z	$U_{eq}/U(\text{\AA}^2)$
N	0.1969 (1)	0.3987 (2)	0.7131 (1)	0.0441 (7)
C(1)	0.2960 (2)	0.4221 (2)	0.7766 (1)	0.0401 (7)
C(2)	0.3490 (2)	0.5071 (2)	0.7634 (2)	0.0477 (9)
C(3)	0.4397 (2)	0.5320 (2)	0.8228 (2)	0.0543 (10)
C(4)	0.4766 (2)	0.4709 (2)	0.8935 (2)	0.0588 (10)
C(5)	0.4235 (2)	0.3866 (3)	0.9054 (2)	0.0614 (11)
C(6)	0.3326 (2)	0.3602 (2)	0.8477 (2)	0.0497 (10)
C(7)	0.2616 (2)	0.2772 (2)	0.6213 (1)	0.0396 (8)
C(8)	0.3649 (2)	0.2743 (2)	0.6456 (2)	0.0488 (8)
C(9)	0.4136 (2)	0.1850 (2)	0.6319 (2)	0.0568 (11)
C(10)	0.3593 (2)	0.0982 (2)	0.5932 (2)	0.0543 (10)
C(11)	0.2574 (2)	0.0996 (2)	0.5696 (2)	0.0527 (10)
C(12)	0.2082 (2)	0.1888 (2)	0.5829 (1)	0.0462 (9)
C(13)	0.2062 (2)	0.3758 (2)	0.6264 (1)	0.0445 (9)
C(14)	0.1299 (2)	0.4930 (3)	0.7023 (2)	0.0704 (13)
C(15)	0.1453 (3)	0.3073 (3)	0.7379 (2)	0.0620 (12)
Cl	-0.0762 (1)	0.3155 (1)	0.5635 (1)	0.0781 (4)
O	0.2785 (3)	0.3707 (2)	0.0806 (2)	0.0887 (12)
H(2)	0.326 (2)	0.553 (3)	0.717 (2)	0.065 (9)
H(3)	0.480 (3)	0.598 (3)	0.822 (2)	0.075 (9)
H(4)	0.548 (3)	0.490 (3)	0.939 (2)	0.086 (11)
H(5)	0.456 (3)	0.343 (3)	0.960 (3)	0.110 (13)
H(6)	0.298 (2)	0.305 (2)	0.855 (2)	0.054 (8)
H(8)	0.401 (2)	0.332 (2)	0.668 (2)	0.054 (8)
H(9)	0.489 (3)	0.184 (2)	0.648 (2)	0.072 (9)
H(10)	0.391 (2)	0.041 (3)	0.582 (2)	0.068 (9)
H(11)	0.219 (2)	0.042 (2)	0.540 (2)	0.066 (9)
H(12)	0.131 (3)	0.192 (2)	0.563 (2)	0.061 (8)
H(131)	0.134 (2)	0.367 (2)	0.590 (2)	0.042 (6)
H(132)	0.240 (2)	0.437 (2)	0.611 (2)	0.046 (7)
H(141)	0.169 (3)	0.552 (3)	0.687 (2)	0.084 (11)
H(142)	0.068 (2)	0.470 (2)	0.663 (2)	0.067 (9)
H(143)	0.119 (3)	0.520 (3)	0.749 (2)	0.082 (11)
H(151)	0.135 (2)	0.318 (2)	0.786 (2)	0.042 (6)
H(152)	0.084 (3)	0.301 (3)	0.691 (2)	0.075 (9)
H(153)	0.187 (3)	0.239 (3)	0.745 (2)	0.076 (10)
H(O1)	0.322 (3)	0.323 (3)	0.074 (2)	0.103 (15)
H(O2)	0.219 (4)	0.351 (4)	0.047 (3)	0.060 (9)

Table 2. Bond distances (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) with e.s.d.'s in parentheses

N—C(1)	1.492 (3)	N—C(13)	1.537 (3)
N—C(14)	1.500 (4)	N—C(15)	1.500 (5)
C(1)—C(2)	1.372 (4)	C(2)—C(3)	1.384 (4)
C(3)—C(4)	1.376 (4)	C(4)—C(5)	1.359 (5)
C(5)—C(6)	1.378 (4)	C(6)—C(1)	1.387 (3)
C(13)—C(7)	1.494 (4)	C(7)—C(8)	1.382 (4)
C(8)—C(9)	1.384 (4)	C(9)—C(10)	1.381 (4)
C(10)—C(11)	1.363 (4)	C(11)—C(12)	1.385 (4)
C(12)—C(7)	1.391 (3)		
C(1)—N—C(13)	111.9 (2)	C(1)—N—C(14)	109.6 (2)
C(1)—N—C(15)	112.4 (2)	C(13)—N—C(14)	106.2 (2)
C(13)—N—C(15)	108.5 (2)	C(14)—N—C(15)	107.9 (3)
N—C(1)—C(2)	118.3 (2)	N—C(1)—C(6)	120.6 (2)
C(2)—C(1)—C(6)	121.1 (3)	C(1)—C(2)—C(3)	119.2 (3)
C(2)—C(3)—C(4)	120.1 (3)	C(3)—C(4)—C(5)	120.0 (3)
C(4)—C(5)—C(6)	121.3 (3)	C(5)—C(6)—C(1)	118.3 (3)
N—C(13)—C(7)	114.9 (2)	C(13)—C(7)—C(8)	121.8 (2)
C(13)—C(7)—C(12)	119.3 (2)	C(12)—C(7)—C(8)	118.6 (3)
C(7)—C(8)—C(9)	120.4 (3)	C(8)—C(9)—C(10)	120.2 (3)
C(9)—C(10)—C(11)	120.0 (3)	C(10)—C(11)—C(12)	120.0 (3)
C(11)—C(12)—C(7)	120.8 (3)		
C(1)—N—C(13)—C(7)	66.5 (3)	C(7)—C(13)—N—C(14)	-173.8 (2)
C(7)—C(13)—N—C(15)	-58.0 (3)	N—C(13)—C(7)—C(8)	-83.1 (3)
N—C(13)—C(7)—C(12)	103.9 (3)		

Hite, 1973; Jellinek, 1957; Senko & Templeton, 1960). The steric strain resulting from the contact between C(15) and C(6) [2.777 (6) Å] accounts for the increment in the C(1)—N—C(15) angle [112.4 (2)°] from the ideal tetrahedral value. The significant increase in the N—C(13)—C(7) angle [114.9 (2)°] from the tetrahedral value is a common feature in molecules having acetylcholine-like structures: 116.8 (2)° in cartinine hydrochloride (Tomita, Urabe, Kim & Fujiwara, 1974), 116.6 (1)° in trimethyl[(*cis*-2-methyl-1,3-oxathiolan-5-yl)methyl]ammonium iodide (Bardi *et al.*, 1983), 112° in choline chloride (Senko & Templeton, 1960), and 113° in muscarine iodide (Jellinek, 1957).

The torsion angle N—C(13)—C(7)—C(8) [−83.1 (3)°], defining the orientation of the phenyl ring [C(7), C(8), C(9), C(10), C(11), C(12)] with respect to the quaternary N, shows that the N⁺—C(13)—C(7)—C(8) system is in the *gauche* conformation. The close similarity of this torsion angle with the corresponding torsion angles in acetylcholine chloride (84.7°) (Herdklotz & Sass, 1970), acetylcholine bromide (77°) (Canepa, Pauling & Sorum, 1966) and L-(+)-muscarine (74°) (Radna, Beveridge & Bender, 1973) shows that the conformation of the N⁺—C—C—C part of the present molecule is similar to that of the active part (N⁺—C—C—O) of acetylcholine and its structural analogues. The other torsion angle C(7)—C(13)—N—C(14) [−173.8 (2)°] compares well with the values of −175° in L-(+)-muscarine (Radna *et al.*, 1973), 171.4°

in acetylcholine chloride (Herdklotz & Sass, 1970) and 180° in acetylcholine bromide (Canepa *et al.*, 1966). This is in good agreement with the expected value of 180° in an antiplanar bond. The intramolecular N...C(8) distance [3.341 (4) Å] is very close to the intramolecular N⁺...O distances of 3.26 Å in acetylcholine chloride (Herdklotz & Sass, 1970) and 3.29 Å in acetylcholine bromide (Canepa *et al.*, 1966). These similarities suggest that the conformation of this molecule may also be stabilized electrostatically (Sundaralingam, 1968).

The Cl[−] ions and the water molecules form hydrogen-bonded chains [O—H 0.89 (3), H...Clⁱ 2.31 (3), O...Clⁱ 3.204 (4) Å, O—H...Clⁱ 173 (2)°; O—H 0.88 (3), H...Clⁱⁱ 2.31 (5), O...Clⁱⁱ 3.174 (4) Å, O—H...Clⁱⁱ 167 (2)°; symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $x, y, \frac{1}{2} - z$]. The O—H and H...Cl distances, similar to those found in tetraethylammonium chloride monohydrate (Loehlin & Kvick, 1978) and choline chloride (Senko & Templeton, 1960), indicate that the hydrogen bonds are weak.

A perspective view of the packing arrangement is shown in Fig. 2. The packing of the ions is determined mainly by Coulombic and van der Waals forces. The Cl[−] ions tend to concentrate around the tetrahedral N atoms. The six shortest N⁺...Cl[−] distances are 4.01 (3), 4.73 (3), 5.72 (3), 6.35 (3), 7.06 (4) and 7.61 (4) Å.

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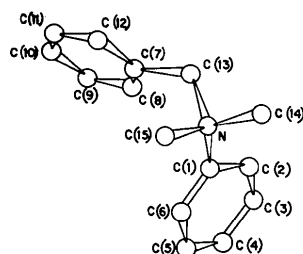


Fig. 1. Projection of the cation.

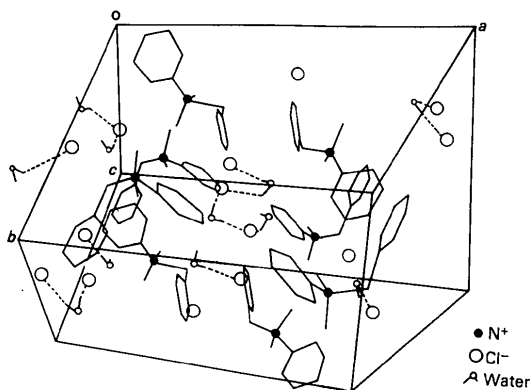


Fig. 2. Perspective view of the packing arrangement.

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