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2,6-Dimethylphenylammonium Chloride at 173 and 293 K

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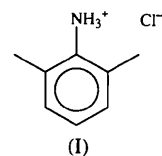
Abstract

The X-ray structure of 2,6-dimethylphenylammonium chloride, $C_8H_{12}N^+Cl^-$, has been determined at 173 and 293 K. The slight distortion of the phenyl ring of the cation can be attributed to the additive effects of the ring substituents. Hydrogen bonds link the ions into infinite sandwich-type layers where the anions act as the sandwich filling.

Comment

The structure of 2,6-dimethylphenylammonium chloride (I) has been investigated in order to compare its $N-H \cdots Cl$ hydrogen-bonding interactions with those of other methyl- or methoxy-substituted phenylammonium chloride derivatives. Such compounds have shown reasonably strong correlations between various parameters; *viz.* $N-H$ bond force constant K versus pK_a (or base strength), ΔK versus pK_a , atomic core level binding energy E_b versus pK_a , ΔK versus ΔE_b and $E_b(Cl\ 2p)$ versus $E_b(N\ 1s)$. These results indicate that the degree of hydrogen bonding in the solids depends

on the type and position of substituents on the aromatic ring of the base (Jiang, James, Liesegang & Day, 1994). The general purpose NDDO molecular orbital method AM1 (Austin Model 1), which is incorporated in the *MOPAC* (version 7.00) package (Stewart & Coolidge, 1993), may be used to calculate net atomic charges based on known crystal structures. Until recently, only two simple methyl- or methoxy-substituted phenylammonium chloride structures were known: for the 4-methyl derivative (Colapietro, Domenicano & Portalone, 1982) and a lower quality data set for the 2-methyl compound (Cameron, Duffin & Singh, 1976), both obtained from room-temperature measurements. Thus, high quality data have been sought for other similarly substituted phenylammonium chlorides and to this end the structure determination of the 2-methoxy derivative as well as a more accurate redetermination of the 2-methyl derivative have already been undertaken (Jiang, Liesegang, James, Skelton & White, 1995). The structure of (I), reported here, expands this series further.



Since the atomic coordinates are most precisely obtained from low-temperature measurements, the determination was originally carried out at 173 K. However, particularly marked changes were observed in the calculated charge on N with a modelled variation of the H-atom position in the $N-H \cdots Cl$ system (Jiang, James, Liesegang & Day, 1994). Therefore, for comparison purposes, the room-temperature atomic coordinates were also required, because the other substituted derivatives had also been measured at this temperature.

Views of (I) at 173 and 293 K, showing the displacement ellipsoids and the atomic numbering, are given in Fig. 1. With the exception of minor changes in the positions of the ammonium H atoms, the structure of (I) at 173 K is the same as that at 293 K. At the higher temperature, the estimated standard deviations of the atomic parameters are larger, which is to be expected as a result of increased thermal vibration. A TLS thermal motion correction (Schomaker & Trueblood, 1968) applied to the atoms of the cation suggested that the bond lengths given in the tables are too short by 0.003–0.005 Å at 173 K and 0.007–0.011 Å at 293 K. This correction reduces the mean differences in the bond lengths at the two temperatures from 0.007 to 0.004 Å, or to 0.003 Å if the anomalously short C(4)—C(5) bond in the structure at 293 K is discounted. The corrections to the bond angles are less than one standard deviation at both temperatures. The slightly high values of the goodness-of-fit parameter (S) for each refinement

may indicate an underestimation of the estimated standard deviations of the atomic and geometric parameters, although refinements with different weighting schemes generally changed parameters by less than one standard deviation.

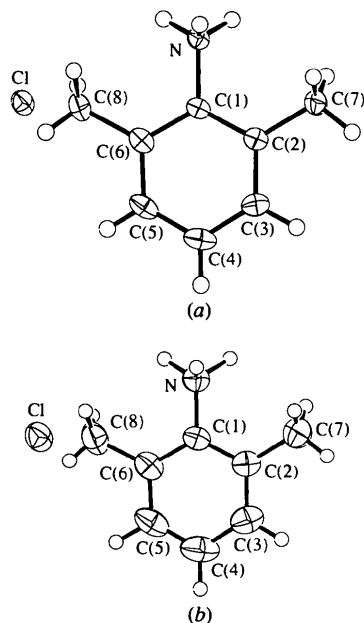


Fig. 1. View of the cation of (I) at (a) 173 K and (b) 293 K showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

Two of the three N—H bonds at 293 K are marginally longer than at 173 K (Table 3). This effect is probably the result of increased thermal motion and an associated increase in the uncertainty of the atomic positional parameters at the higher temperature.

The phenyl ring of the cation is slightly distorted at both temperatures. The C(2)—C(1)—C(6) bond angle is slightly greater than 120° , while the C(1)—C(2)—C(3) and C(1)—C(6)—C(5) angles are slightly less than 120° . Only one other structure containing a 2,6-dimethylphenylammonium cation has been reported in the literature (Cook, Herrmann, Kiprof & Takacs, 1991). The cation in this structure exhibits similar distortions with the C(2)—C(1)—C(6), C(1)—C(2)—C(3) and C(1)—C(6)—C(5) bond angles being $125.2(1)$, $116.7(1)$ and $115.6(1)^\circ$, respectively. All ring C—C—C angles in (I) agree closely with the predicted angles (Table 4) calculated by adding the distortion effects of the individual substituents, which were estimated by Domenicano & Murray-Rust (1979) and Norrestam & Schepper (1981).

The C—C bond lengths within the phenyl ring become progressively shorter with increasing distance

from the N atom. The difference between the shortest and longest bonds is *ca* 0.015 \AA for both the corrected and uncorrected bond lengths at 173 K. This is consistent with the inductive effects of the positively charged N atom, but may also reflect the increasing magnitude of the thermal displacement factors with increasing distance from C(1). The C(1)—N bond length is similar to those found in other phenylammonium cations. The mean value from 66 accurately determined structures ($R < 0.07$) in the Cambridge Structural Database (October 1994 version) (Allen *et al.*, 1991) is $1.466(11) \text{ \AA}$.

The ions interact *via* a complex series of hydrogen bonds to form a layered sandwich structure. Each H atom of the ammonium part of the cation forms a hydrogen bond with one Cl^- anion. The cation thereby interacts with three different anions and each anion accepts three hydrogen bonds, one from each of three different cations (Table 3). There are no bifurcated interactions. The angles subtended at the Cl^- ion by the interacting H atoms range from 104 to 117° . As shown in Fig. 2, the hydrogen bonding forms an infinite two-dimensional network and causes the ions to pack in a layer structure in which the anions are sandwiched between two layers of cations. The layers extend parallel to the *bc* plane of the crystal lattice and there are no significant interactions between adjacent layers. The pattern of hydrogen bonding is the same at 173 and 293 K.

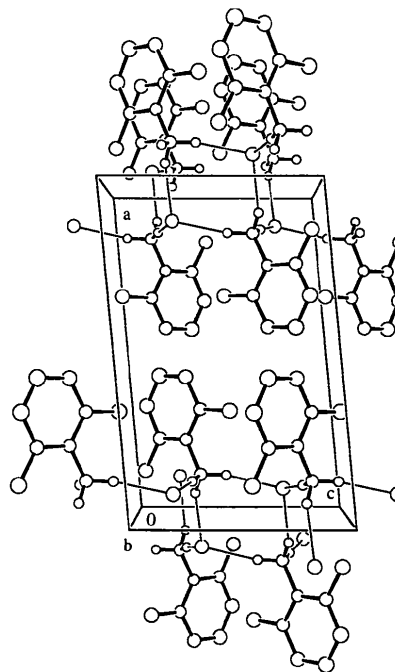


Fig. 2. The packing of (I) in the unit cell at 173 K viewed down *b*. Thin lines show the hydrogen-bonding interactions. Most H atoms have been omitted for clarity.

Experimental

The title compound is obtained by careful addition of concentrated HCl to a chilled ethanol solution of 2,6-dimethylaniline. Crystals suitable for X-ray analysis were obtained by recrystallization from concentrated HCl.

Compound (I) at 173 K*Crystal data*

$C_8H_{12}N^+.Cl^-$
 $M_r = 157.64$
 Monoclinic
 $P2_1/c$
 $a = 12.666 (1) \text{ \AA}$
 $b = 8.552 (2) \text{ \AA}$
 $c = 8.034 (2) \text{ \AA}$
 $\beta = 95.49 (1)^\circ$
 $V = 866.3 (3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.209 \text{ Mg m}^{-3}$

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2861 measured reflections
 2530 independent reflections
 1981 observed reflections
 $[I > 3\sigma(I)]$
 $R_{int} = 0.021$

Refinement

Refinement on F^2
 $R = 0.0342$
 $wR = 0.0413$
 $S = 1.669$
 1981 reflections
 139 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + (0.01F_o)^2]$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 18.5\text{--}20.0^\circ$
 $\mu = 0.368 \text{ mm}^{-1}$
 $T = 173 (1) \text{ K}$
 Plate
 $0.50 \times 0.42 \times 0.10 \text{ mm}$
 Colourless

$\theta_{max} = 30^\circ$
 $h = -17 \rightarrow 17$
 $k = -12 \rightarrow 0$
 $l = 0 \rightarrow 11$
 3 standard reflections monitored every 150 reflections
 intensity decay: insignificant

$(\Delta/\sigma)_{max} = 0.0002$
 $\Delta\rho_{max} = 0.41 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.16 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (I) at 293 K*Crystal data*

$C_8H_{12}N^+.Cl^-$
 $M_r = 157.64$
 Monoclinic
 $P2_1/c$
 $a = 12.766 (2) \text{ \AA}$
 $b = 8.566 (1) \text{ \AA}$
 $c = 8.136 (1) \text{ \AA}$
 $\beta = 94.84 (1)^\circ$
 $V = 886.5 (2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.181 \text{ Mg m}^{-3}$

Data collection

Rigaku AFC-5R diffractometer

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
 Cell parameters from 22 reflections
 $\theta = 12.0\text{--}13.0^\circ$
 $\mu = 0.359 \text{ mm}^{-1}$
 $T = 293 (1) \text{ K}$
 Plate
 $0.40 \times 0.37 \times 0.10 \text{ mm}$
 Colourless

$R_{int} = 0.028$
 $\theta_{max} = 27.5^\circ$

 $\omega/2\theta$ scans

Absorption correction: none

2316 measured reflections
 2031 independent reflections
 1114 observed reflections
 $[I > 3\sigma(I)]$

 $h = -16 \rightarrow 16$ $k = -11 \rightarrow 0$ $l = 0 \rightarrow 10$

3 standard reflections monitored every 150 reflections
 intensity decay: 4%

Refinement

Refinement on F^2
 $R = 0.0465$
 $wR = 0.0390$
 $S = 1.801$
 1114 reflections
 139 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$

$(\Delta/\sigma)_{max} = 0.0003$
 $\Delta\rho_{max} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.19 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$			U_{eq}
	x	y	z	
173 K				
Cl	0.09425 (3)	-0.10032 (4)	0.20388 (4)	0.0275 (1)
N	0.1335 (1)	-0.0588 (2)	0.8254 (2)	0.0217 (4)
C(1)	0.2348 (1)	-0.0040 (2)	0.7716 (2)	0.0207 (4)
C(2)	0.3282 (1)	-0.0684 (2)	0.8509 (2)	0.0233 (4)
C(3)	0.4242 (1)	-0.0198 (2)	0.7962 (2)	0.0289 (5)
C(4)	0.4261 (1)	0.0885 (2)	0.6679 (2)	0.0354 (5)
C(5)	0.3324 (1)	0.1495 (2)	0.5917 (2)	0.0329 (5)
C(6)	0.2340 (1)	0.1050 (2)	0.6416 (2)	0.0250 (4)
C(7)	0.3264 (1)	-0.1875 (2)	0.9885 (2)	0.0321 (5)
C(8)	0.1332 (2)	0.1725 (2)	0.5562 (2)	0.0310 (5)
293 K				
Cl	0.09248 (7)	-0.1016 (1)	0.1977 (1)	0.0527 (3)
N	0.1324 (2)	-0.0602 (4)	0.8242 (4)	0.041 (1)
C(1)	0.2331 (3)	-0.0054 (4)	0.7707 (4)	0.037 (1)
C(2)	0.3251 (3)	-0.0687 (4)	0.8486 (4)	0.044 (1)
C(3)	0.4201 (3)	-0.0197 (5)	0.7953 (5)	0.057 (2)
C(4)	0.4225 (3)	0.0892 (5)	0.6702 (6)	0.069 (2)
C(5)	0.3308 (4)	0.1484 (5)	0.5958 (5)	0.063 (2)
C(6)	0.2334 (3)	0.1034 (4)	0.6442 (4)	0.045 (1)
C(7)	0.3227 (4)	-0.1879 (7)	0.9828 (7)	0.066 (2)
C(8)	0.1343 (4)	0.1702 (6)	0.5590 (6)	0.061 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

	172 K	293 K
N—C(1)	1.470 (2)	1.468 (4)
C(1)—C(2)	1.402 (2)	1.396 (4)
C(1)—C(6)	1.400 (2)	1.389 (4)
C(2)—C(3)	1.395 (2)	1.388 (5)
C(2)—C(7)	1.505 (2)	1.497 (5)
C(3)—C(4)	1.387 (2)	1.382 (5)
C(4)—C(5)	1.385 (3)	1.369 (6)
C(5)—C(6)	1.397 (2)	1.390 (5)
C(6)—C(8)	1.506 (2)	1.505 (5)
N—C(1)—C(2)	117.6 (1)	117.7 (3)
N—C(1)—C(6)	119.2 (1)	119.5 (3)
C(2)—C(1)—C(6)	123.1 (1)	122.8 (3)
C(1)—C(2)—C(3)	117.5 (1)	117.7 (3)
C(1)—C(2)—C(7)	121.9 (1)	121.9 (3)
C(3)—C(2)—C(7)	120.5 (1)	120.4 (4)
C(2)—C(3)—C(4)	120.8 (2)	120.5 (4)
C(3)—C(4)—C(5)	120.3 (2)	120.3 (4)
C(4)—C(5)—C(6)	121.4 (2)	121.6 (4)
C(1)—C(6)—C(5)	116.9 (1)	117.1 (4)
C(1)—C(6)—C(8)	122.7 (1)	122.8 (3)
C(5)—C(6)—C(8)	120.4 (1)	120.2 (4)

Table 3. Hydrogen-bonding geometry (Å, °) for (I)

D—H...A	D—H	H...A	D...A	D—H...A
173 K				
N—H(11)...Cl ⁱ	0.91 (2)	2.32 (2)	3.178 (1)	158 (2)
N—H(12)...Cl ⁱⁱ	0.84 (2)	2.27 (2)	3.099 (2)	172 (2)
N—H(13)...Cl ⁱⁱⁱ	0.96 (2)	2.20 (2)	3.148 (2)	168 (2)
293 K				
N—H(11)...Cl ⁱ	1.02 (4)	2.20 (4)	3.180 (3)	161 (3)
N—H(12)...Cl ⁱⁱ	0.83 (4)	2.27 (4)	3.102 (3)	173 (3)
N—H(13)...Cl ⁱⁱⁱ	1.10 (4)	2.06 (4)	3.143 (3)	169 (3)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, y, 1 + z$.

Table 4. Predicted bond angles (°) within the phenyl ring of a 2,6-dimethylphenylammonium cation

	(a)	(b)
C(2)—C(1)—C(6)	123.8	123.7 (2)
C(1)—C(2)—C(3)	117.3	117.3 (2)
C(2)—C(3)—C(4)	120.6	120.7 (2)
C(3)—C(4)—C(5)	120.7	120.4 (3)
C(4)—C(5)—C(6)	120.6	120.7 (2)
C(5)—C(6)—C(1)	117.3	117.3 (2)

References: (a) Domenicano & Murray-Rust (1979); (b) Norrestam & Schepper (1981).

Although the crystals were anisotropically shaped, an absorption correction was not applied because ψ scans of three reflections produced flat absorption curves and the value of the linear absorption coefficient is small.

MSC/AFC *Diffraction Control Software* (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* software (Molecular Structure Corporation, 1989) was used for data reduction, structure refinement and the preparation of publication material. The structures were solved using *SHELXS86* Patterson methods (Sheldrick, 1990) and molecular graphics were produced using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1275). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 2,2¹-Anhydro-4,6-O-benzylidene-3-deoxy-3-C-[(R)-2-hydroxyethyl]- α -D-allopyranoside at 173 K

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Abstract

The 1,3-dioxane ring in the title compound, C₁₆H₂₀O₅, has an almost undistorted ^αC_{α1} conformation, while the pyranose ring has a more distorted ⁴C₁ conformation. The five-membered C(2,2¹) anhydro ring has an envelope conformation, with C(3) lying out of the plane formed by the other four atoms.

Comment

Many naturally occurring compounds which possess biological activity have furofuran structures. Notable among these are azadirachtin (Broughton, Ley, Slawin, Williams & Morgan, 1986; Ley, Santafianos, Blaney & Simmonds, 1987) and miharamycin A and B (Seto *et al.*, 1983); azadirachtin is an insect anti-feedant (Rembold, 1984; Koul, 1984*a,b*) and miharamycin A and B are active against the rice blast disease caused by *Pyricularia oryzae* (Seto *et al.*, 1983). As a result of increasing interest in using simple sugars as chiral synthons, we are pursuing the search for convenient and efficient approaches to the synthesis of furofuran and related fused-ring systems from readily available sugars and their derivatives. In this paper, we describe the synthesis and crystal structure of the title compound, (I).