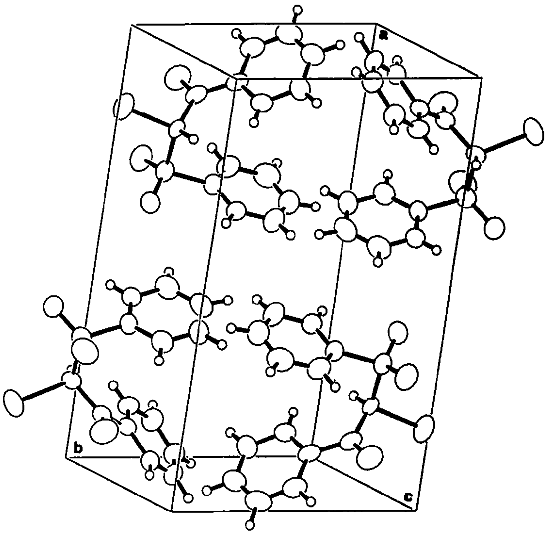

Fig. 2. Perspective view of the unit cell showing the molecular packing.

Fig. 2 shows the molecular packing in the unit cell. Most of the shortest intermolecular O···H and H···H distances correspond to peaks (at 2·45–2·55 Å) in frequency distributions of O···H and H···H interactions described for a considerable number of phenylalanine structures by Gould *et al.* (1985).

We thank Mr L. Hatziarapoglou and Professor A. Varvoglis, Organic Chemistry Laboratory, University of Thessaloniki, Greece, for providing the crystals, and the Academic Computer Center, University of Rhode Island, Kingston, RI, USA, for the use of its computer facilities. One of us (SCK) also thanks the Council for International Exchange of Scholars, Washington, DC, USA, for supporting his work by a Fulbright grant.

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Room-Temperature Phase of *n*-Decylammonium Chloride

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(*Received* 5 *February* 1986; *accepted* 4 *March* 1986)

Abstract. $[NH_3(C_{10}H_{21})]Cl$, $M_r = 193{\cdot}76$, monoclinic, $P2_1$, $a = 5{\cdot}6996\ (4)$, $b = 7{\cdot}1638\ (5)$, $c = 15{\cdot}490\ (1)$ Å, $\beta = 91{\cdot}297\ (5)°$, $V = 632{\cdot}29\ (7)$ Å^3, $Z = 2$, $D_m = 1{\cdot}04$, $D_x = 1{\cdot}02$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54184$ Å, $\mu = 23{\cdot}3$ cm^{-1}, $F(000) = 216$, $T = 296$ K, $R = 0{\cdot}032$ for 426 $[I > 3\sigma(I)]$ reflections. The amphiphilic character of the alkylammonium ion causes crystallization in layers. The polar layers consist of NH_3 groups and Cl atoms; they alternate with the neutral layers consisting of aliphatic chains. These are held together by van der Waals bonds whereas N and Cl atoms are linked by hydrogen bonds to form a two-dimensional honeycomb net.

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0108-2701/86/081076-03$01.50

Introduction. The complex polymorphism of the title compound makes the salt an ideally suited model system for biological membranes. In the solid state alone there exist seven phases, in particular two at room temperature (Gilson, Kertes, Manley, Tsau & Donnay, 1976). One of them is quite disordered and possibly metastable; the other crystallizes nicely and has already been the object of a preliminary structural study (Bayer, 1968). A more detailed knowledge of the structure was, however, necessary for our attempt at interpreting the solid–solid phase transitions (Seliger, Žagar, Blinc, Arend & Chapuis, 1983; Kind *et al.*, 1982) of this type of layer structure. The determination of the room-temperature phase by means of X-ray diffraction is reported in this contribution.

Experimental. Tiny slabs of the title compound grow in a variety of polar solvents and solvent mixtures. They often form pseudo-merohedral twins and invariably develop {100}, {010} and {001} pinacoids. A single-domain crystal could be picked out from a batch crystallized in ethanol and diethyl ether. The crystals perfectly endured irradiation with X-rays: periodically sampled standard intensities fluctuated less than 5% around their mean values and reflection profiles did not broaden during the data collection. Computations performed by *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and figures drawn with the help of *ORTEP*II (Johnson, 1971). Parameters relevant to the measurements and calculations are summarized in Table 1.* Cl atom located from Patterson map; N and C atoms found on subsequent Fourier maps. A difference map based on the anisotropic refinement of non-hydrogen atoms and the inclusion of ideal positions of carbon H atoms was calculated. This yielded two H atoms of the ammonium group; the third atom had to be derived geometrically. In the final refinement, all atoms except skeletal H were refined. The refined H atoms, being, as usual (Hamilton & Ibers, 1968), too close to the N atom, were shifted off so as to produce correct N—H distances by applying a homothetic mapping to coordinates and errors. These corrected positions appear in Table 2 and were used to calculate the distances and angles of Table 3.

Table 1. *Parameters and results relevant to measurements and calculations*

In this table *s* stands for the estimated standard deviation of a stochastic variable.

Crystal:	Volume: 0·0039 mm^3
	Ratio (width/thickness): 10
	Transmission factors: [0·542, 0·928]
Density:	Measured by flotation in benzene and carbon tetrachloride
Space group:	Determined from precession and Weissenberg photographs
Data collection:	Diffractometer: Syntex $P2_1$
	Radiation: Ni-filtered Cu $K\alpha$
	Type of scan: θ:2θ
	Analysis of profiles: Lehmann–Larsen (Schwarzenbach, 1977)
	Scan width: 1° left and right of $K\alpha_1/\alpha_2$
	Scan speed: [2,10]° min^{-1}
	Background: stationary, at each end of scan range during four tenths of the scan time
	Maximal $\sin\theta/\lambda$: 0·42 Å^{-1}; $\pm h \pm k \pm l$
Data reduction:	Scattering factors: neutral atoms (Cromer & Mann, 1968)
	Anomalous-dispersion correction: Cl (Cromer & Liberman, 1970)
	Observations: 428, of which 2 smaller than 3*s* (*s* based on counting statistics)
	Weights: $s^{-2}(F)$
Refinements:	Lattice constants: least-squares of 20 accurately centred reflections with $55° < 2\theta < 58°$
	Positional and thermal parameters: anisotropic (hydrogen atoms isotropic)
	Agreement factors: $R = 0{\cdot}032$, $wR = 0{\cdot}025$, error of an observation of unit weight = 9·7
	Observations per parameter: 3·6
	Largest shift at end of refinement: 0·75*s*

Table 2. *Positional and thermal parameters of the title compound (e.s.d.'s in parentheses)*

$$U_{\rm eq} = \tfrac{1}{3}(\beta_{11} + \beta_{22} + \beta_{33} + 2\beta_{13}\mathbf{a}.\mathbf{c}).$$

	x	y	z	$U_{\rm eq}$(Å^2)
Cl	0·7335 (2)	0·25	−0·03895 (9)	0·0717 (7)
N	0·235 (1)	0·191 (1)	0·0438 (4)	0·065 (5)
H(1)	0·13 (3)	0·25 (7)	0·00 (1)	0·4 (1)
H(2)	0·24 (2)	0·05 (3)	0·048 (9)	0·25 (9)
H(3)	0·40 (2)	0·24 (6)	0·043 (9)	0·23 (8)
C(1)	0·2148 (9)	0·262 (3)	0·1308 (5)	0·065 (3)
C(2)	0·422 (1)	0·201 (1)	0·1903 (5)	0·065 (4)
C(3)	0·404 (1)	0·272 (2)	0·2798 (4)	0·059 (3)
C(4)	0·6062 (9)	0·206 (2)	0·3408 (5)	0·068 (4)
C(5)	0·5965 (9)	0·275 (2)	0·4321 (4)	0·058 (3)
C(6)	0·7988 (9)	0·208 (2)	0·4899 (5)	0·069 (5)
C(7)	0·7939 (9)	0·277 (2)	0·5822 (4)	0·056 (3)
C(8)	0·996 (1)	0·208 (2)	0·6372 (5)	0·067 (4)
C(9)	0·996 (1)	0·277 (3)	0·7304 (4)	0·066 (3)
C(10)	1·200 (1)	0·211 (2)	0·7825 (4)	0·086 (5)

Table 3. *Distances* (Å), *angles* (°) *and torsion angles* (°) (*Klyne & Prelog*, 1960) *in the title compound (e.s.d.'s in parentheses)*

N—Cl	3·172 (6)
N—Cl$^{\rm i}$	3·134 (6)
N—Cl$^{\rm ii}$	3·166 (8)
H(1)—Cl$^{\rm i}$	2·3 (2)
H(2)—Cl$^{\rm ii}$	2·2 (2)
H(3)—Cl	2·3 (1)
N—H(1)—Cl$^{\rm i}$	140 (30)
N—H(2)—Cl$^{\rm ii}$	170 (10)
N—H(3)—Cl	140 (20)
H(1)—N—C(1)—C(2)	−160 (20)

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

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* Lists of structure amplitudes, anisotropic thermal parameters and geometrical parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42891 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The pertinent geometrical features of the structure are summarized in Table 3. (A fuller list is included in the supplementary material.) The C—C distances vary between 1·48 (1) and 1·55 (1) Å; the C—N distance is 1·45 (1) Å and C—C—C(N) angles lie between 112·4 (8) and 115·7 (8)°.

The structure consists of layers built out of N and Cl atoms alternating with layers of *n*-decylammonium cations (Fig. 1). The two types of layers are firmly linked by covalent N—C bonds (Fig. 2).

Each N atom forms hydrogen bonds with three neighbouring Cl atoms, each of which participates in turn in three hydrogen bonds. The resulting hydrogen-bonding scheme resembles a honeycomb (see Fig. 2); according to Kuleshova & Zorky (1980) it can be classified as $L_3^3(6)$ (not distinguishing Cl from N atoms for the sake of classification). A comparison of the N—Cl distances in the title compound (Table 3) with those of $[NH_3(C_{10}H_{21})]_2[CdCl_4]$ or $[NH_3(C_{14}H_{29})]_2[CdCl_4]$ suggests that the hydrogen bonds are stronger in the former compound. This trend is further corroborated by the higher frequencies of the NH_3-deformation vibrations (Rey-Lafon, 1985).

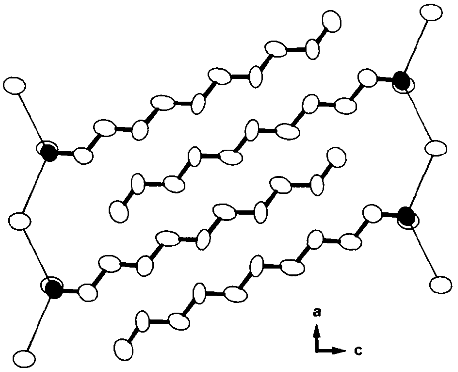

Fig. 1. Projection of the structure on the *ac* plane. All the chains are symmetry-equivalent. Neighbouring chains are related by a twofold screw axis parallel to **b**. Filled ovals represent N atoms.

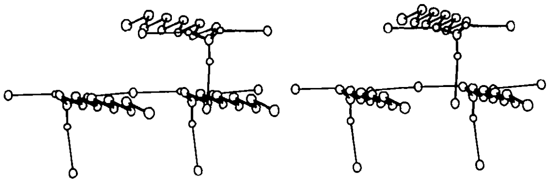

Fig. 2. Stereoscopic representation of the structure of the title compound as viewed along the *c** axis. Radii of H atoms are on an arbitrary scale. The drawing suggests that the ammonium H atoms can indeed be considered as part of a fully (*i.e.* ammonium-hydrogen-atoms-included) extended, tetrahedral chain.

The *n*-decylammonium chains are *intercalated* (see Fig. 1) and held together by van der Waals forces. The chains are all parallel to one direction, which spans the angles $\varphi_a = 65$, $\varphi_b = 89$ and $\varphi_c = 26°$ with the *a*, *b* and *c* axes respectively. C and N atoms lie in a perfect plane (average deviation 0·02 Å). Taking into account the large errors in its position, even the hydrogen atom H(1) appears to take part in this regular zigzag arrangement. The disposition of the C atoms can be described by an idealized, orthorhombic *P* cell with lattice constants $a = 7·16$, $b = 5·18$, $c = 2·56$ Å and symmetry *Pbnm* [packing type O_b (Segerman, 1965)]. The chains are quite densely packed (18·5 Å^2 per chain) and form a surprisingly stable three-dimensional structure.

Let us conclude this report by pointing out the disk shape of the thermal ellipsoids (U_{ij} values are included in the supplementary material). They are approximately perpendicular to the C—C bond on one side and roughly contain the C—C bond on the other side in their equatorial plane (Fig. 1). This arrangement of the thermal ellipsoids differs strongly from the orientation of the disks in $[NH_3(C_{10}H_{21})]_2[CdCl_4]$ or $[NH_3(C_{14}H_{29})]_2[CdCl_4]$. Further investigation – especially in connection with a pretransition phenomenon – will be needed to elucidate this riddle.

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