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Structure of 4-Hydroxy-2,2,6,6-tetramethylpiperidinium Hexanoate

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Abstract. $C_9H_{20}NO^+.C_6H_{11}O_2^-$, $M_r = 273·4$, monoclinic, $P2_1/n$, $a = 17·272\,(7)$, $b = 12·257\,(5)$, $c = 7·884\,(2)$ Å, $\beta = 104·67\,(3)°$, $V = 1614·7\,(5)$ Å^3, $Z = 4$, $D_m = 1·11\,(2)$, $D_x = 1·12$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 0·66$ mm^{-1}, $F(000) = 608$, $T = 298$ K, $R = 0·060$ for 1502 unique observed reflections. There is extensive hydrogen bonding between the piperidinium cations and hexanoate anions leading to the formation of channels running through the crystal parallel to the c axis. The piperidine ring of the cation has a considerably deformed chair conformation.

Introduction. Structural studies on 2,2,6,6-tetramethylpiperidin-4-ol (TMP) and its derivatives have been prompted partly by interest in the conformations of these very crowded molecules and partly because they are intermediates in a number of organic syntheses of industrial interest (Scott, 1983; Jachontov, 1984).

It has been reported (Tamura, Sato & Yoshioka, 1969; Berliner, 1970; Bordeaux & Lajzérowicz, 1974; Cygler, Grabowski, Skolimowski & Skowroński, 1978) that piperidine rings with four methyl substituents generally adopt chair conformations. However, 2,2,6,6-tetramethyl-4-oxopiperidine derivatives display twist and boat conformations (Sato, Yoshioka & Tamura, 1975).

Recently we described the crystal structure of the 1:2 complex of TMP and dodecanoic (lauric) acid (Kettmann, Kellö, Vrábel, Garaj, Karvaš, Göghová & Durmis, 1989). It and related compounds are used as stabilizers for polymers. A number of German, US and USSR patents have been granted on this subject. In order to acquire more detailed information about interaction patterns between fatty acids and TMP bases, we report here on the structure determination of the TMP salt of hexanoic acid.

Experimental. The salt was prepared by mixing at room temperature equimolar amounts of TMP and hexanoic acid dissolved in diethyl ether. Air-stable, colourless, needle-like crystals were recrystallized by slow evaporation from *n*-hexane–acetone solution. Data collected on a crystal 0·25 × 0·15 × 0.40 mm. The crystal density was measured by flotation in bromoform/cyclohexane. Approximate values of lattice parameters calculated from rotation and Weissenberg patterns. Accurate lattice parameters were refined by least squares on the basis of 15 precisely centred reflections with $15 < \theta < 45°$ on a Syntex $P2_1$ four-circle diffractometer using Cu $K\alpha$ radiation filtered by a graphite monochromator. Intensities of 1659 independent reflections collected in range $3 < \theta \leq 50°$, $h = 0$ to 17; $k = 0$ to 12, $l = -7$ to 7 by $\omega/2\theta$ scans, variable rate 4·9 to 29·3° min^{-1} in 2θ, background-to-scan-time ratio 1·0, scan width 2° plus $\alpha_1 - \alpha_2$ dispersion. No significant variation in intensities of two standard reflections (031, 221) measured after every 98 reflections. All intensities corrected for Lorentz and polarization effects, not for absorption or extinction.

Structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the block-diagonal least-squares method. H atoms

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Table 1. *Final positional parameters for non-*H *atoms* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
N(1)	1403 (1)	−153 (1)	602 (2)	2·63 (5)
C(2)	1902 (1)	474 (2)	2182 (2)	3·00 (7)
C(3)	2315 (1)	1409 (2)	1481 (3)	3·53 (7)
C(4)	2790 (1)	1034 (2)	209 (2)	3·47 (7)
C(5)	2220 (1)	484 (2)	−1373 (2)	3·20 (7)
C(6)	1781 (1)	−498 (1)	−859 (2)	2·86 (6)
C(7)	2497 (1)	−283 (2)	3427 (2)	4·02 (7)
C(8)	1301 (1)	911 (2)	3134 (3)	3·93 (7)
C(9)	1075 (1)	−818 (2)	−2404 (3)	3·82 (8)
C(10)	2317 (1)	−1502 (2)	−323 (3)	4·29 (8)
O(1)	3134 (1)	1957 (1)	−455 (2)	4·59 (5)
O(2)	196 (1)	1337 (1)	−912 (2)	4·42 (6)
O(3)	−959 (1)	1945 (1)	−2520 (2)	4·09 (4)
C(11)	−206 (1)	1841 (1)	−2226 (3)	3·24 (6)
C(12)	221 (1)	2365 (2)	−3469 (3)	3·95 (8)
C(13)	637 (1)	3442 (2)	−2746 (3)	4·16 (8)
C(14)	53 (1)	4345 (2)	−2688 (3)	3·77 (7)
C(15)	451 (1)	5430 (2)	−1989 (3)	4·58 (7)
C(16)	157 (1)	6325 (2)	−1994 (3)	5·28 (8)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(4)—O(1)	1·436 (2)	O(1)—H(20)	1·09 (3)
C(2)—C(3)	1·526 (3)	C(11)—O(3)	1·268 (2)
C(3)—C(4)	1·519 (3)	C(11)—O(2)	1·254 (2)
C(4)—C(5)	1·535 (3)	C(11)—C(12)	1·511 (3)
C(5)—C(6)	1·531 (3)	C(12)—C(13)	1·543 (3)
C(6)—C(9)	1·540 (3)	C(13)—C(14)	1·506 (3)
C(6)—C(10)	1·533 (3)	C(14)—C(15)	1·535 (3)
C(6)—N(1)	1·521 (2)	C(15)—C(16)	1·517 (3)
C(2)—N(1)	1·529 (2)	C(2)—C(8)	1·523 (3)
N(1)—H(1)	0·888 (16)	C(2)—C(7)	1·540 (3)
N(1)—H(2)	1·04 (3)		
O(1)—C(4)—C(5)	106·8 (1)	N(1)—C(6)—C(9)	105·3 (1)
O(1)—C(4)—C(3)	110·2 (2)	C(9)—C(6)—C(5)	109·7 (1)
C(2)—C(3)—C(4)	113·2 (2)	C(10)—C(6)—C(9)	108·4 (1)
C(3)—C(2)—N(1)	107·5 (1)	C(10)—C(6)—C(5)	113·5 (2)
C(7)—C(2)—C(8)	109·0 (1)	C(6)—C(5)—C(4)	112·9 (1)
C(7)—C(2)—C(3)	112·6 (1)	C(5)—C(4)—C(3)	109·1 (1)
C(8)—C(2)—C(3)	110·7 (1)	O(3)—C(11)—O(2)	121·9 (2)
C(7)—C(2)—N(1)	111·4 (1)	O(3)—C(11)—C(12)	119·0 (2)
C(8)—C(2)—N(1)	105·4 (1)	O(2)—C(11)—C(12)	119·1 (2)
C(2)—N(1)—C(6)	119·7 (1)	C(11)—C(12)—C(13)	112·5 (2)
N(1)—C(6)—C(5)	108·6 (1)	C(12)—C(13)—C(14)	112·8 (2)
N(1)—C(6)—C(10)	111·1 (1)	C(13)—C(14)—C(15)	113·9 (2)
		C(14)—C(15)—C(16)	112·3 (2)

located by a difference Fourier synthesis. All positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms were refined using 1502 reflections with $I > 1{\cdot}96\sigma(I)$ considered as observed. In the final cycle $R = 0{\cdot}060$, $wR = 0{\cdot}067$, 296 variables, $(\Delta/\sigma)_{\max} = 0{\cdot}32$, function minimized $M = \sum w(|F_o| - |F_c|)^2$ where $w = 1$ if $|F_o| < 22$ and $w = 22/|F_o|$ if $|F_o| \geq 22$. Max. and min. heights in the final difference Fourier synthesis 0·25 and $-0{\cdot}30\ \mathrm{e\ Å^{-3}}$. Scattering factors for uncharged atoms were taken from *International Tables for X-ray Crystallography* (1974). All calculations except those with *MULTAN*78 performed with a local version of the NRC system (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. Positional parameters of non-H atoms and B_{eq} values are listed in Table 1,[*] bond lengths and angles in Table 2. The molecular packing and the atom numbering are shown in Fig. 1.

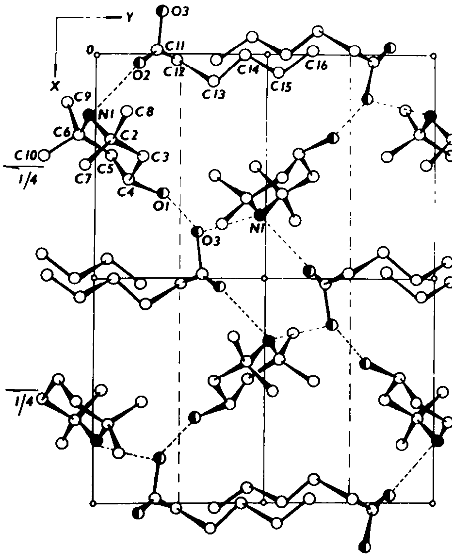

Fig. 1. The crystal structure projected along the *z* axis and numbering scheme.

The unit cell contains four TMP$^+$ cations and four hexanoate anions. The piperidinium N1 atoms form hydrogen bonds to carboxylate O atoms belonging to two different anions [N1···O2 2·800 (2); N1···O3, $(\bar{x}, \bar{y}, \bar{z})$ 2·879 (2) Å]. These hydrogen bonds link pairs of TMP$^+$ cations and pairs of anions into centrosymmetric dimeric units. Within these units open rings formed by alternating NH_2^+ and CO_2^- groups linked by the hydrogen bonds create channels in the crystal running parallel to the *c* axis. The dimeric units are linked together by hydrogen bonds involving the TMP$^+$ hydroxyl group [O1···O3 $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ 2·790 (2) Å]. The TMP$^+$ cation exists in a distorted chair conformation typical of overcrowded piperidine derivatives (Bordeaux & Lajzérowicz 1974; Goaman & Grant, 1964; Lajzérowicz-Bonneteau, 1968; Leiserowitz, 1976). The mean torsion angle in the ring is 53·4° and the individual ring torsion angles [48·0 (2)–60·6 (2)°] are considerably distorted compared with the values for the ideal

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and C—H distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52098 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cyclohexane structure (Hendrickson, 1964; Sato *et al.*, 1975). C—C and C—N bond lengths are in good agreement with values found in other piperidine derivatives (Rees & Weiss, 1971; Birnbaum, 1967). In the anion the C—C bond distances agree with expected values and the aliphatic chain C12—C13—C14—C15—C16 is almost planar, the torsion angles across the C13—C14 and C14—C15 bonds being −179·4 (2) and 178·6 (2)°. The conformation of the ionized carboxyl group [C11—O2 1·254 (2); C11—O3 1·268 (2) Å] expressed by the torsion angle O2—C11—C12—C13 = −77·3 (2)° indicates that the plane of the carboxylic group is almost orthogonal to the plane of the alkyl chain.

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Structure du Bromure de Carboxyméthyl-3 Thiazolium

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Abstract. 3-(Carboxymethyl)thiazolium bromide, $C_5H_6NO_2S^-.Br^+$, $M_r = 224{\cdot}08$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}839\ (1)$, $b = 10{\cdot}047\ (8)$, $c = 11{\cdot}769\ (4)$ Å, $V = 808{\cdot}59\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}840$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 51{\cdot}5$ cm^{-1}, $F(000) = 440$, $T = 290$ K, final $R = 0{\cdot}059$ for 949 observed reflections. The structure was solved by the Patterson method. The cohesion of the crystal is the result of van der Waals interactions and a strong OH···Br hydrogen bond [O···Br = 3·143 (5) Å].

Introduction. Le bromure de carboxyméthyl-3 thiazolium (Fig. 1) est un produit de synthèse étudié dans le cadre d'une recherche d'inhibiteurs potentiels de protéases à sérine. Il est structuralement apparenté au composé porteur d'une chaîne latérale phénylacétamide en position 5 dont la structure cristalline, sous forme de bétaine, a fait l'objet d'une publication récente (Dupont, Dideberg, Sbit, Pirotte & Delarge, 1989).

La détermination de la structure cristalline de ce sel de thiazolium permettra d'établir des comparaisons géométriques dans cette série de molécules peu connues.

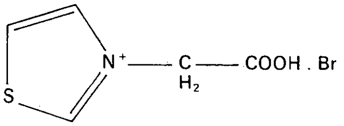

Fig. 1. Formule chimique.

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