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Structure of Piperazinium Suberate Monohydrate, $C_8H_{12}O_4^{2-}.C_4H_{12}N_2^{2+}.H_2O$*

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Abstract. $M_r = 278\cdot35$, triclinic, $P\bar{1}$, $a = 5\cdot8178$ (8), $b = 7\cdot4138$ (6), $c = 8\cdot9971$ (7) Å, $\alpha = 104\cdot54$ (1), $\beta = 90\cdot58$ (1), $\gamma = 100\cdot61$ (1)°, $V = 368\cdot56$ Å^3, $Z = 1$, $D_m = 1\cdot24$, $D_x = 1\cdot25$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1\cdot54178$ Å, $\mu = 0\cdot77$ mm^{-1}, $F(000) = 152$, $T = 296$ K. Final $R = 0\cdot049$ for 1313 observed reflections. The structure consists of a suberate anion and a piperazinium cation both situated on crystallographic centers of symmetry and one water molecule distributed over two sites with an occupancy factor of $\frac{1}{2}$. The C atoms of the suberate anion are coplanar and the carboxylate groups of atoms are inclined by 32° from that plane. Each anion forms four hydrogen bonds to four distinct cations and *vice versa*. The water molecules are also hydrogen-bonded to the carboxylate group.

Introduction. This is the last paper in the series of piperazinium alkanedioates and the search for a structural explanation of the observed variations of densities and melting points in relation to the parity of the number of C atoms in the alkanedioate chain (Vanier, 1982). The structure of piperazinium glutarate (anion with an odd number of C atoms) (Vanier & Brisse, 1982) and the structure of piperazinium succinate and adipate (both anions with an even number of C atoms) (Vanier & Brisse, 1983*a*,*b*) have been reported.

Experimental. Synthesis and recrystallization reported by Vanier (1982), colorless platelets (from water); D_m by flotation in chloroform/monochlorobenzene, m.p. = 457 K; $0\cdot12 \times 0\cdot28 \times 0\cdot30$ mm; Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$; three standard reflections, largest intensity fluctuation: 1·8%; 1446 (hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$) with $2\theta \leq 140\cdot0°$, 1317 with $I \geq 1\cdot96\sigma(I)$, 129 unobserved; Lp correction, no absorption correction; direct methods (*MULTAN*, Main, Lessinger, Woolfson, Germain & Declercq, 1977); anisotropic full-matrix least-squares refinement based on F's, H(calculated) isotropic; final $R = 0\cdot049$ (observed),† $R = 0\cdot055$ (measured), $w = 1$; maximum (shift/σ) = 0·67, mean (shift/σ) = 0·08; final electron-density fluctuations $-0\cdot27$ to $+0\cdot32$ e Å^{-3}; scattering factors for O, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); programs used in this work are the same as those used in Vanier & Brisse (1983*a*).

Discussion. The final atomic coordinates are given in Table 1.† The atomic numbering is shown in Fig. 1 for the suberate anion, that of the piperazinium cation is given in Vanier & Brisse (1983*a*). The bond distances, angles and torsion angles are given in Table 2.

The structure consists of a piperazinium cation, a suberate anion and one water molecule distributed among two centrosymmetrically related sites with an occupancy factor of $\frac{1}{2}$. The cation, located on a center of symmetry at $(0\frac{1}{2}\frac{1}{2})$, has the chair conformation as in all other piperazinium alkanedioates (Vanier & Brisse,

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for* O, N *and* C; $\times 10^3$ *for* H *atoms*), U_{eq}[$\times 10^4$ *for* O, N *and* C; $\times 10^3$ *for* O(W)] *and* U_{iso}($\times 10^3$ *for* H)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso} (Å^2)
O(1)	8191 (2)	4839 (2)	7177 (2)	474 (6)
O(2)	4899 (2)	2807 (2)	6288 (2)	443 (5)
C(1)	6000 (3)	4433 (3)	6977 (2)	317 (6)
C(2)	4657 (4)	6021 (3)	7514 (3)	455 (8)
C(3)	5731 (4)	7554 (3)	8931 (3)	368 (7)
C(4)	4471 (4)	9225 (3)	9294 (3)	405 (8)
N(1)	10197 (3)	1933 (2)	5862 (2)	314 (6)
C(1P)	9500 (4)	1341 (3)	4196 (2)	350 (7)
C(2P)	9468 (4)	351 (3)	6592 (2)	362 (7)
O(W)	9982 (15)	3912 (9)	9614 (8)	162 (4)
H(21)	452 (5)	671 (4)	657 (3)	81 (9)
H(22)	306 (5)	556 (4)	766 (3)	65 (8)
H(31)	575 (4)	701 (3)	985 (3)	59 (7)
H(32)	738 (5)	800 (3)	882 (3)	52 (7)
H(41)	449 (5)	969 (4)	829 (3)	67 (8)
H(42)	278 (5)	876 (3)	941 (3)	61 (8)
H(11P)	997 (4)	237 (4)	372 (3)	59 (7)
H(12P)	777 (4)	104 (3)	410 (2)	41 (6)
H(21P)	770 (4)	3 (3)	649 (3)	46 (6)
H(22P)	1004 (4)	75 (3)	767 (3)	52 (7)
H(1N)	943 (4)	297 (4)	640 (3)	59 (7)
H(2N)	1173 (5)	227 (3)	600 (3)	60 (8)

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* Structural Studies of Compounds with Aliphatic Chains. 10. Part 9: Vanier & Brisse (1983*b*).

† Four reflections given zero weight in final cycles of least-squares refinement.

† Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38424 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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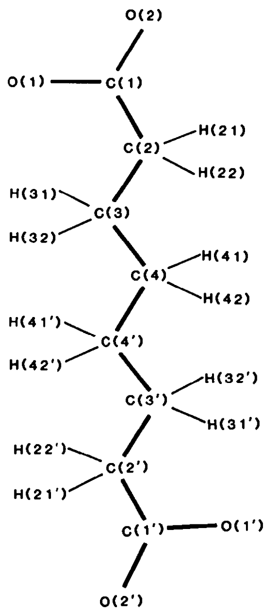

Fig. 1. Atomic numbering of the suberate anion.

Table 2. *Bond distances* (Å), *angles and torsion angles* (°) *in piperazinium suberate monohydrate*

Suberate anion		Piperazinium cation	
C(1)–O(1)	1·255 (2)	N(1)–C(1P)	1·482 (3)
C(1)–O(2)	1·257 (2)	N(1)–C(2P)	1·482 (3)
C(1)–C(2)	1·513 (3)	C(1P)–C(2P)	1·509 (4)
C(2)–C(3)	1·517 (3)		
C(3)–C(4)	1·521 (3)		
C(4)–C(4')*	1·518 (5)		
O(1)–C(1)–O(2)	123·1 (2)	C(1P)–N(1)–C(2P)	111·2 (2)
O(1)–C(1)–C(2)	117·7 (2)	N(1)–C(1P)–C(2P')	110·4 (2)
O(2)–C(1)–C(2)	119·1 (2)	N(1)–C(2P)–C(1P')	110·3 (2)
C(1)–C(2)–C(3)	115·4 (2)		
C(2)–C(3)–C(4)	112·8 (2)		
C(3)–C(4)–C(4')	113·5 (3)		
O(1)–C(1)–C(2)–C(3)	−32·7 (3)	N(1')–C(2P')–C(1P)–N(1)	56·8 (2)
O(2)–C(1)–C(2)–C(3)	150·9 (2)	C(2P)–N(1)–C(1P)–C(2P')	−57·3 (2)
C(1)–C(2)–C(3)–C(4)	172·9 (2)	C(1P)–N(1)–C(2P)–C(1P')	57·2 (2)
C(2)–C(3)–C(4)–C(4')	−179·8 (2)		

* The primed atoms are centrosymmetrically related to the unprimed atoms having the same number. Since the atoms are symmetry-related, the e.s.d.'s include a factor of $\sqrt{2}$.

1982). The suberate anion is also situated on a center of symmetry ($\frac{1}{2}00$) of the unit cell. This anion is almost planar; the actual values of the torsion angles are 172·9 (2), −179·8 (2) and 180° for C(1)–C(2)–C(3)–C(4), C(2)–C(3)–C(4)–C(4') and C(3)–C(4)–C(4')–C(3'), with the other two torsion angles centrosymmetrically related to the first two. The conformation of the chain is therefore *ttttt* (*t* = *trans*). This conformation is similar to that of suberic acid (Housty & Hospital, 1965). It also resembles that of piperazinium adipate (Vanier & Brisse, 1983*b*) since the carboxy groups are tilted by 32° from the plane of the C atoms. The two water molecules are centrosymmetrically related, at 1·58 (1) Å from each other. The occupancy factor of each site being $\frac{1}{2}$, there is only one water molecule per unit cell statistically distributed among two sites. Each piperazinium is hydrogen-bonded to four different suberate anions and *vice versa*. The characteristic distances and angles of this hydrogen-bonding system are as follows: N(1)···O(1) = 2·660 (2), H(1N)···O(1) = 1·68 (3), N(1)–H(1N) = 0·98 (3) Å and N(1)–H(1N)···O(1) = 174 (2)°; N(1)···O(2) = 2·693 (2), H(2N)···O(2) = 1·82 (3), N(1)–H(2N) = 0·88 (3) Å and N(1)–H(2N)···O(2) = 176 (3)°. The water molecules are hydrogen-bonded to O(1) with O(1)···O(*W*) = 2·709 (7) and O(1)···O(*W**) = 2·925 (7) Å. The shortest contacts between O(*W*) and O(2) or N(1) are O(*W*)···O(2) = 4·009 (8) and O(*W*)···N(1) = 3·340 (7) Å. A stereo pair showing the relative dispositions of the structural units is given Fig. 2. There, one can see the arrangement of suberate anions in one plane alternating with another plane containing both the piperazinium cations and the water molecules.

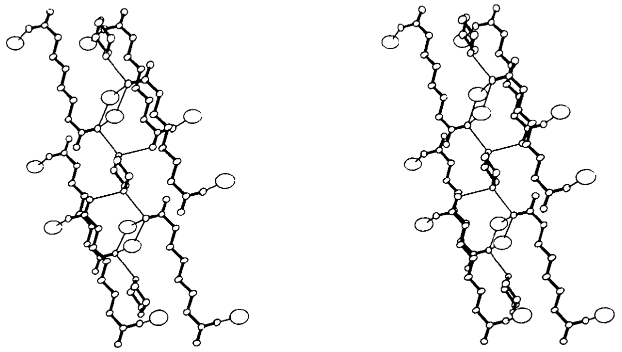

Fig. 2. Stereoview of the unit-cell content of piperazinium suberate monohydrate. The suberate anions are in planes alternating with others containing the piperazinium cations and the water molecules. Both sets of planes are parallel to *bc*. The **a** direction is horizontal.

This disposition of anions and cations is comparable to that observed in piperazinium adipate (Vanier & Brisse, 1983*b*). However, since the suberate anion extends farther than the adipate, there is room for the water molecules in the cation layer.

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