group or for an α,β-unsaturated ketone (expected: *ca* 1670 cm^{-1}). These shifts are due to the unusual hydrogen-bonding arrangement in (I) and are, in fact, fairly typical for catemerically hydrogen-bonded keto carboxylic acids, as is now known from several published examples (Takai, Amagaya & Ogihara, 1977; Jefferies, Payne, Raston & White, 1981; Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Vanderhoff & Thompson, 1991). Hydrogen bonding lowers the IR stretching frequency for all carbonyl groups involved, as observed for the ketone in (I) ($\Delta\nu \simeq 33$ cm^{-1}). The rise seen in (I) in the stretching frequency for the carboxyl ($\Delta\nu \simeq 25$ cm^{-1}) occurs because of the *removal* of hydrogen bonding relative to the normally observed hydrogen-bonded dimer, but is not as great as the increase reported for monomeric carboxylic acids ($\nu \simeq 1760$ cm^{-1}).

It is not clear what causes these molecules to adopt different modes of hydrogen bonding. In each of the two modes we have observed, examples are known of both conjugated and non-conjugated ketones (as well as acids), so the change does not seem attributable merely to polarity effects associated with conjugation. The other major difference between these two compounds is the obvious change in molecular shape, from the near planarity of the bicyclic system in (I) (Fig. 1) to the curvature evident in (II) (Fig. 5), and such a change might reasonably trigger a shift in hydrogen-bonding mode. However, the previously noted 10-carboxy-*cis*-decal-3-one (Chadwick & Dunitz, 1979) is nearly identical to (II) in molecular shape, [and, like (II), has a saturated ketone] and yet the two adopt different hydrogen-bonding modes. Because such slight differences are associated with dramatically different patterns of intermolecular hydrogen bonding in this ring system, it appears that the energy minima represented by these two modes must be similar in energy. It may be that they are more similar here than in the broad structural range of organic compounds, in which we have so far been able to identify more than three dozen simple keto acids which are dimeric, but just over one dozen which are catemeric.

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Structure of *m*-Xylylenediammonium Adipate Monohydrate

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Abstract. $C_8H_{14}N_2^{2+}.C_6H_8O_4^{2-}.H_2O$, $M_r = 300{\cdot}35$, monoclinic, $P2_1/c$, $a = 17{\cdot}968\,(2)$, $b = 5{\cdot}7859\,(7)$, $c = 14{\cdot}844\,(1)$ Å, $\beta = 103{\cdot}614\,(7)°$, $V = 1499{\cdot}9\,(3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}331$, $D_x = 1{\cdot}330$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}85$ mm^{-1}, $F(000) = 648$, $T = 295$ K, $R = 0{\cdot}040$ for 2188 unique reflections. Two *m*-xylylenediammonium cations and adipate anions are held together by two kinds of strong N—H···O hydrogen bonds to form a dimer around an inversion

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center. The dimers are stacked along **b** by van der Waals interactions and two kinds of N—H···O hydrogen bonds to form a column. The columns are held together by an N—H···O hydrogen bond and van der Waals and ionic interactions to form a sheet parallel to (100). The sheets are stacked along **a** by N—H···O and O—H···O hydrogen bonds to form a three-dimensional network.

Introduction. As a part of a systematic investigation of nylon salts, the structures of hexamethylenediammonium terephthalate dihydrate, tetramethylenediammonium terephthalate and ethylenediammonium terephthalate have previously been reported (Moritani, Kashino & Haisa, 1990; Moritani & Kashino, 1991). In the present study the structure of the title compound, a salt between an aromatic diamine and an aliphatic dicarboxylic acid, is reported.

Experimental. Crystals obtained from an aqueous solution by slow evaporation at room temperature: colorless prisms elongated along **b**. D_m by flotation in benzene–CCl_4. Systematic absences: $h0l$ for l odd, $0k0$ for k odd. A crystal with dimensions $0{\cdot}25 \times 0{\cdot}25 \times 0{\cdot}30$ mm was mounted on a Rigaku AFC-5 four-circle diffractometer. Lattice parameters determined with 20 reflections in the range $38 < 2\theta < 42°$ by the least-squares method. Intensities measured up to $(\sin\theta)/\lambda = 0{\cdot}5617$ Å^{-1} by the ω–2θ scan method [scan speed 6° min^{-1} in ω, scan range in ω: $(1{\cdot}2 + 0{\cdot}15\tan\theta)°$], Ni-filtered Cu $K\alpha$ at 40 kV, 200 mA, rotating anode. Background measured for 4 s on either side of the peak; three standard reflections recorded every 97 reflections; the fluctuation was within 2% in F. Lorentz and polarization corrections; no absorption correction. 2336 reflections measured ($h = -20$ to 20, $k = 0$ to 6, $l = 0$ to 16). $R_{\rm int} = 0{\cdot}012$ for 107 $hk0$ reflections. 2188 reflections with $|F_o|$ larger than $\sigma(F_o)$ used in the structure analysis and refinement. The structure was solved by *MULTAN*84 and refined (non-H atoms anisotropically) by a block-diagonal least-squares method; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1{\cdot}0/[\sigma(F_o)^2 - 0{\cdot}0033|F_o| + 0{\cdot}0015|F_o|^2]$. The positions of H atoms were determined from difference Fourier maps and refined isotropically. Correction for secondary extinction applied with $I_{\rm corr} = I_o(1 + 2{\cdot}62 \times 10^{-5} \times I_c)$ for 20 strongest reflections. The final $R = 0{\cdot}040$ for 2188 unique reflections; $wR = 0{\cdot}075$, $S = 1{\cdot}92$. $(\Delta/\sigma)_{\max} = 0{\cdot}30$. $\Delta\rho$ in final difference Fourier map $-0{\cdot}23$ to $+0{\cdot}18$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs: *MULTAN*84 (Main, Germain & Woolfson, 1984), *HBLS-V* and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP*II (Johnson, 1971). Computations were carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

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

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
C(1)	0·80963 (7)	0·2453 (2)	0·85858 (9)	2·51 (5)
C(2)	0·75464 (7)	0·1128 (2)	0·88671 (9)	2·43 (5)
C(3)	0·67824 (7)	0·1808 (2)	0·86788 (8)	2·19 (5)
C(4)	0·65736 (7)	0·3849 (2)	0·8190 (1)	2·62 (5)
C(5)	0·71169 (9)	0·5155 (3)	0·7901 (1)	3·30 (7)
C(6)	0·78747 (8)	0·4481 (3)	0·8098 (1)	3·22 (6)
C(7)	0·89244 (7)	0·1710 (3)	0·8799 (1)	2·99 (6)
C(8)	0·62161 (7)	0·0327 (2)	0·9019 (1)	2·85 (5)
N(9)	0·93280 (6)	0·2420 (2)	0·97518 (8)	2·75 (4)
N(10)	0·54143 (6)	0·0724 (2)	0·85338 (8)	2·74 (5)
C(11)	0·10988 (7)	0·2413 (2)	0·9111 (1)	2·59 (5)
C(12)	0·16240 (8)	0·4036 (2)	0·8744 (1)	2·94 (5)
C(13)	0·24541 (7)	0·3539 (2)	0·92148 (9)	2·77 (5)
C(14)	0·30116 (7)	0·5136 (2)	0·88863 (9)	2·56 (5)
C(15)	0·38417 (8)	0·4443 (2)	0·9284 (1)	2·77 (5)
C(16)	0·43963 (7)	0·5998 (2)	0·89429 (9)	2·33 (5)
O(17)	0·08990 (5)	0·2983 (2)	0·98419 (7)	3·15 (4)
O(18)	0·09010 (6)	0·0539 (2)	0·87069 (8)	4·18 (5)
O(19)	0·47784 (6)	0·5176 (2)	0·84042 (7)	3·32 (4)
O(20)	0·44446 (6)	0·8045 (2)	0·92059 (8)	4·03 (5)
O(21)	−0·01519 (8)	−0·3466 (2)	0·81882 (9)	5·22 (6)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond lengths* (Å) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·390 (2)	C(11)—C(12)	1·520 (2)
C(2)—C(3)	1·392 (2)	C(12)—C(13)	1·518 (2)
C(3)—C(4)	1·391 (2)	C(13)—C(14)	1·525 (2)
C(4)—C(5)	1·380 (2)	C(14)—C(15)	1·523 (2)
C(5)—C(6)	1·380 (2)	C(15)—C(16)	1·515 (2)
C(6)—C(1)	1·387 (2)	C(11)—O(17)	1·264 (2)
C(1)—C(7)	1·509 (2)	C(11)—O(18)	1·250 (2)
C(3)—C(8)	1·506 (2)	C(16)—O(19)	1·263 (2)
C(7)—N(9)	1·487 (2)	C(16)—O(20)	1·244 (2)
C(8)—N(10)	1·469 (2)		

C(6)—C(1)—C(2)	119·1 (1)	C(3)—C(8)—N(10)	114·1 (1)
C(1)—C(2)—C(3)	121·4 (1)	C(11)—C(12)—C(13)	110·1 (1)
C(2)—C(3)—C(4)	118·5 (1)	C(12)—C(13)—C(14)	112·7 (1)
C(3)—C(4)—C(5)	120·2 (1)	C(13)—C(14)—C(15)	111·9 (1)
C(4)—C(5)—C(6)	120·9 (2)	C(14)—C(15)—C(16)	112·0 (1)
C(5)—C(6)—C(1)	119·8 (1)	C(12)—C(11)—O(17)	118·2 (1)
C(6)—C(1)—C(7)	119·9 (1)	C(12)—C(11)—O(18)	119·6 (1)
C(2)—C(1)—C(7)	121·0 (1)	C(15)—C(16)—O(19)	119·1 (1)
C(2)—C(3)—C(8)	119·0 (1)	C(15)—C(16)—O(20)	117·6 (1)
C(4)—C(3)—C(8)	122·5 (1)	O(17)—C(11)—O(18)	122·2 (1)
C(1)—C(7)—N(9)	110·9 (1)	O(19)—C(16)—O(20)	123·3 (1)

	Donor (D)	Acceptor (A)	$D\cdots A$
(1)	N($9^{\rm i}$)	O($17^{\rm ii}$)	2·813 (2)
(2)	N($9^{\rm i}$)	O($17^{\rm iii}$)	2·779 (2)
(3)	N($9^{\rm i}$)	O($18^{\rm iv}$)	2·963 (2)
(4)	N($10^{\rm i}$)	O($19^{\rm i}$)	2·806 (2)
(5)	N($10^{\rm i}$)	O($19^{\rm v}$)	2·833 (2)
(6)	N($10^{\rm i}$)	O($20^{\rm vi}$)	2·693 (2)
(7)	O($21^{\rm i}$)	O($18^{\rm i}$)	2·976 (2)
(8)	O($21^{\rm i}$)	O($18^{\rm vii}$)	2·876 (2)

Symmetry code: (i) x, y, z; (ii) $1 + x, y, z$; (iii) $1 - x, 1 - y, 2 - z$; (iv) $1 - x, -y, 2 - z$; (v) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (vi) $x, -1 + y, z$; (vii) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$.

Discussion. Final atomic parameters are listed in Table 1.* The thermal ellipsoids are shown in Fig. 1 with the atomic numbering. Bond lengths and angles, and the geometry of the hydrogen bonds are listed in Table 2. A stereoscopic view of the crystal structure is shown in Fig. 2.

The benzene ring in the cation is planar within 0·005 (2) Å; the deviations of C(7) and C(8) from the ring plane are 0·005 (2) and 0·023 (2) Å, respectively. The torsion angles for C(2)—C(1)—C(7)—N(9) and C(4)—C(3)—C(8)—N(10) are −83·2 (2) and 20·4 (2)°, respectively. Bond angles for C(4)—C(3)—C(8) and C(3)—C(8)—N(10) are 122·5 (1) and 114·1 (1)°, being larger than the values expected for C(sp^2) and C(sp^3) angles, respectively, because of the steric repulsion between C(4) and N(10) with a distance of 2·893 (2) Å.

The bond lengths and angles in the adipate anion are in agreement with those found in piperazinium adipate (Vanier & Brisse, 1983*b*) and piperazinium glutarate (Vanier & Brisse, 1982). The carbon chain in the anion takes the *trans* zigzag conformation; the torsion angles around C(12)—C(13), C(13)—C(14) and C(14)—C(15) are 179·2 (1), 173·7 (1) and 178·8 (1)°, respectively. The dihedral angles between the plane of the carbon chain and the carboxylate groups involving C(11) and C(16) take larger values, 89·8 (8) and 71·0 (8)°, respectively, than the 1·2 (3)° in piperazinium succinate (Vanier & Brisse, 1983*a*), 29·5 (2)° in piperazinium adipate (Vanier & Brisse, 1983*b*) and 33·1 (2)° in piperazinium suberate monohydrate (Vanier, Bélanger-Gariepy & Brisse, 1983) to accommodate the groups to the hydrogen bonding (Table 2).

The cations and anions in the crystal are held together by six kinds of N—H···O hydrogen bonds and two kinds of O—H···O hydrogen bonds involving the water molecule (Table 2). The long molecular axes of the cations and anions lie nearly parallel to the longest axis, **a**, in a similar way to that observed in poly(*m*-xylylene adipamide) (Ota, Yamashita, Yoshizaki & Nagai, 1966). Two anions and cations related by $\bar{1}$ at ($\frac{1}{2}$, 0, 1) are linked by strong N—H···O hydrogen bonds (2) and (6) to form a dimer. The dimers are stacked along **b** by van der Waals interactions and N—H···O hydrogen bonds (1) and (4) to form a column. The columns related by 2_1 are held together by an N—H···O hydrogen bond (5) and van der Waals and ionic interactions to form a sheet parallel to (100). The water fills up the vacant spaces among the sheets and tightens the structure by hydrogen bonds (7) and (8).

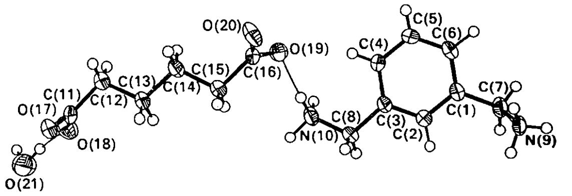

Fig. 1. Thermal ellipsoids (50% probability) with atomic numbering. The H atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2. Hydrogen bonds are shown by thin lines.

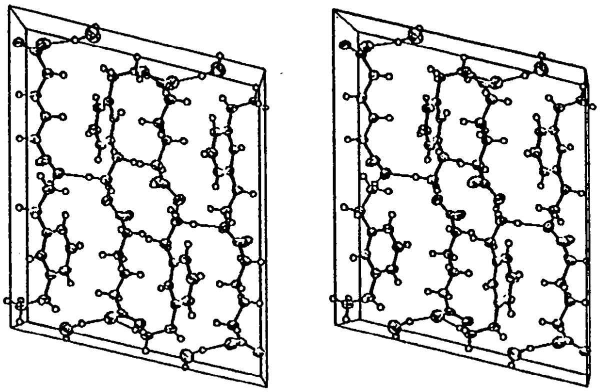

Fig. 2. A stereoscopic view of the molecular packing in the unit cell. The *a* axis points upward, the *c* axis from left to right, and the *b* axis onto the plane of the paper. Hydrogen bonds are shown by thin lines.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53485 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.