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The Crystal Structures of Trimesic Acid, its Hydrates and Complexes. V.* L- (or DL-)Histidinium Trimesate–$\frac{1}{3}$ Acetone

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Abstract

The crystalline complexes of trimesic acid with L- and DL-histidine, $C_6H_{10}N_3O_2^+.C_9H_5O_6^-.\frac{1}{3}C_3H_6O$, are both orthorhombic and have essentially identical cell dimensions: $a = 18{\cdot}097$ (7), $b = 13{\cdot}353$ (5), $c = 6{\cdot}737$ (4) Å, $Z = 4$; however, the space groups are $P2_12_12_1$ and $Pna2_1$ respectively. The structure of the chiral complex has been determined (Mo $K\alpha$, 1148 unique reflections, $R = 0{\cdot}057$). The closely related structure of the racemate was established by analogy from symmetry requirements. The structures contain hydrogen-bonded layers of trimesic acid and histidine moieties extending parallel to (001). The locations of the H atoms and the dimensions of the moieties show that there has been transfer of a proton from one carboxylic acid group of trimesic acid to a N atom of the imidazole ring. The layers contain cavities which are partially occupied by acetone molecules which are azimuthally disordered about their C=O axes. The name appropriate to the salt is accordingly L- (or DL-) histidinium trimesate–$\frac{1}{3}$ acetone. The structures consist of ribbons of cations and anions extending along [010]. Each ribbon of cations has histidinium ions of one chirality only; in the L salt all ribbons are congruent while in the DL salt the chirality alternates in the [100] direction normal to the ribbon axis.

1. Introduction

Trimesic acid (TMA) forms crystalline complexes with various organic molecules; structures have been reported for TMA.H_2O.$\frac{2}{9}$ picric acid and TMA.$\frac{5}{6}H_2O$ (Herbstein & Marsh, 1977), TMA.H_2O.1,4-dioxane (Herbstein & Kapon, 1978) and TMA.Me_2SO (Herbstein, Kapon & Wasserman, 1978). The primary cohesion of the components in these complexes is due to hydrogen bonding.

We have prepared crystalline complexes of TMA with various amino acids, including L- and DL-histidine. Single-crystal photographs of both complexes show very similar diffraction patterns, but with different systematic absences. It was thus evident that determination of the crystal structure of the chiral complex would establish that of the racemate by analogy, from symmetry requirements only.

2. Experimental

Crystals of TMA.L-histidine–$\frac{1}{3}$ acetone (I) and TMA.DL-histidine–$\frac{1}{3}$ acetone (II) were prepared separately by dissolving TMA and L- or DL-histidine in water–acetone solution. Bunches of fine transparent prismatic needles, elongated along [001], were obtained after the solutions were allowed to stand for a few days. A similar complex with DL-histidine, in which one water molecule replaces each one-third molecule of acetone, was prepared from water alone. As the acetone-containing crystals gave better diffraction patterns than the water-containing crystals, the former were used for the structure analysis. After preliminary photography, a single crystal 0·10 × 0·15 × 0·40 mm was sealed in a capillary and mounted on a Philips PW 1100/20 four-circle diffractometer with **c** slightly displaced from the φ axis. Cell dimensions were determined from 22 centered reflections. Crystal data are given in Table 1. The correct formula (*i.e.* including one third of an acetone molecule) was established by the structure analysis.

Table 1. *Crystal data for complex* (I)

L-Histidine. TMA–$\frac{1}{3}$ acetone
$C_6H_9N_3O_2.C_9H_6O_6.\frac{1}{3}[(CH_3)_2CO]$
FW 384·7
Orthorhombic, $P2_12_12_1$*
$Z = 4$, $F(000) = 802{\cdot}7$
$a = 18{\cdot}097$ (7) Å
$b = 13{\cdot}353$ (5)
$c = 6{\cdot}737$ (4)
$V = 1628{\cdot}0$ (13) Å^3
$D_x = 1{\cdot}570$ Mg m^{-3}
$D_m = 1{\cdot}530$ (by flotation in toluene–*s*-tetrabromoethane)
μ(Mo $K\alpha$) = 0·135 mm^{-1}

Chemical analysis of $C_6H_9N_3O_2.C_9H_6O_6.H_2O$; observed (calculated) wt %: C: 47·34 (47·00); H: 4·33 (4·47); N: 11·03 (10·96); O: 37·3 (by difference) (37·57).

* Space group for complex (II) is $Pna2_1$.

* Part IV: Herbstein, Kapon & Wasserman (1978).

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Intensities of 1188 reflections (40 with $I_o = 0$) were measured with graphite-monochromated Mo $K\alpha$ radiation within a 2θ range of 6–44°. The scan speed and width in ω were 1·5° min^{-1} and 1·3° respectively. The background was counted for half the total scanning time on each side of a reflection. Three standard reflections were monitored after every 2 h, but no significant counter or crystal instabilities were detected. Intensities were corrected for Lorentz and polarization factors and converted to structure factors. No absorption corrections were applied as $\mu t \simeq 0{\cdot}02$.

3. Structure solution and refinement

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) with 259 E values >1·20. The E map based on the best set of phases showed all 15 TMA and 7 out of 11 histidine heavy atoms. Structure factors based on 22 atoms with 1148 non-zero reflections gave an initial $R = 0{\cdot}49$. The calculations were carried out with *SHELX* 76 (Sheldrick, 1977). Successive difference syntheses revealed all 26 non-hydrogen atoms, which were refined isotropically to convergence at $R = 0{\cdot}10$. The imidazole ring atoms were identified after all hydrogen bonds had been found. A difference synthesis based on 26 non-hydrogen atoms revealed two peaks 1·17 Å apart with electron densities of 1·1 and 0·8 e Å^{-3}. Atoms in these positions make normal van der Waals contacts with some of the already-identified atoms and the two peaks were therefore considered to demonstrate the presence of a third component filling space left open by the fairly rigid structural framework. The pair of peaks was treated as a C=O group of a solvent acetone with occupancy of $\frac{1}{3}$.

Non-appearance of the methyl groups was attributed to rotational disorder of the acetone molecule about the C–O axis; it is not known whether this is static or dynamic disorder. The structure was then refined anisotropically for the TMA and histidine molecules and isotropically for the C=O group ($R = 0{\cdot}083$). A difference synthesis at this stage revealed the positions of all 15 H atoms. Anisotropic refinement of the C, N and O atoms and isotropic refinement of the H atoms in separate blocks gave $R = 0{\cdot}064$. 28 errant reflections were suppressed and the structure was refined until convergence was reached at $R = 0{\cdot}054$. The errant reflections were remeasured and re-introduced into the structure-factor list. The final values of R and R_w were 0·057 and 0·042 respectively.

Further details about the structure refinement are as follows:

(1) Quantity minimized $\sum w(|F_o| - |F_c|)^2$.

(2) Scattering factors for C, O, N taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965).

(3) Unit weights were used in the earlier stages of the refinement, and $w = k/[\sigma^2(F_o) + |g|F_o^2]$ in the later stages. The refined values of k and g for the final least-squares cycle were 0·6953 and 0·0; thus the standard deviations of the intensities were somewhat underestimated. The final atomic parameters are listed in Table 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34180 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic parameters* ($\times 10^4$ *for* C, N, O *and* $\times 10^3$ *for* H)

E.s.d.'s are given in parentheses for the least significant digit.

	x	*y*	*z*
C*T*(1)	−1374 (3)	7279 (4)	−19 (14)
C*T*(2)	−1962 (3)	6622 (4)	−162 (12)
C*T*(3)	−1847 (3)	5590 (4)	−138 (13)
C*T*(4)	−1131 (3)	5219 (4)	4 (13)
C*T*(5)	−537 (3)	5859 (4)	192 (13)
C*T*(6)	−662 (3)	6889 (4)	143 (13)
C*T*(7)	−1466 (4)	8389 (5)	−78 (16)
C*T*(8)	−2488 (4)	4883 (5)	−217 (13)
C*T*(9)	233 (3)	5510 (5)	395 (13)
O*T*(1)	−890 (3)	8892 (3)	−120 (14)
O*T*(2)	−2106 (2)	8757 (3)	−7 (10)
O*T*(3)	−3124 (2)	5147 (3)	−230 (11)
O*T*(4)	−2282 (2)	3933 (3)	−257 (11)
O*T*(5)	329 (2)	4548 (3)	102 (11)
O*T*(6)	732 (2)	6082 (3)	864 (8)
O*H*(1)	−3223 (2)	2461 (3)	−243 (9)
C*H*(1)	−2942 (3)	1618 (4)	28 (12)
O*H*(2)	−3273 (2)	793 (3)	−22 (10)
C*H*(2)	−2116 (3)	1585 (4)	600 (11)
N*H*(1)	−1990 (3)	679 (3)	1839 (9)
C*H*(3)	−1637 (3)	1547 (5)	−1293 (11)
C*H*(4)	−825 (3)	1558 (5)	−891 (10)
C*H*(5)	274 (3)	933 (5)	−177 (14)
C*H*(6)	−336 (3)	2333 (5)	−700 (11)
N*H*(2)	−428 (3)	697 (4)	−552 (10)
N*H*(3)	345 (3)	1920 (4)	−262 (11)
O*AC*(1)	−106 (1)	321 (1)	343 (3)
C*AC*(1)	−90 (1)	342 (2)	506 (5)
HC*T*(2)	−240 (2)	692 (2)	12 (6)
HC*T*(4)	−103 (3)	456 (3)	14 (10)
HC*T*(6)	−22 (2)	734 (3)	40 (6)
HO*T*(4)	−261 (3)	350 (5)	−18 (11)
HO*T*(5)	92 (4)	433 (5)	−23 (13)
HC*H*(2)	−194 (3)	222 (4)	152 (8)
HC*H*3(1)	−175 (2)	213 (3)	−219 (7)
HC*H*3(2)	−174 (3)	96 (3)	−224 (7)
HC*H*(5)	675 (2)	512 (3)	39 (7)
HC*H*(6)	−44 (2)	303 (3)	−108 (7)
HN*H*1(1)	−228 (2)	92 (3)	284 (5)
HN*H*1(2)	−155 (3)	61 (3)	226 (7)
HN*H*1(3)	−211 (4)	12 (5)	276 (11)
HN*H*(2)	−66 (3)	9 (4)	−19 (9)
HN*H*(3)	77 (2)	222 (3)	24 (9)

The e.s.d.'s of derived quantities (bond lengths and angles, torsion angles) are as follows: σ(C–C, C–N, C–O) $\simeq$ 0·008 Å, σ(C–H, N–H, O–H) $\simeq$ 0·04 Å, σ(C–C–C, C–C–N, C–C–O, O–C–O) $\simeq$ 0·5°, σ(C–C–H, C–N–H, C–O–H) $\simeq$ 2°, $\sigma[\tau$(C–C–C–C), τ(N–C–C–C), τ(N–C–C–O)] $\simeq$ 0·7°.

4. Results and discussion

4.1. *Crystal structure*

4.1.1. *Detailed description.* The structure consists of layers containing hydrogen-bonded TMA and L-histidine moieties, which are disposed about planes normal to **c**, roughly at $z = 0$ and $z = \frac{1}{2}$ (Table 3). A stereoview is given in Fig. 1 and the arrangement of moieties within a layer in Fig. 2.

Table 3. *Deviations of atoms from the mean molecular planes in* Å

Atoms given zero weight in the mean-plane calculations (Schomaker, Waser, Marsh & Bergman, 1959; Waser, Marsh & Cordes, 1973) are marked by asterisks.

1. TMA		2. Histidine		3. Histidine	
Atom	Δ	Atom	Δ	Atom	Δ
C(1)	0·009	N(2)	−0·001	C(1)	−0·018
C(2)	−0·002	N(3)	0·002	C(2)	0·005
C(3)	−0·015	C(4)	0·002	O(1)	0·007
C(4)	−0·036	C(5)	−0·001	O(2)	0·007
C(5)	0·004	C(6)	−0·002	N(1)*	0·672
C(6)	0·002	C(3)*	−0·041	C(3)*	−1·437
C(7)	−0·004				
O(1)*	−0·118				
O(2)*	0·148				
C(8)	0·026				
O(3)*	0·120				
O(4)*	−0·044				
C(9)	0·015				
O(5)*	−0·207				
O(6)*	0·258				

Mean planes defined in crystal coordinates (Å)

1. $-0{\cdot}0869x + 0{\cdot}0080y + 0{\cdot}9962z - 0{\cdot}272$ Å $= 0$.
2. $0{\cdot}2093x - 0{\cdot}0609y - 0{\cdot}9760z - 0{\cdot}145$ Å $= 0$.
3. $-0{\cdot}2324x - 0{\cdot}0741y + 0{\cdot}9698z - 1{\cdot}434$ Å $= 0$.

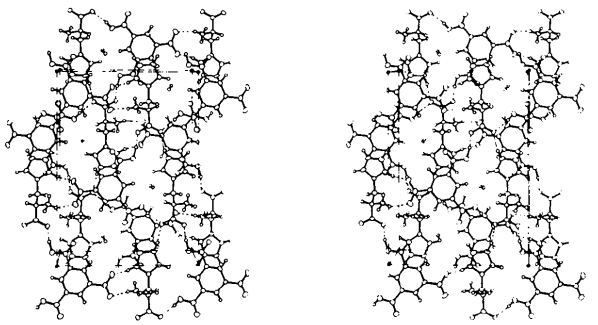

Fig. 1. *ORTEP* (Johnson, 1965) stereoview of TMA.L-histidine–$\frac{1}{3}$ acetone structure. The origin is at the upper left-hand corner of the diagram, **a** running down the page, **b** to the right and **c** up towards the observer.

Four different hydrogen bonds are formed between the reference trimesic acid moiety (coordinates in Table 2) and the neighboring histidine moieties. Two carboxyl groups serve as hydrogen-bond donors and the third as a hydrogen-bond acceptor. There is complete transfer of a proton from the TMA carboxyl group O(1)–C(7)–O(2) to one of the histidine basic N atoms. If one assumes that the normal state of the histidine is zwitterionic with the proton of its carboxyl group moved to the primary amine N(1), then the proton from TMA will be attached at the imidazole N(2). As a result, a neutral layer is formed in which a TMA moiety carries one negative charge and the histidine two positive and one negative charges. This complex is thus the salt L- (or DL-) histidinium trimesate–$\frac{1}{3}$ acetone.

Two histidine molecules are also hydrogen-bonded to each other head to tail *via* N(3) of the reference molecule and O(1) of the molecule related by a screw axis along **a** at $y = \frac{1}{4}$ and $z = 0$.

On the other hand, there are no direct hydrogen bonds or van der Waals contacts between TMA molecules within the layer. Instead, the molecular portions which are free to make direct contacts are separated by cavities left in the hydrogen-bonded frameworks. These cavities are partially occupied by disordered acetone molecules. Every acetone O atom

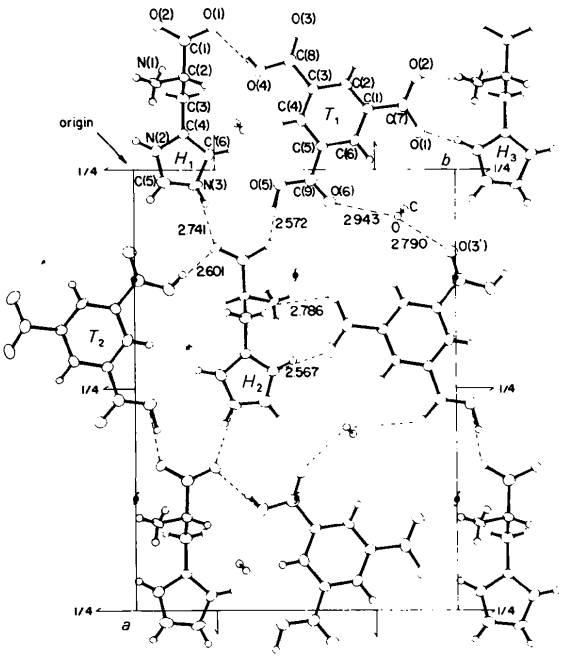

Fig. 2. TMA.L-histidine–$\frac{1}{3}$ acetone. Projection of a layer of moieties lying about $z = 0$ on to (001). The atoms of the reference molecules (coordinates in Table 2) are numbered, while the molecules themselves are numbered in connection with the discussion of the hydrogen-bonding (§ 4.1.3).

makes contacts with O(6) of the reference TMA molecule and O(3) of a molecule related by a screw axis along **a** at $y = \frac{3}{4}$ and $z = 0$. The respective distances are 2·943 and 2·790 Å.

The packing forces between layers along **c** are of the normal van der Waals and hydrogen-bond type. There is no direct overlap between TMA and histidine imidazole rings of adjacent layers. A single hydrogen bond of 2·860 Å exists between N(1) of the reference histidine and O(2) of TMA in the adjacent layer generated by the screw axis along **c** at $x = -\frac{1}{4}$, $y = \frac{1}{2}$.

4.1.2. *Relation between chiral and racemic structures.* The closely related structure of the racemate in projection down **c** can be deduced from the chiral structure by replacement of the atomic x coordinates for $P2_12_12_1$ by $(x - \frac{1}{4})$ in $Pna2_1$ and leaving y and z unchanged (Fig. 3). The figure shows the coincidence of the *n* and *a* glides in $Pna2_1$ with the screw axes along **a** and **b** in $P2_12_12_1$. The screw axes along **c** are common to both space groups. The structures in three dimensions are also closely related if the z coordinate of most of the atoms is essentially zero. This condition is satisfied for the present pair of complexes. There are two atoms of the histidine [N(1) and C(3)] which deviate considerably from the plane $z = 0$ (by 1·24 and 0·87 Å), but their contribution to the structure factors is not dominant.

The structure of the chiral complex can be described in terms of ribbons of cations and anions extending along [010] (Fig. 2). In the structure of the racemate, the chirality is preserved along each ribbon but alternates when one proceeds along **a**, normal to the ribbon axis. This alternation of chirality is due to the glide planes acting along **a**. The next layer of ribbons is identical but is offset due to the *n* glide planes acting normal to **a** and the screw axes acting parallel to **c**.

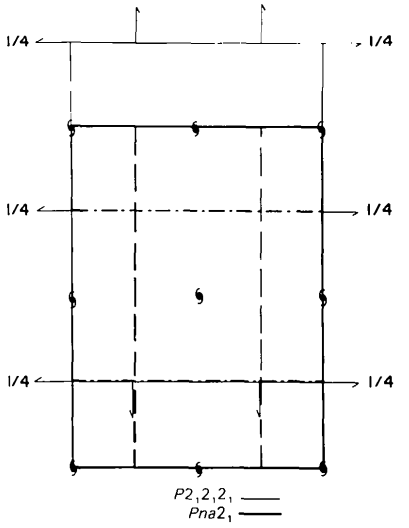

Fig. 3. Superimposition of unit cells of chiral (space group $P2_12_12_1$) and racemic (space group $Pna2_1$) salts [projections on to (001)], showing shift of origin of $x = \frac{1}{4}$ required to match symmetry elements.

Prior examples in which structural relations exist between racemic and optically active structures are known from the amino acid field (Pedone & Benedetti, 1972). L- and DL-alanine, for example, crystallize in space groups $P2_12_12_1$ (Donohue, 1950) and $Pna2_1$ (Simpson & Marsh, 1966); here the (100) planes are occupied exclusively by D- or L-enantiomers. The ribbons in the present complexes contain amino acid molecules of the same chirality separated by optically inactive TMA molecules. The close relation between the structures of the chiral and racemic complexes (and hence between their properties) makes separation of chiral histidine from its racemic mixture *via* the trimesic acid complexes practically impossible.

4.1.3. *The hydrogen bonds.* The hydrogen bonds are shown in Figs. 1 and 2 and can be classified as follows:

(i) O–H···$O^{\frac{1}{2}-}$	2·601 Å	$O(4)^{T1}\cdots O(1)^{H1}$
	2·572	$O(5)^{T1}\cdots O(2)^{H2}$
(ii) N^+–H(primary N)···$O^{\frac{1}{2}-}$	2·860	$N(1)^{H1}\cdots O(2)^{T1}$
N^+–H(primary N)···$O^{\frac{1}{2}-}$	2·786	$N(1)^{H3}\cdots O(2)^{T1}$
N–H(ring N)···$O^{\frac{1}{2}-}$	2·741	$N(3)^{H1}\cdots O(1)^{H2}$
N^+–H(ring N)···$O^{\frac{1}{2}-}$	2·567	$N(2)^{H3}\cdots O(1)^{T1}$

[The numbered histidine (*H*) and trimesic acid moieties (*T*) are shown in Fig. 2].

The O atoms acting as acceptors are all from carboxylate groups and hence are assigned charges of $\frac{1}{2}e$ each. The distances between carboxyl OH and carboxylate $O^{1/2-}$ are smaller by ~0·05 Å than the OH···O distances found between carboxylic acid groups [see Herbstein & Kapon (1978) for some similar distances]. The N–H···O^- and N^+–H···O^- distances fall within the rather broad range found in analogous situations with our extreme values falling at the two ends of the reported range. One O atom of the ionized carboxylate group [O(2)] is bonded to primary N atoms of two different histidines, the longer of these hydrogen bonds contributing to the interlayer cohesion. The angles between the C–O and O···O or N···O vectors are all in the region of 120°, suggesting that sp^2-hybridized lone pairs are involved in the interactions and that the H atoms all lie approximately on these vectors, although their positions have not been determined sufficiently accurately to warrant discussion of the details of these arrangements.

4.2. *The trimesate anion*

The geometry of the trimesate anion is shown in Fig. 4. Apart from the carboxyl O atoms, the anion is essentially planar (Table 3); there are slight tilts and twists of the three carboxyl groups out of the ring plane. The molecule has two neutral carboxyl groups in which the C=O and C–OH bonds are clearly distinguishable,

and one negatively charged carboxyl group with two almost equal bonds [C(7)–O(1) and C(7)–O(2)]. The mean C–C ring and C–C exocyclic distances of 1·389 and 1·488 Å respectively agree well with the values for $TMA.H_2O.\frac{2}{9}PA$ and $TMA.\frac{5}{6}H_2O$ (Herbstein & Marsh, 1977) and for α-TMA (Duchamp & Marsh, 1969).

4.3. L-*Histidinium cation*

The L-histidinium moiety exists in the crystal as a protonated zwitterion. The internal transfer of a proton from the carboxylic group to the primary amine N(1) is well established and here there is also external transfer of a proton from the TMA O(1)–C(7)–O(2) carboxyl group to the available imidazole N(2). The net charge on the cation is +1. The geometry of the L-histidinium cation is shown in Fig. 5. The imidazole ring is planar (Table 3), but there is a slight deviation by C(3) of −0·041 Å from the ring plane, compared with −0·012 in L-histidine dihydrochloride (Kistenmacher & Sorrell, 1974) and 0·02 Å in L-histidine hydrochloride monohydrate (Oda & Koyama, 1972). These deviations from planarity are presumably due to packing effects.

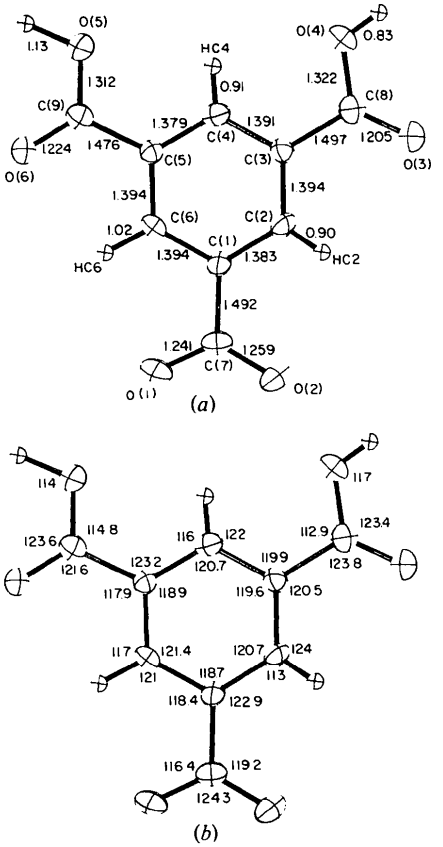

Fig. 4. The trimesate anion: (*a*) bond lengths (Å) and atomic numbering, (*b*) bond angles (°). The thermal ellipsoids are drawn at the 50% probability level.

The three atoms of the carboxyl group and C(2) are approximately coplanar.

The cation exists in the crystal in an open and extended conformation. The torsion angles C(1)–C(2)–C(3)–C(4) and N(1)–C(2)–C(1)–O(2) are 177·5 and −26·2° respectively. They agree with the corresponding values in orthorhombic L-histidine

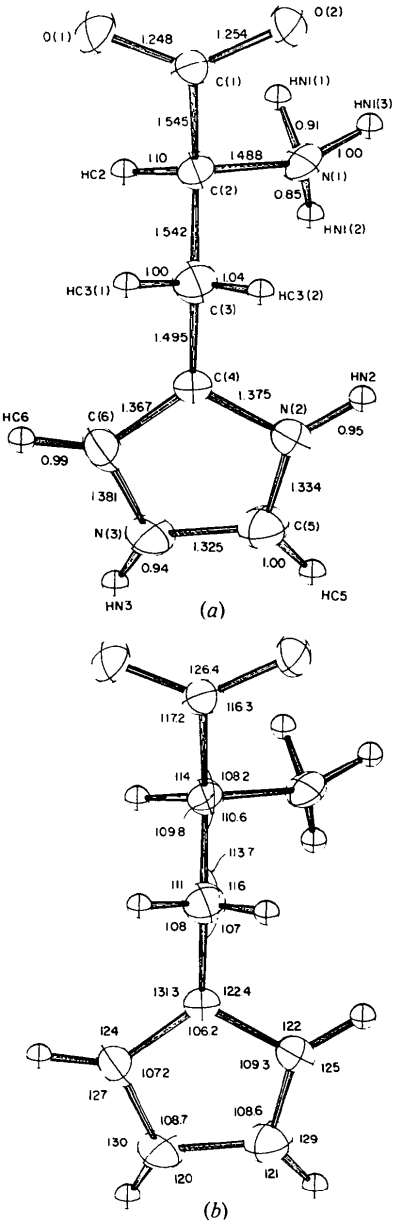

Fig. 5. The L-histidinium cation, (*a*) bond lengths (Å) and atomic numbering, (*b*) bond angles (°). The angles around N(1) are: HN1(1)–N(1)–C(2) = 92°, HN1(1)–N(1)–HN1(2) = 110°, HN1(1)–N(1)–HN1(3) = 71°, HN1(2)–N(1)–C(2) = 115°, HN1(2)–N(1)–HN1(3) = 85°, HN1(3)–N(1)–C(2) = 152°. We infer from this that HN1(3) has refined to an incorrect position, which we did not attempt to improve.

(Madden, McGandy & Seeman, 1972) and L-histidine dihydrochloride (Kistenmacher & Sorrell, 1974). The torsion angle N(2)–C(4)–C(3)–C(2) of 87·6° differs from the corresponding values of −75·1 and −120·3° in L-histidine dihydrochloride and L-histidine hydrochloride monohydrate. These differences are related to the rotational freedom of the imidazole ring which tends to accommodate to the hydrogen-bonding requirements in the crystal structure. This rotational freedom results from the protonation of N(2) which prevents intramolecular hydrogen-bonding with the protonated primary amine N(1) such as is found in orthorhombic L-histidine. In the extended conformation, the imidazole is *gauche* only to the amino group and *trans* to the carboxyl. The angle between the carboxyl and imidazole planes is only 7·7°. All bond lengths and angles in the cation agree well with the corresponding values in other crystal structures.

4.4. *Salt or molecular complex?*

Trimesic acid is a fairly strong acid ($pK_1 = 2{\cdot}12$) and histidine is a fairly strong base ($pK_a = 6{\cdot}10$ for imidazole N, 1·77 for carboxyl H and 9·18 for NH_3^+) and thus it is not surprising that the material crystallizes as a salt. Similar results have been reported, for example, for piperidinium *p*-chlorobenzoate (Kashino, Sumida & Haisa, 1972; pK_a values are 11·21 and 3·98) and for nicotinyl salicylate (Kim & Jeffrey, 1971; pK_a values are 7·85 and 3·00). Examples of hydrogen-bonded molecular complexes are aniline–2,4,5-trichlorophenol (Van Bellingen, Germain, Piret & Van Meerssche, 1971; pK_a values are 4·58 and 6·00) and urea–(oxalic acid)$_2$ (Harkema, Bats, Weyenberg & Feil, 1972; pK_a values are 0·18 and 1·23). These results are all compatible with the conclusions of Johnson & Rumon (1965), from an infrared study of various crystalline combinations of substituted pyridines and benzoic acids, that salts are found for $\Delta pK_a > 3{\cdot}8$ and molecular complexes for $\Delta pK_a < 3{\cdot}8$.

4.5. *The included acetone molecules*

Isomorphous crystals of histidinium trimesate were obtained either with one water molecule (composition from chemical analysis; detailed structure not determined) or one third of an acetone molecule (no chemical analysis; composition inferred from detailed structure analysis). The acetone-containing crystals gave the better diffraction patterns and hence were chosen for structure analysis; indeed at that stage no difference was anticipated between the two sets of crystals. It seems strange that van der Waals bonded acetone should be incorporated in the positions occupied (and this only partially) whereas hydrogen-bonded water could apparently also be accommodated in the space available. However, a detailed discussion would require determination of the water position, which we have not considered worthwhile.

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