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## Location of 'Tailor-Made' Additives in the Crystal and their Effect on Crystal Habit. A Study on the Host-Additive System L-Asparagine-L-aspartic Acid Monohydrate

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### Abstract

The crystal structures of L-asparagine monohydrate and of the solid solution (0.85:0.15) L-asparagine-L-aspartic acid monohydrate were refined using low-temperature (103 K) X-ray diffraction data. The atomic positions of the overlapping (asparagine) CONH<sub>2</sub> and (aspartic acid) CO<sub>2</sub>H groups were resolved by the refinement procedure. The aspartic acid adopts the (commonly observed) synplanar O=C-O-H conformation (1) rather than the alternative antiplanar conformation (2).

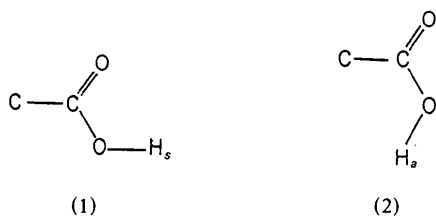
### Introduction

This work is part of a systematic study on the effect of 'tailor-made' additives, present in solution during crystallization (Addadi, Berkovitch-Yellin, Weissbuch, Lahav & Leiserowitz, 1983). The term 'tailor-made' signifies a molecule very similar in structure to that of the host. It was found that such additives have a dramatic effect on crystal growth and habit. The effect was explained in terms of a two-step mechanism: preferential adsorption of the additive on specific crystal faces for which the modified part of the additive points away from the crystal interior. Once bound the additive perturbs the regular deposition of oncoming layers so lowering the rates of growth in these directions, generally accompanied by a concomitant increase in the surface area of these faces. Using appropriate additives it became possible to induce preselected changes in crystal morphology.

In all the host-additive systems that we have studied to date the crystallographic site and molecular conformation of the adsorbed additive were inferred from a variety of experimental and theoretical results (Addadi, Berkovitch-Yellin, Domb, Gati, Lahav & Leiserowitz, 1982; Berkovitch-Yellin, van Mil, Addadi, Idelson, Lahav & Leiserowitz, 1985; Berkovitch-Yellin, 1985) but not from diffraction methods. Thus we searched for a system where we could unambiguously map the atomic positions of the additive from diffraction data better to ascertain the intermolecular interactions involved in effecting the change in crystal morphology. The main difficulty in such an experiment arises from the generally low (<1%) amount of the occluded additive. A system suitable for such an analysis is that in which the additive would induce a significant change in habit through repulsive interactions, and yet be occluded in amounts convincingly detectable by diffraction, e.g. from 5% upwards. These two requirements are not quite compatible. Nevertheless we had found that aspartic acid could be occluded in amounts up to 20% inside the crystal of asparagine H<sub>2</sub>O with a dramatic change in morphology (Addadi *et al.*, 1982). To generalize this finding, namely the pronounced effect of carboxylic acid additives on amide crystals, we studied a wide variety of host-additive systems RCONH<sub>2</sub>/RCO<sub>2</sub>H. We found that the carboxylic acid additives induce dramatic changes in the crystal habit of the corresponding host amide (Berkovitch-Yellin, Addadi, Idelson, Lahav & Leiserowitz, 1982). However, because the carboxyl O atom is a much

weaker proton acceptor than the corresponding amide O atom (Berkovitch-Yellin & Leiserowitz, 1980, 1982; Berkovitch-Yellin, Ariel & Leiserowitz, 1983), there is a large energy loss in replacing an amide-amide hydrogen bond by an amide-carboxyl hydrogen bond at the site of the additive. Thus unless the molecule contains other hydrogen-bonding functional groups, the amount of occluded additive is generally low (1-2%). The system asparagine-aspartic acid satisfied these requirements; the loss in energy is relatively low because the adsorbed additive participates in several intermolecular hydrogen bonds (Fig. 2) and thus a large amount of additive may be occluded. Consequently, this system was chosen for diffraction study.

Asparagine (Asn) resolves spontaneously upon crystallization from aqueous solution, forming a monohydrate in space group  $P2_12_12_1$  (Kartha & De Vries, 1961). The crystals are prismatic in shape exhibiting as many as 18 well-developed faces (Fig. 1a). Additive aspartic acid (Asp), of the same absolute configuration as the host Asn, induces growth of {010} Asn plates (Fig. 1b) due to retardation of growth along the  $b$  axis. This change in habit was explained by the established two-stage mechanism: adsorption of Asp on the {010} crystal faces of Asn followed by hindrance to oncoming Asn layers with a concomitant increase in {010} surface area (Addadi *et al.*, 1982). This deduction was explained on the molecular level as follows: The  $\text{NH}_2$  group of Asn participates in two  $\text{N-H}\cdots\text{O}(\text{carboxylate})$  bonds (Fig. 2). The hydroxyl  $\text{O-H}$  group of Asp may in principle adopt either a synplanar  $\text{O}=\text{C}-\text{O}-\text{H}_s$  (1) or an antiplanar  $\text{O}=\text{C}-\text{O}-\text{H}_a$  (2) conformation. Assuming the carboxyl group adopts the frequently observed synplanar conformation (1) (Leiserowitz, 1976), Asp can be easily adsorbed on the {010} face at an Asn crystallographic site.



In this arrangement the substrate  $(\text{Asn})\text{O}=\text{C}-\text{N}-\text{H}_s\cdots\text{O}(\text{Asn})$  hydrogen bond would be replaced at the site of an additive by an  $(\text{Asp})\text{O}=\text{C}-\text{O}-\text{H}_s\cdots\text{O}(\text{Asn})$  hydrogen bond and the  $(\text{Asn})\text{O}=\text{C}-\text{N}-\text{H}_a\cdots\text{O}(\text{Asn})$  bond will be replaced by an  $(\text{Asp})\text{O}(\text{hydroxyl})\cdots\text{O}(\text{Asn})$  interaction. Assuming this interaction is repulsive, such an Asp molecule would strongly hinder the to-be-attached Asn molecule of an oncoming {010} layer. To clarify these points, namely the conformation of the carboxyl group of Asp and the nature of the  $\text{O}\cdots\text{O}$  interaction

at the site of the additive we undertook a low-temperature X-ray diffraction study of pure L-asparagine monohydrate and of an L-asparagine-L-aspartic acid monohydrate solid solution.

### Experimental

Crystals of pure Asn were obtained by slow evaporation from aqueous solutions of L-asparagine and those of the solid solution Asn-Asp from L-asparagine grown in the presence of 30% L-aspartic acid. The amount of occluded Asp inside the {010} plate crystals

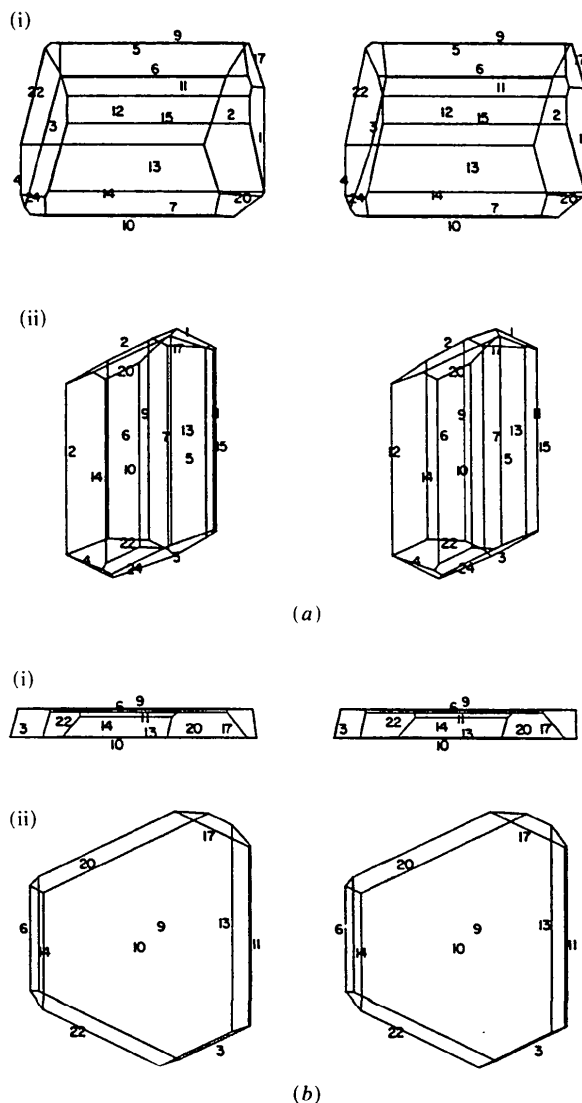


Fig. 1. (a) Crystal morphology of L-asparagine monohydrate. (b) Crystal morphology of L-asparagine monohydrate grown in the presence of L-aspartic acid. The crystals are viewed along the  $c$  axis (i) and the  $b$  axis (ii). The numbering of the faces: (1) (101); (2) (10 $\bar{1}$ ); (3) ( $\bar{1}$ 01); (4) ( $\bar{1}$ 0 $\bar{1}$ ); (5) (011); (6) (01 $\bar{1}$ ); (7) (0 $\bar{1}$ 1); (8) (0 $\bar{1}$  $\bar{1}$ ); (9) (010); (10) (0 $\bar{1}$ 0); (11) (012); (12) (0 $\bar{1}$ 2); (13) (0 $\bar{1}$ 2); (14) (0 $\bar{1}$ 2); (15) (001); (16) (00 $\bar{1}$ ); (17) (111); (18) ( $\bar{1}$ 11); (19) ( $\bar{1}$ 11); (20) (1 $\bar{1}$ 1); (21) (1 $\bar{1}$ 1); (22) ( $\bar{1}$ 1 $\bar{1}$ ); (23) (11 $\bar{1}$ ); (24) ( $\bar{1}$ 11).

of Asn-Asp was determined by HPLC measurements (Weinstein, 1982) from small pieces cut from nine well-shaped and clean crystals grown in the same batch. It was found that about 15% of Asp was occluded in each crystal of Asn-Asp. One of these crystals was chosen for the X-ray intensity measurements.

All X-ray measurements on the single crystals of pure Asn and Asn-Asp were performed at low temperature (about 100K) on a CAD-4 diffractometer. The crystals were cooled by a stream of liquid nitrogen (van Bolhuis, 1971). The cell parameters (Table 1) at this temperature were determined from the angular positions of 25 reflections up to  $\theta = 24^\circ$  (Mo  $K\alpha$  radiation). The agreement between the intensities of several reflections belonging to the eight octants of reciprocal space (i.e.  $hkl$ ,  $\bar{h}\bar{k}l$ ,  $h\bar{k}l$ ,  $\bar{h}kl$  etc.) and the systematic absences for the  $h00$ ,  $0k0$  and  $00l$  reflections denoted  $P2_12_12_1$  symmetry for both pure Asn and Asn-Asp. Details on the X-ray intensity measurements are given in Table 2. The intensities were not corrected for absorption because of the low absorption coefficient of the crystal. The standard deviations in the structure factors were calculated from the equation  $\sigma^2(I - B) = [0.03(I - B)]^2 + I + B$  ( $I$  intensity and  $B$  background).

### Structure refinement

#### Pure asparagine monohydrate

The labelling of the atoms of Asn and Asp is given in Fig. 3. The starting parameters for the refinement were taken from the final coordinates of the room-temperature neutron diffraction analysis (Verbist, Lehmann, Koetzle & Hamilton, 1972). Least-squares refinement was carried out by *SHELX* (Sheldrick, 1976) using the conventional spherical-atom model. The reflection weights were set equal to  $1/\sigma^2(F_o)$ . Extinction corrections were not applied. Several cycles of refinement with anisotropic temperature

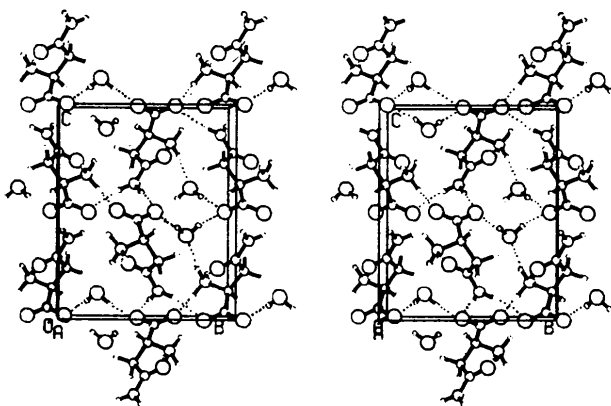


Fig. 2. Stereoscopic view of the packing arrangement of L-asparagine monohydrate along the  $a$  axis.

Table 1. Crystal data at 100K of L-asparagine monohydrate (Asn) and the solid solution L-asparagine-L-aspartic acid monohydrate (0.85:0.15)(Asn-Asp)

	Asn $C_4H_8N_2O_3 \cdot H_2O$	Asn-Asp $0.85C_4H_8N_2O_3 \cdot 0.15C_4H_7NO_4 \cdot H_2O$
$M_r$	132.124	133.108
Space group	$P2_12_12_1$	$P2_12_12_1$
$a$ (Å)	5.584 (1)	5.565 (1)
$b$ (Å)	9.735 (1)	9.774 (2)
$c$ (Å)	11.701 (2)	11.698 (3)
$V$ (Å <sup>3</sup> )	636.11	636.22
$Z$	4	4
$D_x$ (g cm <sup>-3</sup> )	1.3794	1.3894
$\mu$ (Mo $K\alpha$ )	0.127	0.135
$F(000)$	320	320

Table 2. Intensity measurements

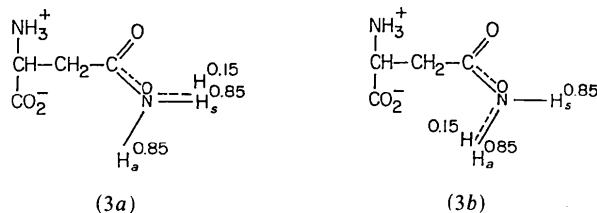
Crystal	Asn	Asn-Asp
Diffractometer		Nonius CAD-4
Monochromator		Graphite
X radiation		Mo $K\alpha$
Crystal temperature		100K
Crystal dimensions (mm)	0.4 × 0.4 × 0.3	0.2 × 0.4 × 0.6
$\theta$ (max)	60°	43°
Range of $h, k, l$	$13 \leq h \leq 13$ , $23 \leq k \leq 23$ , $28 \leq l \leq 28$	$10 \leq h \leq 10$ , $18 \leq k \leq 18$ , $22 \leq l \leq 22$
Scanning mode		$3\omega/2\theta$
Reflection scanning time (s)		60-180
Number of intensity monitor reflections		6
Intensity monitor interval (h)		4
Number of reflections ( $hkl$ ; $\bar{h}\bar{k}l$ ) measured	11063	5350
Number of independent reflections	5339	2672
Number of 'unobserved' reflections		
$I < 3\sigma(I)$	132	52
Agreement between equivalent reflections $R^*$	0.0277	0.0245

\*  $R = \sum |F_o^2 - F_c^2| / \sum F_o^2$ , where  $\bar{F}_o$  is the average value of the Friedel-related structure factors and  $F_o$  is the individual structure factor.

factors for atoms C, N, and O and isotropic H atoms yielded  $R(F) = 0.045$  and  $wR(F) = 0.038$ . The final atomic coordinates, temperature factors and bond lengths are listed in Table 3.\*

#### Asn-Asp solid solution

The challenge was to differentiate between the two possible structures (3a) and (3b), which for 15% occluded Asp, according to the HPLC results, involved differentiating between 0.85e and 1.0e at the two hydrogen sites  $H_s$  and  $H_a$ .



\* Lists of structure factors for L-asparagine monohydrate and L-asparagine-L-aspartic acid monohydrate, together with bond angles relating to Tables 3, 5 and 6, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42143 (50pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Asparagine: spherical-atom model refinement*(a) Atomic coordinates ( $\times 10^4$ ) and their e.s.d.'s in parentheses

	x	y	z
C(1)	-1277 (1)	-569 (1)	349 (1)
C(2)	-3094 (1)	-262 (1)	1300 (1)
C(3)	-2095 (1)	594 (1)	2277 (1)
C(4)	165 (1)	-6 (1)	2793 (1)
N(1)	-4182 (1)	-1561 (1)	1732 (1)
N(2)	1069 (1)	649 (1)	3695 (1)
O(1)	-90 (1)	448 (1)	-15 (1)
O(2)	-1215 (1)	-1759 (1)	-46 (1)
O(3)	1093 (1)	-1055 (1)	2379 (1)
O(4)	2984 (1)	2275 (1)	1129 (1)
H(1)	2078 (32)	1776 (17)	805 (3)
H(2)	3395 (35)	2954 (16)	715 (13)
H(3)	-3156 (24)	-1986 (14)	2252 (11)
H(4)	-4472 (28)	-2163 (13)	1104 (9)
H(5)	-5702 (17)	-1407 (16)	2042 (12)
H(6)	2347 (20)	268 (14)	4093 (10)
H(7)	312 (27)	1389 (12)	4023 (12)
H(8)	-4369 (24)	203 (12)	919 (10)
H(9)	-1720 (28)	1517 (10)	1935 (11)
H(10)	-3350 (21)	603 (15)	2871 (10)

(b) Anisotropic thermal parameters ( $U_{ij}$ ) of the form  $\exp[-2\pi^2(\sum_i a_i^* a_i^* h_i h_i U_{ij})]$  ( $\text{\AA}^2 \times 10^4$ ) and isotropic thermal parameters ( $U$ ) of the form  $\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$  ( $\text{\AA}^2 \times 10^4$ ) and their e.s.d.'s in parentheses

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{23}$	$U_{13}$
C(1)	82 (1)	79 (1)	64 (1)	-3 (1)	8 (1)	4 (1)
C(2)	72 (1)	72 (1)	70 (1)	-5 (1)	3 (1)	6 (1)
C(3)	86 (1)	78 (1)	82 (1)	-19 (1)	0 (1)	9 (1)
C(4)	77 (1)	79 (1)	73 (1)	-10 (1)	0 (1)	-3 (1)
N(1)	79 (1)	86 (1)	78 (1)	-7 (1)	7 (1)	-9 (1)
N(2)	120 (1)	118 (1)	92 (1)	-29 (1)	-25 (1)	-2 (1)
O(1)	131 (1)	91 (1)	113 (1)	8 (1)	37 (1)	-19 (1)
O(2)	123 (1)	84 (1)	93 (1)	-22 (1)	24 (1)	6 (1)
O(3)	94 (1)	96 (1)	121 (1)	-28 (1)	-8 (1)	24 (1)
O(4)	172 (2)	138 (1)	118 (1)	9 (2)	-14 (1)	-27 (1)

	$U$		$U$		$U$
H(1)	333 (29)	H(2)	333 (29)	H(3)	245 (20)
H(4)	245 (20)	H(5)	245 (20)	H(6)	214 (33)
H(7)	289 (38)	H(8)	10 (25)	H(9)	201 (22)
H(10)	201 (22)				

(c) Bond lengths ( $\text{\AA}$ )

C(1)-C(2)	1.535 (1)	C(1)-O(1)	1.266 (1)	C(1)-O(2)	1.247 (1)
C(2)-C(3)	1.521 (1)	C(2)-N(1)	1.491 (1)	C(2)-H(8)	0.953 (14)
C(3)-C(4)	1.515 (1)	C(3)-H(9)	1.005 (11)	C(3)-H(10)	0.989 (13)
C(4)-N(2)	1.333 (1)	C(4)-O(3)	1.244 (1)	N(1)-H(4)	0.953 (13)
N(1)-H(5)	0.938 (11)	N(1)-H(3)	0.935 (14)	N(2)-H(6)	0.928 (13)
N(2)-H(7)	0.921 (13)	O(4)-H(2)	0.850 (17)	O(4)-H(1)	0.786 (18)

Several strategies were undertaken to establish unambiguously the correct structure to minimize the effect of model dependence. The least-squares refinement was initiated with the atoms of Asn only, with parameters taken from Table 3(a). Several cycles yielded  $R(F) = 0.043$ ,  $wR(F) = 0.039$ . The anisotropic and isotropic temperature factors of Asn-Asp were in excellent agreement with the corresponding values from pure Asn except for those of the amide H atoms H(6) [ $0.012(4)$  vs  $0.022(4) \text{\AA}^2$ ] and H(7) [ $0.051(7)$  vs  $0.029(4) \text{\AA}^2$ ]. The high thermal motion of atom H(7) in Asn-Asp, *i.e.*  $0.051 \text{\AA}^2$ , relative to its value in Asn and to that of H(6) in both Asn and Asn-Asp, suggested that atom H(7) in Asn-Asp is deficient in charge. These results may be interpreted in terms of a synplanar  $\text{O}=\text{C}-\text{O}-\text{H}$  conformation (1) for Asp; namely, the hydroxyl H atom almost coincides with atom H(6) of Asn. At this stage the hydroxyl O atom O(5) was inserted at the position

of the amide atom N(2) with a starting occupancy of 0.1. The C(4)-O(5) bond length was constrained to a value of  $1.31 \text{\AA}$  which is an average obtained from several low-temperature X-ray structures. Refinement yielded occupancies of 0.80 (1) and 0.20 (1) for N(2) and O(5) respectively with a distance of  $0.23(1) \text{\AA}$  between them.

To establish further the synplanar conformation of  $\text{O}=\text{C}-\text{O}-\text{H}$  we set the occupancies of  $\text{H}_s$ , *i.e.* H(6), and  $\text{H}_a$ , *i.e.* H(7), to 0.8 and 1.0 respectively. After refinement of the parameters of the atoms of Asn and of O(5), the only atom of Asp which was inserted at this stage, a difference map gave a positive peak of height  $0.26 \text{e \AA}^{-3}$  at the position of  $\text{H}_s$  and a negative peak of  $-0.16 \text{e \AA}^{-3}$  at  $\text{H}_a$ . Reversing the situation by assigning occupancies of 1.0 and 0.8 to  $\text{H}_s$  and  $\text{H}_a$  respectively yielded a difference map with a peak of  $0.19 \text{e \AA}^{-3}$  at the position of  $\text{H}_s$  and no density at that of  $\text{H}_a$ . This test indicated that the total electron charge at the  $\text{H}_s$  position is higher than at  $\text{H}_a$ .

The refinement was continued as follows: The amide group  $\text{CCONH}_2$  was treated as a rigid group with internal geometry taken from the pure Asn structure. The atoms of  $\text{CCO}_2\text{H}_s$  were introduced restraining their various intramolecular distances to averaged values taken from published carboxylic acid crystal structures. The overlapping atoms of the  $\text{CCONH}_2$  and  $\text{CCO}_2\text{H}_s$  groups were constrained to have the same temperature factors. Each molecular site thus contained the moiety  $\text{H}_3\text{NCHCO}_2$  common to Asn and Asp and the amide and carboxyl moieties,  $\text{CH}_2\text{CONH}_2$  and  $\text{CH}_2\text{CO}_2\text{H}$ . During refinement the carboxyl group  $\text{CCO}_2$  proved to be coplanar within  $0.01 \text{\AA}$  and thus  $\text{CCO}_2\text{H}$  was eventually refined as a planar rigid body. At this stage  $R(F)$  converged to 0.0358,  $wR(F)$  to 0.0349 and the occupancies of the amide and carboxyl groups to 0.839 and 0.161 respectively. The isotropic temperature factors of the amide and hydroxyl atoms H(6) and H(6') were each equal to  $0.021(3) \text{\AA}^2$  and that of the amide atom H(7)  $0.028(3) \text{\AA}^2$ . These values matched excellently with the corresponding values of the pure Asn refinement (Table 3b).

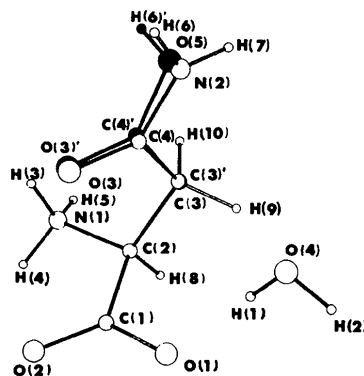


Fig. 3. Atom numbering of asparagine, aspartic acid and water.

Table 4. Asparagine-aspartic acid: results of refinement of various models to ascertain the conformation of the CO<sub>2</sub>H group (i.e. syn 1 or anti 2)

Atom	Model (a)		Model (b)		Model (c)	
	H(6)	H(7)	H(6)	H(7)	H(6)	H(7)
Occupancy	1.0	0.84	0.84	1.02	0.92	0.92
$U$ (Å <sup>2</sup> )	0.023 (3)	0.031 (3)	0.015 (3)	0.042 (3)	0.023 (3)	0.043 (3)
$R$	0.0357		0.0357		0.0357	
$wR$	0.0349		0.0349		0.0349	

In order to ascertain further that the hydroxyl H atom H(6') lies in the synplanar position, refinement was continued on three models (Table 4) which differed in the values of the fixed occupancies attached to the atoms H(6) and H(7). The hydroxyl H atom H(6') was not inserted. The resulting agreement factors of these three models are identical. Nevertheless model (a) is the most probable since the  $U$  values of H(6) and H(7) best fit those of the corresponding atoms in pure Asn (Table 3b). This conclusion is further substantiated by a plot (Fig. 4) of the difference in temperature factors  $|\Delta U|$  between corresponding atoms of pure Asn and of Asn-Asp for the three models. Excluding atoms H(6) and H(7),  $|\Delta U|$  is maximally 0.004 Å<sup>2</sup> for all atoms. For model (a),  $|\Delta U|$  of atoms H(6) and H(7) is in this same range of 0.004 Å<sup>2</sup>; for model (b), however, their  $|\Delta U|$  values are significantly larger than 0.004 Å<sup>2</sup>. The high  $|\Delta U|$  value of H(7) for model (c) is also distinctly higher than 0.004 Å<sup>2</sup>. This analysis clearly indicates that model (a) is the most reasonable, from which we deduce a distinct preference for the synplanar O=C-O-H<sub>s</sub> conformation of the carboxyl group of Asp, in agreement with all the other tests applied above.

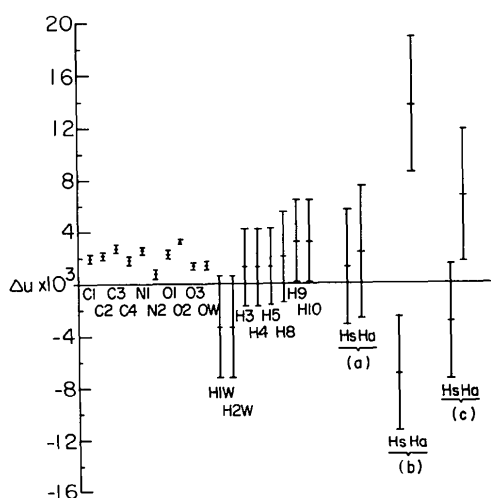


Fig. 4. Differences in temperature factors between the corresponding atoms of Asn and Asn-Asp and the estimated standard deviations for models (a), (b) and (c) (Table 4). These differences were the same for all the atoms in the three models, but for atoms H<sub>s</sub> and H<sub>a</sub>.

Table 5. Asparagine-aspartic acid: spherical-atom model refinement

(a) Atomic coordinates ( $\times 10^4$ ) and their e.s.d.'s

	x	y	z
C(1)	-1212 (1)	-556 (1)	338 (1)
C(2)	-3038 (1)	-254 (1)	1287 (1)
C(3)	-2059 (2)	593 (1)	2269 (1)
C(4)	211 (2)	5 (1)	2789 (1)
N(1)	-4122 (1)	-1554 (1)	1710 (1)
N(2)	1097 (2)	657 (1)	3697 (1)
O(1)	-17 (1)	460 (1)	-20 (1)
O(2)	-1144 (1)	-1737 (1)	-57 (1)
O(3)	1166 (2)	-1033 (1)	2374 (1)
O(4)	3000 (1)	2287 (1)	1145 (1)
H(1)	2076 (25)	1772 (17)	808 (12)
H(2)	3363 (27)	2943 (16)	703 (13)
H(3)	-3169 (22)	-1954 (16)	2230 (11)
H(4)	-4415 (24)	-2171 (14)	1051 (10)
H(5)	-5551 (17)	-1375 (17)	2002 (13)
H(6)	2388 (2)	287 (1)	4092 (1)
H(7)	320 (2)	1392 (1)	4022 (1)
H(8)	-4288 (22)	231 (14)	920 (12)
H(9)	-1713 (25)	1547 (9)	1908 (12)
H(10)	-3287 (20)	565 (15)	2855 (10)
C(3')	-2037 (7)	585 (4)	2273 (4)
C(4')	128 (7)	-103 (4)	2816 (4)
O(3')	1049 (7)	-1121 (4)	2418 (4)
O(5)	922 (7)	504 (4)	3760 (4)
H(6')	2229 (7)	129 (4)	4123 (4)

(b) Anisotropic thermal parameters ( $U_{ij}$ ) of the form  $\exp[-2\pi^2(\sum_i \sum_j a_i^* a_j^* h_i h_j U_{ij})]$  (Å<sup>2</sup>  $\times 10^4$ ) and isotropic thermal parameters ( $U$ ) of the form  $\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$  (Å<sup>2</sup>  $\times 10^4$ ) and their e.s.d.'s in parentheses

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	
C(1)	95 (2)	104 (2)	79 (2)	-7 (2)	0 (2)	9 (2)	
C(2)	94 (2)	86 (2)	97 (2)	-7 (2)	7 (2)	15 (2)	
C(3)	111 (2)	96 (2)	120 (2)	-29 (2)	16 (2)	7 (2)	
C(4)	95 (2)	86 (2)	92 (2)	-14 (2)	20 (2)	-26 (2)	
N(1)	113 (2)	101 (2)	101 (2)	-10 (2)	-1 (2)	-7 (2)	
N(2)	112 (3)	125 (4)	117 (2)	-42 (2)	-8 (2)	-22 (2)	
O(1)	156 (2)	114 (2)	128 (2)	18 (2)	27 (2)	-11 (2)	
O(2)	144 (2)	120 (2)	125 (2)	-46 (2)	27 (2)	-2 (2)	
O(3)	118 (2)	102 (2)	135 (2)	-27 (2)	8 (2)	11 (2)	
O(4)	177 (2)	159 (2)	133 (2)	13 (2)	-11 (2)	-29 (2)	
C(3')	111 (2)	96 (2)	120 (2)	-29 (2)	16 (2)	7 (2)	
C(4')	95 (2)	86 (2)	92 (2)	-14 (2)	20 (2)	-26 (2)	
O(3')	118 (2)	102 (2)	135 (2)	-27 (2)	8 (2)	11 (2)	
O(5)	112 (3)	125 (4)	117 (2)	-42 (2)	-8 (2)	-22 (2)	
$U$							
H(1)	298 (23)		H(2)	298 (23)		H(3)	256 (20)
H(4)	256 (20)		H(5)	256 (20)		H(6)	208 (26)
H(7)	275 (29)		H(8)	131 (23)		H(9)	227 (21)
H(10)	227 (21)		H(6')	208 (26)			

(c) Bond lengths (Å)

C(1)-C(2)	1.534 (1)	C(1)-O(1)	1.266 (1)	C(1)-O(2)	1.244 (1)
C(2)-C(3)	1.521 (4)	C(2)-C(3)	1.517 (1)	C(2)-N(1)	1.491 (1)
C(2)-H(8)	0.945 (13)	C(3)-C(4)	1.515 (2)	C(3)-H(9)	1.042 (10)
C(3)-H(10)	0.968 (11)	C(4)-N(2)	1.333 (2)	C(4)-O(3)	1.244 (1)
N(1)-H(4)	0.992 (13)	N(1)-H(3)	0.897 (13)	N(1)-H(5)	0.883 (11)
N(2)-H(6)	0.928 (2)	N(2)-H(7)	0.921 (1)	O(4)-H(1)	0.820 (15)
O(4)-H(2)	0.848 (15)	H(9)-C(3')	1.048 (11)	H(10)-C(3')	0.974 (12)
C(3)-C(4')	1.519 (6)	C(4)-O(5)	1.329 (6)	C(4)-O(3')	1.212 (6)
O(5)-H(6')	0.918 (6)				

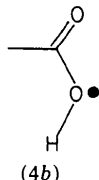
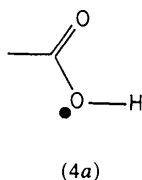
To ascertain that the atoms of the two overlapping amino acid H<sub>3</sub>NCHCO<sub>2</sub> moieties of Asn and of Asp occupy identical positions, these two moieties were refined as rigid bodies. The resulting distances between the overlapping atoms were less than 0.03 Å, which clearly indicated that the H<sub>3</sub>NCHCO<sub>2</sub> moieties of Asp and Asn coincide.

Final atomic coordinates, temperature factors and bond lengths are given in Table 5.\*

\* See deposition footnote.

### Structure refinement with deformation functions

The spherical-atom model definitely indicates a strong preference for the synplanar O=C-O-H<sub>s</sub> conformation of Asp. The disadvantage of the spherical-atom model is that the deformation charge in bonds and lone pairs is in the same range as the fraction of the electron we are looking for (Berkovitch-Yellin & Leiserowitz, 1977). Therefore to substantiate further the synplanar O=C-O-H<sub>s</sub> model we took into account the bonding and lone-pair densities of Asn-Asp using deformation functions (Hirshfeld, 1976, 1977). The deformation parameters were derived by deformation refinement of pure asparagine (Wang, 1983). The deformation parameters of the carboxyl group of Asp were taken from the final refinement of a dicarboxylic acid derivative (Eisenstein, 1981). The starting atomic parameters  $x$ ,  $y$ ,  $z$ ,  $U$  were taken from the spherical-atom refinement of Asn-Asp. The hydroxyl H atom was excluded at this stage. The Asn and Asp atoms, occupying the same atomic sites, were refined with the same thermal parameters. The occupancies of CCONH<sub>2</sub> and CCO<sub>2</sub> were each kept fixed at 0.84 and 0.16 in the initial stages of the deformation refinement. Several cycles of refinement of atomic positional and thermal parameters using weights equal to  $1/\sigma^2(F_o^2)$  yielded  $R(F) = 0.0262$  and  $wR(F^2) = 0.0456$ . The 'absent' hydroxyl H atom H(6') was located as follows: Using the deformation parameters of the hydroxyl O atom, the lone-pair electrons were inserted in turn in the two alternative models *anti* (4a) and *syn* (4b) respectively.



Several cycles of refinement were carried out for each model, in which the occupancies of the amide H atoms H(6) and H(7) were not constrained but refined freely. The results for models (a) and (b) are as follows:

	Occupancy of			
	$R(F)$	$wR(F^2)$	H(6)	H(7)
(a)	0.0259	0.0451	1.00 (2)	0.73 (2)
(b)	0.0258	0.0448	0.91 (2)	0.82 (2)

Both refinements yielded the same  $R$  factors; nevertheless in both cases the resulting occupancy of H(6) is higher than that of H(7). It is therefore clear that the hydroxyl atom H(6') lies in the synplanar position. At this stage atom H(6') was added in a synplanar position.

For the final determination of the composition of Asn-Asp, the occupancies of CCONH<sub>2</sub> and CCO<sub>2</sub>H

of Asn and Asp respectively were varied in steps from 0.83/0.17 to 0.86/0.14. At each step the atomic parameters were refined. A plot of  $R(F)$  and  $wR(F^2)$  versus occupancy, given in Fig. 5, shows that the most probable composition of Asn-Asp is 0.846/0.154. This result is in excellent agreement with the composition obtained from HPLC.

The final atomic coordinates, temperature factors and bond lengths are listed in Table 6.\*

### Discussion

A primary purpose of this study was to locate the aspartic acid occluded in the crystal of an Asn-Asp solid solution. It was found that the amino acid moieties H<sub>3</sub>NCHCO<sub>2</sub> of Asn and Asp occupy identical atomic positions. The calculated distances between the corresponding overlapping atoms of the CCO<sub>2</sub>H and CCONH<sub>2</sub> groups range from 0.02 to 0.2 Å (Table 7). These distances are less than the theoretical resolving power of 0.3 Å ( $=0.6\lambda/2 \sin \theta_m$ ;

\* See deposition footnote.

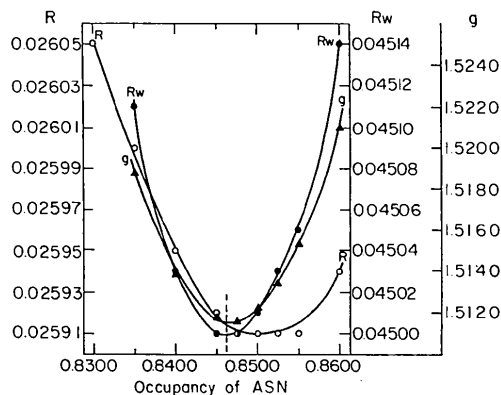


Fig. 5. Plot of  $R(F)$ ,  $wR(F^2)$  and  $g\{[\sum w(F_o^2 - F_c^2)^2]/(n-p)]$ , where  $n$  is the number of observations and  $p$  the number of parameters} as a function of the occupancies of the groups CCONH<sub>2</sub> and CCO<sub>2</sub>H of Asn and Asp respectively.

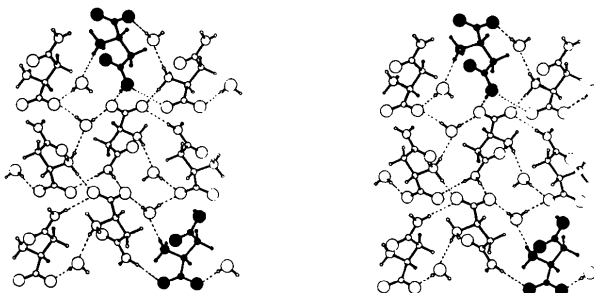


Fig. 6. Stereoscopic view of the packing arrangement of the solid solution 0.85:0.15 L-asparagine-L-aspartic acid monohydrate. Two arbitrary sites are occupied by aspartic acid molecules (filled atoms).

Table 6. Asparagine-aspartic acid: structure refinement with deformation functions

(a) Atom coordinates ( $\times 10^4$ ) and their e.s.d.'s

	x	y	z
C(1)	-1212 (1)	-556 (1)	339 (1)
C(2)	-3043 (1)	-255 (1)	1289 (1)
C(3)	-2062 (1)	594 (1)	2268 (1)
C(4)	209 (2)	5 (1)	2791 (1)
N(1)	-4122 (1)	-1554 (1)	1711 (1)
N(2)	1091 (2)	655 (1)	3693 (1)
O(1)	-20 (2)	456 (2)	-19 (1)
O(2)	-1143 (1)	-1738 (2)	-58 (1)
O(3)	1160 (2)	-1029 (2)	2375 (1)
O(4)	3004 (2)	2287 (1)	1149 (2)
H(1)	1880 (29)	1751 (22)	720 (17)
H(2)	3494 (34)	3006 (20)	639 (17)
H(3)	-3098 (39)	-2026 (22)	2305 (18)
H(4)	-4418 (30)	-2202 (21)	1087 (20)
H(5)	-5739 (45)	-1338 (20)	2073 (14)
H(6)	2579 (53)	210 (25)	4079 (19)
H(7)	113 (49)	1556 (27)	3975 (19)
H(8)	-4355 (66)	257 (29)	926 (20)
H(9)	-1723 (33)	1515 (45)	1983 (17)
H(10)	-3241 (60)	698 (16)	2891 (31)
C(3)'	-2037	585	2273
C(4)'	128	-103	2816
O(3)'	1049	-1121	2418
O(5)	922	504	3760
H(6)'	2307	49	4095

(b) Anisotropic thermal parameters ( $U_{ij}$ ) of the form  $\exp[-2\pi^2(\sum_i \sum_j a_i^* a_j^* h_i h_j U_{ij})]$  ( $\text{\AA}^2 \times 10^3$ ) and their e.s.d.'s in parentheses

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{23}$	$U_{13}$
C(1)	99 (2)	93 (2)	82 (2)	7 (2)	-10 (2)	5 (2)
C(2)	91 (2)	84 (2)	96 (2)	16 (1)	-5 (1)	6 (2)
C(3)	112 (2)	92 (2)	118 (2)	8 (2)	-28 (2)	17 (2)
C(4)	91 (2)	86 (2)	95 (2)	-19 (2)	-18 (2)	17 (2)
N(1)	109 (2)	100 (2)	97 (2)	-7 (2)	-10 (1)	-1 (1)
N(2)	106 (3)	123 (3)	115 (3)	-15 (3)	-43 (2)	-11 (2)
O(1)	149 (3)	110 (3)	121 (3)	-14 (2)	19 (2)	29 (3)
O(2)	144 (3)	114 (3)	124 (3)	-2 (2)	-49 (2)	26 (3)
O(3)	116 (3)	104 (3)	133 (3)	15 (3)	-33 (3)	0 (4)
O(4)	165 (4)	148 (4)	125 (4)	-25 (4)	10 (2)	-7 (2)
H(1)	455 (140)	514 (109)	421 (104)	148 (132)	106 (104)	158 (117)
H(2)	413 (75)	474 (174)	516 (145)	86 (91)	-241 (155)	-113 (79)
H(3)	501 (111)	295 (75)	640 (116)	-77 (80)	-75 (90)	225 (118)
H(4)	385 (90)	351 (100)	612 (129)	-66 (67)	346 (106)	42 (69)
H(5)	561 (156)	282 (74)	391 (75)	-103 (79)	28 (55)	-91 (92)
H(6)	432 (105)	278 (78)	355 (87)	-49 (85)	62 (67)	63 (85)
H(7)	397 (94)	297 (107)	501 (95)	52 (92)	-19 (81)	56 (75)
H(8)	254 (70)	371 (70)	325 (64)	-49 (66)	-2 (59)	-106 (60)
H(9)	454 (82)	239 (79)	404 (71)	-108 (70)	-1 (67)	51 (65)
H(10)	345 (73)	500 (88)	227(63)	107 (71)	-12 (58)	158 (72)
C(3)'	112	91	118	8	-28	17
C(4)'	91	86	95	-19	-18	17
O(3)'	116	104	133	15	-33	0
O(5)	106	123	115	15	-43	-11
H(6)'	435	285	355	-51	58	64

(c) Bond lengths ( $\text{\AA}$ )

C(1)-C(2)	1.536 (1)	C(1)-O(1)	1.262 (2)	C(1)-O(2)	1.246 (2)
C(2)-C(3)'	1.521	C(2)-C(3)	1.516 (1)	C(2)-N(1)	1.489 (1)
C(2)-H(8)	0.982 (33)	C(3)-C(4)	1.518 (1)	C(3)-H(10)	0.987 (35)
C(3)-H(9)	0.979 (41)	C(4)-N(2)	1.326 (2)	C(4)-O(3)	1.240 (2)
N(1)-H(5)	1.016 (23)	N(1)-H(3)	1.010 (21)	N(1)-H(4)	0.980 (22)
N(2)-H(7)	1.087 (26)	N(2)-H(6)	1.038 (27)	O(4)-H(1)	0.958 (19)
O(4)-H(2)	0.962 (20)	H(9)-C(3)'	0.986	H(10)-C(3)'	0.992
C(3)'-C(4)'	1.519	C(4)'-O(5)	1.329	C(4)'-O(3)'	1.212
O(5)-H(6)'	0.972				

$\theta_m$  is the maximum Bragg angle) as dictated by the diffraction data. Nevertheless, we believe the separations are meaningful by virtue of the refinement procedure. The overlap between the two molecules is depicted in Fig. 3. It was furthermore established that the carboxyl group of Asp adopts the commonly observed synplanar  $\text{O}=\text{C}-\text{O}-\text{H}$  conformation (Fig. 3), which is in agreement with that assumed in

Table 7. Asparagine-aspartic acid: intermolecular distances ( $\text{\AA}$ ) between overlapping atoms of the amide group of Asn and the carboxyl group of Asp

C(3)···C(3)'	0.018 (1)
C(4)···C(4)'	0.118 (1)
O(3)···O(3)'	0.120 (2)
N(2)···O(5)	0.192 (1)
H(5)···H(6)'	0.22

accounting for the effect of additive Asp on the crystal growth and habit of Asn.

The packing arrangement of the Asn-Asp solid solution is depicted in Fig. 6. The N(2)-H(6)···O(1) distance of 2.87  $\text{\AA}$  in Asn is replaced at the site of the additive by an O(5)-H(6)···O(1) H-bond of distance 2.85  $\text{\AA}$ , the N(2)-H(7)···O(2) bond of 3.01  $\text{\AA}$  is replaced by an O(5)···O(2) distance of 3.1  $\text{\AA}$ . This increase of 0.1  $\text{\AA}$ , not imposed by the refinement procedure, indicates a repulsive interaction between O(5) and O(2). In fact, the repulsive nature of this interaction was invoked to account for the distorted hydrogen-bonding geometry in the crystal structure of benzamide-succinic acid (Huang, Leiserowitz & Schmidt, 1973). The O···O repulsion energy has been calculated to be about 4-8  $\text{kJ mol}^{-1}$  in several amide(host)-carboxylic acid(guest) systems (Berkovitch-Yellin *et al.*, 1985).

The replacement of an attractive N-H···O bond along the **b** direction in Asn by a repulsive O···O interaction is consistent with the difference in cell dimensions between pure Asn and the Asn-Asp solid solution containing 15% occluded Asp (see Table 1); there is a distinct increase in the length of the *b* axis by 0.039 (2)  $\text{\AA}$  and a shortening of the *a* and *c* axes by 0.019 and 0.003  $\text{\AA}$  respectively.

Thus we may definitely conclude that the {010} plate-like shape of the Asn-Asp crystal is induced by O(hydroxyl)···O(carboxylate) repulsion along the *b* axis with the carboxyl group of adsorbed Asp exhibiting a synplanar  $\text{O}=\text{C}-\text{O}-\text{H}$  conformation.

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## Trimesic Acid, Its Hydrates, Complexes and Polymorphism. VIII.\* Interstitial Complexes of $\alpha$ - and (the Hypothetical) $\gamma$ -Trimesic Acid

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### Abstract

Interstitial complexes of  $\alpha$ -trimesic acid [TMA; Duchamp & Marsh (1969). *Acta Cryst.* **B25**, 5-19] have been prepared with guests such as Br<sub>2</sub> and acetone (composition TMA. $\frac{1}{6}$ X), and with hydroquinone and resorcinol (composition TMA. $\frac{1}{12}$ X). These complexes are isomorphous with  $\alpha$ -TMA; e.g. TMA. $\frac{1}{6}$ Br<sub>2</sub> is monoclinic, *C2/c* with  $a = 26.510$  (2),  $b = 16.449$  (5),  $c = 26.580$  (7) Å,  $\beta = 91.80$  (1)°,  $Z = 48$ . The structure was refined to  $R = 11.1\%$ . Determination of the structure showed that the Br<sub>2</sub> molecules are accommodated in a considerably disordered manner in cavities around  $0, \frac{1}{2}, \frac{1}{4}$ . High-temperature studies show that  $\alpha$ -trimesic acid transforms enantiotropically to a polycrystalline  $\beta$ -phase at  $\sim 543$  K which melts at  $\sim 603$  K. Single crystals of a third phase,  $\gamma$ , are formed by condensation of the vapour on cold surfaces. The  $\gamma$ -phase is isostructural [orthorhombic, *I222*,  $a = 24.225$  (7),  $b = 15.364$  (5),  $c = 16.562$  (6) Å,  $Z = 24$ ] with TMA.I<sub>5</sub> [Herbstein, Kapon & Reisner (1981). *Proc. R. Soc. (London) Ser. A*, **376**, 301-318]. The structure was refined to  $R = 8.4\%$ . The channel along  $0, 0, z$  which contains the linear I<sub>5</sub> anions in TMA.I<sub>5</sub> was found to be empty in  $\gamma$ -TMA. The cavity around  $\frac{1}{2}, 0, \frac{1}{2}$ , which contains disordered water molecules in TMA.I<sub>5</sub>, here accommodates disordered TMA and various benzenedicarboxylic acids, which are presumed to stabilize the  $\gamma$ -phase.

\* Part VII: Herbstein, Kapon & Reisner (1981).

### Introduction

The crystal structure of  $\alpha$ -trimesic acid (TMA; 1,3,5-benzenetricarboxylic acid) is characterized by the mutual triple catenation of pleated hexagonal networks of hydrogen-bonded TMA molecules (Duchamp & Marsh, 1969). Analogous mutual triple catenation of TMA networks has been found in TMA.0.7H<sub>2</sub>O.0.09HI<sub>5</sub>(TMA.I<sub>5</sub>) where the networks are planar and so arranged as to leave channels in which the pentaiodide ions are constrained from their usual V-shape to a linear configuration (Herbstein, Kapon & Reisner, 1981). The  $\alpha$ -TMA structure is tightly packed but nevertheless complexes of composition TMA. $\frac{1}{6}$ Br<sub>2</sub> and TMA. $\frac{1}{12}$ I<sub>2</sub> have been reported (Herbstein, 1968), with the halogen molecules presumably located in interstitial sites. Furthermore, we have found (unpublished results) that  $\alpha$ -TMA appears to undergo phase transitions at high temperatures [the melting point of TMA is given as  $\sim 653$  K (*Dictionary of Organic Compounds*, 1965)]. Interrelationships between these facets of the structural chemistry of trimesic acid are presented here.

### Interstitial complexes of $\alpha$ -TMA

#### Experimental

Trimesic acid was crystallized from saturated aqueous solutions of the five guest molecules studied here (for picric acid as a guest see Appendix 1). Deep-red and deep-purple crystals, respectively, of