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Structures of the crystalline supramolecular associates of imidazole with 1,1′-binaphthyl-8,8′-dicarboxylic acid and 2,2′-dihydroxy-1,1′-binaphthyl. Spatial similarity of the acid associate crystal packing to the active site of a serine protease

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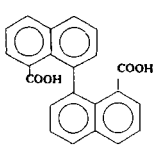
Crystal structure analysis of the imidazole associates with 1,1′-binaphthyl-8,8′-dicarboxylic acid (1), [1a, triclinic, P1, a = 7.569(4), b = 8.393(2), c = 8.634(1) Å, α = 93.21(2), β = 106.88(3), γ = 105.17(3)°, D_c = 1.36 g/cm³, Z = 1, R = 0.045 for 1031 data] and with 2,2′-dihydroxy-1,1′-binaphthyl (2), [2a, tetragonal $P4_12_12$, a = 8.519(1), c = 29.821(2), D_c = 1.30 g/cm³, Z = 4, R = 0.051 for 1236 reflections] revealed 1:1 and 1:2 stoichiometry, respectively. Spontaneous resolution occur during crystallization in both compound crystals. 1a is a salt-like associate with hydrogen bonds between the carboxylate and imidazolium ion pairs while the neutral 2a has also well defined hydrogen bonds between *host* and *guest* molecules. In a modeling experiment corresponding Brookhaven Protein Data Bank atomic coordinates from the active site of the bacterial serine protease enzyme Subtilisin BPN were fitted to the crystal packing of the small molecule associate 1a crystal. The relative displacement of the ion pair components and a symmetry related carboxyl function in 1a has fair steric resemblance to similar moieties in the active site of Subtilisin (Δ_{ave} = 0.24 Å for 9 fitted atoms). The agreement in the results of two fully independent and totally different (i.e. a native protein active site and an artificial small molecule associate) crystal structure determinations underlines the assumed conceptual similarity of crystals ("giant supramolecules") to protein sequences optimized through evolution.

INTRODUCTION

The imidazole moiety of the amino acid histidine is a fascinating component in chemistry[1] and biochemistry[2] as well. It has also been used in several modelling experiments. Both chemical[3] and structural[4] modelling attempts have been reported to elucidate the role of this facile chemical group. We aimed our efforts at the creation of non-covalently bound molecular associates in the solid state.[5] It was hoped that the resulting molecular associates supply information as to the behaviour of imidazole in chemically differing environments. Both the acid (**1**) and the alcohol (**2**)



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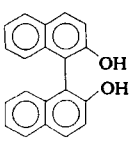

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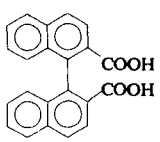

3

1a: 1.imidazole 1:1

2a : 2.imidazole 1:2

components of the title crystals were deemed to be attractive since the acid is a structural isomer of the successful inclusion host 1,1′-binaphthyl-2,2′-dicarboxylic acid (**3**)[6] while binaphthol (**2**), apart from being a widely used resolving agent,[7] offered an opportunity for mimicking the important hydroxyl function in many biochemical systems.[8] At the onset of this investigation we assumed that switching of the carboxylic functions of the host acid from the 2,2′ to the 8,8′ positions will help us in getting a ternary inclusion with imidazole and an alcohol eventually.

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Formation of a ternary solid state associate was noted for **1** with pyridine and acetic acid (1:1:1).[9] Apparently all known salt structures of **1** with pyridine easily form *intra*molecular -COOH···COO$^-$ hydrogen bonds. These are assumed to stabilize salt associates of such dicarboxylic acids.

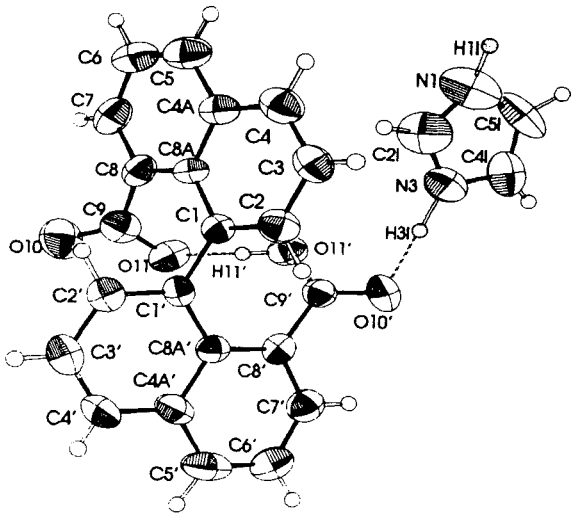

Figure 1 Perspective view of **1a** with internal hydrogen bonds dashed.

DISCUSSION

Molecular structures

The molecular shapes of both title associates (**1a** and **2a**) are presented in Figs 1 and 2. A summary of the experimental and crystallographic data is in Table 1, while Table 2 contains the final atomic coordinates for both **1a** and **2a**. Relevant bonding geometry is in Tables 3 and 4.

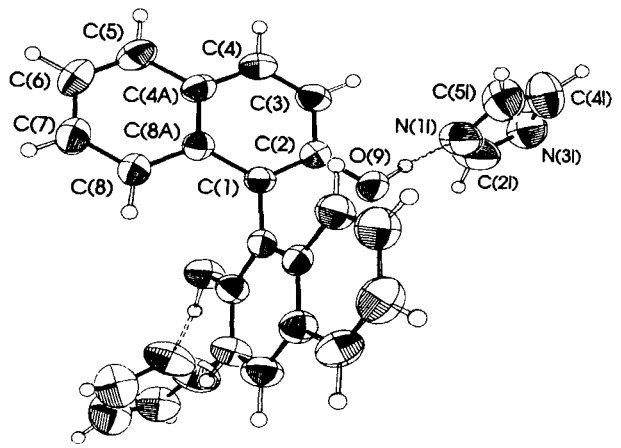

Figure 2 Perspective view of **2a** with internal hydrogen bonds dashed.

Table 1 Summary of crystal data and experimental details

Compound	*1a*	*2a*
Formula	$C_{25}H_{18}N_2O_4$	$C_{26}H_{22}N_4O_2$
F.W.	410.43	422.49
Crystal size (mm):	0.12 × 0.22 × 0.35	0.20 × 0.40 × 0.50
Radiation	CuKα,λ = 1.54184 Å	CuKα,λ = 1.54184 Å
Temperature	296(1) K	296(1) K
Space group	**P1**	$P4_12_12$
a	7.569(4) Å	8.519(1) Å
b	8.393(2) Å	8.519(1) Å
c	8.634(1) Å	29.821(2)
α	93.21(2)	90
β	106.88(3)	90
γ	105.17(3)°	90
V	501.3(6) Å^3	2164.0(7) Å^3
Z	1	4
D_C(g/cm^3)	1.36	1.30
μ(cm^{-1})	7.2	6.4
Scan width, ω°	0.5 + 0.14*tan θ	0.4 + 0.14*tan θ
Maximum 2θ	150.0°	150.0°
No. of refl./total	1924	1460
unique	1695	1337
No. of refl. $F_0^2 > 3*\sigma(F_0^2)$	1031	1236
Parameters refined	277	145
R factor, unweighted	0.045	0.051
$R_{weighted}$	0.045	0.046
R_{total}	0.087	0.080
Esd of obs. of unit weight	1.28	0.80
Largest shift Δ/σ	0.95	0.29
Residual e.d. (e/Å^3)	0.13(3)	0.19(3)

Table 2 (a) Fractional atomic coordinates for **1a**

Atom	*x/a*	*y/b*	*z/c*	*B(eq)/B*
C(1)	0.8506	0.7140	0.2980	2.37(6)
C(2)	1.0479(6)	0.7577(5)	0.3596(5)	3.16(7)
C(3)	1.1444(6)	0.6879(6)	0.4883(5)	3.69(8)
C(4)	1.0398(6)	0.5704(6)	0.5550(6)	3.91(8)
C(4a)	0.8363(6)	0.5211(5)	0.4977(5)	3.13(7)
C(5)	0.7260(7)	0.3932(5)	0.5606(6)	3.9(1)
C(6)	0.5355(7)	0.3456(6)	0.5086(6)	4.19(9)
C(7)	0.4365(6)	0.4296(6)	0.3941(6)	4.37(9)
C(8)	0.5350(6)	0.5569(5)	0.3292(5)	3.29(7)
C(8a)	0.7392(5)	0.6001(5)	0.3737(5)	2.57(6)
C(9)	0.4178(6)	0.6580(6)	0.2287(5)	3.69(9)
O(10)	0.2747(5)	0.5900(5)	0.1102(4)	6.14(8)
O(11)	0.4698(4)	0.8159(3)	0.2790(4)	3.84(5)
C(1')	0.7636(5)	0.7679(5)	0.1399(4)	2.59(6)
C(2')	0.6683(6)	0.6453(6)	0.0081(5)	3.69(8)
C(3')	0.6039(7)	0.6789(7)	−0.1523(6)	4.75(9)
C(4')	0.6403(7)	0.8389(7)	−0.1787(5)	4.84(9)
C(4a')	07296(6)	0.9745(6)	−0.0478(5)	3.30(7)
C(5')	0.7650(6)	1.1392(6)	−0.0808(6)	4.29(9)
C(6')	0.8519(6)	1.2705(6)	0.0426(6)	3.92(9)
C(7')	0.9002(6)	1.2366(6)	0.2014(6)	3.61(8)
C(8')	0.8658(5)	1.0790(5)	0.2437(5)	2.61(6)
C(8a')	0.7882(5)	0.9410(5)	0.1150(5)	2.55(6)
C(9')	0.9116(6)	1.0679(5)	0.4218(5)	3.18(6)
O(10')	1.0639(4)	1.1574(4)	0.5188(4)	5.18(6)
O(11')	0.7775(4)	0.9784(3)	0.4739(3)	3.41(5)
N(1)	1.2454(6)	0.9214(6)	1.0056(5)	4.8(1)
C(2i)	1.1557(8)	0.9268(7)	0.8531(7)	5.2(1)
N(3)	1.1643(6)	1.0798(5)	0.8263(5)	4.6(1)
C(4i)	1.2647(7)	1.1810(7)	0.9736(7)	5.9(1)
C(5i)	1.3150(8)	1.0809(8)	1.0829(7)	6.4(1)
H(2)	1.127	0.844	0.308	3.5(8)
H(3)	1.274	0.713	0.521	5.4(9)
H(4)	1.107	0.524	0.643	6(1)
H(5)	0.796	0.354	0.647	5.7(9)
H(6)	0.468	0.256	0.552	6(1)
H(7)	0.303	0.402	0.357	6(1)
H(2')	0.649	0.526	0.034	5.2(9)
H(3')	0.555	0.595	−0.242	4.4(9)
H(4')	0.606	0.860	−0.274	4.5(9)
H(5')	0.716	1.152	−0.194	5.2(9)
H(6')	0.877	1.382	0.021	7(1)
H(7')	0.961	1.325	0.289	5.4(9)
H(2i)	1.101	0.835	0.774	6(1)
H(4i)	1.288	1.293	0.985	6(1)
H(5i)	1.401	1.112	1.192	8(1)
H(3i)	1.115	1.119	0.702	10(1)
H(1i)	1.335	0.841	1.058	14(2)
H(11')	0.686	0.905	0.389	13(2)

The important structural features of the **1a** associate are connected with the salt formation. A comparison (c.f. Fig. 3) of the relevant bond lengths between **1a** and the related imidazole/imidazolium associates of the 2,2--diacid **3**[4b] indicates that proton transfer occurred in **1a** i.e. a proton from one of the -COOH groups was displaced to the imidazolium unit. This result underines that the initial assumption was partly

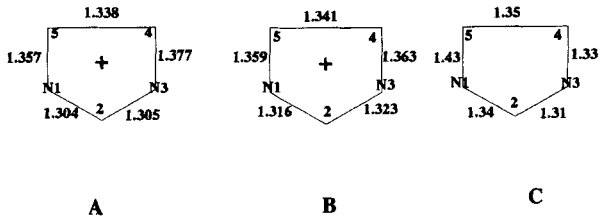

Figure 3 Imidazole ring bond distances in the imidazole associates **1a** (**A**), 3.imidazolium.H_2O 1:2:2[4b] (**B**) and in 3.imidazole 1:2 (**C**). Standard deviations albeit not indicated are generally in the order of magnitude of the last significant digits.

correct. Due to the easily formed internal hydrogen bridge the environment based on molecule **1** can stabilize an ion pair more than **3** can, i.e. without the use of additional components like water molecules.[4b]

This change can be also visualized in terms of some characteristic dihedral angles of the **1** and **3** host molecules in the proper environments (c.f. Table 5). One can note that the geometry of **1** assumes an intermediary state between the ionic and (partly) neutral forms of the imidazole associates of **3**. The inclination of the naphtalene rings is no longer perpendicular and the carboxyl/carboxylate inclination angles correspond to intermediate values as found for the extremes in the other two structures.

The molecular structure of **2a** does not feature any unexpected bonding dimension. The most remarkable observation pertains to the matching of the molecular symmetry with a twofold crystallographic rotor.

Aggregate structures

A basic difference in the packing between the imidazole associates of the 2,2' isomer of 1,1'-binaphthyl-dicarboxylic acid (**3**) and **1** is the loss of the center of symmetry in the crystal lattice of the latter associate (Fig. 4). Both of the 2,2'-diacid associates are formed

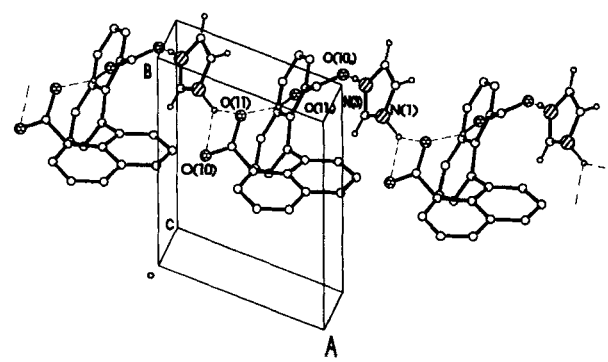

Figure 4 Packing excerpt in **1a** with H-bonds indicated in dashed lines. Skeleton H atoms are omitted for clarity, O and N atoms are highlighted with different shading.

Table 3 Bond distances (Å) of non-hydrogen atoms and of some relevant hydrogen atoms in **1a**

C(1)–C(2)	1.370(3)	C(8)–C(9)	1.513(5)	C(7')–C(8')	1.371(5)
C(1)–C(8a)	1.421(3)	C(9)–O(10)	1.230(5)	C(8')–C(8a')	1.429(6)
C(1)–C(1')	1.485(4)	C(9)–O(11)	1.289(5)	C(8')–C(9')	1.488(6)
C(2)–C(3)	1.392(6)	C(1')–C(2')	1.370(6)	C(9')–O(10')	1.229(5)
C(3)–C(4)	1.361(6)	C(1')–C(8a')	1.452(5)	C(9')–O(11')	1.305(4)
C(4)–C(4a)	1.411(4)	C(2')–C(3')	1.399(7)	O(11')–H(11')	0.912(3)
C(4a)–C(5)	1.415(5)	C(3')–C(4')	1.345(7)	N(1)–C(2i)	1.304(7)
C(4a)–C(8a)	1.416(5)	C(4')–C(4a')	1.428(7)	N(1)–C(5i)	1.357(8)
C(5)–C(6)	1.320(4)	C(4a')–C(5')	1.399(6)	N(1)–H(1i)	1.102(4)
C(6)–C(7)	1.400(6)	C(4a')–C(8a')	1.414(6)	C(2i)–N(3)	1.305(6)
C(7)–C(8)	1.380(6)	C(5')–C(6')	1.365(7)	N(3)–C(4i)	1.377(7)
C(8)–C(8a)	1.419(3)	C(6')–C(7')	1.379(7)	N(3)–H(3i)	1.128(4)
C(4i)–C(5i)	1.338(8)	C(1)–C(1)	1.489(3)		

Table 4 Bond distances (Å) in **2a**

C(1)–C(2)	1.374(4)	C(4)–C(4a)	1.404(5)	C(7)–C(8)	1.377(5)
C(1)–C(8a)	1.429(4)	C(4a)–C(5)	1.434(5)	C(8)–C(8a)	1.415(4)
C(2)–C(3)	1.406(5)	C(4a)–C(8a)	1.413(4)	N(1i)–C(2i)	1.340(6)
C(2)–O(9)	1.367(4)	C(5)–C(6)	1.356(5)	N(1i)–C(5i)	1.310(5)
C(3)–C(4)	1.347(5)	C(6)–C(7)	1.411(5)	C(2i)–N(3i)	1.316(5)
N(3i)–C(4i)	1.309(6)	C(4i)–C(5i)	1.348(7)		

Table 4 (b) Fractional atomic coordinates for **2a**

Atom	*x/a*	*y/b*	*z/c*	*B(eq)/B*
C(1)	0.7191(3)	0.3794(3)	0.73479(8)	3.1(1)
C(2)	0.6614(3)	0.4365(3)	0.69500(9)	3.5(1)
C(3)	0.7560(4)	0.5232(4)	0.66536(9)	4.4(1)
C(4)	0.9065(4)	0.5549(4)	0.6759(1)	4.5(1)
C(4a)	0.9717(3)	0.5036(4)	0.7166(1)	3.9(1)
C(5)	1.1301(4)	0.5401(4)	0.7290(1)	4.9(1)
C(6)	1.1908(4)	0.4913(5)	0.7687(1)	5.4(1)
C(7)	1.0975(4)	0.4023(4)	0.7984(1)	5.2(1)
C(8)	0.9454(4)	0.3640(4)	0.7872(1)	4.3(1)
C(8a)	0.8779(3)	0.4152(3)	0.74639(9)	3.3(1)
O(9)	0.5083(2)	0.4075(3)	0.68411(6)	4.7(1)
N(1i)	0.4032(3)	0.5549(4)	0.61164(9)	6.6(1)
C(2i)	0.2994(5)	0.6726(6)	0.6087(1)	7.5(2)
N(3i)	0.2501(4)	0.6866(4)	0.5670(1)	6.4(1)
C(4i)	0.3313(5)	0.5886(6)	0.5424(1)	7.7(2)
C(5i)	0.4262(5)	0.5079(5)	0.5703(1)	6.9(2)
H(3)	0.714	0.555	0.636	5.1(7)
H(4)	0.971	0.612	0.654	3.3(5)
H(5)	1.192	0.600	0.707	5.0(6)
H(6)	1.301	0.525	0.777	6.6(7)
H(7)	1.145	0.376	0.825	5.1(6)
H(8)	0.887	0.298	0.809	5.9(8)
H(9)	0.470	0.477	0.656	7.5(8)
H(2i)	0.237	0.719	0.637	8.1(9)
H(3i)	0.182	0.768	0.559	10(1)
H(4i)	0.316	0.589	0.510	8(1)
H(5i)	0.508	0.437	0.561	7(1)

Table 5 Inclination of characteristic planes (°) of **1** and **3** host molecules in their imidazole associates. A, B and C notations are as for Fig. 3. N_1 and N_2 denotes naphtalene planes, taken always with their respective -COOH/COO− groups. Deprotonated acid groups and their inclination are marked by an *

Planes	*A*	*B*	*C*
N_1/N_2	66.0(1)	81.6(1)	87.7(2)
N_1/COO*	57.7(3)*	74.5(1)*	50.4(5)
N_2/COOH	51.8(2)	50.6(1)	25.2(3)

around centres of symmetry[4b] while in **1a** the lattice lacks even this simplest of symmetries, i.e. the crystal lattice is built from pure 3D-translations maintaining endless hydrogen bonding contacts (Table 6). It is indicated, that hydrogen bonding at H1 of the imidazolium has a bifurcated nature. This is a plausible consequence of the steric positions of the oxygen atoms of the carboxylate acceptor.

The packing in structure **2a** shows helical turns of imidazole and binaphtol molecules associated mainly through hydrogen bonds as shown in Fig. 5. The hydrogen bond linking imidazole with **2** is a well defined contact as shown by the respective geometries.

Table 6 Hydrogen bond geometries in **1a** and **2a**. Distances are in (Å), angles in °. E.s.d.s are given for parameters where all atoms were refined

Acceptor		*H---Donor (Å)*		*A···H--D Angle*		*A···D (Å)*
O(10′)	1.59	H(3i)	1.13	N(3)	172	2.708(6)
$O(10)_{1+x,y,1+z}$	2.14	H(1i)	1.10	N(1)	134	3.015(7)
$O(11)_{1+x,y,1+z}$	1.94	H(1i)	1.10	N(1)	134	2.817(6)
O(11)	1.58	H(11′)	0.91	O(11′)	153	2.433(4)
$O(9)_{0.5-x,0.5+y,1.25-z}$	2.02	H(3i)	0.93	N(3i)	156	2.896(4)
O(9)	1.07	H(9)	1.59	N(1i)	171	2.655(4)

Table 7 Final cartesian coordinates from a least-squares adjustment of translational coordinates and Euler angles of Model B (**1a** with a COO^- at 1 + x, y, 1 + z) to Model A (SUBTILISIN active site). First 9 atoms were fitted (W202 site in enzyme (in fact a SO_4^{2-} anion) is matched to COOH)

Assumed model (A, Subtilisin)				Fitted model (B, **1a**)				
Atm/Res	*XO*	*YO*	*ZO*	*Atom*	*XO*	*YO*	*ZO*	*Δ (Å)*
Nδ64	20.1	24.0	23.8	N1	20.339	24.106	23.741	0.268
Cγ64	19.8	23.0	23.1	C5I	19.823	23.028	23.099	0.036
Cδ264	19.5	23.3	21.9	C4I	19.523	23.388	21.847	0.106
Nε264	20.0	24.6	21.8	N3	19.851	24.721	21.734	0.204
Cε164	20.2	25.0	23.0	C2I	20.343	25.090	22.886	0.204
Oδ132	21.0	24.7	26.4	O10	21.269	24.618	26.564	0.325
Oδ232	20.3	22.8	26.4	O11	20.132	22.758	26.206	0.260
Cγ32	20.9	23.6	26.9	C9	20.631	23.655	26.988	0.288
O202	19.3	26.9	19.6	O10′	19.189	26.535	19.835	0.448
				Other atoms				
Oγ221	21.4	27.0	20.6	O11′	21.273	27.247	19.895	0.758

Final Euler angles and translations (Å) for Model B*

$E_A = 14.11$ $E_B = 148.81$ $D_C = -103.19$ $X_{TR} = 26.708$ $Y_{TR} = 33.526$ $Z_{TR} = 22.501$

Statistics for 9 fitted atom pairs

	$\Delta(X)^2$	$\Delta(Y)^2$	$\Delta(Z)^2$	Distance
Average	0.0318	0.0208	0.0168	0.0238 Å

* For details see ref. [4b].

Comparison of the crystal structure of ***1a*** *with a subtilisin active site.* Modelling experiments were carried out using atomic coordinates of *Subtilisin BPN* from the Protein Data Bank.[10] The agreement of structural motifs observed in two totally independent systems seemed to be less precise first as compared for the imidazol dihydrate associate of **3**. However, closer scrutiny and subsequent least-squares fitting of imidazole moieties of HIS64 and the packing generated pattern in **1a** crystal by a numeric procedure[11] yielded comparable atomic positions between those in the enzyme's active site and of the packing pattern in **1a**. The agreement pertains to a fair matching of 9 fitted atoms ($\Delta_{ave} = 0.24$ Å, c.f. Table 7). In the model used for the fitting the following atoms are matched: atoms of the carboxylate moiety in **1a** with ASP32 (three atoms), those of the imidazolium ion in **1a** to HIS64 (five sites) and O10′ oxygen of the next, translation related carboxyl function of molecule **1a** in the crystal. Interestingly, this latter position corresponds to a site designated as a water molecule W202 in the enzyme. However, this atomic site was proved to be a *sulphate anion* i.e. a negatively charged species by subsequent analysis.[10b] "Water" 202 comes close and probably forms a hydrogen bond to the γ oxygen of SER221 of the enzyme. The other oxygen (O11′) atom of the above said crystal carboxyl approaches then the Oγ221 position by 0.76 Å. These results underlines our former conclusion[4b] on the steric similarity of supramolecular crystalline aggregates to those of the active site geometry in serine protease enzymes. It is also plausible to assume on such basis that electrostatic

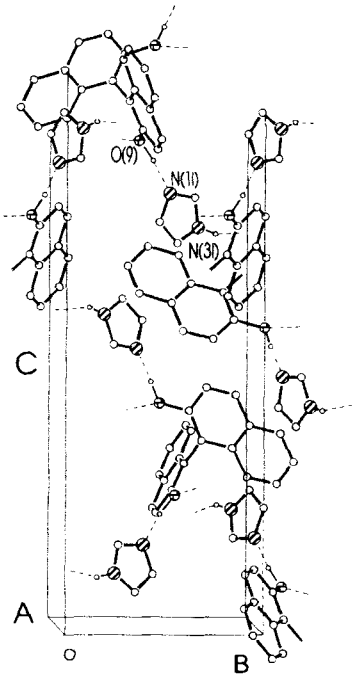

Figure 5 Packing in **2a**. Molecules at top and bottom of the unit cell are cropped, designations are as for Fig. 4.

similarity persists in this case as well.[4b] The assumption that serine protease enzymes are triggered for catalysis even in their native form is supported by observing independently anions in the active cleft of such enzymes[2d] and by partially negative charged moieties in **1a** and related crystals[4b] at comparable displacements. Presence of sulphate anions separated well from their counter cations is also seen plausibly in the crystals of simple salt complexes.[20] It is quite possible then that an enzyme does have the ability in an aqueous milieu to sustain such an environment.

EXPERIMENTAL

Synthesis

Host compounds **1**[9] and **2**[12] were prepared according to the literature: **1** (87%, m.p. 308–310 °C), **2** (58%, m.p. 215 °C).

Crystal growth

1a Suitable single crystals for X-ray diffraction were grown with the hope of obtaining a ternary inclusion of **1** with imidazole and an alcohol. Dilute 1:2 molar ratio solutions of **1** and imidazole were prepared in ethylacetate. After carefully mixing, a solution of three molar equivalents of ethanol in ethylacetate was also added. Relative small crystals appeared in several hours which contrary to expectations, do not include alcohol. Variations of simple alcohols and additional water in the system did not yield crystals of appreciable quality for an X-ray study.

2a Suitable crystals for X-ray diffraction were obtained by slow cooling of a hot solution of **2** and imidazole in methanol.

Crystallography

Experimental data are summarized in Table 1. Preliminary examinations and data collections were performed for both crystals with CuK_α radiation (λ = 1.54184 Å) on an Enraf-Nonius CAD4 computer controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator.

1a A pale yellow rhombohedron crystal measuring 0.12 × 0.22 × 0.35 mm was mounted in a glass capillary in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $25 < \theta < 38°$, measured by the computer controlled diagonal slit method of centering. The triclinic cell parameters and calculated volume are **a** = 7.569(4), **b** = 8.393(2), **c** = 8.634(1) Å, α = 93.21(2), β = 106.88(3), γ = 105.17(3)°, **V** = 501.3(6) Å^3. For **Z** = 1 and F.W. = 410.43 the calculated density is 1.36 g/cm^3. The lack of systematic absences and the Z value indicated the space group to be **P1** (# 1). The data were collected at a temperature of 296(1)K using the ω-2θ scan technique. The scan rate varied from 1 to 20 °/min (in ω). Data were collected to a maximum 2θ of 150.0° (minimum 2θ = 3.0°). The scan range (in °) was determined as a function of θ to correct for the separation of the K_α doublet.[13] Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. A total of 1924 reflections were collected ($h_{min} = 0$, $h_{max} = 9$, $k_{min} = -10$, $k_{max} = 10$, $l_{min} = -10$, $l_{max} = 10$) of which 1695 were unique. As a check on crystal and electronic stability three standards were measured every 60 min. No decay correction was necessary. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 7.2 cm^{-1} for CuK_α radiation. An empirical spherical absorption correction[14] was applied. Relative transmission coefficients ranged from 0.814 to 1.515 with an average value of 0.991. Extinction correction was not performed.

2a A transparent bipyramidal crystal measuring ca. 0.20 × 0.40 × 0.50 mm was mounted on a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $35 < \theta < 39°$. The tetragonal cell parameters and calculated volume are

$\mathbf{a} = 8.519(1), \mathbf{c} = 29.821(2)$ Å, $\mathbf{V} = 2164.0(7)$ Å^3. From the systematic absences and from subsequent least-squares refinement, the space group was determined to be $\mathbf{P4_12_12}$ (# 92). The data were collected under similar conditions as for **1a** including temperature and scanning. A total of 1460 reflections were collected ($h_{min} = 0$, $h_{max} = 10$, $k_{min} = 0$, $k_{max} = 10$, $l_{min} = 0$, $l_{max} = 37$) of which 1337 were unique, non-zero and not systematically absent. Lorentz and polarization corrections were applied to the data. The linear absorption correction[14] was applied. Relative transmission coefficients ranged from 0.865 to 1.193 with an average value of 0.989.

Structure model and refinement

The initial structure models were obtained by direct methods for both crystals.

1a Using 301 reflections ($E_{min} = 1.30$) and 2898 relationships, a total of 31 phase sets were produced. Twenty-one atoms were located from an E-map prepared from the "best" phase set. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|Fo| - |Fc|)^2$ and the weight **w** is defined as $4Fo^2/\sigma(Fo^2)^2$. The standard deviation on intensities, $\sigma(F_0^2)$, is defined as $\sigma(F_0^2) = ([\mathbf{S}^2(\mathbf{C} + \mathbf{R}^2\mathbf{B}) + (\mathbf{p}F_0^2)^2]/\mathbf{Lp})^2$, where **S** is the scan rate, **C** is the total integrated peak count **R** is the ratio of scan time to background counting time, **B** is the total background count, **Lp** is the Lorentz-polarization factor, and the parameter **p** is a factor introduced to downweight intense reflections. Here p was set to 0.050. Scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in Fc;[16] the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] Only 1031 reflections having their intensities greater than $3.0*\sigma(I)$ were used in the refinements. The final cycle of refinement included 277 variable parameters and converged (largest $\Delta/\sigma = 0.95$) with unweighted and weighted agreement factors of $R = 0.045$ and $R_w = 0.045$. The standard deviation of an observation of unit weight was 1.28. The highest peak in the final difference Fourier had a height of 0.13 eÅ^{-3}.

2a Six phase sets were produced using 180 reflections ($E_{min} = 1.48$, 3511 relationships). Sixteen atoms were located from an E-map prepared from the 'best' phase set. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares like for **1a** except that the weight w was defined as 1.0 for all observed reflections. Scattering factors applied were as for **1a**. Only the 1236 reflections with $\mathbf{I} > 3.0\sigma(\mathbf{I})$ were used in the refinements. The final cycle included 145 variable parameters and converged (largest $\Delta/\sigma = 0.29$) with unweighted and weighted agreement factors of $R = 0.051$ and $R_w = 0.046$. The S value and the highest residual density were 0.80 and 0.19 eÅ^{-3}, respectively. All calculations were performed on a PDP-11/34 128Kw minicomputer using SDP-PLUS and local programs.[19]

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