Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

(1*R*,3*S*)-Camphoric acid as a building block in supramolecular chemistry: adducts with organic polyamines

Choudhury M. Zakaria,[a]† George Ferguson,[a,b] Alan J. Lough[c] and Christopher Glidewell[a]*

[a]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, UK, [b]Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and [c]Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6

† On leave from Department of Chemistry, University of Rajshahi, Rajshahi, Bangladesh.

Correspondence e-mail: cg@st-andrews.ac.uk

Received 27 November 2002
Accepted 10 December 2002

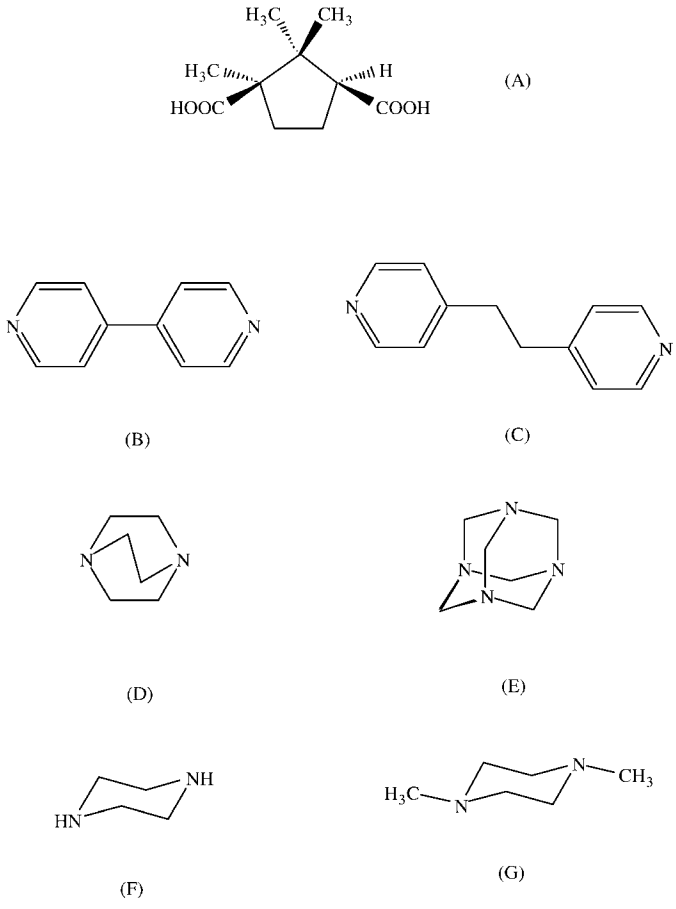
(1*R*,3*S*)-Camphoric acid [(1*R*,3*S*)-1,2,2,-trimethylcyclopentane-1,3-dicarboxylic acid, $C_{10}H_{16}O_4$] forms adducts with a range of amines in which the acid component may be the neutral molecule, the mono-anion $(C_{10}H_{15}O_4)^-$ or the di-anion $(C_{10}H_{14}O_4)^{2-}$. The structures generated by the hard hydrogen bonds take the form of chains in the 1:1 adducts (II) and (III) formed with 4,4′-bipyridyl and 1,2-bis(4-pyridyl)-ethane. There are single sheets in the hydrated 1:1 adduct (IV) formed with 1,4-diazabicyclo[2.2.2]octane, and pairwise-interwoven sheets in the 2:1 adduct (V) formed with hexamethylenetetramine. Three-dimensional frameworks are present in the salt-like 1:1 adduct (VI) formed with piperazine and in the hydrated 3:1 adduct (VII) formed with *N*,*N*′-dimethylpiperazine. This latter adduct contains both neutral $C_{10}H_{16}O_4$ and anionic $(C_{10}H_{15}O_4)^-$ units. In (II), (III) and (IV), the chain and sheet substructures are linked by C—H···O hydrogen bonds to form three-dimensional frameworks. The monoclinic polymorph of camphoric acid itself (I) has been reinvestigated.

1. Introduction

We have recently studied the supramolecular structures of a range of adducts formed by the enantiopure carboxylic acids (2*R*,3*R*)-tartaric acid and (*S*)-malic acid with organic amines (Farrell *et al.*, 2002*a*,*b*). While the primary aim of these studies was the comparison of the structural behaviour of the enantiopure acids on the one hand and their racemic analogues on the other, it became clear that both acids could exhibit a degree of conformational flexibility, specifically by rotation about the C2—C3 bond. This flexibility was only partially moderated by the formation of intramolecular hydrogen bonds. Accordingly, we have now turned to the enantiopure and essentially rigid dicarboxylic acid (1*R*,3*S*)-camphoric acid [(1*R*,3*S*)-1,2,2,-trimethylcyclopentane-1,3-dicarboxylic acid, $C_{10}H_{16}O_4$] (*A*, see scheme below). Here we report the molecular and supramolecular structures of the adducts formed by this acid with a representative selection of organic amines, namely the heteroaromatic diamines 4,4′-bipyridyl (*B*) and 1,2-bis(4-pyridyl)ethane (*C*), the cage amines 1,4-diazabicyclo[2.2.2]octane (DABCO) (*D*) and hexamethylenetetramine (*E*), and the saturated monocyclic diamines piperazine (*F*) and *N*,*N*′-dimethylpiperazine (*G*).

In addition we have reinvestigated the monoclinic polymorph of camphoric acid itself (I). The adducts discussed here are camphoric acid–4,4′-bipyridyl (1/1), $C_{10}H_{16}O_4\cdot C_{10}H_8N_2$ (II); camphoric acid–1,2-bis(4-pyridyl)ethane (1/1), $C_{10}H_{16}O_4\cdot C_{12}H_{12}N_2$ (III); camphoric acid–DABCO–water (1/1/1) $C_{10}H_{16}O_4\cdot C_6H_{12}N_2\cdot H_2O$ (IV); camphoric acid–hexamethylenetetramine (2/1), $(C_{10}H_{16}O_4)_2\cdot C_6H_{12}N_4$ (V);

camphoric acid–piperazine (1/1), $C_{10}H_{16}O_4{\cdot}C_4H_{10}N_2$ (VI); and camphoric acid-*N*,*N*′-dimethylpiperazine–H_2O (3/1/2), $(C_{10}H_{16}O_4)_3{\cdot}C_6H_{14}N_2{\cdot}(H_2O)_2$ (VII).



Very little use has been made to date of camphoric acid as a building block for supramolecular chemistry, but we note here the recently reported 1:1 adduct formed with 2-aminopyrimidine (Goswami *et al.*, 2000). Although described as a heterodimer, the structure actually contains a rather elegant chain of rings generated by paired O—H···N and N—H···O hydrogen bonds, while the chains are loosely linked into sheets by a single very weak C—H···O hydrogen bond.

2. Experimental

2.1. Syntheses

Stoichiometric quantities of camphoric acid and the appropriate amine, which were arranged to give equal numbers of carboxyl groups and amino N atoms, were separately dissolved in methanol solution. The pairs of solutions were mixed and the mixtures were set aside to crystallize, to give analytically pure (II)–(VII). Analyses: (II) found C 67.3, H 6.8, N 7.8%, $C_{20}H_{24}N_2O_4$ requires C 67.4, H 6.8, N 7.9%; (III) found C 68.7, H 8.3, N 7.3%, $C_{22}H_{28}N_2O_4$ requires C 68.7, H 7.3, N 7.3%; (IV) found C 58.4, H 9.1, N 9.0%, $C_{16}H_{30}N_2O_5$ requires C 58.2, H 9.2, N 8.5%; (V) found C 57.8, H 8.1, N 10.6%, $C_{26}H_{44}N_4O_8$ requires C 57.8, H 8.2, N 10.4%; (VI) found C 58.4, H 9.2, N 9.8%, $C_{14}H_{26}N_2O_4$ requires C 58.7, H 9.2, N 9.8%; (VII) consistent analysis not obtained, $C_{36}H_{66}N_2O_{14}$ requires C 57.6, H 8.9, N 3.7%. Crystals of (II)–(VII) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples. The crystals of camphoric acid (I) were also grown from methanol. In a similar way we have prepared 1:1 adducts (VIII) and (IX), respectively, of camphoric acid with 1,2-diaminoethane and with 1,2-bis(4-pyridyl)ethene, but for neither of these have crystals of adequate quality yet been obtained. Analyses: (VIII) found C 55.8, H 9.6, N 11.0%, $C_{12}H_{24}N_2O_4$ requires C 55.4, H 9.3, N 10.8%; (IX) found C 68.8, H 7.9, N 7.4%, $C_{16}H_{28}N_2O_4$ requires C 69.1, H 6.9, N 7.3%.

2.2. Data collection, structure solution and refinement

Diffraction data for (I)–(VII) were collected at 150 (1) K using a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data-collection and refinement are summarized in Table 1, together with details of the software employed.

For (I), the systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups: $P2_1$ was selected, and confirmed by the successful structure analysis. For (II), the systematic absences indicated one of the two enantiomorphous space groups $P3_121$ and $P3_221$. Compound (III) is triclinic, and the space group $P1$ was selected and confirmed by the successful structure analysis. For each of (V)–(VII), the space group $P2_12_12$ was uniquely assigned from the systematic absences; likewise space group $P2_12_12_1$ was assigned to (IV). For (II), the correct space group was assigned from the known absolute configuration of the starting (1*R*,3*S*)-camphoric acid, and for each of the remaining compounds the absolute structure was likewise set by reference to this known configuration. The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based on $P = (F_o^2 + 2F_c^2)/3$ was employed in order to reduce statistical bias (Wilson, 1976), and in all refinements the Friedel equivalents were merged. For (I) and (III), where Z' = 2 and 4, respectively, *ADDSYM* (Spek, 2003) revealed no additional symmetry. In (II), the carboxyl H atoms were included in the refinement at locations identified from difference maps. This refinement lead to O—H distances of 1.03 and 1.05 Å. All other H atoms were included in the refinements as riding atoms with distances O—H 0.84 Å (carboxyl) or 0.90 Å (water), N—H 0.92 or 0.93 Å, and C—H 0.95–1.00 Å.

In (II), the amine component is ordered across a twofold rotation axis, while the camphoric acid component is disordered across a different twofold axis. For (III), Z' = 4, and all four independent acid components show orientational disorder, while two of the diamines are fully ordered and the other two exhibit positional disorder. All components were initially refined with individual occupancy factors, but it soon became apparent that the disorder could be adequately treated with one pair of tied occupancy factors, which refined

Table 1
Experimental table.

	I	II	III	IV
Crystal data				
Chemical formula	$C_{10}H_{16}O_4$	$C_{10}H_{16}O_4{\cdot}C_{10}H_8N_2$	$C_{12}H_{12}N_2{\cdot}C_{10}H_{16}O_4$	$C_6H_{13}N_2^+{\cdot}C_{10}H_{15}O_4^-{\cdot}H_2O$
M_r	200.23	356.41	384.46	330.42
Cell setting, space group	Monoclinic, $P2_1$	Trigonal, $P3_121$	Triclinic, $P\overline{1}$	Orthorhombic, $P2_12_12_1$
a, b, c (Å)	7.7206 (3), 11.6677 (5), 12.5830 (5)	6.7302 (10), 6.7302 (10), 34.345 (7)	8.5318 (2), 10.3775 (2), 23.3884 (5)	7.031 (3), 11.252 (5), 21.8177 (12)
α, β, γ (°)	90.00, 105.653 (2), 90.00	90.00, 90.00, 120.00	99.819 (8), 95.478 (8), 90.787 (9)	90.00, 90.00, 90.00
V (Å^3)	1091.46 (8)	1347.3 (4)	2030.17 (8)	1726.06 (14)
Z, Z'	4, 2	3, 0.5	4, 4	4, 1
D_x (Mg m^{-3})	1.219	1.318	1.258	1.272
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	2608	1103	9230	1768
θ range (°)	2.8–27.5	3.5–26.0	2.6–27.4	2.6–25.0
μ (mm^{-1})	0.09	0.09	0.09	0.09
Temperature (K)	150 (1)	150 (1)	150 (1)	150 (1)
Crystal form, colour	Needle, colourless	Block, colourless	Block, colourless	Plate, colourless
Crystal size (mm)	0.30 × 0.12 × 0.12	0.35 × 0.32 × 0.30	0.36 × 0.28 × 0.18	0.38 × 0.32 × 0.11
Data collection				
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	None	None	None	None
T_{min}	–	–	–	–
T_{max}	–	–	–	–
No. of measured, independent and observed parameters	9392, 2608, 2126	4738, 1103, 889	34201, 9230, 7063	7008, 1768, 1423
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.043	0.034	0.064	0.058
θ_{max} (°)	27.5	26.0	27.4	25.0
Range of h, k, l	$0 \Rightarrow h \Rightarrow 10$ $0 \Rightarrow k \Rightarrow 15$ $-16 \Rightarrow l \Rightarrow 15$	$0 \Rightarrow h \Rightarrow 8$ $-6 \Rightarrow k \Rightarrow 0$ $-41 \Rightarrow l \Rightarrow 42$	$0 \Rightarrow h \Rightarrow 11$ $-13 \Rightarrow k \Rightarrow 13$ $-30 \Rightarrow l \Rightarrow 29$	$0 \Rightarrow h \Rightarrow 8$ $0 \Rightarrow k \Rightarrow 13$ $0 \Rightarrow l \Rightarrow 25$
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.105, 1.05	0.038, 0.097, 1.05	0.049, 0.138, 1.03	0.050, 0.139, 1.05
No. of reflections	2608	1103	9230	1768
No. of parameters	264	164	1272	246
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.1361P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.131P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.2326P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 0.4401P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.001	<0.001	0.001	<0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.14	0.15, −0.17	0.26, −0.20	0.31, −0.17
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*	None
Extinction coefficient	0.022 (6)	0.014 (4)	0.032 (4)	

	V	VI	VII
Crystal data			
Chemical formula	$2(C_{10}H_{16}O_4){\cdot}C_6H_{12}N_4$	$C_4H_{12}N_2^{2+}{\cdot}C_{10}H_{14}O_4^{2-}$	$C_6H_{16}N_2^{2+}{\cdot}C_{10}H_{16}O_4{\cdot}$-$2(C_{10}H_{15}O_4)^-{\cdot}2H_2O$
M_r	540.65	286.37	750.91
Cell setting, space group	Orthorhombic, $P2_12_12$	Orthorhombic, $P2_12_12$	Orthorhombic, $P2_12_12$
a, b, c (Å)	19.9172 (8), 6.7515 (3), 10.6272 (4)	19.1277 (4), 7.5743 (6), 10.6920 (12)	13.5730 (4), 22.05 (8), 6.8417 (2)
α, β, γ (°)	90.00, 90.00, 90.00	90.00, 90.00, 90.00	90.00, 90.00, 90.00
V (Å^3)	1429.05 (10)	1549.0 (2)	2047.62 (11)
Z, Z'	2, 0.5	4, 2 × 0.5 = 1	2, 0.5
D_x (Mg m^{-3})	1.256	1.228	1.218
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	1866	1776	2095
θ range (°)	2.8–27.4	2.9–26.0	3.0–25.0
μ (mm^{-1})	0.09	0.09	0.09

Table 1 (continued)

	V	VI	VII
Temperature (K)	150 (1)	150 (1)	150 (1)
Crystal form, colour	Block, colourless	Block, colourless	Plate, colourless
Crystal size (mm)	0.34 × 0.32 × 0.30	0.35 × 0.30 × 0.28	0.28 × 0.22 × 0.10
Data collection			
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	None	None	None
T_{min}	–	–	–
T_{max}	–	–	–
No. of measured, independent and observed parameters	5749, 1866, 1651	6537, 1776, 1373	10832, 2095, 1634
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.039	0.057	0.061
θ_{max} (°)	27.4	26.0	25.0
Range of h, k, l	$0 \Rightarrow h \Rightarrow 25$ $0 \Rightarrow k \Rightarrow 8$ $0 \Rightarrow l \Rightarrow 13$	$0 \Rightarrow h \Rightarrow 23$ $0 \Rightarrow k \Rightarrow 9$ $0 \Rightarrow l \Rightarrow 13$	$0 \Rightarrow h \Rightarrow 16$ $0 \Rightarrow k \Rightarrow 26$ $0 \Rightarrow l \Rightarrow 8$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.080, 1.02	0.059, 0.149, 1.20	0.039, 0.099, 1.02
No. of reflections	1866	1776	2095
No. of parameters	179	266	279
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.1756P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0089P)^2 + 1.4657P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.001	0.001	<0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.13	0.18, −0.17	0.17, −0.16
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*
Extinction coefficient	0.022 (6)	0.036 (5)	0.016 (2)

Computer programs: *Kappa-CCD server software* (Nonius, 1997); *DENZO-SMN* (Otwinowski & Minor, 1997); *SHELXS*97 (Sheldrick, 1997*b*); *SHELXL*97 (Sheldrick, 1997*a*); *PLATON* (Spek, 2003); *PRPKAPPA* (Ferguson, 1999).

to values 0.8469 (14) and 0.1531 (14). Because of the disorder, numerous *DFIX* restraints involving standard bond lengths were employed during the refinement cycles. All the carboxyl H atoms of the major forms of the camphoric acid units were clearly revealed in difference maps, but for the minor forms the carboxyl H atoms were positioned by geometrical calculation. The DABCO unit in (IV) is disordered over two orientations, whose occupancy factors refined to values of 0.826 (5) and 0.174 (5), while the HMTA unit in (V) is fully ordered across a twofold rotation axis. There are two independent camphorate anions in (VI), both of which are disordered across twofold rotation axes, while in (VII) there is a neutral camphoric acid molecule that is disordered across a twofold rotation axis as well as a camphorate anion that is fully ordered in a general position, while the protonated *N*,*N*′-dimethylpiperazine unit lies across a different twofold axis.

Supramolecular analyses were performed and the diagrams were prepared with the aid of *PLATON* (Spek, 2003). Details of hydrogen-bond dimensions and of molecular conformations are given in Tables 2 and 3.[1]

Figs. 1–19 show the molecular components, with the atom-labelling schemes, and aspects of the supramolecular structures.

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0144). Services for accessing these data are described at the back of the journal.

3. Results and discussion

3.1. Crystallization characteristics and molecular constitutions

All co-crystallizations were carried out using mixtures that contained equal numbers of carboxylic acid and N-acceptor moieties in the, perhaps naive, expectation that the formation of hard hydrogen bonds, whether of N—H···O type where ions are formed or of O—H···N type where neutral molecular species persist, would control the stoichiometries of the resulting products. In the event, the expected 2:1 ratio of acid to amine is observed in the adduct (V), while the expected 1:1 adducts are formed in (II), (III) and (VI). However, (IV) and (VII) are both stoichiometric hydrates in which the water molecules are fully integrated into the supramolecular structures, and in (VII) the expected 1:1 ratio of acid to amine is not observed. Instead, there are three times as many camphoric acid units, some neutral and some ionized, as there are diamine units. Thus even the stoichiometric compositions of at least two of these adducts are unexpected and, in the case of (VII) at least, far from predictable.

Compounds (II), (III) and (V) all consist of neutral components, whereas in (IV), (VI) and (VII) the diamine components are all protonated. In (IV), there is a single H-atom transfer from the acid to the amine, which gives the singly charged ions $[\{(C_6H_{12}N_2)H\}^+]$ and $[(C_{10}H_{15}O_4)^-]$. In (VI), there is a double transfer to produce the ions $[\{H_2N(CH_2CH_2)_2NH_2\}^{2+}]$ and $[(C_{10}H_{14}O_4)^{2-}]$. A doubly

Table 2
Hydrogen-bond parameters (Å, °).

D—H···A	H···A	D···A	D—H···A
(I)			
O12—H12···O23	1.83	2.670 (2)	178
O14—H14···O21^{i}	1.83	2.667 (3)	175
O22—H22···O13^{ii}	1.82	2.657 (3)	171
O24—H24···O11	1.80	2.637 (2)	178
(II)†			
O1—H1···N11^{iii}	1.69	2.732 (16)	175
O3—H3···N11	1.68	2.666 (10)	159
C15—H15···O2^{iv}	2.44	3.293 (19)	149
C15—H15···O4^{v}	2.53	3.425 (19)	156
(III)			
O2*A*—H2*A*···N1*B*	1.82	2.656 (54)	173
O1*C*—H1*C*···N2*B*	1.80	2.614 (4)	163
O3*C*—H3*C*···N1*D*	1.82	2.652 (6)	174
O2*E*—H2*E*···N2*D*	1.85	2.686 (6)	175
O4*E*—H4*E*···N1*F*	1.82	2.635 (5)	162
O3*G*—H3*G*···N2*F*	1.84	2.658 (4)	166
O1*G*—H1*G*···N1*H*	1.83	2.650 (7)	167
O4*A*—H4*A*···N2*H*^{vi}	1.80	2.639 (6)	176
C13*F*—H13*F*···O3*E*^{vii}	2.55	3.332 (6)	140
C17*B*—H17*E*···O1*A*^{vii}	2.47	3.308 (5)	142
C25*B*—H25*B*···O2*C*^{viii}	2.50	3.272 (5)	138
C27*F*—H27*G*···O4*G*^{viii}	2.30	3.182 (5)	147
C16*B*—H16*B*···O3*E*^{ix}	2.56	3.382 (5)	145
C22*D*—H22*D*···O3*A*^{x}	2.56	3.429 (9)	152
C22*H*—H22*H*···O1*E*^{x}	2.52	3.386 (5)	151
C26*F*—H26*F*···O2*C*^{x}	2.48	3.279 (5)	142
C12*H*—H12*H*···O4*C*^{xi}	2.50	3.379 (10)	153
(IV)			
N2—H2···O1	1.69	2.598 (4)	165
O4—H4···N1^{xii}	1.81	2.646 (4)	172
O5—H51···O1	2.02	2.894 (4)	164
O5—H52···O2^{viii}	1.92	2.810 (4)	169
(V)			
O2—H2···N2^{xiii}	1.88	2.684 (2)	159
O4—H4···N1	1.89	2.728 (2)	175
(VI)‡			
N1—H1*A*···O11^{xiv}	1.80	2.70 (2)	168
N1—H1*A*···O13^{xv}	1.75	2.65 (2)	165
N1—H1*B*···O12^{xvi}	1.76	2.64 (2)	160
N1—H1*B*···O14	1.75	2.64 (3)	162
N4—H4*A*···O22^{xvii}	1.85	2.756 (12)	169
N4—H4*A*···O24^{xviii}	1.70	2.598 (11)	165
N4—H4*B*···O21^{xix}	1.78	2.677 (14)	165
N4—H4*B*···O23	1.81	2.698 (15)	163
(VII)			
N1—H1···O11	2.20	2.989 (3)	142§
N1—H1···O12	1.95	2.811 (3)	154§
O3—H31···O11	1.84	2.708 (3)	162
O3—H32···O12^{xx}	1,82	2.696 (3)	166
O14—H14···O3^{xxi}	1.76	2.599 (3)	174
O22—H22···O11^{xxii}	1.87	2.683 (18)	164
O24—H24···O11	1.78	2.598 (17)	165

Symmetry codes: (i) $1+x, y, -1+z$; (ii) $-1+x, y, 1+z$; (iii) $-x, -x+y, \frac{1}{3}-z$; (iv) $-1-x+y, -x, -\frac{1}{3}+z$; (v) $-1+y, x, -z$; (vi) $3+x, 3+y, 2+z$; (vii) $-1+x, y, z$; (viii) $1+x, y, z$; (ix) $1+x, 1+y, 1+z$; (x) $-1+x, -1+y, -1+z$; (xi) $-2+x, -2+y, -1+z$; (xii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (xiii) $x, 1+y, -1+z$; (xiv) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (xv) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (xvi) $-x, -y, z$; (xvii) $-\frac{1}{2}+x, \frac{3}{2}-y, -z$; (xvii) $\frac{1}{2}-x, -\frac{1}{2}+y, -z$; (xix) $1-x, 2-y, z$; (xx) $x, y, -1+z$; (xxi) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (xxii) $-x, 1-y, z$. † O1 and O3 are alternative sites in disordered molecule, as are O2 and O4 (see §3.3). ‡ For details of alternative and near-equivalent atom sites see §3.5. § Three-centre N—H···$(O)_2$ system: sum of angles at H1, 359°.

protonated diamine $[\{MeHN(CH_2CH_2)_2NHMe\}^{2+}]$ is also present in (VII), but this compound rather unexpectedly contains not only two mono-anions $[(C_{10}H_{15}O_4)^-]$ but also a neutral $[C_{10}H_{16}O_4]$ molecule.

Only in (I) and (V) is there no disorder. The diamines are disordered in (II) and (IV), while two of the four independent diamines in (III) are disordered. The camphoric acid units are disordered in (II), (III) and (VI), across twofold rotation axes in (II) and (VI). In (VII), the neutral camphoric acid molecule is also disordered across a twofold axis, while the $[(C_{10}H_{15}O_4)^-]$ anion is fully ordered.

3.2. Molecular conformations and dimensions

It is striking that the independent diamine components in (III) adopt two quite different conformations (Table 3, Fig. 6), in which the ordered amines (types *D* and *H*) are virtually planar. The disordered amines, whether in their major orientations (types *B* and *F*) or the corresponding minor forms (types *V* and *Y*), have one pyridyl ring nearly coplanar with the central C—CH_2—CH_2—C unit, while the other ring is nearly orthogonal to this plane. In contrast, the bipyridyl component of (II) has only a modest dihedral angle between the two ring planes.

In (IV), the N—C—C—N torsional angles in the DABCO component indicate only a very marked deviation from the idealized D_{3h} ($\bar{6}m2$) molecular symmetry. The twist of the molecule from D_{3h} symmetry may be regarded as an internal rotation about the N···N vector, while in the D_{3h} conformation the neighbouring CH_2 groups are all eclipsed. For isolated DABCO molecules in the gas phase (Yokozeki & Kuchitsu, 1971) the internal dynamics indicate a very broad potential well for the twist motion, which is best fitted by a harmonic quartic potential function that has an energy minimum corresponding to a twist of *ca* 10° from the D_{3h} geometry. However, with this in mind it is of interest to compare the conformation in (IV) with that in the adduct formed with *N*-(phosphonomethyl)iminodiacetic acid, where the mean N—C—C—N torsional angle is even larger at −17.2 (2)° (Bowes *et al.*, 2002). The intramolecular distances and angles present no unexpected features.

3.3. Supramolecular structures – hard hydrogen bonds generate chains

3.3.1. (1*R*,3*S*)-Camphoric acid (I). The structure of camphoric acid was investigated some years ago by Barnes *et al.* (1991). These authors reported two polymorphs: an ordered monoclinic polymorph (space group $P2_1$, $Z' = 2$), which is obtained from aqueous solution, and a disordered orthorhombic polymorph (space group $P2_12_12_1$, $Z' = 2$), which was crystallized from acetone. The structure of the monoclinic form was described using a non-reduced cell and refined from room-temperature data, where only *ca* 60% of the reflections were labelled 'observed', only to $R = 0.069$. The H atoms of the carboxyl groups were not located, but nonetheless the main feature of the supramolecular aggregation was the formation of chains.

Table 3
Selected dihedral and torsional angles (°).

(II)			
(N11—C16)^(N11^{i}—C16^{i})	15.8 (2)		
(III)			
C13*B*—C14*B*—C17*B*—C27*B*	−1.7 (6)	C13*F*—C14*F*—C17*F*—C27*F*	80.3 (5)
C14*B*—C17*B*—C27*B*—C24*B*	−178.4 (4)	C14*F*—C17*F*—C27*F*—C24*F*	176.5 (3)
C17*B*—C27*B*—C24*B*—C23*B*	102.9 (5)	C17*F*—C27*F*—C24*F*—C23*F*	2.7 (5)
C13*D*—C14*D*—C17*D*—C27*D*	4.5 (4)	C13*H*—C14*H*—C17*F*—C27*H*	1.7 (4)
C14*D*—C17*D*—C27*D*—C24*D*	179.5 (3)	C14*H*—C17*H*—C27*H*—C24*H*	179.6 (3)
C17*D*—C27*D*—C24*D*—C23*D*	−1.4 (4)	C17*H*—C27*H*—C24*H*—C23*H*	−5.0 (4)
C13*V*—C14*V*—C17*V*—C27*V*	7 (3)	C13*Y*—C14*Y*—C17*Y*—C27*Y*	−78 (3)
C14*V*—C17*V*—C27*V*—C24*V*	177 (2)	C14*Y*—C17*Y*—C27*Y*—C24*Y*	−176 (2)
C17*V*—C27*V*—C24*V*—C23*V*	78 (3)	C17*Y*—C27*Y*—C24*Y*—C23*Y*	−4 (3)
(IV)			
N1—C11—C21—N2	10.2 (4)	N11—C31—C41—N12	−4 (2)
N1—C12—C22—N2	9.1 (4)	N11—C32—C42—N12	−3 (2)
N1—C13—C23—N2	9.7 (4)	N11—C33—C43—N12	−7 (2)

Symmetry code: (i) $y, x, -z$.

We have now reinvestigated the monoclinic polymorph of (1*R*,3*S*)-camphoric acid using a larger data set, which was collected at 150 (1) K and in which over 80% of the reflections are 'observed'. The resulting structure is fully ordered, including the H atoms of the carboxyl groups, all of which were clearly visible in difference maps. Within the asymmetric unit (Fig. 1), atom O12 in molecule 1 acts as hydrogen-bond donor to O23 in molecule 2, while O24 in molecule 2 acts as donor to O11 in molecule 1, so generating the $R_2^2(8)$ motif so characteristic of carboxylic acids (Fig. 2). Likewise O14 in molecule 1 at (x, y, z) acts as donor to O21 in molecule 2 at $(1 + x, y, -1 + z)$, and O22 in molecule 2 at (x, y, z) acts as donor to O13 in molecule 1 at $(-1 + x, y, 1 + z)$, thus generating further $R_2^2(8)$ motifs. The combination of the four O—H···O hydrogen bonds generates by translation a $C_2^2(16)[R_2^2(8)][R_2^2(8)]$ chain of rings (Bernstein *et al.*, 1995) that runs parallel to the $[10\bar{1}]$ direction (Fig. 2). Two such chains run through each unit cell; these chains are related by the 2_1 screw axis, but there are no direction-specific interactions between adjacent chains. Aside from the choice of unit cell, this structure differs from that reported earlier primarily in terms of the enantiomorph; the structure described by Barnes *et al.* (1991) is that of (1*S*,3*R*)-camphoric acid, although these authors do not specify how the stereochemistry was assigned.

3.3.2. Camphoric acid–4,4′-bipyridyl (1/1) (II). In this 1:1 adduct, both components are neutral with no evidence of any transfer of H atoms from O to N. The bipyridyl unit is fully ordered and lies across a twofold rotation axis in $P3_121$, which is selected as that at $z = 0$, while the camphoric acid molecule is disordered across a twofold rotation axis that is selected as that at $z = \frac{1}{6}$, in order to form a connected asymmetric unit (Fig. 3). Hence in the two orientations of the acid unit, the sites occupied by the hydroxyl atoms O3 and O1^{iii} (see

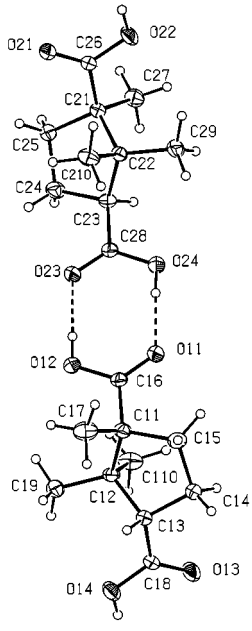


Figure 1
The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

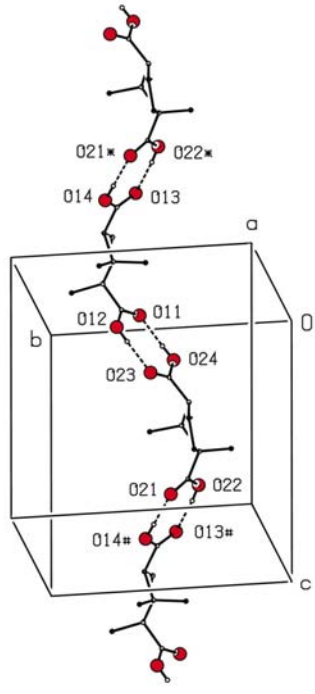


Figure 2
Part of the crystal structure of (I) showing the formation of a chain of rings along $[10\bar{1}]$. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 + x, y, -1 + z)$ and $(-1 + x, y, 1 + z)$, respectively.

Table 2) are nearly coincident (Fig. 4). For the orientation shown in Fig. 3, hydroxyl O1 acts as hydrogen-bond donor to N11 at $(-x, -x+y, \frac{1}{3}-z)$, which lies in the bipyridyl unit across the twofold axis at $z = \frac{1}{3}$. Propagation of the two independent O—H···N hydrogen bonds (Table 2) produces a $C_2^2(17)$ spiral chain generated by the 3_1 screw axis along $(0, 0, z)$ (Fig. 5).

Adjacent spirals are linked into a continuous bundle by a C—H···O hydrogen bond in which a single donor in the bipyridyl unit interacts with two alternative acceptors in the camphoric acid unit. Aromatic C15 at (x, y, z), which lies in the spiral chain along $(0, 0, z)$, acts as donor either to O2 at $(-1-x+y, -x, -\frac{1}{3}+z)$ or to O4 at $(-1+y, x, -z)$ according to the orientation of the camphoric acid unit concerned, which itself lies in the chain along $(-1, 0, z)$. Propagation of these interactions by both the rotation and the screw axes links all of the spiral chain into a single framework (Fig. 5).

3.3.3. Camphoric acid–1,2-bis(4-pyridyl)ethane (1/1) (III). Although the stoichiometry of (III) is simple, with a 1:1 ratio of camphoric acid and 1,2-bis(4-pyridyl)ethane units, the constitution is more complex, partly because $Z' = 4$, which is an unusually high value for the triclinic system (Wilson, 1993; Brock & Dunitz, 1994). Of the four independent diamine units present, two are fully ordered, while the other two exhibit positional disorder. All four of the camphoric acid units exhibit orientational disorder. However, during the course of the refinement it was found that the two orientations of each of the disordered components occurred with very unequal site occupancies. In fact, a single tied pair of site-occupancy factors proved sufficient to model the structure satisfactorily. The resulting structure consists entirely of neutral camphoric acid molecules and neutral bipyridyl units, with no evidence for any transfer of H atoms from N to O.

The independent components (Fig. 6) are linked by O—H···N hydrogen bonds into continuous chains in which the acid and the diamine units alternate. The supramolecular structure will be discussed primarily in terms of the major component at each site along the chain, as the behaviour of the minor components is not significantly different. Within the asymmetric unit, the fully ordered and major disordered components are linked by seven O—H···N hydrogen bonds.

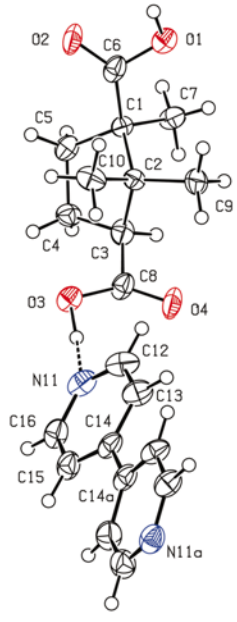


Figure 3
The independent molecular components of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. For the sake of clarity, only one orientation of the acidic component is shown: the atoms marked 'a' are at the symmetry position $(y, x, -z)$.

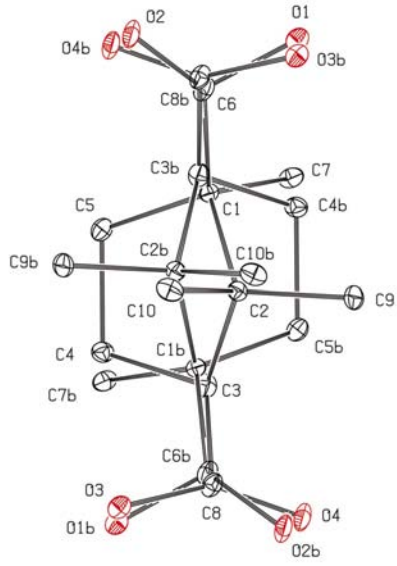


Figure 4
The two orientations of the disordered acid unit in (II) showing the near coincidence of the O sites in the two forms. Displacement ellipsoids are drawn at the 10% probability level. For the sake of clarity, H atoms are omitted. The atoms marked 'b' are at the symmetry position $(-x, -x+y, \frac{1}{3}-x)$.

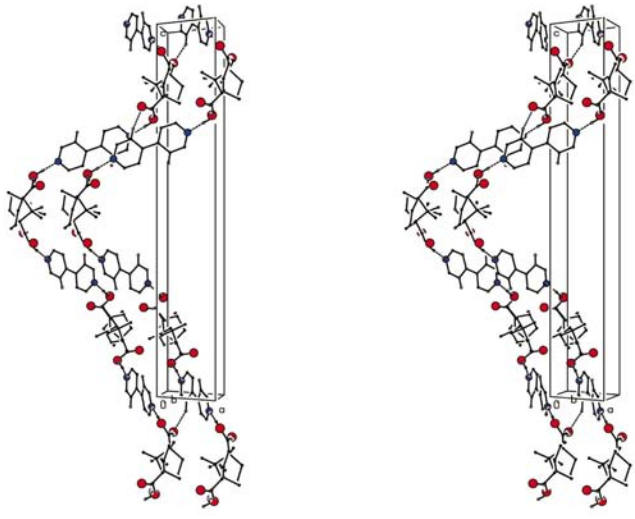


Figure 5
Stereoview of part of the crystal structure of (II) showing the linking of the $C_2^2(17)$ spiral chains by the C—H···O hydrogen bond.

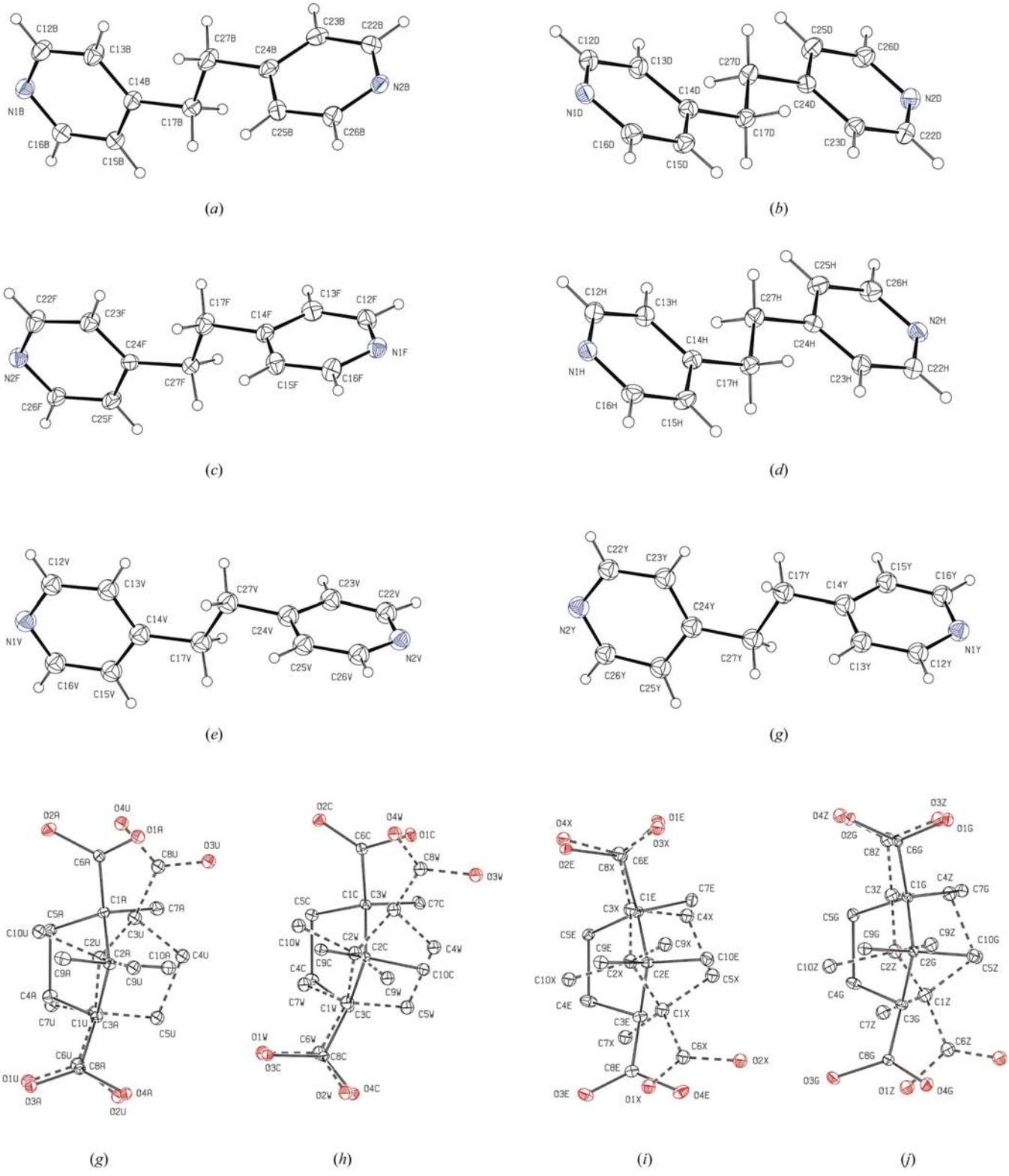


Figure 6
The independent molecular components of (III) showing the atom-labelling scheme. Parts (*a*)–(*f*) show the amine components; those with atom labels suffixed *D* and *H* are fully ordered with unit occupancy, those suffixed *B* and *F* have occupancy 0.8469 (14), and those suffixed *V* and *Y* have occupancy 0.1531 (14). Parts (*g*)–(*j*) show the corresponding pairs of major [full lines, occupancy 0.8469 (14)] and minor [broken lines, occupancy 0.1531 (14)] orientations of the camphoric acid components. Displacement ellipsoids are drawn at the 30% probability level in parts (*a*)–(*f*) and at the 10% probability level in parts (*g*)–(*j*). For the sake of clarity, H atoms are omitted in parts (*g*)–(*j*).

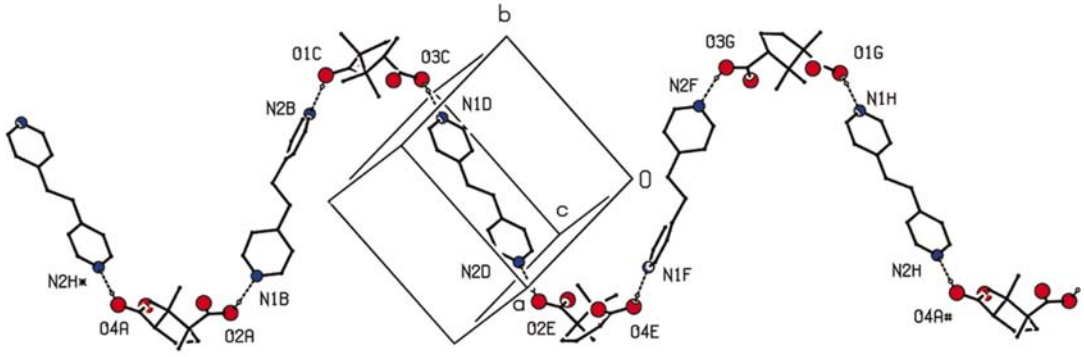


Figure 7
Part of the crystal structure of (III) showing the formation of a $C_8^8(76)$ chain along [332]. For the sake of clarity, only the major orientations of the disordered components are shown and H atoms bonded to C are omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(3 + x, 3 + y, 2 + z)$ and $(-3 + x, -3 + y, -2 + z)$, respectively.

In addition, atom O4*A* at (x, y, z) acts as hydrogen-bond donor to N2*H* at $(3 + x, 3 + y, 2 + z)$, so generating by translation a $C_8^8(76)$ chain that runs parallel to the [332] direction (Fig. 7). At two of the eight independent molecular sites along this chain there are fully ordered diamines, and at each of the other six there is a statistical distribution of the major and minor orientations of either the diamine or the acid, as the case may be. Because each component acts either as a double donor or as a double acceptor of hydrogen bonds, no correlation of the molecular orientations at adjacent sites is necessary. In particular, the pattern of the hard hydrogen bonds is the same, whether major or minor orientations are involved. Thus O2*U* in one of the minor components acts as hydrogen-bond donor to N2*H* at $(3 + x, 3 + y, 2 + z)$, which again completes the formation of the [332] chain.

Adjacent [332] chains are linked by a large number of rather weak, but cooperatively reinforcing, C—H···O hydrogen bonds. Again, we consider here only the major orientations of the disordered components, as the behaviour of the minor components is similar (Table 2). Atoms C13*F* and C17*B* in diamines at (x, y, z) act as hydrogen-bond donors, respectively, to O3*E* and O1*A* at $(-1 + x, y, z)$, while C25*B* and C27*F* act as donors to O2*C* and O4*G* at $(1 + x, y, z)$, so generating for each interaction a chain along [100]. Atom C16*B* at (x, y, z) acts as donor to O3*E* at $(1 + x, 1 + y, 1 + z)$, while C22*D*, C22*H* and C26*F* act as donors to O3*A*, O1*E* and O2*C*, all at $(-1 + x, -1 + y, -1 + z)$: each of these interactions generates a chain along [111]. Finally, C12*H* at (x, y, z) acts as hydrogen-bond donor to O4*C* at $(-2 + x, -2 + y, -1 + z)$, so generating a chain parallel to [221]. The formation of a continuous three-dimensional framework can most easily be seen by considering the combination of the [111], [221] and [332] chains, which together generate a $(1\bar{1}0)$ sheet, while adjacent $(1\bar{1}0)$ sheets are linked by the [100] chains.

3.4. Hard hydrogen bonds generate sheets

3.4.1. Camphoric acid–DABCO–water (1/1/1) (IV). Compound (IV) is a monohydrated 1:1 adduct of 1,4-diaza bicyclo[2.2.2]octane and camphoric acid. The constitution of

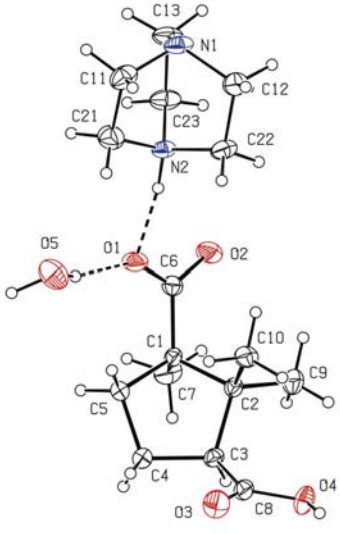


Figure 8
The independent components of (IV) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only the major orientations of the ionic components are shown.

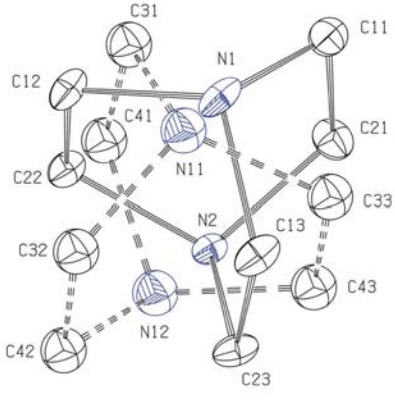


Figure 9
The two orientations of the disordered cation on (IV). Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, H atoms are omitted

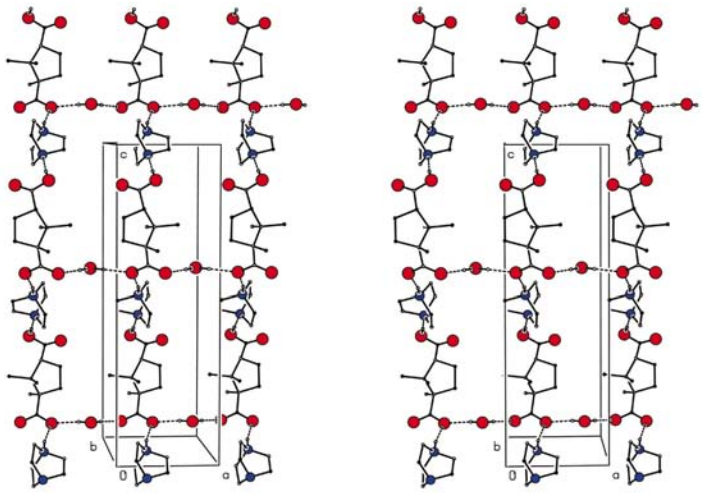


Figure 10
Stereoview of part of the crystal structure of (IV) showing the formation of a puckered (010) sheet. For the sake of clarity, only the major orientations of the ionic components are shown, and H atoms bonded to C are omitted.

(IV) is that of a salt $\{[(C_6H_{12}N_2)H]^+\}\cdot[(C_{10}H_{15}O_4)^-]\cdot H_2O$ (Fig. 8). The anion shows no overall orientational disorder, although the unionized carboxyl group based on C8 shows some local disorder over two orientations of this substituent. The cation exhibits orientational disorder of the entire cage with the same site occupancies as for the disordered carboxyl group (Fig. 9), but the neutral water molecule is fully ordered. For the sake of simplicity only the major components of the cation and anion will be considered in the discussion of the supramolecular structure.

Within the asymmetric unit (Fig. 8), the protonated N2 acts as hydrogen-bond donor to carboxylate O1, as does the water O5, *via* H51. There are thus only two hard hydrogen bonds, one each of O—H···O and O—H···N types, which link these three-component units: the resulting supramolecular structure takes the form of deeply puckered sheets, whose formation is readily analysed in terms of two simple chain motifs. Water O5 at (x, y, z) acts as hydrogen-bond donor, *via* H52, to carboxylate O2 in the anion at ($1+x$, y, z), so generating by translation a $C_2^2(6)$ chain running parallel to the [100] direction, while carboxyl O4 at (x, y, z) acts as donor to N1 in the cation at ($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$), thus producing a $C_2^2(13)$ chain running parallel to the [001] direction and generated by the 2_1 screw axis along ($\frac{1}{2}$, 0, z). The combination of the [100] and [001] chains generates a (010) sheet built from a single type of $R_8^7(36)$ ring (Fig. 10).

Two sheets pass through each unit cell; these sheets are disposed about the planes $y=0$ and $y=\frac{1}{2}$ and are related to one another by the 2_1 screw axes along [010]. Although the sheets are deeply puckered, they are not interwoven; the supramolecular structure defined by the direction-specific interactions is thus two dimensional.

3.4.2. Camphoric acid–hexamethylenetetramine (2/1) (V). In this 2:1 adduct (Fig. 11), where both components are neutral with no transfer of H atoms from O to N, each camphoric acid molecule forms O—H···N hydrogen bonds to two hexamethylenetetramine (HMTA) molecules and each HMTA accepts hydrogen bonds from four camphoric acid molecules: all the H atoms are fully ordered. The behaviour of HMTA as a fourfold acceptor of O—H···N hydrogen bonds is highly unusual, although it has been observed in the 2:1 adduct formed with 2,2′-biphenols (MacLean *et al.*, 1999). Normally HMTA behaves as a twofold acceptor of hydrogen bonds (Dahl & Hassel, 1971; Mak *et al.*, 1978; Mahmoud & Wallwork, 1979; Ferguson *et al.*, 1995; Coupar, Glidewell *et al.*, 1997; Meehan *et al.*, 1997). Rather less frequently, HMTA behaves as an acceptor of just one hydrogen bond (Mak *et al.*, 1986; Coupar, Glidewell *et al.*, 1997) or of three hydrogen bonds (Jordan & Mak, 1970; de Bruyn *et al.*, 1996; Coupar, Ferguson *et al.*, 1997).

In adduct (V), the HMTA lies on a twofold rotation axis in $P2_12_12$, which is chosen for convenience as that along ($\frac{1}{2}$, $\frac{1}{2}$, z); atoms C3 and C4 lie on this axis. The camphoric acid molecule lies in a general position and just two O—H···N hydrogen bonds generate the supramolecular structure, which takes the form of pairwise interwoven sheets built from $R_8^8(48)$ rings. Within the asymmetric unit (Fig. 11) O4 acts as hydrogen-bond donor to N1. O2 at (x, y, z) acts as donor to N2 in the HMTA molecule at (x, $1+y$, $-1+z$), so generating a $C_2^2(12)$ chain running parallel to the [01$\bar{1}$] direction (Fig. 12). The action of the twofold rotation axis generates a second $C_2^2(12)$ chain

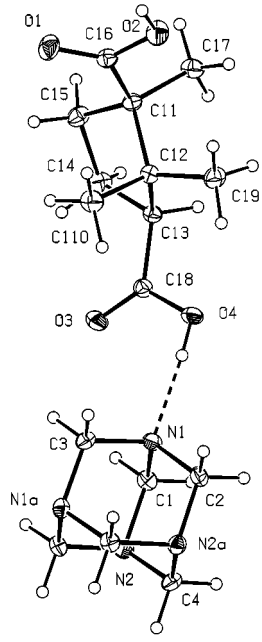


Figure 11
The molecular components of (V) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' are at the symmetry position ($1-x$, $1-y$, z).

running parallel to the [011] direction, so that the reference HMTA molecule accepts hydrogen bonds from the four camphoric acid molecules at (x, y, z), $(x, -1 + y, 1 + z)$, $(1 - x, 1 - y, z)$ and $(1 - x, 2 - y, 1 + z)$ (Fig. 12). The combination of the [011] and [01$\bar{1}$] chains generates a (100) sheet built from a single type of $R_8^8(48)$ ring. This sheet takes the form of a (4,4) net (Batten & Robson, 1998) if the HMTA molecules are regarded as the nodes of the net with the camphoric acid molecules as spacer units between the nodes. The reference (100) sheet lies within the domain $0.26 < x < 0.74$, and there is a second sheet, which is related to the first by the action of the 2_1 screw axes, in the domain $0.76 < x < 1.24$. In the reference sheet there are HMTA molecules at $(x, y, n + z)$ for n = zero or even integers but not at $(x, y, n + z)$ for n = odd integers, and two such nets are thus required to define each domain fully. The individual sheets are sufficiently puckered to allow pairwise interweaving: thus in each domain of x, two sheets are interwoven (Fig. 13), but there are no significant interactions between the paired sheets in adjacent domains.

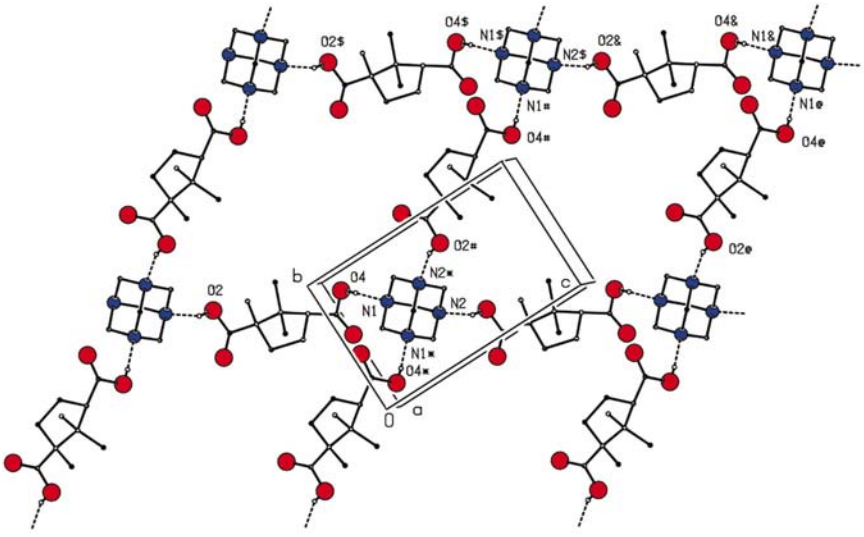


Figure 12
Part of the crystal structure of (V) showing the formation of a (100) sheet built from $R_8^8(48)$ rings. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or at sign (@) are at the symmetry positions $(1 - x, 1 - y, z)$, $(1 - x, 2 - y, 1 + z)$, $(x, 1 + y, 1 + z)$, $(x, y, 2 + z)$ and $(1 - x, 1 - y, 2 - z)$, respectively.

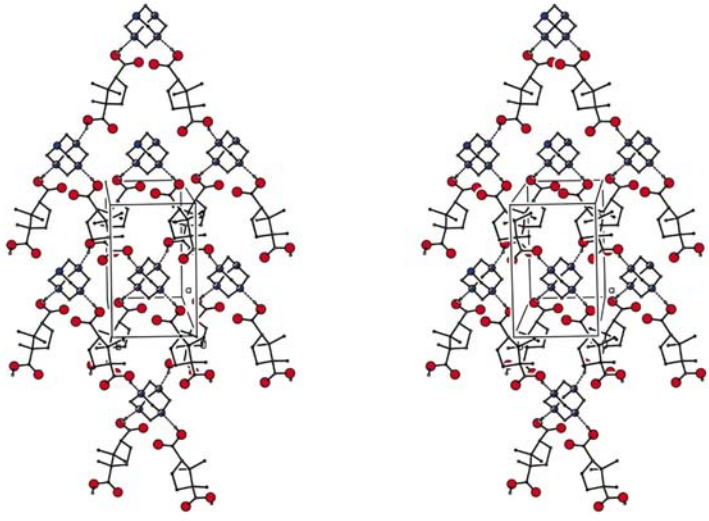


Figure 13
Stereoview of part of the crystal structure of (V) showing the pairwise interweaving of (100) sheets.

3.5. Hard hydrogen bonds generate frameworks

3.5.1. Camphoric acid–piperazine (1/1) (VI). Compound (VI) is a simple salt $[H_2N(CH_2CH_2)_2NH_2]^{2+}\cdot[C_{10}H_{14}O_4]^{2-}$, in which complete transfer of two H atoms from O to N has occurred (Fig. 14). The cation lies in a general position and is, in fact, nearly centrosymmetric, as it adopts the usual chair conformation. There are two independent anions, both of which are disordered across twofold rotation axes in $P2_12_12$. These axes are chosen as those along $(0, 0, z)$ for anion 1, which contains atoms O1n (n = 1, 2, 3, 4), and $(\frac{1}{2}, 1, z)$ for anion 2, which contains atoms O2n (n = 1, 2, 3, 4). The ionic components are linked by N—H···O hydrogen bonds into a three-dimensional framework, which is most readily analysed *via* the substructure approach (Gregson *et al.*, 2000) in terms of chain formation and the linking of these chains to form the framework.

At the local level, each anion site contains a single orientation of the (1*R*,3*S*)-camphorate(2−) ion, in which all four carboxylate O atoms form N—H···O hydrogen bonds, each with a different cation: similarly each cation forms N—H···O hydrogen bonds with four different anions. While the orientational disorder of the camphorate ions complicates matters somewhat, it is necessary only to recognize that the sites of the carboxylate atoms O11–O14 at (x, y, z) lie very close to those of the atoms O13, O14, O11 and O12, respectively, at $(-x, -y, z)$. Likewise the sites of O21–O24 at (x, y, z) lie very close to the sites of O23, O24, O21 and O22, respectively, at $(1 - x, 2 - y, z)$. Thus N1 at (x, y, z) acts as hydrogen-bond donor, *via* H1*B* (the equatorial H at N1), either to O14 at (x, y, z) or to O12 at $(-x, -y, z)$; the identity of the acceptor depends solely on which orientation of the camphorate ion is present at that particular site. Similarly, all the other N—H···O hydrogen bonds in (VI) (Table 2) have alternative acceptors that depend on the local anion orientation. It is thus possible, without serious loss of precision in the descriptive analysis, to consider just one orientation of each anion

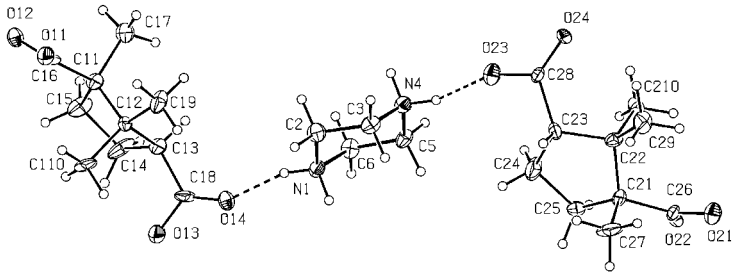


Figure 14
The independent components of (VI) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity only one orientation is shown for each of the disordered anions.

while retaining the effect of the twofold rotation axes on the propagation of the cation sites: the important point is that in each orientation the anion acts as a fourfold acceptor of N—H···O hydrogen bonds.

Within the selected asymmetric unit (Fig. 14), the cation centroid lies near $(\frac{1}{4}, \frac{1}{2}, \frac{1}{4})$, and N1 and N4 act as hydrogen-bond donors, *via* the equatorial H1*B* and H4*B*, to O14 and O23, respectively. At the same time, N1 and N4 similarly act as donors, respectively, to O12 at $(-x, -y, z)$ and to O21 at $(1-x, 2-y, z)$, where the acceptors occupy sites close to O14 and O23 at (x, y, z) (Table 2). The twofold axis along $(0, 0, z)$ generates another cation centred near $(-\frac{1}{4}, -\frac{1}{2}, \frac{1}{4})$, in which N1 at $(-x, -y, z)$ acts as donor to O11 at (x, y, z) [or to O13 at $(-x, -y, z)$ in the alternative anion orientation], while N4 at $(-x, -y, z)$ acts as donor to O22 at $(-1+x, -2+y, z)$ [or to O24 at $(-x, -y, z)$]. Propagation of these hydrogen bonds then generates a $C_4^4(26)$ chain running parallel to the [120] direction (Fig. 15). The action of the 2_1 axes generates a similar chain running parallel to the $[1\bar{2}0]$ direction, so that there are by translation two sets of $C_4^4(26)$ chains inclined to one another at *ca* 77°. Hydrogen bonds, which are formed by the two axial N—H bonds of the cation, link the individual chains of this criss-cross stack into a continuous framework.

Atom N1 at (x, y, z) lies in a [120] chain: this atom acts as hydrogen-bond donor, *via* the axial H1*A*, to O12 at $(\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$, which lies in a $[1\bar{1}0]$ chain. In turn N1 at $(\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$ acts as donor to O12 at $(1+x, y, z)$ in the adjacent [120] chain, so producing a $C_2^2(10)$ chain running parallel to the [100] direction and generated by the 2_1 axis along $(x, \frac{1}{4}, \frac{1}{2})$ (Fig. 16). In a similar fashion, N4 at (x, y, z) acts as donor, *via* H1*A*, to O21 at $(-\frac{1}{2}+x, \frac{3}{2}-y, -z)$, so producing another $C_2^2(10)$ chain along [100], this time generated by the 2_1 axis along $(x, \frac{3}{4}, 0)$. The combination of these two chain motifs generates a (011) sheet containing $R_6^6(32)$ and $R_8^8(46)$ rings that alternate in checkerboard fashion (Fig. 16). The (011) sheets are linked by the [120] and $[1\bar{2}0]$ chains into a single framework.

3.5.2. Camphoric acid–*N*,*N*′-dimethylpiperazine–water (3/1/2) (VII). Compound (VII) is unusual in that it contains both a neutral camphoric acid molecule $C_{10}H_{16}O_4$ and two mono-anions $(C_{10}H_{15}O_4)^-$ as well as a doubly protonated diamine $[MeN(CH_2CH_2)_2NMeH_2]^{2+}$. The cation lies across a twofold rotation axis in $P2_12_12$, which is selected as that along $(\frac{1}{2}, \frac{1}{2}, z)$, and the neutral camphoric acid molecule is disordered across another twofold rotation axis, this time along $(0, \frac{1}{2}, z)$. The camphorate anion and the water molecule lie in general positions giving an overall constitution $[\{MeN(CH_2CH_2)_2NMe\}H_2]\cdot[C_{10}H_{16}O_4]\cdot[(C_{10}H_{15}O_4)^-]_2\cdot\cdot[H_2O]_2$. The four independent molecular components are extensively linked by hydrogen bonds of O—H···O and N—H···O types into a three-dimensional framework. As usual in such cases, the choice of asymmetric unit allows considerable discretion, but it is, in fact, possible to select a very compact asymmetric unit (Fig. 17) in which the camphorate anion accepts hydrogen bonds from the other three components, at a common site O11 (Table 2).

The application of the substructure approach (Gregson *et al.*, 2000) to the analysis of the three-dimensional supramolecular structure shows that just two of the molecular components, the camphorate anion and the water molecule (the two components in general positions), combine to form rather simple sheets. These sheets are linked both by the cations and by the neutral camphoric acid molecules into a composite pillared-layer structure that contains two types of pillar.

The sheet formation can in turn be analysed very simply in terms of two one-dimensional motifs. The water molecule based on O3 is linked, *via* H31, to carboxylate O11 within the

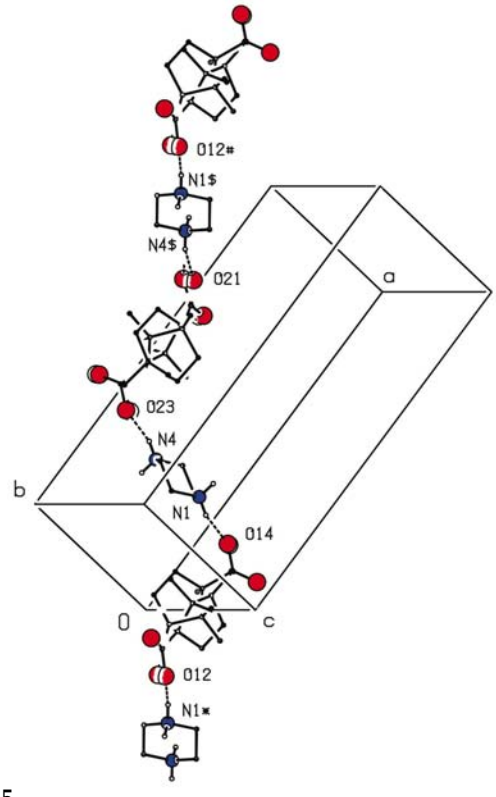


Figure 15
Part of the crystal structure of (VI) showing the formation of a $C_4^4(26)$ chain along [120]. For the sake of clarity, H atoms bonded to C are omitted, and only one orientation of each disordered anion is shown. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(-x, -y, z)$, $(-1+x, -2+y, z)$ and $(1-x, 2-y, z)$, respectively.

asymmetric unit. In addition, O3 at (x, y, z) is linked, *via* H32, to carboxylate O12 at $(x, y, -1 + z)$, so generating by translation a $C_2^2(6)$ chain running parallel to the [001] direction (Fig. 18). A second chain results from the involvement of the water molecule as an acceptor as well as a donor of hydrogen bonds. Carboxyl O14 in the camphorate anion at (x, y, z) acts as hydrogen-bond donor to water O3 at $(-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$, while O14 at $(-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ acts as donor to O3 at $(-1 + x, y, z)$, thus producing a $C_2^2(10)$ chain running parallel to the [100] direction and generated by the 2_1 axis along $(x, \frac{1}{4}, \frac{1}{2})$. The combination of the $C_2^2(6)$ and $C_2^2(10)$ chains generates a (010) sheet built from a single type of $R_6^6(26)$ ring (Fig. 18). This sheet lies in the domain $0.10 < y < 0.40$, and there is a second such sheet in the domain $0.60 < y < 0.90$, which is related to the first by the rotation axes.

Adjacent (100) sheets are linked both by the cations and by the neutral camphoric acid molecules. Atom N1 at (x, y, z) lies in the cation across $(\frac{1}{2}, \frac{1}{2}, z)$ and acts as donor to both O11 and O12 at (x, y, z) in a planar three-centre $N-H\cdots(O)_2$ hydrogen bond. These carboxylate O atoms are components of a camphorate anion in the $0.10 < y < 0.40$ sheet. The symmetry-related N1 in the same cation across $(\frac{1}{2}, \frac{1}{2}, z)$ is at $(1 - x, 1 - y, z)$, and this atom acts as donor to O11 and O12 in the camphorate anion at $(1 - x, 1 - y, z)$, which forms part of the $0.60 < y < 0.90$ sheet. Similarly, in the neutral camphoric acid molecule across $(0, \frac{1}{2}, z)$, the carboxyl O24 atoms at (x, y, z) and at $(-x, 1 - y, z)$ act as donors, respectively, to O11 at (x, y, z), which is part of the $0.10 < y < 0.40$ sheet, and to O11 at $(-x, 1 - y, z)$, which is part of the $0.60 < y < 0.90$ sheet. Hence adjacent anionic sheets are linked by two types of pillar, one cationic and the other neutral (Fig. 19). Propagation of these connections by the 2_1 axes of the space group causes each adjacent pair of sheets to be linked in the same manner, so that all the (010) sheets are linked into a single three-dimensional framework.

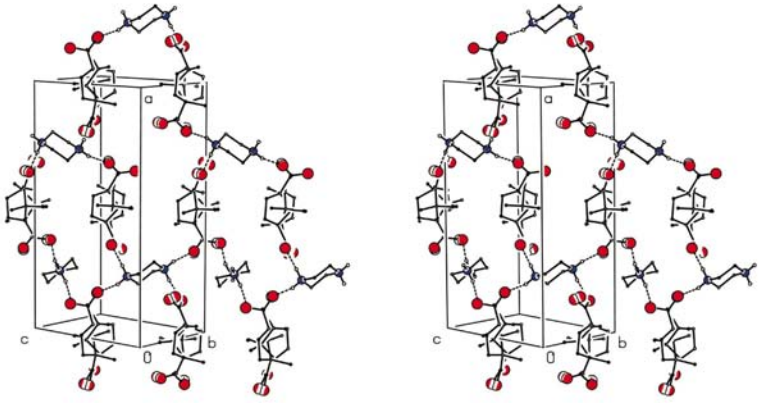


Figure 16
Stereoview of part of the crystal structure of (VI) showing the combination of $C_2^2(10)$ spiral chains along [100] to form a (011) sheet of $R_6^6(32)$ and $R_8^8(46)$ rings. For the sake of clarity, H atoms bonded to C are omitted, and only one orientation of each disordered anion is shown.

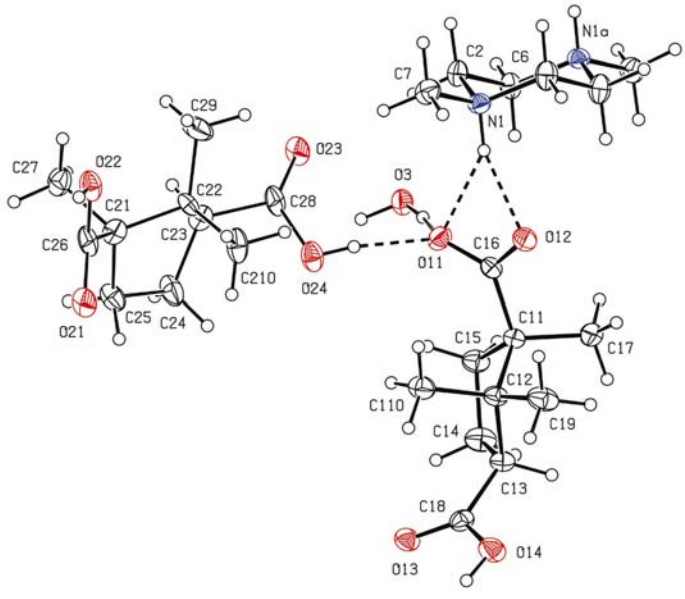


Figure 17
The independent components of (VII) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity only one orientation of the disordered anion is shown. The atoms marked 'a' are at the symmetry position $(1 - x, 1 - y, z)$.

4. Concluding comments

The results reported here, for a series of adducts formed by a single acid with a range of rather simple and closely related amines, encompass a wide variety of molecular constitutions and supramolecular arrangements. The nature of the acid components present, whether neutral species, mono-anions or di-anions, is not readily predictable. For example, while the di-anion $(C_{10}H_{14}O_4)^{2-}$ is present in the adduct formed with piperazine, in the adduct formed by the closely related diamine *N*,*N*′-dimethylpiperazine both neutral $C_{10}H_{16}O_4$ and mono-anionic $(C_{10}H_{15}O_4)^-$ are present. Similarly, the adducts formed by the closely related heteroaromatic amines 4,4′-bipyridyl (trigonal, $P3_121$, $Z' = 0.5$) and 1,2-bis(4-pyridyl)ethane (triclinic, $P1$, $Z' = 4$) exhibit widely different crystallographic properties, even though in both cases the principal substructure is a chain of alternating acid and diamine molecules. These observations mean that no one supramolecular structure could readily be predicted, even with detailed foreknowledge of all the others in this series. This fact in turn may mean that attempts to apply simple principles of crystal engineering to the design and construction

of specific supramolecular structures in systems such as those described here will require predictive models that are considerably more sophisticated than those currently available.

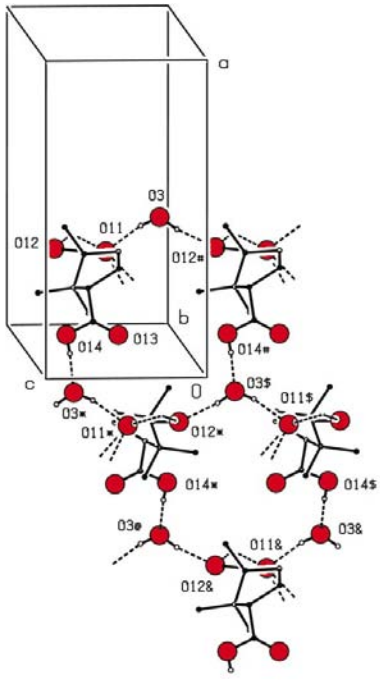


Figure 18
Part of the crystal structure of (VII) showing the formation of a (010) sheet of $R_6^6(26)$ rings built from anions and water molecules only. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or at (@) sign are at the symmetry positions $(-\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$, $(x, y, -1+z)$, $(-\frac{1}{2}+x, \frac{1}{2}-y, -z)$, $(-1+x, y, -1+z)$ and $(-1+x, y, z)$, respectively.

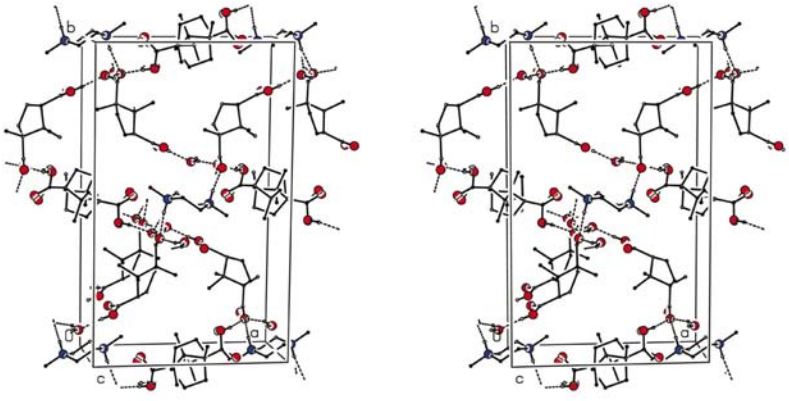


Figure 19
Stereoview of part of the crystal structure of (VII) showing the linking of (010) sheets by the cations and the neutral camphoric acid molecules.

X-ray data were collected at the University of Toronto using a Nonius Kappa-CCD diffractometer purchased with funds from NSERC Canada.

References

Barnes, J. C., Paton, J. D., Blyth, C. S. & Howie, R. A. (1991). *Acta Cryst.* C**47**, 1888–1892.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1460–1494.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bowes, K. F., Ferguson, G., Glidewell, C. & Lough, A. J. (2002). *Acta Cryst.* C**58**, o467–o469.
Brock, C. P. & Dunitz, J. D. (1994). *Chem. Mater.* **6**, 1118–1127.
Bruyn, P. J. de, Gable, R. W., Potter, A. C. & Solomon, D. H. (1996). *Acta Cryst.* C**52**, 466–468.
Coupar, P. I., Ferguson, G., Glidewell, C. & Meehan, P. R. (1997). *Acta Cryst.* C**53**, 1978–1980.
Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.
Dahl, T. & Hassel, O. (1971). *Acta Chem. Scand.* **25**, 2168–2174.
Farrell, D. M. M., Ferguson, G., Lough, A. J. & Glidewell, C. (2002*a*). *Acta Cryst.* B**58**, 272–288.
Farrell, D. M. M., Ferguson, G., Lough, A. J. & Glidewell, C. (2002*b*). *Acta Cryst.* B**58**, 530–544.
Ferguson, G. (1999). *PRPKAPPA. A WordPerfect* 5.1 *Macro to Formulate and Polish CIF Format Files from the SHELXL*97 *Refinement of Kappa-CCD Data.* University of Guelph, Canada.
Ferguson, G., Glidewell, C., Lewis, A. & Zakaria, C. M. (1995). *J. Organomet. Chem.* **492**, 229–234.
Goswami, S., Mukherjee, R., Ghosh, K., Razak, I. A., Sundara Raj, S. S. & Fun, H.-K. (2000). *Acta Cryst.* C**56**, 477–478.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* B**56**, 39–57.
Jordan, T. H. & Mak, T. C. W. (1970). *J. Chem. Phys.* **52**, 3790–3794.
MacLean, E. J., Glidewell, C., Ferguson, G., Gregson, R. M. & Lough, A. J. (1999). *Acta Cryst.* C**55**, 1867–1870.
Mahmoud, M. M. & Wallwork, S. C. (1979). *Acta Cryst.* B**35**, 2370–2374.
Mak, T. C. W., Chen, X.-M., Shi, K.-L., Yao, J.-X. & Zheng, C. (1986). *J. Cryst. Spectrosc. Res.* **16**, 639–646.
Mak, T. C. W., Yu, W.-H. & Lam, Y.-S. (1978). *Acta Cryst.* B**34**, 2061–2063.
Meehan, P. R., Gregson, P. R., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* C**53**, 1637–1640.
Nonius (1997). *Kappa-CCD Server Software.* Windows 3.11 Version. Nonius B V, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.
Wilson, A. J. C. (1993). *Acta Cryst.* A**49**, 795–806.
Yokozeki, A. & Kuchitsu, K. (1971). *Bull. Chem. Soc. Jpn*, **44**, 72–77.