Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

meso-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane as a building block in supramolecular chemistry; salts formed with 2,2′-biphenol, 4,4′-biphenol, 4,4′-thiodiphenol, 4,4′-sulfonyldiphenol, 3- and 4-hydroxybenzoic acids, 3,5-dihydroxybenzoic acid and phenylphosphonic acid; supramolecular structures in zero, one, two and three dimensions

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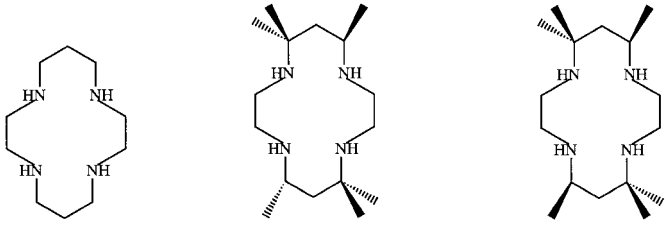
Received 1 March 1999
Accepted 28 April 1999

The structure of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–2,2′-biphenol (1/2), $(C_{16}H_{36}N_4).(C_{12}H_{10}O_2)_2$ (1), is a salt $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4C_6H_4O]^-$: the cations are centrosymmetric with two protons held within the N_4 cavity of the macrocycle by N—H···N hydrogen bonds, and the phenolate anions contain intramolecular O—H···O$^-$ hydrogen bonds. The ions are linked into a finite centrosymmetric aggregate by means of N—H···O hydrogen bonds. *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane–4,4′-thiobiphenol–methanol (1/2/2), $(C_{16}H_{36}N_4).(C_{12}H_{10}O_2S)_2.(CH_4O)_2$ (2), and *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–4,4′-sulfonylbiphenol–methanol (1/2/2), $(C_{16}H_{36}N_4).(C_{12}H_{10}O_4S)_2.(CH_4O)_2$ (3), are isomorphous: each is a salt, $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4SC_6H_4O]^-.2MeOH$ (2) and $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4SO_2C_6H_4O]^-.2MeOH$ (3), and in each the phenolate anions are linked by O—H···O$^-$ hydrogen bonds into chains; antiparallel pairs of chains are cross-linked by the cations to form molecular ladders, with neutral methanol molecules acting as spacer units. In *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–3-hydroxybenzoic acid–methanol (1/2/2) (4), 3-hydroxybenzoate anions form chains, again cross-linked in pairs by the $[C_{16}H_{38}N_4]^{2+}$ cations to form molecular ladders, different from those in (2) and (3) in that the neutral methanol units are pendent from the ladders, rather than forming a part of it. *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane–4-hydroxybenzoic acid–methanol (1/2/1) (5) is again a salt, $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4COO]^-.MeOH$: chains of 4-hydroxybenzoate anions are continuously cross-linked by two different types of $[C_{16}H_{38}N_4]^{2+}$ cation into a two-dimensional net. Only one of the two types of cation is linked to the chains *via* neutral methanol spacer units. *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane–phenylphosphonic acid–water (1/4/2) (6) is a salt, $[C_{16}H_{40}N_4]^{4+}.4[C_6H_5PO_3H]^-.2H_2O$, containing the centrosymmetric tetraprotonated amine units, which have a conformation quite different from the *trans*-III conformation uniformly found in the $[C_{16}H_{38}N_4]^{2+}$ cations. The phenylphosphonate anions and the water molecules are linked into chains of fused rings, which are linked by the cations into two-dimensional nets. In

meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane–3,5-dihydroxybenzoic acid (1/2) (7), the 3,5-dihydroxybenzoate anions in the unsolvated salt $[C_{16}H_{38}N_4]^{2+}.2[(HO)_2C_6H_3COO]^-$ are linked into continuous two-dimensional nets, which are in turn linked by the centrosymmetric cations to form a three-dimensional framework. *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane–4,4′-biphenol (1/3) (8) is a salt containing both neutral and anionic biphenol units, $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4C_6H_4O]^-.[HOC_6H_4C_6H_4OH]$. The two types of biphenol unit form two-dimensional nets and these nets are linked by the cations to form three independent, three-dimensional frameworks which are fully interwoven, but not bonded to one another.

1. Introduction

The tetraaza macrocycle 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$ cyclam (i), is strongly basic and readily captures two protons to form a dication $[C_{10}H_{26}N_4]^{2+}$, in which two H atoms are held in the interior N_4 cavity of the ring by means of intramolecular N—H···N hydrogen bonds. There are four external N—H bonds roughly normal to the ring and hence this dication can act as a fourfold donor in hydrogen-bond formation, in which the geometric arrangement of the hydrogen bonds is pre-determined. Cyclam is thus a versatile building block for crystal engineering purposes (Ferguson *et al.*, 1998*a*, 1999).



Closely related to cyclam are the *meso* and racemic 5,5,7,12,12,14-hexamethyl analogues tet-a (ii) and tet-b (iii), having respectively C_i and C_2 molecular symmetry. These hexamethyl derivatives differ from the parent cyclam in their *N*-alkylation behaviour: whereas cyclam is readily tetra-*N*-alkylated, both tet-a and tet-b undergo only di-*N*-alkylation, at N1 and N8. The other two N sites, N4 and N11, appear to be protected by the adjacent gem-dimethyl substituents and the resulting dialkylated product from tet-a is centrosymmetric (Hay *et al.*, 1996). If this steric shielding of two of the N sites also applied to the hydrogen-bonding behaviour of the dications formed from tet-a and tet-b, then these cations should provide two quite distinct hydrogen-bonding building blocks. The centrosymmetric tet-a dication should have two N—H bonds active as hydrogen-bond donors, one on each face of the macrocycle, whereas in the tet-b dication the two active N—H bonds are expected to be on the same face of the macrocycle.

In this paper we report on the results of a structural investigation of some adducts formed between tet-a, and some simple phenolic and acidic compounds which demonstrate the versatility of tet-a in supramolecular chemistry: architectures ranging between zero-dimensional and three-dimensional are found. In most cases, the tet-a moiety is found as the doubly protonated dication $[C_{16}H_{38}N_4]^{2+}$ with two protons held by N—H···N hydrogen bonds within the N4 cavity of the macrocycle and with four exterior N—H bonds: in a single example, the 1:4 adduct with phenylphosphonic acid, the tet-a is protonated at all four N atoms and there are thus no intramolecular hydrogen bonds. 2,2′-Biphenol forms the 1:2 salt $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4C_6H_4O]^-$ (1), while 4,4′-thiodiphenol, $S(C_6H_4OH)_2$, 4,4′-sulfonyldiphenol, $SO_2(C_6H_4OH)_2$, and 3-hydroxybenzoic acid, HOC_6H_4COOH, all form methanol-solvated salts of 1:2:2 stoichiometry, (2)–(4), respectively: $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4SC_6H_4O]^-.2MeOH$ (2), $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4SO_2C_6H_4O]^-.2MeOH$ (3), and $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4COO]^-.2MeOH$ (4); 4-hydroxybenzoic acid forms a 1:2:1 methanol-solvated salt $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4COO]^-.MeOH$ (5), and phenylphosphonic acid forms an aquated salt of 1:4:2 stoichiometry $[C_{16}H_{40}N_4]^{4+}.4[C_6H_5PO_3H]^-.2H_2O$ (6). 3,5-Dihydroxybenzoic acid $(HO)_2C_6H_3COOH$ forms an unsolvated 1:2 salt $[C_{16}H_{38}N_4]^{2+}.2[(HO)_2C_6H_3COO]^-$(7), and 4,4′-biphenol forms an unsolvated 1:3 compound (8) containing both neutral and deprotonated biphenol units $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4C_6H_4O]^-.[HOC_6H_4C_6H_4OH]$. The structure analyses reported here demonstrate that (1) forms finite, zero-dimensional supramolecular aggregates, (2)–(4) all form one-dimensional molecular ladders, and (5) and (6) both form two-dimensional networks. In (7) and (8) the phenolic components form two-dimensional network substructures, linked by the cations to form three-dimensional frameworks: in (7), a single framework defines the entire crystal structure, while in (8) there are three identical but independent interwoven frameworks.

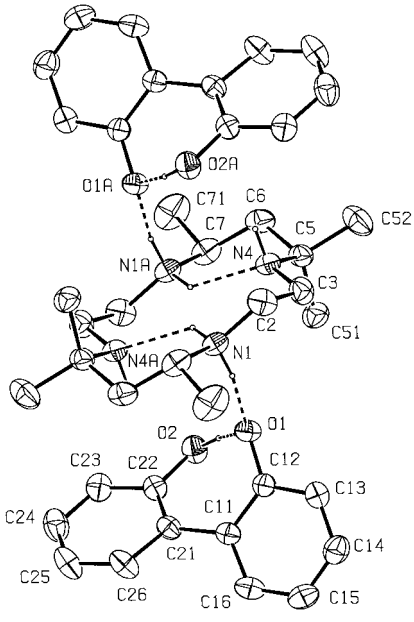
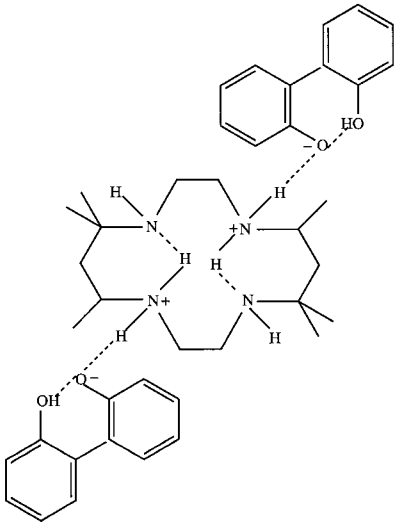


Figure 1
The molecular aggregate in (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

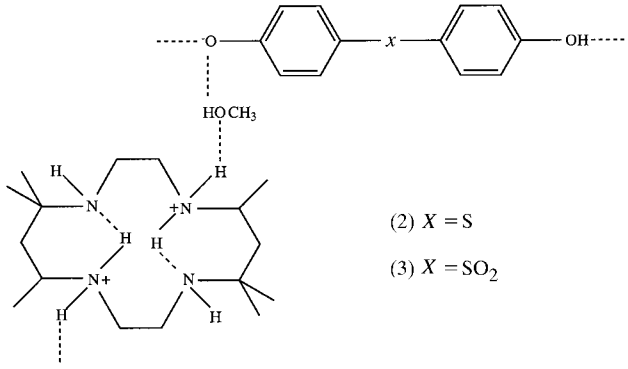
2. Experimental

2.1. Synthesis

Tet-a was prepared by the literature method (Hay *et al.*, 1975). Compounds (1)–(8) were prepared by co-crystallizing tet-a with the appropriate phenol or acid from solutions in methanol exposed to the laboratory atmosphere: the amine and the phenol were separately dissolved in methanol, and these solutions were mixed to give stoichiometric ratios of amine-to-phenol in the range 2:1–1:2. For each system the

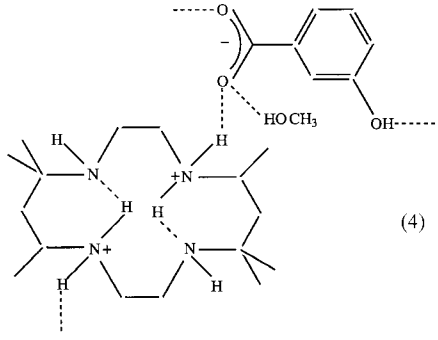


(1)

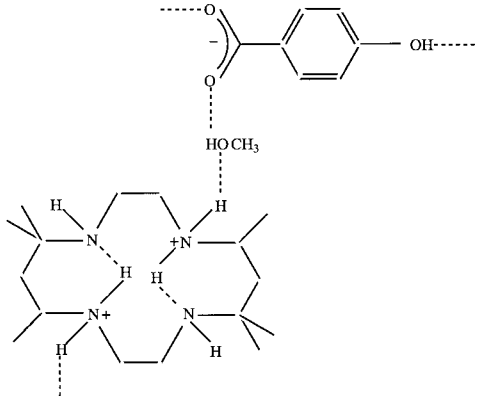


(2) $X = S$

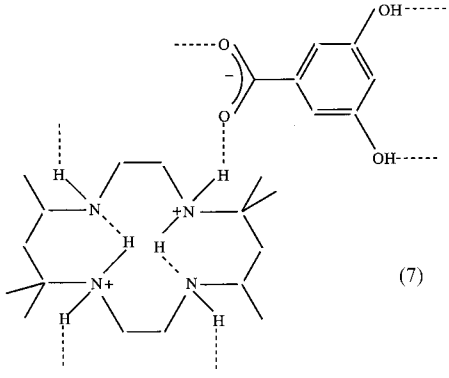
(3) $X = SO_2$



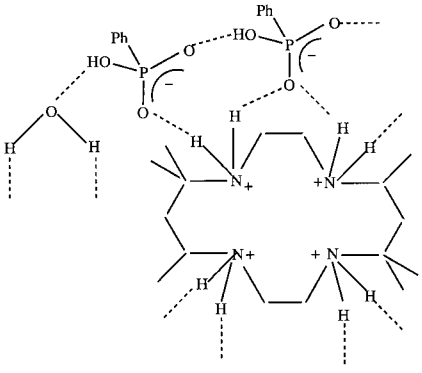
(4)



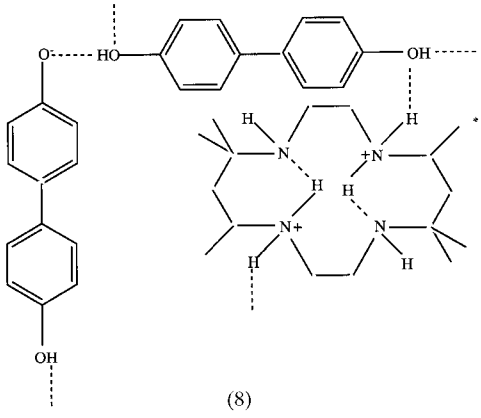
(5)



(7)



(6)



(8)

Table 1
Experimental details.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$C_{16}H_{38}N_4^{2+}.2C_{12}H_9O_2^-$	$C_{16}H_{38}N_4^{2+}.2C_{12}H_9O_2S^-.2CH_4O$	$C_{16}H_{38}N_4^{2+}.2C_{12}H_9O_4S^-.2CH_4O$	$C_{16}H_{38}N_4^{2+}.2C_7H_5O_3^-.2CH_4O$	$C_{16}H_{38}N_4^{2+}.2C_7H_5O_3^-.CH_4O$
Chemical formula weight	656.89	785.11	849.09	624.81	592.77
Cell setting	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P2_1/c$	$P2_1/c$	$P\overline{1}$	$P\overline{1}$
a (Å)	8.6323 (19)	10.659 (5)	10.7736 (10)	8.0814 (9)	9.4481 (7)
b (Å)	9.943 (3)	17.892 (5)	18.1167 (18)	10.1981 (12)	9.8905 (6)
c (Å)	12.582 (2)	11.679 (5)	11.5532 (14)	10.7800 (16)	18.0942 (12)
α (°)	98.783 (17)	90	90	79.789 (10)	88.704 (5)
β (°)	102.785 (15)	103.107 (5)	101.136 (9)	80.728 (10)	78.675 (4)
γ (°)	115.746 (11)	90	90	80.280 (10)	77.525 (4)
V (Å^3)	909.8 (4)	2169.3 (15)	2212.5 (4)	853.89 (19)	1618.43 (19)
Z	1	2	2	1	2
D_x (Mg m^{-3})	1.199	1.202	1.275	1.215	1.216
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	7	25	25	18 522
θ range (°)	7.89–18.58	7.3–11.7	8.41–13.4	8.73–17.36	4.2–26.4
μ (mm^{-1})	0.077	0.172	0.18	0.087	0.086
Temperature (K)	294 (1)	294 (1)	294 (1)	294 (1)	100 (1)
Crystal form	Needle	Plate	Plate	Block	Block
Crystal size (mm)	0.39 × 0.19 × 0.17	0.45 × 0.4 × 0.35	0.42 × 0.33 × 0.12	0.42 × 0.29 × 0.21	0.35 × 0.2 × 0.2
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless
Data collection					
Diffractometer	Enraf–Nonius CAD-4	Rigaku AFC-7*S*	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Nonius KappaCCD
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	ω scans
Absorption correction	None	None	None	None	None
No. of measured reflections	3375	3947	4294	3169	18 522
No. of independent reflections	3375	3802	4091	3169	6587
No. of observed reflections	2146	2602	2056	1794	2949
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.000	0.005	0.010	0.000	0.091
θ_{max} (°)	25.45	25	25.42	25.44	26.41
Range of h, k, l	$-10 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 12$ $-15 \rightarrow l \rightarrow 15$	$0 \rightarrow h \rightarrow 12$ $-3 \rightarrow k \rightarrow 21$ $-13 \rightarrow l \rightarrow 13$	$-13 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 21$ $0 \rightarrow l \rightarrow 13$	$-9 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 12$ $-12 \rightarrow l \rightarrow 13$	$0 \rightarrow h \rightarrow 11$ $-11 \rightarrow k \rightarrow 12$ $-22 \rightarrow 1 \rightarrow 22$
No. of standard reflections	3	3	3	3	–
Frequency of standard reflections	Every 120 min	Every 120 min	Every 120 min	Every 120 min	–
Intensity decay (%)	0.2	1.3	0.5	1.0	0
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0523	0.0375	0.0461	0.0482	0.0520
$wR(F^2)$	0.1334	0.1030	0.1077	0.1183	0.1199
S	1.030	1.042	0.958	0.943	0.843
No. of reflections used in refinement	3375	3802	4091	3169	6587
No. of parameters used	221	250	266	206	394
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.0289P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.5476P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0	0	0	0	0.001

Table 1 (continued)

	(1)	(2)	(3)	(4)	(5)
$\Delta\rho_{max}$ (e Å^{-3})	0.156	0.175	0.192	0.165	0.237
$\Delta\rho_{min}$ (e Å^{-3})	−0.189	−0.162	−0.209	−0.142	−0.221
Extinction method	None	*SHELXL*97 (Sheldrick, 1997)	*SHELXL* (Sheldrick, 1997)	*SHELXL* (Sheldrick, 1997)	*SHELXL* (Sheldrick, 1997)
Extinction coefficient	0	0.0079 (8)	0.0022 (6)	0.017 (4)	0.0048 (11)
Computer programs					
Data collection	*CAD*-4-*PC* (Enraf–Nonius, 1992)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*CAD*-4-*PC* (Enraf–Nonius, 1992)	*CAD*-4-*PC* (Enraf–Nonius, 1992)	*KappaCCD* (Nonius, 1998)
Cell refinement	*SET*4 and *CELDIM* in *CAD*-4-*PC* (Enraf–Nonius, 1992)	*MSC/AFC* (Molecular Structure Corporation, 1988)	*SET*4 and *CELDIM* in *CAD*-4-*PC* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* in *CAD*-4-*PC* (Enraf–Nonius, 1992)	*DENZO* (Nonius, 1998)
Data reduction	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DENZO* (Nonius, 1998)
Structure solution	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)
Structure refinement	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)
Preparation of material for publication	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson, 1988)	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson, 1988)	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson, 1988)	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson, 1988)	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson, 1988)

	(6)	(7)	(8)
Crystal data			
Chemical formula	$C_{16}H_{40}N_4^{4+}.4C_6H_6O_3P^-.2H_2O$	$C_{16}H_{38}N_4^{2+}.2C_7H_5O_4^-$	$C_{16}H_{38}N_4^{2+}.\ C_{12}H_{10}O_2.2C_{12}H_9O_2^-$
Chemical formula weight	952.86	592.72	843.09
Cell setting	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.7391 (2)	8.9162 (13)	9.9634 (10)
b (Å)	26.1558 (7)	11.8903 (10)	18.8981 (19)
c (Å)	10.7871 (2)	14.5229 (18)	12.2344 (11)
β (°)	107.267 (13)	100.419 (7)	97.725 (7)
V (Å^3)	2354.57 (9)	1514.3 (3)	2282.7 (4)
Z	2	2	2
D_x (Mg m^{-3})	1.344	1.300	1.227
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	22 140	25	25
θ range (°)	4.1–26.4	9.59–19.4	10.0–18.41
μ (mm^{-1})	0.227	0.094	0.08
Temperature (K)	100 (1)	294 (1)	294 (1)
Crystal form	Block	Plate	Plate
Crystal size (mm)	0.3 × 0.25 × 0.15	0.41 × 0.41 × 0.29	0.28 × 0.22 × 0.04
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Nonius KappaCCD	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	ω scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	None	None	None
No. of measured reflections	22 140	3595	4427
No. of independent reflections	4796	3470	4232
No. of observed reflections	3777	2576	2138
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.065	0.009	0.012
θ_{max} (°)	26.38	27.41	25.43

Table 1 (continued)

	(6)	(7)	(8)
Range of h, k, l	$-10 \rightarrow h \rightarrow 10$ $-32 \rightarrow k \rightarrow 32$ $-13 \rightarrow l \rightarrow 12$	$-11 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 15$ $0 \rightarrow l \rightarrow 18$	$-12 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 22$ $0 \rightarrow l \rightarrow 14$
No. of standard reflections	–	3	3
Frequency of standard reflections	–	Every 120 min	Every 120 min
Intensity decay (%)	0	0.2	0.6
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0402	0.0419	0.0527
$wR(F^2)$	0.1011	0.1116	0.1262
S	1.032	1.052	0.931
No. of reflections used in refinement	4796	3470	4232
No. of parameters used	293	195	286
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0360P)^2 + 1.8098P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.2636P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0	0
$\Delta\rho_{max}$ (e Å^{-3})	0.300	0.213	0.192
$\Delta\rho_{min}$ (e Å^{-3})	−0.499	−0.196	−0.174
Extinction method	None	None	*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient	0	0	0.0055 (8)
Computer programs			
Data collection	*KappaCCD* (Nonius, 1998)	*CAD*-4-*PC* (Enraf–Nonius, 1992)	*CAD*-4-*PC* (Enraf–Nonius, 1992)
Cell refinement	*DENZO* (Nonius, 1998)	*SET*4 and *CELDIM* in *CAD*-4-*PC* (Enraf–Nonius, 1992)	*SET*4 and *CELDIM* in *CAD*-4-*PC* (Enraf–Nonius, 1992)
Data reduction	*DENZO* (Nonius, 1998)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)
Structure solution	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)
Structure refinement	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 (Sheldrick, 1997)
Preparation of material for publication	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson 1988)	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson 1988)	*NRCVAX*96 (Gabe *et al.*, 1989), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1998), *PREP*8 (Ferguson 1988)

same product was formed regardless of the starting stoichiometry. Analyses: (1) found: C 73.5, H 8.6, N 8.6%; $C_{40}H_{56}N_4O_4$ requires: C 73.1, H 8.6, N 8.5%; (2) found: C 64.6, H 8.4, N 7.2%; $C_{42}H_{64}N_4O_6S_2$ requires: C 64.2, H 8.2, N 7.1%; (3) found: C 59.5, H 7.8, N 6.6%; $C_{42}H_{64}N_4O_{10}S_2$ requires: C 59.4, H 7.6, N 6.6%; (4) found: C 61.1, H 9.1, N 8.9%; $C_{32}H_{56}N_4O_8$ requires: C 61.5, H 9.0, N 9.0%; (5) found C 62.4, H 9.2, N 9.5%; $C_{31}H_{52}N_4O_7$ requires: C 62.8, H 8.8, N 9.5%; (6) found C 50.0, H 7.1, N 5.8%; $C_{40}H_{68}N_4P_4O_{14}$ requires: C 50.4, 7.2, N 5.9%; (7) found: C 61.0, H 8.3, N 9.5%; $C_{30}H_{48}N_4O_8$ requires: C 60.8, H 8.2, N 9.5%; (8) found: C 74.0, H 7.8, N 6.7%; $C_{52}H_{66}N_4O_6$ requires: C 74.1, H 7.9, N 6.7%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Diffraction data for compounds (1), (3), (4), (7) and (8) were collected at 294 (1) K using an Enraf–Nonius CAD-4 diffractometer; data for (2) were collected at 294 (1) K using a Rigaku AFC-7*S* diffractometer; data for (5) and (6) were collected at 100 (1) K using a Nonius Kappa CCD diffractometer: in all cases graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) was employed. Other details of cell data, data collection and refinement are summarized in Table 1. Compounds (1), (4) and (5) are all triclinic: for each the space group $P\bar{1}$ was selected and confirmed by the successful structure analysis. For each of the compounds (2), (3), (6), (7) and (8) the space group $P2_1/c$ was uniquely determined from the systematic absences. The structures were all solved by direct methods using *NRCVAX* (Gabe *et al.*, 1989) and refined with all data on F^2 using *SHELXL*97 (Sheldrick, 1997). A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). No absorption corrections were necessary. All H atoms were located from difference maps and all were included in the refinements as riding atoms. It was apparent at an early stage in the refinements that two H atoms had been transferred to each tet-a unit in (1)–(5), (7) and (8), and that four H atoms had been transfered to the tet-a unit in (6). All H atoms are fully ordered, except for the methyl H atoms of the methanol component in (2); these H atoms were modelled with two sets of sites, offset by a 60° rotation about the C—O bond and each with 0.50 occupancy. Except in (6), H atoms bonded to N are

labelled as H*nA* (axial) or H*nE* (equatorial). The diagrams were prepared with the aid of *PLATON* (Spek, 1998). Hydrogen-bond dimensions are presented in Table 2 and other selected dimensions in Table 3.[1]

3. Results and discussion

3.1. Co-crystallization behaviour

For each of (1)–(8), co-crystallization of tet-a and the appropriate hydrogen-bond donor compound from solutions in methanol gave only a single product, irrespective of the initial molar ratios of acceptor:donor, within the range 2:1–1:2. This is typical of the behaviour previously observed in systems of this type (Coupar *et al.*, 1997; Ferguson *et al.*, 1998*a*). In each of (1)–(5) and (7), the resulting molar ratio of tet-a to hydrogen-bond donor is 1:2, and these ratios, deduced from analytical data (§2.1), were readily interpreted in terms of the formation of the cation $[C_{16}H_{38}N_4]^{2+}$ by transfer to the initially neutral tet-a molecule of a single proton from each of two donor molecules. Similarly, the 1:4 ratio on tet-a to phenylphosphonic acid in (6) was readily interpreted in terms of fourfold protonation of tet-a by the rather stronger acid, thus forming the cation $[C_{16}H_{40}N_4]^{4+}$. Less easily understood was the 1:3 ratio in (8).

However, many of the compounds studied here are solvated, either by methanol or, in the case of (6), by water; in every such case the solvent molecules participate in the hydrogen-bonding scheme. In no case studied here is there any passive solvation (Shivanyuk *et al.*, 1997; Ferguson *et al.*, 1998). The structure analysis of (8) (§3.2) makes clear that the protonation of the tet-a component gives the usual dication $[C_{16}H_{38}N_4]^{2+}$: while two of the 4,4′-biphenol units are anionic, the third is neutral and can be regarded as playing a similar role in (8) to that played by the neutral methanol molecules in (2)–(5).

3.2. Supramolecular structures

3.2.1. Finite aggregates, (1). The structure of (1) is built from centrosymmetric three-component aggregates (Fig. 1). A doubly protonated tet-a moiety lies across a centre of inversion and this dication is linked to the two mono-deprotonated biphenol units, each by means of a single N—H···O hydrogen bond. The constitution of this aggregate thus confirms the 1:2 tet-a:biphenol stoichiometry deduced from elemental analysis.

The dication adopts the *trans*-III conformation commonly observed in $[cyclamH_2]^{2+}$ salts (Adam *et al.*, 1994; Ferguson *et al.*, 1998*a*), with a remarkably flat heavy-atom skeleton having almost perfect staggering about all the C—C and C—N bonds. There are two intra-ring N—H···N hydrogen bonds, and the exterior N—H bonds are all axial and approximately normal to the plane of the macrocycle. The methyl substituent at C7 is equatorial and the exterior N—H bond at N4, adjacent to the gem-dimethyl unit, plays no role in the hydrogen bonding.

The biphenolate anion forms an intramolecular O—H···O hydrogen bond and in consequence of the near-linearity of this hydrogen bond, the two aryl rings are twisted from coplanarity by *ca* 40°. Finally, N1 acts as hydrogen-bond donor, *via* its axial

Table 2
Hydrogen-bond dimensions.

(1)			
O2···O1	2.488 (2)	O2—H2···O1	162
N1···O1	2.584 (3)	N1—H1*A*···O1	160
N1···N4^{i}	2.818 (3)	N1—H1*E*···N4^{i}	136
(2)			
O1···O24	2.591 (3)	O1—H1···O24	172
O14···O24^{ii}	2.568 (2)	O14—H14···O24^{ii}	174
N1···O1	2.733 (3)	N1—H1*A*···O1	168
N1···N4^{i}	2.792 (2)	N1—H1*E*···N4^{i}	139
(3)			
O1···O24	2.632 (3)	O1—H1···O24	175
O14···O24^{ii}	2.571 (3)	O14—H14···O24^{ii}	174
N1···O1	2.749 (3)	N1—H1*A*···O1	166
N1···N4^{i}	2.801 (3)	N1—H1*E*···N4^{i}	137
(4)			
O3···O2^{ii}	2.596 (2)	O3—H3···O2^{ii}	175
O4···O1	2.752(3)	O4—H4···O1	171
N1···O1	2.815 (2)	N1—H1*A*···O1	145†
N1···O3^{iii}	3.202 (2)	N1—H1*A*···O3^{iii}	126†
N1···N4^{i}	2.793 (2)	N1—H1*E*···N4^{i}	138
(5)			
O1···O41	2.740 (3)	O1—H1···O41	167
O34···O41	2.637 (3)	O34—H34···O41	175
O44···O32^{iv}	2.650 (3)	O44—H44···O32^{iv}	173
N11···O32	3.098 (2)	N11—H11*A*···O32	145
N14···O31^{v}	2.656 (3)	N14—H14···O31^{v}	177
N21···O1	2.976 (3)	N21—H21*A*···O1	154
N24···O42^{i}	2.746 (3)	N24—H24*A*···O42^{i}	169
N14···N11^{v}	2.811 (3)	N14—H14*E*···N11^{v}	128
N24···N21^{i}	2.867 (3)	N24—H24*E*···N21^{i}	139
(6)			
O11···O23	2.496 (2)	O11—H11···O23	152
O21···O1	2.616 (2)	O21—H21···O1	171
O1···O22^{vi}	2.707 (2)	O1—H1···O22^{vi}	169
O1···O13^{vii}	2.744 (2)	O1—H2···O13^{vii}	178
N1···O12	2.692 (2)	N1—H1*B*···O12	171
N1···O13^{vii}	2.750 (2)	N1—H1*A*···O13^{vii}	164
N4···O12	2.753 (2)	N4—H4···O12	164
N4···O22	2.637 (2)	N4—H4*B*···O22	163
(7)			
O3···O1^{vi}	2.677 (2)	O3—H3···O1^{vi}	168
O5···O1^{viii}	2.676 (2)	O5—H5···O1^{viii}	172
N4···O2	2.742 (2)	N4—H4*A*···O2	168
N1···O3^{ix}	3.100 (2)	N1—H1*A*···O3^{ix}	143
N4···N1^{i}	2.846 (2)	N4—H4*E*···N1^{i}	137
(8)			
O14···O24	2.477 (2)	O14—H14···O24	166
O34···O24^{x}	2.601 (2)	O34—H34···O24^{x}	167
N1···O14	2.742 (3)	N1—H1*A*···O14	172
N1···N4^{i}	2.820 (3)	N1—H1*E*···N4^{i}	141

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-1+x, y, z$; (iii) $1+x, y, z$; (iv) $x, -1+y, z$; (v) $-x, 2-y, -z$; (vi) $-x, 1-y, -z$; (vii) $-x, 1-y, 1-z$; (viii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ix) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (x) $-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$. † Three-centred N—H···(O)$_2$ system: angle O1···H1*A*···O3^{iii} is 89°, so that the sum of the angles around H1*A* is 360°.

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0090). Services for accessing these data are described at the back of the journal.

Table 3
Selected molecular dimensions (Å, °).

(*a*) C—N distances in the cations

Compound	N1—C2	N1—C7′	N4—C3	N4—C5	Site of protonation
(1)	1.480 (3)	1.497 (2)	1.463 (2)	1.488 (2)	N1
(2)	1.489 (2)	1.500 (2)	1.466 (2)	1.492 (2)	N1
(3)	1.483 (3)	1.503 (3)	1.463 (3)	1.493 (3)	N1
(4)	1.482 (2)	1.506 (3)	1.468 (3)	1.493 (3)	N1
(5)†					
Cation 1	1.456 (3)	1.479 (3)	1.489 (3)	1.505 (3)	N14
Cation 2	1.480 (3)	1.479 (3)	1.495 (3)	1.513 (3)	N24
(6)	1.499 (2)	1.512 (2)	1.493 (3)	1.519 (2)	N1 and N4
(7)	1.471 (2)	1.487 (2)	1.492 (2)	1.524 (2)	N4
(8)	1.479 (3)	1.505 (3)	1.455 (3)	1.494 (3)	N1

† In (5) atoms are numbered N11, C21 *etc*. in cation 1 and N21, C22 *etc*. in cation 2 (see Fig. 7).

(*b*) Selected dimensions for anionic and neutral components

(1)			
C12—O1	1.329 (2)	C22—O2	1.357 (2)
C11—C12—O1	121.2 (2)	C21—C22—O2	122.3 (2)
C13—C12—O1	120.1 (2)	C23—C22—O2	117.1 (2)
Dihedral angle between aryl rings: 39.6 (1)			
(2)			
C11—S1	1.781 (2)	C21—S1	1.780 (2)
C14—O14	1.355 (2)	C24—O24	1.328 (2)
C1—O1	1.402 (3)		
C11—S1—C21	101.1 (1)		
C13—C14—O14	118.4 (2)	C23—C24—O24	121.9 (2)
C15—C14—O14	123.0 (2)	C25—C24—O24	121.4 (2)
C21—S1—C11—C12	85.4 (2)	C11—S1—C21—C22	85.9 (2)
C21—S1—C11—C16	−94.5 (2)	C11—S1—C21—C26	−93.7 (2)
(3)			
C11—S1	1.759 (3)	C21—S1	1.753 (3)
S1—O11	1.441 (2)	S1—O12	1.436 (2)
C14—O14	1.347 (3)	C24—O24	1.318 (3)
C1—O1	1.413 (3)		
C11—S1—C21	105.4 (1)	O11—S1—O12	119.7 (1)
C13—C14—O14	118.3 (3)	C23—C24—O24	121.7 (3)
C15—C14—O14	122.7 (3)	C25—C24—O24	121.7 (2)
C21—S1—C11—C12	87.3 (3)	C11—S1—C21—C22	83.7 (2)
C21—S1—C11—C16	−90.8 (2)	C11—S1—C21—C26	−94.6 (2)
(4)			
C1—O1	1.261 (3)	C1—O2	1.248 (3)
C13—O3	1.361 (2)	C41—O4	1.392 (3)
O1—C1—O2	123.9 (2)		
C12—C13—O3	117.3 (2)	C14—C13—O3	122.8 (2)
O1—C1—C11—C12	−3.0 (3)	O2—C1—C11—C12	178.4 (2)
O1—C1—C11—C16	176.4 (2)	O2—C1—C11—C16	−2.2 (3)
(5)			
C37—O31	1.260 (3)	C47—O41	1.274 (3)
C37—O32	1.270 (3)	C47—O42	1.253 (3)
C34—O34	1.369 (3)	C44—O44	1.364 (3)
C1—O1	1.407 (3)		
O31—C37—O32	123.3 (2)	O41—C47—O42	123.2 (2)
C33—C34—O34	118.1 (2)	C43—C44—O44	122.6 (2)
C35—C34—O34	122.4 (2)	C45—C44—O44	117.5 (2)

Table 3 (continued)

O31—C37—C31—C32	7.4 (3)	O41—C47—C41—C42	−13.5 (3)
O31—C37—C31—C36	−171.8 (2)	O41—C47—C41—C46	165.9 (2)
O32—C37—C31—C32	−172.4 (2)	O42—C47—C41—C42	167.2 (2)
O32—C37—C31—C32	−172.4 (2)	O42—C47—C41—C42	167.2 (2)
O32—C37—C31—C36	8.5 (3)	O42—C47—C41—C46	−13.4 (3)
(6)			
P1—O11	1.560 (1)	P2—O21	1.577 (2)
P1—O12	1.520 (1)	P2—O22	1.513 (2)
P1—O13	1.504 (1)	P2—O23	1.496 (2)
P1—C11	1.803 (2)	P2—C21	1.798 (2)
O11—P1—O12	111.3 (1)	O21—P2—O22	109.4 (1)
O11—P1—O13	108.2 (1)	O21—P2—O23	111.8 (1)
O12—P1—O13	115.3 (1)	O22—P2—O23	114.6 (1)
O11—P1—C11	105.6 (1)	O21—P2—C21	103.2 (1)
O12—P1—C11	106.3 (1)	O22—P2—C21	108.8 (1)
O13—P1—C11	109.6 (1)	O23—P2—C21	108.4 (1)
O11—P1—C11—C12	−23.6 (2)	O21—P2—C21—C22	−98.6 (2)
O12—P1—C11—C12	94.8 (2)	O22—P2—C21—C22	17.5 (2)
O13—P1—C11—C12	−140.0 (2)	O23—P2—C21—C22	142.7 (2)
(7)			
C1—O1	1.262 (2)	C1—O2	1.241 (2)
C13—O3	1.364 (2)	C15—O5	1.357 (2)
O1—C1—O2	124.5 (1)		
C12—C13—O3	122.1 (1)	C14—C15—O5	122.4 (1)
C14—C13—O3	117.1 (1)	C16—C15—O5	117.1 (1)
O1—C1—C11—C12	23.5 (2)	O2—C1—C11—C12	−158.2 (1)
O1—C1—C11—C16	−156.4 (1)	O2—C1—C11—C16	21.9 (2)
(8)			
C14—O14	1.360 (3)		
C24—O24	1.337 (3)	C34—O34	1.358 (3)
C13—C14—O14	122.2 (2)	C15—C14—O14	120.2 (2)
C23—C24—O24	121.4 (2)	C25—C24—O24	121.8 (2)
C33—C34—O34	123.6 (2)	C35—C34—O34	118.1 (2)
C33—C34—O34	123.6 (2)	C35—C34—O34	118.1 (2)
Dihedral angle between aryl rings C2*n* and C3*n* (*n* = 1–6): 34.1 (1)			

N—H bond, to the deprotonated oxygen O1 of the biphenol. N1 thus acts as a double donor of hydrogen bonds and O1 as a double acceptor: in each case, one interaction is intermolecular and one intramolecular. The structure of (1) may thus be regarded as equivalent to a diagonal slice of the one-dimensional polymeric structure formed by the 1:2 adduct of the same 4,4′-sulfonyldiphenol with cyclam, the unmethylated analogue of tet-a (Ferguson *et al.*, 1999).

The two N—H···N hydrogen bonds within the centrosymmetric cation generate an $R_2^2(10)$ motif (Bernstein *et al.*, 1995) in (1), and indeed in all of the compounds studied here, while the intramolecular O—H···O hydrogen bond in the phenolate anion (Fig. 1) generates an $S(7)$ motif. The linkages between the cation and the anions are of type *D*, so that the overall graph-set descriptor can be written as $D_5^5(12)$ $[R_2^2(10)]$: it has

been noted (Bernstein *et al.*, 1995) that $D[R]$ patterns are likely to be commonly encountered in centrosymmetric systems containing more than one crystallographically distinct moiety. The most common type of $D[R]$ pattern hitherto observed involves just two independent types of hydrogen bond in a centrosymmetric motif $D_3^3(n)$ $[R]$, where the length n takes values between 9 and 20 (Bernstein *et al.*, 1995; Patterson *et al.*, 1998), and indeed $D_3^3(10)$ $[R_2^2(10)]$ would be observed in (1), but for the two additional hydrogen bonds in the $S(7)$ motifs.

The salt-type constitution of (1) is in sharp contrast to that of the 1:1 adduct formed between 2,2′-biphenol and 1,10-phenanthroline (Lavender, Gregson *et al.*, 1999): in this case, no proton transfer occurs and the neutral biphenol molecule is bound to the phenanthroline *via* a three-centre $O-H\cdots(N)_2$ hydrogen bond, as opposed to the $N-H\cdots O$ hydrogen bond in (1).

3.2.2. One-dimensional structures. *Compounds (2) and (3):* Compounds (2) and (3) are isomorphous and both are methanol-solvated salts $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4XC_6H_4O]^-.2MeOH$, where the spacer X represents S in (2) and SO_2 in (3). Their structures consist of molecular ladders. Antiparallel chains of phenolate anions $[HOC_6H_4XC_6H_4O]^-$ linked by $O-H\cdots O$ hydrogen bonds form the uprights of the ladders, and centrosymmetric amine dications form the rungs, linked to the uprights *via* the neutral methanol molecules acting as spacer units.

In each of (2) and (3), the asymmetric unit consists of one half of a diprotonated amine, one phenolate anion and a neutral methanol molecule (Figs. 2 and 3). The phenolate anions are linked into chains running parallel to the [100] direction (Fig. 4): the hydroxyl oxygen O14 at (x, y, z) acts as a donor to the anionic oxygen O24 at $(-1+x, y, z)$ to form a $C(12)$ chain generated by translation. The dication lies across a centre of inversion and, as in (1), there are two fully ordered H atoms held within the N4 cavity by means of $N-H\cdots N$ hydrogen bonds. The ladder is formed by the linking of the amine dications to the [100] chains: within the asymmetric unit, the N1 atom acts as a donor, *via* the external axial H1A, to the methanol oxygen O1, which in turn acts as a donor to the anionic O24. In this way, the dications are suspended, *via* the linking methanol molecules, between pairs of chains forming a single type of $R_{12}^{10}(50)$ ring (Fig. 4). Again as in (1), the N atom adjacent to the gem-dimethyl unit plays no role in the intermolecular hydrogen bonding.

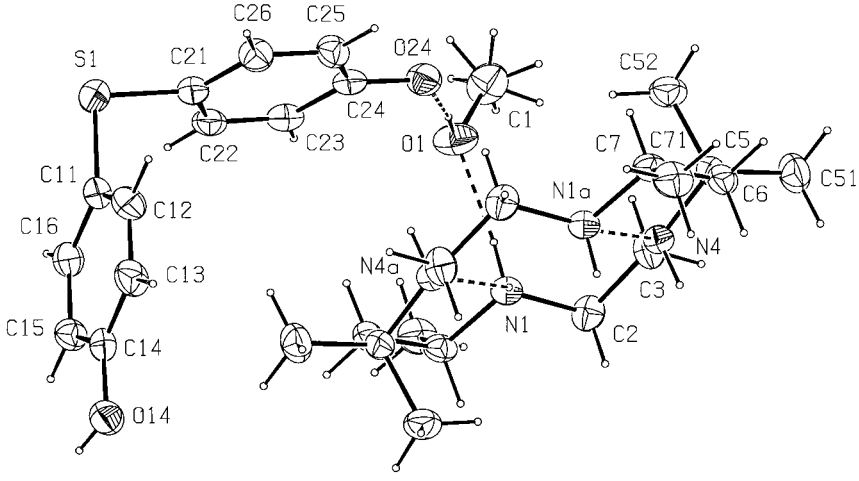


Figure 2
The molecular aggregate in (2): atoms are depicted as in Fig. 1.

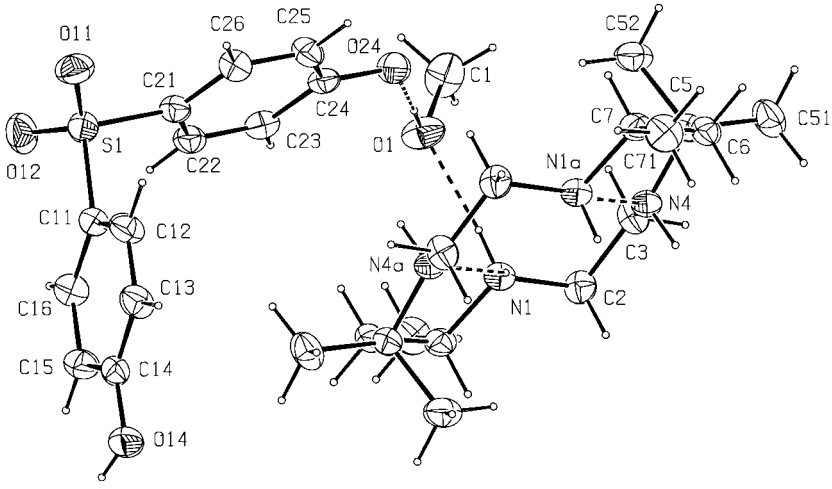


Figure 3
The molecular aggregate in (3): atoms are depicted as in Fig. 1.

Two of these ladders run through each unit cell. The ladder whose rungs are built of the cations centred at $(\frac{1}{2}, (n+1)/2, \frac{1}{2})$ (n = zero or integer) lies within the domain $0.22 < z < 0.75$. A similar ladder, whose rungs are those cations centred at $(\frac{1}{2}, n, 0)$ (n = zero or integer), lies within the domain $-0.25 < z < 0.28$. These two ladders are related to one another by the action of both the glide plane at $y = 0.25$ and the screw axis along $(\frac{1}{2}, y, \frac{1}{4})$.

Compound (4): The structure of (4) (Fig. 5) shows interesting similarities to, as well as differences from, the structures of (2) and (3). The basic supramolecular architecture in (4) is still that of a molecular ladder (Fig. 6) with the uprights now built from chains of 3-hydroxybenzoate anions: the hydroxyl oxygen O3 at (x, y, z) acts as a donor to the carboxylate oxygen O2 at $(-1+x, y, z)$, thus producing by translation a $C(7)$ chain running parallel to the [100] direction. The centrosymmetric cations, again with two fully ordered H atoms within the cavity, are in (4) linked directly to the carboxylate chains without the intervention of the methanol molecules. Instead, the methanol molecules are pendent from the molecular ladder with the methanol oxygen

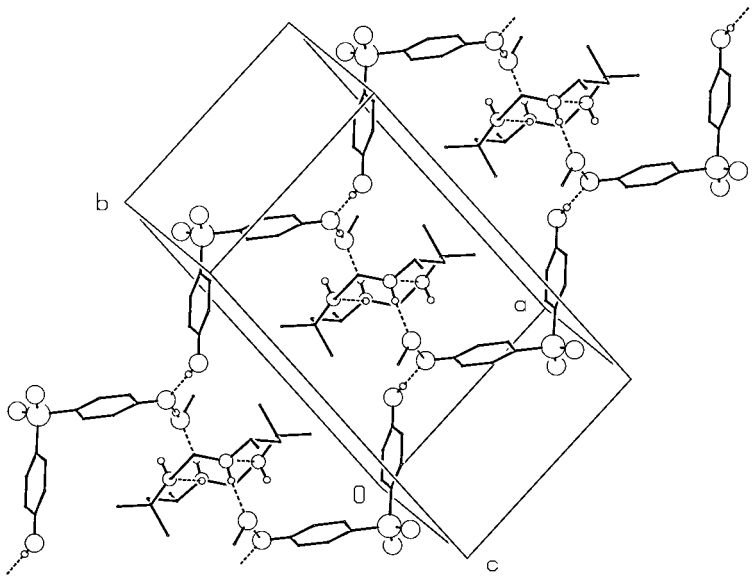


Figure 4
Part of the crystal structure of (3), showing the formation of the molecular ladder parallel to [100]. The ladder in (2) is virtually identical, except for the absence of the sulfone O atoms. For the sake of clarity, H atoms bonded to carbon are omitted.

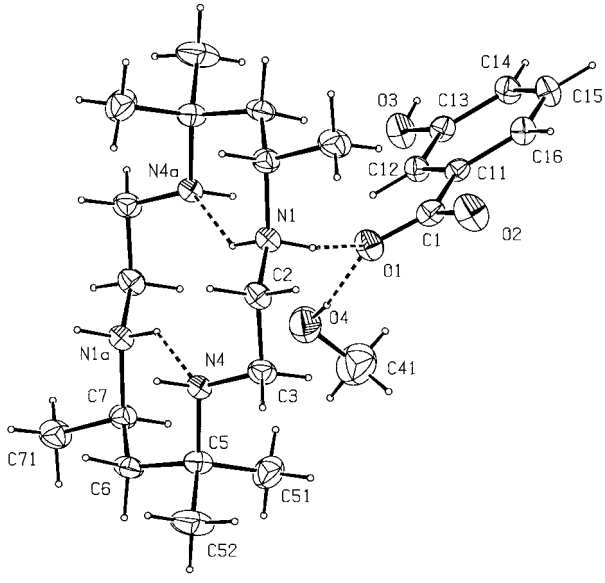


Figure 5
The molecular aggregate in (4): atoms are depicted as in Fig. 1.

O4 acting as a hydrogen-bond donor, but not as an acceptor: the carboxylate oxygen O1, on the other hand, acts as a double acceptor of hydrogen bonds, from both N1 and O4. In contrast to (2) and (3), only one molecular ladder runs through each unit cell.

Although N4 does not act as a hydrogen-bond donor, the mutual disposition of the cations and the oxygen-rich segments of the carboxylate chains is such that N1 at (x, y, z) acts as a donor in a planar three-centre N—H···$(O)_2$ system: as well as acting as a donor to carboxylate oxygen O1 at (x, y, z), N1 at (x, y, z) is also a donor to phenolic oxygen O3 at $(1 + x, y, z)$. Thus, two types of ring can be identified between the rungs of the ladder in (4): the including atoms O2 are of $R_8^8(36)$ type, while those excluding O2 are of $R_6^6(28)$ type (Fig. 6). The formation of similar three-centre hydrogen-bonding systems is prevented in (2) and (3) by the intervention of the methanol spacer, while no such development is necessary in cyclam salts (Ferguson *et al.*, 1998*a*), since all four of the axial N—H bonds are active in hydrogen-bond formation.

3.2.3. Two-dimensional structures. *Compound (5):* In (2) and (3) the tet-a cations are connected to the phenolate chains *via* methanol molecules acting as linker units, whereas in (4) the cations are connected directly to the anion chains while the methanol molecules are pendent units. Both modes of connection are observed in (5). 4-Hydroxybenzoate anions form chains and these chains are linked by the tet-a cations: however, there are two independent cations, both centrosymmetric, one of which is linked directly to the chains by means of four N—H···O hydrogen bonds, while the other forms two N—H···O bonds directly to phenolate anions and another two to intervening methanol molecules. Moreover, the linking pattern differs from that in (4), so that instead of pairwise linking of the chains to form a one-dimensional ladder, the linking is continuous, giving a two-dimensional sheet. In (2), (3) and (4) each anion chain is linked by the cations to just one other anion chain: in (5), however, each anion chain is linked to two others *via* the two different types of cation.

As usual, each tet-a unit has captured two protons, in this case from the 4-hydroxybenzoic acid units: the asymmetric unit consists of two independent 4-hydroxybenzoate units, two independent half-molecules of the tet-a cation and a neutral methanol molecule (Fig. 7). The cations both lie across centres of inversion, so that the overall stoichiometry tet-a:acid:methanol is 1:2:1 with $Z = 2$. One of the cations, that containing N11 and N14, exhibits rotational disorder equivalent to a 180° rotation of a fraction 0.584 (5) of the cations about a line joining the midpoint of the C12—C13 bond and the centre of inversion at (0, 1, 0). The net effect of this disorder is to distribute the axial methyl groups between two sites on C15 and C17 with s.o.f.s of 0.584 (5) and 0.416 (5) with the corresponding axial H atoms similarly disorderd with s.o.f.s of 0.416 (5) and 0.584 (5). All the other atoms in this cation site are fully ordered.

Within the asymmetric unit (Fig. 7), hydroxyl oxygen O34 acts as a donor to carboxylate oxygen O41; hydroxyl O44 at (x, y, z) similarly acts as a donor to carboxylate O32 at $(x, -1 + y, z)$, thus generating a $C_2^2(16)$ chain running parallel to the [010] direction. Two such chains, related by centres of inversion, and thus are antiparallel, run through each unit cell. Each type of cation utilizes all four of its axial N—H bonds in forming links to pairs of these anion chains. Cations of type 1 (containing N11) centred at $(0, n, 0)$ (n = zero or integer) link

the anion chains at (x, z) and $(-x, -z)$, while cations of type 2 (containing N21) centred at $(\frac{1}{2}, \frac{1}{2} + n, \frac{1}{2})$ (n = zero or integer) link the anion chains at (x, z) and $(1 - x, 1 - z)$: in this manner a continuous two-dimensional sheet parallel to $(10\bar{1})$ is generated (Fig. 8). Type 1 cations are linked directly to the anion chains: within one cation, N11 at (x, y, z) and N14 at $(-x, 2 - y, -z)$ act as donors to the carboxylate O atoms O32 and O31, respectively, at (x, y, z), while the other two N atoms in the same cation, centred at (0, 1, 0), are donors to O32 and O31 at $(-x, 2 - y, -z)$, thus linking the (x, z) and $(-x, -z)$ chains. For the type 2 cations, two of the N—H···O hydrogen bonds have carboxylate oxygen as the acceptor and two have methanol oxygen as the acceptor. N21 at (x, y, z) acts as a donor to methanol O1 at (x, y, z) and this in turn acts as a donor to carboxylate O41 at (x, y, z): in the same cation, N24 at $(1 - x, 1 - y, 1 - z)$ acts as a donor directly to O42 at (x, y, z). The other two N atoms in this cation, which is centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, are donors, one *via* methanol and one directly, to the carboxylate O atoms O41 and O42 at $(1 - x, 1 - y, 1 - z)$: hence, the chains at (x, z) and $(1 - x, 1 - z)$ are linked.

The two types of linkage of the cations to the [010] chains generate two types of centrosymmetric ring in the $(10\bar{1})$ network: there are $R_8^6(46)$ rings centred at $(0, \frac{1}{2} + n, 0)$ (n = zero or integer) and $R_{10}^8(50)$ rings centred at $(\frac{1}{2}, n, \frac{1}{2})$ (n = zero or integer), thus generating a checker-board pattern of the two types of ring on the $(10\bar{1})$ plane.

Compound (6): In (6) the stoichiometric ratio of tet-a to phenylphosphonic acid units is 1:4. The tet-a is tetra-protonated to form the unusual cation $[C_{16}H_{40}N_4]^{4+}$, in which each nitrogen is of $R_2NH_2^+$ type: there is thus no intramolecular N—H···N hydrogen bonding and all eight of the N—H bonds participate in the intermolecular hydrogen bonding. The asymmetric unit (Fig. 9) consists of one half of a tet-a tetracation, two independent phenylphosphonate anions, $[C_6H_5PO_3H]^-$, and one neutral water molecule, consistent with the 1:4:2 molar ratio of tet-a:acid:water deduced from elemental analysis (§2.1).

The overall structure is built of two-dimensional tripartite layers. The central slice of each layer is polar, consisting of the cations, the water molecules and the PO_3H fragments of the anions: the two outer, non-polar slices of the layer are composed of phenyl groups. Within the two-dimensional layer, it is possible to identify a one-dimensional substructure generated solely by the phenylphosphonate anions and the water molecules.

Within the asymmetric unit, phenylphosphonate anions are linked in pairs: O11 in anion 1 (containing P1) acts as a donor to anionic O23 in anion 2 (containing P2) and these pairs of anions are further linked by water molecules. The anion pair at (x, y, z) acts as an acceptor, *via* O22, from O1 at $(-x, 1 - y, -z)$ and, *via* O13, from O1 $(-x, 1 - y, 1 - z)$: in this manner, a $C_3^3(10)$ chain is produced running parallel to [001]. Pairs of antiparallel chains are linked into a chain of fused rings: O21 at (x, y, z) in one chain acts as a donor to the water molecule also at (x, y, z), but forming part of the second chain. This produces a sequence of alternating small and large rings: $R_4^4(12)$ rings centred at $(0, \frac{1}{2}, n)$ (n = zero or integer) and $R_6^6(20)$ rings centred at $(0, \frac{1}{2}, \frac{1}{2} + n)$ (n = zero or integer; Fig. 10). The chain of fused rings has a polar centre layer, but the outer edges consist solely of non-polar phenyl groups. In adducts of phenylphosphonic acid with diamines (Ferguson, *et al.*, 1998*b*), the acid units retain either the cyclic dimeric $R_2^2(8)$ motif or the extended $C(4)$ chain motif, both of which can be identified in the parent acid (Weakley, 1976): neither motif is identifiable in the structure of (6).

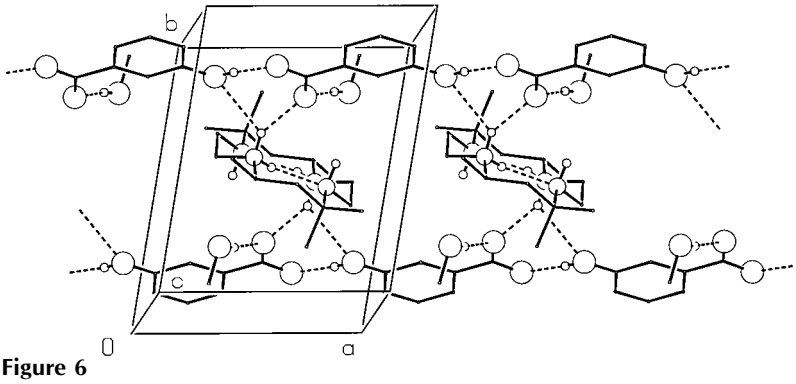


Figure 6
Part of the crystal structure of (4), showing the formation of the molecular ladder parallel to [100]: atoms are depicted as in Fig. 4.

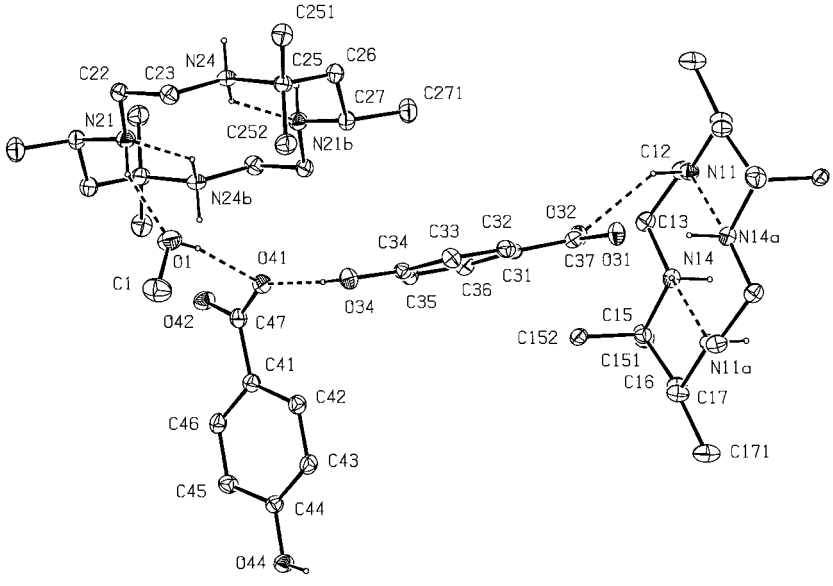


Figure 7
The molecular aggregate in (5): atoms are depicted as in Fig. 1. Only the major cation orientation is shown.

These one-dimensional anion/water arrays are then linked by the cations into a two-dimensional network: the binding of the cations to the anion chains is elaborate. Within the asymmetric unit (Fig. 9 and Table 2), both N1 and N4 act as hydrogen-bond donors, *via* H1*B* and H4*A*, respectively, to O12, while N4 also acts as a donor, *via* H4*B*, to O22, generating a double-ring motif. The fourth independent N—H bond, N1—H1*A* at (x, y, z), forms a hydrogen bond with O13 at $(-x, 1-y, 1-z)$: the symmetry-related N1—H1*A* bond, at $(1-x, 1-y, 1-z)$, in the same cation forms a hydrogen bond to O13 at $(1+x, y, z)$. Hence, anion 1 at (x, y, z) is linked *via* the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ to anion 1 at $(1+x, y, z)$: in turn anion 1 at (x, y, z) links the two cations centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively, thus forming a $C_2^2(10)$ chain parallel to [100]. The interaction of these [100] chains with the [001] chains built from anions and water molecules then produces the two-dimensional network parallel to (010) built from a single type of $R_{10}^8(36)$ ring (Fig. 11).

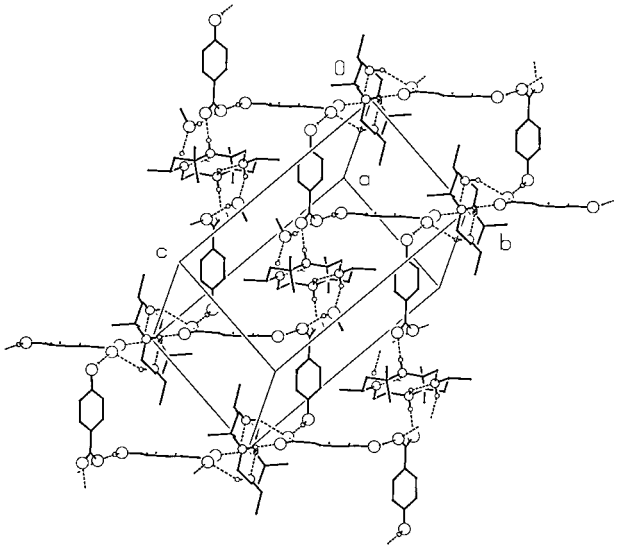


Figure 8
Part of the crystal structure of (5), showing the two-dimensional sheet parallel to $(10\bar{1})$: atoms are depicted as in Fig. 4. Only the major cation orientation is shown.

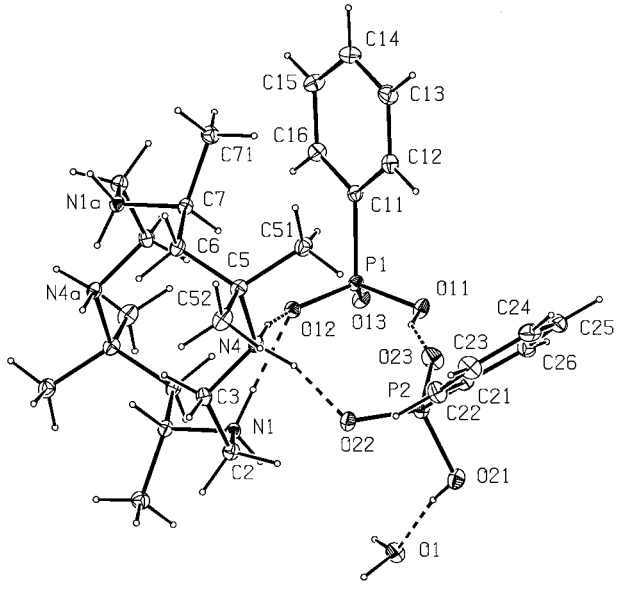


Figure 9
The molecular aggregate in (6): atoms are depicted as in Fig. 1.

The (010) network lies in the domain $\frac{1}{4} < y < \frac{3}{4}$ and a second identical network, related to the first by the action of the 2_1 screw axes, lies in the domain $-\frac{1}{4} < y < \frac{1}{4}$. The outer surface of each such layer consists entirely of phenyl rings, but there are no contacts between neighbouring layers which are significantly shorter than the sum of van der Waals radii.

3.2.4. Three-dimensional structures. *Compound (7):* The incorporation of a second hydroxyl group in the carboxylic acid component, 3,5-dihydroxybenzoic acid, in (7) leads to the development of a three-dimensional structure, as compared to the one-dimensional structure generated by 3-hydroxybenzoic acid in (4) and the two-dimensional structure generated by 4-hydroxybenzoic acid in (5). Just as it was possible to identify a one-dimensional substructure, built solely from anions and water molecules, in the two-dimensional structure of (6), so too within the three-dimensional framework in (7) it is possible to identify a two-dimensional substructure generated solely by the carboxylate anions.

Compound (7) is again a salt $[C_{16}H_{38}N_4]^{2+}\cdot 2[(HO)_2C_6H_3COO]^-$ (Fig. 12) with the cations lying across centres of inversion. Unlike (1)–(4) and (8), the site of protonation in the cation is N4, adjacent to the gem-dimethyl group: in all the other examples reported here, protonation occurs at N1, remote from the gem-dimethyl group.

The 3,5-dihydroxybenzoate anions generate a two-dimensional network parallel to the (100) plane: each of the

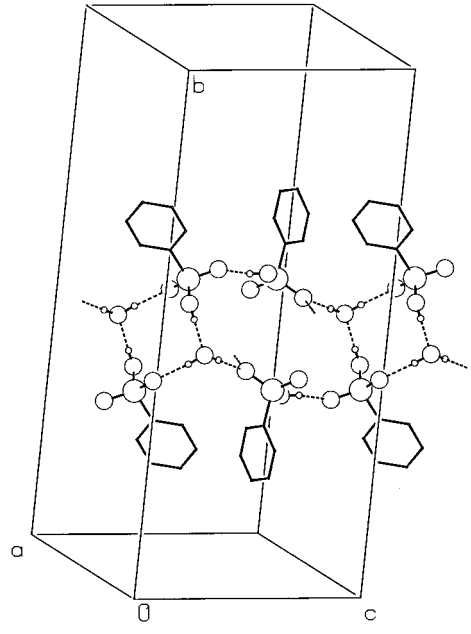


Figure 10
Part of the crystal structure of (6), showing the chain of fused rings parallel to [001]: atoms are depicted as in Fig. 4.

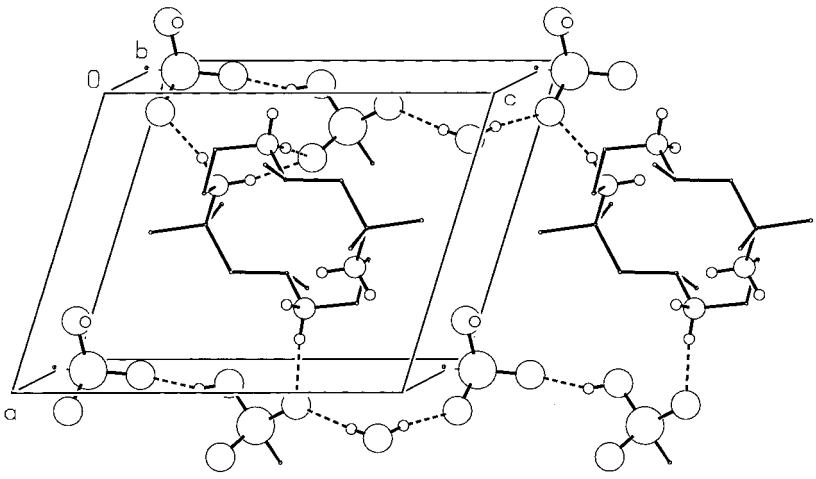


Figure 11
Part of the crystal structure of (6), showing the two-dimensional net parallel to (010). For the sake of clarity, phenyl group atoms other than C11 and C21 are omitted.

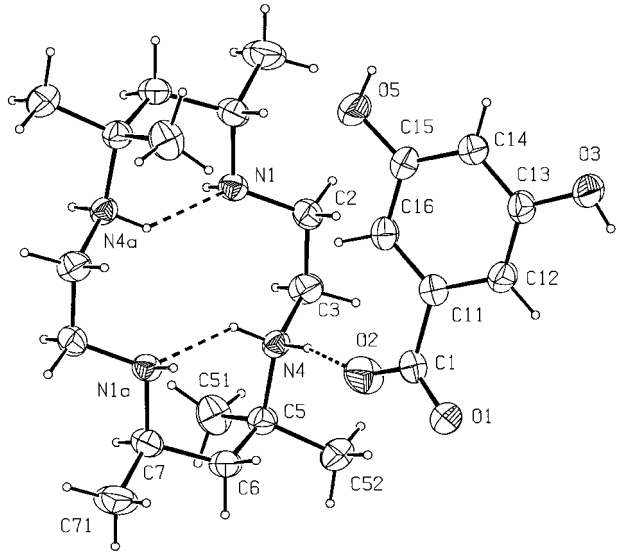


Figure 12
The molecular aggregate in (7): atoms are depicted as in Fig. 1.

hydroxyl O atoms acts as a hydrogen-bond donor, with the carboxylate oxygen O1 acting as an acceptor in each case. Hydroxyl O3 at (x, y, z) acts as donor to O1 at $(-x, 1-y, -z)$, while O3 at $(-x, 1-y, -z)$ in turn acts as donor to O1 at (x, y, z). These interactions thus generate a cyclic, centrosymmetric $R_2^2(14)$ dimer centred at (0, 0.5, 0): this dimeric unit is, of course, quite different from the normal $R_2^2(8)$ dimer commonly formed by simple, unfunctionalized carboxylic acids. Formation of the $R_2^2(14)$ dimer does not involve the hydroxyl oxygen O5, but O5 at (x, y, z) acts as a donor to O1 at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, while O5 at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ acts as a donor to O1 at $(x, -1+y, z)$ so producing a $C(7)$ spiral chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(0, y, 0.25)$. Propagation of these interactions by means of the space-group symmetry serves to generate a two-dimensional network built of alternating large $R_6^4(30)$ and small $R_2^2(14)$ rings, both centrosymmetric in a checkerboard pattern (Fig. 13). The large rings are centred at the Wyckoff *a* sites and the small rings at the *c* sites.

This two-dimensional network lies entirely within the domain $-0.34 < x < +0.34$ and a single network utilizes all the anions within one unit cell. Neighbouring networks, stacked along the [100] direction, are linked by the cations which are centred at the Wyckoff *b* sites. N1 at (x, y, z) is a donor to phenolic oxygen O3 at $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$, while the symmetry-related N1 in the same cation, which is at $(1-x, 1-y, 1-z)$, acts as a donor to the phenolic O3 at $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$. These two O3 atoms, linked to the N1 atoms in the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, in fact form parts of two separate anion networks, separated by a unit translation along [100]: hence, the cations serve to link adjacent anion networks into a three-dimensional framework (Fig. 14). As well as the less sterically shielded N1, the other N atom N4 adjacent to the gem-dimethyl group also forms N—H···O hydrogen bonds, which likewise serve to link adjacent anion networks. Atoms of type N4 at (x, y, z) and $(1-x, 1-y, 1-z)$, components of the same cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ act, respectively, as donors to the carboxylate oxygen O2 at (x, y, z) and $(1-x, 1-y, 1-z)$, which are in turn components of the two separate anion nets, again separated by a unit translation along [100].

Hence, in (7) all four of the exterior axial N—H bonds are engaged in the formation of N—H···O hydrogen bonds.

Compound (8): In (8) the molar ratio of tetramine to biphenol is 1:3 and this compound contains, in addition to the usual centrosymmetric doubly protonated amine, both anionic and neutral biphenol species, thus $[C_{16}H_{38}N_4]^{2+}.2[HOC_6H_4C_6H_4O]^-.[HOC_6H_4C_6H_4OH]$ (Fig. 15). The biphenolate anions lie in general positions, but the neutral biphenol molecules lie across centres of inversion. With the amine dications centred at the Wyckoff *b* sites and the neutral biphenol molecules at the *c* sites, these two components thus generate alternating layers parallel to (100). As in (7), it is possible in (8) to identify a two-dimensional substructure composed solely of the neutral and anionic biphenol species. These two-dimensional nets are then linked by the dications into three independent interwoven three-dimensional frameworks, but it is convenient to analyse first the substructure generated by the phenolic components.

The biphenolate anions $[HOC_6H_4C_6H_4O]^-$ are linked by O—H···O$^-$ hydrogen bonds to form a $C(11)$ chain running parallel to the [201] direction and generated by the glide plane at $y = 0.25$. Hydroxyl oxygen O34 at (x, y, z) acts as a donor to anionic O24 at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, while hydroxyl O34 in the same molecule at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ acts as a donor to O24 at $(-2+x, y, -1+z)$ (Fig. 16). Four such chains run

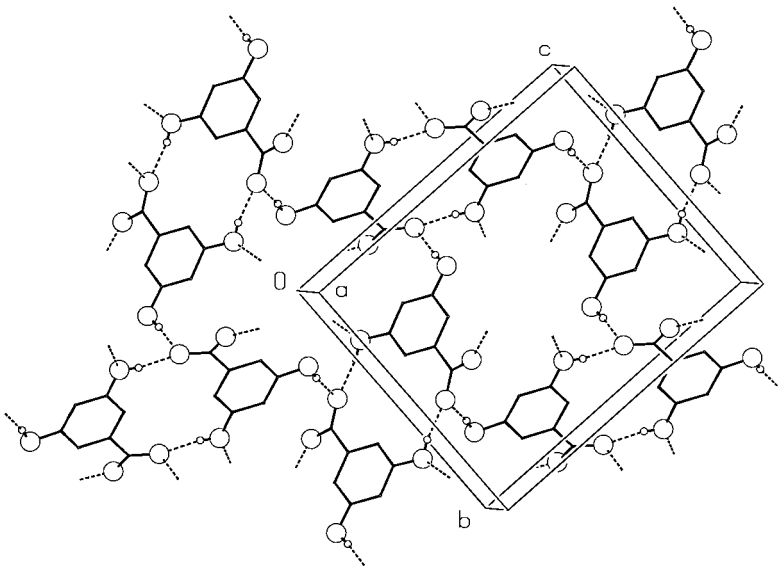


Figure 13
Part of the crystal structure of (7), showing the two-dimensional net parallel to (100) and built from 3,5-dihydroxybenzoate anions: atoms are depicted as in Fig. 4. The dangling hydrogen bonds in the large $R_6^4(30)$ rings arise from the cations (see Fig. 14).

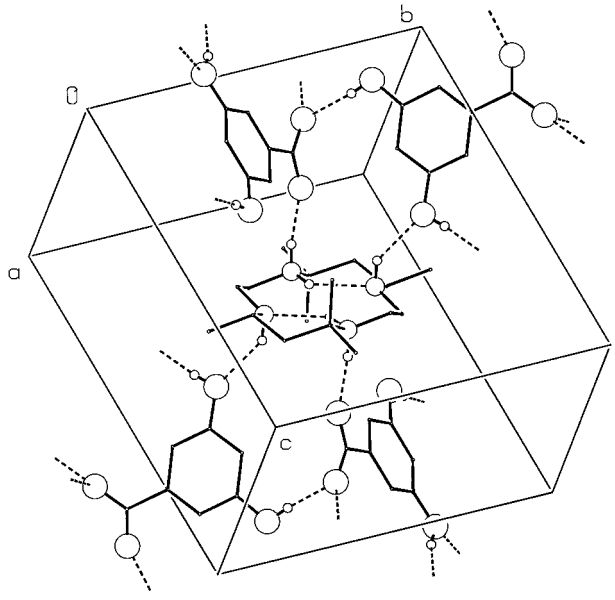


Figure 14
Part of the crystal structure of (7), showing the linking of the (100) nets by the cations: atoms are depicted as in Fig. 4.

through each unit cell and pairs of adjacent and antiparallel chains are linked by neutral and centrosymmetric biphenol molecules to form a two-dimensional net.

Atom O14 at (x, y, z) is part of the neutral biphenol centred at $(1, \frac{1}{2}, 0)$ and acts as a donor to O24 at (x, y, z): O14 at $(2-x, -y, -z)$ is part of the neutral biphenol centred at $(1, -\frac{1}{2}, 0)$ and acts as a donor to O24 at $(2-x, -y, -z)$. The adjacent O24 atoms in these two chains are in the anions at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ and $(1-x, -\frac{1}{2}+y, -\frac{1}{2}-z)$, respectively, and these two O24 sites are acceptors from the two O14 atoms in the neutral biphenol centred at $(0, 0, -\frac{1}{2})$. In this manner a $C_3^2(24)$ chain is produced, running parallel to the [010] direction, and generated by the 2_1 screw axis along $(\frac{1}{2}, y, -\frac{1}{4})$. The interaction of the two types of chain, along [201] and [010], generates a two-dimensional net, parallel to $(20\bar{1})$ and built from a single type of $R_8^6(70)$ ring (Fig. 16). This net uses only one half of the biphenol moieties within the unit cell, so that two such nets, offset by a unit translation along [100] but not interwoven, are required to fully define the biphenol substructure. As in (5), this substructure is two-dimensional, but the nets are connected by the cations to form a three-dimensional system.

The tet-a cation is centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with a symmetry-related cation centred at $(\frac{1}{2}, 0, 0)$: there are thus two cations per unit cell. Each cation is linked, *via* N—H···O hydrogen bonds, to two centrosymmetric, neutral biphenol molecules. Each neutral biphenol thus acts, in its capacity as a hydrogen-bond acceptor, as a link between a pair of cations and, in its capacity as a hydrogen-bond donor, as a link between pairs of phenolate chains. In order to assess the role of the cations in the development of the overall supramolecular structure, it is convenient to trace the connections between different cation units.

The cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is connected to those centred at $(\frac{3}{2}, \frac{1}{2}, -\frac{1}{2})$ and $(-\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ by the neutral biphenol molecules centred at $(1, \frac{1}{2}, 0)$ and $(0, \frac{1}{2}, 1)$, respectively. These interactions thus generate a $C_3^3(18)$ $[R_2^2(10)]$ chain-of-rings (Bernstein *et al.*, 1995) running parallel to the $[10\bar{1}]$ direction (Fig. 17). A similar chain-of-rings containing the cation centred at $(\frac{3}{2}, 0, 1)$ is connected to the first by means of the anions at (x, y, z) and $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$. Atom O14 at (x, y, z) is an acceptor from N1 at (x, y, z) and as a donor to O24 at (x, y, z): this latter oxygen is an acceptor from O34 at $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$, while in the same anion O24 at $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$ is an acceptor from O14 at $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$, which in turn is an acceptor from N1 at $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$. This N1 lies in the cation centred at $(\frac{3}{2}, 0, 1)$. Repetition of this sequence of hydrogen bonds, starting with the symmetry-related N1 in the same cation, N1 at $(2-x, -\frac{1}{2}+y, \frac{3}{2}-z)$ leads to N1 at $(1-x, -y, 1-z)$, which is part of the cation centred at $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$. The centre of inversion in the cation at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ means that this cation is directly connected to the cation at $(-\frac{1}{2}, 1, 0)$ in exactly the same way as to the cation at $(\frac{3}{2}, 0, 1)$, while the cation at $(-\frac{1}{2}, 1, 0)$ is in turn linked similarly to that at $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$. Hence, a $C_6^5(24)$ $[R_2^2(10)]$ chain-of-rings connecting cell-centring cations *via* cell-edge cations runs parallel to the [010] direction (Fig. 18).

As well as being directly linked to the cell-edge cations centred at $(\frac{3}{2}, 0, 1)$ and $(-\frac{1}{2}, 1, 0)$, the cell centring cation at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is, by a different sequence of hydrogen bonds, also linked to the cell-edge cations at $(\frac{3}{2}, 1, 1)$ and $(-\frac{1}{2}, 0, 0)$. N1 at (x, y, z), part of the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is connected, *via* O14, to O24 at (x, y, z). O34 in the anion at (x, y, z) is a donor to O24

at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, and this anionic oxygen is similarly linked, *via* an O14, to N1 at $(-1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$. This N1 forms part of the cation centred at $(-\frac{1}{2}, 0, 0)$, and repetition of this sequence, starting from the symmetry-related N1 of the same cation, N1 at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ leads to the cation centred at $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$. The centre of inversion in the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ cation leads, *via* a similar sequence, to the cations centred at $(\frac{3}{2}, 1, 1)$ and $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$.

The importance of the sequences of hydrogen-bonding connections between neighbouring tet-a units lies in their role in defining the multiplicity of the framework. The tet-a units centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{5}{2}, \frac{1}{2}, \frac{3}{2})$ are both directly linked to those centred at $(\frac{3}{2}, 0, 1)$ and $(\frac{3}{2}, 1, 1)$: in an entirely similar way, the tet-a units centred at $(\frac{1}{2}, \frac{1}{2}, \frac{7}{2})$ and $(-\frac{3}{2}, \frac{1}{2}, \frac{5}{2})$ are both directly linked to those centred at $(-\frac{1}{2}, 0, 3)$ and $(-\frac{1}{2}, 1, 3)$. The tet-a units at $(\frac{3}{2}, 0, 1)$ and $(-\frac{1}{2}, 0, 3)$ are components of one $[10\bar{1}]$ chain, while those centred at $(\frac{3}{2}, 1, 1)$ and $(-\frac{1}{2}, 1, 3)$ are components of a second, parallel $[10\bar{1}]$ chain. Thus, direct connections running parallel to [201] can be traced between the tet-a units centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{7}{2})$: however, no such connections can be found from either of these tet-a units to those centred at $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{5}{2})$, respectively. The intersection of the $[10\bar{1}]$ and the [201] chains involving both biphenol and tet-a moieties leads to the generation of a two-dimensional net, parallel to (010) and built of a single type of $R_{12}^{10}(66)$ ring (Fig. 19). The combination of these nets and the [010] chain-of-rings, which have both neutral and anionic phenolate units in common, generates a continuous three-dimensional framework. The lack of connections between the tet-a units at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and those at $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{5}{2})$ demonstrates that there must be three independent and interpenetrating frameworks (Fig. 19).

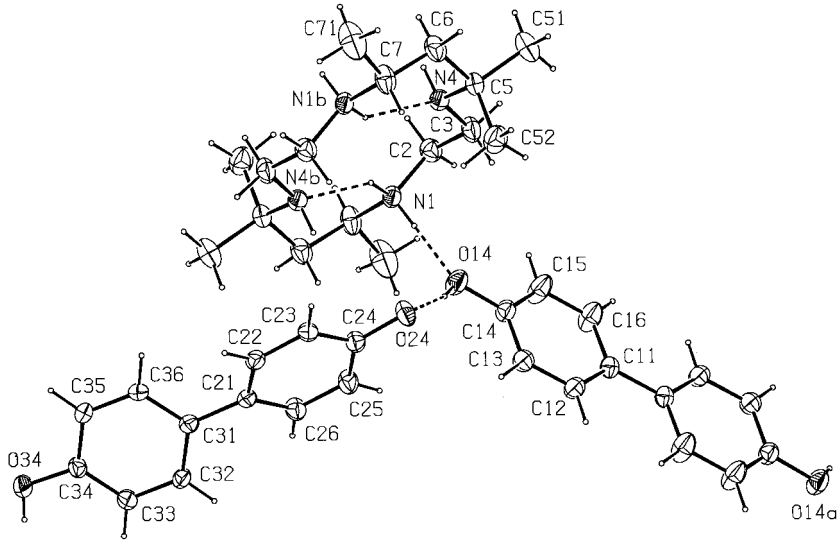


Figure 15
The molecular aggregate in (8): atoms are depicted as in Fig. 1.

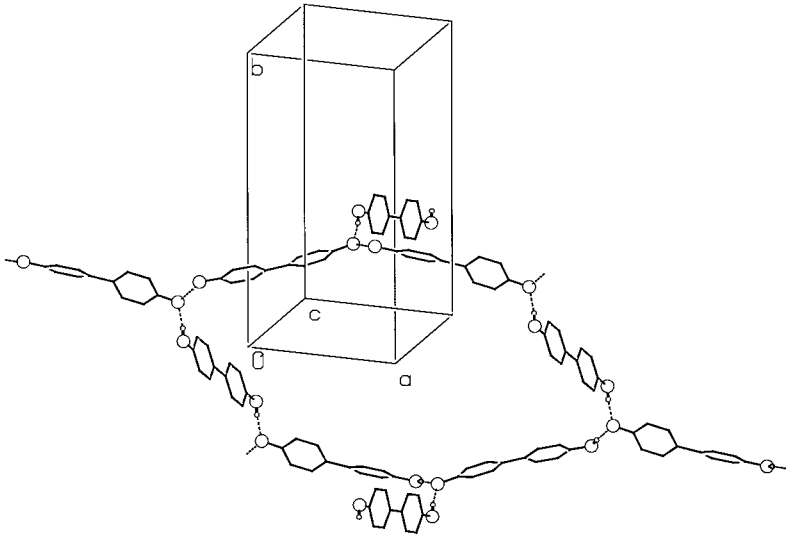


Figure 16
Part of the crystal structure of (8), showing the $R_8^6(70)$ net parallel to $(20\bar{1})$, built from $C(11)$ chains parallel to [201] and $C_3^2(24)$ chains parallel to [010]: atoms are depicted as in Fig. 4.

3.3. Hydrogen-bond dimensions

With the exception of the intramolecular N—H···N hydrogen bonds within the tet-a dications $[C_{16}H_{38}N_4]^{2+}$, all the hydrogen bonds (Table 2) are of two types: O—H···O and N—H···O. Neither O—H···N nor intermolecular N—H···N hydrogen bonds are observed.

All the O—H···O hydrogen bonds are short for their type: the O···O distances range from 2.488 (2) Å for the intramolecular hydrogen bond in the phenolate anion of (1) to 2.752 (3) Å observed in (4). Similarly, the O—H···O angles are tightly clustered around the expected value of 160°, with the extreme values of 175 and 152° observed in (5) and (6), respectively. These are, therefore, all strong O—H···O hydrogen bonds, as expected where each such bond involves one charged component (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994). However, even for the very short (less than 2.50 Å) O···O distances in (1), (6) and (8), there is no evidence for a symmetrical, or near-symmetrical, placing of the proton between the two O atoms, as sometimes found in very short O···H···O systems (Emsley, 1980).

The N—H···O hydrogen bonds (Table 2) can be divided into four categories, as each component, donor and acceptor, can independently be either neutral or charged. The four possibilities can thus be represented as follows: type (*a*), N^+—H···O^-; type (*b*), N^+—H···O; type (*c*), N—H···O^-; type (*d*), N—H···O. It may be expected (Aakeröy &

Seddon, 1993; Gilli *et al.*, 1994) that type (*a*) are the strongest and type (*d*) the weakest, and the N···O distances and N—H···O angles in Table 2 certainly support this. The data in Table 2 indicate that the type (*a*) bonds range in length from 2.584 (3) Å in (1) to 2.742 (2) Å for the N4···O2 hydrogen bond in (7): the N^+—H···O^- angles range from 160° in (1) to 177° for the N14—H14*A*···O31 interaction in (5), with a mean value of 167°. There are fewer examples of the other three types: type (*b*) is represented by the N1···O1 hydrogen bonds in (2) and (3), and type (*c*) occurs in (5), N11···O32, while very long type (*d*) bonds, both having N—H···O angles less than 160°, are observed in (5) (N21···O1) and (7) (N1···O3).

In addition to these four types, there is a three-centre N—H···$(O)_2$ system in (4), in which the donor N1 is charged, one acceptor (O1) is anionic and the other (O3) is neutral. The N···O distance involving the anionic acceptor is significantly shorter than that involving the neutral acceptor (Table 2), again consistent with the notion that hydrogen bonds involving ionic components are stronger than those involving only neutral components.

The dimensions of the N—H···N hydrogen bonds indicate minor variations in the shape of the $[C_{16}H_{38}N_4]^{2+}$ cations: in (5), the two independent cations exhibit significantly different N···N distances.

3.4. Molecular conformations and dimensions

3.4.1. Conformation of the tet-a cations. In all the examples studied here the cations, whether $[C_{16}H_{40}N_4]^{4+}$ in (6) or $[C_{16}H_{38}N_4]^{2+}$ in all of the other systems, always lie across centres of inversion. In (1)–(5), (7) and (8) the dication $[C_{16}H_{38}N_4]^{2+}$ adopts the *trans*-III conformation found in many metal complexes of neutral tet-a type (Barefield *et al.*, 1986).

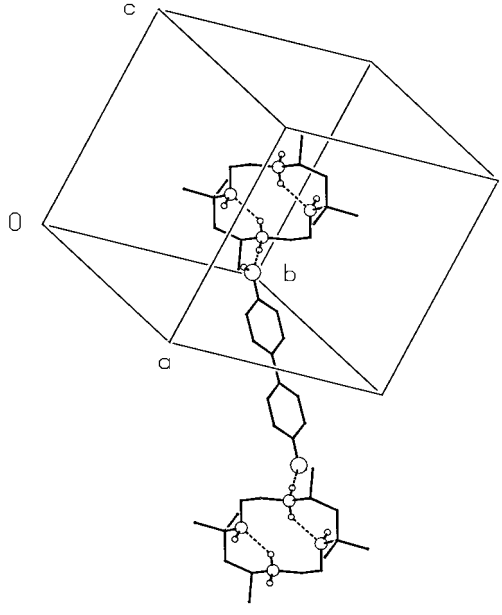


Figure 17
Part of the crystal structure of (8), showing the $C_3^3(18)$ $[R_2^2(10)]$ chain-of-rings parallel to $[10\bar{1}]$: atoms are depicted as in Fig. 4.

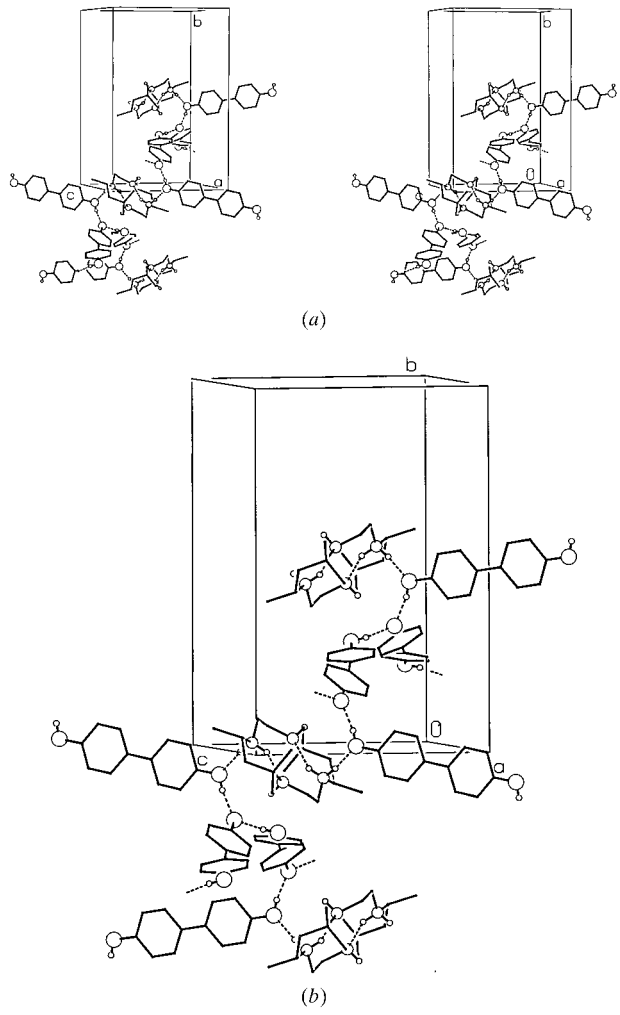


Figure 18
Stereoview of part of the crystal structure of (8), showing the $C_6^5(24)$ $[R_2^2(10)]$ chain-of-rings parallel to [010]: atoms are depicted as in Fig. 4.

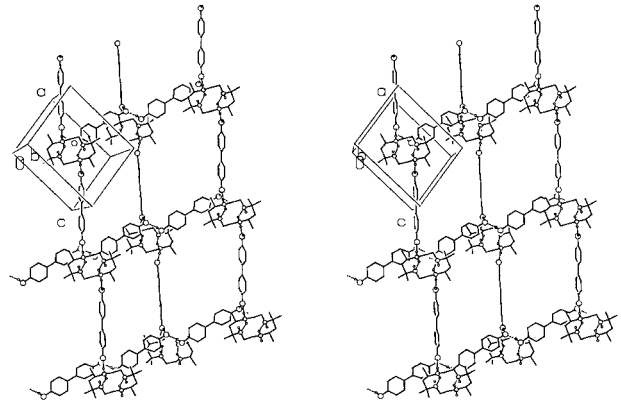
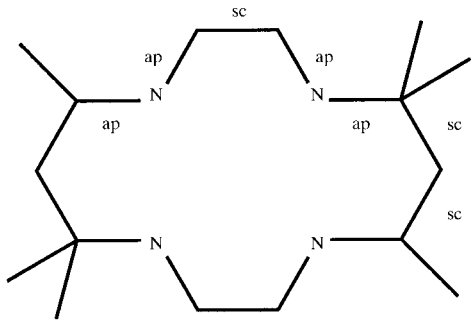
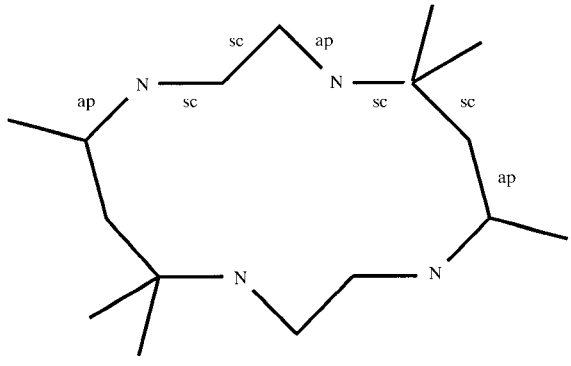


Figure 19
Stereoview of a slice of the three-dimensional structure in (8), parallel to (010) and showing one of the three independent frameworks: atoms are depicted as in Fig. 4.

In this conformation the N atoms are sufficiently close for the formation of intramolecular N—H···N hydrogen bonds (Table 2) and there are four axial N—H bonds, two on each face of the disc-like cation. In this conformation, there is almost perfect staggering about all the C—N and C—C bonds within the macrocycle, with the synclinal torsional angles (shown below) all within 5° of ± 60° and the antiperiplanar torsional angles all within 5° of 180°. Four of the exocyclic methyl groups lie in equatorial sites, and two in axial sites.



(*a*)



(*b*)

By contrast, the conformation of $[C_{16}H_{40}N_4]^{4+}$ in (6) [Fig. 9, and (*a*) and (*b*) above] produces a much more open, almost rectangular, macrocycle, doubtless resulting from a combination of increased electrostatic repulsion between adjacent cationic N atoms and the lack of any intramolecular N—H···N hydrogen bonds. The N1···N4 and N1···N4^{i} [(i) $1-x$, $1-y$, $1-z$)] distances are 3.191 (2) and 4.194 (2) Å, respectively; these values are similar to the values of 3.296 and 4.151 Å for the corresponding distances in the solvated salt $[C_{16}H_{40}N_4]^{4+}(Cl^-)_3(OH^-)[Mo^{V}(OH)(OH_2)Cl_4]$ (Minacheva *et al.*, 1994). The corresponding N···N distances in the diprotonated cation $[C_{16}H_{38}N_4]^{2+}$, by contrast, span the ranges 2.858 (3)–2.993 (3) and 2.792 (2)–2.868 (3) Å, respectively. All eight of the N—H bonds in $[C_{16}H_{40}N_4]^{4+}$, four on each face, are available for hydrogen bonding: for each of the N atoms, the two N—H bonds are on the same face of the cation.

3.4.2. C—N distances in the tet-a cations. In adducts of cyclam with phenols, the internal protons of the $[cyclamH_2]^{2+}$ cations are sometimes ordered and sometimes disordered over the four possible protonation sites (Ferguson *et al.*, 1998*a*, 1999). However, in the $[C_{16}H_{38}N_4]^{2+}$ cations studied here, the internal protons are always fully ordered. The C—N distances, particularly N1—C2 and N4—C3 in the sterically unencumbered N—C—C—N bridge, show clear variation depending on the site of protonation (Table 3). Bonds to protonated N, of type $R_2NH_2^+$, are significantly longer than bonds to neutral N, of type R_2NH. This mirrors the pattern observed in $[cyclamH_2]^{2+}$ cations (Ferguson *et al.*, 1998*a*): a very similar pattern of C—N bond lengths is observed in the non-centrosymmetric $[C_{16}H_{38}N_4]^{2+}$ cations in the perchlorate salt (Hu *et al.*, 1997).

3.4.3. Anionic and neutral components. In the bis-phenol components of (1), (2), (3) and (8) there are clear differences in the geometry involving the ionized and neutral hydroxyl O atoms (Table 3). First, the C—O$^-$ distances are all significantly shorter that the corresponding C—O(H) distances; second, the two independent C—C—O angles are always virtually identical in the case of C—O$^-$, but differ by 4–5° in the case of C—O(H).

The conformations of the heavy atom skeletons in the bis-phenolate components in (2) and (3) are both of approximate C_2 symmetry, and neither is far from C_{2v} symmetry. In (4) and (5) the carboxyl groups in the hydroxybenzoate anions are virtually coplanar with the aryl rings, whereas in (7) the carboxyl group is twisted away from coplanarity with the aryl ring by *ca* 22.5°.

3.5. Comparison of tet-a and cyclam

There are a number of points at which the behaviour of tet-a in (1)–(8) may be compared and contrasted with that of cyclam in the salts formed with 2,2′-biphenol (Ferguson *et al.*, 1999) and with 4,4′-thiodiphenol and 4,4′-sulfonyldiphenol (Ferguson *et al.*, 1998*a*). First, both tet-a and cyclam form doubly protonated dications, $[C_{16}H_{38}N_4]^{2+}$ and $[C_{10}H_{26}N_4]^{2+}$, respectively, with these bis-phenols with two interior protons held by N—H···N hydrogen bonds. However, while in all of the tet-a dications reported here these protons are fully ordered, in salts of the $[cyclamH_2]^{2+}$ cation, they are sometimes ordered and sometimes disordered: thus, in the salt formed with 4,4′-thiodiphenol, the interior protons of the centrosymmetric $[cyclamH_2]^{2+}$ cation are disordered over two sets of sites with s.o.f. 0.81 (3) and 0.19 (3) (Ferguson *et al.*, 1998*a*).

Secondly, whereas in cyclam systems all four axial N—H bonds of the $[cyclamH_2]^{2+}$ cation are involved in the hydrogen-bonding scheme (Nave & Truter, 1974; Ferguson *et al.*, 1998*a*, 1999), in the corresponding doubly protonated tet-a cations studied here, only in (7) are all four axial N—H bonds active in hydrogen-bond formation: it is interesting to note that (7) is the only example observed here in which protonation of the tet-a occurs at the more sterically hindered N4, adjacent to the gem-dimethyl group, rather than at N1.

Despite the unexpected behaviour of the cations in (7), there is nonetheless clear evidence that the axial N—H sites in $[C_{16}H_{38}N_4]^{2+}$ are sterically more congested than those in $[C_{10}H_{26}N_4]^{2+}$. The adducts of both 4,4′-thiodiphenol and 4,4′-

sulfonyldiphenol with tet-a and cyclam are all molecular ladders: in the cyclam adducts the cations $[C_{10}H_{26}N_4]^{2+}$ are bonded directly to the anion chains using all four axial N—H bonds, while the cations $[C_{16}H_{38}N_4]^{2+}$ in (2) and (3) employ only the less-sterically hindered axial N—H bonds and, even then, are connected to the anion chains *via* methanol spacer units. Tet-a and cyclam both form 1:2 adducts with 2,2′-biphenol and the basic architectural unit is the same for both adducts. However, whereas tet-a employs only two axial N—H bonds in supramolecular bonding, and thus forms the finite aggregate observed in (1), cyclam, using all four axial N—H bonds, forms a one-dimensional aggregate, a chain of fused rings (Ferguson *et al.*, 1999).

3.6. Behaviour of 2,2′-biphenol and its monoanion

The monoanion $[C_{12}H_9O_2]^-$ in (1) contains a strong intramolecular O—H···O$^-$ hydrogen bond: similar intramolecular hydrogen bonds are found for this anion in its salts with $[cyclamH_2]^{2+}$ (Ferguson *et al.*, 1999) and with $[NBu_4]^+$ (Swamy *et al.*, 1991). There appear to be no well characterized examples of this anion which do not contain such an intramolecular hydrogen bond. However, the neutral 2,2′-biphenol molecule sometimes contains an intramolecular O—H···O hydrogen bond, when it acts as a chain-terminating unit (Swamy *et al.*, 1991; Lavender, Gregson *et al.*, 1999), but in other examples, both hydroxyl groups are involved in forming hydrogen bonds to other acceptors, so that in these cases the biphenol molecule acts as a chain-builder (Lavender, Ferguson & Glidewell, 1999; Chen *et al.*, 1996)

4. Conclusions

In the compounds studied here the tet-a units have captured two protons, as expected, in all except (6), where the combination with phenylphosphonic acid, an acid somewhat stronger than substituted benzoic acids and considerably stronger than phenols, leads to the formation of a tetraprotonated cation. Of those compounds containing the diprotonated tet-a unit, (1)–(4) and (8) all show the hydrogen-bonding behaviour deduced from the alkylation properties of tet-a, in that only the two axial N–H bonds remote from the sterically congested gem-dimethyl substituents are active as hydrogen-bond donors. However, in (5) and (7) all the axial N—H bonds are active. In (7) it is the more sterically hindered N atom which is protonated. The factors determining the site of protonation to form the $[C_{16}H_{38}N_4]^{2+}$ cation, in the solid state, which in (1)–(4) and (8) is coincident with the active axial N—H donor site, are not yet clear: protonation sites in solids cannot be reliably deduced from those found in solution.

The other feature of (1)–(8) which is of importance in the future design of self-assembled molecular materials is the dependence of the dimensionality of the supramolecular aggregate upon subtle changes in the constitution of the molecular building blocks. This is illustrated by the change from a one-dimensional to a two-dimensional structure upon changing the acidic components from 3-hydroxybenzoic acid in (4) to the 4-isomer in (5); even more striking is the change from a finite, zero-dimensional aggregate to a multiple three-dimensional framework structure upon changing from 2,2′-biphenol in (1) to the 4,4′-isomer in (8).

RMG thanks EPSRC (UK) for financial support; GF and AJL thank NSERC (Canada) for research grants.

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