Crystal Engineering Using Bis- and Tris-phenols. Adducts with 1,4,8,11-Tetraazacyclotetradecane (Cyclam): Isolated Ladders in the Adduct with 4,4'-Thiodiphenol, Tethered Ladders in the Adduct with 4,4'-Sulfonyldiphenol and Two Interwoven Three-Dimensional Networks in the Adduct with 1,1,1-Tris(4-hydroxyphenyl)ethane

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Abstract

The structure of 4,4'-thiodiphenol–1,4,8,11-tetraazacyclotetradecane (2/1), $(C_{12}H_{10}O_2S)_2.C_{10}H_{24}N_4$ (1), monoclinic, $P2_1/c$, $a = 11.1602$ (12), $b = 10.8084$ (12), $c = 14.001$ (2) Å, $\beta = 103.127$ (10)°, with $Z = 2$, contains phenolate anions $[HOC_6H_4SC_6H_4O]^-$ and diprotonated cyclam cations $[C_{10}H_{26}N_4]^{2+}$: these cations have the centrosymmetric *trans*-III conformation and the two additional protons are contained within the N_4 cavity of the macrocycle, held by three-centre hydrogen bonds. The phenolate anions form chains, held together by $O—H\cdots O$ hydrogen bonds, and pairs of these chains are cross-linked into ladders by the $[cyclamH_2]^{2+}$ cations by means of $N—H\cdots O$ hydrogen bonds. The structure of 4,4'-sulfonyldiphenol–1,4,8,11-tetraazacyclotetradecane (2/1), $(C_{12}H_{10}O_4S)_2.C_{10}H_{24}N_4$ (2), triclinic, $P\bar{1}$, $a = 10.9345$ (10), $b = 11.0060$ (10), $c = 14.350$ (2) Å, $\alpha = 79.532$ (10), $\beta = 86.739$ (10), $\gamma = 87.471$ (10)°, with $Z = 2$, contains phenolate anions $[HOC_6H_4SO_2C_6H_4O]^-$ and cyclam dications $[C_{10}H_{26}N_4]^{2+}$: the phenolate anions are linked into antiparallel chains, cross-linked by the cyclam cations. There are two distinct types of ladder in the structure running along (0, y, 0) and ($\frac{1}{2}$, y, $\frac{1}{2}$), respectively, and these bundled ladders are tied together by $C—H\cdots O$ hydrogen bonds to form a continuous three-dimensional array. In 1,1,1-tris(4-hydroxyphenyl)ethane–1,4,8,11-tetraazacyclotetradecane–methanol (2/1/1), $(C_{20}H_{18}O_3)_2.C_{10}H_{24}N_4.CH_4O$ (3), triclinic, $P\bar{1}$, $a = 8.2208$ (11), $b = 16.245$ (2), $c = 17.337$ (2) Å, $\alpha = 81.694$ (13), $\beta = 89.656$ (14), $\gamma = 86.468$ (12)°, with $Z = 2$, the structure contains centrosymmetric diprotonated cyclam cations of precisely the same type as found in (1), phenolate anions $[(HOC_6H_4)_2C(CH_3)C_6H_4O]^-$ and neutral methanol molecules. The molecular components are linked together by nine different types of hydrogen bond, five of $O—H\cdots O$ type and four of $N—H\cdots O$ type, to form chains running in the [001], [010] (two sets), [211] and [21$\bar{1}$] directions. The combination of these chain motifs generates two independent three-dimensional networks which are fully interwoven, but not bonded to one another.

1. Introduction

Hydrogen-bonded adducts formed between simple bis- or tris-phenols and simple polyamines exhibit an extremely wide range of supramolecular architectures: these include chains, chains-of-rings, ladders, double and triple helices, sheets, and interwoven three-dimensional arrays (Coupar *et al.*, 1996*a,b*, 1997; Ferguson, Bell *et al.*, 1997; Ferguson, Coupar & Glidewell, 1997). For the most part, these adducts are built from very simple supramolecular synthons (Desiraju, 1995), such as $O—H\cdots O$, $O—H\cdots N$ and $N—H\cdots O$, where the hydrogen bonds are formed between neutral molecular tektons. It is now well established that hydrogen bonds formed between charged components are significantly stronger than those where both the hydrogen-bond donor and acceptor are neutral (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994). In order to exploit this property in supramolecular adducts of polyphenols, it is therefore necessary to employ a polyamine which can effect the complete transfer of at least one proton from each molecule of the polyphenol to the amine. We reasoned that cyclam (1,4,8,11-tetraazacyclododecane, $C_{10}H_{24}N_4$) would be highly basic towards phenols, since two protons could be transferred into the N_4 cavity where each could be captured by a pair of closely adjacent N atoms, rather in the manner of the well known proton sponge 1,8-bis(dimethylamino)naphthalene (Alder *et al.*, 1968; Brzezinski *et al.*, 1991): in the resulting $[cyclamH_2]^{2+}$ dication, there should still be four exterior $N—H$ bonds capable of forming hydrogen bonds to the phenolic component of the adduct.

Here we report the realisation of this idea in the adducts of cyclam with 4,4'-thiodiphenol, $S(C_6H_4OH)_2$, 4,4'-sulfonyldiphenol, $SO_2(C_6H_4OH)_2$, and 1,1,1-tris(4-hydroxyphenyl)ethane, $CH_3C(C_6H_4OH)_3$ (1)–(3), respectively. Each of these adducts has a cyclam:polyphenol ratio of 1:2 and, in addition, (3) contains one molecule of methanol per cyclam, which forms an integral part of the hydrogen-bonding network: in each adduct there is transfer to the cyclam of a single proton from each molecule of the phenol. Consequently, these salt-like adducts must be formulated as (1)
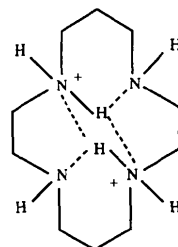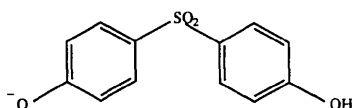
$[C_{10}H_{26}N_4]^{2+}.2[HOC_6H_4SC_6H_4O]^-$, (2) $[C_{10}H_{26}N_4]^{2+}.-$
$2[HOC_6H_4SO_2C_6H_4O]^-$, and (3) $[C_{10}H_{26}N_4]^{2+}.-$
$2[(HOC_6H_4)_2C(CH_3)C_6H_4O]^-.CH_3OH$. In each of (1)–
(3) the cyclam is found to have captured two protons
which are held in the N_4 cavity of the macrocycle, while
each N atom also acts as a hydrogen-bond donor to
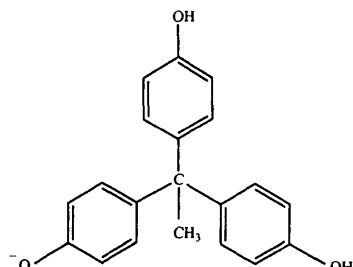phenolate anions, by means of the exterior N—H
bonds.
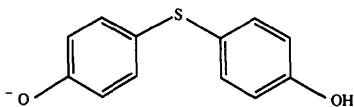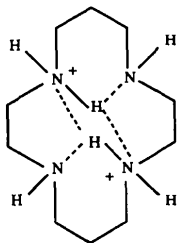
(1)
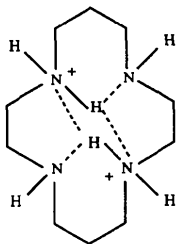
(2)

(3)

2. Experimental

2.1. Synthesis

Compounds (1), (2) and (3) were prepared by co-
crystallizing cyclam with the appropriate polyphenol
from solutions in methanol. Analyses: (1) found: C 64.0,
H 6.9, N 8.8%; $C_{34}H_{44}N_4O_4S_2$ requires: C 64.1, H 7.0, N
8.8; (2) found: C 58.2, H 6.5, N 8.0%; $C_{34}H_{44}N_4O_8S_2$
requires: C 58.3, H 6.3, N 8.0%; (3) found: C 72.3, H 7.6,
N 6.7%; $C_{51}H_{64}N_4O_7$ requires: C 72.5, H 7.6, N 6.6%.
Crystals suitable for single-crystal X-ray diffraction
were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Details of cell data, data collection and refinement
are summarized in Table 1. For (1) the space group

$P2_1/c$ was uniquely determined by the systematic
absences ($h0l$ absent if $l = 2n + 1$; $0k0$ absent if $k = 2n +
1$). Compounds (2) and (3) are both triclinic; space
group $P\bar{1}$ was selected and confirmed in each case by
the successful structure analysis. The structures were
solved by direct methods (Gabe et al., 1989). A
weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was
employed, in order to reduce statistical bias (Wilson,
1976). H atoms bonded to carbon were positioned on
geometric grounds; initial coordinates for H atoms
bonded to N or O were obtained from difference maps.
In each compound it rapidly became obvious that
complete transfer of one hydroxyl H had occurred from
each phenol molecule to the cyclam component and
that in (1) and (3) these additional H atoms in the
cyclams were each disordered over two independent
sites. All the H atoms were included in the refinements
as riding atoms and the site-occupation factors of the
disordered H atoms were refined. Examination of the
structures using PLATON (Spek, 1995a) showed that
there were no solvent-accessible voids in the lattices.
The diagrams were prepared using ORTEPII (Johnson,
1976), as implemented in PLATON, and with
PLUTON (Spek, 1995b). Final fractional coordinates
are presented in Table 2 and selected dimensions in
Table 3.†

3. Results and discussion

3.1. Co-crystallization behaviour

Compounds (1), (2) and (3) result from the co-crys-
tallization of cyclam with the appropriate phenol from
methanol solutions: the product obtained with each
phenol is independent of the phenol:cyclam molar ratio
in the initial solution (within the range 1:2–2:1), as
typically found in systems of this type (Coupar et al.,
1997). When, for a given system, analytically identical
materials were isolated using different starting ratios of
the components, powder X-ray diffraction showed that
these were the same polymorph: this again is typical of
systems of this type and suggests that in general such
systems probably have rather simple phase diagrams.

3.2. Crystal structures and molecular packing

3.2.1. Compound (1). The asymmetric unit consists of
half a doubly protonated cyclam, $[C_{10}H_{26}N_4]^{2+}$, lying
across the centre of inversion at the origin and a
phenolate anion $[HOC_6H_4SC_6H_4O]^-$ lying in a general
position, consistent with the 2:1 bis-phenol:cyclam ratio
deduced from the elemental analysis. In the cyclam
dication (Fig. 1) the additional protons are within the

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† Lists of atomic coordinates, anisotropic displacement parameters
and structure factors have been deposited with the IUCr (Reference:
AB0380). Copies may be obtained through The Managing Editor,
International Union of Crystallography. 5 Abbey Square. Chester
CH1 2HU, England.

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{34}H_{44}N_4O_4S_2$	$C_{34}H_{44}N_4O_8S_2$	$C_{51}H_{64}N_4O_7$
Chemical formula weight	636.85	700.85	845.06
Cell setting	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.1602 (12)	10.9345 (10)	8.2208 (11)
b (Å)	10.8084 (12)	11.0060 (10)	16.245 (2)
c (Å)	14.001 (2)	14.350 (2)	17.337 (2)
α (°)		79.532 (10)	81.694 (13)
β (°)	103.127 (10)	86.739 (10)	89.656 (14)
γ (°)		87.471 (10)	86.468 (12)
V (Å^3)	1644.7 (3)	1694.5 (3)	2286.6 (5)
Z	2	2	2
D_x (Mg m^{-3})	1.286	1.374	1.227
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	25	25
θ range (°)	10.31–17.89	9.57–16.99	10.05–18.00
μ (mm^{-1})	0.206	0.215	0.082
Temperature (K)	294 (1)	294 (1)	294 (1)
Crystal form	Plate	Block	Block
Crystal size (mm)	0.33 × 0.19 × 0.09	0.20 × 0.20 × 0.20	0.42 × 0.31 × 0.28
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	Gaussian (North *et al.*, 1968)	None	None
T_{min}	0.9628	–	–
T_{max}	0.9817	–	–
No. of measured reflections	4130	5895	8108
No. of independent reflections	3747	5895	8108
No. of observed reflections	2023	3246	4835
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.006	–	–
θ_{max} (°)	27.41	25.00	27.20
Range of h, k, l	$-14 \to h \to 14$	$-12 \to h \to 12$	$-10 \to h \to 10$
	$0 \to k \to 13$	$0 \to k \to 13$	$0 \to k \to 19$
	$0 \to l \to 18$	$-16 \to l \to 17$	$-20 \to l \to 22$
No. of standard reflections	3	3	3
Frequency of standard reflections (min)	720	120	120
Intensity decay (%)	No decay, variation 0.5	No decay, variation 1.5	No decay, variation 1.0
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0454	0.0437	0.0516
$wR(F^2)$	0.1160	0.1234	0.1223
S	0.964	0.972	1.001
No. of reflections used in refinement	3747	5895	8108
No. of parameters used	205	436	582
H-atom treatment	H parameters constrained	H parameters constrained	H parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0550P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	-0.001	0.000	0.006
$\Delta\rho_{max}$ (e Å^{-3})	0.181	0.236	0.235
$\Delta\rho_{min}$ (e Å^{-3})	-0.192	-0.320	-0.202
Extinction method	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	None
Extinction coefficient	0.0013 (9)	0.0017 (8)	–
Source of atomic scattering factors	International Tables for Crystallography (1992, Vol. C)	International Tables for Crystallography (1992, Vol. C)	International Tables for Crystallography (1992, Vol. C)

Table 1 (cont.)

	(1)	(2)	(3)
Computer programs			
Data collection	CAD-4 (Enraf–Nonius, 1992)	CAD-4 (Enraf–Nonius, 1992)	CAD-4 (Enraf–Nonius, 1992)
Cell refinement	SET4 and CELDIM (Enraf–Nonius, 1992)	SET4 and CELDIM (Enraf–Nonius, 1992)	SET4 and CELDIM (Enraf–Nonius, 1992)
Data reduction	DATRD2 in NRCVAX96 (Gabe et al., 1989)	DATRD2 in NRCVAX96 (Gabe et al., 1989)	DATRD2 in NRCVAX96 (Gabe et al., 1989)
Structure solution	SOLVER in NRCVAX96	SHELXS86 (Sheldrick, 1985)	SOLVER in NRCVAX96
Structure refinement	NRCVAX96 and SHELXL93 (Sheldrick, 1993)	NRCVAX96 and SHELXL93 (Sheldrick, 1993)	NRCVAX96 and SHELXL93 (Sheldrick, 1993)
Preparation of material for publication	NRCVAX96, SHELXL93 and WordPerfect macro PRPCIF97 (Ferguson, 1997)	NRCVAX96, SHELXL93 and WordPerfect macro PRPCIF97 (Ferguson, 1997)	NRCVAX96, SHELXL93 and WordPerfect macro PRPCIF97 (Ferguson, 1997)

N_4 cavity of the macrocycle, but are disordered over two independent sites covalently bonded to N31 or N34 and having site occupancies of 0.81 (3) and 0.19 (3), respectively. At each site the internal hydrogen participates in a three-centre hydrogen bond: when the site covalently bonded to N31 at (x, y, z) is occupied, hydrogen bonding occurs to the N34 sites at both (x, y, z) and $(-x, -y, -z)$, while an internal hydrogen covalently bound to N34 is hydrogen bonded to the N31 atoms at both (x, y, z) and $(-x, -y, -z)$. This disorder may be a manifestation of the mobility of the internal hydrogens; such mobility has been observed in several tetraazaannulenes by means of ^{15}N CP-MAS NMR,
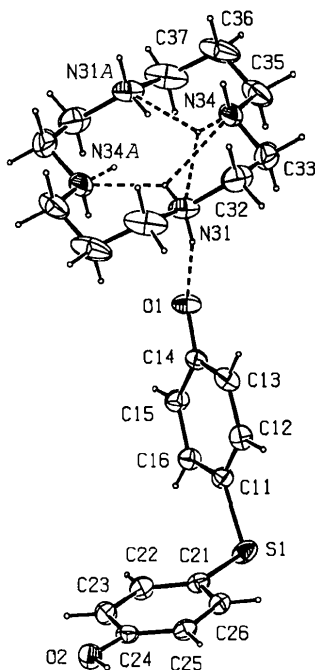

Fig. 1. View of the molecular aggregate in (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, the internal hydrogen bonds in the [cyclamH$_2$]$^{2+}$ cation are shown for only two of the four N atoms.

although the interpretation of the spectra was in terms of simple $N-H\cdots N$ hydrogen bonds, rather than in terms of three-centre hydrogen bonds (Limbach et al., 1987). By contrast, in two previously characterized salts of the $[C_{10}H_{26}N_4]^{2+}$ cation, bis(perchlorate) (Nave & Truter, 1974) and bis-(4-tert-butylbenzoate) (Adam et al., 1994), the hydrogens are all ordered.

The phenolate anions form hydrogen-bonded chains running parallel to the [100] direction: O2 in the phenolate at (x, y, z) acts as a hydrogen-bond donor to O1 in the anion at $(1 + x, y, z)$. There is a similar anti-parallel chain generated by the centre of inversion at the origin and this pair of chains is cross-linked by means of the cyclam dications; the four exterior $N-H$ bonds of each cation form $N-H\cdots O$ hydrogen bonds to four different phenolate anions. The overall structural motif is thus that of a ladder, in which the pairs of phenolate chains represent the uprights and the cyclam dications the rungs (Fig. 2). The N31 atom at (x, y, z) acts as a hydrogen-bond donor to O1 in the phenolate at (x, y, z), while N34 at (x, y, z) acts as a donor to O2 at $(1 - x, -y, -z)$: similarly, the symmetry-related N31 and N34 atoms at $(-x, -y, -z)$ act as donors to O1 at $(-x, -y, -z)$ and O2 at $(-1 + x, y, z)$, respectively. Each cyclam dication also forms two $C-H\cdots O$ hydrogen bonds: C36 at (x, y, z) acts, via H36A, as a donor to O1 at $(-x, -y, -z)$, so reinforcing the effect of the $N31-H31A\cdots O1$ hydrogen bond.

This ladder utilizes only half the unit-cell contents and it lies largely in that half of the unit cell having $-0.25 < y < +0.25$: there is another identical ladder lying largely in the half of the unit cell with $+0.25 < y < +0.75$ and related to the first ladder by the action of the glide plane. The entire structure therefore consists of an infinite bundle of ladders, parallel to [100], with no contacts between adjacent ladders less than the sum of the van der Waals' radii: in particular, there are no short contacts involving the S atom.

The overall topology of this structure provides an interesting contrast with that of the stoichiometrically similar 2:1 adduct formed between 4,4'-thiodiphenol and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Ferguson, Coupar & Glidewell, 1997), where again hydrogen-

Table 2. *Fractional atomic coordinates and anisotropic displacement parameters (Å²)*

Table 2 (cont.)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
(1)				
S1	0.55042 (5)	0.18244 (6)	−0.41081 (5)	0.0574 (2)
O1	0.19678 (12)	0.05855 (15)	−0.16811 (10)	0.0549 (4)
O2	1.01827 (15)	−0.0778 (2)	−0.24402 (13)	0.0559 (4)
C11	0.4520 (2)	0.1362 (2)	−0.3339 (2)	0.0421 (5)
C12	0.4569 (2)	0.1952 (2)	−0.2456 (2)	0.0488 (6)
C13	0.3752 (2)	0.1658 (2)	−0.1884 (2)	0.0483 (6)
C14	0.2813 (2)	0.0799 (2)	−0.21933 (15)	0.0415 (5)
C15	0.2794 (2)	0.0186 (2)	−0.3075 (2)	0.0484 (6)
C16	0.3636 (2)	0.0455 (2)	−0.3634 (2)	0.0477 (5)
C21	0.6911 (2)	0.1050 (2)	−0.35868 (14)	0.0424 (5)
C22	0.6989 (2)	−0.0224 (2)	−0.3606 (2)	0.0482 (6)
C23	0.8087 (2)	−0.0823 (2)	−0.3220 (2)	0.0482 (5)
C24	0.9141 (2)	−0.0143 (2)	−0.28236 (15)	0.0417 (5)
C25	0.9069 (2)	0.1138 (2)	−0.28223 (15)	0.0438 (5)
C26	0.7960 (2)	0.1725 (2)	−0.31893 (14)	0.0431 (5)
N31	0.1724 (2)	0.0845 (2)	0.01429 (14)	0.0610 (6)
C32	0.1420 (3)	0.2076 (3)	0.0489 (2)	0.0863 (10)
C33	0.0174 (3)	0.2486 (3)	−0.0061 (2)	0.0882 (10)
N34	−0.0765 (2)	0.1606 (2)	0.00709 (14)	0.0628 (6)
C35	−0.2000 (3)	0.1943 (3)	−0.0494 (2)	0.0921 (11)
C36	−0.2979 (3)	0.1025 (4)	−0.0365 (2)	0.0983 (12)
C37	−0.2829 (2)	−0.0238 (4)	−0.0755 (2)	0.0956 (11)
(2)				
S1	−0.19379 (7)	0.58018 (7)	0.39996 (6)	0.0407 (2)
O11	−0.0629 (2)	0.20579 (19)	0.16514 (15)	0.0532 (6)
O12	0.0707 (2)	1.0298 (2)	0.23810 (17)	0.0547 (6)
O13	−0.1519 (2)	0.5339 (2)	0.49370 (14)	0.0522 (6)
O14	−0.32208 (19)	0.6098 (2)	0.38916 (16)	0.0545 (6)
C11	−0.1493 (3)	0.4720 (3)	0.3281 (2)	0.0346 (7)
C12	−0.2072 (3)	0.4742 (3)	0.2441 (2)	0.0442 (8)
C13	−0.1760 (3)	0.3875 (3)	0.1890 (2)	0.0435 (8)
C14	−0.0880 (3)	0.2935 (3)	0.2163 (2)	0.0417 (8)
C15	−0.0299 (3)	0.2949 (3)	0.3001 (2)	0.0438 (8)
C16	−0.0583 (3)	0.3826 (3)	0.3548 (2)	0.0423 (8)
C21	−0.1155 (3)	0.7160 (3)	0.3533 (2)	0.0351 (7)
C22	−0.1790 (3)	0.8184 (3)	0.3058 (2)	0.0384 (7)
C23	−0.1190 (3)	0.9246 (3)	0.2687 (2)	0.0414 (8)
C24	0.0074 (3)	0.9302 (3)	0.2764 (2)	0.0407 (8)
C25	0.0698 (3)	0.8275 (3)	0.3252 (2)	0.0468 (8)
C26	0.0094 (3)	0.7209 (3)	0.3628 (2)	0.0425 (8)
S2	0.30089 (8)	−0.54428 (7)	0.11274 (6)	0.0401 (2)
O21	0.4345 (2)	−0.17764 (18)	0.33432 (14)	0.0472 (6)
O22	0.5701 (2)	−1.0104 (2)	0.24847 (18)	0.0562 (7)
O23	0.3387 (2)	−0.4977 (2)	0.01576 (15)	0.0526 (6)
O24	0.17263 (19)	−0.5626 (2)	0.13570 (16)	0.0511 (6)
C31	0.3519 (3)	−0.4430 (3)	0.1818 (2)	0.0365 (7)
C32	0.2991 (3)	−0.4436 (3)	0.2722 (2)	0.0401 (8)
C33	0.3308 (3)	−0.3587 (3)	0.3246 (2)	0.0410 (8)
C34	0.4134 (3)	−0.2660 (3)	0.2876 (2)	0.0357 (7)
C35	0.4695 (3)	−0.2701 (3)	0.1977 (2)	0.0419 (8)
C36	0.4394 (3)	−0.3578 (3)	0.1461 (2)	0.0408 (8)
C41	0.3794 (3)	−0.6868 (3)	0.1490 (2)	0.0337 (7)
C42	0.5064 (3)	−0.6920 (3)	0.1447 (2)	0.0424 (8)
C43	0.5689 (3)	−0.8013 (3)	0.1773 (2)	0.0430 (8)
C44	0.5055 (3)	−0.9078 (3)	0.2126 (2)	0.0395 (8)
C45	0.3778 (3)	−0.9036 (3)	0.2120 (2)	0.0386 (8)
C46	0.3155 (3)	−0.7929 (3)	0.1825 (2)	0.0376 (7)
N51	−0.0666 (3)	0.1841 (2)	−0.01893 (19)	0.0561 (8)
C52	−0.1867 (4)	0.1688 (4)	−0.0552 (3)	0.0738 (12)
C53	−0.2433 (3)	0.0537 (4)	−0.0039 (3)	0.0720 (12)
N54	−0.1652 (3)	−0.0557 (3)	−0.0122 (2)	0.0533 (8)

	x	y	z	U_{eq}
C55	−0.2154 (4)	−0.1696 (4)	0.0412 (3)	0.0740 (12)
C56	−0.1336 (5)	−0.2807 (4)	0.0350 (3)	0.0817 (14)
C57	−0.0104 (5)	−0.2827 (3)	0.0767 (3)	0.0768 (13)
N61	0.3688 (2)	−0.1322 (2)	0.50927 (18)	0.0461 (7)
C62	0.2605 (3)	−0.0524 (3)	0.5281 (3)	0.0621 (10)
C63	0.2675 (3)	0.0745 (3)	0.4678 (3)	0.0585 (10)
N64	0.3761 (3)	0.1366 (2)	0.48555 (19)	0.0493 (7)
C65	0.3920 (4)	0.2564 (3)	0.4207 (2)	0.0585 (10)
C66	0.5036 (4)	0.3211 (3)	0.4399 (3)	0.0595 (10)
C67	0.6230 (4)	0.2535 (3)	0.4253 (3)	0.0611 (10)
(3)				
O14	0.1521 (3)	0.68430 (12)	0.17751 (12)	0.0675 (6)
O24	0.3743 (2)	0.13079 (11)	0.05043 (10)	0.0571 (5)
O34	1.04648 (19)	0.30286 (10)	0.40224 (9)	0.0470 (4)
C1	0.6293 (3)	0.42272 (14)	0.14160 (12)	0.0426 (6)
C3	0.7293 (3)	0.47006 (15)	0.07589 (13)	0.0527 (6)
C11	0.4934 (3)	0.48650 (14)	0.16022 (12)	0.0415 (5)
C12	0.5356 (3)	0.56051 (15)	0.18510 (14)	0.0514 (6)
C13	0.4206 (3)	0.62514 (16)	0.19144 (14)	0.0545 (7)
C14	0.2608 (3)	0.61724 (16)	0.17321 (13)	0.0501 (6)
C15	0.2146 (3)	0.54372 (15)	0.15233 (13)	0.0502 (6)
C16	0.3308 (3)	0.47896 (15)	0.14536 (13)	0.0452 (6)
C21	0.5584 (3)	0.34582 (14)	0.11452 (12)	0.0415 (5)
C22	0.5416 (3)	0.33650 (15)	0.03672 (13)	0.0458 (6)
C23	0.4787 (3)	0.26637 (15)	0.01447 (13)	0.0472 (6)
C24	0.4303 (3)	0.20259 (15)	0.06993 (13)	0.0463 (6)
C25	0.4420 (3)	0.21152 (15)	0.14754 (13)	0.0515 (6)
C26	0.5043 (3)	0.28224 (15)	0.16883 (13)	0.0524 (6)
C31	0.7403 (3)	0.39299 (14)	0.21265 (13)	0.0414 (5)
C32	0.8982 (3)	0.36060 (17)	0.20351 (14)	0.0564 (7)
C33	0.9986 (3)	0.33001 (16)	0.26586 (14)	0.0547 (7)
C34	0.9454 (3)	0.32928 (13)	0.34210 (13)	0.0390 (5)
C35	0.7860 (3)	0.35966 (13)	0.35238 (13)	0.0423 (6)
C36	0.6866 (3)	0.39059 (14)	0.28893 (13)	0.0431 (6)
O44	0.6468 (2)	−0.26662 (9)	0.63656 (10)	0.0543 (4)
O54	0.9548 (2)	0.28153 (12)	0.54358 (11)	0.0669 (6)
O64	0.19881 (19)	0.16339 (10)	0.93121 (9)	0.0495 (4)
C2	0.4333 (3)	0.07391 (13)	0.64212 (12)	0.0405 (5)
C4	0.2982 (3)	0.08861 (15)	0.57893 (13)	0.0536 (7)
C41	0.4991 (3)	−0.01768 (13)	0.64779 (11)	0.0375 (5)
C42	0.3915 (3)	−0.08121 (14)	0.65775 (12)	0.0416 (5)
C43	0.4413 (3)	−0.16338 (14)	0.65547 (12)	0.0428 (6)
C44	0.6037 (3)	−0.18510 (13)	0.64283 (12)	0.0398 (5)
C45	0.7142 (3)	−0.12478 (14)	0.63758 (13)	0.0452 (6)
C46	0.6622 (3)	−0.04209 (14)	0.63975 (13)	0.0439 (6)
C51	0.5701 (3)	0.13228 (13)	0.61672 (12)	0.0418 (6)
C52	0.6314 (3)	0.13779 (15)	0.54143 (13)	0.0552 (7)
C53	0.7591 (3)	0.18642 (16)	0.51664 (14)	0.0593 (7)
C54	0.8290 (3)	0.23287 (15)	0.56649 (13)	0.0508 (6)
C55	0.7701 (3)	0.22897 (15)	0.64151 (13)	0.0536 (7)
C56	0.6429 (3)	0.17971 (14)	0.66575 (13)	0.0473 (6)
C61	0.3634 (3)	0.09233 (13)	0.72033 (12)	0.0386 (5)
C62	0.2512 (3)	0.15917 (15)	0.72322 (13)	0.0527 (7)
C63	0.1978 (3)	0.18299 (16)	0.79226 (14)	0.0559 (7)
C64	0.2521 (3)	0.13998 (14)	0.86351 (13)	0.0411 (5)
C65	0.3611 (3)	0.07168 (14)	0.86155 (12)	0.0423 (6)
C66	0.4152 (3)	0.04862 (14)	0.79141 (12)	0.0421 (6)
N71	0.0970 (2)	−0.11278 (14)	−0.00764 (13)	0.0594 (6)
N74	0.1214 (2)	0.00438 (13)	0.10248 (12)	0.0532 (5)
C72	0.2294 (3)	−0.12038 (18)	0.05038 (17)	0.0689 (8)
C73	0.1734 (3)	−0.08495 (17)	0.12167 (16)	0.0620 (7)
C75	0.0436 (3)	0.04046 (19)	0.16808 (16)	0.0676 (8)
C76	−0.0131 (4)	0.13064 (19)	0.14166 (18)	0.0751 (9)
C77	−0.1487 (3)	0.14253 (19)	0.08171 (17)	0.0715 (8)
N81	1.0772 (3)	0.42150 (14)	0.59428 (12)	0.0597 (6)

Table 2 (cont.)

	x	y	z	U_{eq}
N84	0.8204 (3)	0.54973 (13)	0.56308 (12)	0.0591 (6)
C82	0.9880 (4)	0.45395 (18)	0.65761 (15)	0.0716 (8)
C83	0.8188 (4)	0.48349 (19)	0.63181 (17)	0.0767 (9)
C85	0.6577 (4)	0.5742 (2)	0.5293 (2)	0.0813 (9)
C86	0.6641 (4)	0.63564 (19)	0.45584 (18)	0.0751 (9)
C87	0.7482 (4)	0.60190 (19)	0.38824 (17)	0.0741 (9)
O9	−0.1070 (2)	0.67689 (15)	0.08539 (11)	0.0765 (6)
C9	−0.0670 (4)	0.66046 (19)	0.00975 (17)	0.0790 (9)

bonded chains of bis-phenols are cross-linked by DABCO molecules attached by means of O—H···N hydrogen bonds, rather than the N—H···O bonds as in (1). However, the disposition of the cross-linkers differs between the two structures; whereas in (1) all the cyclam dications attached to a given chain are on the same side of that chain, leading to ladder formation, in the DABCO adduct the cross-linkers alternate from side to side of a given chain: consequently, instead of pairwise coupling into ladders, the chains are linked into a continuous two-dimensional sheet.

3.2.2. *Compound (2)*. In (2) the asymmetric unit (Fig. 3) consists of two independent phenolate anions [HOC$_6$H$_4$SO$_2$C$_6$H$_4$O]$^-$ and two independent half-molecules of the doubly protonated cyclam [C$_{10}$H$_{26}$N$_4$]$^{2+}$ lying across the centres of inversion at (0, 0, 0) and ($\frac{1}{2}$, 0, $\frac{1}{2}$). The two types of phenolate anion give rise to two independent chains, each running parallel to the [010] direction. In one of the chains O12 in the anion at (x, y, z) acts as a donor to the deprotonated oxygen O11 at (x, 1 + y, z), while in the other O22 at (x,

y, z) acts as a donor to the deprotonated oxygen O21 at (x, −1 + y, z). Each of these chains is accompanied by an antiparallel analogue generated by the centres of inversion at (0, 0, 0) and ($\frac{1}{2}$, 0, $\frac{1}{2}$), respectively. These two pairs of chains are linked into two ladders by the [cyclamH$_2$]$^{2+}$ cations, but in slightly different ways. In the first, type 1, ladder running along (0, y, 0) N51 of the cyclam cation at (x, y, z) acts as a donor to the anionic oxygen O11 in the same asymmetric unit, while N54 also at (x, y, z) acts as a donor to O12 at (−x, 1 − y, −z): this cyclam cation thus utilizes all four exterior N—H bonds in the formation of N—H···O hydrogen bonds (Fig. 4), so that this ladder is similar to those in (1). However, in the second, type 2, ladder running along ($\frac{1}{2}$, y, $\frac{1}{2}$), only two of the four exterior N—H bonds are involved in the hydrogen bonding (Fig. 5): N61 acts as a donor to the anionic oxygen O21, but N64 forms no N—H···O hydrogen bonds.

In addition to the O—H···O and N—H···O hydrogen bonds which generate the individual ladders, there are C—H···O hydrogen bonds, involving the sulfone O atoms as acceptors, which serve to tie all the ladders together. C56 of the cyclam dication at (x, y, z) in a type 1 ladder acts as a donor, *via* its axial hydrogen H56A to the sulfone O24 atom in the bis-phenol anion at (−x, −1 − y, −z): this hydrogen bond has the effect of linking the type 1 ladder along (0, y, 0) to the type 2 ladder along (−$\frac{1}{2}$, y, −$\frac{1}{2}$). In an entirely similar way, the type 2 ladder along ($\frac{1}{2}$, y, $\frac{1}{2}$) is linked to the type 1 ladder running along (0, y, 1): C66 in the cyclam cation at (x, y,
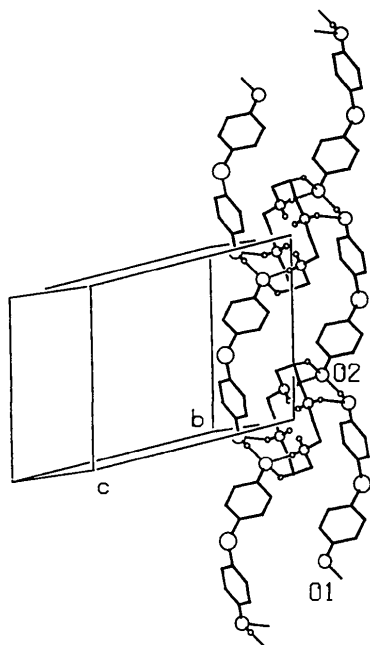

Fig. 2. Packing diagram of part of the crystal structure of (1), showing the formation of the ladders parallel to [100].
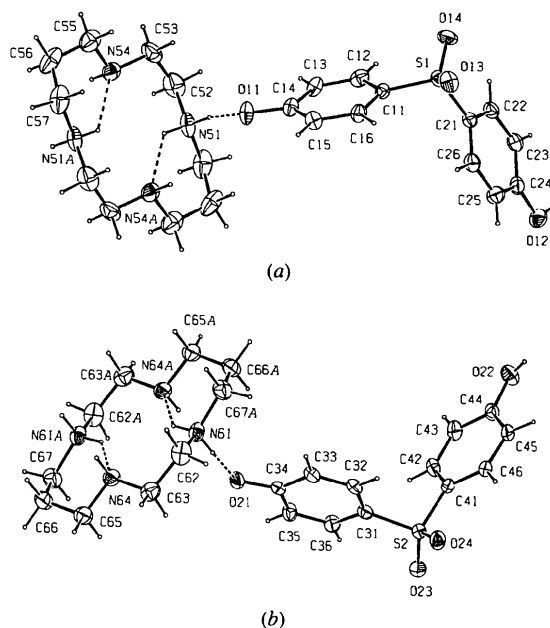

(a)

(b)

Fig. 3. View of the molecular aggregates in (2), (a) giving rise to ladders of type 1 and (b) giving rise to ladders of type 2. Atoms are depicted as in Fig. 1. For the sake of clarity, some of the internal hydrogen bonds in the cation are omitted.

Table 3. *Selected molecular dimensions (Å, °)*

Table 3 (*cont.*)

(1)

S1—C11	1.776 (2)	S1—C21	1.783 (2)
O1—C14	1.328 (2)	O2—C24	1.352 (2)
N31—C32	1.481 (3)	N31—C37^i	1.484 (3)
N34—C33	1.458 (3)	N34—C35	1.471 (3)

C11—S1—C21	103.21 (9)	C33—N34—C35	112.5 (2)
C32—N31—C37^i	115.5 (2)		

C21—S1—C11—C12	81.9 (2)	C21—S1—C11—C16	−102.0 (2)
C11—S1—C21—C22	66.3 (2)	C11—S1—C21—C26	−116.3 (2)

O2···O1^{ii}	2.512 (2)	O2—H2···O1^{ii}	172
N31···O1	2.644 (2)	N31—H31A···O1	162
N31···N34	2.877 (3)	N31—H31E···N34	109
N31···N34^i	2.847 (3)	N31—H31E···N34^i	135
N34···O2^{iii}	3.354 (3)	N34—H34A···O2^{iii}	157
C36···O1^i	3.323 (4)	C36—H36A···O1^i	133

(2)

S1—C11	1.748 (3)	S1—C21	1.761 (3)
S2—C31	1.748 (3)	S2—C41	1.762 (3)
S1—O13	1.442 (2)	S1—O14	1.437 (2)
S2—O23	1.437 (2)	S2—O24	1.437 (2)
O11—C14	1.326 (4)	O12—C24	1.337 (4)
O21—C34	1.312 (3)	O22—C44	1.341 (3)
N51—C52	1.467 (5)	N51—C57^i	1.499 (5)
N54—C53	1.464 (5)	N54—C55	1.458 (5)
N61—C62	1.486 (4)	N61—C67^{iv}	1.488 (4)
N64—C63	1.454 (4)	N64—C65	1.480 (4)

C11—S1—O13	108.0 (1)	C21—S1—O13	108.0 (1)
C11—S1—O14	108.1 (1)	C21—S1—O14	106.7 (1)
O13—S1—O14	118.8 (1)	C11—S1—C21	106.8 (1)
C31—S2—O23	107.5 (1)	C41—S2—O23	108.3 (1)
C31—S2—O24	108.4 (1)	C41—S2—O24	107.6 (1)
O23—S2—O24	118.2 (1)	C31—S2—C41	106.3 (1)
C52—N51—C57^i	116.1 (3)	C53—N54—C55	112.9 (3)
C62—N61—C67^{iv}	114.8 (3)	C63—N64—C65	112.7 (3)

C21—S1—C11—C12	−83.1 (3)	C21—S1—C11—C16	98.1 (3)
C11—S1—C21—C22	107.7 (3)	C11—S1—C21—C26	−71.7 (3)
C41—S2—C31—C32	−83.1 (3)	C41—S2—C31—C36	100.3 (3)
C31—S2—C41—C42	−56.9 (3)	C31—S2—C41—C46	122.3 (2)

O12···O11^v	2.484 (3)	O12—H1···O11^v	175
O22···O21^{vi}	2.513 (3)	O22—H2···O21^{vi}	163
N51···N54	2.878 (4)	N51—H51A···N54	110

(1)

N51···N54^i	2.864 (5)	N51—H51A···N54^i	134
N51···O11	2.698 (3)	N51—H51B···O11	163
N54···O12^{vii}	3.312 (4)	N54—H54A···O12^{vii}	160
N61···N64	2.920 (3)	N61—H61A···N64	107
N61···N64^{iv}	2.793 (4)	N61—H61A···N64^{iv}	135
N61···O21	2.700 (3)	N61—H61B···O21	156
C16···O13	2.935 (4)	C16—H16···O13	102
C22···O14	2.873 (4)	C22—H22···O14	105
C36···O23	2.918 (4)	C36—H36···O23	102
C42···O23^{viii}	3.264 (4)	C42—H42···O23^{viii}	148
C46···O24	2.910 (4)	C46—H46···O24	105
C56···O24^{ix}	3.298 (5)	C56—H56A···O24^{ix}	137
C66···O14^x	3.244 (5)	C66—H66B···O14^x	134

(3)

O14—C14	1.376 (3)	O44—C44	1.369 (3)
O24—C24	1.367 (3)	O54—C54	1.363 (3)
O34—C34	1.341 (3)	O64—C64	1.348 (2)
C1—C3	1.543 (3)	C2—C4	1.548 (3)
C1—C11	1.541 (3)	C2—C41	1.541 (3)
C1—C21	1.544 (3)	C2—C51	1.537 (3)
C1—C31	1.540 (3)	C2—C61	1.531 (3)
N71—C72	1.474 (3)	N81—C82	1.460 (3)
N71—C77^i	1.487 (3)	N81—C87^{xi}	1.484 (3)
N74—C73	1.478 (3)	N84—C83	1.486 (3)
N74—C75	1.478 (3)	N84—C85	1.472 (3)
O9—C9	1.409 (3)		

C72—N71—C77^i	113.0 (2)	C82—N81—C87^{xi}	114.2 (2)
C73—N74—C75	113.8 (2)	C83—N84—C85	113.4 (2)

C3—C1—C11—C12	−59.6 (3)	C4—C2—C41—C42	−51.8 (3)
C3—C1—C11—C16	112.9 (2)	C4—C2—C41—C46	124.9 (2)
C3—C1—C21—C22	−19.5 (3)	C4—C2—C51—C52	−48.0 (3)
C3—C1—C21—C26	162.0 (2)	C4—C2—C51—C56	134.1 (2)
C3—C1—C31—C32	−41.1 (3)	C4—C2—C61—C62	−39.3 (3)
C3—C1—C31—C36	144.1 (2)	C4—C2—C61—C66	145.6 (2)

O9···O64^x	2.632 (3)	O9—H9···O64^x	155
O14···O9	2.689 (3)	O14—H14···O9	171
O24···O64^{xii}	2.502 (2)	O24—H24···O64^{xii}	174
O44···O34^{xiii}	2.659 (2)	O44—H44···O34^{xiii}	172
O54···O34	2.541 (2)	O54—H54···O34	169
N71···N74	2.900 (3)	N71—H71A···N74	106
N71···N74^i	2.800 (3)	N71—H71A···N74^i	128
N71···O64^{xiv}	2.870 (2)	N71—H71B···O64^{xiv}	157
N74···O24	3.053 (3)	N74—H74A···O24	165
N81···O54	2.797 (3)	N81—H81B···O54	169
N84···O34^{xi}	2.836 (3)	N84—H84A···O34^{xi}	174
N84···N81	2.870 (3)	N84—H84B···N81	107
N84···N81^{xi}	2.832 (3)	N84—H84B···N81^{xi}	132

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 + x, y, z$; (iii) $1 - x, -y, -z$; (iv) $1 - x, -y, 1 - z$; (v) $x, 1 + y, z$; (vi) $x, -1 + y, z$; (vii) $-x, 1 - y, -z$; (viii) $1 - x, -1 - y, -z$; (ix) $-x, -1 - y, -z$; (x) $-x, 1 - y, 1 - z$; (xi) $2 - x, 1 - y, 1 - z$; (xii) $x, y, -1 + z$; (xiii) $2 - x, -y, 1 - z$; (xiv) $-x, -y, 1 - z$.

z) acts as a donor to the sulfone O14 atom at ($-x, 1 - y, 1 - z$), again *via* the axial C—H bond. The third independent C—H···O interaction has the effect of linking two ladders of type 2: C42 in the anion at (x, y, z) acts as a donor to the sulfone O23 atom in the anion at ($1 - x, -1 - y, -z$), so linking the type 2 ladder along ($\frac{1}{2}, y, \frac{1}{2}$) to that along ($\frac{1}{2}, y, -\frac{1}{2}$). When these three independent C—H···O hydrogen bonds are propagated through the structure by translation and by the action of the centres of inversion, their net effect is to tie all the ladders together to form a continuous three-dimensional network. C56 at (x, y, z) acts as a donor to O24 at ($-x, -1 - y, -z$) and O21 in the same bis-phenolate anion acts as an acceptor from N61 at ($-x, -1 - y, -z$). C66, also at ($-x, -1 - y, -z$), acts as a donor to O14 at ($x, -2 + y, -1 + z$) and O11 in the same anion is an acceptor from N51 at ($x, -2 + y, -1 +$

z). The neighbouring C56 at $(-x, -2 - y, -1 - z)$ in the same $[cyclamH_2]^{2+}$ cation is a donor to O24 at $(x, -1 + y, -1 + z)$, while within the same asymmetric unit N61 acts as a donor to O21: C66 in this same unit $(x, -1 + y, -1 + z)$ is a donor to O14 at $(-x, -y, -z)$,
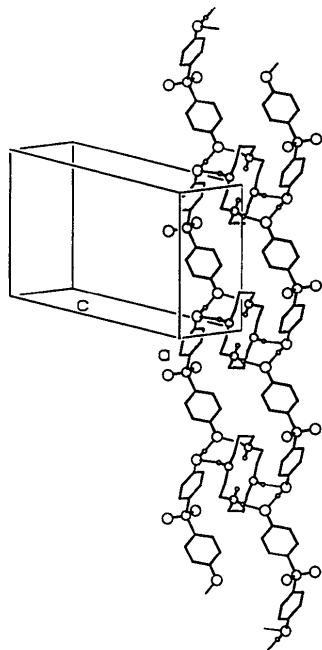

Fig. 4. Packing diagram of part of the crystal structure of (2), showing the formation of type 1 ladders, parallel to [010].
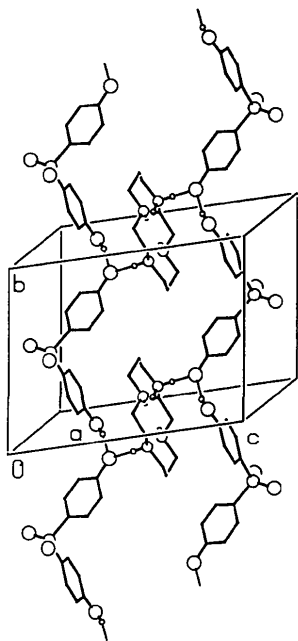
while N51 at $(-x, -y, -z)$ acts as a donor to O11 at $(-x, -y, -z)$. N51 at $(-x, -y, -z)$ occurs in the same $[cyclamH_2]^{2+}$ cation as C56 at (x, y, z) and hence the linking of these four ladders by means of C—H$\cdots$O hydrogen bonds generates a ring motif containing four $[cyclamH_2]^{2+}$ cations, two of each type, and four bis-phenolate anions, again two of each type (Fig. 6). Thus the type 1 ladder running along $(0, y, 0)$ is linked, as a donor, to the type 2 ladders along $(\frac{1}{2}, y, \frac{1}{2})$ and $(-\frac{1}{2}, y, -\frac{1}{2})$ and as an acceptor to those along $(\frac{1}{2}, y, -\frac{1}{2})$ and $(-\frac{1}{2}, y, \frac{1}{2})$. The type 2 ladder running along $(\frac{1}{2}, y, \frac{1}{2})$ is linked, as a donor, to the type 1 ladders along $(0, y, 1)$ and $(1, y, 0)$, and as an acceptor to those along $(0, y, 0)$ and $(1, y, 1)$. In addition, the type 2 ladder along $(\frac{1}{2}, y, \frac{1}{2})$ is linked as both a donor and an acceptor to the type 2 ladders running along $(\frac{1}{2}, y, -\frac{1}{2})$ and $(\frac{1}{2}, y, \frac{3}{2})$: C42 in the bis-phenol at (x, y, z) acts as a donor to O23 at $(1 - x, -1 - y, -z)$, while C42 in this second bis-phenolate unit at $(1 - x, -1 - y, -z)$ acts as a donor to O23 at (x, y, z), thus forming a cyclic centrosymmetric motif (Fig. 7).

In addition to these intermolecular C—H$\cdots$O hydrogen bonds, there are a number of intramolecular C—H$\cdots$O hydrogen bonds: each of the four sulfone O atoms acts as an acceptor from one of the ortho-C—H bonds in the neighbouring aryl rings (Table 3).

3.2.3. *Compound (3).* The asymmetric unit of (3) (Fig. 8) consists of two molecules of the tris-phenol 1,1,1-tris(4-hydroxyphenyl)ethane and one molecule of methanol, all lying in general positions, together with

Fig. 5. Packing diagram of part of the crystal structure of (2), showing the formation of type 2 ladders, parallel to [010].
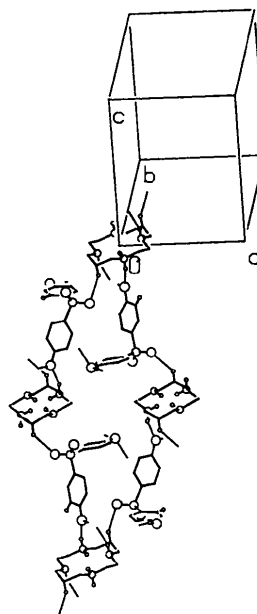

Fig. 6. Packing diagram of part of the crystal structure of (2), showing the $R_8^8(54)$ rings linking the type 1 ladders running along $[0, y, 0]$ and $[0, y, -1]$ and the type 2 ladders running along $[-\frac{1}{2}, y, -\frac{1}{2}]$ and $[\frac{1}{2}, y, -\frac{1}{2}]$.

two independent half-molecules of cyclam lying across the centres of inversion at (0, 0, 0) and (1, $\frac{1}{2}$, $\frac{1}{2}$), respectively: consequently, the molecular components tris-phenol, cyclam and methanol are present in the molar ratio 2:1:1. For the sake of convenience, the tris-phenol molecules containing O14 and O44 will be
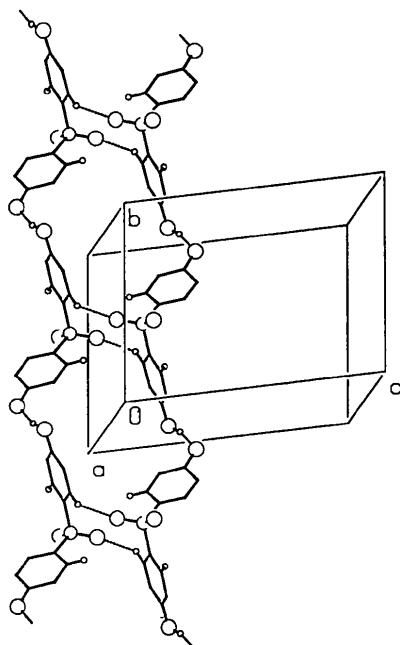

Fig. 7. Packing diagram of part of the crystal structure of (2), showing the $R_2^2(10)$ rings linking pairs of type 2 ladders, running along [$\frac{1}{2}$, y, $\frac{1}{2}$] and [$\frac{1}{2}$, y, $-\frac{1}{2}$].
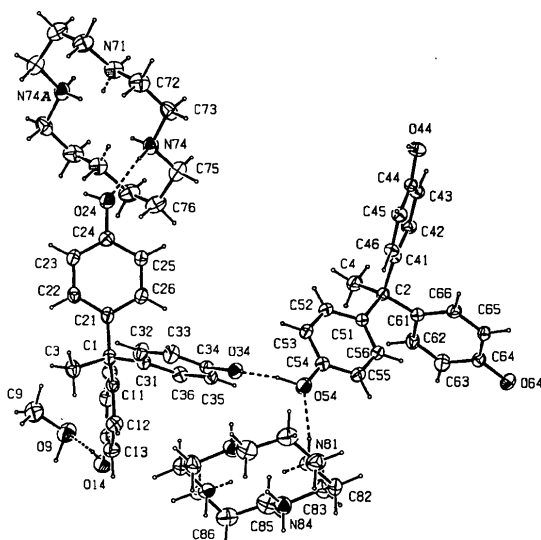
Fig. 8. View of the molecular aggregate in (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, the internal hydrogen bonds in the cations are omitted.

denoted here as tris-phenol molecules 1 and 2, while the cyclams containing N71 and N81 will be denoted as cyclam molecules 1 and 2. The structure analysis shows that, as in (1) and (2), each of the phenols has trans-ferred one proton, from O34 and O64, respectively, to a cyclam component: consequently, each independent cyclam in the structure is doubly protonated. Just as in (1), the centrosymmetric cations $[C_{10}H_{26}N_4]^{2+}$ in (3) contain two hydrogens in the N_4 cavity; each of the interior hydrogens is disordered over two sites and each forms a three-centred hydrogen bond, as in (1): in (3), the occupancies of the two interior sites are 0.61 (3) and 0.39 (3) in cyclam 1 and 0.56 (3) and 0.44 (3) in cyclam 2.

The independent molecular tektons which comprise the structure of (3) are linked together into two inde-pendent, but interwoven, three-dimensional networks by a range of hydrogen bonds, all of O—H···O and N—H···O types. In both the independent tris-phenol molecules, one of the OH groups acts solely as a hydrogen-bond donor (O14 and O44 in the two mole-cules, respectively); the other OH group (O24 and O54) acts as both donor and acceptor; the deprotonated O atoms (O34 and O64) act as triple acceptors, of two O—H···O and one N—H···O hydrogen bonds in each case. The methanol molecule acts as both a donor and an acceptor of O—H···O hydrogen bonds, while all of the exterior axial N—H bonds in the cyclam dications act as a donors in N—H···O hydrogen bonds; there are no O—H···N hydrogen bonds in the structure of (3) and the only N—H···N interactions are those within the cyclam dications.

The formation of the three-dimensional networks is best described in terms of the one-dimensional chains which intersect to form these networks. There are chains running parallel to the [001] direction which are built from the tris-phenol molecules only: O54 in the tris-phenol, molecule 2, at (x, y, z) acts as a hydrogen-bond donor to the deprotonated oxygen O34 in mole-cule 1, also at (x, y, z), while O24 at (x, y, z) acts as a donor to the deprotonated oxygen O64 in the tris-phenol at (x, y, −1 + z) (Fig. 9). Repetition of these two independent O—H···O⁻ hydrogen bonds thus gener-ates a chain and there is an anti-parallel chain of the same type, generated by the action of the centre of inversion at the origin. In addition to these chains running parallel to the [001] direction, there are two independent sets of chains running parallel to [010]. O14 in the tris-phenol at (x, y, z) acts as a hydrogen-bond donor to the methanol O9 atom also at (x, y, z) and this in turn acts as a donor to the deprotonated O64 atom in the unit at (−x, 1 − y, 1 − z); O24 also in the tris-phenol molecule at (x, y, z) acts as an acceptor from N74, also at (x, y, z), while N71 in the same cyclam acts as a donor to O64 at (−x, −y, 1 − z). This sequence of four different hydrogen bonds, two each of O—H···O and N—H···O types, generates the first type of [010]

chain (Fig. 9); the second type of [010] chain involves the other cyclam cations, containing N81 and N84. O44 in the tris-phenol molecule 2 at (x, y, z) acts as a donor to the deprotonated O34 in the unit at $(2 - x, -y, 1 - z)$, while O54 in molecule 2 at (x, y, z) acts as an acceptor from N81 at (x, y, z), while N84 in the same cyclam acts as a donor to O34 at $(2 - x, 1 - y, 1 - z)$. The resulting sequence of three hydrogen bonds, one of O—H···O type and two of N—H···O type, completes the second [010] chain (Fig. 10). Each type of [010] chain involves just one of the two independent cyclam dications, although both independent molecules of the tris-phenol participate in both chain types. As with the

Fig. 9. Packing diagram of part of the crystal structure of (3), showing the [001] chain and the [010] chain involving cyclam dication 1.

[001] chains, each of the types of [010] chain has a counterpart generated by a centre of inversion and running in an anti-parallel direction. The nature of the three-dimensional network depends upon the spacial relations of the three types of chain described above.

The [001] chain is built from two types of tris-phenol molecule within the same asymmetric unit at (x, y, z). The first of the [010] chains links tris-phenol 1 at (x, y, z) to tris-phenol 2 at $(-x, 1 - y, 1 - z)$, while the second of the [010] chains links tris-phenol 2 at (x, y, z) with tris-phenol 1 at $(2 - x, 1 - y, 1 - z)$, two cells displaced along [100] from the tris-phenol 2 at $(-x, 1 - y, 1 - z)$. Hence, the interaction of these three types of chain generates a three-dimensional array, itself best described in terms of chains involving both types of cyclam (Fig. 11). N74 in the cyclam at (x, y, z) is a donor to O24, also at (x, y, z); in the same tris-phenol molecule O34 is an acceptor from N84 at $(2 - x, 1 - y, 1 - z)$; the symmetry-related N84 in the same cyclam molecule is at (x, y, z) and acts as a donor to O34 at $(2 - x, 1 - y, 1 - z)$, while O24 in this same tris-phenol at $(2 - x, 1 - y, 1 - z)$ is an acceptor from N74 at $(2 - x, 1 - y, 1 - z)$; the symmetry-related N74 in this cyclam is at $(2 + x, 1 + y, 1 + z)$. Hence, a repetition of two independent types of N—H···O hydrogen bond generates a chain running parallel to [211] and in an entirely similar fashion the N71···O64 and N81···O54 interactions generate another chain, running parallel to [21$\bar{1}$] (Table 3 and Fig. 11). The occurrence of a repeat period spanning two unit cells in the [100] direction indicates that there are two independent three-dimensional networks in the structure of (3). There are, in fact, short routes between the individual [001] chains of a given network which are separated by two repeat units along [100] and these take the form of spirals. As
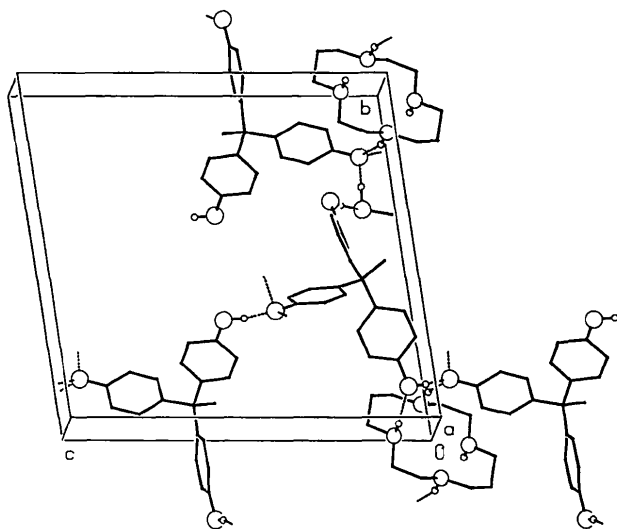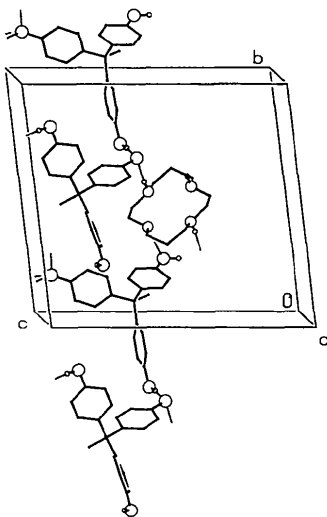

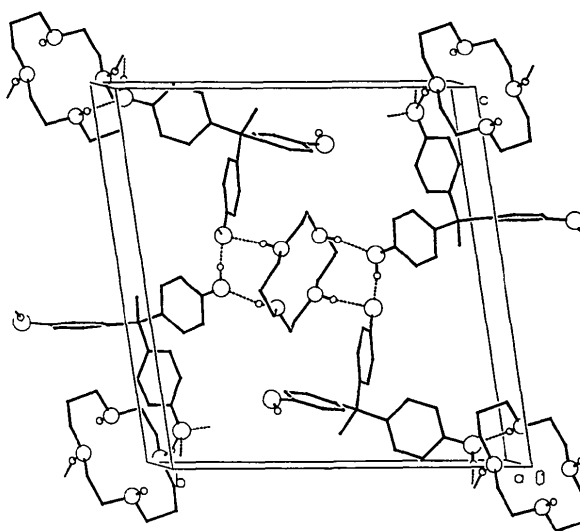Fig. 10. Packing diagram of part of the crystal structure of (3), showing the [010] chain involving cyclam dication 2.

Fig. 11. Packing diagram of part of the crystal structure of (3), showing the [211] and [21$\bar{1}$] chains.

described earlier (Fig. 9), O34 at (x, y, z) is linked via a combination of covalent and hydrogen bonds to O54 at $(-x, 1 - y, 1 - z)$; N84 and N81 in the cyclam at $(2 - x, 1 - y, 1 - z)$ act as donors to O34 at (x, y, z) and to O54 at $(2 - x, 1 - y, 1 - z)$, respectively, so generating a spiral about an axis parallel to [100]: there are two such spirals, of opposite helicity, running through each unit cell.

3.3. Molecular conformations and dimensions

3.3.1. The $[cyclamH_2]^{2+}$ cation. It is perhaps surprising that the structure of cyclam itself has not been reported, although several $[cyclamH_2]^{2+}$ salts and a number of metal complexes of cyclam have been structurally characterized. For a cyclam system in which the four N atoms are constrained to be coplanar, as found in (1)–(3), there are five possible isomeric arrangements of the four axial N—H bonds, two of which are consistent with centrosymmetry (Barefield et al., 1986). All the independent cations in compounds (1)–(3) in fact adopt the same centrosymmetric structure having the pairs of axial N—H bonds on the same side of the molecular plane separated by three-carbon loops: this is the trans-III isomer, examples of which are found both in the 4:1 adduct of 4-tert-butylbenzoic acid with cyclam (Adam et al., 1994) and in [Ni(cyclam)]I$_2$ (Adam et al., 1991). The overall molecular shape of the heavy-atom skeleton in this cation is remarkably flat and disc-like and there is almost perfect staggering about all the C—C and C—N bonds (Table 3 and Figs. 1, 3 and 8). The C—C bond lengths are unexceptional, but the C—N bond lengths show a systematic variation with the degree of protonation of the N atom, as judged by the site-occupation factors of the internal equatorial hydrogens: where the internal H atoms are disordered, (1) and (3), the mean C—N bond lengths range from 1.483 (3) Å when the s.o.f. is 0.81 (3) Å in (1) to 1.465 (7) Å when the s.o.f. is 0.19 (3) Å, also in (1), with intermediate values for the various sites in (3) (Table 3): in (2), where the internal H atoms are fully ordered, the mean value of the C—N bond lengths for protonated and unprotonated N atoms (corresponding to s.o.f.'s of unity and zero) are 1.488 (11) and 1.461 (10) Å, respectively. In the simple salt [cyclamH$_2$](ClO$_4$)$_2$, where the additional hydrogens are fully ordered (Nave & Truter, 1974), the corresponding values are 1.497 and 1.467 Å, respectively. The intramolecular hydrogen bonds are all three-centred; for each occupied site, the intra-cavity hydrogen is covalently bonded to one nitrogen and hydrogen bonded to two others (Table 3, Figs. 1, 3 and 8): the hydrogen bonds are necessarily rather short for N—H···N interactions as the N···N distances are constrained by the overall size and shape of the cyclam macrocycle and, as expected, the sum of the three angles around these H atoms is close to 360° in each case (Table 3). This arrangement of three-centre

hydrogen bonds involving all four of the N atoms may contribute to the stability and the ease of formation of the $[cyclamH_2]^{2+}$ cations in these compounds.

3.3.2. The phenolate anions. In each compound the C—O⁻ bonds are significantly shorter than the C—O(H) bonds (Table 3). The conformation of the heavy-atom skeleton of the phenolate anion [HOC$_6$H$_4$SC$_6$H$_4$O]⁻ in (1), as defined by the C—S—C—C torsional angles (Table 3) is close to C_2 symmetry; .in (2) the conformations of both the independent phenolate anions are close to C_2, presumably constrained to be such by the intramolecular C—H···O hydrogen bonds; the conformation of one of the phenolate anions in (3), that centred on atom C2, is not far from C_3 symmetry.

3.4. Hydrogen-bonding motifs and dimensions

3.4.1. Motifs. The chain-forming motif in (1), which involves only the phenolate anions, can be described by the graph set $C(12)$ (Etter, 1990; Bernstein et al., 1995), while the cross-links formed by the cyclam dication joining O1 at (x, y, z) to O2 at $(1 - x, -y, -z)$ have graph set DD. The large centrosymmetric rings between the rungs of the ladder have unitary- and binary-level graph sets $N_1 = DD$, $N_2 = R_4^4(34)$; the smaller rings at the ends of each rung of the ladder, described by two N—H···O and one O—H···O hydrogen bonds, have $N_1 = DDD$, $N_2 = R_3^2(10)$; finally, the $R_3^2(10)$ rings are subdivided by the C—H···O hydrogen bonds into $R_2^1(6)$ and $R_3^2(8)$ sections. In (2) the two independent chain-forming motifs involving only the phenolate anions can both be described by the graph-set descriptor $C(12)$ and the cross-links formed by the cyclam dications have graph set DD. In the ladders of type 1 the small and large rings, within and between the rungs of the ladder, have graph sets $R_3^2(10)$ and $R_4^4(34)$, while in the ladders of type 2 all the rings involving the rungs of the ladder are the same with graph set $R_6^4(46)$. All the intramolecular C—H···O hydrogen bonds in (2) form $S(5)$ motifs, while the cyclic motifs linking the ladders together (Figs. 6 and 7) have graph-set descriptors $R_8^8(54)$ and $R_2^2(10)$, respectively. In (3) the [001] chain formed from tris-phenol species only can be described by the unitary- and binary-level graph sets $N_1 = DD$, $N_2 = C_2^2(24)$. The two types of [010] chain may be described as follows: the chain which contains cyclam dication 1 has $N_1 = DDDD$, $N_2 = C_4^3(21)$, while that involving cyclam dication 2 has $N_1 = DDD$, $N_2 = C_3^2(19)$. The difference between these two chains which influences their graph sets is the incorporation of methanol into only one of them; for each of the binary-level graph sets the number of acceptors is less than the number of donors since each chain includes a double acceptor of hydrogen bonds, O64 and O34, respectively. The [211] and [2Ī1] chains, neither of which involves the methanol components, and both of which link different

centres of inversion, each contain only two distinct types of hydrogen bond, both of $N-H\cdots O$ type: the graph-set descriptors are $N_1 = DD$, $N_2 = C_4^4(42)$. The spiral motifs in (3), linking [001] chains two cells apart in the [110] direction, are built from two phenolate anions, one cyclam dication and one methanol molecule, and contain four independent hydrogen bonds, two each of $O-H\cdots O$ and $N-H\cdots O$ types, and the graph-set descriptors are $N_1 = DDDD$, $N_2 = C_4^4(31)$. The small rings (Fig. 11), which include N71, N74, O24 and O64, have $N_1 = DDD$, $N_2 = R_3^2(10)$.

3.4.2. *Dimensions.* The intermolecular hydrogen-bond distances are nearly all short (Table 3). The $O\cdots O$ distances range from 2.479 (5) to 2.680 (4) Å and the shorter distances are, in general, associated with deprotonated O atoms as acceptors; despite this shortness, there is no indication in any of the $O-H\cdots O$ interactions for a symmetrical or near-symmetrical placing of the proton between the two O atoms, as sometimes found in short $O\cdots H\cdots O$ systems (Emsley, 1980). In both (1) and (2) there are marked differences between the $N\cdots O$ distances involving the neutral and anionic O atoms, with the bonds to the deprotonated O atoms always shorter by at least 0.5 Å; by contrast, in (3) no clear pattern can be found for the $N\cdots O$ distances in the four independent $N-H\cdots O$ hydrogen bonds.

References

Aakeröy, C. B. & Seddon, K. R. (1993). *Chem. Soc. Rev.* **22**, 397–407.

Adam, K. R., Antolovich, M., Atkinson, I. M., Leong, A. J., Lindoy, L. F., McCool, B. J., Davis, R. L., Kennard, C. H. L. & Tasker, P. A. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1539–1540.

Adam, K. R., Antolovich, M., Brigden, L. G., Leong, A. J., Lindoy, L. F., Baillie, P. J., Uppal, D. K., McPartlin, M., Shah, B., Proserpio, D., Fabbrizzi, L. & Tasker, P. A. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2493–2501.

Alder, R. W., Bowman, P. S., Steel, W. R. S. & Winterman, D. R. (1968). *J. Chem. Soc. Chem. Commun.* pp. 723–724.

Barefield, E. K., Biancchi, A., Billo, E. J., Connolly, P. J., Paoletti, P., Summers, J. S. & van Derveer, D. G. (1986). *Inorg. Chem.* **25**, 4197–4202.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Brzezinski, B., Grech, E., Malarski, Z. & Sobczyk, L. (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 857–859.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996a). *Acta Cryst.* C**52**, 2524–2528.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996b). *Acta Cryst.* C**52**, 3052–3055.

Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.

Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.

Emsley, J. (1980). *Chem. Soc. Rev.* **9**, 91–124.

Enraf–Nonius (1992). *CAD-4-PC Software.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Ferguson, G. (1997). *PRPCIF97. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL93 Programs.* University of Guelph, Canada.

Ferguson, G., Bell, W., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 534–543.

Ferguson, G., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 513–520.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Gilli, P., Bertolasi, V., Ferretti, V. & Gilli, G. (1994). *J. Am. Chem. Soc.* **116**, 909–915.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Limbach, H. H., Wehrle, B., Zimmermann, H., Kendrick, R. D. & Yannoni, C. S. (1987). *J. Am. Chem. Soc.* **109**, 929–930.

Nave, C. & Truter, M. R. (1974). *J. Chem. Soc. Dalton Trans.* pp. 2351–2354.

North, A. C. T., Philips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1995a). *PLATON. Molecular Geometry Program.* July 1995 Version. University of Utrecht, The Netherlands.

Spek, A. L. (1995b). *PLUTON. Molecular Graphics Program.* July 1995 Version. University of Utrecht, The Netherlands.

Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.