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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1292). Services for accessing these data are described at the back of the journal.

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A chain of fused $R_2^2(10)$ and $R_6^4(12)$ rings in the hydrogen-bonded structure of 1,4,8,11-tetraazacyclotetradecane–2,2′-biphenol (1/2)

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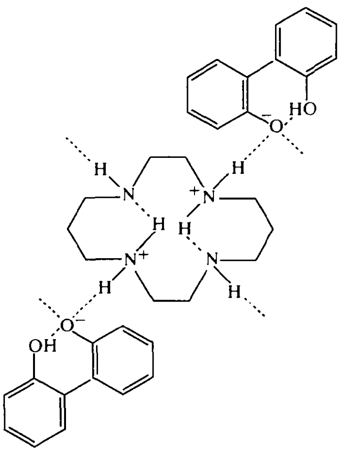
Abstract

The title compound is a salt, *i.e.* 4,11-diaza-1,8-diazoniacyclotetradecane bis[2-(2-hydroxyphenyl)phenolate], $C_{10}H_{26}N_4^{2+}\cdot 2HOC_6H_4C_6H_4O^-$. The centrosymmetric cation contains two intramolecular N—H···N hydrogen bonds, with an N···N distance of 2.865 (2) Å, and the anion contains an intramolecular O—H···O hydrogen bond, with an O···O distance of 2.486 (2) Å. The ions are linked into continuous chains by means of two types of N—H···O hydrogen bond having N···O distances of 2.682 (2) and 3.273 (2) Å.

Comment

The macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane (cyclam, $C_{10}H_{24}N_4$) forms adducts with both 4,4′-thiodiphenol and 4,4′-sulfonyldiphenol of 1:2 stoichiometry which are salts $[\text{cyclamH}_2]^{2+}\cdot 2[HOC_6H_4X\text{-}C_6H_4O]^-$, where X = S or SO_2 (Ferguson *et al.*, 1998). In each of these adducts, the bis-phenol molecules have each transferred one proton to the cyclam, and the resulting phenolate anions are linked by means of O—H···O hydrogen bonds. Pairs of antiparallel chains are then linked by centrosymmetric $[\text{cyclamH}_2]^{2+}$ cations to form molecular ladders.

While the disposition of the hydroxy groups in 4,4′-disubstituted bis-phenols is ideal for the formation of extended chains, this is by no means obviously the case for 2,2′-biphenol, where the formation of an intramolecular O—H···O hydrogen bond is a plausible alternative. We report here the formation and structure of the 1:2 adduct (I), formed between cyclam and 2,2′-biphenol. The resulting structure is a one-dimensional hydrogen-bonded polymer, but this takes the form of a chain-of-rings (Bernstein *et al.*, 1995), rather than that of a molecular ladder (Ferguson *et al.*, 1998).



(I)

The constitution of the 1:2 adduct (I) is that of a salt, $[C_{10}H_{26}N_4]^{2+}\cdot 2[HOC_6H_4C_6H_4O]^-$, in which the asymmetric unit consists of one phenolate anion and one half of a $[\text{cyclamH}_2]^{2+}$ cation lying across a centre of inversion (Fig. 1). As observed previously

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in similar [cyclamH_2]$^{2+}$ salts (Ferguson *et al.*, 1998), two protons are held by means of N—H···N hydrogen bonds within the N_4 cavity of the macrocycle in an $R_2^2(10)$ motif (Bernstein *et al.*, 1995), leaving four axial N—H bonds, all of which participate in the hydrogen bonding, which are essentially normal to the mean plane of the centrosymmetric macrocycle (Fig. 2). The phenolate anion, in which the two aryl rings are inclined at an angle of 42.1 (1)°, contains an intramolecular O—H···O hydrogen bond in an *S*(7) motif.

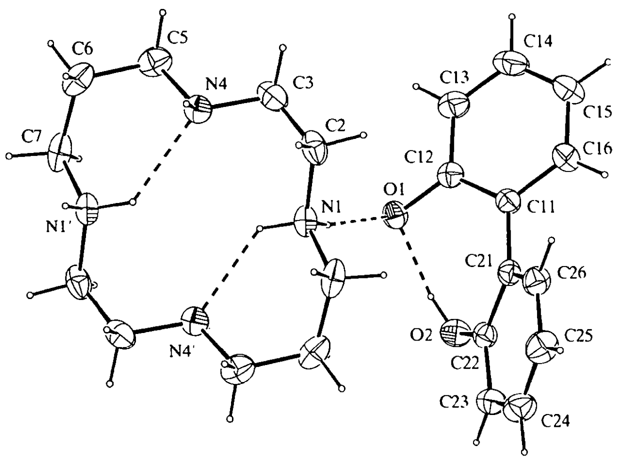

Fig. 1. A view of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

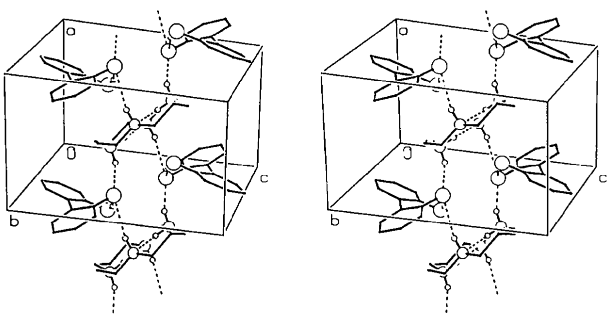

Fig. 2. A view of part of the crystal structure of (I), showing the chain of fused $R_2^2(10)$ and $R_6^4(12)$ rings running parallel to [100].

The cations and anions are linked by N—H···O hydrogen bonds into a chain-of-rings (Bernstein *et al.*, 1995) running parallel to the [100] direction; each N atom acts as a donor, but only the deprotonated O1 atom acts as an acceptor of N—H···O hydrogen bonds. This anionic O atom thus acts as a triple acceptor, while the neutral O2 atom acts only as a hydrogen-bond donor (Table 2). Atom O1 at (*x*, *y*, *z*) acts as acceptor from N1 at (*x*, *y*, *z*) and from N4 at ($-1+x$, *y*, *z*), while N4 at (*x*, *y*, *z*) is a donor to O1 at ($1+x$, *y*, *z*). Adjacent cations are thus linked by pairs of phenolate anions to form a chain of $R_6^4(12)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ (n = 0 or integer), alternating with the $R_2^2(10)$ rings centred at $(n+\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (n = 0 or integer) (Fig. 2). The N1—H1*E*···N4^{i} [symmetry code: (i) $1-x$, $1-y$, $1-z$] unit is common to rings of both types, so that the two types of ring are, in effect, fused. Of the four independent hydrogen bonds within the structure (Table 2), those of the N—H···N and O—H···O types are both intramolecular; the two N—H···O hydrogen bonds are sufficient to generate the supramolecular structure. There are no contacts between the individual chains closer than the sum of the van der Waals radii, and just one chain runs through each unit cell. Along the chain, there is a $C_2^1(7)$ motif defining the repeat unit, so that the entire chain-of-rings with pendent *S*(7) rings may be designated as $S(7)C_2^1(7)[R_2^2(10)][R_6^4(12)]$. The N4···O1^{ii} [symmetry code: (ii) $1+x$, *y*, *z*] hydrogen bond is significantly longer, and thus presumably weaker, than the N1···O1 type (Table 2). Although in the N4···O1^{ii} interaction both donor and acceptor are charged, leading to the expectation of short strong hydrogen bonds (Aakeröy & Seddon, 1993; Gilli *et al.*, 1994), the weakness inferred from the observed N···O distance may be related to the fact that the N4 atom is acting as a double donor of hydrogen bonds, while O1 is acting as a triple acceptor. If the N4···O1^{ii} interaction were to be discounted, the structure (Fig. 2) could alternatively be envisaged as the finite centrosymmetric three-component aggregate whose hydrogen-bonding motif can be designated as $D_3^3(12)[R_2^2(10)]$; such *D*[*R*] patterns are expected to be commonly observed in multi-component centrosymmetric aggregates (Bernstein *et al.*, 1995).

The [cyclamH_2]$^{2+}$ cations adopt the usual *trans*-III conformation (Barefield *et al.*, 1986; Adam *et al.*, 1994; Ferguson *et al.*, 1998), in which the heavy-atom skeleton is remarkably flat and disc-like (Fig. 2), with almost perfect staggering about all of the C—C and C—N bonds (Table 1).

The C—N bonds associated with the protonated N1 atom are significantly longer than those associated with the unprotonated N4 atom (Table 1). The observed C—N bond lengths in (I) are almost identical to the corresponding mean distances in cyclam–4,4′-sulfonyldiphenol (1/2) of 1.488 (11) and 1.461 (10) Å, respectively (Ferguson *et al.*, 1998). As normally observed for bis-phenolate monoanions, the C—O$^-$ bond is significantly shorter than the C—O(H) bond (Table 1). All other bond lengths are typical of their types (Allen *et al.*, 1987); so too are the interbond angles.

As commonly found in phenol–amine adducts (Coupar *et al.*, 1997; Ferguson *et al.*, 1998), the stoichiometry of the product is independent of the composition of the co-crystallization mixture over fairly wide limits. Systems of this type probably have rather simple phase diagrams and rather deep wells on their potential-energy surfaces.

Experimental

Equimolar quantities of cyclam and 2,2′-biphenol were dissolved separately in methanol. The solutions were mixed and the mixture was set aside to crystallize, yielding analytically pure (I). Analysis: found C 71.0, H 7.6, N 9.8%; $C_{34}H_{44}N_4O_4$ requires C 71.3, H 7.7, N 9.8%. The same product was obtained using a variety of molar ratios of cyclam and 2,2′-biphenol in the range 1:2 to 2:1. Crystals suitable for single-crystal X-ray diffraction analysis were selected directly from the analytical sample.

Crystal data

$C_{10}H_{26}N_4^{2+}\cdot 2C_{12}H_9O_2^-$
$M_r = 572.73$
Triclinic
$P\bar{1}$
$a = 7.3635\,(7)$ Å
$b = 9.8643\,(10)$ Å
$c = 11.4142\,(15)$ Å
$\alpha = 110.845\,(8)°$
$\beta = 99.069\,(12)°$
$\gamma = 92.998\,(9)°$
$V = 759.83\,(15)$ Å^3
$Z = 1$
$D_x = 1.252$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.69–17.58°$
$\mu = 0.082$ mm^{-1}
$T = 294\,(1)$ K
Plate
0.42 × 0.36 × 0.17 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3486 measured reflections
3486 independent reflections
2278 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 27.41°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity variation: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.111$
$S = 1.030$
3486 reflections
192 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.0479P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.217$ e Å^{-3}
$\Delta\rho_{\min} = -0.144$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.054 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C12	1.335 (2)	C3—N4	1.462 (2)
O2—C22	1.355 (2)	N4—C5	1.461 (2)
N1—C2	1.484 (2)	C5—C6	1.515 (2)
N1—C7$^{\rm i}$	1.489 (2)	C6—C7	1.508 (3)
C2—C3	1.498 (2)		
C16—C11—C21—C26	40.8 (2)	N1—C2—C3—N4	65.6 (2)
C12—C11—C21—C26	−138.3 (2)	C2—C3—N4—C5	−178.3 (1)
C16—C11—C21—C22	−138.1 (2)	C3—N4—C5—C6	178.3 (1)
C12—C11—C21—C22	42.8 (2)	N4—C5—C6—C7	−64.9 (2)
C7$^{\rm i}$—N1—C2—C3	−168.6 (1)	C5—C6—C7—N1$^{\rm i}$	72.0 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	0.82	1.70	2.486 (2)	161
N1—H1*A*···O1	0.90	1.82	2.682 (2)	159
N1—H1*E*···N4$^{\rm i}$	0.90	2.15	2.865 (2)	135
N4—H4*A*···O1$^{\rm ii}$	0.90	2.40	3.273 (2)	165

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 + x, y, z$.

H atoms were treated as riding atoms (C—H 0.93 and 0.97, N—H 0.90 and O—H 0.82 Å).

Data collection: *CAD-4-PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*96. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

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