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The First Crystal Structure Analysis of Cyclododeca-2,8-diyne-1,10-diols

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Abstract

Cyclododeca-2,8-diyne-1,10-diol, (6), $C_{12}H_{16}O_2$, and 1,10-dimethylcyclododeca-2,8-diyne-1,10-diol, (11), $C_{14}H_{20}O_2$, have been prepared and their structures determined. Both crystallize in centrosymmetric space groups and the molecules have approximate C_2 symmetry. For compound (6), the lengths of the triple bonds are 1.184 (3) ($C2\equiv C3$) and 1.189 (3) Å ($C8\equiv C9$). The bond angles at the triple bonds ($C1—C2\equiv C3$ and $C8\equiv C9—C10$) deviate by less than 6° from 180°. For compound (11), the lengths of the triple bonds are 1.190 (3) ($C2\equiv C3$) and 1.188 (3) Å ($C8\equiv C9$), and the bond angles at the triple bonds are close to 175.5°. In both compounds, the two 3-hexyne chains maintain a 'crossed' arrangement whereas the two alkylene chains are arranged in a manner similar to that described for unsubstituted cyclododecane.

Comment

Medium-sized ring compounds are of considerable interest because of their unique structure and transannular reactivity (Dunitz & Meyer, 1965; Johnson, 1986; Gleiter, Merger, Irngartinger & Nuber, 1993). The cyclododecadiynediols (6) and (11) (see schemes in *Experimental*) have been prepared for an investigation of reactions of the juxtaposed triple bonds with doubly functionalized reagents and in order to determine the influence of different substitution patterns at the propargylic centres on the structure of such ring compounds.

The expected C_2 symmetry of *rac*-(6) and *rac*-(11) is apparent from the structure analysis. For (6)

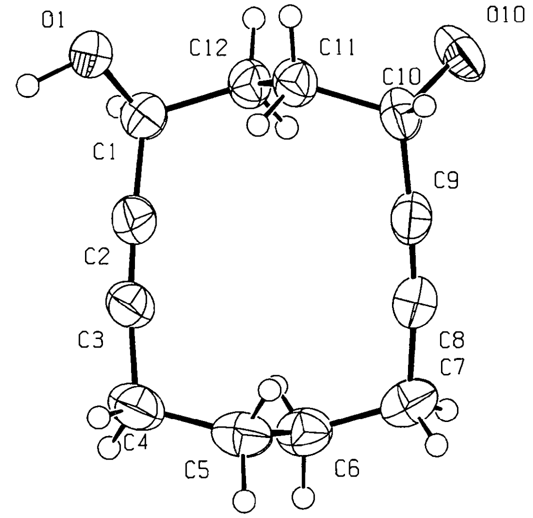


Fig. 1. Perspective view of (6). Displacement ellipsoids are shown at the 50% probability level.

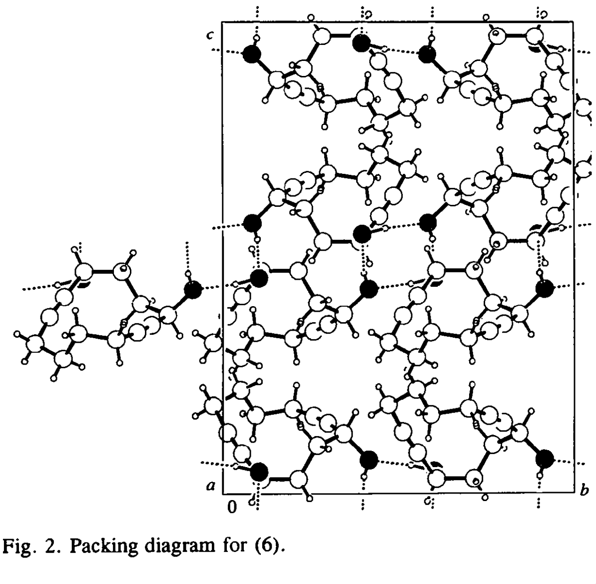


Fig. 2. Packing diagram for (6).

and (11), the orientation of the two alkylene chains relative to each other corresponds to the 'crossed' arrangement described for unsubstituted cyclododecane (Dale, 1978). In *rac*-(6), the lengths of the two triple bonds, 1.184 (3) (C2≡C3) and 1.189 (3) Å (C8≡C9), are very similar. The bond angles at the triple bonds are 177.3 (2) (C1—C2≡C3), 173.8 (2) (C2≡C3—C4), 174.4 (2) (C7—C8≡C9) and 176.2 (2)° (C8≡C9—C10). The transannular distances of the two alkyne units are 3.885 (3) (C2···C9) and 3.923 (4) Å (C3···C8). In compound (11), the lengths of the two triple bonds, 1.190 (3) (C2≡C3) and 1.188 (3) Å (C8≡C9), deviate only slightly from each other. The angles at the triple bonds, 175.5 (3) (C1—C2≡C3), 175.9 (3) (C2≡C3—C4) and 175.3 (3)° (C7—C8≡C9 and C8≡C9—C10), are almost the same. The transannular distances of the two alkyne moieties in *rac*-(11) are 3.929 (3) (C2···C9) and 3.926 (4) Å (C3···C8). These structural features are well within the ranges found for cyclododecadiynes and cyclodecadiynes in the Cambridge Structural Database (Allen *et al.*, 1979). Other salient features of the diols (6) and (11) are the bond angles at other centres. In (11), the bond angle (C2—C1—C12) at the quaternary C atom, is 109.1 (2)°, whereas the adjacent bond angle (C1—C12—C11) is close to 115°, and the value at the corresponding location (C4—C5—C6) is 113.9 (2)°. This is reminiscent of the bond-angle situation at quaternary C atoms of type $(H_3C)_2C(C)_2$ (Keese & Meyer, 1993). In (6), the bond angle C2—C1—C12 is 111.5 (2)°. At the CH_2 centres, bond angles close to 114° have been observed. It is apparent that the bonds as well as the dihedral angles deviate from the average values expected for open-chain alkynes.

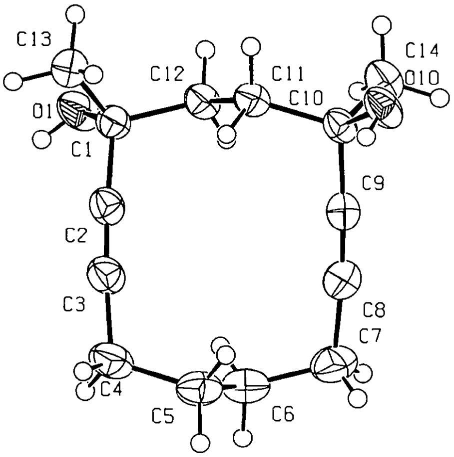


Fig. 3. Perspective view of (11). Displacement ellipsoids are shown at the 50% probability level.

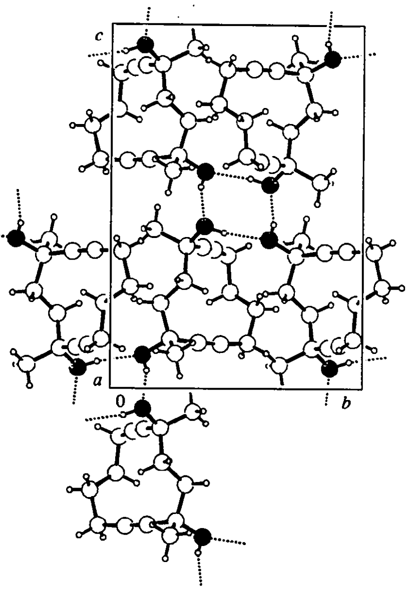
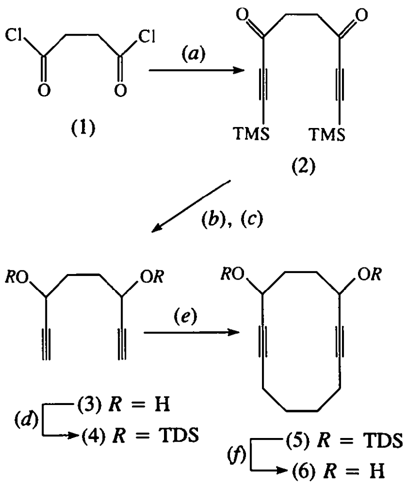


Fig. 4. Packing diagram for (11).

Hydrogen bonding can be seen in the cell packing diagrams of *rac*-(6) and *rac*-(11) (Figs. 2 and 4, respectively). For *rac*-(6), symmetry-related molecules are hydrogen bonded to form two-dimensional chains extending in the **b** direction (Fig. 2). The hydrogen-bond lengths are 1.736 (3) (HO1···O10^{i}) and 1.909 (3) Å (HO10···O1^{ii}), with hydrogen-bond angles of 172.8 (3) (O1—HO1···O10^{i}) and 168.3 (3)° (O10—HO10···O1^{ii}). In *rac*-(11), symmetry-related molecules are hydrogen bonded to give a three-dimensional network (Fig. 4). The lengths of the hydrogen bonds are 2.037 (3) (HO1···O10^{iii}) and 1.987 (3) Å (HO10···O1^{iv}), and lie in the same range as those in *rac*-(6). In (11), the bond angles are 161.9 (3) (O1—HO1···O10^{iii}) and 161.7 (3)° (O10—HO10···O1^{iv}), and thus differ by 6–11° from those determined for *rac*-(6). [Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, -z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

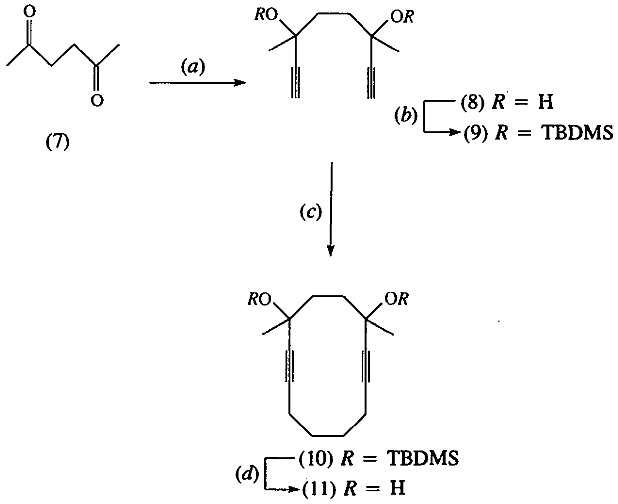
Experimental

Compound (6) was prepared by a sequence of six steps. Addition of bis(trimethylsilyl)acetylene to succinyl dichloride, (1), in a Friedel–Crafts acylation led to the diyne diol (2) (see scheme below; TMS is trimethylsilyl). Reduction of the carbonyl groups with sodium borohydride, followed by treatment with silver nitrate/potassium cyanide yielded a 1:1 mixture of *meso*- and *rac*-(3). After silylation of the hydroxy groups with thexyldimethylsilyl (TDS) chloride, (4) was deprotonated with ^{n}BuLi and alkylated with 1,4-dibromobutane to give (5) in 41% isolated yield, which was transformed to (6) by deprotection of the silyloxy groups with TBAF (tetrabutyl ammonium fluoride) in THF. After chromatographic purification, the diastereomeric mixture of (6) was recrystallized from ether at room temperature. The *meso* compound formed white needles, whereas *rac*-(6) gave pure colourless prisms with m.p. 427–428 K, which were easily separated from one another.



(*a*) $MeCl_2$, $AlCl_3$, TM5—C≡C—TMS
(*b*) $NaBH_4.CeCl_3$, MeOH
(*c*) (i) $AgNO_3$, $EtOH/H_2O$; (ii) KCN, H_2O
(*d*) DMF, imidazole, 2 TDS chloride
(*e*) (i) THF, 243 K, 2^nBuLi; (ii) RT, DMPU, 1,4-dibromobutane
(*f*) TBAF, THF

Compound (11) was prepared by a sequence of four steps. Addition of acetonylacetone, (7), to ethynylmagnesium chloride gave a 1:1 mixture of *meso*- and *rac*-(8). After silylation of the hydroxy groups with *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMS triflate), (9) was deprotonated with ^{n}BuLi and alkylated with 1,4-dibromobutane to give (10) in 43% isolated yield, which was deprotected with TBAF in THF to a diastereomeric mixture of (11) in 98% yield. Pure *rac*-(11) was obtained by flash chromatography, followed by recrystallization from ether at room temperature. *rac*-(11) forms colourless hexagonal crystal plates with m.p. 417 K, which can be easily separated from the white needles of *meso*-(11).



(*a*) THF, 273 K, 2 ClMgC≡CH
(*b*) THF, NEt_3, 2 TBDMS triflate
(*c*) (i) THF, 253 K, 2^nBuLi;
(ii) RT, DMPU, 1,4-dibromobutane
(*d*) TBAF, THF

Compound (6)

Crystal data

$C_{12}H_{16}O_2$
$M_r = 192.25$
Orthorhombic
Pbca
$a = 8.526\,(1)$ Å
$b = 13.857\,(1)$ Å
$c = 18.519\,(1)$ Å
$V = 2187.9\,(3)$ Å^3
$Z = 8$
$D_x = 1.167$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.0$–$18.0°$
$\mu = 0.078$ mm^{-1}
$T = 294\,(2)$ K
Prism
0.57 × 0.49 × 0.46 mm
Colourless

Data collection

Stoe AED-2 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1919 measured reflections
1919 independent reflections
1036 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 24.97°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 22$
3 standard reflections frequency: 60 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0444$
$wR(F^2) = 0.0929$
$S = 0.882$
1919 reflections
138 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.128$ e Å^{-3}
$\Delta\rho_{min} = -0.120$ e Å^{-3}

Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0120 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (6)*

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

	x	y	z	U_{eq}
O1	0.1317 (2)	0.60278 (11)	0.04670 (9)	0.0555 (5)
O10	0.4394 (2)	0.91546 (11)	0.07005 (11)	0.0575 (5)
C1	0.2972 (3)	0.60913 (14)	0.03123 (12)	0.0459 (6)
C2	0.3876 (3)	0.5543 (2)	0.08474 (13)	0.0464 (6)
C3	0.4649 (3)	0.5132 (2)	0.12800 (13)	0.0486 (6)
C4	0.5677 (3)	0.4724 (2)	0.18383 (13)	0.0598 (7)
C5	0.6704 (3)	0.5513 (2)	0.21601 (12)	0.0578 (7)
C6	0.7885 (3)	0.5934 (2)	0.16302 (12)	0.0547 (7)
C7	0.8231 (3)	0.6997 (2)	0.17568 (13)	0.0591 (7)
C8	0.6836 (3)	0.7584 (2)	0.16080 (12)	0.0496 (6)
C9	0.5653 (3)	0.7992 (2)	0.14595 (12)	0.0461 (6)
C10	0.4156 (3)	0.84413 (14)	0.12467 (13)	0.0442 (6)
C11	0.2974 (2)	0.76862 (14)	0.10050 (11)	0.0443 (6)
C12	0.3425 (3)	0.71510 (14)	0.03129 (11)	0.0445 (6)

Table 2. *Selected geometric parameters (Å, °) for (6)*

O1—C1	1.443 (3)	C5—C6	1.522 (3)
O10—C10	1.429 (2)	C6—C7	1.521 (3)
C1—C2	1.467 (3)	C7—C8	1.467 (3)
C1—C12	1.518 (3)	C8—C9	1.189 (3)
C2—C3	1.184 (3)	C9—C10	1.474 (3)

C3—C4	1.469 (3)	C10—C11	1.520 (3)
C4—C5	1.523 (3)	C11—C12	1.530 (3)
O1—C1—C2	110.4 (2)	C8—C7—C6	110.6 (2)
O1—C1—C12	107.9 (2)	C9—C8—C7	174.4 (2)
C2—C1—C12	111.5 (2)	C8—C9—C10	176.2 (2)
C3—C2—C1	177.3 (2)	O10—C10—C9	111.0 (2)
C2—C3—C4	173.8 (2)	O10—C10—C11	111.2 (2)
C3—C4—C5	110.0 (2)	C9—C10—C11	111.2 (2)
C6—C5—C4	113.8 (2)	C10—C11—C12	114.5 (2)
C7—C6—C5	113.6 (2)	C1—C12—C11	113.9 (2)
C1—C2—C3—C4	23 (7)	C7—C8—C9—C10	−8 (6)
C4—C5—C6—C7	147.4 (2)	C10—C11—C12—C1	143.2 (2)

Compound (11)

Crystal data

$C_{14}H_{20}O_2$
$M_r = 220.30$
Monoclinic
$P2_1/n$
$a = 8.115$ (2) Å
$b = 10.4765$ (11) Å
$c = 15.093$ (4) Å
$\beta = 94.59$ (3)°
$V = 1279.1$ (5) Å^3
$Z = 4$
$D_x = 1.144$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7 reflections
$\theta = 17.5$–$21.0°$
$\mu = 0.075$ mm^{-1}
$T = 293$ (2) K
Hexagonal plate
$0.38 \times 0.38 \times 0.38$ mm
Colourless

Data collection

Stoe AED-2 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1666 measured reflections
1666 independent reflections
1537 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 22.49°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 16$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0515$
$wR(F^2) = 0.1094$
$S = 1.215$
1666 reflections
154 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.7847P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.128$ e Å^{-3}
$\Delta\rho_{\min} = -0.149$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0139 (18)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (11)*

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

	x	y	z	$U_{\rm eq}$
O1	0.4214 (2)	0.6269 (2)	0.40731 (13)	0.0499 (6)
O10	0.1487 (2)	0.8711 (2)	0.05671 (11)	0.0447 (5)
C1	0.3392 (3)	0.7353 (2)	0.36387 (15)	0.0355 (6)
C2	0.4475 (3)	0.8486 (2)	0.3738 (2)	0.0380 (6)
C3	0.5410 (3)	0.9363 (3)	0.3774 (2)	0.0416 (7)
C4	0.6566 (3)	1.0438 (2)	0.3751 (2)	0.0494 (7)
C5	0.6912 (3)	1.0766 (2)	0.2800 (2)	0.0470 (7)
C6	0.7863 (3)	0.9737 (3)	0.2344 (2)	0.0494 (7)
C7	0.7359 (3)	0.9630 (3)	0.1355 (2)	0.0601 (8)
C8	0.5685 (3)	0.9092 (3)	0.1196 (2)	0.0476 (7)
C9	0.4337 (3)	0.8642 (2)	0.1132 (2)	0.0398 (6)
C10	0.2711 (3)	0.8002 (2)	0.11050 (15)	0.0341 (6)
C11	0.2161 (3)	0.7905 (2)	0.20503 (15)	0.0344 (6)
C12	0.3177 (3)	0.6974 (2)	0.26574 (15)	0.0364 (6)
C13	0.1753 (3)	0.7566 (3)	0.4037 (2)	0.0505 (7)
C14	0.2819 (3)	0.6710 (2)	0.0651 (2)	0.0471 (7)

Table 4. *Selected geometric parameters (Å, °) for (11)*

O1—C1	1.447 (3)	C5—C6	1.522 (4)
O10—C10	1.438 (3)	C6—C7	1.520 (4)
C1—C2	1.478 (4)	C7—C8	1.473 (4)
C1—C13	1.519 (4)	C8—C9	1.188 (3)
C1—C12	1.530 (3)	C9—C10	1.478 (4)
C2—C3	1.190 (3)	C10—C14	1.523 (3)
C3—C4	1.467 (4)	C10—C11	1.532 (3)
C4—C5	1.525 (4)	C11—C12	1.533 (3)
O1—C1—C2	109.6 (2)	C8—C7—C6	111.1 (2)
O1—C1—C13	108.8 (2)	C9—C8—C7	175.3 (3)
C2—C1—C13	112.0 (2)	C8—C9—C10	175.3 (3)
O1—C1—C12	104.4 (2)	O10—C10—C9	110.9 (2)
C2—C1—C12	109.1 (2)	O10—C10—C14	105.5 (2)
C13—C1—C12	112.7 (2)	C9—C10—C14	109.4 (2)
C3—C2—C1	175.5 (3)	O10—C10—C11	108.7 (2)
C2—C3—C4	175.9 (3)	C9—C10—C11	109.3 (2)
C3—C4—C5	111.2 (2)	C14—C10—C11	113.0 (2)
C6—C5—C4	113.9 (2)	C10—C11—C12	114.6 (2)
C7—C6—C5	113.0 (2)	C1—C12—C11	115.3 (2)
C1—C2—C3—C4	38 (6)	C7—C8—C9—C10	−41 (6)
C4—C5—C6—C7	145.7 (2)	C10—C11—C12—C1	146.8 (2)

For both (6) and (11), hydroxy H atoms were located from difference maps and refined isotropically. Remaining H atoms were modelled as riding atoms $\{U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}[{\rm C(H_2)}]$ or $1.5U_{\rm eq}[{\rm C(H_3)}]\}$.

Data collection: *DIF*4 (Stoe, 1986*a*, 1996*a*) for (6); *STADI*4 (Stoe, 1986*a*, 1996*a*) for (11). Cell refinement: *DIF*4 for (6); *STADI*4 for (11). Data reduction: *REDU*4 (Stoe, 1986*b*, 1996*b*) for (6); *X-RED* (Stoe, 1986*b*, 1996*b*) for (11). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLUTON*/*PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 3073-3075

Tetraprotonated Tetra(2-pyridyl)pyrazine: Pyrazine-2,3,5,6-tetra(2-pyridinium) Tetrachloride Dihydrate

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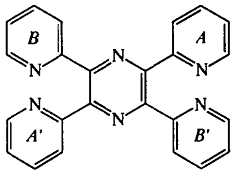
Abstract

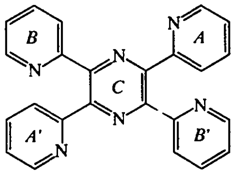
In the tetraprotonated form of tetra(2-pyridyl)pyrazine, $C_{24}H_{20}N_6^{4+}.4Cl^-.2H_2O$, all four pyridine groups are protonated. The structure possesses a crystallographic centre of symmetry. The four pyridinium-H atoms are hydrogen bonded to two Cl^- anions, forming NH···Cl···HN units. In the crystal, two more Cl^- anions and two water molecules of crystallization form a hydrogen-bonded chain that threads its way through the tetra-cations.

Comment

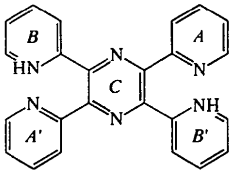
The ligand tetra(2-pyridyl)pyrazine (tppz) was first synthesized by Goodwin & Lions in 1959. The structures of two polymorphs have been reported previously. When recrystallized from $CHCl_3$ (Bock, Vaupel, Näther, Ruppert & Havlas, 1992) or CH_2Cl_2 (Greaves & Stoeckli-Evans, 1992), the monoclinic form tppz-I is normally obtained. A tetragonal form, tppz-II, has also been observed (Greaves & Stoeckli-Evans, 1992). Both forms possess C_i symmetry, the difference being in the orientation of the pyridine rings with respect to the pyrazine ring. A recent paper by Bailey, Grabarczyk, Hanks, Newton & Pennington (1996) describes the solid-state interconversion of polymorphs of tppz. We have been investigating the coordination chemistry of this ligand with first-row transition metals and have synthesized a number of mononuclear and binuclear complexes (Graf, Greaves & Stoeckli-Evans, 1993; Graf & Stoeckli-Evans, 1994; Graf, Stoeckli-Evans, Escuer & Vicente, 1996).



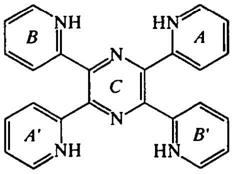
tppz-I



tppz-II



tppz-H2



tppz-H4

Bock and co-workers (Bock, Ruppert *et al.*, 1992) have shown that tppz exhibits proton-sponge properties, and that the reaction of tppz-I with 1*N* HCl leads to the formation of the diprotonated form, tppz-H2 (Bock, Vaupel *et al.*, 1992) in which two opposing pyridine rings (*B* and *B′*) were protonated and hydrogen bonded to two Cl^- anions. The orientation of the pyridine rings with respect to the pyrazine ring remains unchanged. They then studied the exchange of this preferred electron-rich proton-acceptor anion, Cl, for the phenyl-substituted tetraphenylborate. X-ray analysis revealed the formation of a second form of tppz-H2 in which intramolecular hydrogen bonds were formed. The two opposing protonated pyridine rings (*B* and *B′*) are now hydrogen bonded intramolecularly to the adjacent pyridine-N atoms of rings *A′* and *A*, respectively.

The reaction of tppz-I with 2*N* HCl gave a white powder. When recrystallized from ethanol, very pale blue transparent crystals were produced but this material proved to be amorphous (no diffraction spots were observed). When recrystallized from water, large clear transparent blocks were formed. The structure analysis revealed a tetraprotonated form, tppz-H4 (Fig. 1). All four pyridine N atoms are protonated and the rings are rotated 180° from their original positions to hydrogen bond to two Cl^- anions (Cl1) situated above and below the plane of the pyrazine-N atoms (Fig. 2). Details of the hydrogen bonding are given in Table 3. The orientation of the pyridinium rings with respect to the central pyrazine ring is very different from that observed in the diprotonated form tppz-H2.2Cl (Bock, Vaupel *et al.*, 1992). In tppz-H2.2Cl, pyridine ring *A* has moved into the plane of the pyrazine ring and the dihedral angle between rings *A* and *C* is 16.6° compared with

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