organic compounds

The 1:1 adduct of 5-methylbenzene-1,3-diol (orcin) and 1,4-diaza-bicyclo[2.2.2]octane

Zhi-Min Jin,[a]* Chen-Shui Lin,[a] Hai-Bin Wang,[b] Mao-Lin Hu,[c] Liang Shen[d] and Liang-Ren Huang[e]

[a]College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China, [b]College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China, [c]Department of Chemistry, Wenzhou Normal College, Wenzhou, Zhejiang 325003, People's Republic of China, [d]Department of Chemistry, Hangzhou Teachers' College, Hangzhou, People's Republic of China, and [e]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China
Correspondence e-mail: zimichem@sina.com

In the title adduct, $C_6H_{12}N_2·C_7H_8O_2$, the orcin and 1,4-diazabicyclo[2.2.2]octane moieties are held together by O—H···N hydrogen bonds. One-dimensional chiral hydrogen-bonded chains are formed along the *b* axis. Neighbouring chains are held together principally by van der Waals interactions and are interrelated by translation, resulting in a chiral layer.

Comment

Chiral crystals can be formed through self-assembly even from achiral molecules (Jacques *et al.*, 1981). It is possible to synthesize substances asymmetrically from such crystals by solid-state reactions (Elgavi *et al.*, 1973; Green *et al.*, 1979; Sakamoto, 1997). Furthermore, chiral crystallization is relevant to the origin of chiral compounds in nature (Addadi & Lahav, 1979). The design of chiral crystalline complexes from different achiral molecules (Koshima *et al.*, 1996, 1997, 1998, 1999; Koshima & Honke, 1999) is an active field. It has been
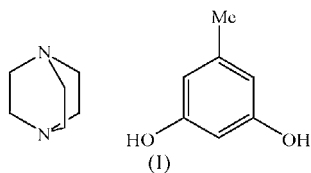
reported previously that a resorcinol–urea adduct crystallizes in chiral space group $P2_12_12_1$ (Pickering & Small, 1982). In our case, the chiral crystal of the title adduct, (I), was synthesized from two achiral compounds, namely 5-methylresorcinol (orcin) and 1,4-diazabicyclo[2.2.2]octane (DABCO). The structure and chirality of (I) are discussed here.

There are two crystallographically independent molecules each of DABCO and orcin in the unit cell of (I) (Fig. 1). In the structure of (I), the orcin and DABCO moieties are linked by O1—H1···N1, O2—H2···N3, O3—H3···N4[i] and O4—H4···N2[ii] hydrogen bonds (Fig. 2 and Table 2; symmetry codes as in Table 2).

The resorcinol hydroxy group may be arranged in one of the conformations depicted in the scheme below. In (I), the orcin hydroxy groups assume the first conformation, which is in contrast with the third conformation, observed in the resorcinol–urea (1/1) adduct (Pickering & Small, 1982), and the second conformation, observed in the resorcinol–isonicotinamide (1/2) adduct (Vishweshwar *et al.*, 2003). The orcin molecules are pseudo-C_2 symmetrically related.

Conformation 1   Conformation 2   Conformation 3
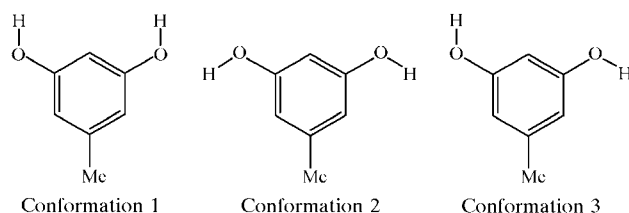
As shown in Fig. 2, one-dimensional chiral hydrogen-bonded chains are formed along the *b* axis, with the screw-pitch equal to the length of the *b* axis. The chain can be described in graph-set notation (Etter, 1990; Grell *et al.*, 2000) as $C_4^4(22)$. Neighbouring chains in the (001) plane are associated with each other principally by van der Waals interactions and are interrelated by translation, thus resulting in a chiral layer. There are four kinds of chiral layer in the crystal of (I). C—H···O hydrogen bonds (Table 2) play an important role in stabilizing the chiral structure. Neighbouring chiral layers are related to each other *via* C5—H5B···O2[iii], C6—H6A···O3[iii] and C10—H10A···O1[iv] hydrogen bonds (symmetry codes as in Table 2).

There are four C—H···π interactions in the crystal, namely C8—H8A[iii]···π(C13–C18) (3.30 Å), C7—H7B[iii]···π(C13–C18) (3.36 Å), C1—H1B($x + \frac{1}{2}$, $\frac{3}{2} - y$, $2 - z$)···π(C20–C25) (3.37 Å) and C2—H2A($x + \frac{1}{2}$, $\frac{3}{2} - y$, $2 - z$)···π(C20–C25)
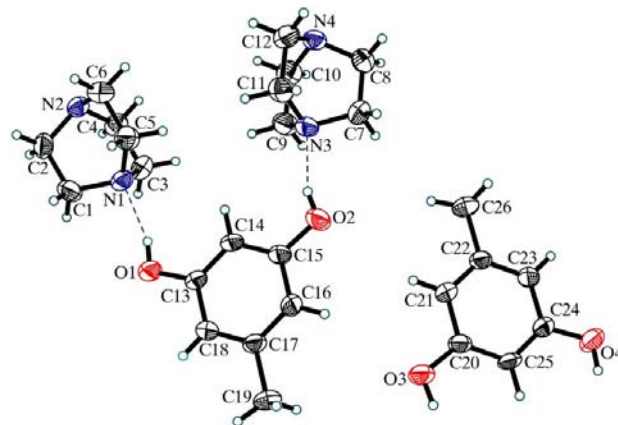

Figure 1
The orcin and DABCO moieties of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.
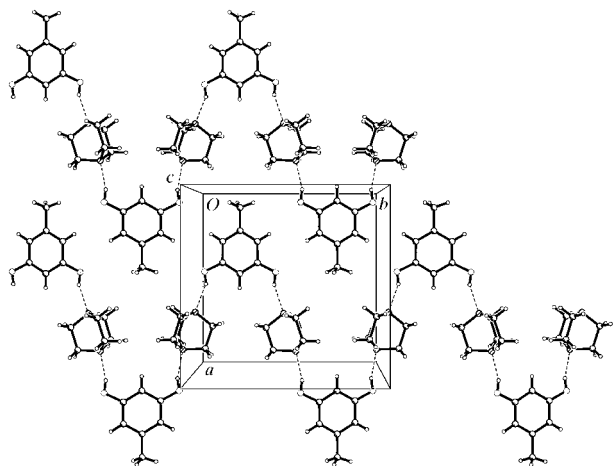
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Figure 2
Part of the crystal structure of (I), showing the infinite chiral chains along the *b* axis. Hydrogen bonds are indicated by dashed lines.

(3.30 Å), where the values in parentheses indicate the distance between the H atom and the centroid of the phenyl ring (see Table 2 for symmetry code). As a result of the balance of C—H···O and C—H···π interactions, the two orcin molecules that are bridged by a DABCO molecule are fixed at a dihedral angle of 30.8 (3)°.

DABCO may assume one of four conformations, namely ordered and non-distorted, ordered and distorted, disordered and non-distorted, or disordered and distorted (Nimmo & Lucas, 1976). The disordered conformations are frequently observed, such as in DABCO–biphenol (1/1) (Ferguson *et al.*, 1998), DABCO–perchloric acid (1/1) (Katrusiak, 2000) and DABCO–maleic acid (1/2) (Sun & Jin, 2002). In (I), both of the DABCO molecules are ordered and they are almost non-distorted, as indicated by N—C—C—N torsion angles with mean values of 1.2 (4) and 0.9 (4)°, respectively, for atoms N1/N2 and N3/N4.

Experimental

Equimolar quantities of DABCO and orcin were mixed and dissolved in sufficient water by heating to a temperature where a clear solution resulted. Single crystals of (I) were formed by allowing the resulting solution to stand overnight at 293 K.

Crystal data

$C_6H_{12}N_2 \cdot C_7H_8O_2$
$M_r = 236.31$
Orthorhombic, $P2_12_12_1$
$a = 12.2569$ (6) Å
$b = 12.5985$ (6) Å
$c = 16.8506$ (9) Å
$V = 2602.0$ (2) Å^3
$Z = 8$
$D_x = 1.206$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 346 reflections
$\theta = 2.4$–23.0°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
$0.46 \times 0.42 \times 0.38$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
13 862 measured reflections
2645 independent reflections
2129 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 25.2°$
$h = -11 \rightarrow 14$
$k = -15 \rightarrow 14$
$l = -20 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.157$
$S = 1.06$
2645 reflections
307 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1095P)^2 + 0.08P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.456 (4)	O1—C13	1.357 (3)
N1—C1	1.459 (4)	O2—C15	1.364 (3)
N1—C3	1.478 (4)	C13—C14	1.390 (4)
N2—C2	1.462 (4)	C13—C18	1.396 (3)
N2—C6	1.473 (4)	C14—C15	1.384 (4)
N2—C4	1.479 (4)	C15—C16	1.390 (3)
C1—C2	1.540 (4)	C16—C17	1.386 (4)
C3—C4	1.531 (4)	C17—C18	1.379 (4)
C5—C6	1.540 (4)	C17—C19	1.515 (4)
N1—C1—C2—N2	1.2 (4)	N3—C7—C8—N4	0.3 (4)
N1—C3—C4—N2	−0.5 (4)	N3—C9—C10—N4	2.3 (4)
N1—C5—C6—N2	2.0 (4)	N3—C11—C12—N4	−0.2 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.91	2.704 (3)	162
O2—H2···N3	0.82	1.92	2.706 (3)	161
O3—H3···N4^i	0.82	1.93	2.697 (3)	155
O4—H4···N2^{ii}	0.82	1.95	2.710 (3)	153
C5—H5B···O2^{iii}	0.97	2.63	3.576 (4)	164
C6—H6A···O3^{iii}	0.97	2.69	3.417 (4)	132
C10—H10A···O1^{iv}	0.97	2.62	3.369 (4)	134

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 + x, y - 1, z$; (iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$.

All H atoms were placed in calculated positions and allowed to ride on their parent atoms at distances of 0.82–0.97 Å, with isotropic displacement parameters 1.2–1.5 times U_{eq} of the parent atoms. Because of the lack of atoms heavier than oxygen and the short measuring wavelength of Mo radiation, no useful absolute structure parameter could be refined.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1016). Services for accessing these data are described at the back of the journal.

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