

Health for a grant in support of the purchase of a Bruker CCD SMART diffractometer (3S06GM08102-25S1/M1HREV).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1124). Services for accessing these data are described at the back of the journal.

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o-Phenylenediamine Pyrocatechol Hemihydrate Complex

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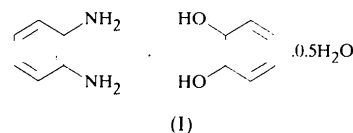
Abstract

A well defined supramolecular structure, C₆H₈N₂·C₆H₆O₂·0.5H₂O, is generated by molecular recognition between pyrocatechol and *o*-phenylenediamine in the presence of water. They spontaneously self assemble

through a unique network of hydrogen bonds around a twofold axis.

Comment

The development of solid state structures which are able to exhibit new physical and chemical properties (Hanesian *et al.*, 1994) is the basis of crystal engineering. The self-assembling complementarity of diamine/diol motifs provides convincing evidence that the engineering of highly organized supramolecular structures based on molecular recognition can now be extended to include 'weak' hydrogen-bonding interactions. The X-ray structure analysis of the title compound, (I), supports this viewpoint.



The asymmetric unit consists of one molecule each of *o*-phenylenediamine, pyrocatechol and water. In the crystal, the water molecules lie on the twofold axis and they are linked to the pyrocatechol molecules through an O2—H···O3ⁱⁱⁱ hydrogen bond (Table 3 and Fig. 2). The diamine molecules are connected to the water molecules by O3—H···N2^{iv} hydrogen bonds between O3 and N2^{iv}. The diol and diamine molecules themselves are involved in N—H···O hydrogen bonds (N2···O1 and N1···O2¹). This hydrogen-bonded network forms a supramolecular structure around the twofold axis. The neighbouring molecular assemblies are interlinked by O1—H1O1···N1ⁱⁱ hydrogen bonds. Due to the hydrogen bonding, both the N atoms and water O atoms exhibit full tetra-coordination. The hydrogen-bonded assembly in this structure is significantly different from the supramolecular helicate structures observed for the 1:1 complex of *trans*-1,2-diaminocyclohexane and (1*S*,2*S*)-*trans*-1,2-cyclohexanediol (Hanesian *et al.*, 1994), which may be due to the presence of water molecules. The C—N, C—O and C—C lengths observed in this structure agree with the reported values (Allen *et al.*, 1987). The dihedral angle between the mean planes through the diamine and diol moieties is 25.87 (3)°. The

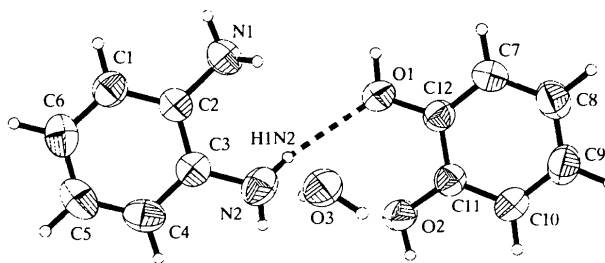


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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diamine and diol molecules translated one unit cell along the *b* direction are stacked stepwise without any π - π stacking interactions with minimum short contacts for C1...C4 [3.662 (2) Å] and C7...C10 [3.543 (2) Å].

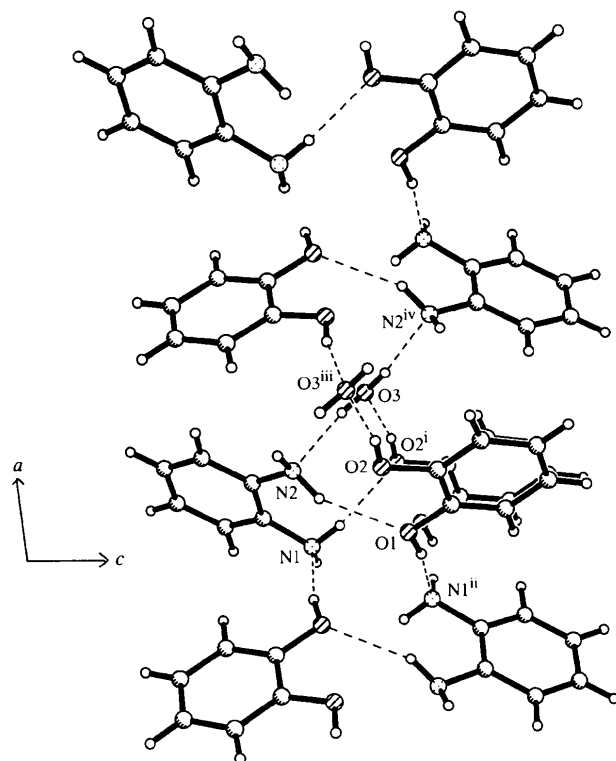


Fig. 2. Hydrogen-bonding network viewed down the *b* axis.

Experimental

Single crystals were grown by slow evaporation of a 1:1 mixture of *o*-phenylenediamine and pyrocatechol in a chloroform and acetone solution.

Crystal data

C₆H₈N₂·C₆H₆O₂·0.5H₂O

M_r = 227.26

Monoclinic

*P*2/*c*

a = 9.0498 (2) Å

b = 5.2275 (1) Å

c = 25.0771 (2) Å

β = 97.71°

V = 1175.62 (4) Å³

Z = 4

D_x = 1.284 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 4441 reflections

θ = 1.31–33.1°

μ = 0.091 mm⁻¹

T = 293 (2) K

Thin plate

0.68 × 0.44 × 0.08 mm

Colourless

Data collection

Siemens SMART diffractometer with CCD area detector

ω scans

2016 reflections with

$I > 2\sigma(I)$

R_{int} = 0.024

θ_{\max} = 27.50°

Absorption correction: none

7110 measured reflections

2692 independent reflections

h = -11 → 11

k = 0 → 6

l = 0 → 32

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.041

wR(*F*²) = 0.107

S = 1.057

2692 reflections

211 parameters

All H-atom parameters refined

w = 1/[σ²(*F_o*²) + (0.0391*P*)² + 0.1889*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.158 e Å⁻³

Δρ_{min} = -0.113 e Å⁻³

Extinction correction:

SHELXTL

Extinction coefficient:

0.011 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O1	0.14028 (13)	0.3317 (3)	0.79384 (4)	0.0751 (4)
O2	0.31302 (14)	0.7177 (2)	0.77498 (4)	0.0699 (4)
O3	1/2	0.0847 (3)	3/4	0.0541 (4)
N1	0.0534 (2)	-0.0708 (3)	0.68937 (5)	0.0558 (3)
N2	0.2664 (2)	0.3174 (3)	0.68079 (6)	0.0621 (4)
C1	0.0724 (2)	-0.1942 (3)	0.59639 (6)	0.0556 (4)
C2	0.11620 (13)	-0.0389 (3)	0.64043 (5)	0.0445 (3)
C3	0.21536 (14)	0.1617 (3)	0.63568 (5)	0.0477 (3)
C4	0.2681 (2)	0.1981 (3)	0.58642 (7)	0.0621 (4)
C5	0.2229 (2)	0.0411 (4)	0.54290 (7)	0.0682 (5)
C6	0.1247 (2)	-0.1550 (4)	0.54779 (6)	0.0650 (4)
C7	0.2357 (2)	0.3374 (3)	0.88909 (6)	0.0540 (4)
C8	0.3270 (2)	0.4523 (4)	0.93123 (6)	0.0633 (4)
C9	0.4149 (2)	0.6565 (4)	0.92126 (6)	0.0639 (4)
C10	0.4133 (2)	0.7475 (3)	0.86931 (6)	0.0544 (4)
C11	0.32189 (14)	0.6346 (3)	0.82708 (5)	0.0473 (3)
C12	0.23165 (14)	0.4281 (3)	0.83721 (5)	0.0478 (3)

Table 2. Selected bond lengths (Å)

O1—C12	1.371 (2)	N1—C2	1.430 (2)
O2—C11	1.369 (2)	N2—C3	1.419 (2)

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ... <i>A</i>	<i>D</i> — <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
N2—H1N2...O1	0.93 (3)	2.33 (2)	3.196 (2)	154 (2)
N1—H2N1...O2 ⁱ	0.88 (2)	2.36 (2)	3.162 (2)	150 (2)
O1—H1O1...N1 ⁱⁱⁱ	0.92 (2)	1.90 (2)	2.806 (2)	169 (2)
O2—H1O2...O3 ⁱⁱⁱ	0.90 (2)	1.80 (2)	2.687 (2)	168 (2)
O3—H1O3...N2 ^{iv}	0.89 (2)	1.95 (2)	2.824 (2)	164 (2)

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

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω . The crystal-to-detector distance was 4 cm and the detector swing angle was -35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analysing the duplicate reflections. It was found to be negligible.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically.

Data collection: *SMART* (Siemens, 1996a). Cell refinement: *SAINT* (Siemens, 1996b). Data reduction: *SAINT*. Program(s)

used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995).

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Fibleucin from *Fibraurea chloroleuca* Miers

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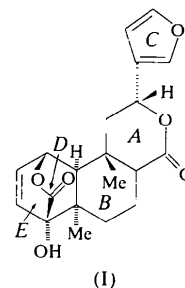
Abstract

In the title compound, 9-(3-furyl)-1,4,4a,5,9,10,10a,10b-octahydro-4-hydroxy-4a,10a-dimethyl-1,4-etheno-3*H*,7*H*-benzo[1,2-*c*:3,4-*c'*]dipyran-3,7-dione, C₂₀H₂₀O₆, the pyran ring adopts a conformation intermediate between sofa and half-chair. All other six-membered rings are in the boat conformation. The furan ring is planar and is

equatorially attached. The crystal structure is stabilized by O—H···O and C—H···O intermolecular hydrogen bonds.

Comment

The title compound, (I), was first isolated from the plant *Fibraurea chloroleuca* Miers and identified by Ito & Furukawa (1969). It had been located in a crude methanol extract a few years earlier and it was found to possess antitumour and antifungal activity (Nakanishi *et al.*, 1965). The present X-ray structure determination was carried out in order to elucidate the molecular conformation.



Most of the bond lengths and angles in the structure agree with those observed in the epoxy derivative of this compound, (–)-fibrarin (Dampawan *et al.*, 1986). The fused rings, A and B, and the six-membered rings, D and E, formed by the lactone bridge, all adopt the boat conformation. Ring C is in a conformation which is intermediate between half-chair and sofa,

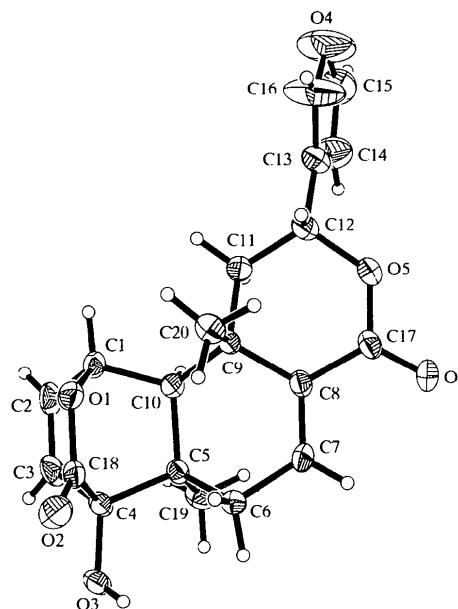


Fig. 1. The structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

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