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2,5-Diphenyl-3,6-dihydroxy-1,4-benzoquinone (polyporic acid)

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Key indicators

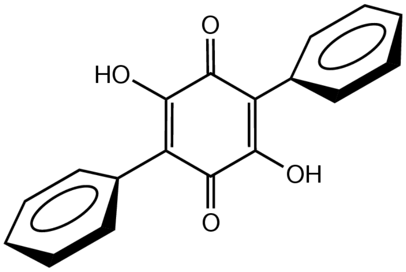
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.110
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{18}H_{12}O_4$, is a naturally occurring product found in several genera of fungi and lichens. Its structure is composed of a 1,4-benzoquinone moiety 2,5-disubstituted with phenyl rings and 3,6-disubstituted with hydroxyl groups. The angle between the planes of the phenyl rings and that of the benzoquinone is 45.24 (8)°. Intermolecular hydrogen bonding produces infinite molecular chains. The molecule has crystallographic inversion symmetry.

Comment

Polyporic acid, (I), is currently the only known benzoquinone naturally occurring in lichens (Huneck & Yoshimura, 1996). While the sole published paper on the chemical identity of synthesized polyporic acid states that the MS and ^{1}H NMR data for (I) are in agreement with the expected structure, no mass spectral data or numerical proton-shift values are actually provided in the publication (Dallacker & Ditgens, 1975). This study was undertaken to provide crystallographic data affording the definitive structural characterization of polyporic acid which, for almost 50 years, has been known in the scientific literature without any substantive information about its absolute structure.



(I)

The molecule, shown in Fig. 1, is composed of a benzoquinone moiety 2,5-disubstituted with phenyl rings and 3,6-disubstituted with hydroxyl groups. A center of symmetry, located at the center of the benzoquinone moiety, relates the two halves of the molecule. Only minor deviations from expected geometry were noted. There is minor distortion of the bond angles involving O1 and O2 as shown in Table 1, perhaps a result of the hydrogen bonding. The phenyl rings are rotated 45.24 (8)° with respect to the central ring, as would be expected, and all ring systems are essentially flat. A hydrogen bond involving the hydroxyl group and the carbonyl oxygen results in the linking of individual molecules into infinite one-dimensional chains which propagate in the [100] direction as shown in Fig. 2; Table 2 gives the hydrogen-bond

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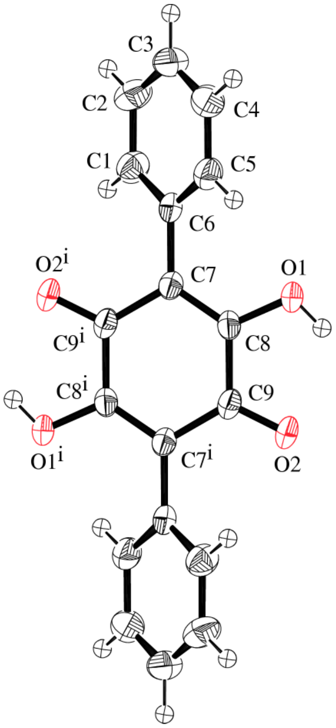

Figure 1
The molecular structure and atom-numbering scheme for (I) with displacement ellipsoids at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

geometry. The molecular packing is shown in Fig. 3 with the molecular chains normal to the plane of the paper; nine individual chains can be seen. The packing produces double-layers of phenyl rings which sandwich single-layers of benzoquinone rings. It is conceivable, given the packing arrangement and high electron density of the aromatic rings, that polyporic acid might be a strong conductor in the solid state.

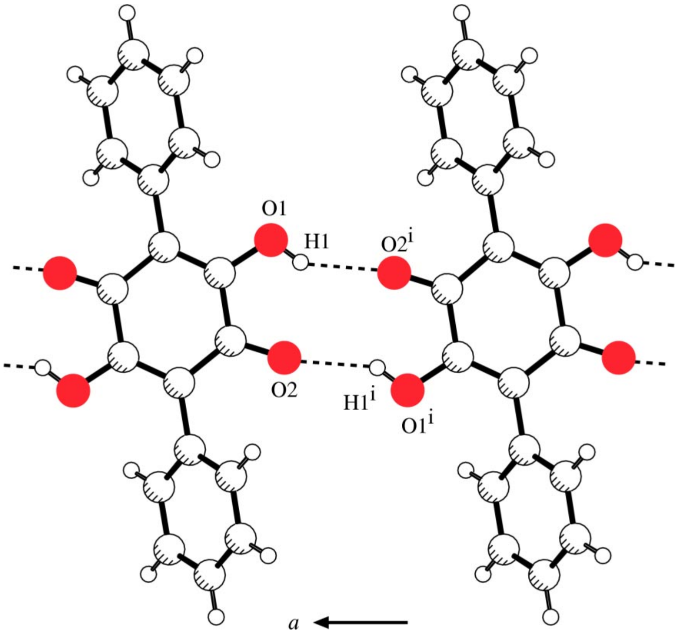

Figure 2
The hydrogen bonding in (I) and the resultant infinite molecular chains propagating in the [100] direction.

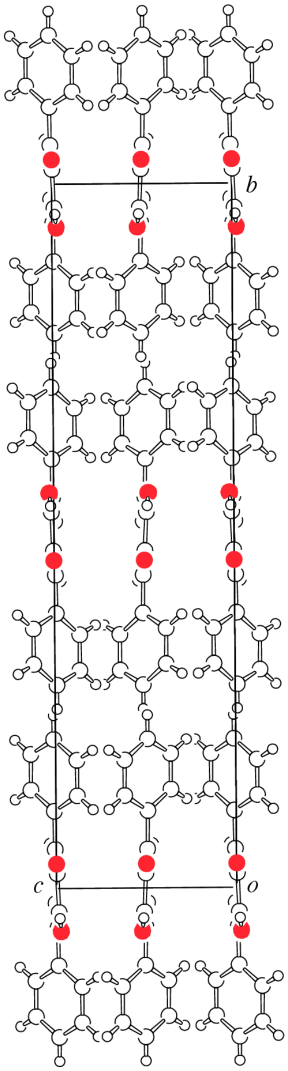

Figure 3
The molecular packing in (I) as viewed down [100].

Experimental

Polyporic acid occurs naturally in several genera of higher fungi (Basidiomycetes) including *Polyporus* and *Fomes* (Murray, 1952; Huneck & Yoshimura, 1996; Huneck, 2001). In addition, it occurs in the tropical lichen species *Pseudocyphellaria coronata*. Polyporic acid was isolated as follows: 100 g of dried *P. coronata* (collected in Waikato, New Zealand in July 2000) was continuously extracted with one litre of MeOH overnight. The red–brown extract was concentrated *in vacuo* to give a red solid. The red solid (12 g) was purified by column chromatography on Sephadex L-50 (eluent: 9:1 CH_2Cl_2–MeOH) to give fractions containing polyporic acid totaling 200 mg. This crude material was further purified by preparative TLC (eluent: 9:1 CH_2Cl_2–MeOH) to give 80 mg of pure polyporic acid (0.08% yield dry weight). This material was recrystallized from hot acetone to give purple prisms, m.p. 579–581 K, used in the X-ray study. The structure of polyporic acid so determined is in agreement with that suggested by its ^{1}H NMR (300 MHz) and ^{13}C NMR (125 MHz) spectra, as well as EIMS low-resolution mass spectra. The EI mass spectrum shows a sharp peak at 292 mass units corresponding to the molecular weight for polyporic acid, while the ^{1}H NMR spectrum shows the presence of five aromatic protons, indicative of the two equivalent phenyl side-chains determined by the crystallographic study.

Crystal data

$C_{18}H_{12}O_4$
$M_r = 292.28$
Orthorhombic, *Pbca*
$a = 7.323$ (3) Å
$b = 26.980$ (4) Å
$c = 6.897$ (4) Å
$V = 1362.7$ (9) Å^3
$Z = 4$
$D_x = 1.425$ Mg m^{-3}

Mo Kα radiation
Cell parameters from 25 reflections
$\theta = 20.8$–24.3°
$\mu = 0.10$ mm^{-1}
$T = 296$ K
Prism, dark red
0.49 × 0.39 × 0.33 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
1201 measured reflections
1201 independent reflections
796 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0^\circ$

$h = 0 \rightarrow 8$
$k = 0 \rightarrow 32$
$l = 0 \rightarrow 8$
3 standard reflections
every 199 reflections
intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.110$
$S = 1.02$
1201 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.1614P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C8	1.332 (2)	C7—C8	1.349 (2)
O2—C9	1.223 (2)	C7—C9$^{\rm i}$	1.458 (2)
C6—C7	1.486 (2)	C8—C9	1.507 (3)
O1—C8—C7	121.74 (16)	C8—C7—C9$^{\rm i}$	115.66 (16)
O1—C8—C9	114.36 (15)	C7—C8—C9	123.88 (16)
O2—C9—C8	116.35 (16)	C8—C7—C6	124.10 (15)
O2—C9—C7$^{\rm i}$	123.22 (17)	C9$^{\rm i}$—C7—C6	120.24 (15)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O2$^{\rm i}$	0.82	2.06	2.796 (2)	149

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

The location of the hydroxyl H atom was determined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997). All H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR*92 (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*; software used to prepare material for publication: *TEXSAN, SHELXL*97 and *PLATON* (Spek, 2000).

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