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CRYSTAL STRUCTURE OF A 1:2 MOLECULAR COMPLEX OF 2,5-BIS(2,4-DIMETHYLPHENYL)HYDROQUINONE AND ETHANOL

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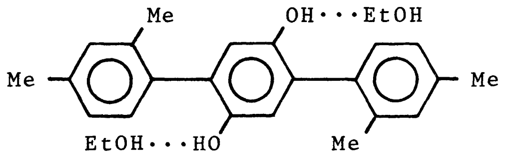
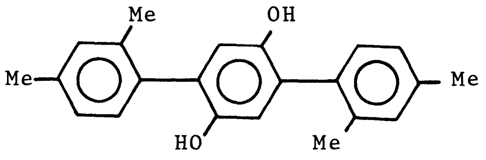
A centrosymmetric 1:2 hydrogen-bonded adduct of 2,5-bis(2,4-dimethylphenyl)hydroquinone and ethanol has been determined by X-ray crystallography. Its layer-type architecture is conducive to the replacement of ethanol by various alcohols to yield a series of isostructural molecular complexes.

As a sequel to our recent studies on molecular inclusion involving acetylenic diols,[1,2] it was found that 2,5-diarylhydroquinones form 1:2 crystalline complexes with ethanol and other alcohols. We now report our X-ray analysis of the title complex (**1**), which is of interest in relation to ethanol extraction from its aqueous solution obtained by fermentation of biomass.

Complex **1** was prepared from slow crystallization of 2,5-bis(2,4-dimethylphenyl)hydroquinone (**2**)[3] in ethanol. The plate-shaped crystals rapidly turn opaque upon exposure to air and are easily deformed by cutting with a blade. A single crystal of dimensions 0.44 x 0.42 x 0.26 mm^3 was fished out of the mother liquor and quickly sealed in a 0.5 mm diameter Lindemann glass capillary partly filled with ethanol at its tip portion.



1



2

Crystal data of $C_{22}H_{22}O_2 \cdot 2C_2H_6O$ (1) are as follows: monoclinic, a = 7.410(2), b = 13.696(6), c = 12.288(5) Å, β = 101.85(2)°, V = 1220.5(7) $Å^3$, D_m (flotation in aqueous KI) = 1.11(1) g cm^{-3}, Z = 2, D_c = 1.117 g cm^{-3}, systematic absences: $h0\ell$ with h odd, $0k0$ with k odd, space group $P2_1/a$ (No. 14), Mo-$K\alpha$ radiation (graphite-monochromatized), λ = 0.71069 Å, μ = 0.69 cm^{-1}.

Intensities ($2\theta_{max}$ = 40°) were measured on a Nicolet R3m diffractometer system using the ω-2θ scan technique (2.02 to 8.37° min^{-1}), with a scan range from 1° below $K\alpha_1$ to 1° above $K\alpha_2$ and background counts taken for half the scan time at each end. The crystal remained stable throughout the diffraction experiment, as three standard reflections monitored every 50 data measurements showed only random deviations within 1% of their mean values. The intensities (1017 unique reflections) were processed with the learnt-profile procedure,[4] and corrected for Lorentz and polarization factors but not for absorption.

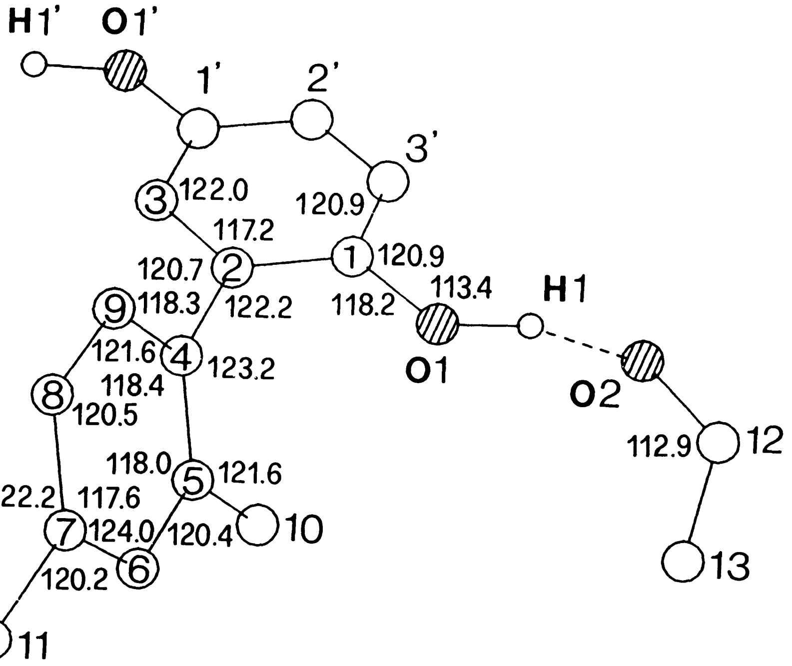


Fig. 1. Atom labelling in the asymmetric unit of complex 1 and selected bond angles (standard deviations about 0.4°).

Space group considerations require that 2 possesses a center of symmetry.5) Structure solution by the direct method based on negative quartets6) revealed the positions of all non-hydrogen atoms in the asymmetric unit (Fig. 1). The C atoms comprising the 2,4-dimethylphenyl group and the two O atoms were varied anisotropically, the remaining C atoms isotropically, and all H atoms (which showed up in a difference map) were included with assigned isotropic thermal parameters in the calculation of structure factors. Convergence for 878 observed data $[|F_o|>3\sigma(|F_o|)]$ and 120 variables was reached at $R \equiv \Sigma||F_o|-|F_c||/\Sigma|F_o|$ = 0.066, with residual extrema in the final difference map lying between 0.28 and -0.23 $e\text{Å}^{-3}$.7)

Figure 2 shows a stereoscopic view of the molecular packing. Diarylhydroquinone 2 occupies a centrosymmetric site and forms donor hydrogen bonds [O(1)-H···O(2) = 2.617(6) Å] to a pair of ethanol molecules. Neighboring 2·2EtOH aggregates related by the *a* glide are further linked by weaker hydrogen bonds [O(1)··· H-O(2)" = 2.751(6) Å] to yield infinite zigzag chains of hydroxyl groups running parallel to *a*. The crystal structure of 1 is thus characterized by a stacking of hydrogen-bonded layers normal to *c*, with only weak van der Waals interaction between layers related by the 2_1 axis parallel to *b*. All inter-layer contacts between C(12) and C(13) of the ethanol molecule and other C atoms exceed 3.75 Å.

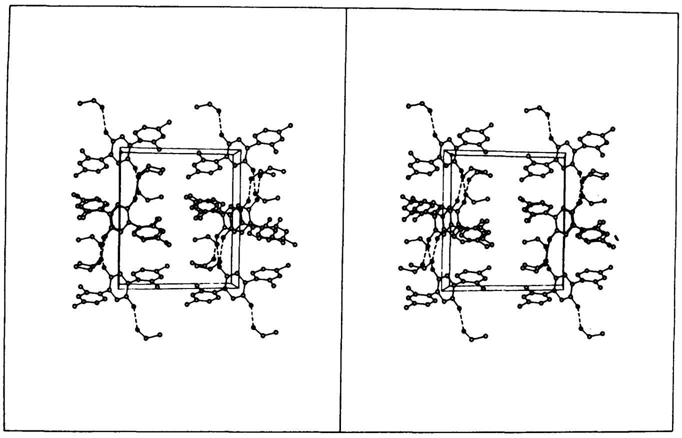


Fig. 2. Stereodrawing of the molecular packing in 1. Hydrogen bonds in the 2·2EtOH aggregates are indicated by dotted lines, and those between aggregates have been omitted for clarity. The origin of the unit cell lies at the upper left corner, with *a* towards the reader, *b* downwards, and *c* from left to right.

The existence of a series of crystalline complexes isostructural with **1** can be rationalized since ethanol may be replaced by another alcohol, but not water, with no alteration in the pattern of molecular packing and hydrogen bonding.

The relative orientation of the phenyl and hydroquinone rings of **2** is described by the torsion angle C(1)-C(2)-C(4)-C(9) = 117.5(5)°; the C-C-O angles at C(1) (Fig. 1) exhibit the well established inequality due to the steric influence of the phenolic H atom.8) Similar repulsion between pairs of *o*-substituents are manifested in the exo-ring bond angles at C(2), C(4), and C(5).

References

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5) The molecular center of **2** is located at (0, 1/2, 0), namely Wyckoff position 2(*c*); the other half of the centrosymmetric molecule can be generated from the atoms in the asymmetric unit by the symmetry transformation (-*x*, 1-*y*, -*z*).

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7) All computations were performed with the SHELXTL program package. Analytic expressions of atomic scattering factors with anomalous dispersion correactions were taken from "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. 4, pp. 99, 149, The weighting scheme employed for the blocked-cascade least-squares refinement and analysis of variance was $w = [\sigma^2(|F_o|) + 0.0006|F_o|^2]^{-1}$. Tables of atomic coordinates and bond distances are available on request from the Director of the Cambridge Crystallographic Data Centre.

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