

Design of a New Host Compound, 2,2-Di(*p*-hydroxyphenyl)propane,
and Crystal Structure of Its 1:1 Complex with Methylhydrazine

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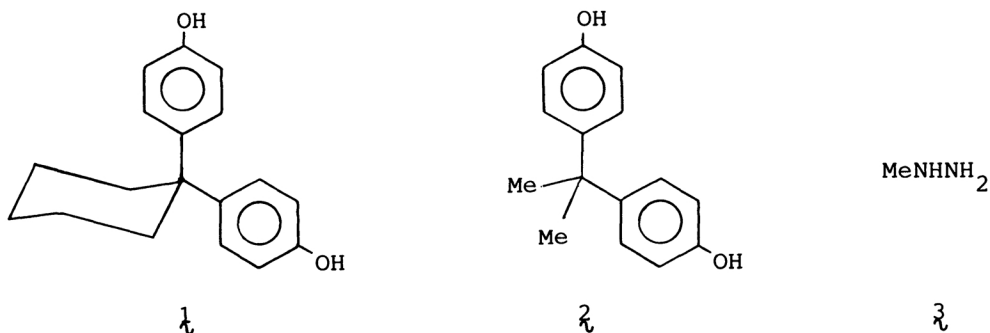
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A new host compound, 2,2-di(*p*-hydroxyphenyl)propane, which exhibits high inclusion ability towards phenols, amines, and hydrazines, has been designed. The crystal structure of its 1:1 complex with methylhydrazine comprises centrosymmetric cyclic dimeric units consolidated by O-H...N hydrogen bonding.

Recently we reported that 1,1-di(*p*-hydroxyphenyl)cyclohexane (**1**) is a good host compound for the efficient separation of cyclohexanol and cyclohexanone, since it forms a 1:1 complex with cyclohexanol more easily than cyclohexanone.¹⁾ The crystal structures of both complexes were also reported.¹⁾ In order to gauge the role of the cyclohexane ring of **1** in the above complexation, it was replaced with two methyl groups in our design of the new host 2,2-di(*p*-hydroxyphenyl)propane (**2**). Compound **2** shows high inclusion ability towards phenols, amines, and hydrazines (Table 1), as well as high selectivity for isomers of these guest species. For example, when a solution of **2** (2.28 g, 10 mmol) and a 1:1 mixture of *m*- and *p*-cresol (2.16 g, 20 mmol) in benzene (10 ml) was kept at room temperature for 10 h, a 1:1 complex of **2** with *p*-cresol (2.79 g) was



obtained, which upon heating in vacuo after recrystallization from benzene gave p-cresol (0.57 g, 53%). This result is in contrast with that of λ , which includes m-cresol selectively.

Table 1. Inclusion Complexes of λ with Phenols, Amines, and Hydrazines

Guest	Complex	Host/Guest Ratio	Mp $\theta_m/^\circ\text{C}$	Guest	Complex	Host/Guest Ratio	Mp $\theta_m/^\circ\text{C}$
Phenol	needle	1:1 ^{a)}	94-95	NH ₃	needle	--- ^{b)}	not clear
<u>o</u> -Cresol	---	---	---	MeNH ₂	needle	1:1 ^{c)}	not clear
<u>m</u> -Cresol	needle	1:1 ^{a)}	91-92	EtNH ₂	prism	1:1 ^{c)}	84-86
<u>p</u> -Cresol	prism	1:1 ^{a)}	110-112	Me ₂ NH	---	---	---
Resorcinol	---	---	---	NH ₂ NH ₂	prism	1:1 ^{c)}	86-90
Hydroquinone	prism	1:1 ^{a)}	135	MeNHNH ₂	prism	1:1 ^{c)}	105-108

a) The ratio was determined by Thermal Gravity measurement. b) The complex was too labile for measurement. c) The ratio was determined from NMR data.

The most interesting and important finding in regard to λ is its high inclusion ability towards hydrazines. Extraction of hydrazines from aqueous solution, which is a difficult problem in the chemical industry, can be performed efficiently with the use of λ . For example, when a mixture of λ (2.0 g, 8.77 mmol) and 50% aqueous methylhydrazine (λ) (0.81 g, 8.77 mmol) was kept at room temperature for 12 h, a 1:1 complex (λ) of λ with λ was formed as colorless hygroscopic prisms (2.21 g, 92%), which upon heating at 150 °C gave anhydrous λ (0.20 g, 49%). In a similar way, a 1:1 complex of λ with hydrazine was obtained in 96% yield from λ and 30% hydrazine. Extraction of amines from aqueous solution can also be easily achieved.

The nature of the complex (λ) has been elucidated by means of X-ray crystallography. A selected crystal of dimensions 0.48 x 0.46 x 0.40 mm³ was sealed inside a 0.5 mm Lindemann glass capillary, and intensity data were collected on Nicolet R3m diffractometer at 22 °C using Mo-K α radiation ($\theta = 0.71069$ Å) as described previously.²⁾

Crystal data: λ , C₁₆H₂₂N₂O₂, FW = 274.36, monoclinic, space group P2₁/a, $a = 11.398(2)$, $b = 9.352(1)$, $c = 14.538(5)$ Å, $\beta = 97.12(2)^\circ$, $V = 1567.3(6)$ Å³, $Z = 4$, $F(000) = 592$, D_m (flotation in CCl₄/hexane) = 1.15, $D_c = 1.163$ g cm⁻³, $\mu = 0.72$ cm⁻¹, $2\theta_{\text{max}} = 50^\circ$, 2289 unique reflections. Absorption correction ($\mu_r = 0.016$, transmission factors 0.936 to 0.943) was applied by fitting a pseudo-ellipsoid to the azimuthal scan data of 20 strong reflections over a range of 2θ -values.³⁾ The structure was solved by direct phase determination guided by negative quartets.⁴⁾ All non-hydrogen atoms in the asymmetric unit (Fig. 1) were varied anisotropically. The methyl and phenyl ring H atoms were generated geometrically, and all others could be located in a difference map except the one bonded to N1. All these H atoms were included in structure factor

calculations with assigned isotropic temperature factors. Refinement of 1572 observed data [$|F_o| > 3\sigma(|F_o|)$] on 190 parameters using the weighting scheme $w = [\sigma^2(|F_o|) + 0.001|F_o|^2]^{-1}$ converged to $R = 0.071$. All computations were performed on a Data General Nova 3 minicomputer with the SHELXTL package.^{5,6)}

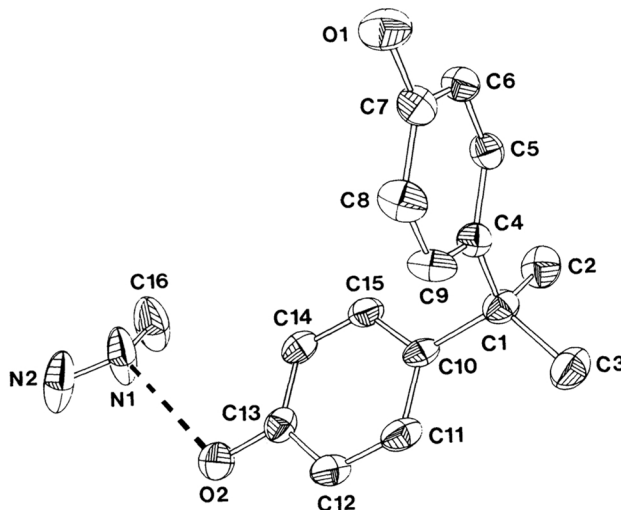
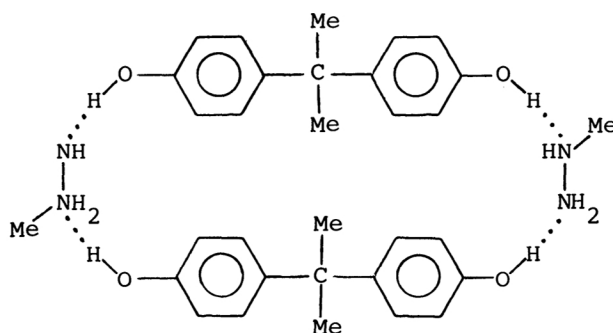


Fig. 1. Host-guest interaction and atom labelling in **4**, with the O-H...N hydrogen bond represented by a broken line. Thermal ellipsoids are drawn at the 30% probability level. Selected molecular dimensions (bond lengths in Å, angles in degrees, standard deviations in parentheses): C1-C2 1.534(6), C1-C3 1.543(7), C1-C4 1.542(5), C1-C10 1.537(6), C7-O1 1.364(5), C13-O2 1.372(5), C2-C1-C3 107.2(4), C4-C1-C10 107.7(8), C6-C7-O1 118.5(4), C8-C7-O1 122.7(3), C12-C13-O2 118.6(4), C14-C13-O2 122.8(4); C16-N1 1.481(8), N1-N2 1.222(6), C16-N1-N2 117.9(5); O2...N1 2.797(7), O1...N2' 2.769(7), C7-O1...N2' 117.3(6), C13-O2...N1 111.3(6), N2-N1...O2 107.9(8), C16-N1...O2 117.1(8), N1-N2...O1' 135.1(9).

As illustrated in Fig. 1, the two molecular components are connected by the O2-H...N1 hydrogen bond. A second independent hydrogen bond of the type O1-H...N1', where the primed superscript denotes the symmetry transformation $(-x, 1-y, -z)$, also occurs, thereby resulting in a centrosymmetric cyclic dimer as represented by the following diagram:



Geometrical details of the scheme of hydrogen bonding and selected molecular dimensions are given in the legend of Fig. 1. A stereoview of the molecular packing in **4** (Fig. 2) clearly shows the cyclic hydrogen-bonded dimeric unit located at the inversion center $(0, \frac{1}{2}, 0)$.

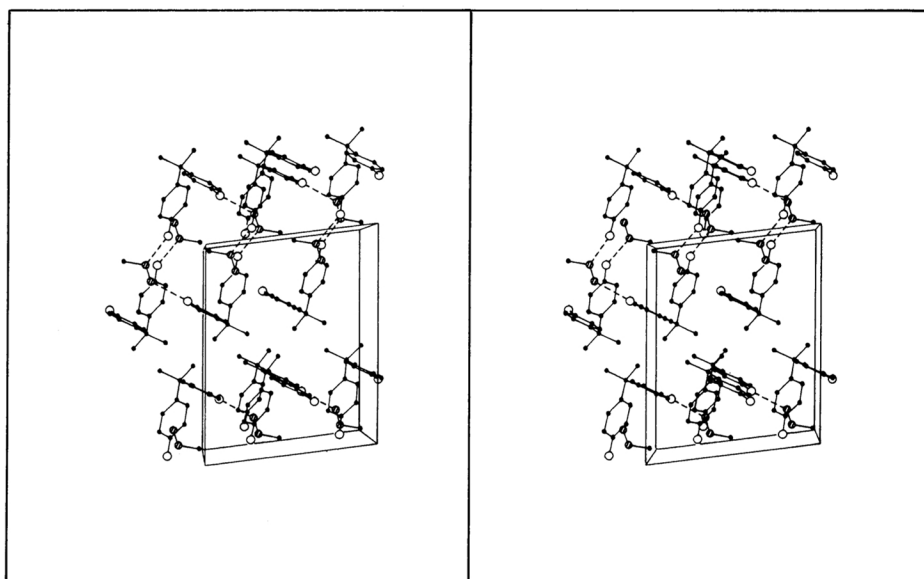


Fig. 2. Stereodrawing of the crystal structure of **4**. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader, and *c* downwards. Broken lines represent O-H...N hydrogen bonds.

Molecular association to give cyclic dimers, which accounts for the highly efficient inclusion of **3** by **2**, requires that the guest molecule be capable of forming two acceptor hydrogen bonds with its neighboring host molecules. Of the guest species listed in Table 1, hydrazine is envisaged to behave in the same manner as methylhydrazine. Both resorcinol and hydroquinone satisfy the above criterion, but many other structural possibilities exist in addition to the formation of cyclic dimers. Less organized structures are expected for the 1:1 complexes of **2** with phenol, cresols, ammonia, and the simple aliphatic amines.

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