

A Complex in Which the Carbonyl Oxygen Atom of a Simple Ketone Accepts Two Intermolecular Hydrogen Bonds

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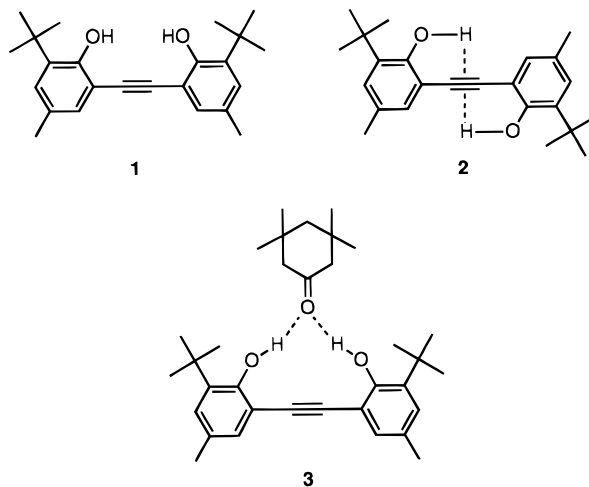
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Carbonyl oxygen atoms have two formal lone pairs of electrons in sp^2 orbitals.² In principle, both pairs are available for interaction with Brønsted or Lewis acids. As a result, simultaneous binding of two or more Brønsted or Lewis acids by simple ketones is plausible, even though ketones are among the least basic carbonyl compounds.³ Such multiple coordination can be expected to have a variety of interesting consequences.^{4–10} Of particular importance is the possibility that ketones interacting with multiple Brønsted or Lewis acids may experience an unusually high degree of electrophilic activation.^{5–9} Structures in which the carbonyl oxygen atom of relatively simple ketones interacts *intramolecularly* with two nearby sites of Brønsted acidity are well-known,⁴ and analogues involving two intramolecular sites of Lewis acidity have also been characterized.⁵ In both cases, the multiple interactions have marked effects on the geometry, spectroscopic properties, and reactivity of the bound carbonyl group. Carbonyl compounds that are more basic than simple ketones can interact *intermolecularly* with multiple sites of Brønsted or Lewis acidity.^{6,7,10} In contrast, complexes in which simple ketones interact *intermolecularly* with multiple Brønsted acids

are extremely uncommon,^{11,12} and analogues involving multiple Lewis acids are unknown. In this note, we establish that doubly hydrogen-bonded complexes of simple ketones can be formed with 2,2'-(1,2-ethynediyl)-bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**),¹³ which is particularly well designed to serve as a convergent donor of two hydrogen bonds.¹⁴

Evaporation of solvent from an equimolar mixture of diphenol **1** and 3,3,5,5-tetramethylcyclohexanone in pentane produced colorless crystals of a 1:1 adduct in 98% yield. Its IR spectrum (Nujol) revealed a sharp band at 1670 cm^{-1} and a broader band at 3329 cm^{-1} . In contrast, the carbonyl stretching band of the free ketone appears at 1717 cm^{-1} under similar conditions, and the OH stretching region of the IR spectrum of diphenol **1** contains a sharp peak at 3502 cm^{-1} , which indicates that both OH groups are equivalent and doubly π -bonded to the central triple bond in the approximately symmetric manner suggested by structure **2**.¹³ Together, these data suggest that the 1:1 adduct has the novel structure **3**, in



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(2) For discussions of the electronic structure of carbonyl compounds, see: Wiberg, K. B.; Marquez, M.; Castejon, H. *J. Org. Chem.* **1994**, *59*, 6817. Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018.

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which the two OH groups of diphenol **1** are oriented convergently and act as donors of two hydrogen bonds to the oxygen atom of the ketone. In this structure, the *tert*-butyl groups play an important role by favoring a convergent orientation of the hydrogen atoms of the OH groups and by disfavoring self-association of diphenol **1** by intermolecular hydrogen bonding. Double hydrogen bonding of the bound ketone has a notable effect on the position of its carbonyl band, which shifts by 47 cm^{-1} to a lower frequency in the adduct.

An X-ray crystallographic study confirmed that the doubly hydrogen-bonded structure **3** is adopted in the solid state. The results of this study, which are sum-

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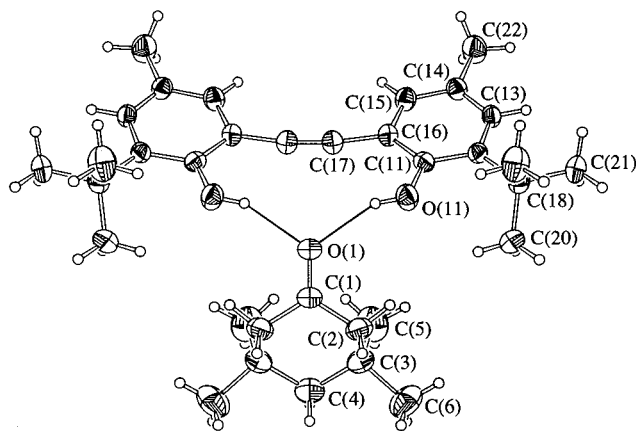


Figure 1. ORTEP view of the structure of the doubly hydrogen-bonded adduct **3** formed by the interaction of diphenol **1** and 3,3,5,5-tetramethylcyclohexanone. Non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and hydrogen bonds are represented by narrow lines.

marized in Figure 1, show that the hydrogen bonds are equivalent by symmetry and have several interesting features. In particular, the intermolecular O(1)⋯O(11) distances are relatively short (2.780(2) Å), suggesting that both hydrogen bonds are moderately strong. However, the distances are somewhat longer than those normally seen in singly hydrogen-bonded adducts of simple ketones and phenols (2.73–2.78 Å),¹⁵ and they are also longer than those observed in a related doubly hydrogen-bonded 1:2 adduct of acetone and 4-hydroxybiphenyl (2.745(2) Å).¹² The observed lengthening may indicate that the average strength of a hydrogen bond in a doubly bonded adduct is slightly lower than that in a singly bonded analogue, or it may simply reflect constraints imposed by the rigid geometry of diphenol **1**. Indeed, the O(1)⋯H–O(11) angles (150.4(1)°) show that the hydrogen bonds in adduct **3** deviate more substantially from linearity than those in unconstrained analogues.^{11,12,15} Moreover, the C(11)–C(17)–C(17a) angle (171.85(12)°) reveals that the triple bond is slightly deformed, possibly in order to make the hydrogen bonds more nearly linear. The angle C(1)–O(1)⋯O(11) (118.26(5)°) and the dihedral angle C(2)–C(1)–O(1)⋯O(11) (2.33(4)°) are both similar to those found in related structures, and they confirm that both hydrogen bonds lie close to the carbonyl plane along the directions defined by the formal sp² lone pairs on oxygen.¹⁶

We have observed that diphenol **1** also forms solid 1:1 adducts with other carbonyl compounds. Their IR spec-

tra suggest that they are analogous to adduct **3**, but we did not determine their structures by X-ray crystallography. Although double hydrogen bonding is a salient feature of the interaction of diphenol **1** with simple ketones in the solid state, it is not always strong enough to be retained in solution. For example, the IR spectrum of a 0.2 M solution prepared by dissolving adduct **3** in CH₂Cl₂ showed only bands at 1707 and 3506 cm⁻¹, which are characteristic of free 3,3,5,5-tetramethylcyclohexanone and diphenol **1** under the same conditions. It is possible that more stable adducts will be formed by related diphenols with convergent OH groups that cannot form weak intramolecular hydrogen bonds such as those present in structure **2**. Nevertheless, our spectroscopic and crystallographic studies confirm that simple ketones, despite their inherently weak basicity, can accept multiple intermolecular hydrogen bonds.

Experimental Section

1:1 Adduct of 2,2'-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1) and 3,3,5,5-Tetramethylcyclohexanone. A mixture of diphenol **1** (15.9 mg, 0.0448 mmol)¹³ and 3,3,5,5-tetramethylcyclohexanone (6.9 mg, 0.045 mmol) in pentane (1 mL) was stirred at 25 °C for 10 min. Evaporation of solvent then left a crystalline colorless residue of the 1:1 adduct **3** (22.3 mg, 0.0442 mmol, 98%): mp 110 °C; IR (Nujol) 3329, 1670 cm⁻¹.

X-ray Crystallographic Study of the 1:1 Adduct 3 of 2,2'-(1,2-Ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (1) and 3,3,5,5-Tetramethylcyclohexanone.¹⁷ Crystals of 1:1 adduct **3** belong to the orthorhombic space group *Pnma* with *a* = 9.542(2) Å, *b* = 26.567(6) Å, *c* = 12.398(2) Å, α = 90°, β = 90°, γ = 90°, *V* = 3142.9(10) Å³, *D*_{calcd} = 1.067 g cm⁻³, and *Z* = 4. Data were collected at 293 K, and the structure was refined to *R*1 = 0.039, *wR*2 = 0.080 for 3041 reflections with *I* > 2.00 σ(*I*).

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters, and distances to weighted least-squares planes for the 1:1 adduct of 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (**1**) and 3,3,5,5-tetramethylcyclohexanone (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(17) The authors have deposited X-ray crystallographic data, a description of the structure determination, and tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and refined and calculated hydrogen atom coordinates with the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.