p-Benzoquinone 2,3,5,6-Tetrakis(diisopropyl phosphonate): A Novel, Highly Bent *p*-Benzoquinone

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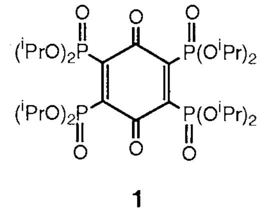
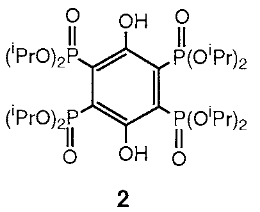
Multiple introduction of phosphonate groups around the quinone oxygen greatly deforms the *p*-benzoquinone ring through the steric and electronic repulsion. The repulsion produces not a boat but a chair conformation with a bent angle as large as 17.8°.

The chemistry of highly bent benzene derivatives such as short-bridged cyclophanes has been intensively investigated in recent years,[1] as exemplified by the work reported by Tobe *et al.*[2] in which ingenious valence isomerization of Dewar benzene precursors was employed to obtain highly strained cyclophanes. On the other hand, the structurally related quinone ring is more flexible than the benzene ring. Hence, quinone rings are easily deformed to release the steric energy in the sterically congested quinone systems, [3-6] although the planar quinone ring is quite normal.[7] Some interesting examples of quinone structures bent primarily due to steric effect have already been reported. The transition-metal complexes of *p*-benzoquinone have the boat conformation[3] and the *p*-quinone skeleton in a natural product, Conacytone, deviates from planarity.[4] On the other hand, the chair conformation was found in the *p*-benzoquinone skeleton of 2,3,5,6-tetrakis(phenylthio)benzoquinone[5] and in 2,3,5,6-tetraphenyl-*p*-benzoquinone.[6]

We now propose a new approach for obtaining a bent quinone system. Introducing sterically bulky groups with electronegative atoms such as oxygen as close as possible to the quinone oxygen would give a bent quinone ring structure by the mutual steric and electrostatic repulsion between quinone oxygens and electronegative functional groups such as phosphoryl ones. The steric bulk of alkyl groups introduced would also contribute to the stabilization of such a bent quinone structure, since the quinone ring is embedded deeply into the lipophilic environment constructed by bulky alkyl groups. Our first target compound to test this proposal is *p*-benzoquinone 2,3,5,6-tetrakis(diisopropyl phosphonate) (**1**),[8] since, judging from an examination of molecular models, P = O oxygen atoms are placed very close to the quinone oxygen atoms and eight bulky isopropyl groups obviously construct the steric barrier surrounding the quinone ring. Herein, we wish to report the molecular structures of **1** and its reference compound, hydroquinone 2,3,5,6-tetrakis(diisopropyl phosphonate) (**2**),[8] by X-ray crystal structure analysis.



1



2

Reaction of chloranil with triisopropyl phosphite in benzene under reflux gave **1** (30%), which was hydrogenated to give **2** (99%). Single crystals of **1** and **2** were obtained by recrystallization from the mixed solvent of ethyl acetate and hexane (1:1). Molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively.[9,10]

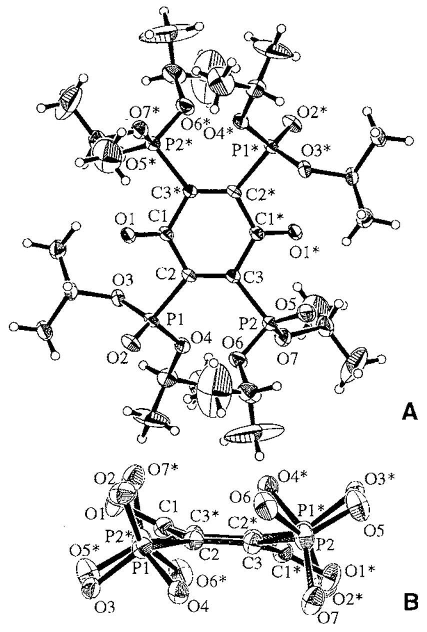
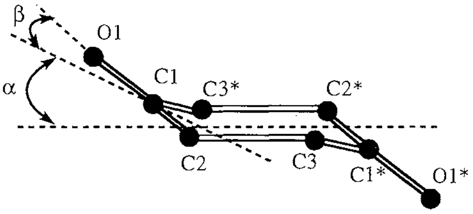


Figure 1. ORTEP drawings of **1** with 30% probability thermal ellipsoids. **A**: top view. **B**: side view, isopropyl groups of peripheral were omitted for clarity.

Since the center of the quinone ring of **1** is located at a center of symmetry, only half of the structure is crystallographically independent (Figure 1). Two types of bond distances were observed in the six-membered ring; the bond distances C1-C2 (1.494(5) Å) and C3-C1* (1.493(5) Å) are longer than that of C2-C3 (1.349(5) Å). As expected, the benzoquinone skeleton is deformed from the normal planar structure to give a chair conformation (Figure 1B). The P-O oxygen atoms O(3) and O(5*) are located below the quinone ring, while the P-O oxygen atoms O(2) and O(7*) above it. The interatomic distances O(1)--O(3) (2.929(4) Å) and O(1)--O(5*) (2.898(4) Å) are shorter than O(1)--O(2) (3.302(4) Å) and O(1)--O(7*) (3.356(4) Å), indicating that the oxygen atoms O(3) and O(5*) push quinone oxygen atom O(1) upward. The O(1)--O(3)



and O(1)--O(5*) distances are slightly longer than the total of two van der Waals radii of oxygen atoms (2.8 Å), suggesting repulsion between the oxygen atoms. The deformation angle (α) of the quinone ring (the angle between the planes defined by C1-C2-C3* and C2-C3-C2*-C3*) is 17.8°. This value is quite bigger than that of 2,3,5,6-tetraphenyl-*p*-benzoquinone (7.0°) which has simple steric bulkiness by four phenyl groups.[6] The deformation angle (β) (the angle between the C(1)-O(1) bond and the C1-C2-C3* plane) of **1** is 1.3°, suggesting that O(1) atom is pushed away by O(3) and O(5*) atoms. The peripheral eight isopropyl groups construct a remarkable lipophilic outer shell and the chair quinone structure is embedded deeply into the lipophilic environment (Figure 1A).

Similar to compound **1**, the center of the benzene ring of **2** is also located at a center of symmetry and therefore half of the structure is crystallographically independent (Figure 2). In sharp contrast to the quinone counterpart described above, the C-C bond lengths of the six-membered ring of **2** are essentially equivalent (C(1)-C(2) 1.413(3) Å, C(2)-C(3) 1.412(3) Å, C(1)-C(3*) 1.415(3) Å) and the benzene ring is planar within 0.015 Å (Figure 2B). In addition, the P = O oxygen atom O(2) is hydrogen-bonded to the hydroxyl group O(1)-H(1) (O(1)---O(2) 2.457(2) Å), eventually releasing the electrostatic repulsion between O(1) and O(2).

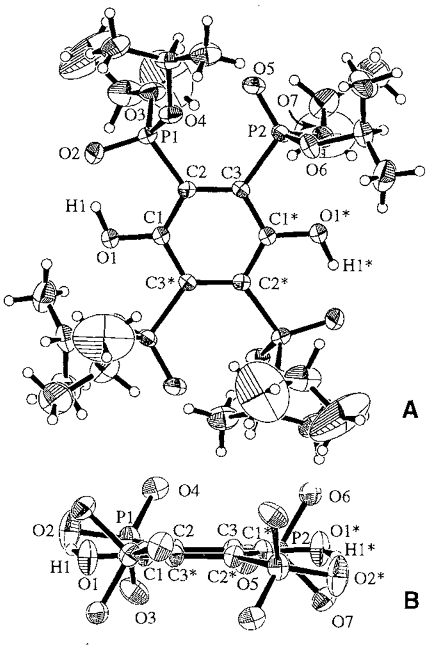


Figure 2. ORTEP drawings of **2** with 30% probability thermal ellipsoids. **A**: top view. **B**: side view, isopropyl groups of peripheral were omitted for clarity.

We may conclude that the proposed approach works indeed at least with the quinone and produces the unusual chair conformation of quinone skeleton by steric and electrostatic repulsion between the quinone oxygen and phosphonate groups in the adjacent substituent. The clear chair structure with such a large distortion angle is rarely seen for simple *p*-benzoquinone in the literature. This kind of structural alternation between benzoquinone and hydroquinone is quite interesting and attractive and could be employed as a tool for controlling the physical and chemical properties of quinone derivatives.[11] Works along this line are currently in progress.

References and Notes

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9 Crystallographic data for **1**: $C_{30}H_{56}O_{14}P_4$, M = 764.66, triclinic, $P\bar{1}$, a = 11.485(2) Å, b = 12.186(3) Å, c = 8.087(1) Å, α = 98.92(2)°, β = 101.01(1)°, γ = 66.92(1)°, V = 1018.0(3) Å^3, Z = 1, D_{calcd} = 1.247 gcm^{-3}, μ = 2.43 cm^{-1}, F(000)=408.00, 2Θmax = 55°, Mo Kα radiation, of 4912 reflections measured, 4677 were unique. The structure was solved by direct methods (SHELXS-86) and refined by full matrix least-squares method. The final R and Rw factors were 0.051 and 0.070 for 2346 reflections with I > 3.00 σ(I), respectively.

10 Crystallographic data for **2**: $C_{30}H_{58}O_{14}P_4$, M = 766.67, triclinic, $P\bar{1}$, a = 10.894(2) Å, b = 12.665(3) Å, c = 8.093(3) Å, α = 94.45(3)°, β = 104.37(2)°, γ = 76.61(2)°, V = 1052.0(5) Å^3, Z = 1, D_{calcd} = 1.210 gcm^{-3}, μ = 2.35 cm^{-1}, F(000)=410.00, 2Θmax = 55°, Mo Kα radiation, of 5180 reflections measured, 4840 were unique. The structure was solved by direct methods (SHELXS-86) and refined with full matrix least-squares method. Hydrogen atom (H1) of hydroxyl group was found by difference synthesis. The final R and Rw factors were 0.049 and 0.086 for 3604 reflections with I > 3.00 σ(I), respectively.

11 Preliminary experiment of cyclic voltammogram measurements of **1** in acetonitrile showed that the first and the second reduction potentials are -0.196 and -0.970 V vs. SCE, respectively.