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Preparation, Crystal Structure and Photochemistry of a Novel Molecular Compound between Duroquinone and Durene

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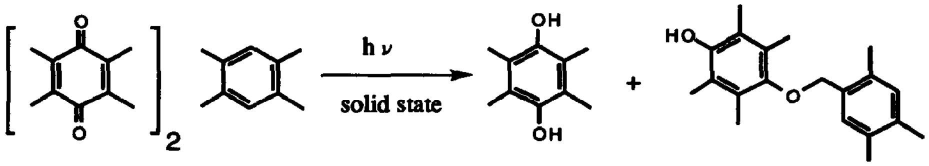
Abstract: A 2:1 crystalline molecular compound (3) of duroquinone (1) and durene (2) has been prepared in two ways of evaporating the solution and solidifying the melt. The crystal structure of 3 was determined by X-ray crystallography. Irradiation of 3 caused the intermolecular hydrogen abstraction reaction, which was specific in the solid state, to give durohydroquinone (4) and a photoadduct (5).

A large number of solid-state photoreactions in the crystals of one component has been studied since Cohen and Schmidt have reported the dimerization of *trans*-cinnamic acids in the solid state.[1] However, solid-state photoreactions between different two organic molecules have been undeveloped.[2-6] One aim is to find new photoreactive molecular compounds composed of different molecules, followed by making clear the correlation of the photoreaction with the molecular arrangement in the crystal. We discovered a novel 2:1 molecular compound 3 of duroquinone 1 and durene 2, which is constructed from two directions of layer structure in the crystal lattice. UV irradiation of the crystal of 3 caused intermolecular hydrogen abstraction which was specific in the solid state. In the crystal, the distances between quinone oxygens and surrounding methyl hydrogens are short enough to permit abstraction of the hydrogens producing the durosemiquinone radicals.



Molecular Compound 3 4 5

Scheme I

A yellow single crystal of **3** was easily obtained by the slow evaporation of an ethyl acetate solution of 1:2 to 2:1 molar ratio of **1** and **2** at room temperature. The polycrystal of **3** was also prepared by melting and resolidifying the mixture of 2:1 molar ratio of **1** and **2**. It was confirmed that the crystal of **3** obtained by the melting-resolidifying process is identical with the single crystal of **3** as shown by the occurrence of the same new peaks in the powder X-ray diffraction, the solid-state ^{13}C CP/MAS NMR and IR spectra. The melting point is 95°C appearing between the melting points of **1** (112°C) and **2** (79°C). The structure of **3**[7] was determined by the single crystal X-ray analysis (Fig. 1). The crystal is triclinic, space group $P\bar{1}$, $Z=6$; there are three molecules (including two duroquinones and one durene per molecule) in the unsymmetric unit of the unit cell. The rings 1 and 2 are occupied by both duroquinone and durene; the occupancy of each one is about 0.5, respectively. The rings 3, 4, 5 and 8 are the duroquinones. The rings 6 and 7 are the durenes. There is an inversion center in each center of ring 9 and ring 10 which correspond to one duroquinone, therefore. Totally, there are six duroquinones (ring 1+2, 3, 4, 5, 8, 9+10) and three durenes (ring 1+2, 6, 7) in the unit cell. The disorder of the rings 1 and 2 may be the reason why the R value is relatively high as 0.11. The rings 7, 4, 2, 3 and 8 are nearly parallel, which are stacked along an almost straight line, and the distances of the ring centers are in the range 3.4-3.6 Å. The other rings 6, 9, 1, 5 and 10 are nearly parallel each other and approximately perpendicular to the rings 7, 4, 2, 3 and 8. The ring center distances between 6 and 9 and also 5 and 10 are 3.5 Å. Other ring center distances are 5-6 Å. The layer stacking structure suggested that the crystal of **3** might be a CT complex. A very weak CT complex having a CT absorption band at 339 nm was formed in a concentrated cyclohexane solution of **1** (0.01 M) and **2** (0.1 M). However we conclude that there is a minor contribution of CT interaction for the formation of the crystalline molecular compound.

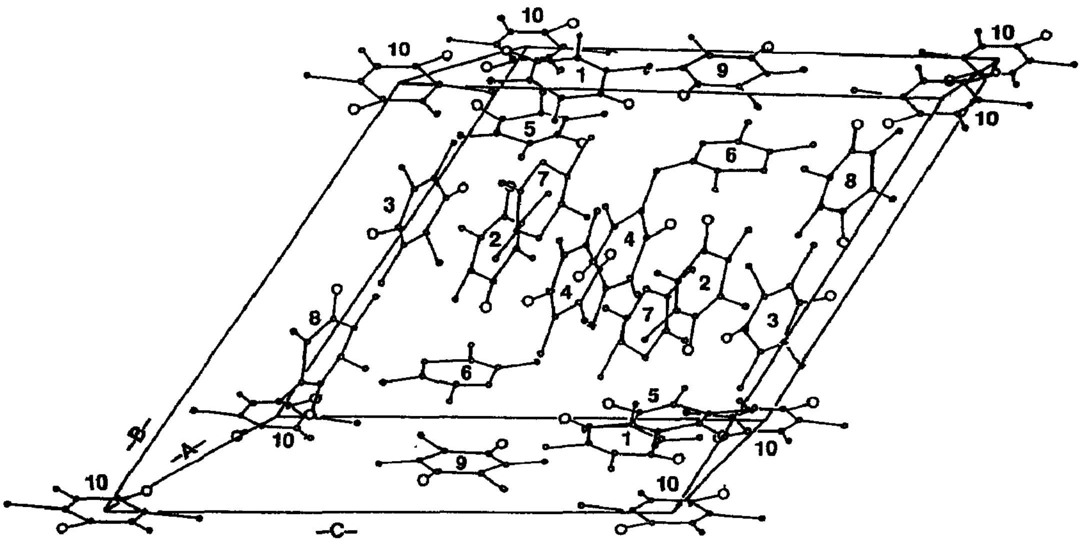


Figure 1. Packing diagram in the unit cell of the molecular compound **3**.
Large circles are oxygen atoms and small circles are carbon atoms.

Twenty mg of the crystal 3 was placed between two Pyrex glass plates in about 5 cm-diameter circle, put into a sealed Pyrex glass vessel and irradiated with a 400 W high-pressure mercury lamp under argon for 20 h in a water bath at 10 °C. The light strength at 360 nm measured with a UV radiometer was about 40 mW cm^{-2}. The irradiation gave durohydroquinone 4 in 20% yield and a photoadduct 5[8] in 6% yield as main products. The hydroquinone 4 was separated by washing the irradiated solid sample with hexane and identified by comparison with an authentic sample. The photoadduct 5 was separated by a preparative HPLC and the structure was elucidated by elemental analysis and spectral data.[8] The same results were obtained for the photoreaction of the crystals of 3 prepared either by the recrystallization or the melting-resolidifying process. For comparison, the irradiation of the solution of a 2:1 mixture of 1 and 2 in acetonitrile or benzene gave two unidentified products, which were also obtained by the irradiation of the solution of 1 alone. The products have absorption maxima at 245 nm and 276 nm, respectively, as shown by the HPLC measurement with a phototodiode array detector. However, these products could not be separated due to the instability, and their properties were not consistent with those of o-quinone methide and diduroquinone which were reported as the products in the flash photolysis of the solution of 1[9]. In conclusion, the intermolecular hydrogen abstraction photoreaction in Scheme I is thus specific to the solid state.

The steady-state ESR spectrum of 3 in the solid state was measured under UV irradiation at -100°C (Fig. 2). The ESR signal is assigned to be the durosemiquinone radical by a g-value of 2.0051[10] and by a hyperfine structure with a peak to peak width of 0.62 mT. The semiquinone radical is stable since about half of the radical intensity remained after stopping irradiation followed by standing at 30°C for 1 h. However, the duryl radical was not observed. Irradiation of 1 alone also gave the identical ESR signal but the strength was weak; it is consistent with the lower yield of 4 (4%). We now give a possible solid-state photoreaction mechanism. The duroquinone oxygen excited by UV irradiation of 3 abstracts the surrounding methyl hydrogens of 1 and 2 to form the semiquinone radical. The disproportionation reaction of two semiquinone radicals gives durohydroquinone 4 and the starting duroquinone 1. On the other hand, the radical coupling of the semiquinone radical and the duryl radical produces the photoadduct 5.

Figure 2. ESR spectrum of 3 in the solid state under UV irradiation at -100°C.

One of the essential factors for the formation of the semiquinone radical is that the distances between quinone oxygens and methyl hydrogens are short enough to abstract the hydrogen; Scheffer[11] estimated the distances to be 2.2-2.7 Å. In the crystal of 3 (Fig. 1), the quinone oxygen is surrounded by a number of methyl groups of 1 and 2. Although the positions of the hydrogen atoms in the crystallographic analysis could not be determined at this time, the shorter O···C distances are in the range 3.2-3.8 Å.[12] Further refinement of the structure will become possible more precise discussion about the correlation of the reactivity with not only O···H distances but also C=O···H angles[11].

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7 Crystal data for 3: $C_{30}H_{38}O_4$ (two duroquinones and one durene), triclinic, $P\bar{1}$, a=16.106(7) Å, b=17.580(9) Å, c=18.759(7) Å, α=58.48(3)°, β=63.49(3)°, γ=65.85(3)°, V=3943 Å^3, Mr=462.63, z=6, Dx=1.169 g cm^{-3}, μ=0.709 cm^{-1}, F(000)=1500. Intensity data were collected from a crystal 0.3x0.4x0.3 mm, with an Enraf-Nonius CAD4 diffractometer, Mo K_α radiation, by ω-2θ scans in the range $2° \leq \theta \leq 23°$ and 3215 observed [$I > 3\sigma(I)$] reflections of the total 11247 independent reflections were corrected for LP factors. Structure solution was by the direct method and successive difference Fourier maps. The hydrogen atoms were not found. The final refinement by full matrix least-square method with anisotropic thermal parameters was converged with unweighted and weighted agreement factors of 0.11 and 0.12. The highest peak on the final difference Fourier map has a height of 0.63 e/A^3.

8 Selected data for 5: white crystal, m.p. 138-139°C; elemental analysis, calcd. for $C_{20}H_{26}O_2$ C 80.50%, H 8.78%, found C 80.48%, H 8.78%; UV (MeOH) λ_{max} 278 nm; IR (KBr) 3410 cm^{-1} (br, OH); ^{1}H NMR [$(CD_3)_2CO$] 2.09 (s, 12H), 2.14 (s, 6H), 2.23 (s, 3H), 4.52 (s, 2H), 6.84 (s, 1H), 7.15 (s, 1H).

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12 For example, the distances between one quinone oxygen of the ring 9 and two methyl carbons of the ring 6 are 3.3 Å and 3.6 Å.

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