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Solid-State Photochemistry of the Mixed Crystals between Benzoquinones and Polymethylbenzenes

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Abstract: Nine mixed crystals combined 1,4-benzoquinone (**1**), 2,5-xyloquinone (**2**) and duroquinone (**3**) with durene (**a**), pentamethylbenzene (**b**) and hexamethylbenzene (**c**) were prepared by a melting-resolidifying process and characterized by powder X-ray diffractometry, DSC and IR. Only the mixed crystal of **3** and **a** formed a 2:1 novel molecular crystal (**4**); other eight mixed crystals were simple polycrystalline mixtures of the two components. Irradiation of the molecular crystal **4** (**3/a**) and the mixed crystals **1/a**, **1/b** and **3/b** caused intermolecular hydrogen abstraction to give hydroquinones and in some cases adducts. Product selectivities in the solid state were different from those in solution. Correlation between the crystal structure and the reactivity of **4** is discussed.

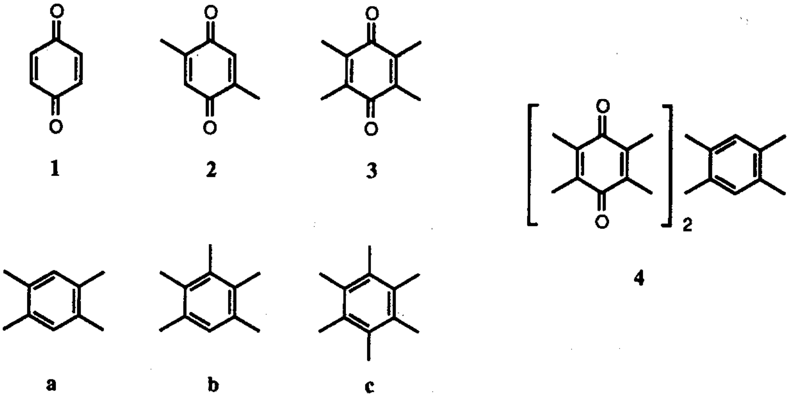
INTRODUCTION

Since photodimerization of *trans*-cinnamic acids in the solid state was reported by Cohen and Schmidt,[1] solid-state photochemistry has been almost limited in the crystals composed of one or similar two components.[2-4] In this context we started the study of solid-state photochemistry in the mixed crystals between two different organic molecules.[5-11] Quinone chemistry has been already developed in the every area including structure, complex formation, synthesis and photochemistry.[12] However the solid-state photochemistry was known only on the dimerization of pure quinone crystals.[13-17] In a preliminary communication[7] we have reported the preparation and crystal structure of a molecular compound (**4**) between duroquinone (**3**) and durene (**a**) and its photochemical hydrogen abstraction. The crystal **4** is a novel type of molecular crystal having no hydrogen bonding and no CT interaction. It was thought that similarity of the molecular shapes of **3** and **a** was a factor required for the formation of the crystalline molecular compound. This finding led us to further study of a series of the mixed crystals between benzoquinones and polymethylbenzenes. We selected 1,4-benzoquinone (**1**), 2,5-xyloquinone (**2**) and duroquinone (**3**) as the benzoquinones, and durene (**a**), pentamethylbenzene (**b**) and hexamethylbenzene (**c**) as the polymethylbenzenes (Scheme 1). The preparation and characterization of other eight mixed crystals combined **1**–**3** with **a**–**c** and their photoreactivity are described in addition to the details for the molecular crystal **4**. For a comparison their photoreactions were also carried out in solution.

RESULTS AND DISCUSSION

Preparation and characterization of the mixed crystals between benzoquinones and polymethylbenzenes

A yellow 2:1 molecular compound **4** of duroquinone (**3**) and durene (**a**) was prepared by slow evaporation of the ethyl acetate solution. The melting point is 95 °C between those of **3** (112 °C) and **a** (79 °C). The crystal structure of **4**[7] is shown in 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



Scheme 1

cell. The rings 1 and 2 are occupied in disorder by duroquinone or durene; the occupancy of each one is about 0.5. The rings 3, 4, 5 and 8 are duroquinones. The rings 6 and 7 are durenes. There is an inversion center in each center of ring 9 and ring 10 corresponding to one duroquinone. 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 crystal has two directions of stackings; the rings 7, 4, 2, 3 and 8 are nearly parallel, and are stacked along an almost straight line. 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 parllel to each other and approximately perpendicular to the rings 7, 4, 2, 3 and 8. The ring center distances between rings 6 and 9 and also rings 5 and 10 are 3.5 Å. Other ring center distances are 5–6 Å.

Some other characterizations for **4** were performed. The IR spectrum (KBr) of **a** had absorption bands at 870 cm^{-1} and 1740 cm^{-1} due to the C–CH_3 out-of-plane vibration

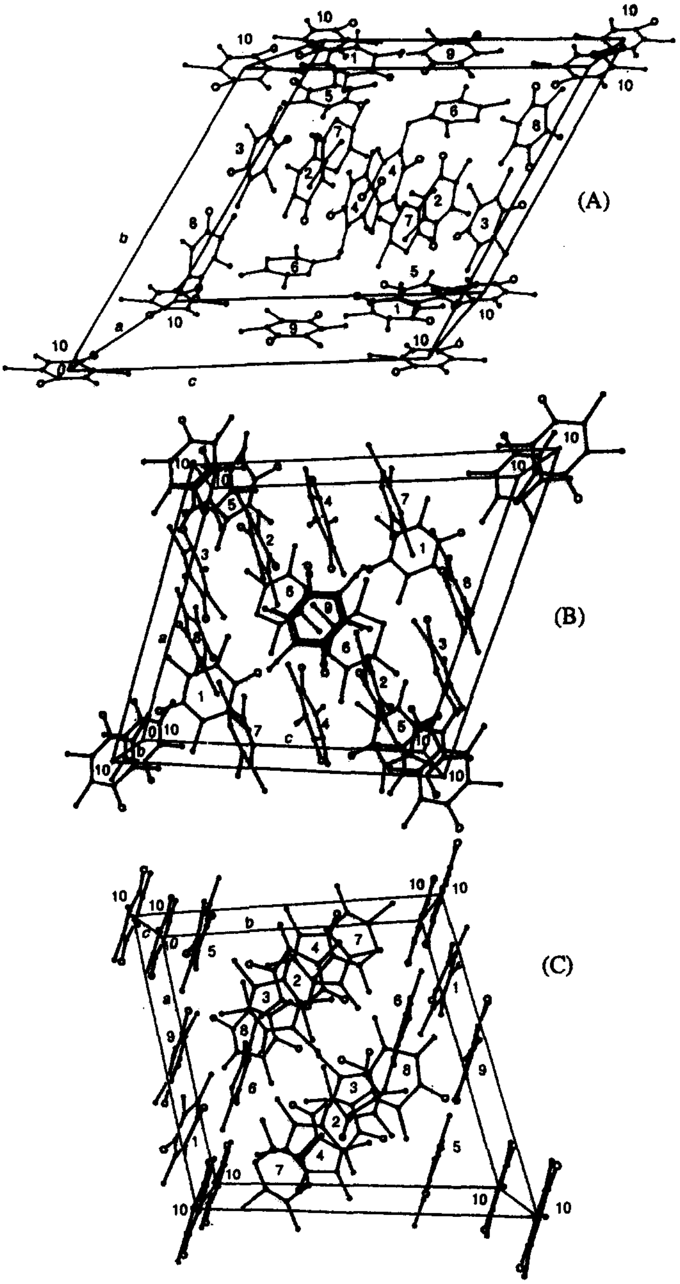


Fig. 1. Packing views of molecular crystal 4.
(A), (B) and (C) show a-, b- and c-axis reflections, respectively. Large circles are oxygen atoms and small circles are carbon atoms.

Table 1. Solid-state ^{13}C CP-MAS NMR of the molecular crystal **4** and its components, duroquinone **3** and durene **a**

Carbon	Chemical shift, ppm		
	Duroquinone **3**	Durene **a**	Molecular crystal **4**
CH_3	11.4, 12.8		11.7, 12.7(m)
		19.0	19.4, 20.2(m)
ArC-H		131.0	131.0(m)
ArC-CH_3		134.2	133.3(m), 134.0(m)
	139.8, 140.8		139.1(m)
C=O	183.9		184.3(m), 185.9(m)

(m) Multiple peak

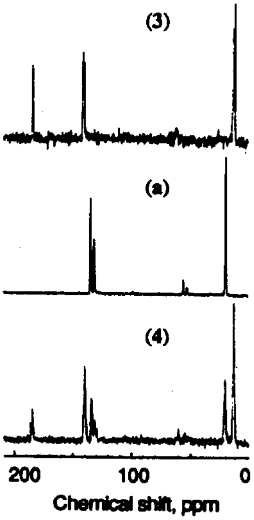


Fig. 2. Solid-state ^{13}C CP-MAS NMR spectra of molecular crystal **4** and its components duroquione **3** and durene **a**

and its overtone, respectively. The out-of-plane vibration band of **a** in **4** shifted to two separate bands 880 cm^{-1} and 985 cm^{-1} and the overtone band disappeared. The solid-state ^{13}C CP-MAS NMR spectra of **4** and its components **3** and **a** were measured by using glycine as an external standard (Fig. 2 and Table 1). The methyl and aromatic carbons of **3** have two separate peaks because two kinds of carbon environment in the crystal **3** exist due to the asymmetric stacking of the molecular plane along {100}.[16] The NMR spectrum of **4** is not the same as the sum of the components **3** and **a**; the chemical shifts of **4** were slightly different from those of the components and the peaks were splitted to multiplet. These reflect[18] that molecular packing in the unit cell of **4** is complicated (Fig.1). Thus the solid-state ^{13}C CP-MAS NMR spectra give us some qualitative information of the carbon environment in the crystal. Fluorescence spectra of **4** and its components **3** and **a** were measured by a front faced arrangement; **4** had no fluorescence though **a** had fluorescence at 292 nm.

Phase diagram of **3** and **a** was constructed by DSC measurement and powder X-ray diffractometry (PXD) of the solid phase. Figure 3 shows the formation of a 2:1 molecular compound **4**, of which the melting point is 95°C. The eutectic points of **4** and **3**, and **a** and **4** were 94°C and 69°C, respectively; the former was very near to the melting point of **4**. We also prepared a large size (30 x 8 i.d. mm) of the single crystal **4** by the Bridgeman method based on slow crystal growth. The prepared single crystal column had two cleavage faces, which were coincident with the two perpendicular layer structure (Fig. 1). The melting point, IR and PXD patterns were in accord with those of the single crystal obtained by slow evaporation of the ethyl acetate solution.

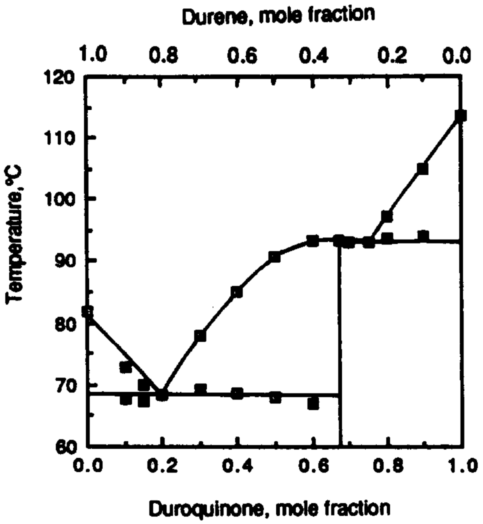


Fig. 3. **Phase diagram of duroquinone 3 and durene a**

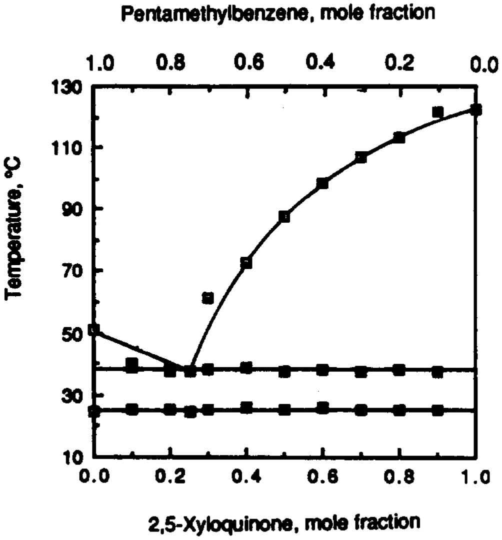


Fig. 4. Phase diagram of 2,5-xyloquinone 2 and pentamethylbenzene b

We prepared eight mixed crystals 1,4-benzoquinone **1**, 2,5-xyloquinone **2** and duroquinone **3** as the quinones combined with durene **a**, pentamethylbenzene **b** and hexamethylbenzene **c** as the polymethylbenzenes by resolidifying the 1:1 melts (Scheme 1). As the results of characterization by PXD, IR and DSC, it was confirmed that six mixed crystals **1/a**, **1/b**, **1/c**, **2/a**, **2/c** and **3/c** were simple mixtures of the two components. In the cases of **2/b** and **3/b**, the IR spectra were the same as the sum of their components spectra in spite of the appearance of some new PXD peaks. To verify the contradictory data, the phase diagrams between **2** and **b**, and **3** and **b** were constructed by DSC and PXD. Figure 4 indicates that the mixed crystal **2/b** is a simple

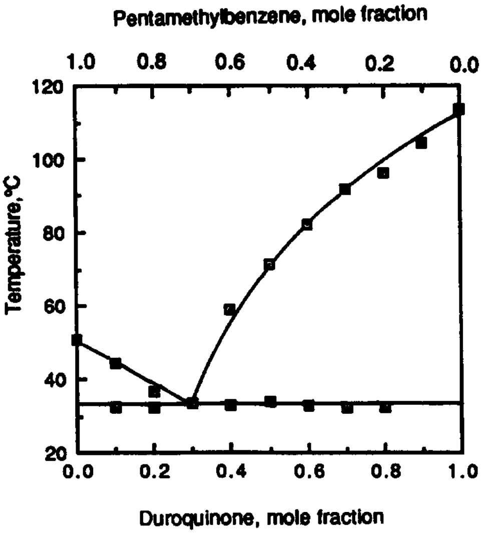


Fig. 5. Phase diagram of duroquinone 3 and pentamethylbenzene b

Table 2. CT bands between benzoquinones 1–3 and polymethylbenzenes in cyclohexane a–c

Methylbenzene	Wavelength maximum of CT band, nm (ε)[a]		
	1,4-Benzoquinone 1	2,5-Xyloquinone 2	Duroquinone 3
Durene a	363 (48)	351 (37)	330 (30)
Pentamethylbenzene b	383 (87)	363 (63)	350 (51)
Hexamethylbenzene c	406 (148)	385 (79)	370 (59)

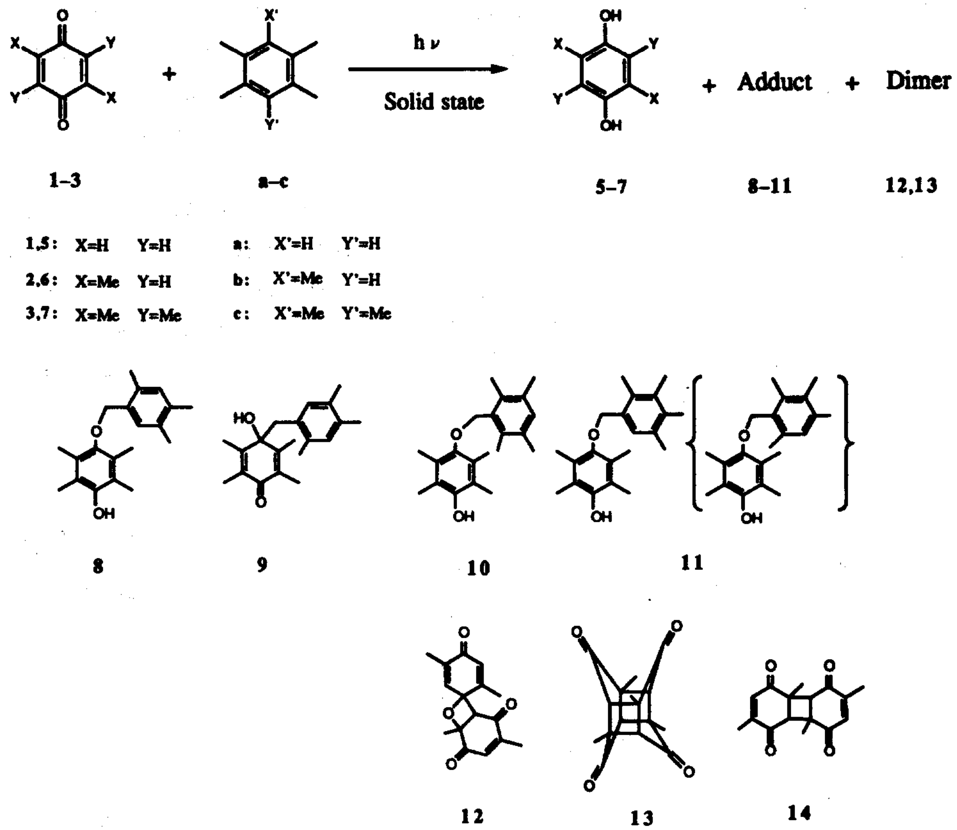
a Apparent ε values calculated from absorbance of 0.01M quinone solutions containing 0.1 M polymethylbenzene.

mixture having an eutectic point at 38°C and a phase transformation at 26°C, which is that of **b**. The phase diagram of **3** and **b** was a typical simple mixture which had an eutectic point at 33°C (Fig. 5).

On the other hand, it is well known that CT complexes of quinones and polymethylbenzenes are formed in the solutions. We measured the absorption spectra of the mixtures of **1–3** and **a–c** in cyclohexane (Table 2), as well as those of the mixed crystals of **1–3** and **a–c** and the molecular crystal **4**, which showed no CT band. These results indicate that the CT complexes are formed only in the solutions but not in the crystal states. Probably the similarity of the molecular shapes between **3** and **a** is a factor forming the molecular crystal **4**. This kind of crystal having almost no CT interation and no hydrogen bonding is novel.

Photoreaction of the mixed crystals and relationship between the reactivity and the structure

We have already reported the photochemical intermolecular hydrogen abstraction of the molecular crystal **4**.[7] More detailed data are shown in Scheme 2 and Table 3. Photoproducts obtained were durohydroquinone (**7**) and two adducts (**8**) and (**9**). Duroquinone **3** in cyclohexane has absorption bands at 267 nm ($\pi-\pi^*$, allowed), 330 nm ($\pi-\pi^*$, forbidden) and 432 nm (n–π^*, forbidden) with ε 21,000, 233 and 27, respectively. We examined wavelength dependence of the reactivity because the last two wavelengths are known to be in relation to photoreactivity.[12] Irradiation with a high-pressure mercury lamp which has strong emission lines in shorter wavelengh region gave higher yield of **7** due to the $\pi-\pi^*$ excitation of the 330 nm band. While the n–π^* excitation at 432 nm by using a xenon short arc lamp which has continuous wavelength distribution led to much production of **9**. The reason that any products were not obtained by the irradiation of 290-410 nm light with xenon lamp through a UV transparent filter is the weakness of 330 nm light component. Influence of the irradiation temperature on the yield of **9** was not observed, while **7** and **8** were not obtained at low temperature. Yields of **7** obtained by the irradiation of duroquinone crystal **3** alone were low.



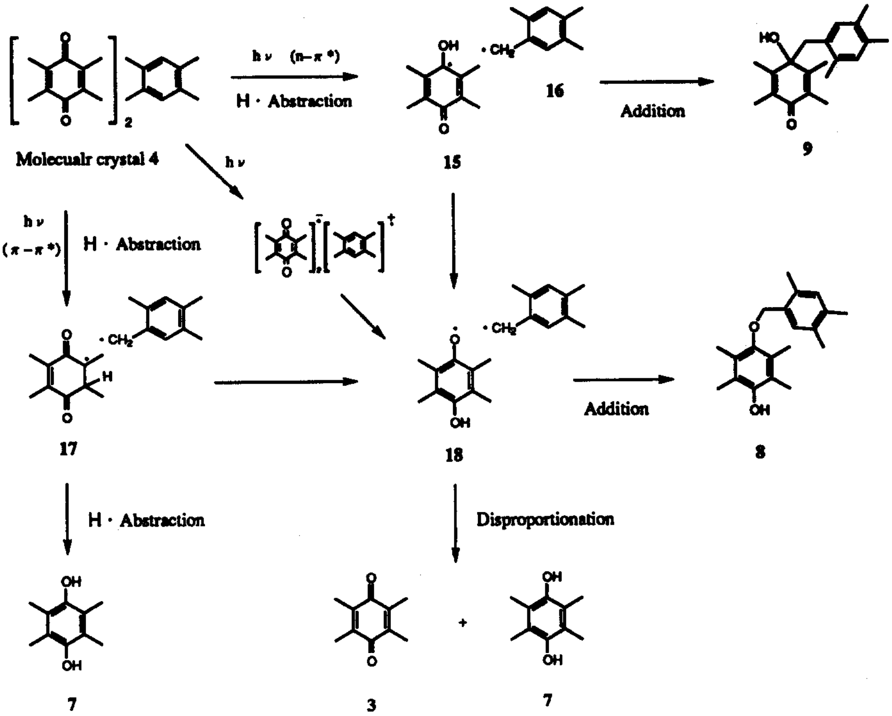
Scheme 2

Table 3. Photoreaction of a molecular crystal 4 of duroquinone 3 and durene a, and 3 alone

	Irrad. temp.	Irrad. wavelength		Conversion, %		Yield, %		
Crystal	°C	nm	lamp	3	a	7	8	9
4	10	>290	a	64	51	20	7	3
4	10	>290	b	48	46	4	3	16
4	10	290-410	c	33	15	-	-	-
4	10	>390	d	42	41	3	3	20
4	-50	>290	b	31	44	-	-	15
3	10	>290	a	56	-	4	-	-
3	10	>290	b	39	-	1	-	-

a Hg lamp. b Xe lamp. c Xe lamp with a UV transparent filter. d Xe lamp with a UV cut filter.

Scheme 3 shows a possible reaction mechanism. The key point is hydrogen abstraction to generate two quinone radicals **15** and **17** by the $\pi-\pi^*$ and $n-\pi^*$ excitation at 330 and 432 nm, respectively. An adduct **9** is fastly produced by subsequent radical coupling of **15** and **16**. Hydroquinone **7** is formed via two paths. One is repeated hydrogen abstraction of **17** from $-CH_3$ of an adjacent molecule. Another path is the disproportionation of semiquinone radical **18** produced by rearrangement of **15** and **17**. We measured ESR spectrum of **4** under UV irradiation at −100°C in the solid state (Fig. 6). The ESR signal was assigned to **18** by the g-value of 2.0051, the peak to peak width of 2.97 mT and the hyperfine structure with the peak to peak width of 0.69 mT. This radical was stable since about half of the signal strength remained after stopping UV irradiation and keeping in the dark at 30 °C for 1 h. Thus hydrogen abstraction of **3** from **a** in **4** is possible because **4** has a layer stacking structure with a shorter ring center distance of 3.5 Å, e.g., between rings



Scheme 3

6 (**a**) and 9 (**3**), and also 5 (**a**) and 10 (**3**) as described in the previous Section and Fig. 1. In addition, if the oxygen atom of the quinone C=O can directly abstract to give **18**, the shorter C=O···H_3C– distances are estimated in the range 2.2–2.8 Å from the crystal data; they are short enough[19] to abstract hydrogen in the crystal lattice.

We also considered a photoinduced electron transfer (PET) process preceeding the hydrogen transfer. Free energies (ΔG) for the electron transfer between benzoquinones and polymethylbenzenes in acetonitrile by the Rehm and Weller equation[20,21] were calculated (Table 4). All ΔG values obtained were negative, indicating that a mechanism involving such an electron transfer may be possible in Scheme 3.

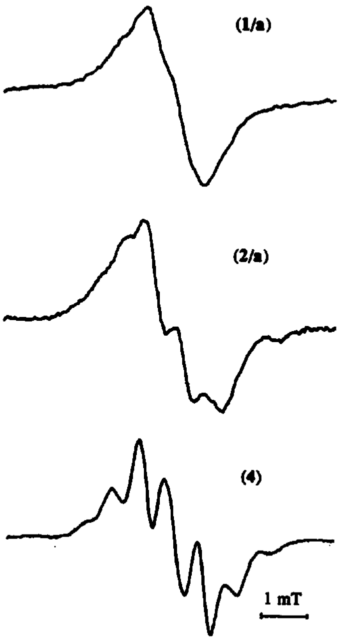


Fig. 6. ESR spectra of mixed crystals 1/a and 2/a and molecular crystal 4 under UV irradiation at −100°C in the solid state.

Solid-state photoreactivity of other 1:1 simple polycrystalline mixtures of quinones **1**–**3** and polymethylbenzenes **a**–**c** prepared by the melting-resolidifying procedure was investigated under irradiation with a high-pressure mercury lamp. The results are shown in Table 5, together with photoreaction of the quinones alone. Irradiation of the mixed crystals with **1** and **3** caused hydrogen abstraction reaction which was similar to that of the molecular crystal **4** to give the corresponding hydroquinones **5** and **6**. Particularly in the cases of **1/a**, **1/b** and **3/b** relatively high yields were obtained. Irradiation of **3/b** gave also two adducts **10** and **11** in low yields; it is similar to

Table 4. Free energies for the photoinduced electron transfer between benzoquinones 1–3 and polymethylbenzenes a–c in acetonitrile

	ΔG, kcal mol^{-1}		
Methylbenzene	1,4-Benzoquinone 1	2,5-Xyloquinone 2	Duroquinone 3
Durene a	-56.1	-53.2	-48.3
Pentamethylbenzene b	-56.3	-53.5	-48.6
Hexamethylbenzene c	-58.1	-55.3	-50.4

Table 5. Photoreactions in the mixed crystals of benzoquinones **1–3** and polymethylbenzenes **a–c**

Mixed crystal or quinone	Conversion, % Quinone	Polymethylbenzene	Yield, % Hydroquinone	Adduct	Dimer
1	53		(**5**) 2		-
1/a	74	54	29	-	-
1/b	92	72	36	-	-
1/c	35	10	4	-	-
2	94		(**6**) 3		(**12**) 8 (**13**) 31
2/a	96	28	3	-	6 30
2/b	96	31	3	-	6 30
2/c	96	40	4	-	4 30
3	65		(**7**) 4		-
3/b	82	46	23	(**10**) 3 (**11**) 3	-
3/c	56	12	6	-	-

the photoreaction of the molecular crystal **4**. In addition, detection of many small peaks in HPLC analysis and production of some insoluble polymers indicate that polymerization of the quinones occurred; it is the reason that the conversions of **1** and **3** were high.

On the other hand irradiation of xyloquinone **2** and the mixed crystals **2/a**, **2/b** and **2/c** mainly caused dimerization of **2** to give oxetane dimer **12**[13] and box-dimer **13**[14] (Scheme 2). While hydrogen abstraction reaction hardly caused, different from the mixed crystals with **1** and **3**. Failure in detection of (2+2) cyclobutane dimer **14**[12,13] indicates that the cyclobutane dimer **14** formed at the early stage was totally changed to **13** due to the prolonged irradiation (24 h). The yields of **12** and **13** from the mixed crystals **2/a**, **2/b** and **2/c** were similar to those from **2**, supporting that the mixed crystals are simple polycrystalline mixtures of **2** and polymethylbenzenes. The occurrence of the (2+2) dimerization of **2** is due to the sufficient parallel overlapping of C=C and C=O of the quinone ring in the crystal lattice.[15] On the other hand the crystal structures of **1** and **3** are not suitable for the dimerization.[16,17]

The same reaction mechanism as in Scheme 3 can be applied for these simple polycrystalline mixtures. In this case the reactions proceed at the interface of the component crystallites.[8] ESR signals detected under UV irradiation of **1/a** and **2/a** at −100 °C in the solid state were assigned to the corresponding semiquinone radicals by the g-values of 2.0049 and 2.0039, the peak to peak widths of 1.30 and 1.76, respectively, and the hyperfine structure of **2/a** with the peak to peak width of 0.69 mT (Fig. 6). One of the reasons for the relatively high yields of the hydroquinones obtained by the irradiation of **1/a**, **1/b** and **3/b** is that the sizes of

Table 6. Yields of hydroquinones 5–7 by photoreaction in acetonitrile

Substance	Conversion, %		Yield, %
	Quinone	Durene a	Hydroquinone
1	57		(5) 5
1-a	93	61	28
2	73		(6) 5
2-a	84	63	43
3	99		(7) -
3-a	71	34	-

the crystallites are small enough to generate high concentrations of the semiquinone radicals followed by disproportionation. Assuming that another reason may be the mobility of the molecules in the mixed crystals, the results (Table 5) that the high photoreactivity of the mixed crystals with **a** (79 °C) or **b** (54 °C) having a low melting point is reasonable. In fact the reactivity of the mixed crystals **1/c** and **3/c** with **c** having a high melting point of 167°C was low.

Irradiation of quinones **1**–**3** with durene **a** in acetonitrile was carried out for a comparison (Table 6). We have reported[7] that irradiation of a solution of **3** and **a** in acetonitrile or benzene did not give durohydroquinone **7** but other two products.[22] However, photoreaction of **1** and **2** with **a** in acetonitrile caused hydrogen abstraction to give **5** and **6**, respectively.

In conclusion, irradiation of the molecular crystal between duroquinone and durene causes intermolecular hydrogen abstraction in the crystal lattice to give hydroquinone and two adducts. In the case of the simple mixtures of benzoquinones and polymethylbenzenes similar hydrogen abstraction occurs at the interface of the component crystallites.

EXPERIMENTAL SECTION

General procedure

^{1}H NMR spectra were measured on a 60 MHz JEOL PMX-60 spectrometer with tetramethylsilane as an internal standard. Solid-state ^{13}C CP-MAS NMR spectra were taken on a Bruker MSL-200 specrometer by using glycine as an external standard. IR specra were recorded on a JASCO FT/IR-8300 spectrophotometer. UV and fluorescence spectra were measured on a Shimadzu UV-3100 spectrophotometer and an RF-5000 spectrofluorophotometer, respectively. Powder X-ray diffractograms (PXD) were taken on a Rigaku Geigerflex by using a Cu-target X-ray tube equipped with RAD-C system. Differential scanning calorimetry (DSC) was done on a Rigaku Thermoflex TAS-200 DSC8230D and melting points were not corrected. HPLC with a photodiode-array detector were used for determining the products on a Waters HPLC system (C_{18} column, MeOH-H_2O). All the reagents employed were commercially available.

Preparation of mixed crystals

Mixed crystals were prepared by melting 1:1 mixtures of **1**–**3** and **a**–**c** followed by resolidifying and pulverizing in a mortar. The mixed crystals were characterized by PXD, IR and DSC. Preparation of a single crystal **4** by slow evaporation of the solution of **3** and **a** in ethyl acetate has already been described.[7] A large size (30 x 8 i.d.mm) of the single crystal **4** was also prepared by the Bridgeman method under the following conditions; upper heating bath (silicone oil) at 114°C, lower cooling bath (glycerol) at 28°C, taking down rate of the glass tube packed of **4** at about 2 cm per day and final annealing at 65°C for 2 days.

Solid-state photoreaction

Twenty mg of a pulverized mixed crystal was placed between two Pyrex glass plates and irradiated with a 400 W high-pressure mercury lamp under argon at 10°C for 24 h. A 500 W xenon short arc lamp was also used with or without a filter to examine the wavelength dependence of the product selectivity. Irradiated mixed crystals were analyzed by HPLC. Yield of product **13** was calculated from the weight after filtration.

Irradiation of **2** (500 mg) in a preparative scale with a 400 W high-pressure mercury lamp under argon at 10°C for 24 h followed by filtration and column chromatography (silica gel, benzene-ethyl acetate) gave dimer **12** in 8% yield. The residue was washed with ethyl acetate and dried to give white solid in 31% yield, which was identified to be box-dimer **13** by the decomposition at about 250°C and the IR(KBr) 1700, 1715 cm^{-1}.[13] **12**: m.p. 174°C (from ethyl acetate); ^1H NMR ($CDCl_3$) consistent with the literature,[12] δ 6.89 (q, J=1.5 Hz, 1H), 6.56 (q, J=1.5 Hz, 1H), 6.07 (q, J=1.5 Hz, 1H), 3.94 (s, 1H), 2.27 (d, J=1.5 Hz, 3H), 2.06 (d, J=1.5, 3H), 1.79 (d, J=1.5 Hz, 3H), 1.70 (s, 3H); IR(KBr), 2990, 2990, 1675, 1645, 1625, 1460, 1375, 1275, 1155, 985, 960, 900, 760 cm^{-1}.

Preparative solid-state photoreaction of **4** (500 mg) with a 400 W high-pressure mercury lamp under argon at 10 °C for 24 h followed by preparative HPLC separation gave an adduct **8** in 6% yield. **8**: white crystal, m.p. 138-139 °C; ^1H NMR (acetone-d_6) δ 7.15(s, 1H), 6.84 (s, 1H), 4.52 (s, 2H), 2.23 (s, 3H), 2.14 (s, 6H), 2.09 (s, 12H); IR (KBr) 3400, 2910, 1460, 1250, 1075, 895 cm^{-1}; UV (MeOH) λ_{max} 278 nm. Analysis calculated for $C_{20}H_{26}O_2$: C, 80.50, H, 8.78%. Found: C, 80.48, H, 8.78%. Another preparative irradiation of **4** (1110 mg) with a 500 W xenon short arc lamp under agron at 10 °C for 20 h followed by removal (700 mg) of the starting **3** by crystallizing from THF–MeOH and preparative HPLC separation of the filtrate gave an adduct **9** in 7% yield. **9**: colorless stickey liquid, ^{1}H NMR ($CDCl_3$) δ 1.73-2.12 (m, 21H), 2.40 (s, 1H), 2.93 (s, 2H), 6.53 (s, 1H), 6.73 (s, 1H); IR (KBr) 3416, 2922, 1666, 1614, 1509, 1453, 1375, 1034, 871, 755 cm^{-1}; UV (MeCN) λ_{max} 218 (sh, log ε 4.13), 244 nm (4.02). Analysis calculated for $C_{20}H_{26}O_2$: C, 80.50, H, 8.78%. Found: C, 80.73, H, 8.78 %.

Irradiation of the mixed crystal **3/b** in a preparative scale (500 mg) with a 400 W high-pressure mercury lamp under argon at 10°C for 24 h followed by HPLC separation gave two adduct **10** and **11** in the same 3% yields. **10**: m.p. 128.9-131.2°C; ^{1}H NMR (acetone-d_6) δ 6.72-6.79 (m, 1H), 4.91 (s, 1H), 4.85 (s, 1H), 2.30 (s, 3H), 2.20 (s, 9H), 2.11 (s, 6H), 2.05 (s, 6H); IR (KBr), 3410, 2910, 1462, 1242, 1075, 955, 860 cm^{-1}. Analysis calculated for $C_{21}H_{28}O_2$: C, 80.72; H, 9.03%. Found: C, 79.72; H, 8.97%. **11**: m.p. 145.8-147.3°C; ^{1}H NMR (acetone-d_6) δ 7.10 (s, 1H), 4.61 (s, 2H), 2.26 (s, 6H), 2.19 (s, 6H), 2.15 (s, 12H); IR (KBr), 3400, 2920, 1455, 1245, 1076, 960, 872, 760 cm^{-1}. Analysis calculated for $C_{21}H_{28}O_2$: C, 80.72; H, 9.03%. Found: C, 79.35; H, 8.75%. Slightly low contents of carbon analyzed in **10** and **11** may be due to some impurity because of no further purification after preparative HPLC separation; they were not very stable and decomposed gradually in air.

Solution photoreaction

An acetonitrile solution (10 ml) containing **1–3** (0.05 M) and **a** (0.05 M) in a Pyrex test tube was irradiated with a 400 W high-pressure mercury lamp under argon-bubbling at 10°C for 24 h. The irradiated solution was analyzed by HPLC. A quinone solution containing no polymethylbenzenes was irradiated for comparison.

2,5-Xylohydroquinone **6** as an HPLC standard was prepared by external irradiation of 0.1 M 2,5-xyloquinone in ethanol (15 ml) with a 400 W high-pressure mercury lamp for 50 h under argon bubbling at room temperature, followed by filtration and recrystallization from ethyl acetate-benzene.[23]

X-Ray crystallographic analysis

Crystal data for **8**:[7] $C_{30}H_{38}O_4$ (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 0.3 x 0.4 x 0.3 mm, with an Enraf-Nonius CAD4 diffractometer, Mo K α radiation, by ω –2 θ scans in the range $2° \leq \theta \leq 23°$ and 3215 observed [I>3 σ (I)] reflections of the total 11247 independent reflections were corrected for LP factors. Structure solution was done 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.

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