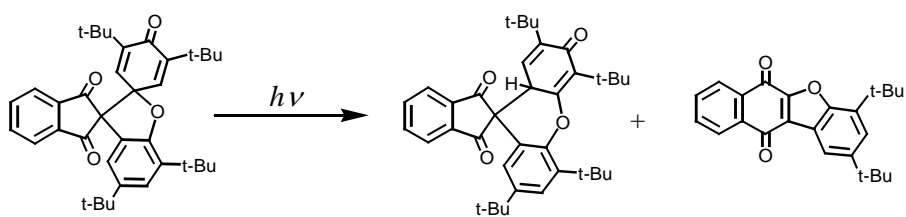


Graphical Abstract



Photorearrangements in Spiro-Conjoined Cyclohexa-2,5-dien-1-one

Masaya Suzuki,^a Kazunori Imai,^a Hidetsugu Wakabayashi,^a Atsuko Arita,^b Kohei Johmoto,^b Hidehiro Uekusa^b and Keiji Kobayashi^{a,*}

^a*Department of Chemistry, Graduate School of Material Science, Josai University
Keyakidai, Sakado, Saitama 350-0295, Japan*

^b*Department of Chemistry and Material Science, Tokyo Institute of Technology, Ookayama,
Meguro-ku, Tokyo 152-8551, Japan*

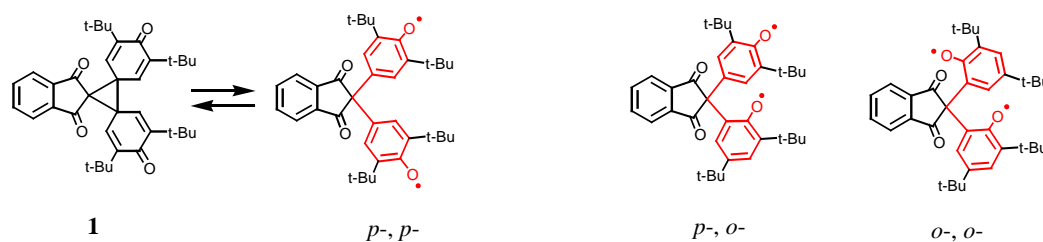
Abstract— The unexpected formation of cyclohexa-2,5-dien-1-one (**6**) spiro-conjoined with a dihydrobenzofuran framework, and the photochemical behavior of this compound in solution as well as in the solid state are described. The photoreaction of **6** in solution affords two rearranged products, one (**7**) accompanied by the enlargement of the oxygen heterocyclic ring and the other (**8**) accompanied by cyclopentadienone fragmentation. In the solid state, the former is the sole photoproduct of both solvated and desolvated crystals. The desolvated crystals were obtained as polycrystalline solids by thermal release of solvent molecules, and its structure was elucidated by ab initio determination from X-ray powder diffraction data followed by the Rietveld refinement.

Keywords: Solid-state Photoreaction, Photorearrangement, Solvate Crystal, X-ray Powder Diffraction, Rietveld refinement,

1. Introduction

Diradicals are a focus of increasing interest because of their importance in gaining an understanding of spin-spin interactions.¹ Recently, we have reported interesting dynamic behavior that involves bond dissociation and regeneration via diradical species;² the cyclopropane ring of compound **1** has been found to exist in solution in fast equilibrium with diradicals via the dissociation of the C-C bond of trispiro-conjoined cyclopropane. In the solid state, on the other hand, **1** exhibits slow interconversion between ring-opened and ring-closed forms. Thus, when heated to 180 °C, **1** undergoes homolytic bond dissociation to generate a diradical, which persists and gradually regenerates the cyclopropane ring as temperature is decreased. This cycle of reversible bond dissociation and recombination via a diradical is accompanied by a color change. The diradical derived from **1** consists of two bisphenoxy radicals in which the fundamental framework bearing the radical centers is bis(*p*-hydroxyphenyl)methane (*p,p*-isomer). Thus, it is interesting to determine whether similar dynamic behavior to that observed in the *p,p*-isomer occurs

in *o*, *p*- and *o*, *o*-isomeric forms (Scheme 1). In this context, we have prepared their possible precursor compounds and investigated their photochemical and thermal properties, particularly in the solid state. Herein, we describe unusual photoinduced rearrangements in spirocyclohexadienone compound **6** occurring not only in solution but also in the solid state. For the latter, solvated and desolvated crystals were used to gain insight to the comparative photoreactivity upon solid-state irradiation.

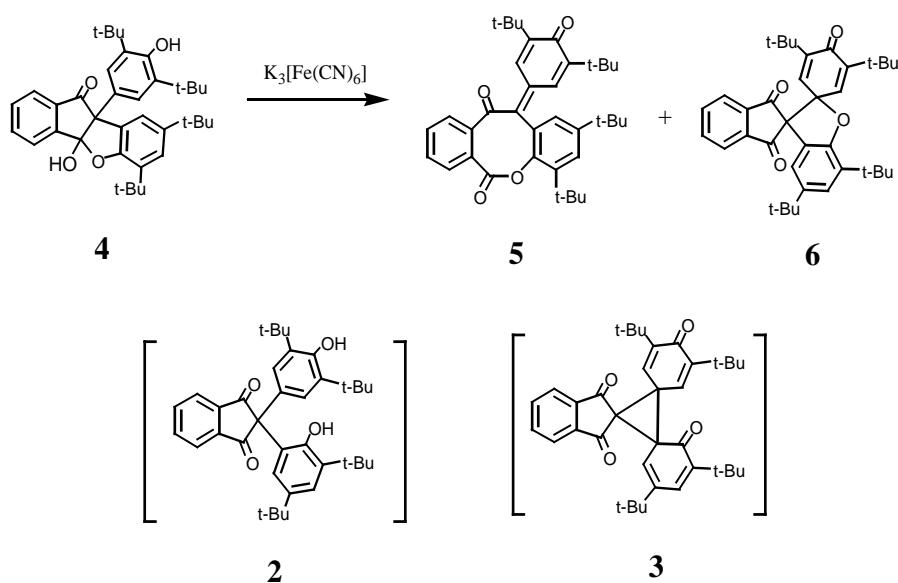


Scheme 1. Isomeric diradicals based on bis(hydroxyphenyl)methane.

2. Results and discussion

2.1. Preparation of precursor for *p*,*o*- isomer

As a possible precursor for the generation of *p*, *o*-diradicals, we chose 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1H-indene-1,3(2H)-dione (**2**), which is expected to afford cyclopropane compound **3** by oxidation similarly to **1**. Compound **2** was prepared by the reactions of ninhydrin with 2,6-di-*tert*-butylphenol and then with 2,4-di-*tert*-butylphenol. The product actually has an intramolecular hemiacetal structure, **4**, rather than the expected dihydroxyphenyl structure.³ Compound **4** was oxidized by potassium hexacyanoferrate (III) in a similar reaction to that for **1**. The product, however, was not the cyclopropane compound **3**, but the ring-expanded lactone **5** (52%) and the spiro-conjoined cyclohexa-2,5-dien-1-one **6** (24%) (Scheme 2). The oxidation of (*p*-hydroxyphenyl)(*o*-hydroxyphenyl)methane compounds has been known to frequently afford spiro-cyclohexadienone compounds.⁴ Therefore, **4** is assumed to exist in equilibrium with the ring-opened form which could be oxidized to afford **6**.



Scheme 2. Oxidation of **4**.

The structures of **5** and **6** were elucidated by $^1\text{H-NMR}$ and mass spectrometry and confirmed by X-ray analysis (Figs. 1 and 2). The quinonoid compound **5**, an orange solid, exhibits two sets of two doublets weakly coupled to each other and four methyl signals due to the *tert*-butyl groups along with multiplets for four aromatic protons. In the X-ray crystallographic analysis, appreciable thermal motion in the *tert*-butyl groups of the benzene ring was observed, however, the results clearly indicate the structure of **5**. The eight-membered ring is distorted into a tub structure with an $\text{O}=\text{C}---\text{C}=\text{C}$ torsional angle of 49.54° . On the other hand, the dihedral angle of $\text{C}(\text{ph})-\text{C}(=\text{O})---\text{O}-\text{C}(\text{ph})$ is 10.63° .

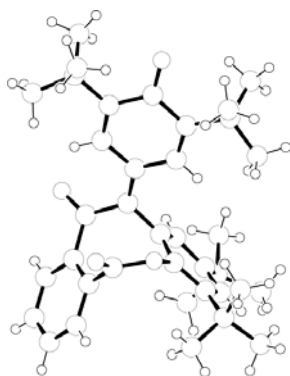


Figure 1. X-ray structure of **5**.

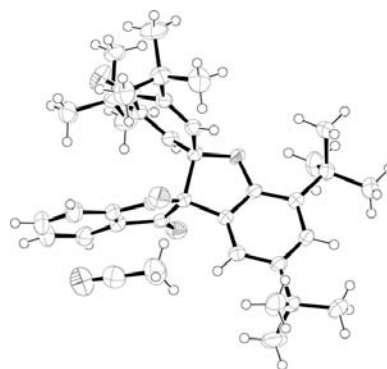
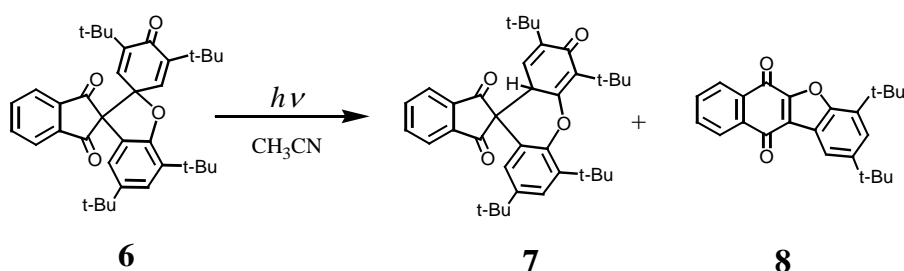


Figure 2. X-ray structure of acetonitrile solvate crystal of **6**.

Single crystals of **6** suitable for X-ray studies were obtained by the slow evaporation of the solvent from acetonitrile solution. X-ray analysis revealed that the crystals are solvated by MeCN molecules in a ratio of **6**:MeCN = 1:1. These solvent molecules are embedded in a channel-like column and not released after five days at room temperature. The ^1H NMR spectrum of **6** at room temperature and even at high temperatures showed no evidence that dynamic molecular motion occurs in **6**. When **6** was heated to above its melting point (234 °C), no decomposition was observed. We carried out a photoreaction of **6**, expecting to find a photoreaction via the *p*, *o*-isomeric bis(phenoxy) radical, which would be formed if the single bond connecting the spiro carbon and oxygen atoms undergoes hemolytic bond cleavage.

2.2 Photolysis in solution

An acetonitrile solution of compound **6** (ca 1.2 mmol/L) was irradiated with a high-pressure mercury lamp through a Pyrex filter under nitrogen at room temperature. Distinct photoreactions were induced as probed by the ^1H NMR analysis of the reaction mixture, which clearly shows two photoproducts, i.e., **7** and **8**, along with starting compound **6** in a ratio of **7** : **8** : **6** = 1 : 2 : 3 (Scheme 3). The photoproduct **8** was isolated by gel permeation chromatography (GPC) and its structure was elucidated by NMR and mass spectrometry. The ^1H NMR spectrum exhibited a set of AA'BB' signals in the aromatic region due to four protons and two slightly coupled doublets attributed to a 1,2,3,5-tetra-substituted benzene ring. The chemical shifts of these latter signals are in fair agreement with those reported for a similar benzoquinone-fused benzofuran derivative.⁵ Eventually, the structure of **8** was confirmed by X-ray analysis. Although the results are not good enough to provide accurate structural parameters because of the poor crystallinity of the single crystal employed for data collection, they are still satisfactory for revealing the gross structure of **8**.



Scheme 3. Photoreaction of **6**.

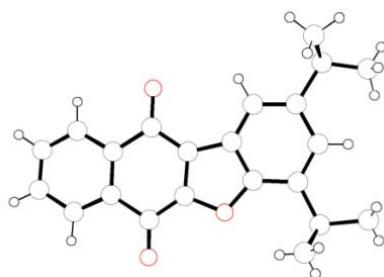


Figure 3. X-ray structure of **8**.

On the other hand, the separation of **6** and **7** could neither be achieved by GPC even after 10 cycles nor by recrystallization from various solvents. The structure of **7** was elucidated on the basis of the spectral data from a sample in which **6** and **7** coexist. The mass spectrum of this sample was not distinguishable from that of pure **6**, indicating that the concomitant photoproduct is an isomer of **6**. In Fig. 4, the ^1H NMR spectrum of the sample is shown, for which the signals attributed to **7** are indicated by asterisks. The ^1H signal at 2.98 ppm, which is assigned to the methine proton, is weakly coupled to the signal at 7.06 ppm ($J=3.6$ Hz), indicating the presence of the CH-CH=C framework. In ^{13}C NMR, at least 28 signals are assigned to photoproduct **7** by eliminating 21 signals due to **6**. These include the signals due to three carbonyl carbons (202.0, 200.0 and 192.9 ppm) and the *quart*- and *tert*-carbons at the spiro-conjoined positions (63.9 and 50.8 ppm, respectively). In the IR spectrum, an OH stretching band was not observed. On the basis of these results, the structure of the photoproduct was determined to be **7**, which includes the partial structure of the keto form of a phenol. It is rather surprising that **7** fails to undergo enolization by treatment with acid, although there have been many examples of such rearrangements that are known as cyclohexadienone-phenol rearrangements.⁶

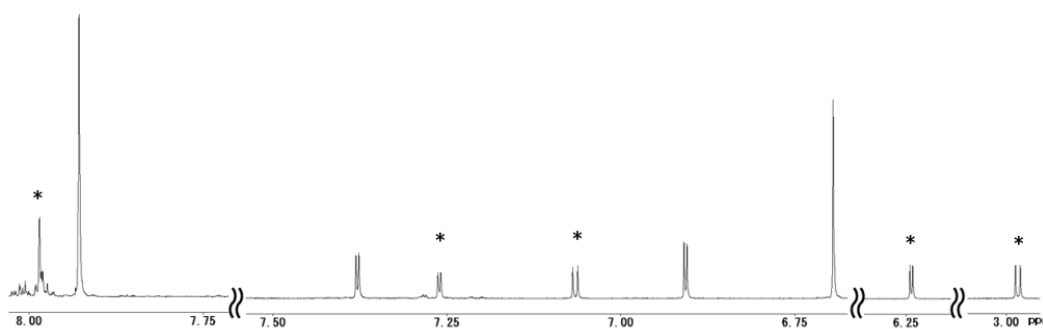
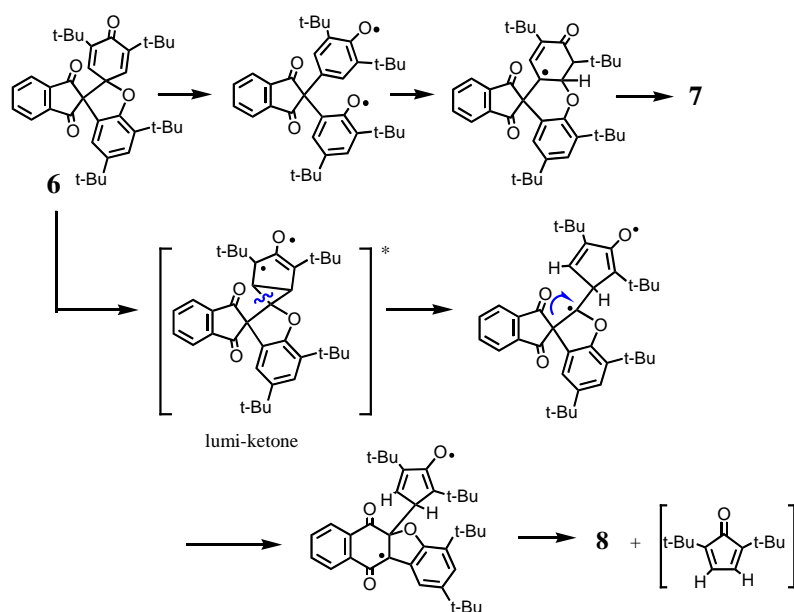


Figure 4. NMR spectrum (in CD_3CN) of photoproduct **7** coexisting with **6**. Signals due to **7** are indicated by asterisks (*). The methyl protons of *tert*-butyl groups are outside this scale.

A plausible mechanism of the photorearrangement of **6** to **7** involves the homolytic cleavage of the C-O bond of the five-membered oxygen ring to form the *p*-, *o*- diradical isomer shown in Scheme 1. The recombination of the diradical to furnish the six-membered ring followed by hydrogen migration results in the formation of **7**. The carbon-oxygen bond linked to the 4 position of cyclohexa-2,5-dien-1-one has been known to undergo direct photochemical cleavage.⁷ Alternatively, as observed in the photochemistry of 2,4,6-tri-*tert*-butyl-4-methoxy-cyclohexadienones,⁸ the photoexcited transformation to a bicyclo[3.1.0]hexanone framework would be involved.⁹ This latter mechanism also accounts for the formation of **8** as shown in Scheme 4. Thus, the formation of **8** could be rationalized analogously to the photoreaction of 4-*tert*-butylperoxy-4-methyl-2,6-di-*tert*-butylcyclohexadienone, wherein 1,5-di-*tert*-butylcyclopentadienone is formed via a lumiketone-type intermediate followed by radical rearrangement.¹⁰ Such a photoprocess for **6** would result in the elimination of the 2,5-di-*tert*-butylcyclopentadienone fragment. In the mass spectra of the photoreaction mixture, the molecular ion peak assignable to 2,5-di-*tert*-butylcyclopentadienone was detected at $m/z = 191$.



Scheme 4. Plausible reaction paths to **7** and **8**.

2.3 Photolysis in the solid state

Upon recrystallization from acetonitrile, **6** was obtained as solvate crystals including **6**:CH₃CN in a 1:1 ratio. The polycrystalline solid of **6** was held among Pyrex plates and irradiated with a mercury lamp at room temperature. After 3 h, the solid was dissolved in CDCl₃ and its NMR spectrum was recorded, which showed the existence of **7** as the sole product with a 15% yield; the other compound **8** obtained in solution photochemistry was not detected. The distinct photochemical behavior in the solid state from that in solution suggests that the lattice-controlled reaction is induced in the solid state.¹¹ The solvate acetonitrile was retained in the photoproduct after photoirradiation, as observed in the NMR spectrum.¹² XRD studies revealed the occurrence of haloes in the XRD profiles after photoirradiation (Fig. 5). This observation indicates that the solid-state reaction results in the collapse of the crystalline phase to form an amorphous phase in ca. 15% of the entire solid. This was also the case for photoirradiation of single crystals of **6**, although the conversion of **6** to **7** was as low as 5% after 48 h irradiation.

Single crystals of **6** became opaque when acetonitrile was released by heating to 80 °C. It was revealed on the basis of the XRD studies that the resulting solids were in a new crystalline phase (Fig. 5). Then, in order to examine the effect of crystal environment on the reaction, the solid-state photoreaction of desolvated **6** was also carried out. The result was the formation of **7** as a single product in ca. 10% yield after 40 h irradiation. The XRD profiles after photoirradiation again exhibited haloes. The conversion of **6** to **7** should be accompanied by an appreciable structural change that disturbs the crystalline environment around the reaction sites. A mismatching between the reactant and product in terms of molecular structure would induce a collapse to the amorphous phase at reaction sites.¹³

We were able to elucidate the crystal structure of desolvated crystals of **6** by ab initio structure determination from X-ray powder diffraction data followed by the Rietveld refinement, which entails refining the parameters of a structural model to supply a calculated X-ray powder diffraction pattern similar to the observed one.¹⁴ Figure 5(d) shows the Rietveld refinement plot for desolvated crystals of **6**. The molecular packing is similar before and after the loss of acetonitrile in the sense that the molecules are aligned along the *b*-axis (Fig. 6), although the space group changes from *P*-1 to *P*2₁. It is interesting to note that achiral solvate crystals are transformed into chiral crystals by elimination of solvent molecules; the molecules of **6** are in a chiral structure because of deformation of the five-membered oxygen heterocycle from a planar geometry. With the crystal structures of solvated and desolvated **6** in hand, we carried out a comparative investigation of their photoreactivity, considering that solid state reactions under lattice control depend on the crystalline environment. The photoreactions were monitored by examining the decrease in IR absorbance at 1714 and 1647 cm⁻¹ upon the irradiation of the sample compressed in KBr pellets. However, the results were not

in agreement with our expectation, indicating that there are no appreciable differences in the reaction rate. It might be assumed, at least from this observation, that degradation of the crystalline state into an amorphous phase does not play a role in controlling the rate.

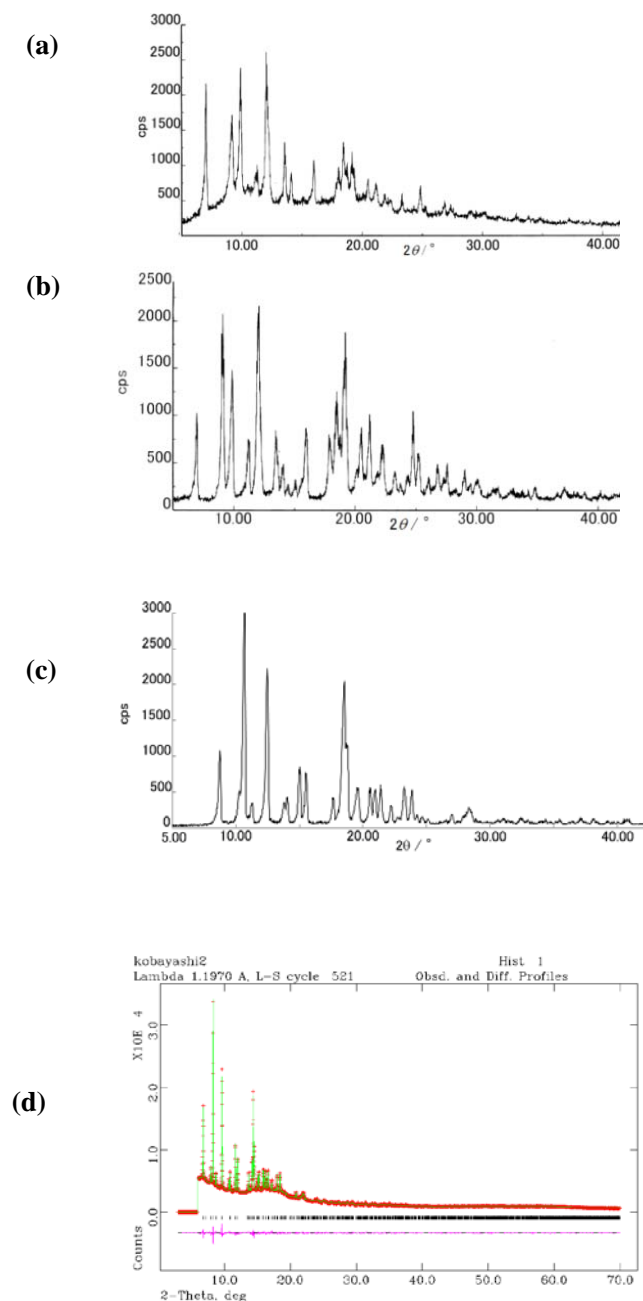


Figure 5. XRD profiles of **6**. (a) Solvate crystal of **6**·CH₃CN after photoirradiation, (b) solvated crystal of **6**·CH₃CN before photoirradiation, (c) desolvated solids of **6** obtained after heating, and (d) Rietveld refinement plot for desolvated **6**.

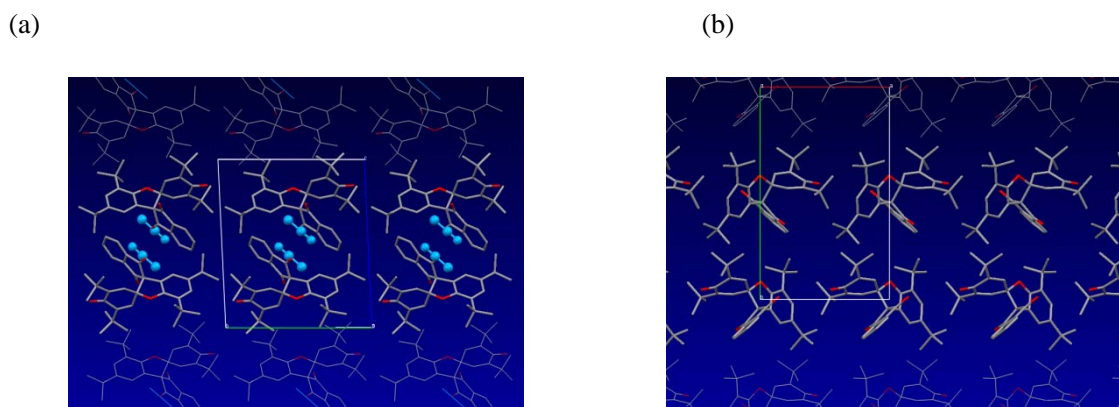


Figure 6. Crystal structures of (a) **(6)**(CH₃CN) and (b) desolvated **6**.

2.4. Attempted preparation of precursor of *o*-, *o*- isomer

In our attempts to synthesize the *o*-, *o*-diradical isomer, as represented in Scheme 1, 2,2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1H-indene-1,3(2H)-dione (**9**) was chosen as the appropriate precursor. To prepare **9**, ninhydrin was reacted with 2,4-di-*tert*-butylphenol in acetic acid in the presence of a small amount of sulfuric acid. Contrary to our expectation, the product was the benzofurane-condensed lactone **10** (20%). Although the reactions of ninhydrin with *p*-substituted phenols in the presence of ZnCl₂ have been reported to give this type of lactone,¹⁵ their structural characterization is unequivocal. We carried out an X-ray analysis of a single crystal obtained by recrystallization from benzene and unambiguously determined the structure of the product (Fig. 7). The crystal of **10** includes benzene molecules located in a channel running along the *a*-axis. The eight-membered ring has a tub structure with torsional angle of 42.06° for C-C—C-O.

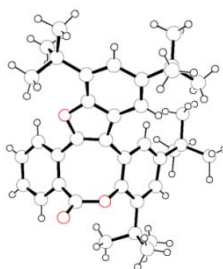
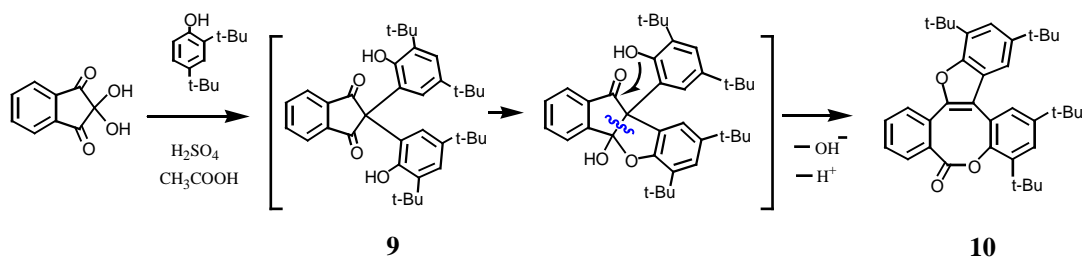


Figure 7. X-ray structure of **10**. Solvated benzene molecules are omitted for clarity

A plausible mechanism of the formation of **10** is shown in Scheme 5 and is based on analogous systems.¹⁶ Cleavage at the carbon-carbon bond of the intramolecular hemiacetal structure produces an eight-membered lactone ring, and acid-catalyzed hemiacetal formation at the carbonyl unit leads to the formation of a furan ring. In spite of all our effort including the use of milder reaction conditions, we could not isolate a hemiacetal intermediate.



Scheme 5. Plausible reaction path to **10**.

3. Conclusions

We have observed the unexpected formation of a novel cyclohexadienone compound incorporated in the dispiro framework upon the oxidation of intramolecular hemiacetal compounds. The photoirradiation of this compound in acetonitrile induced a rearrangement, resulting in the expansion of the oxygen heterocyclic ring, leaving the cyclohexadienone moiety intact. Another photoproduct was accompanied by the fragmentation of the cyclopentadienone skeleton to afford benzofuranonaphthoquinone. Photoirradiation in the solid state afforded only the former as a product of solvated crystals as well as of desolvated crystals, for which the crystal structure was determined by powder X-ray diffraction. In both solvated and desolvated crystals, the photoreaction induced an amorphous phase at the reacted sites.

4. Experimental

4-1. General

All melting points were determined using a Yanaco MS-500V apparatus and are uncorrected. The IR spectra were obtained on a Shimadzu FTIR-8200PC spectrometer. The ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded using a JEOL α -500

spectrometer. Chemical shifts are given in δ values (ppm) using TMS as the internal standard. Mass spectra were taken on a Shimadzu GCMS-QP5050A mass spectrometer. Elementary combustion analyses were recorded using a Yanaco CHN CORDER MT-6 analyzer. All reactions were monitored by TLC employing a 0.25 mm silica gel plate (Merck 60F 254). Gel permeation chromatography (GPC) was performed using two columns (GAIGEL 1H and 2H) on an LC-908 recycling preparative HPLC. Column chromatography was carried out on silica gel (Merck 60N spherical).

4-1-1: Preparation of 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1H-indene-1,3(2H)-dione (4)

To a solution of 2-hydroxy-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1H-indene-1,3(2H)-dione (3.0 g, 8.2 mmol) in acetic acid (30 mL) was added a small amount of *p*-toluenesulfonic acid (ca. 10 mg) and 2,4-di-*tert*-butylphenol (2.0 g, 9.8 mmol) at room temperature. The mixture was heated at reflux for 4 h. Aqueous work up, extraction with dichloromethane, and drying over anhydrous Mg_2SO_4 afforded a reddish solution. After the solvent was removed under reduced pressure, the resulting solids were washed with hexane for decoloration and recrystallized from acetonitrile to give **4** (4.2 g, 92 %) as a white solid.

4: M.p. 268-269 °C. IR (Nujol); 3630, 3298, 1701 cm^{-1} . ^1H NMR (CDCl_3); δ 1.24 (9H, s), 1.32 (18H, s), 1.37 (9H, s), 3.05 (1H, bs), 5.27 (1H, bs), 6.73 (2H, s), 7.20 (1H, d, $J=2.4$ Hz), 7.21 (1H, $J=2.4$), 7.55 (1H, t, $J=7.2$ Hz), 7.77 (1H, $J=7.0$ Hz), 7.87 (1H, d, $J=7.6$ Hz), 8.00 (1H, d, $J=7.9$). C^{13} NMR ($\text{DMSO-}D_6$); δ 29.06, 29.20, 30.23, 31.52, 33.98, 34.22, 34.96, 68.97, 69.30, 113.03, 120.17, 122.77, 124.56, 125.85, 126.01, 127.80, 130.54, 131.53, 134.80, 136.10, 137.82, 142.81, 151.89, 152.04, 152.86, 201.59. MS (m/z); 554(M^+), 539, 498. Anal. Calcd for $\text{C}_{37}\text{H}_{46}\text{O}_4$: C, 80.11; H, 8.36 %. Found: C, 79.08 ; H, 8.14%.

4-1-2. Oxidation of 4

To a solution of potassium hexacyanoferrate (III) (3.5 g) and sodium hydroxide (0.8 g) in 15 mL water was added **4** (1.0 g, 1.8 mmol) dissolved in CHCl_3 (50 mL) at 25 °C. The mixture was stirred for 1 h. After aqueous work up, extraction with chloroform (300 mL), drying over anhydrous Mg_2SO_4 , and evaporation of the solvent under reduced pressure, the residual solid was chromatographed on silica gel with benzene and dichloromethane as eluents to give **5** (0.52 g, 52%) and **6** (0.24 g, 24%).

2,4-di-*tert*-butyl-12-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)-11,12-dihydro-6H-dibenzo[b,f]oxocin-6,11-dione (5): reddish brown crystals. Mp 207-209 °C. IR (Nujol); 1747, 1664, 1624 cm^{-1} . ^1H -NMR (CD_3CN): δ 6.63 (1H, d, $J=2.6$ Hz), 7.15 (1H, d, $J=2.4$ Hz), 7.43 (1H,

d, $J=2.6$ Hz), 7.51 (1H, d, $J=2.3$ Hz), 7.53 (1H, m), 7.66 (2H, m), 7.80 (1H, m). MS (m/z); 552 (M^+). Anal. Calcd for $C_{37}H_{44}O_4$: C, 80.45; H, 7.97 %. Found: C, 80.08 ; H,8.11%.

3,5,5',7'-tetra-tert-butylspiro[[2,5]cyclohexadiene-1,2'-[2,3]dihydrobenzofuran-3',2''-[2H]indene]-1'',3'',4-trione (6): yellow crystals. Mp 234 °C. IR (Nujol); 1714, 1672, 1647 cm^{-1} . 1H NMR ($CDCl_3$): δ 1.04 (18H, s), 1.25 (9H, s), 1.43 (9H, s), 6.65 (1H, d, $J=1.8$ Hz), 6.75 (2H, s), 7.31 (1H, d, $J=1.8$ Hz), 7.84 (2H, dd, $J=3.1$ Hz, $J=3.1$ Hz), 7.93 (2H, dd, $J=3.1$ Hz, $J=3.1$ Hz). ^{13}C -NMR ($CDCl_3$): δ 28.95, 29.32, 31.66, 34.46, 34.62, 34.82, 73.77, 85.57, 119.24, 123.59, 124.60, 124.82, 133.38, 136.18, 137.44, 142.86, 144.60, 147.56, 156.43, 185.34, 196.90. MS (m/z); 552 (M^+). Anal. Calcd for $C_{37}H_{44}O_4$: C, 80.45; H, 7.97 %. Found: C, 80.56 ; H,8.24 %.

4-2. Photoreaction of 6

An acetonitrile solution of compound **6** (1.2 mmol/L) was irradiated with a high-pressure Hg lamp (Riko UVL-400HA) through a Pyrex filter under nitrogen at 0°C. After irradiation for 1 h the solvent was removed under reduced pressure without heating. The resulting residue was chromatographed on GPC (JAL-gel, GPL) to afford two fractions; one, a mixture of **6** and **7**, and the other, **8**. The percent conversion was determined by NMR of the crude reaction mixture after evaporation.

Solid state irradiation was carried out for samples (ca. 25 mg) held between Pyrex glasses or dispersed in compressed KBr pellets under atmospheric environment at room temperature. The irradiated solids were dissolved in $CDCl_3$ for analysis by NMR. The IR spectra were obtained from KBr pellets on a BioRad FTS-3000 FT-IR spectrophotometer.

2',4',5',7'-tetra-tert-butyl-3-hydroxy-spiro[[2H]indene-2,9'-[9H]xanthene]-1,3-dione (7) -- keto form: By subtracting the signals due to **6** in 1H and ^{13}C NMR spectra the following signals are assignable to **7**. 1H NMR (CD_3CN): δ 0.49 (9H, s), 1.02 (9H, s), 1.08 (9H, s), 1.40 (9H, s), 2.98 (1H, d, $J=3.6$ Hz), 6.24 (1H, d, $J=1.9$ Hz), 7.06 (1H, d, $J=3.6$ Hz), 7.26 (1H, d, $J=1.9$ Hz), 8.00 (4H, m). ^{13}C NMR ($CDCl_3$): δ 202.0, 200.0, 192.9, 154.5, 153.5, 151.2, 144.6, 143.0, 140.8, 136.7, 135.8, 132.4, 125.2, 124.1, 123.5, 115.6, 63.9, 50.8, 34.4, 34.2, 32.5, 32.1, 29.3, 28.7, 27.4, 26.2. Anal. Calcd for $C_{37}H_{44}O_4$: C, 80.45; H, 7.97 %. Found: C, 80.72; H,7.88 %.

2,4-di-tert-butylbenzo[b]naphtho[2,3-d]furan-6,11-dione (8): 1H NMR (CD_3CN): δ 1.51 (9H, s), 1.43 (9H, s), 7.64 (1H, d, $J=2.1$ Hz), 7.84 (2H, m), 8.10 (1H, d, $J=2.1$ Hz), 8.18 (2H, m). ^{13}C NMR ($CDCl_3$): δ 29.96, 31.69, 34.75, 35.26, 117.47, 123.14, 124.27, 124.50, 126.64, 126.81, 132.61, 133.40, 133.72, 133.95, 135.70, 149.53, 153.20, 153.47, 175.25, 181.88. MS (m/z); 360

(M⁺), 344. Anal. Calcd for C₂₄H₂₄O₃: C, 80.00; H, 6.67 %. Found: C, 80.26 ; H, 6.29 %.

4-3. Reaction of ninhydrin with 2,4-di-*tert*-butylphenol

To a solution of ninhydrin (3.02 g, 17 mmol) in acetic acid (30 mL) was added 2,4-di-*tert*-butylphenol (6.97 g, 34 mmol) and a drop of conc sulfuric acid. The mixture was heated at reflux for 4 h. Aqueous work up, extraction with dichloromethane (300 mL), and drying over anhydrous Mg₂SO₄ afforded a reddish solution. After the solvent was removed under reduced pressure, the resulting solids were chromatographed on silica gel with benzene as eluent to give **10** (1.82 g, 20%).

2,4,12,14-tetra-*tert*-butyl-6H-dibenzo[b.f]benzofuro[3,2-d]oxocin-6-one (10): Mp 216-217 °C. IR (Nujol); 1732, 1248 cm⁻¹. ¹H NMR (CDCl₃): δ 6.61 (1H, d, *J*=1.8 Hz), 6.80 (1H, q, *J*=1.5 Hz), 6.87 (1H, d, *J*=3.1 Hz), 7.28 (1H, *J*=1.8 Hz), 7.89 (4H, m). MS (m/z); 536 (M⁺). Anal. Calcd for C₃₇H₄₄O₃: C, 82.78; H, 8.18 %. Found: C, 82.26 ; H,8.04 %.

4-4. Single-crystal X-ray crystallography

X-ray crystallographic data were collected at cryogenic temperature (-50 °C) for **6** and at ambient temperature for others on a Rigaku-RAPID imaging plate two-dimensional area detector using graphite monochromatized Mo-Kα radiation(λ =0.71073 Å). All crystallographic calculations were performed using CrystalStructure crystallographic software.¹⁷ Crystal data have been submitted to CCDC, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

Crystal data for **5**: C₃₇H₄₄O₄, *P*-2₁/*c* (#14), *a*=9.4641(9), *b*=24.3590(20), *c*=14.6422(11) Å, β=104.825(3) °, *V*=3263.2(5) Å³, *Z*=4, *D*_{calc}=1.125 g/cm³, *R*₁=0.1241, *wR*₂=0.3521, CCDC-813921. Crystal data for (**6**)(CH₃CN): C₃₉H₄₇O₄N, *P*-1(#2), *a*=9.7554(5), *b*=12.5742(5), *c*=14.6696(8) Å, α=85.6750(15), β=77.3860(15), γ=82.0220(14) °, *V*=1737.13(14) Å³, *Z*=2, *D*_{calc}=1.135 g/cm³, *R*₁=0.0467, *wR*₂=0.1520, CCDC-813922. Crystal data for **8**. C₂₄H₂₄O₃, *Pnma* (#62), *a*=15.1070(13), *b*=7.1473(5), *c*=18.1696(14) Å, *V*=1961.9(3) Å³, *Z*=4, *D*_{calc}=1.220 g/cm³, *R*₁=0.1231, *wR*₂=0.1924. CCDC-813923. Crystal data for (**10**)₂(benzene)₃: C₄₆H₅₃O₃, *P*-1(#2), *a*=9.57324(5), *b*=15.2267(7), *c*=15.2332(7) Å, α=66.0570(9), β=77.3180(15), γ=84.2820(16) °, *V*=1979.83(16) Å³, *Z*=2, *D*_{calc}=1.097 g/cm³, *R*₁=0.1097, *wR*₂=0.2720, CCDC-813924.

4-5. Powder X-ray diffraction

The synchrotron X-ray powder diffraction data for the polycrystalline sample of the desolvated **6** were recorded at ambient temperature on beamline 4B2 (parallel beam optics) at the PF synchrotron facility using a wavelength of 1.197040(7) Å. The sample was loaded into a borosilicate glass capillary (2.0 mm diameter) and was used for the diffraction measurement in transmission mode. The powder X-ray diffraction pattern was indexed using the program DICVOL04.¹⁸ The structure solution was carried out using the simulated annealing method incorporated in the program DASH.¹⁹ The best structure obtained in the structure solution calculation was used as the initial structural model for Rietveld refinement, which was carried out using the GSAS program.²⁰

Crystal data for **6**: C₃₇H₄₄O₄, P2₁ (#4), monoclinic, *a*=10.3569(3), *b*=16.5705(4), *c*=9.7932(4) Å, β =102.5746(1) °, *V*=1640.39(10) Å³, *Z*=2, *D*_{calc}=1.119 g/cm³, R_p=0.0215, R_{wp}=0.0287, CCDC-818653..

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research (C) from MEXT (Nos. 21550048 and 21550008). Part of this work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2009G658).

References and notes

1. (a) *Diradicals*; Borden, W. T., Ed.: Wiley, New York, 1982; (b) Rajca, A. *Chem. Rev.* **1994**, *94*, 871; (c) Adam, W.; van Barneld, C.; Emmert, O.; Harrer, H. M.; Kita, F.; Kumar, A. S.; Maas, W.; Nau, W. M.; Reddy, S. H. K.; Wirz, J. *Pure Appl. Chem.* **1997**, *69*, 735.
2. Kiyohara, S.; Ishizuka, K.; Wakabayashi, H.; Miyamae, H.; Kanazumi, M.; Kato, T.; Kobayashi, K. *Tetrahedron Lett.* **2007**, *48*, 6877.
3. (a) Hashimoto, S.; Sakuma, N.; Wakabayashi, H.; Miyamae, H.; Kobayashi, K. *Chem. Lett.* **2008**, *37*, 696; (b) Das, S.; Frohlich, R.; Pramanik, A. A. *Org. Lett.* **2006**, *8*, 4263; (c) Na, J. E.; Lee, K. Y.; Seo, J.; Kim, J. N.; *Tetrahedron Lett.* **2005**, *46*, 4505.
4. (a) Tsuge, O.; Watanabe, H.; Kanemasa, S. *Chem. Lett.* **1984**, 1415; (b) Dean, F. M.; Herbin, G. A.; Matkin, D. A.; Price, A. W.; Robinson, M. L. *J. Chem. Soc. Perkin Trans. 1*, **1980**, 1986; (c) Bennett, D. J.; Dean, F. M.; Herbin, G. A.; Matkin, D. A.; Price, A. W.;

- Robinson, M. L. *J. Chem. Soc., Perkin Trans. 1*, **1980**, 1978; (d) Feringa, B. Wynberg, H.; *Tetrahedron Lett.*, **1977**, 447; (e) Katoh, T.; Ohmori, O.; Iwasaki, K.; Inoue, M. *Tetrahedron*, **2002**, 58, 1289.
5. Tashiro, M.; Yoshiya, H.; Fukata, G. *J. Org. Chem.* **1981**, 46, 3784.
 6. Frimer, A. A. ; Marks, V.; Sprecher, M.; Gilinsky-Sharon, P. *J. Org. Chem.* **1994**, 59, 1831. and refereces cited there.
 7. (a) Taub, D.; Kuo, C. H.; Slates, H. L.; Wender, N. L. *Tetrahedron*, **1963**, 19, 1; (b) Hewgill, F. R.; Raston, C. L.; Skelton, B. W.; Webb, R. J.; White, A. H. *Aust. J. Chem.* **1983**, 36, 1603.
 8. (a) Matsuura, T.; Ogura, K. *J. Am. Chem. Soc.* **1967**, 89, 3846; (b) Matsuura, T.; Meng, J-B.; Ito, Y.; Irie, M.; Fukuyama, K. *Tetrahedron*, **1987**, 43, 2451.
 9. (a) Schaffner, K.; Demuth, M. in *Rearrangements in Ground and Excited States* vol. 3, de Mayo, P. Ed, Academic Press, New York, 1980, pp 281-348; (b) Schultz, A. G. *Pure Appl. Chem.* **1988**, 60, 981. (c) Schuster, D. I. *Acc. Chem. Res.* **1978**, 11, 65.
 10. (a) Lind, H.; Winkler, T.; Loeliger, H. *J. Polym. Sci. Part C*, **1976**, 225; (b) Zimmerman, H. E.; Keese, R.; Nasielski, J.; Sweton, J. S. *J. Am. Che. Soc.* **1966**, 88, 4895.
 11. The NMR analysis could not reveal if acetonitrile molecules were retained in the amorphous region where the reactions took place. It would be reasonable to assume that the solvate has been lost in such a region.
 13. Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, 6, 217.
 14. Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, 2, 65.
 15. Roussey, J-C.; Laude, B. *C. R. Acad. Sc., Ser. C*, **1979**, 288, 225.
 16. Das, S.; Frohlich, R.; Pramanik, A. *Synlett*, **2006**, 207.
 17. CrystalStructure, Ver.3. 7, Rigaku Corporation, Tokyo, 2005.
 18. (a) Boultif, A; Louer, D. *J. Appl. Crystallogr.* **1991**, 24, 987; (b) Boultif, A.; Louer, D. *J. Appl. Crystallogr.* **2004**, 37, 724.
 19. David, W. I. F.; Shankland, K.; van de Streek, J.; Pidcock, E.; Motherwell, W. D. S.; Cole, J. C. *J. Appl. Crystallogr.* **2006**, 39, 910.
 20. Larson, A. C.; Von Dreele, R. B. GSAS, Los Alamos Laboratory Report No. LA-UR-86-748, 1987, 19.