Reactions of lithium phenylacetylenide and lithium 3,3-dimethylbut-1-ynide with 3,6-di-*tert*-butyl-1,2-benzoquinone. Molecular structure of 2,5-di-*tert*-butyl-8-(3,6-di-*tert*-butyl-1,2-benzoquinon-4-yl)-8-phenylocta-2,4,6,7-tetraen-1,6-olide

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Reactions of 3,6-di-*tert*-butyl-1,2-benzoquinone with PhC≡CLi and Bu^{t}C≡CLi are multistage processes. In the first stage, nucleophilic 1,2-addition of the organometallic compound to *o*-benzoquinone occurs to form the corresponding hydroxycyclohexadienone derivative. In polar solvents, the latter undergoes rearrangement through insertion of the oxygen atom into the ring to form a new allenic organolithium compound. The reaction of the newly formed organometallic compound with the initial *o*-quinone occurs either as a one-electron transfer to yield lithium semiquinolate and a dimerization product, *viz.*, 4,4′-bi(2,5-di-*tert*-butyl-9,9-dimethyldeca-2,5-dien-7-yn-1,6-olide), or as the 1,4-addition to yield 2,5-di-*tert*-butyl-8-(3,6-di-*tert*-butyl-1,2-benzoquinon-4-yl)-8-phenylocta-2,4,6,7-tetraen-1,6-olide. The structure of the latter compound was established by X-ray diffraction analysis and by NMR and IR spectroscopy.

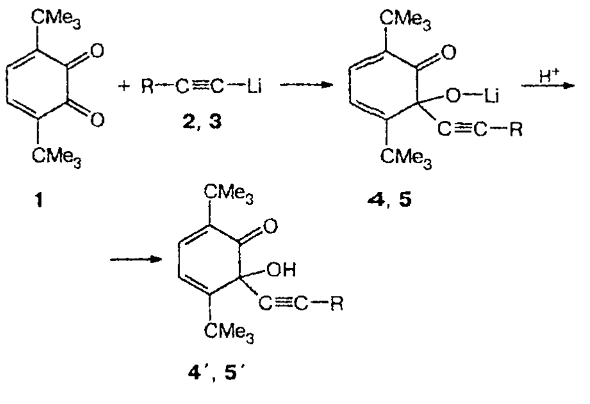
Key words: *o*-benzoquinones, organometallic compounds, acetylene-allene rearrangement, X-ray diffraction analysis.

Reactions of *o*-quinones with compounds containing an active methylene group allow preparation of new *o*-benzoquinones[1,2] with diverse steric and electronic properties, which can be used in the directed synthesis of *o*-benzosemiquinone complexes of transition metals.[3] Studies of reactions of organometallic compounds with 3,6-di-*tert*-butyl-1,2-benzoquinone (**1**) demonstrated that the reactions with alkyl derivatives of Zn, Cd, and Al [4,5] proceeded according to two concurrent mechanisms involving one-electron transfer to form alkoxyphenols and nucleophilic 1,2- and 1,4-addition of an organometallic compound to *o*-quinone at one of the carbonyl groups. The ratio between these directions depends mainly on the nature of the organometallic compound, the polarity of the solvent, and the temperature.

The use of organolithium compounds in reactions with compound **1** allowed one to synthesize sterically hindered *o*-benzoquinones containing various substituents. To prepare *o*-quinones containing alkyne fragments, we used lithium phenylacetylenide and lithium 3,3-dimethylbut-1-ynide (**2** and **3**, respectively) as reagents.

The reactions of *o*-quinone (**1**) with RC≡CLi (**2** or **3**) in toluene afforded cyclohexadienones (**4** or **5**) (Scheme 1) as a result of nucleophilic 1,2-addition of lithium acetylenides at one of the carbonyl groups of *o*-quinone. After hydrolysis of the reaction mixture with AcOH, products **4′** and **5′** were isolated in ~50% yields with respect to the initial *o*-quinone and identified by NMR and IR spectroscopy.

Scheme 1



R = Ph (**2**, **4**, **4′**) or Bu^t (**3**, **5**, **5′**)

The IR spectra of compounds **4′** and **5′** have characteristic absorption bands of the carbonyl group at 1670 cm^{-1} and of the hydroxy groups at 3410 and 3440 cm^{-1}. These parameters are similar to those of hydroxycyclo-

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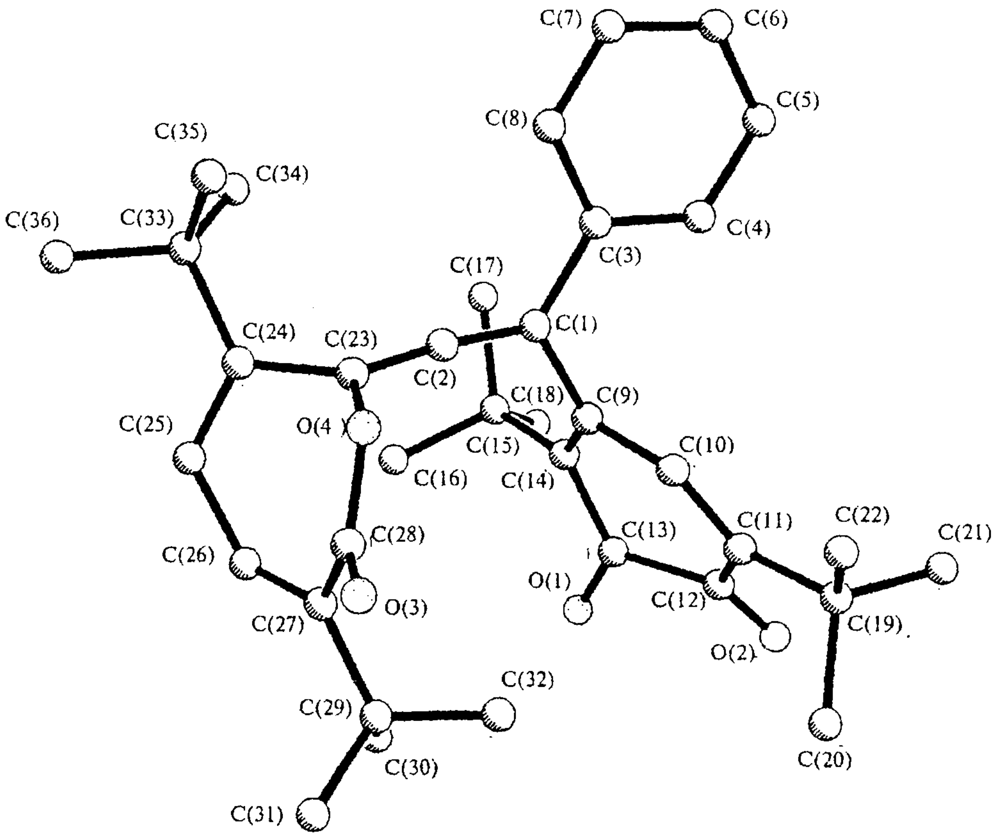


Fig. 1. Molecular structure of **6′**.

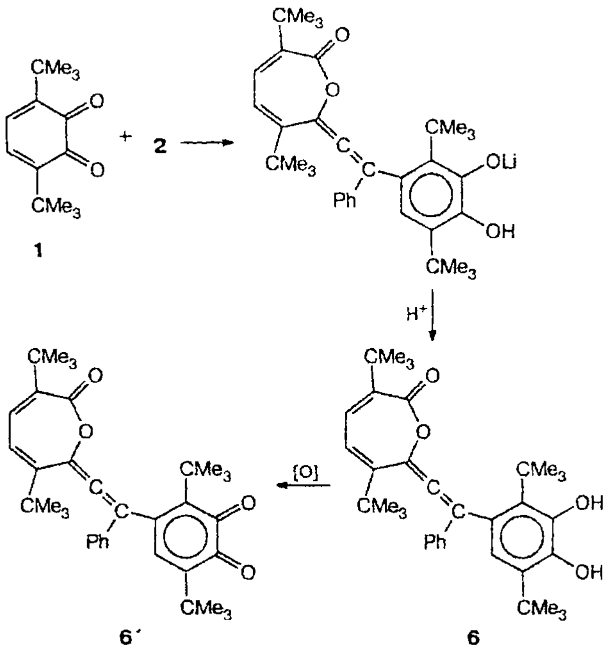
hexadienones, which we have prepared previously.[4,5]

The shape of the absorption band of the hydroxy group in the IR spectrum is indicative of the presence of an intramolecular hydrogen bond. This conclusion is confirmed also by the ^1H NMR spectroscopic data. Thus the chemical shift of the proton of the OH group depends only slightly on the temperature, which is indicative of the absence of intermolecular hydrogen bonds, and the spin-spin coupling constant between the proton of the OH group and the proton of the aromatic ring has a small value (0.4 Hz), which is a reflection of slow (in the NMR time scale) exchange of the hydroxy proton. On the whole, the ^1H and ^{13}C NMR spectra completely confirm structures **4′** and **5′**.

The reaction of *o*-quinone **1** with PhC≡CLi (**2**) in ether afforded pyrocatechol (**6**), which contains a substituent with a complex structure at position 4, in high yield (Scheme 2). Pyrocatechol **6** was oxidized to the corresponding *o*-benzoquinone (**6′**).

The presence of the 3,6-di-*tert*-butyl-*o*-benzoquinone fragment in lactone **6′** was established by NMR and IR spectroscopy and confirmed by ESR spectroscopy. When compound **6′** was reduced with metallic potassium, the ESR spectrum of the corresponding semiquinone (SQ) showed hyperfine interaction of the unpaired electron

Scheme 2



with only one proton of the aromatic ring, A_H = 3.25 Oe, g = 2.0042.

X-ray diffraction analysis of compound **6′** demonstrated that the seven-membered ring of lactone is nonplanar (Fig. 1). The torsion angles between the mean plane of the central fragment O(4)—C(28)—C(24)—C(25) (planar to within 0.02 Å) and the planes of the O(4)—C(23)—C(24) and C(25)—C(26)—C(27)—C(28) fragments (the latter is planar to within 0.04 Å) are 61.2° and 36.3°, respectively. The torsion angles in the lactone substituent are as follows: C(2)—C(23)—C(24)—C(33), −71.4°; C(2)—C(23)—C(24)—C(25), 110.9°; C(23)—C(24)—C(25)—C(26), −4.2°; C(24)—C(25)—C(26)—C(27), 37.2°; C(25)—C(26)—C(27)—C(28), 10.4°; C(26)—C(27)—C(28)—O(4), −47.1°; and C(27)—C(28)—O(4)—C(23), −0.3°.

Table 1. Bond lengths (*d*) in lactone **6′**

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(13)	1.216(3)	O(2)—C(12)	1.203(4)
O(3)—C(28)	1.200(4)	O(4)—C(23)	1.425(4)
O(4)—C(28)	1.357(4)	C(1)—C(2)	1.311(3)
C(1)—C(3)	1.486(4)	C(1)—C(9)	1.514(4)
C(2)—C(23)	1.309(3)	C(3)—C(4)	1.373(4)
C(3)—C(8)	1.386(4)	C(4)—C(5)	1.390(5)
C(5)—C(6)	1.360(6)	C(6)—C(7)	1.366(5)
C(7)—C(8)	1.383(5)	C(9)—C(10)	1.483(4)
C(9)—C(14)	1.348(3)	C(10)—C(11)	1.332(4)
C(11)—C(12)	1.478(3)	C(11)—C(19)	1.525(5)
C(12)—C(13)	1.545(4)	C(13)—C(14)	1.484(5)
C(14)—C(15)	1.538(4)	C(15)—C(16)	1.527(4)
C(15)—C(17)	1.529(6)	C(15)—C(18)	1.531(4)
C(19)—C(20)	1.539(6)	C(19)—C(21)	1.525(4)
C(19)—C(22)	1.524(4)	C(23)—C(24)	1.475(4)
C(24)—C(25)	1.330(4)	C(24)—C(33)	1.526(5)
C(25)—C(26)	1.463(6)	C(26)—C(27)	1.329(5)
C(27)—C(28)	1.491(4)	C(27)—C(29)	1.531(5)
C(29)—C(30)	1.536(4)	C(29)—C(31)	1.529(5)
C(29)—C(32)	1.520(5)	C(33)—C(34)	1.531(5)

On the whole, the C—C, C=C, C—O, and C=O bond lengths in the lactone (Table 1) are close to the corresponding average values for six-membered lactones.[6] Note that compound **6′** is apparently the first example of compounds containing the seven-membered lactone ring whose structure was determined by X-ray diffraction analysis.

The C(1)C(2)C(23) fragment is nonlinear (the C(1)—C(2)—C(23) angle is 173.4(4)°). The C(1)—C(2) and C(2)—C(23) bond lengths (1.311(3) and 1.309(3) Å, respectively) are close to the average value of the C=C bond length in olefin fragments (1.307 Å).[6] The C(2)—C(23)—C(24) angle (130.9(3)°) is substantially larger than the C(2)—C(23)—O(4) and O(4)—C(23)—C(24) angles (116.6(3)° and 112.5(2)°, respectively). The differences in the angles at the C(1) atom are less significant. The C(9)—C(1)—C(2), C(9)—C(1)—C(3), and C(3)—C(1)—C(2) angles are 117.4(3)°, 118.0(2)°, and 124.0(3)°, respectively. The sums of the three angles at the C(1) and C(23) atoms are 359.4° and 360.0°, respectively.

The C(9)—C(14) benzoquinone fragment of molecule **6′** is also nonplanar. The C(12) and C(13) atoms deviate from the mean plane of the ring in opposite directions by −0.13 and 0.17 Å, respectively (Table 2). The bond lengths and bond angles in the benzoquinone fragment (see Tables 1 and 2, respectively) are also close to the values typical of these groups.[7]

Table 2. Bond angles (ω) in lactone **6′**

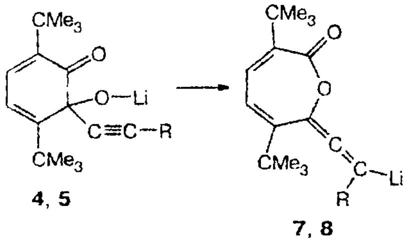
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(23)—O(4)—C(28)	117.4(2)	C(25)—C(24)—C(33)	125.7(3)	C(12)—C(13)—C(14)	119.9(2)
C(2)—C(1)—C(9)	117.4(3)	C(25)—C(26)—C(27)	128.5(3)	C(9)—C(14)—C(15)	128.4(3)
C(1)—C(2)—C(23)	173.4(4)	C(26)—C(27)—C(29)	123.6(3)	C(14)—C(15)—C(16)	109.8(3)
C(1)—C(3)—C(8)	120.9(2)	O(3)—C(28)—O(4)	116.1(3)	C(16)—C(15)—C(17)	109.9(3)
C(3)—C(4)—C(5)	120.8(3)	O(4)—C(28)—C(27)	120.4(3)	C(16)—C(15)—C(18)	109.7(2)
C(5)—C(6)—C(7)	120.0(3)	C(27)—C(29)—C(31)	110.3(3)	C(11)—C(19)—C(20)	110.2(3)
C(3)—C(8)—C(7)	120.3(3)	C(27)—C(29)—C(32)	110.7(3)	C(20)—C(19)—C(21)	110.2(3)
O(1)—C(9)—C(14)	127.5(3)	C(31)—C(29)—C(32)	109.8(3)	C(20)—C(19)—C(22)	107.5(3)
C(9)—C(10)—C(11)	127.0(2)	C(24)—C(33)—C(35)	109.7(3)	O(4)—C(23)—C(2)	116.6(3)
C(10)—C(11)—C(19)	124.4(2)	C(24)—C(33)—C(36)	111.6(3)	C(2)—C(23)—C(24)	130.9(3)
C(2)—C(12)—C(11)	125.8(3)	C(35)—C(33)—C(36)	108.9(2)	C(23)—C(24)—C(33)	119.3(2)
C(11)—C(12)—C(13)	116.2(2)	C(2)—C(1)—C(3)	124.0(3)	C(24)—C(25)—C(26)	123.1(3)
C(1)—C(13)—C(14)	123.7(3)	C(3)—C(1)—C(9)	118.0(2)	C(26)—C(27)—C(28)	120.0(3)
C(9)—C(14)—C(13)	113.5(3)	C(1)—C(3)—C(4)	120.6(3)	C(28)—C(27)—C(29)	116.0(3)
C(13)—C(14)—C(15)	118.1(2)	C(4)—C(3)—C(8)	118.5(3)	O(3)—C(28)—C(27)	123.5(4)
C(14)—C(15)—C(17)	111.9(2)	C(4)—C(5)—C(6)	120.0(3)	C(27)—C(29)—C(30)	110.1(3)
C(14)—C(15)—C(18)	110.3(3)	C(6)—C(7)—C(8)	120.3(3)	C(30)—C(29)—C(31)	108.9(3)
C(17)—C(15)—C(18)	105.2(3)	C(1)—C(9)—C(10)	110.0(2)	C(30)—C(29)—C(32)	107.0(3)
C(11)—C(19)—C(21)	109.2(3)	C(10)—C(9)—C(14)	122.4(3)	C(24)—C(33)—C(34)	109.3(2)
C(11)—C(19)—C(22)	111.1(3)	C(10)—C(11)—C(12)	114.7(3)	C(34)—C(33)—C(35)	108.1(3)
C(21)—C(19)—C(22)	108.6(2)	C(12)—C(11)—C(19)	120.8(3)	C(34)—C(33)—C(36)	109.3(3)
O(4)—C(23)—C(24)	112.5(2)	O(2)—C(12)—C(13)	118.0(2)		
C(23)—C(24)—C(25)	114.9(3)	O(1)—C(13)—C(12)	116.3(3)		

The IR spectrum of compound **6′** has absorption bands of the lactone and quinone carbonyl groups and of allene at 1725, 1680, and 1950 cm^{-1}, respectively.

In subsequent studies, the use of the NMR and IR spectroscopic data substantially simplified the problem of identification of other analogous products.

The formation of the seven-membered lactone fragment is possible only in the case of rearrangements of the primary products **4** and **5** under the reaction conditions. Previously, it has been reported that metal-containing cyclohexadienone products of type **4** undergo transformations.[4,5] In the case of alkyl and aryl derivatives, this results in the replacement of the *tert*-butyl fragment to form the corresponding catecholate. In the present case, the rearrangement is accompanied by insertion of the O atom into the ring, the formation of the allenic fragment, and migration of the Li atom to the allenic C atom to form a new organolithium compound (Scheme 3).

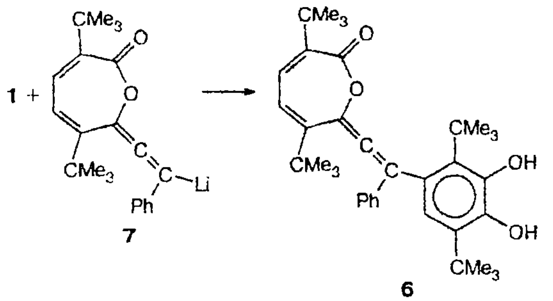
Scheme 3



R = Ph (**4**, **7**) or Bu^t (**5**, **8**)

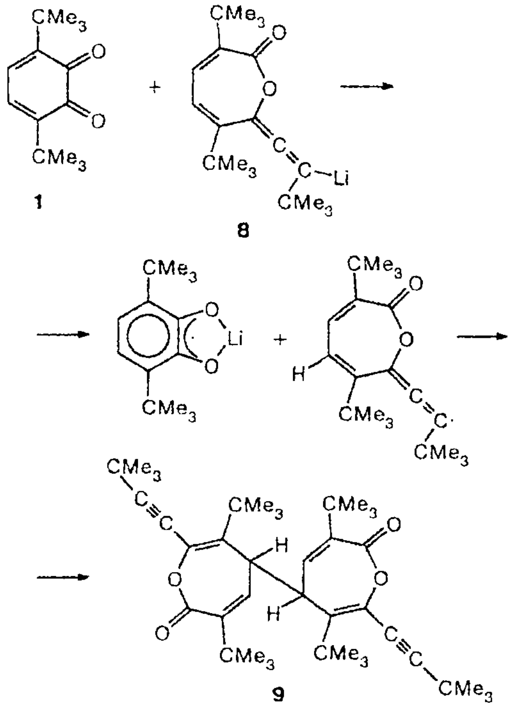
The reactions of organolithium compounds **7** and **8** with *o*-quinone **1** occur through different mechanisms. Phenyl derivative **7** reacts with *o*-quinone **1** according to the mechanism of nucleophilic 1,4-addition (Scheme 4) to give pyrocatechol **6**.

Scheme 4



Under analogous conditions, *tert*-butyl derivative **8′** reacts with the initial *o*-quinone **1** according to the mechanism of one-electron transfer to form lithium *o*-semiquinolate and dimeric product **9** (Scheme 5).

Scheme 5



In the first stage of this conversion, compound **8** is oxidized to form an allenic radical, which is rapidly rearranged to give a more stable isomer and then dimerizes. In the ^1H NMR spectrum of compound **9**, a rather large spin-spin coupling constant between the protons 4 and 4′ (10.7 Hz) is observed, which is indicative of the *meso* configuration.

The major effect of the nature of the solvent on the reactions of *o*-quinone **1** with acetylenides **2** or **3** is manifested in the change in the rate constant of the acetylene-allene rearrangement, which is ionic in character. In a solvating medium, this rate and, correspondingly, the rate of the reaction with the initial *o*-quinone, as expected, increased substantially.

The resulting *o*-benzoquinone **6′** readily underwent one-electron reduction to the corresponding semiquinone derivative not only under the action of alkali metals but also under the action of metallic thallium. The ESR spectrum of the product has a doublet with A_H = 3.3 Oe; A_{Tl} = 56.6 Oe; g = 1.9986. When a mixture of compound **6′** and $Mn_2(CO)_{10}$ was irradiated with visible light, the semiquinone complex $(SQ)Mn(CO)_4$ formed. The ESR spectrum of the complex has the following parameters: A_H = 3.2 Oe; A_{Mn} = 7.4 Oe; g = 2.0039. We also prepared the complex $(SQ)Cu(PPh_3)_2$. Its ESR spectrum at room temperature has the following parameters: A_H = 3.1 Oe; A_{Cu} = 11.3 Oe; A_P = 18.5 Oe (2 P); g = 2.0055. The central components of phosphorus triplets are substantially broadened compared to the analogous complex, namely, semiquinone derivative **1**.[8]

This is primarily indicative of steric crowding of the semiquinone under study.

Experimental

The IR spectra were recorded on a Specord-80 instrument. The ESR spectra were measured on a Bruker ER-200D-SRC instrument. The ^{1}H and ^{13}C NMR spectra were obtained on a Tesla BS-567A instrument.

Lithium phenylacetylenide and lithium 3,3-dimethylbut-1-ynide were prepared according to a known procedure.[10]

3,6-Di-*tert*-butyl-2-hydroxy-2-phenylethynylcyclohexa-3,5-dienone (4′). A solution of lithium phenylacetylenide **2** (1.05 g, 0.01 mol) in toluene (50 mL) was gradually added to a solution of *o*-quinone **1** (2.2 g, 0.01 mol) in toluene (60 mL). The color of the initial *o*-quinone disappeared and the solution turned bright-green. The reaction mixture was kept at 30 °C for 1 h and hydrolyzed with aqueous AcOH. The organic layer was washed with water until the reaction became neutral. After the removal of toluene, the solid residue was recrystallized from MeOH. The yield of product **4′** was 1.6 g (50%), m.p. 113–115 °C. Found (%): C, 82.49; H, 8.24. $C_{22}H_{26}O_2$. Calculated (%): C, 82.00; H, 8.13. IR, ν/cm^{-1}: 1640, 1670 (C=O), 2240 (C≡C), 3440 (OH). ^{1}H NMR (CDCl$_3$), δ: 1.16 (s, 6 H, 2 Me); 1.26 (s, 9 H, 6-Bu^t); 1.36 (s, 9 H, 3-Bu^t); 4.45 (s, 1 H, OH); 5.95 (d, 1 H, 4-H, *J* = 7 Hz); 6.72 (d, 1 H, 5-H, *J* = 7 Hz); 7.3 (m, 5 H, Ph). ^{13}C NMR (CDCl$_3$), δ: 28.8 (q, 6-C($\underline{C}H_3)_3$); 29.7 (q, 3-C($\underline{C}H_3)_3$); 33.9 (s, 6-CMe$_3$); 37.3 (s, 3-CMe$_3$); 76.6 (s, COH); 81.7, 87.7 (both s, C≡C); 116.0 (d, 4-C); 122.2 (s, 1′-C); 128.1 (d, 3′,5′-C); 128.4 (d, 4′-C); 131.7 (d, 2′,6′-C); 135.6 (d, 5-C); 141.4 (s, 3-C); 157.6 (s, 6-C); 199.6 (s, C=O).

3,6-Di-*tert*-butyl-2-hydroxy-2-(3,3-dimethylbut-1-ynyl)cyclohexa-3,5-dienone (5′). The reaction of **1** with **3** was carried out according to the above-described procedure. Product **5′** was isolated in a yield of 1.65 g (66%), m.p. 137 °C. Found (%): C, 79.29; H, 10.10. $C_{20}H_{30}O_2$. Calculated (%): C, 79.40; H, 10.02. ^{1}H NMR (CDCl$_3$), δ: 1.11 (s, 9 H, 2′-Bu^t); 1.23 (s, 9 H, 6-Bu^t); 1.30 (s, 9 H, 3-Bu^t); 4.36 (s, 1 H, OH); 5.87 (d, 1 H, 4-H, *J* = 6.8 Hz); 6.66 (d, 1 H, 5-H, *J* = 6.8 Hz).

2,5-Di-*tert*-butyl-8-(2,5-di-*tert*-butyl-3,4-dihydroxyphenyl)-8-phenylocta-2,4,6,7-tetraen-1,6-olide (6). A solution of lithium phenylacetylenide **2** (1.3 g, 0.013 mol) in ether (30 mL) was gradually added to a solution of *o*-quinone **1** (3.0 g, 0.013 mol) in ether (50 mL). The reaction mixture was kept at 30 °C for 1.5 h. The color of the solution changed from pale-green to dark-green. The mixture was hydrolyzed with AcOH. The ethereal layer was washed with water until the reaction became neutral and dried with MgSO$_4$. The solvent was removed. The solid residue was recrystallized from hexane. Lactone **6** was obtained in a yield of 3.2 g (48%), m.p. 175–177 °C. ^{1}H NMR ((CD$_3$)$_2$CO), δ: 1.12 (s, 9 H, 5-Bu^t); 1.18 (s, 9 H, 2-Bu^t); 1.32 (s, 9 H, 2-Bu^t); 1.41 (s, 9 H, 5′-Bu^t); 6.25 (d, 1 H, 4-H, *J* = 5.6 Hz); 6.45 (s, 1 H, 6′-H); 6.66 (d, 1 H, 3-H, *J* = 5.6 Hz); 7.2–7.4 (m, 7 H, Ph, 2 OH).

2,5-Di-*tert*-butyl-8-(3,6-di-*tert*-butyl-1,2-benzoquinon-4-yl)-8-phenylocta-2,4,6,7-tetraen-1,6-olide (6′). Pyrocatechol **6** (2 g) was dissolved in ether (100 mL) and mixed with an aqueous solution of $K_3Fe(CN)_6$ (30 g), KOH (3 g), and Na_2CO_3 (5 g). The color of the solution changed from yellow to dark-green. The organic layer was separated, the solvent was removed, and the solid residue was recrystallized from methanol. Compound **6′** was obtained as dark-brown crystals in a yield of 1.5 g (70%), m.p. 170–172 °C. Found (%): C, 79.89; H, 8.11. $C_{36}H_{44}O_4$. Calculated (%): C, 79.96; H, 8.20. IR, ν/cm^{-1}: 1725, 1680 (C=O), 1950 (C=C=C). ^{1}H NMR (CDCl$_3$), δ: 1.12 (s, 18 H, 3′,6′-Bu^t); 1.20 (s, 9 H, 2-Bu^t); 1.25 (s, 9 H, 5-Bu^t); 6.18 (d, 1 H, 4-H, *J* = 5.6 Hz); 6.37 (s, 1 H, 5′-H); 6.61 (d, 1 H, 3-H, *J* = 5.6 Hz); 7.3–7.5 (m, 5 H, Ph). ^{13}C NMR ((CD$_3$)$_2$CO), δ: 28.8, 29.1, 29.5, 30.3 (C($\underline{C}H_3)_3$).

4,4′-Bi(2,5-di-*tert*-butyl-9,9-dimethyldeca-2,5-dien-7-yn-1,6-olide) (9). A solution of lithium 3,3-dimethylbut-1-ynide **3** (1.1 g, 0.013 mol) in ether (20 mL) was gradually added to a solution of *o*-quinone **1** (3.0 g, 0.013 mol) in ether (50 mL). The color of the solution changed from green to bright-blue. After 2 h, the reaction mixture was hydrolyzed with AcOH. The organic layer was separated and washed until the reaction became neutral. Then ether was removed. The solid residue

Table 3. Atomic coordinates (×10^3) and equivalent isotropic thermal parameters (×10^2) in the structure of **6′**

Atom	*x*	*y*	*z*	*U*/Å*
O(1)	−1005	2283(2)	768	67(1)
O(2)	−1833(2)	90(2)	1337(2)	70(1)
O(3)	4591(3)	2377(4)	5189(2)	110(1)
O(4)	4942(2)	1877(2)	3870(2)	47(1)
C(1)	3158(3)	366(2)	1699(2)	37(1)
C(2)	3926(3)	1255(2)	2233(2)	40(1)
C(3)	3588(3)	−848(3)	1387(2)	39(1)
C(4)	2743(3)	−1819(3)	962(2)	53(1)
C(5)	3143(3)	−2962(3)	678(3)	66(1)
C(6)	4378(4)	−3112(3)	793(3)	73(1)
C(7)	5226(3)	−2143(3)	1190(3)	74(1)
C(8)	4840(3)	−1011(3)	1490(3)	60(1)
C(9)	1765(2)	498(2)	1523(2)	34(1)
C(10)	1457(3)	−283(2)	2253(2)	39(1)
C(11)	317(3)	−460(3)	2292(2)	40(1)
C(12)	−718(3)	263(3)	1545(2)	46(1)
C(13)	−312(3)	1351(3)	1006(2)	44(1)
C(14)	901(3)	1247(2)	851(2)	40(1)
C(15)	1054(3)	2039(3)	13(2)	46(1)
C(16)	1400(4)	3424(3)	353(3)	80(1)
C(17)	2056(3)	1466(4)	−332(3)	79(1)
C(18)	−178(3)	2019(3)	−898(3)	67(1)
C(19)	49(3)	−1354(3)	3018(2)	50(1)
C(20)	−621(4)	−613(4)	3595(3)	85(1)
C(21)	−778(3)	−2467(3)	2452(3)	75(1)
C(22)	1274(3)	−1901(3)	3766(3)	68(1)
C(23)	4644(3)	2108(2)	2847(2)	38(1)
C(24)	5220(3)	3304(3)	2666(2)	44(1)
C(25)	4737(3)	4381(3)	2869(2)	56(1)
C(26)	3656(3)	4399(3)	3181(3)	56(1)
C(27)	3377(3)	3575(3)	3765(2)	48(1)
C(28)	4323(3)	2589(3)	4327(2)	59(1)
C(29)	2186(3)	3676(3)	4013(2)	54(1)
C(30)	1108(4)	4309(4)	3155(3)	86(1)
C(31)	2456(4)	4486(4)	4943(3)	78(1)
C(32)	1728(4)	2349(3)	4161(3)	81(1)
C(33)	6321(3)	3221(3)	2311(2)	52(1)
C(34)	5817(3)	2811(4)	1226(3)	71(1)
C(35)	7265(3)	2206(3)	2909(3)	67(1)
C(36)	7006(3)	4507(3)	2419(3)	74(1)

* Equivalent isotropic parameters *U* were determined as 1/3 of the trace of the orthogonalized *U*(*i*,*j*) tensor.

was recrystallized from acetone. Dilactone **9** was isolated in a yield of 2.1 g (51%), m.p. 181 °C. Found (%): C, 79.29; H, 10.10. $C_{40}H_{58}O_4$. Calculated (%): C, 79.38; H, 10.02. IR, ν/cm^{-1}: 1725 (C=O); 2240 (C≡C). ^{1}H NMR ($CDCl_3$), δ: 1.16 (s, 9 H, Bu^t); 1.18 (s, 9 H, Bu^t); 1.24 (s, 9 H, Bu^t); 3.78 (m, $\underline{\mathrm{AA}}$'XX', 1 H, 4-H, J_{AX} = 9.2 Hz, $J_{AA'}$ = 10.7 Hz); 6.68 (m, AA'$\underline{\mathrm{XX}}$', 1 H, 5-H).

X-ray structural analysis of compound **6'** was carried out on a Siemens P3/PC diffractometer (20 °C, Mo-Kα radiation, graphite monochromator, 2θ/θ-scanning technique in the range of $2 \le 2\theta \le 48°$). The crystals are monoclinic, at 20 °C a = 11.380(2) Å, b = 10.400(2) Å, c = 14.614(3) Å, β = 111.93(3)°, V = 1604.4(8) Å^3, space group Pn, Z = 2, d_{calc} = 1.119 g cm^{-3}, μ(Mo-Kα) = 0.071 mm^{-1}. A total of 3798 independent reflections were measured of which 2406 reflections with $F > 6\sigma(F)$ were used in the refinement of the structure. The structure was solved by direct methods in combination with difference electron density syntheses. The positions of the hydrogen atoms were calculated from geometric considerations. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the H atoms were refined using the riding model with variable isotropic thermal parameters. In the final stage of the refinement, the following weighting scheme was used: $W^{-1} = \sigma^2(F) + 0.0008F^2$. The final values of the R factors were as follows: R = 0.039, R_w = 0.047, S = 1.23 for the observed reflections.

All calculations were carried out using the SHELX PLUS program package.[9] The bond lengths and bond angles are given in Tables 1 and 2, respectively. The atomic coordinates and equivalent isotropic temperature factors are given in Table 3.

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