

New sterically hindered di-*o*-quinones of the biphenyl series

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New di-*o*-quinones of the biphenyl series, namely, 2,2'-dialkyl-5,5'-di-*tert*-butylbiphenyl-3,4,3',4'-diquinones, were synthesized. Their structures were established by IR and NMR spectroscopy. The molecular structure of 2,2'-dimethyl-5,5'-di-*tert*-butylbiphenyl-3,4,3',4'-diquinone was established by X-ray structural analysis. The structure is characterized by orthogonal (the torsion angle is 82.9°) mutual arrangement of *o*-benzoquinone fragments. ESR studies demonstrated that chemical reduction of diquinone proceeds in four one-electron stages to form paramagnetic mono- and trianions as intermediates. Quinopyrocatechols, which are intermediates in the synthesis of di-*o*-quinones, were isolated and characterized.

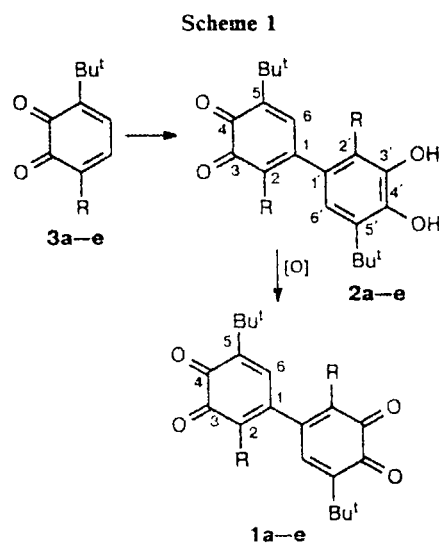
Key words: synthesis, di-*o*-quinones, structure, IR spectroscopy, NMR, X-ray structural analysis.

o-Semiquinone complexes of transition metals are of exceptional interest as objects of studies of various intramolecular electronic and magnetic interactions because of the presence of a variable-valence metal ion bonded to a free-radical ligand whose oxidation state can change reversibly. New phenomena such as "stray valence",¹ redox isomerism in solution²⁻⁴ and in the solid phase,^{5,6} and the photo(thermo)mechanical effect^{7,8} were first found and studied in *o*-semiquinone complexes. Studies of the magnetic properties of *o*-semiquinone complexes of transition metals have demonstrated that many of them are characterized by strong ferromagnetic metal–ligand exchange interactions (in some cases, these interactions are as large as 200 cm⁻¹).⁹⁻¹¹ Ferromagnetic exchange interactions between ligands have been observed in a number of *o*-semiquinone complexes of metals.¹²

These results were obtained for normal sterically hindered *o*-quinones. If additional free-radical centers are introduced into a molecule, the use of di-*o*-quinones as ligands makes it possible to obtain new intramolecular channels of electron–electron interactions, which are impossible in derivatives of ordinary *o*-quinones. Thus, for example, there is a good probability that in radical dianions of di-*o*-quinones of the biphenyl series with a mutual orthogonal arrangement of the *o*-semiquinone rings, the exchange interaction of unpaired electrons will be ferromagnetic, and therefore, in binuclear complexes with a bridging di-*o*-semiquinone ligand, a four-center chain can occur with continuous ferromagnetic exchange along it.

Apparently, radical anions of di-*o*-quinones as bridging ligands are promising switches in the design of polymeric metallocomplex compounds used in molecular-electronic devices.^{13,14}

Some di-*o*-quinones of the biphenyl series have been described.¹⁵ However, the data on sterically hindered di-*o*-quinones of this type and their derivatives that can be used as a basis for target metallocomplexes are unavailable in the literature. This work is devoted to the



synthesis and investigation of the structures and properties of new di-*o*-quinones, namely, 2,2'-dialkyl-5,5'-di-*tert*-butylbiphenyl-3,4,3',4'-diquinones (**1a–e**). The intermediate products of the synthesis, namely, the corresponding quinopyrocatechols (**2a–e**), were characterized.

Results and Discussion

Acid-catalyzed dimerization of *o*-benzoquinones **3a–e** yielded di-*o*-quinones **1a–e** (Scheme 1).

Intermediate quinopyrocatechols **2a–e** were oxidized to di-*o*-quinones by potassium ferricyanide in an alkaline medium.

An alternative procedure for the synthesis of di-*o*-quinones **1a–e** is redox coupling of *o*-semiquinolates of

alkali metals or thallium(I) followed by oxidation of the salts of "dihydroxydiphenokinones" formed by concentrated nitric acid (Scheme 2).

The structures of the new compounds were established by IR, NMR, and ESR spectroscopy (Tables 1 and 2). The IR spectra of quinones **1a–e** have characteristic bands (1660–1680 cm⁻¹) that correspond to the stretching vibrations of carbonyl groups and are typical of all *o*-quinones. The ¹H NMR spectra of these compounds are similar. In these spectra, signals of 6,6' protons ($\delta = 6.22$ –6.57) and signals of protons of *tert*-butyl groups ($\delta = 1.11$ –1.27) are present.

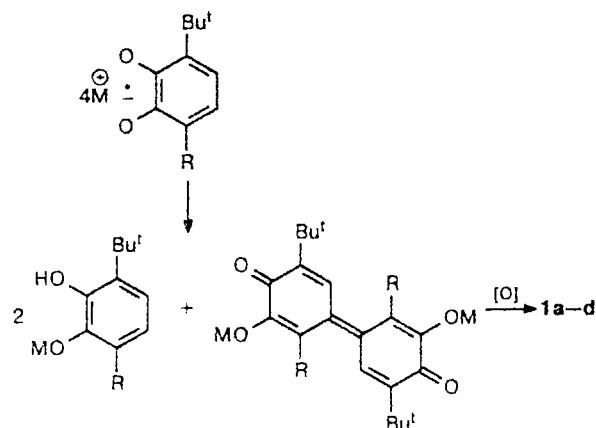
Note that in the NMR spectra of di-*o*-quinones **1c–e**, atropoisomerism, caused by hindered rotation of the quinone fragments with respect to each other, has been observed.¹⁶ Atropoisomerism manifests itself in

Table 1. Parameters of the ¹H NMR and IR spectra of quinopyrocatechols and di-*o*-quinones

Com- pound	δ_{H}	Assignment, <i>J</i> /Hz	ν_{CO} /cm ⁻¹	ν_{OH} /cm ⁻¹
2a	1.23	5-C(CH ₃) ₃	1640; 1680	3450
	1.40	5'-C(CH ₃) ₃		
	1.74	2-CH ₃		
	2.11	2'-CH ₃		
	5.14	OH		
	5.28	OH		
	6.62	6-H		
	6.66	6'-H		
2b	0.94	2-CH ₃ (t), <i>J</i> = 7.5	1665; 1685	3500
	1.14	2'-CH ₃ (t)		
	1.23	5-C(CH ₃) ₃		
	1.41	5'-C(CH ₃) ₃		
	2.05	2-CH ₂ (q)		
	2.53	2'-CH ₂ (q)		
	5.60	OH		
	5.73	OH		
	6.56	6-H		
	6.62	6'-H		
2c	0.78	2-CH ₃ (t), <i>J</i> = 7.0	1655; 1680	3360; 3480
	0.90	2'-CH ₃ (t), <i>J</i> = 7.0		
	1.22	5-C(CH ₃) ₃		
	1.41	5'-C(CH ₃) ₃		
	1.7— —2.3	2,2'-(CH ₂ CH ₂) (m)		
	2.49	2,2'-CH ₂ CH ₂ CH ₃ (t)		
	5.50	OH		
	5.93	OH		
	6.59	6-H		
	6.68	6'-H		
2d	1.01	5-C(CH ₃) ₃	1660; 1680	3390; 3495
	1.33	5'-C(CH ₃) ₃		
	3.35	2-CHHPh (d), <i>J</i> = 14.0		
	3.66	2-CHHPh (d), <i>J</i> = 14.0		
	3.78	2'-CH ₂ Ph (s)		
	4.78	3'-OH		
	5.86	4'-OH		
	6.45	6-H		
	6.56	6'-H		
	6.8— —7.3	2,2'-Ph (m)		

Com- pound	δ_{H}	Assignment, <i>J</i> /Hz	ν_{CO} /cm ⁻¹
2e	1.11	2-(CH ₃)CH(CH ₃) (d), <i>J</i> = 7.0	1660;
	1.17	2-(CH ₃)CH(CH ₃) (d), <i>J</i> = 7.0	1680;
	1.22	5-C(CH ₃) ₃	1685
	1.34	2'-(CH ₃)CH(CH ₃) (d), <i>J</i> = 7.0	
	1.40	2'-(CH ₃)CH(CH ₃) (d), <i>J</i> = 7.0	
	1.41	5'-C(CH ₃) ₃	
	2.50	2-(CH ₃)CH(CH ₃) (sept), <i>J</i> = 7.0	
	2.90	2'-(CH ₃)CH(CH ₃) (sept), <i>J</i> = 7.0	
	5.25	OH	
	5.49	OH	
1a	6.50	6-H	
	6.57	6'-H	
	1.27	C(CH ₃) ₃	1648;
	1.90	CH ₃	1670;
1b	6.57	6-H	1680
	1.05	CH ₃ (t), <i>J</i> = 7.5	
	1.27	C(CH ₃) ₃	
	2.31	CH ₂ (q), <i>J</i> = 7.5	
1c	6.57	6-H	
	0.90	CH ₃ (t), <i>J</i> = 7.0	1665;
	1.26	C(CH ₃) ₃	1680
	1.50	CH ₂ CH ₂ CH ₃ (m)	
	2.16	CHHCH ₂ CH ₃ (m)	
	2.30	CHHCH ₂ CH ₃ (m)	
	6.56	6-H	
	1.11	C(CH ₃) ₃	1660
1d	3.29	CHHPh (d), <i>J</i> = 14.8	1680
	3.83	CHHPh (d), <i>J</i> = 14.8	
	6.22	6-H	
	6.9— —7.3	Ph (m)	
1e	1.24	(CH ₃)CH(CH ₃) (d), <i>J</i> = 6.8	1660;
	1.26	C(CH ₃) ₃	1680;
	1.27	(CH ₃)CH(CH ₃) (d), <i>J</i> = 6.9	1685
	2.58	(CH ₃)CH(CH ₃) (sept), <i>J</i> = 6.8	
	6.49	6-H	

Scheme 2



magnetic nonequivalence of the protons of substituents R and in additional splitting of the corresponding components owing to geminal spin-spin coupling (see Table 1).

The *o*-quinone nature of compounds **1a–e** is responsible for their ability to form radical anions of *o*-semiquinones when they undergo one-electron reduction by alkali metals and (or) thallium. The parameters of the ESR spectra of the paramagnetic derivatives obtained by reducing solutions of di-*o*-quinones by potassium metal are given in Table 2. It is of note that the spectral parameters of the radical anions strongly depend on the nature of the substituents R, the cations, and the solvents.

In this work, the structure and properties of di-*o*-quinone **1a** were studied in more detail. The structure of **1a** was established by X-ray structural analysis. Its stepwise chemical reduction was studied by ESR spectroscopy.

X-ray structural analysis demonstrated that molecule **1a** contains two *o*-benzoquinone residues that are linked through a C–C bond (Fig. 1) and are planar to within ± 0.003 Å. The O atoms deviate from the mean planes of these fragments in opposite directions: the deviations of the O(1), O(2), O(3), and O(4) atoms are -0.23 , 0.15 , 0.20 , and -0.19 Å, respectively.

Table 2. Parameters of the ESR spectra of radical anions of di-*o*-quinones (THF; potassium "mirror"; 290 K)

Radical anion of di- <i>o</i> -quinone	g_i	A (mT)			
		$A(H_S)$	$A(H_{S'})$	$A(H_R)$	$A(H_{R'})$
1a ^{•−}	2.0049	0.260	0.020	0.110 (3 H)	0.130 (3 H)
1a ^{3•−}	2.0050	0.337	0.023	0.033 (3 H)	0.019 (3 H)
1b ^{•−}	2.0046	0.279	—	0.102 (2 H)	—
1c ^{•−}	2.0045	0.279	—	0.110 (2 H)	—
				0.017 (2 H)	—
1d ^{•−}	2.0040	0.292	—	0.051 (1 H)	—
1e ^{•−}	2.0048	0.282	—	—	—

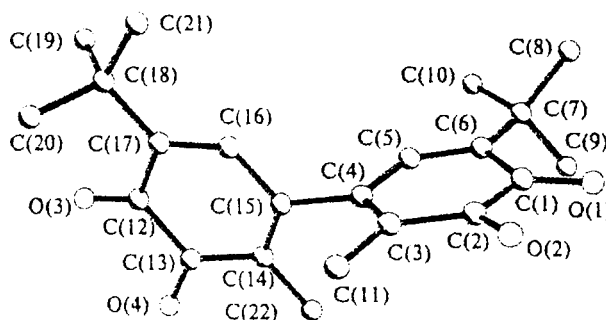


Fig. 1. Overall view of molecule **1a**. H atoms are omitted.

The principal bond lengths and bond angles in **1a** are given in Table 3. The C=O (1.211(4)–1.220(4) Å) and C(O)–C(O) (1.551(4) and 1.548(5) Å) bond lengths are typical of the *o*-quinones.¹⁷ The dihedral angle ω be-

Table 3. Principal bond lengths (d) and bond angles (φ) in the structure of **1a**

Bond	$d/\text{Å}$	Bond	$d/\text{Å}$
O(1)–C(1)	1.214(4)	C(7)–C(9)	1.534(6)
O(2)–C(2)	1.218(4)	C(7)–C(10)	1.529(5)
O(3)–C(12)	1.220(4)	C(12)–C(13)	1.548(5)
O(4)–C(13)	1.211(4)	C(12)–C(17)	1.474(4)
C(1)–C(2)	1.551(4)	C(13)–C(14)	1.464(4)
C(1)–C(6)	1.473(4)	C(14)–C(15)	1.347(4)
C(2)–C(3)	1.459(4)	C(14)–C(22)	1.491(5)
C(3)–C(4)	1.347(4)	C(15)–C(16)	1.468(4)
C(3)–C(11)	1.498(5)	C(16)–C(17)	1.345(4)
C(4)–C(5)	1.470(4)	C(17)–C(18)	1.533(4)
C(4)–C(15)	1.499(4)	C(18)–C(19)	1.542(5)
C(5)–C(6)	1.349(4)	C(18)–C(20)	1.534(6)
C(6)–C(7)	1.514(4)	C(18)–C(21)	1.525(6)
C(7)–C(8)	1.534(5)		
Angle	φ/deg	Angle	φ/deg
O(1)–C(1)–C(2)	117.3(3)	O(3)–C(12)–C(13)	117.3(3)
O(1)–C(1)–C(6)	123.7(3)	O(3)–C(12)–C(17)	123.8(3)
C(2)–C(1)–C(6)	119.0(3)	C(13)–C(12)–C(17)	118.9(3)
O(2)–C(2)–C(1)	118.3(3)	O(4)–C(13)–C(12)	117.8(3)
O(2)–C(2)–C(3)	122.3(3)	O(4)–C(13)–C(14)	122.8(3)
C(1)–C(2)–C(3)	119.4(3)	C(12)–C(13)–C(14)	119.3(3)
C(2)–C(3)–C(4)	117.1(3)	C(13)–C(14)–C(15)	116.8(3)
C(2)–C(3)–C(11)	118.6(3)	C(13)–C(14)–C(22)	118.2(3)
C(4)–C(3)–C(11)	124.3(3)	C(15)–C(14)–C(22)	124.9(3)
C(3)–C(4)–C(5)	122.7(3)	C(4)–C(15)–C(14)	120.6(3)
C(3)–C(4)–C(15)	121.3(2)	C(4)–C(15)–C(16)	116.3(2)
C(5)–C(4)–C(15)	116.0(2)	C(14)–C(15)–C(16)	123.2(3)
C(4)–C(5)–C(6)	126.0(3)	C(15)–C(16)–C(17)	125.4(3)
C(1)–C(6)–C(5)	115.1(3)	C(12)–C(17)–C(18)	115.7(3)
C(1)–C(6)–C(7)	120.5(2)	C(12)–C(17)–C(18)	120.5(3)
C(5)–C(6)–C(7)	124.3(3)	C(16)–C(17)–C(18)	123.7(3)
C(6)–C(7)–C(8)	110.5(3)	C(17)–C(18)–C(19)	109.4(3)
C(6)–C(7)–C(9)	109.1(3)	C(17)–C(18)–C(20)	109.6(3)
C(8)–C(7)–C(9)	109.9(3)	C(19)–C(18)–C(20)	109.6(4)
C(6)–C(7)–C(10)	111.6(3)	C(17)–C(18)–C(21)	110.6(3)
C(8)–C(7)–C(10)	107.7(3)	C(19)–C(18)–C(21)	108.1(4)
C(9)–C(7)–C(10)	108.1(3)	C(20)–C(18)–C(21)	109.5(3)

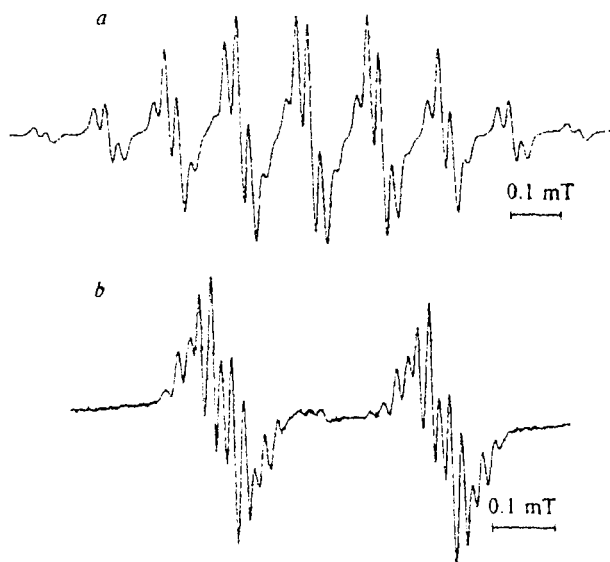


Fig. 2. Isotropic ESR spectra of $1a^{\bullet-}$ (a) and $1a^{3\bullet-}$ (b) (THF; potassium "mirror"; 290 K).

tween the planes of the *o*-quinone fragments of $1a$ is 82.9° , i.e., these fragments are approximately orthogonal to each other.

Compound $1a$ is bifunctional, which could be seen when its chemical reduction was monitored by ESR spectroscopy. When a solution of $1a$ in dimethyl ether was reduced by potassium, a paramagnetic radical monoanion ($1a^{\bullet-}$) was first generated. The ESR spectrum of $1a^{\bullet-}$ is shown in Fig. 2, a. Further reduction of $1a^{\bullet-}$ yielded a non-paramagnetic dianion ($1a^{2-}$). Reduction of $1a^{2-}$ gave the paramagnetic radical trianion ($1a^{3\bullet-}$). However, the ESR spectrum of $1a^{3\bullet-}$ differs substantially from that of the radical monoanion (Fig. 2, b and Table 2), which is indicative of a substantial difference in the distribution of spin density in these radicals. Because the probability of delocalization of the unpaired electron over the second ring is determined by, among other factors, the torsion angle ω , a substantial difference in the parameters of the hyperfine structures may reflect the fact that this angle varies in going from one state to another. The final product of the reduction of $1a$ is a diamagnetic tetraanion.

Quinopyrocatechols $2a-e$ are formed as initial products of coupling of the corresponding *o*-quinones $3a-e$ (see Scheme 1). The synthesis of $2a-e$ was not the aim of this work. However, these compounds were isolated as intermediates and characterized by IR and NMR spectroscopy. The structural similarity of $2-e$ can be seen in their 1H NMR spectra (see Table 1).

The 1H NMR spectra of quinopyrocatechols $2a-e$ contain double sets of signals of protons. The number and the character of the components of these sets are analogous to those in the 1H NMR spectra of the

corresponding di-*o*-quinones. The signals of the protons of the substituents in the quinone ring are shifted upfield of those of the related di-*o*-quinones, whereas the signals of the protons of the substituents in the pyrocatechol ring are shifted downfield. Like for di-*o*-quinones $1c-e$, magnetic nonequivalence of protons of substituents *R* was observed in the 1H NMR spectra of quinopyrocatechols $2c-e$, which is caused by atropoisomerism.

The IR spectra of compounds $2a-e$ have absorption bands in the $1640-1680\text{ cm}^{-1}$ region along with intense bands in the $3400-3500\text{ cm}^{-1}$ region, which correspond to the characteristic stretching vibrations of carbonyl groups of the *o*-quinone fragment of the molecule. The intensities and shapes of the bands are typical of vibrations of hydroxy groups observed in the IR spectra of hindered pyrocatechols and phenols.¹⁸

Experimental

The IR spectra were recorded on a Specord M-80 spectrometer. The electronic absorption spectra were obtained on a Specord M-40 spectrometer. The NMR spectra were recorded on Tesla BS-567A (100 MHz) and Varian (300 MHz) spectrometers with HMDS as the internal standard. The ESR spectra were obtained on a Bruker ER 200D-SRC radio-spectrometer (9.5 GHz).

X-ray structural analysis of compound $1a$ was carried out on a Siemens P3/PC diffractometer (Mo-K α -radiation, $2\theta/\theta$ -scanning technique in the range of $2 < 2\theta < 50^\circ$, 2852 measured reflections, 1686 independent reflections with $F > 4\sigma(F)$). The unit cell parameters are as follows: $a = 10.430(2)$, $b = 18.528(4)$, $c = 21.148(4)$ Å; $V = 4087(1)$ Å³, $d_{\text{calc}} = 1.152\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.078\text{ mm}^{-1}$, $Z = 8$ for $C_{22}H_{26}O_4$, space group *Pbca*. The structure was solved by direct methods in combination with differential Fourier syntheses. All nonhydrogen atoms were refined with anisotropic thermal parameters. Positions of hydrogen atoms were located from the differential synthesis and refined with isotropic thermal parameters. The final values of the *R* factors were as follows: $R = 0.044$ and $R_w = 0.047$. The following weighting scheme was used: $w = 1/[\sigma^2(F) + 0.0003F^2]$. In the final cycle of the refinement, the value of $(\Delta/\sigma)_{\text{av}}$ was 0.001. The maximum peaks in the final difference synthesis were 0.16 and $-0.17\text{ (e}^- \cdot \text{Å}^{-3})$. All calculations were carried out using the SHELXTL PLUS program package.¹⁹ The principal bond lengths and bond angles in $1a$ are given in Table 3. The atomic coordinates and equivalent isotropic temperature factors are given in Table 4.

3-R-6-*tert*-Butylbenzoquinones-1,2 ($3a-e$) were synthesized according to procedures reported previously.^{20,21}

Quinopyrocatechols $2a-e$. A KU-2-8 cation-exchange resin (10 g) and 2–3 drops of H_2SO_4 were added to a solution of 3-R-6-*tert*-butylbenzoquinone-1,2 ($3a-e$) (1 g) in acetone (20 mL). The reaction mixture was thermostatically controlled at 30°C for 24 h (in the case of $3e$, for 5 days). The cation-exchange resin was separated and washed with acetone. The solution was evaporated. The residue was dissolved in a 25 : 1 heptane–ether mixture and chromatographed on a column with silochrom (C-120). A brown fraction was collected. The solvent was replaced with a heptane–toluene mixture, and dark-brown crystals of quinopyrocatechols were isolated. Quinopyrocatechol $2a$, yield 60%. M.p. 178°C . Found (%): C, 74.08; H, 7.90. $C_{22}H_{28}O_4$. Calculated (%): C, 74.16;

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal factors, U_{iso}^* ($\times 10^3$) in the structure of **1a**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/\text{\AA}^2$
O(1)	-1219(2)	8320(2)	5771(1)	89(1)
O(2)	-1740(2)	9401(1)	4960(1)	62(1)
O(3)	5131(2)	9248(1)	2616(1)	69(1)
O(4)	3335(3)	8239(2)	2413(1)	88(1)
C(1)	-387(3)	8494(2)	5400(1)	47(1)
C(2)	-731(3)	9076(2)	4901(1)	43(1)
C(3)	140(3)	9205(2)	4373(1)	38(1)
C(4)	1264(3)	8847(2)	4377(1)	34(1)
C(5)	1638(3)	8359(2)	4893(1)	38(1)
C(6)	905(3)	8174(2)	5393(1)	36(1)
C(7)	1320(3)	7658(2)	5909(1)	44(1)
C(8)	1145(5)	8005(3)	6562(2)	69(2)
C(9)	514(6)	6967(3)	5865(3)	85(2)
C(10)	2732(4)	7449(3)	5842(2)	73(2)
C(11)	-267(4)	9718(3)	3864(2)	59(1)
C(12)	4224(3)	9222(2)	2980(1)	44(1)
C(13)	3259(3)	8595(2)	2892(2)	49(1)
C(14)	2299(3)	8458(2)	3383(1)	39(1)
C(15)	2224(3)	8941(2)	3857(1)	35(1)
C(16)	3061(3)	9577(2)	3901(2)	38(1)
C(17)	4022(3)	9737(2)	3501(1)	39(1)
C(18)	4887(3)	10401(2)	3572(2)	49(1)
C(19)	6282(4)	10155(3)	3680(3)	73(2)
C(20)	4813(6)	10861(3)	2970(2)	80(2)
C(21)	4476(5)	10854(3)	4139(2)	72(2)
C(22)	1458(4)	7811(2)	3314(2)	58(1)

*Equivalent isotropic thermal factors were determined as $1/3$ of the spur of the orthogonalized $U(i,j)$ tensor.

H, 7.87. **2b**, yield 50%. M.p. 112 °C. Found (%): C, 75.23; H, 8.45. $\text{C}_{24}\text{H}_{32}\text{O}_4$. Calculated (%): C, 75.00; H, 8.33. **2c**, yield 50%. M.p. 153 °C. Found (%): C, 75.79; H, 8.81. $\text{C}_{26}\text{H}_{36}\text{O}_4$. Calculated (%): C, 75.73; H, 8.74. **2d**, yield 60%. M.p. 118 °C. Found (%): C, 80.24; H, 7.27. $\text{C}_{34}\text{H}_{36}\text{O}_4$. Calculated (%): C, 80.31; H, 7.09. **2e**, yield 10%. Found (%): C, 75.91; H, 8.90. $\text{C}_{26}\text{H}_{36}\text{O}_4$. Calculated (%): C, 75.73; H, 8.74.

2,2'-Dialkyl-5,5'-di-*tert*-butylbiphenyl-3,4,3',4'-diquinones (1a–e). **A.** An ethereal solution of quinopyrocatechol obtained by the above-described procedure was oxidized by potassium ferricyanide in an alkaline medium for 1–2 h. The color of the solution changed from brown to green. After oxidation, the mixture was chromatographed on a column with silochrom (C-120) using a 50 : 1 heptane–ethyl acetate mixture as the eluent. The green fraction that eluted last was concentrated, and greenish-brown crystals of the corresponding di-*o*-quinone were obtained. Di-*o*-quinone **1a**, yield 55%. M.p. 197 °C. Found (%): C, 74.30; H, 7.61. $\text{C}_{22}\text{H}_{26}\text{O}_4$. Calculated (%): C, 74.58; H, 7.34. **1b**, yield 45%. M.p. 124 °C. Found (%): C, 75.30; H, 7.93. $\text{C}_{24}\text{H}_{30}\text{O}_4$. Calculated (%): C, 75.39; H, 7.85. **1c**, yield 45%. M.p. 133 °C. Found (%): C, 75.99; H, 8.11. $\text{C}_{26}\text{H}_{34}\text{O}_4$. Calculated (%): C, 76.10; H, 8.29. **1d**, yield 55%. M.p. 117 °C. Found (%): C, 80.46; H, 7.00. $\text{C}_{34}\text{H}_{34}\text{O}_4$. Calculated (%): C, 80.63; H, 6.72. **1e**, yield 7%. M.p. 200 °C. Found (%): C, 75.21; H, 8.40. $\text{C}_{26}\text{H}_{34}\text{O}_4$. Calculated (%): C, 75.10; H, 8.29.

B. A solution of thallium *o*-semiquinolate in THF, which was obtained from the corresponding *o*-quinone **3a–e** (0.005 mmol) according to a procedure similar to the synthesis

of thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate,¹⁹ was concentrated *in vacuo*. The residue was kept for 2–3 h. The solid residue was dissolved in glacial acetic acid (10 mL) and oxidized by concentrated HNO_3 . Then ether was added. The organic layer was washed with water until the reaction became neutral. Then the reaction mixture was processed according to procedure **A**. The yields of di-*o*-quinones **1a–d** synthesized according to this procedure were 30–35%. We failed to obtain di-*o*-quinone **1e**.

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