New Bis-o-Benzoquinoid Ligands with Ethylene Bridge and Their Metal Complexes

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Abstract. The treatment of di-*o*-quinone 4,4'-(ethane-1,2-diyl)-bis(3,6-di-*tert*-butyl-*o*-benzoquinone) (Q–CH₂–CH₂–Q, **1**) leads to its rearrangement to form di-*p*-quinomethide 4,4'-(ethane-1,2-diylidene)bis(2-hydroxy-3,6-di-*tert*-butyl-cyclohexa-2,5-dienone) (**2**). The subsequent oxidation of **2** by an alkaline solution of K₃[Fe(CN)₆] yielded the new di-*o*-quinone 4,4'-(ethene-1,2-diyl)bis(3,6-di-*tert*-butyl-*o*-benzoquinone) (Q–CH=CH–Q, **3**), which contains an ethylene bridge. The formation of mono- and poly-reduced derivatives of **2** and **3** with potas-

1. Introduction

An important area in modern coordination chemistry is the search of compounds that act as molecular magnetic materials [1]. Redox-active dioxolene ligands such as o-quinones and related compounds are prospective objects for the composition of molecules with novel electronic structures [2]. The diversity of electronic structures of the formed complexes is influenced by the three different forms of such ligands: quinone, semiquinone and catecholate. Transition metal semiguinone complexes are interesting in the viewpoint of investigating their intra- and intermolecular electronic and magnetic interactions (metal-ligand, ligand-ligand etc.). The integration of two and more semiquinone moieties in one organic tetra- or hexadentate ligand allows the formation of polynuclear structures and the organization of new molecular magnetic exchange channels, which are impossible for the derivatives of simple o-quinones [3]. Therefore, the synthesis of novel bis- or tris-o-quinones is expected to be important for the preparation of complexes revealing new interesting magnetic and electronic properties. Along these investigations, a number of different bis-o-quinones were synthesized and characterized [3, 4]. Among them (Scheme 1) are bis-o-quinones such as 1,1'-spirobis(3,3-dimethylindanequinone-5,6) (A) [4a]; p-terphenyldiquinone-3,4,3',4' (B) [4b], bis-o-quinones (C) with a linker L, which affects the conformation and, consequently, exchange coupling of semiguinone derivatives [4c]; a bis-o-quinone

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 [a] G. A. Razuvaev Institute of Organometallic Chemistry Russian Academy of Sciences Tropinina 49 603950 Nizhny Novgorod GSP-445, Russian Federation sium, thallium was studied by EPR technique. The dinuclear thallium derivative of **3**, Tl(SQ–CH=CH–SQ)Tl, was found to exist in the diamagnetic quinomethide form. The most stable derivatives of **2** and **3** are triphenyltin(IV) bis-*p*-quinomethide-phenolate (**4**) and triphenylan-timony(V) bis-catecholate (**5**), which have been synthesized and isolated. The molecular structures of **2**, **3**, and **5** were characterized by single-crystal X-ray diffraction.

based on indeno[1,2]indene (D) [4d] and 4,4-bis-*o*-benzoquinones (E) [4e, f]. The next type of bis-*o*-benzoquinones is presented by 4,4'-(ethane-1,2-diyl)-bis(3,6-di-*tert*-butyl-*o*-benzoquinone) (Q–CH₂–CH₂–Q, **1**) [5].



Scheme 1.

In this paper we report on the synthesis and characterization of bis-*o*-quinones containing ethylene bridge between *o*-benzoquinone parts, and their reduced derivatives, particularly the tetra electron reduced derivative bis-triphenylantimony(V) biscatecholate.



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2. Results and Discussion

2.1. Synthesis and Characterization

Di-*o*-quinone 4,4'-(ethane-1,2-diyl)-bis(3,6-di-*tert*-butyl-*o*-benzoquinone) (Q-CH₂-CH₂-Q, 1) rearranged into 4,4'-(ethane-1,2-diylidene)bis(2-hydroxy-3,6-di-*tert*-butyl-cyclohexa-2,5-dienone) (2) upon it was treated in toluene for 4 hours at 70 °C (Scheme 2).





Compound 2 was isolated from dioxane as deep colored crystalline powder, which is stable in air. The color of the amorphous powder of 2 is cherry-red. It is hardly soluble in common organic solvents, but reasonably soluble in dioxane. Its crystal structure was determined by X-ray diffraction studies.

Subsequent oxidation of **2** by alkaline solution of potassium hexacyanidoferrate gives new di-o-quinone 4,4'-(ethene-1,2-diyl)bis(3,6-di-tert-butyl-o-benzoquinone) (Q-CH=CH-Q, **3**) (Scheme 3). Dark red crystals of **3** suitable for X-ray analysis were grown from a toluene solution.





Compounds 2 and 3 were characterized by NMR and IR spectroscopy. Noteworthy, both compounds 2 and 3 have a symmetrical structure in solution in accordance with their ¹H and ¹³C NMR spectra. The ¹H NMR spectrum of 2 contains two singlet signals assigned to two pairs of nonequivalent *tert*-butyl proton groups at 1.35 and 1.61 ppm and the integral intensity of 18 protons per singlet. Two equivalent ring protons appear as singlet signal at 8.20 ppm whereas two protons of a =CH–CH= bridging moiety give a singlet signal at 7.68 ppm. Another singlet signal at 8.15 ppm is assigned to hydroxyl protons. The ¹H NMR spectrum of **3** shows two singlet signals from two pairs of *tert*-butyls protons (1.27 and 1.42 ppm), one singlet signal from two benzoquinone protons (7.27 ppm) and one singlet signal from ethylene protons (6.95 ppm).

The comparison of the IR spectra of **2** and **3** gives interesting results. The absorption bands of the carbon–oxygen vibrations v(C=O) for **3** are observed at 1676 and 1648 cm⁻¹. In the case of quinomethide **2**, those are shifted to 1591 cm⁻¹. The stretch-

ing vibrations of the OH groups in 2 give a signal at 3213 cm⁻¹. It allows the assumption of intramolecular interactions between hydroxyl and carbonyl groups. The X-ray studies corroborate this supposition (see below).

2.2. Crystal Structures of 2 and 3

The crystal structures of 2 and 3 were determined by singlecrystal X-ray diffraction (Figure 1 and Figure 2, respectively). The selected bond lengths and angles of 2 are listed in Table 1.



Figure 1. PLATON [6] view of 2. Hydrogen atoms of *tert*-butyl groups and the rings are omitted for clarity.

In the crystal structure of 2, the molecules are disposed in an inversion center. The quinomethide structure of 2 is corroborated by *p*-quinoid type distortion: the carbon-carbon bonds C(2)-C(3) and C(5)-C(6) are of double character and distinctly shorter than the ordinary C(1)-C(2), C(3)-C(4), C(4)-C(5) and C(1)-C(6) bonds (Scheme 4). Scheme 4 also shows the structure of related diethylstilbestrolquinone [7] to compare the quinomethide fragments of these molecules. The difference in the C=C bond lengths in the cyclohexadiene and methylene fragments of these molecules, and also in the C-C bond lengths of the bridging chain is obvious. In the case of diethylstilbestrolquinone, the ordinary C-C bond length (1.469 Å) of the C=C-C=C moiety tends to a value of 1.478(12) Å, which is usual for unconjugated units [8], whereas the same bond length in 2 [1.406(10) Å] is shorter than even in butadiene. This observation can be rationalized by a different conjugation degree. In contrast to the nonplanar diethylstilbestrolquinone molecule [7], compound 2 is planar, and thus, both quinomethide fragments are strongly conjugated. The torsion angle O(1)-C(1)-C(2)-O(2) is only $1.29(4)^{\circ}$.

The C(2)–O(2) distance of 1.357(6) Å is close to the ordinary C–O bond lengths in different phenols (1.359–1.362 Å) [8], it evidences the hydroxyl character of this group. The O(1)···H(2) distance [1.78(2) Å] is shorter than the sum of Van der Waals radii of hydrogen and oxygen atoms (2.7 Å [9]) or close intramolecular O···H (2.15 Å) contacts [10]. Thus, the intramolecular hydrogen bond is realized in molecule **2**. The O(1)–C(1)–C(2)–O(2)–H(2) fragment is practically planar, the mean deviation from plane is 0.033 Å.



Figure 2. PLATON view of two independent molecules of 3. Hydrogen atoms of tert-butyl groups and the rings are omitted for clarity.

Table 1. Selected bond lengths /Å and angles /° in 2.

bond /Å		angle /°	
O(1)–C(1)	1.246(6)	O(1)-C(1)-C(6)	124.8(4)
O(2) - C(2)	1.357(6)	O(1)-C(1)-C(2)	115.9(4)
C(1) - C(6)	1.446(7)	C(6)-C(1)-C(2)	119.3(4)
C(1) - C(2)	1.486(7)	O(2)-C(2)-C(3)	125.1(4)
C(2) - C(3)	1.361(7)	O(2)-C(2)-C(1)	110.3(4)
C(3) - C(4)	1.451(7)	C(3)-C(2)-C(1)	124.6(4)
C(3) - C(8)	1.544(7)	C(7)-C(4)-C(5)	116.8(4)
C(4) - C(7)	1.391(7)	C(7) - C(4) - C(3)	122.4(4)
C(4) - C(5)	1.452(7)	C(5)-C(4)-C(3)	120.7(4)
C(5) - C(6)	1.342(6)	C(6) - C(5) - C(4)	125.2(4)
C(6) - C(12)	1.528(7)	C(5)-C(6)-C(1)	115.7(4)
C(7)–C(7a)	1.406(10)	C(4)-C(7)-C(7a)	127.4(6)



Scheme 4.

Selected bond lengths and angles in the molecular structure of compound **3** are given in Table 2. The crystals of **3** contain two crystallographically independent molecules in the unit cell, the first molecule is in common position (A) and the other molecule is disposed on the C_2 axis (B). Both molecules reveal the usual *o*-quinoid distortion: two double C=C bonds [C(3)–

C(4), C(5)-C(6) and C(10)-C(11), C(9)-C(14) in A and C(33)-C(34), C(35)-C(36) in B] are separated by an ordinary C-C bond [C(4)-C(5), C(9)-C(10) in A, and C(34)-C(35) in B]. Carbon–oxygen bonds [O(1)–C(1) 1.215(2) Å, O(2)–C(2)1.213(2) Å, O(3)–C(12) 1.217(2) Å, O(4)–C(13) 1.221(2) Å in A; O(5)–C(32) 1.218(2) Å, O(6)–C(31) 1.220(2) Å in B] are of double bond character and are in the range of usual carbonyl bonds of carbonyl compounds 1.19–1.23 Å [8, 11]. In crystals of 3,5-di-tert-butyl-o-benzoquinone, double C=C bonds are 1.347, 1.348 Å, C=O bonds are 1.221, 1.223 Å [12]. The double [1.341–1.343(2) Å] and ordinary [1.471(2), 1.467(2) Å in A and 1.463(2) Å in B] carbon-carbon bond lengths of the ethylene bridge in both molecules A and B in 3 (Table 2) are similar to those in compounds with a C=C-C=C fragment (C=C, 1.331-1.341 Å; C-C, 1.460-1.470 Å) [8]. In contrast to the molecular structure of 2, the C-O groups in both molecules of 3 are twisted against each other. The torsion angles O(1)-C(1)-C(2)-O(2), O(3)-C(12)-C(13)-O(4) in the first molecule of 3 and O(5)-C(33)-C(34)-O(6) in the second molecule of 3 are 22.82(15), 34.55(15) and 23.34(15)°, respectively.

It should be noted that the shortened O····H distances between oxygen atoms and hydrogen atoms of tert-butyl groups are found in both molecules. These distances vary in the range of 2.30(2)-2.44(2) Å in **2** and 2.30(2)-2.41(2) Å in **3** and are significantly shorter than the sum of Van der Waals radii of above-mentioned atoms. However, we observed a twist conformation of the C–O groups for 3 but not for 2 (the molecule is practically planar). Apparently, the main reason for this structural difference in molecules 2 and 3 is the formation of an intramolecular O···H hydrogen bond in 2. In other words, the intramolecular O····H bond in 2 gives additional hardness (stability) of the O(1)-C(1)-C(2)-O(2) fragments in 2 relative to analogous fragments in 3. Consequently, the energy of intermolecular O···H interactions in 2 should be lower than the energy of the O(1)–H(2) bond. In order to check this assumption, we carried out DFT calculations with the PC-Gamess (Firefly) program [13]. These calculations showed that the planar

Table 2. Se	elected bond	lengths /Å	and angles	/°	in	3.
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bond /Å angle /°				
First independent molecule of 3 (A)				
O(1)-C(1)	1.215(2)	O(1)-C(1)-C(6)	124.99(16)	
O(2) - C(2)	1.213(2)	O(1)-C(1)-C(2)	117.22(14)	
O(3) - C(12)	1.217(2)	C(6)-C(1)-C(2)	117.22(14)	
O(4)–C(13)	1.221(2)	O(2)–C(2)–C(3)	124.09(16)	
C(1)–C(6)	1.473(2)	O(2)-C(2)-C(1)	115.95(15)	
C(1)–C(2)	1.553(2)	C(3)-C(2)-C(1)	119.83(13)	
C(2)–C(3)	1.478(2)	C(3)-C(4)-C(5)	121.76(14)	
C(3)–C(4)	1.373(2)	C(3)-C(4)-C(7)	123.29(15)	
C(4) - C(5)	1.470(2)	C(5)-C(4)-C(7)	114.92(14)	
C(4) - C(7)	1.471(2)	C(8)-C(7)-C(4)	124.05(15)	
C(5)-C(6)	1.340(2)	C(7)-C(8)-C(9)	126.33(15)	
C(7)-C(8)	1.343(2)	C(14)-C(9)-C(8)	122.22(15)	
C(8)–C(9)	1.467(2)	C(14)-C(9)-C(10)	122.12(14)	
C(9)-C(14)	1.373(2)	C(8)-C(9)-C(10)	115.45(14)	
C(9)-C(10)	1.473(2)	O(3)-C(12)-C(11)	125.61(16)	
C(10)–C(11)	1.348(2)	O(3)–C(12)–C(13)	117.74(15)	
C(11)-C(12)	1.474(2)	C(11)-C(12)-C(13)	116.64(13)	
C(12)–C(13)	1.549(2)	O(4)-C(13)-C(14)	124.07(16)	
C(13)–C(14)	1.478(2)	O(4)-C(13)-C(12)	116.48(14)	
		C(14)-C(13)-C(12)	119.28(13)	
Second independent molecule of 3 (B)				
O(5)–C(32)	1.218(2)	O(6)-C(31)-C(36)	125.11(15)	
O(6)–C(31)	1.220(2)	O(6)-C(31)-C(32)	117.16(14)	
C(31)–C(36)	1.467(2)	C(36)–C(31)–C(32)	117.59(13)	
C(31)–C(32)	1.548(2)	O(5)-C(32)-C(33)	123.78(16)	
C(32)–C(33)	1.478(2)	O(5)-C(32)-C(31)	115.61(14)	
C(33)–C(34)	1.372(2)	C(33)–C(32)–C(31)	120.28(13)	
C(34)–C(45)	1.463(2)	C(33)–C(34)–C(45)	122.88(14)	
C(34)–C(35)	1.472(2)	C(33)-C(34)-C(35)	121.62(14)	
C(35)–C(36)	1.343(2)	C(45)-C(34)-C(35)	115.45(13)	
C(45)-C(45a)	1.341(3)	C(45a)-C(45)-C(34)	125.68(19)	

framework in 2 and the twisted distortion between the C-O groups in 3 remained after geometry optimization. The torsion O-C-C-O angles are 0.14° in 2 and 33.46, 33.42° in 3. Consequently, these phenomena are mainly due to intramolecular interactions than intermolecular interactions in the crystal. In order to understand the nature of these phenomena, we performed calculations with the application of *Bader*'s theory [14, 15]. According to the observed critical points (3,-1), both complexes have intramolecular hydrogen bonds between the oxygen atoms of C=O groups and the hydrogen atoms of tBu groups. There are two O(1)-H(tBu) and one O(2)-C(9) bond paths in one part of 2-hydroxy-3,6-di-tert-butyl-cyclohexa-2,5dienone and the same in other part of molecule 2. The same situation is observed for 3, in which two O(1)-H(*t*Bu) and one O(2)-H(tBu) bond paths exist, the same is observed in the other part of the molecule. In order to evaluate the energy of these interactions, we used the correlated equation of Espinosa [16]. According to this equation, the energy of intramolecular O(1)–H(2) hydrogen bond is 12.2 kcal·mol⁻¹ and is noticeably larger than the energy of two intramolecular O(1)-H(tBu) and one O(2)–C(9) interactions (9.4 kcal·mol⁻¹). Thus, the intramolecular O(1)-H(2) hydrogen bond stabilizes the planar conformation in 2. The energy of two O(1)-H(tBu) and one O(2)-H(*t*Bu) intramolecular hydrogen bonds in **3** is 8.6 kcal·mol⁻¹,

which is close to the energy of the similar hydrogen bonds in **2**. However, the absence of an additional stabilization of the O-C-C-O fragment leads to the twisted conformation of this fragment in **3**, which is due to Pauli repulsion between the two carbonyl groups.

2.3. EPR Study of the Derivatives of 3

The formation of mono- and polyreduced derivatives is a well known feature of *o*-quinones and related ligands [4d, 4f, 11, 17].

It was unexpected that some of radical-anionic derivatives of di-o-quinone **3** were found to be quite unstable. For instance, the interaction of **3** with thallium amalgam is accompanied by a rapid color change to deep violet but, however, the reaction mixture is EPR silent. The latter fact can be rationalized by the rearrangement chain including disproportionation of the mononuclear product and the existence of the diamagnetic quinomethide salt of the dianionic derivative (Scheme 5).





Scheme 5.

The same observations were made when the tetra-reduced derivative $Tl_2(Cat-CH=CH-Cat)Tl_2$ was treated with neutral di-*o*-quinone **3** (Scheme 5). Despite the amount of **3**, there are no EPR signals in the reaction mixture although the color change reflects the processing of the reaction. This fact implies that mono- and tri-thallium adducts are not stable and undergo disproportionation to diamagnetic forms.

An EPR spectrum of mono-reduced derivative of **3**, (Q–CH= CH–SQ)^{$\dot{}$ K⁺, was obtained when an excess of di-*o*-quinone (**3**) was treated with potassium in THF media (Figure 3). The hyperfine structure (HFS) of spectrum [triplet (1:1:1) of doublets}



with $A_i(2H) = 3.6 \text{ G}$, $A_i(H) = 1.95 \text{ G}$, $g_i = 2.0042$] is caused by unpaired electron hyperfine coupling (HFC) with three protons where two of them are equivalent by pure accident.

3436 3438 3440 3442 3444 3446 3448 Figure 3. The X-band EPR spectrum of $(Q-CH=CH-SQ)^{-}K^{+}$, the reduced derivative of 3 with potassium (THF, 298 K) (top spectrum) and the simulation (bottom spectrum).

The bigger HFS constant ($A_i(2H) = 3.6$ G) can be attributed to the ring proton and the second proton of methylene group whereas the first methylene proton gives rise to the splitting of 1.95 G. So, the delocalization of an unpaired electron over both *o*-quinonic fragments in (Q–CH=CH–SQ)^{\pm} takes place. The presence of additional lines in the EPR spectrum of (Q– CH=CH–SQ)^{\pm}K⁺, which are probably due to *cis–trans* isomerism of this (Q–CH=CH–SQ) K derivative are noteworthy. The spin density distribution in *cis-* and *trans*-isomers should be undoubtedly different from each other. To our regret, the low concentration of the second product in solution does not allow to distinguish its spectrum EPR unequivocally.

2.4. Binuclear Tin and Antimony Derivatives of 2 and 3

Di-*p*-quinomethide (2) is a suitable starting agent for the preparation of dianionic derivatives of di-*o*-quinone (3). It reacts readily with organometallic bases such as Ph_3SnOH (Scheme 6). During the reaction of 2 with Ph_3SnOH in THF the color of mixture turned to dark-violet, and a microcrystal-

line dark-blue powder precipitated after the solvent change to hexane. By using NMR and IR spectroscopy, it was determined as diamagnetic triphenyltin(IV) bis-*p*-quinomethide-phenolate (4).

Triphenylstibine is a convenient two-electron reductant for o-quinones [18]. The addition of a toluene solution of Ph₃Sb to a solution of **3** at room temperature (molar ratio 2:1) (Scheme 7) effects a color change from green-brown to deep yellow within one hour. The crystalline product **5** was obtained by slow evaporation of the solvent.

Bis-catecholate complex Ph₃Sb(Cat–CH=CH–Cat)SbPh₃ (**5**) has a symmetrical structure in solution, which is corroborated by its ¹H NMR spectrum. The aliphatic region contains two singlet signals (at 1.44 and 1.59 ppm) assigned to two pairs of *tert*-butyl protons, a singlet signal at 6.98 ppm is due to the ethylene bridge protons. Two protons of aromatic moieties (fragments C₆H₁) appear as one singlet signal at 6.76 ppm and multiplet signals at 7.42–7.50 and 7.74–7.90 ppm are due to the phenyl protons of triphenylantimony(V) units. The ¹H NMR spectrum also contains signals of the solvent toluene (singlet at 2.36 ppm and multiplets at 7.15–7.26 ppm).

The symmetrical structure of bis-catecholate **5** maintains in crystals. Its molecular structure is shown in Figure 4. Selected bond lengths and angles are listed in Table 3. X-ray diffraction analysis corroborates the presence of co-crystallized solvent: the unit cell contains one toluene molecule per complex molecule.

Each antimony atom adopts a distorted square-planar arrangement where two oxygen atoms of the catecholate ligand and two of three phenyl carbon atoms form the basal plane of the pyramid and the third phenyl carbon atom is in apical position. This arrangement was observed for a number of triphenylantimony(V) catecholates [18, 19]. The bond angles at the basal plane are not equal: O(1)-Sb(1)-C(28) has a value of 144.14(5)° whereas the angle O(2)-Sb(1)-C(16) has 155.53(5)°. The planes of Cat-ligands in CatSbPh₃-fragments are nearly coplanar. At the same time, the plane formed by ethylene bridge [C(30)-C(15)-C(15')-C(3')] is rotated at 47.13(5)° regarding planes of Cat-ligands. The apical Ph groups of each Sb^V catecholate fragment occupy trans-positions relatively to each other. The deflection of each antimony atom from the basal plane O(1)-O(2)-C(16)-C(28) of pyramid is 0.495(2) Å. The Sb–O bonds [Sb(1)–O(1) 2.0086(11) Å, Sb(1)-O(2) 2.0381(11) Å] are in good agreement with the sum of the covalent radii of the corresponding elements (1.41+ 0.66 = 2.05 Å [9, 20]).

The oxygen–carbon bond lengths [O(1)–C(1) 1.3653(18), O(2)–C(6) 1.3579(19) Å] are in the range of ordinary O–C bond lengths in other triphenylantimony(V) catecholates (1.34–1.37 Å) [18,19]. The ring carbon–carbon distances of 1.403(2) Å are in average close to aromatic C–C bond lengths in catecholates [18, 19] or, for instance, in benzene (1.399 Å) [8].

The single C–C bond lengths [C(3)–C(15) 1.494(2) Å] of the ethylene bridge in **5** are elongated relative to those in neutral bis-*o*-quinone (**3**) [1.463(2)–1.471(2) Å], whereas the length of the double bond C(15)–C(15a) [1.314(3) Å] is shorter than



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Scheme 6.



Scheme 7.



Figure 4. PLATON view of 5. Hydrogen atoms of tert-butyl groups and the rings are omitted for clarity.

Table 3. Selected	bond	lengths /Å	and	angles	/°	in	5.
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bond /Å		angle /°	
Sb(1)–O(1)	2.0086(11)	O(1)–Sb(1)–O(2)	78.42(4)
Sb(1)–O(2)	2.0381(11)	O(1)-Sb(1)-C(22)	107.14(5)
Sb(1)–C(22)	2.0976(14)	O(2)-Sb(1)-C(22)	98.56(5)
Sb(1)–C(28)	2.1278(15)	O(1)-Sb(1)-C(28)	144.14(5)
Sb(1)–C(16)	2.1414(15)	O(2)-Sb(1)-C(28)	85.50(5)
O(1) - C(1)	1.3653(18)	C(22)-Sb(1)-C(28)	106.82(6)
O(2) - C(6)	1.3579(19)	O(1)-Sb(1)-C(16)	83.28(5)
C(1) - C(6)	1.405(2)	O(2)-Sb(1)-C(16)	155.53(5)
C(1)-C(2)	1.406(2)	C(22)-Sb(1)-C(16)	102.28(5)
C(2) - C(3)	1.416(2)	C(28)-Sb(1)-C(16)	100.44(6)
C(3) - C(4)	1.405(2)	O(1)-C(1)-C(6)	114.20(13)
C(3)–C(15)	1.494(2)	O(1)-C(1)-C(2)	121.87(13)
C(4) - C(5)	1.392(2)	C(6)-C(1)-C(2)	123.93(14)
C(5) - C(6)	1.395(2)	O(2)-C(6)-C(5)	123.10(13)
C(15)-C(15a)	1.314(3)	O(2)-C(6)-C(1)	115.93(13)
		C(5)-C(6)-C(1)	120.97(14)
		C(15a)-C(15)-C(3)	123.83(19)

that of the same bond in **3**. They slightly differ from usual single and double C–C bond lengths (1.51-1.54 and 1.30-1.33 Å, respectively) [8] because of the formation of a conjugate system in a binuclear molecule.

Investigations on the crystal structure showed that molecules of **5** are packed in stacks, shifted relatively to each other (Figure 5). Interestingly, hydrogen atoms of apical Ph rings are directed towards the center of benzene rings of catecholate ligands (T-shape arrangement). The "H---center of π -system" distance is 2.52(2) Å [the "C-H-center of π -system" angle is 170.9°; the H---C distances vary in the range of 2.80(3)–2.98(2) Å]. Apparently, these structural characteristics could be interpreted as the demonstration of C(H)– π -system interactions (<3.05 Å [21]).

We found that the repetition of the reaction between di-*o*quinone (**3**) and triphenylstibine (molar ratio 1:1) did not lead to mononuclear catecholate Ph₃Sb(Cat–CH=CH–Q) in contrast to 4,4'-bis(3-methyl-6-*tert*-butyl-*o*-benzoquinone) (see type E of di-*o*-quinones on Scheme 1), which was shown to react with



Figure 5. View of crystal packing fragment of 5. The hydrogen and carbon atoms of *tert*-butyl groups and hydrogen atoms of the rings are omitted for clarity.

Ph₃Sb in 1:2 molar ratio forming binuclear bis-catecholate Ph₃Sb(Cat–Cat)SbPh₃ and in 1:1 molar ratio forming mononuclear Ph₃Sb(Cat–Q) [18a]. In our case, reaction of **3** and Ph₃Sb in 1:1 molar ratio yielded the mixture of bis-catecholate (**5**) and an initial di-*o*-quinone (**3**) (Scheme 8).

Q-CH=CH-Q + Ph₃Sb
$$\xrightarrow{(1:1)}$$
 1/2 Ph₃Sb(Cat-CH=CH-Cat)SbPh₃ + 1/2 3
3 5

Scheme 8.

This evidenced that the doubly reduced derivatives of di-o-quinone **3** exist as quinomethide salts (both o-quinone fragments are one-electron reduced). The products prepared by the two-electron reduction of one of the two o-quinone fragments were not stable and disproportionated to an initial di-o-quinone (**3**) and a bis-catecholate derivative (like **5**).

3. Experimental Section

3.1. General Considerations

Starting materials were commercially available (Aldrich, Fluka, Strem) unless otherwise noted. Triphenyltin hydroxide and triphenylantimony were of reagent grade. 4,4'-(Ethane-1,2-diyl)-bis(3,6-di-*tert*-butyl-*o*-benzoquinone) Q–CH₂–CH₂–Q (1) was prepared according to literature procedure [5a]. Solvents were purified by standard methods [22]. All manipulations with samples for EPR investigations as well as syntheses of complexes 4 and 5 were carried out in vacuo.

¹H NMR spectra were recorded with a Bruker AVANCE DPX-200 spectrometer, by using CDCl₃ as solvent and tetramethylsilane as internal standard. IR spectra were recorded with a FSN 1201 Fourier spectrometer. UV/Vis spectra were taken with a Perkin–Elmer lambda 25 spectrometer. X-band EPR spectra were recorded with a "Bruker ER 200 D-SRC" spectrometer with thermostat ER 4111 T. The standard for *g* factor was DPPH (g = 2.0037). The C, H analysis of compounds was performed with an Euro EA 3000 elemental analyzer.

The intensities data were collected with a SMART APEX diffractometer (graphite-monochromated, Mo- K_{α} -radiation, ω - and θ -scan technique, $\lambda = 0.71073$ Å). The structures were solved by direct methods and were refined on F^2 using SHELXTL package [23]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **3** and **5** were found from Fourier syntheses of electron density and were refined isotropically, whereas hydrogen atoms in **2** were placed in calculated positions and were refined in the riding model. SADABS [24] was used to perform area-detector scaling and absorption corrections. Summary of crystal and refinement data are presented in Table 4.

DFT calculations were carried out by the PC-Gamess (Firefly) program using B3LYP functional and 6-311 (2p,2d) basis set. Optimizations were performed without constraint, and the nature of the stationary points was confirmed by calculation of vibrational frequencies.

3.2. Syntheses

4,4'-(Ethane-1,2-diylidene)bis(2-hydroxy-3,6-di-tert-butyl-

cyclohexa-2,5-dienone) (2): 4,4'-(ethane-1,2-diyl)-bis(3,6-di-tert-butyl-o-benzoquinone) (Q-CH2-CH2-Q, 1) (2 g, 4.3 mmol) in toluene (20 mL) was heated to 70-80 °C for 4 h. The obtained precipitate was recrystallized from dioxane, filtered off and washed with n-hexane. Crystals of 2 suitable for single-crystal X-ray analysis were collected after prolonged crystallization from toluene solution. Yield 1.42 g (71 %). $T_{\rm m}$ = 250–251 °C. Elemental analysis: calcd. (%) for C₃₀H₄₂O₄: C, 77.21; H, 9.07; found: C, 77.07; H, 8.93. IR (Nujol), v = 1591 s (C=O); 3213 s (OH) cm⁻¹. UV/Vis (70 °C, toluene): $\lambda =$ 494.42 nm (ε = 46200 m⁻¹·cm⁻¹). ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.35$, 1.61 (both s, 18H, 2 *t*Bu); 7.68 (s, 2H, methyne protons of = CH-CH = bridge); 8.15 (s, 2 H, 2 OH); 8.20 (s, 2H, 2 C_6H_1). ¹³C NMR (50 MHz, CDCl₃, 25 °C, TMS): $\delta = 28.9$, 36.1[C(CH₃)₃, C'(C'H₃)₃]; 32.9 [C(13), C(14), C(15)]; 34.9 [C(9), C(10), C(11)]; 127.0 [C(7)]; 130.4 [C(5)]; 136.1 [C(4)]; 142.7 [C(2)]; 148.4 [C(6)]; 180.1 [C(1)=O(1)].

4,4'-(Ethene-1,2-diyl)bis(3,6-di-*tert***-butyl-***o***-benzoquinone)** (Q-CH=CH-Q, 3): A solution of K_3 [Fe(CN)₆] (1 g) and KOH (3 g) in

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Table 4. Summary of crystal and refinement data.

	2	3	5·toluene
Formula	C ₃₀ H ₄₂ O ₄	C ₄₅ H ₆₀ O ₆	C ₇₃ H ₇₈ O ₄ Sb ₂
Formula weight	466.64	696.93	1262.91
Temperature /K	100(2)	100(2)	100(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	Pbca	$P\overline{1}$
Unit cell dimensions	-		
a /Å	10.124(2)	12.0726(9)	11.0695(12)
b /Å	10.856(3)	20.1445(14)	11.3986(12)
c /Å	11.705(3)	32.163(2)	13.6607(15)
$\alpha /^{\circ}$	90	90	103.388(2)
β /°	92.958(5)	90	113.273(2)
y /°	90	90	90.681(2)
Volume /Å ³	1284.7(5)	7822(1)	1530.0(3)
Z	2	8	1
Calculated density /Mg·m ⁻³	1.206	1.184	1.362
Absorption coefficient /mm ⁻¹	0.078	0.077	0.932
F(000)	508	3024	642
Crystal size /mm	$0.30 \times 0.25 \times 0.08$	$0.20 \times 0.15 \times 0.08$	$0.16 \times 0.16 \times 0.16$
Theta range for data collection	2.01 to 20.16	2.02 to 29.02	1.85 to 29.07
Limiting indices	$-9 \le h \le 9$	$-16 \le h \le 16$	$-14 \le h \le 14$
	$-10 \le k \le 10$	$-27 \le k \le 27$	$-15 \le k \le 11$
	$-11 \le l \le 11$	$-43 \le l \le 43$	$-18 \le l \le 15$
Reflections collected / unique	5704 / 1192 [R(int) = 0.0396]	78056 / 10388 [R(int) = 0.0519]	11381 / 7923 [R(int) = 0.0155]
Reflections with $I > 2\sigma(I)$	1035	8355	7414
Completeness to theta	$\theta = 20.16, 96.8 \%$	$\theta = 29.02, 99.6 \%$	$\theta = 29.07, 96.7 \%$
Max. and min. transmission	0.9938 and 0.9770	0.9939 and 0.9848	0.8653 and 0.8653
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1192 / 0 / 162	10388 / 0 / 700	7923 / 19 / 510
Goodness-of-fit on F^2	1.071	1.100	1.098
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0754,	R1 = 0.0717,	R1 = 0.0309,
	wR2 = 0.2032	wR2 = 0.1631	wR2 = 0.0755
R indices (all data)	R1 = 0.0814,	R1 = 0.0886,	R1 = 0.0337,
· · · ·	wR2 = 0.2079	wR2 = 0.1722	wR2 = 0.0771
Largest diff. peak / hole / e ·A ⁻³	0.397 / -0.238	0.640 / -0.242	1.228 / -0.511

water (200 mL) was added to a hot solution of 2 (1 g, 2.2 mmol) in toluene (500 mL). The reaction mixture was stirred until the red color disappeared. Toluene was reduced to a volume of 100 mL at atmospheric pressure and dark red-brown crystals of 3 suitable for X-ray diffraction were obtained after slow cooling of the solution. Yield 0.92 g (92 %). $T_{\rm m} = 256-257$ °C. Elemental analysis: calcd. (%) for C₃₀H₄₀O₄: C, 77.55; H, 8.68; found: C, 77.27; H, 8.31. **IR** (Nujol): *v* = 1655 s. (C=O), 1685 s. (C=O) cm⁻¹. UV/Vis (50 °C, toluene): $\lambda =$ 423.25 nm (ε = 14384 m⁻¹·cm⁻¹). ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.27$, 1.41 (both s, 18H, 2 *t*Bu); 6.95 (s, 2H, methyne protons of -CH=CH- bridge); 7.28 (s, 2H, 2 C₆H₁). ¹³C NMR (50 MHz, CDCl₃, 25 °C, TMS): δ = 29.00, 31.58 [C(CH₃)₃, C'(C'H₃)₃]; 35.09 [C(20), C(21), C(22)]; 36.67 [C(16), C(17), C(18)]; 133.19 [C(7)]; 137.28 [C(5)]; 140.38 [C(4)]; 148.66 [C(3)]; 148.99 [C(6)]; 182.79, 186.22 [C=O, C'=O']. DEPT (50 MHz, CDCl₃, 25 °C, TMS): $\delta = 29.00, 31.58 [C(CH_3)_3, C'(C'H_3)_3]; 137.28 [C(5)H and$ C(10)H]; 133.19 [C(7)H and C(8)H].

Triphenyltin(IV) *p*-quinomethide-phenolate (4): A solution of 2 (0.042 g, 0.09 mmol) in THF (50 mL) was added to a sample of Ph₃SnOH (0.066 g, 0.18 mmol). The color of the solution turned dark-violet. After solvent change to *n*-hexane, **4** precipitated as microcrystalline powder. It was filtered, washed with *n*-hexane and dried in vacuo. Yield 0.078 g (75 %). Elemental analysis: calcd. (%) for C₆₆H₇₀O₄Sn₂: C, 68.04; H, 6.01; Sn, 20.45; found: C, 68.23; H, 6.22; Sn, 19.74. **IR** (Nujol): v = 1462 (C–O) cm⁻¹. **UV/Vis** (50 °C, THF):

 $\lambda_1 = 471.67 \text{ nm}, \lambda_2 = 764.87 \text{ nm}.$ ¹**H NMR** (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.31$, 1.61 (both s, 18H, 2 *t*Bu); 7.61 (s, 2H, methyne protons of –CH=CH– bridge); 7.43–7.49, 7.75–7.79 (m, 30 H, 6 C₆H₅ of 2 SnPh₃); 8.20 (s, 2H, 2 C₆H₁).

Triphenylantimony(V) bis-catecholate (5): 1. A solution of triphenylstibine (0.155 g, 0.44 mmol) in toluene (20 mL) was added to a solution of di-*o*-quinone **3** (0.1 g, 0.22 mmol) in toluene (50 mL). After 1 h, the reaction was finished and the solution color turned from greenbrown to deep-yellow. Crystals of **5**-toluene suitable for X-ray diffraction were obtained after solvent evaporation in vacuo. Yield 0.224 g (81 %). $T_{\rm m} = 210-211$ °C (decomp.). Elemental analysis: calcd. (%) for C₆₆H₇₀O₄Sb₂·C₇H₈: C, 69.43; H, 6.22; Sb, 19.28; found: C, 69.02; H, 6.33; Sb, 20.18. **IR** (Nujol): v = 693 s, 718 s (Ph); 1256 s, 1306 s (C–O) cm⁻¹. ¹H **NMR** (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.44$, 1.59 (both s, 18H, 2 *t*Bu); 2.36 (s, 3 H,CH₃ of toluene); 6.76 (s, 2H, 2 C₆H₁); 6.98 (s, 2H, methyne protons of –CH=CH– bridge); 7.15–7.26 (m, 5 H, Ph of toluene); 7.44–7.49, 7.75–7.79 (m., 30 H, 6 C₆H₅ of 2 SbPh₃).

2. A solution of triphenylstibine (0.078 g, 0.22 mmol) in toluene (10 mL) was added to a solution of di-*o*-quinone (3) (0.100 g, 0.22 mmol) in toluene (50 mL), which caused brightening of the solution. Upon evaporation of the solvent in vacuo, first the crystals of initial di-*o*-quinone (3) precipitated followed by the crystals of complex 5 (0.058 g, yield 21 %) and afterwards an inseparable mixture of 3 and 5 was formed.



Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. CCDC-732316 for **2**, CCDC-732317 for **3** and CCDC-732318 for **5**-toluene. Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk).

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