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5-{5-(Bicyclo[2.2.1]hept-2-enyl)hydroxymethyl}-3,6-di-*tert*-butyl-*o*-benzoquinone and Related Polymers. Synthesis and Some Properties

A. V. Safronova, L. N. Bochkarev, N. O. Druzhkov, Yu. A. Kurskii, E. V. Baranov, and G. A. Abakumov

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, ul. Tropinina 49, Nizhny Novgorod, 603950 Russia
e-mail: lnb@iomc.ras.ru

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Abstract—A norbornene-containing *ortho*-quinone, 5-{5-(bicyclo[2.2.1]hept-2-enyl)hydroxymethyl)-3,6-di-*tert*-butyl-*o*-benzoquinone, was synthesized by the nucleophilic addition of 5-(hydroxymethyl)bicyclo[2.2.1] hept-2-ene to 3,6-di-*tert*-butyl-*o*-benzoquinone. The structure of the compound was established by the X-ray analysis. The monomer obtained undergoes metathesis polymerization in the presence of Grubbs catalyst of the third generation with the formation of polynorbornene containing quinone fragments in the side chains.

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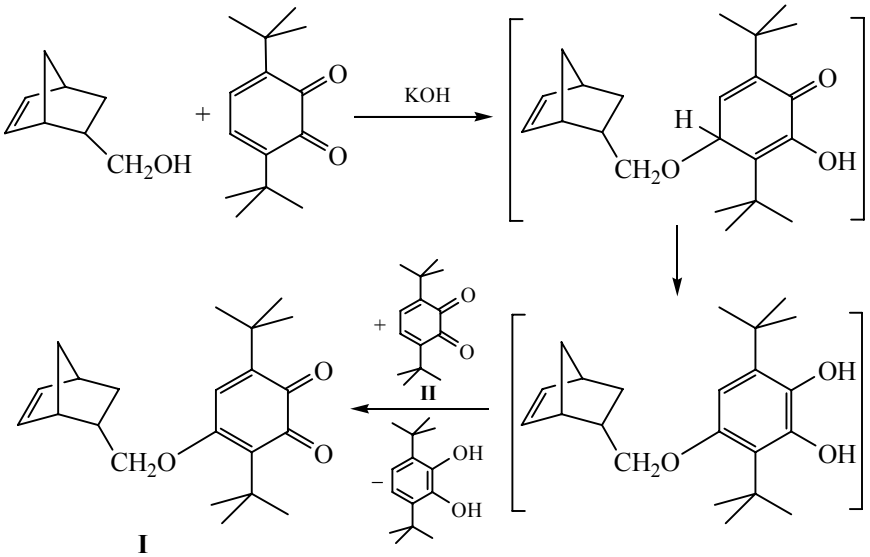
Sterically hindered *o*-quinones are redox-active ligands capable of forming semiquinone and catecholate complexes with various metals [1, 2]. Several semiquinone complexes of Rh, Co, Ir, Cu, Ni, and Mn exhibit temperature-induced redox isomerism [3]. Triarylantimony catecholate derivatives can reversibly absorb molecular oxygen [4, 5]. Properties of semiquinone and catecholate metallocomplexes are largely determined by the nature of substituents in the quinone moiety [6, 7]. One of the most convenient methods for introducing different substituents in the *o*-quinone ligands is alkoxylation [8]. In this study, we used this method to prepare a norbornene-containing 3,6-di-*tert*-butyl-*o*-benzoquinone (**I**), which has typical properties of sterically hindered *o*-quinone and is capable of forming a carbon-chain polymers with quinone fragments in side chains.

We found that reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone (**II**) with 5-(hydroxymethyl)bicyclo[2.2.1]hept-



2-ene at 100°C in the presence of a catalytic amount of potassium hydroxide led to the formation of new 5-{5-(bicyclo[2.2.1]hept-2-enyl)hydroxymethyl}-3,6-di-*tert*-butyl-*o*-benzoquinone (**I**).

In the initial stages of the reaction the quinone adds alcohol to form alkoxypyrocatechol, which is oxidized subsequently by the parent 3,6-di-*tert*-butyl-*o*-benzoquinone (**II**) to alkoxyquinone **I**.

After final purification by column chromatography alkoxyquinone **I** was isolated in 42% yield as dark red crystals, stable in air, easily soluble in common organic solvents. According to NMR spectroscopy data (see Experimental) compound **I** in $CDCl_3$ solution exists as *endo*- and *exo*-isomers in a 4:1 ratio.

Structure of the norbornene-substituted quinone **I** was determined by X-ray diffraction analysis. The X-ray study showed that a single-crystal of the compound contained only the *endo*-isomer (Fig. 1). The unit cell contains two independent molecules (**A** and **B**) with close values of their geometric characteristics (Table 1). Therefore while further discussing the structure of the quinone **I** we considered only the geometric parameters of molecule **A**. The six-membered ring is not flat, the average deviation of carbon atoms C^1–C^6 from the plane of the ring is 0.051 Å. Oxygen atoms O^1 and O^2 are turned into opposite directions relative to the six-membered ring plane at 0.465 and 0.224 Å, respectively. The O^1–C^2 and O^2–C^3 distances are 1.232(4) and 1.209(3) Å, which is close to the length of the C=O double bond (1.21 Å [9]). The most shortened distances in the six-membered rings are observed between the atoms C^4–C^5 and C^6–C^1, 1.336(3) and 1.358(3) Å respectively, which are close to the length of the C=C double bond (1.317 Å [9]). The length of the single bond O^3–C^{15} is 1.438(3) Å. The O^3–C^6 distance is markedly shortened, being 1.344(3) Å, which is typical of the O–C_{sp^2} bond (1.354 Å [9]). The length of the double bond C^{19}–C^{20} in the norbornene fragment (NBE) is 1.3298 (9) Å.

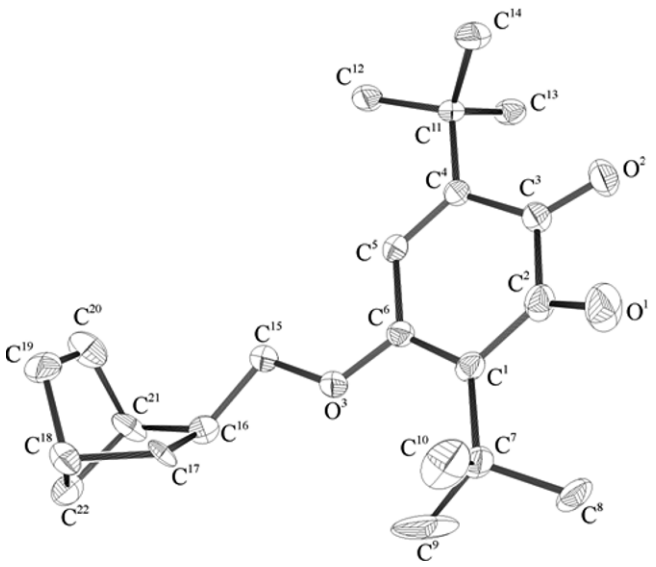


Fig. 1. Structre of 5-{5-(bicyclo[2.2.1]hept-2-enyl)hydroxymethyl}-3,6-di-*tert*-butyl-*o*-benzoquinone (**I**) (thermal ellipsoids with 30% probability, the hydrogen atoms are omitted).

Table 1. Selected bond lengths (*d*) and bond angles (ω) in quinone **I** molecule

Parameter	A	B
Bond		
O^1–C^2	1.232(4)	1.211(3)
O^2–C^3	1.209(3)	1.221(3)
C^1–C^2	1.454(4)	1.452(4)
C^2–C^3	1.557(4)	1.543(4)
C^3–C^4	1.466(3)	1.465(3)
C^4–C^5	1.336(3)	1.344(3)
C^5–C^6	1.477(3)	1.474(3)
C^6–C^1	1.358(3)	1.375(3)
O^3–C^6	1.344(3)	1.346(3)
O^3–C^{15}	1.438(3)	1.428(3)
C^{15}–C^{16}	1.526(3)	1.531(3)
C^{19}–C^{20}	1.3298(9)	1.3300(9)
Angle ω		
$C^6O^3C^{15}$	122.6(2)	122.5(2)
$C^{15}C^{16}C^{17}$	109.8(1)	110.0(2)

The marked difference should be noted in the O^1–C^2 and O^2–C^3 distances in the molecule **A** [1.232(4), 1.209(3) Å] compared with the analogous distances in the molecule **B** [1.211(3), 1.221(3) Å]. The analysis of the crystal packing shows that the oxygen atom O^1 in the molecule **A** is involved in the formation of intermolecular contact with the hydrogen atom H^{20B} of the norbornene fragment in the second independent molecule of quinone **B**. The distance $O^{1A}\cdots H^{20B}$ is 2.151 Å (Fig. 2), which corresponds to a short O···H

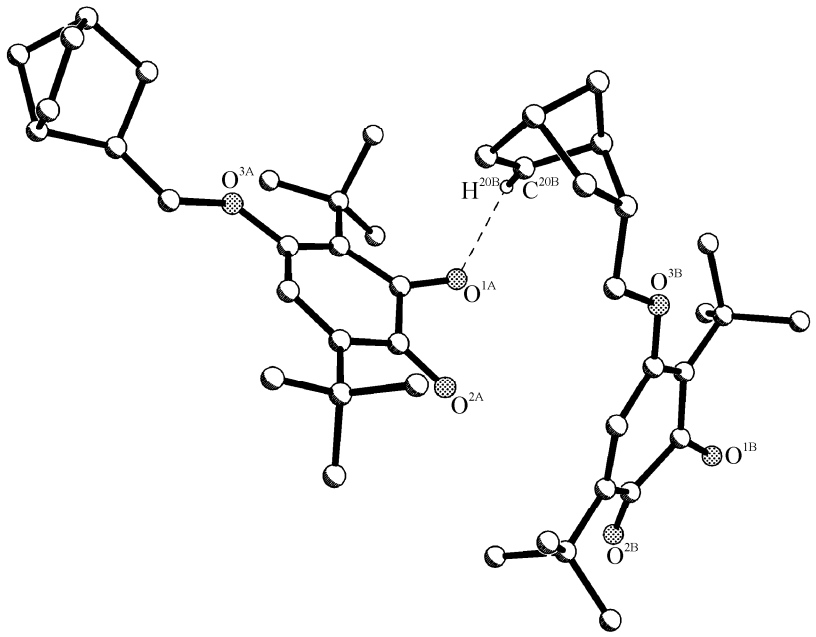
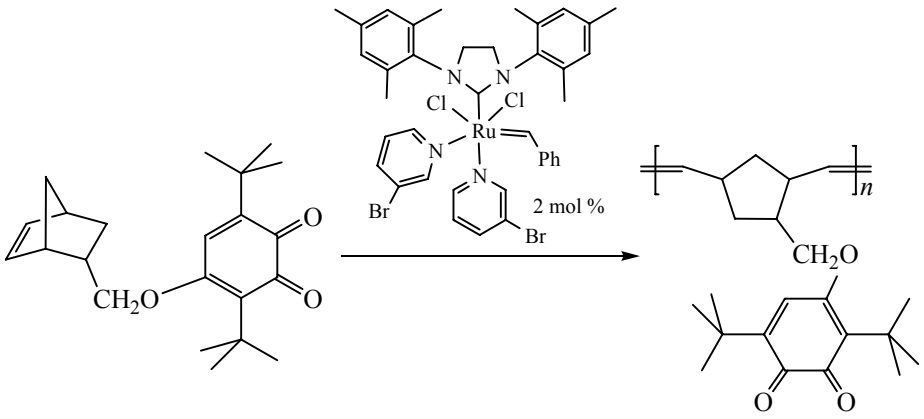


Fig. 2. Fragment of crystal packing of quinone **I**.

interactions (2.15 Å [10]) and is close by the value to the H–O···H distance in a hydrogen bond (2.1 Å [11]).

The norbornene-containing *o*-quinone **I** is reduced easily by metallic potassium to the corresponding *o*-semiquinone. The ESR spectrum of the corresponding potassium semiquinonate (g_i = 2.0066) has hyperfine structure caused by the hyperfine interaction of the unpaired electron with the proton of the aromatic ring [$a_i(H_{ring})$ = 3.68 Oe]. In addition, the ESR spectrum has a hyperfine structure due to two protons of methylene group, $a_i[H(CH_2)]$ = 0.27 Oe.

Compound **I** was brought into the metathesis polymerization in the presence of the Grubbs catalyst of the third generation:



The reaction proceeds in the methylene chloride medium at room temperature and is completed in 1 h. The yield of the reprecipitated polymer was 97% (M_w = 30300, M_n = 22100, M_w/M_n = 1.37). The resulting polymer product is a stable in air substance of dark brown color, well soluble in THF, methylene chloride, and chloroform. The IR spectrum of polymer includes strong absorption bands in the range of 1640–1680 cm^{-1} corresponding to the characteristic stretching vibrations of carbonyl group C=O in the quinoid fragment. The bands at 720 cm^{-1} and 960 cm^{-1} refer to the deformation vibrations of C–H bonds at the double

carbon–carbon bonds in the polymer backbone. The ^{1}H and ^{13}C NMR spectra (see Experimental) confirm the composition of the polymer product.

Reaction of the quinone-containing polymer with metallic potassium leads to the reduction of the *o*-quinone fragments to the corresponding anion radicals. The signals in the ESR spectrum of the reduced polymer (g_i = 2.0050) are significantly broadened compared with the corresponding line in the spectrum of the semiquinonate monomer, up to 1.27 Oe, which prevents observation of the superfine interaction with the methylene group protons. The hyperfine coupling constants of the unpaired electron with the proton of the quinoid ring is 3.12 Oe.

Thus, we synthesized and structurally characterized a new norbornene-containin *o*-quinone. The compound can be subjected to the metathesis polymerization to form a carbon-chain polymer with quinone fragments in the side chains. The *o*-quinone fragments in the polymer retain the ability to form anion-radicals at the interaction with metallic potassium.

EXPERIMENTAL

The polymerization was carried out in evacuated glass ampules using standard Schlenk technique. The solvents used were thoroughly purified and degassed according to the procedures described in [12]. The reaction duration was monitored using TLC.

The IR spectra were recorded on a FTIR FSM 1201 spectrometer. The samples of compounds were prepared as suspensions in mineral oil. The NMR spectra were recorded on a Bruker DPX-200 spectrometer (^{1}H NMR: 200 MHz, ^{13}C NMR: 50 MHz). Chemical shifts are given in ppm relative to tetramethylsilane as internal reference. The ESR spectra were obtained on a Bruker ER-200D-SRC spectrometer with ER 4105DR double resonator and ER 4111 VT thermocontroller. As a reference at determining the values of the *g*-factor was used diphenylpicrylhydrazyl.

The single crystals of compound **I** for the X-ray analysis were obtained by crystallization from hexane. The experimental sets of intensities were measured at 100(2) K on an automatic diffractometer Bruker AXS SMART APEX (graphite monochromator, MoK_α radiation, φ–ω scanning, λ=0.71073 Å). The structure is solved by the direct method using the SHELXTL software [13] and refined by full-matrix least-square method with respect to F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined in the *rider* model. The SADABS software [14] was used for the introduction of corrections for extinction. In each independent molecule the norbonene fragment and one of the two *tert*-butyl groups are disordered over two position s, and were refined with occupancies of 0.5. Selected bond lengths and angles are listed in Table 1. The main crystallographic characteristics and parameters of X-ray experiment are listed in Table 2.

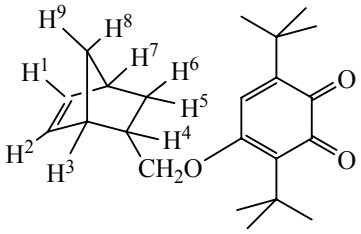
Table 2. The main crystallographic data, parameters of X-ray diffraction experiment and refinements for quinone **I** structure

Parameter	Value
Empirical formula	$C_{22}H_{30}O_3$
Molecular weight	342.46
Crystal size, mm	0.52×0.34×0.15
Crystal system	Triclinic
Space group	*P*-1
a, Å	11.5727(9)
b, Å	11.9088(9)
c, Å	14.4798(11)
α, deg	87.109(2)
β, deg	76.467(2)
γ, deg	89.398(2)
V, Å^3	1937.7(3)
Z	4
d_{calc}, g cm^{-3}	1.174
μ, mm^{-1}	0.076
F(000)	744
Domain of θ measurements, deg	1.45–26.00
Indices of change in *h*, *k*, *l*	$-14 \le h \le 14$ $-14 \le k \le 14$ $-17 \le l \le 17$
Number of measured reflections	16411
Number of independent reflections	7547
R_{int}	0.0413
Q-factor (F^2)	1.086
R_1/wR_2 [$I > 2\sigma(I)$]	0.1057/0.2861
R_1/wR_2 (for all reflections)	0.1732/0.3255
Residual electron density(ρ_{max}/ρ_{min}), *e* Å^{-3}	0.841/–0.543

The polymer molecular weight distribution was determined by gel permeation chromatography on a Knauer chromatograph with a Smartline RID 2300 differential refractometer as a detector, with a set of two Phenomenex columns with Phenogel sorbent, pore size 10^4 and 10^5 Å. THF was used as eluent (2 ml min^{-1}, 40°C). Calibration of columns was performed using 13 polystyrene standards.

The initial 3,6-di-*tert*-butyl-*o*-benzoquinone was synthesized as described in [15], 5-(hydroxymethyl)-bicyclo[2.2.1]hept-2-ene (5-norbornene-2-methanol) (Aldrich) was used without further purification. Grubbs catalyst of the third generation was synthesized as described in [16].

5-{5-(Bicyclo[2.2.1]hept-2-enyl)hydroxymethyl}-3,6-di-*tert*-butyl-*o*-benzoquinone (I). To a mixture of 5-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene (2.08 g, 16.77 mmol) and KOH (0.1 g, 1.81 mmol) was added in small portions 3,6-di-*tert*-butyl-*o*-benzoquinone (3.71 g, 16.86 mmol). The reaction mixture was heated at 100ºC for 2 h to complete the dissolution of the parent quinone. Then was added by portions another 3.00 g (13.65 mmol) of 3,6-di-*tert*-butyl-*o*-benzoquinone. The reaction mixture was heated for 6 h at 100ºC. After cooling to room temperature, the reaction mixture was dissolved in 100 ml of diethyl ether and added to a solution containing 10 g of $K_3[Fe(CN)_6]$, 3 g of Na_2CO_3, and 0.2 g of KOH in 100 ml of water. The mixture was stirred at room temperature for 30 min. The ether layer was then separated and washed with water (2×150 ml). After removing the solvent, the residue was dried in a vacuum for 1 h at 100ºC. The product was purified by column chromatography (eluent hexane–ethyl acetate, 1:50), 2.40 g (42%) of compound **I** was isolated as dark red crystals. Found, %: C 77.05, H 8.84. $C_{22}H_{30}O_2$. Calculated, %: C 77.16, H 8.83. IR spectrum (ν, cm^{-1}): 1683 s, 1638 s (C=O), 1620 s, 1546 s, 1462 s, 1376 s, 1301 s, 1236 s, 1197 s, 1164sr, 1075, 1021, 976, 884, 720 (C–H at *cis*-C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): *endo*-isomer (80%), 0.61 d.d.d. (1H, H^5, ^2J 12.1, $^3J_{4-5}$ 4.2, $^3J_{5-7}$ 2.8), 1.24 s and 1.34 s (9H, two $C(CH_3)_3$), 1.3–1.4 m (1H, H^8), 1.5–1.6 m (1H, H^9), 1.94 d.d.d. (1H, H^6, ^2J 12.1, $^3J_{4-6}$ 9.3, $^3J_{6-7}$ 3.8), 2.54 m (1H, H^4), 2.89 m (1H, H^7), 3.03 m (1H, H^3), 3.68 t and 3.79 d.d (two 1H, OCH_2, ^2J 9.0, ^3J 9.0 and ^3J 6.6), 6.00 dd (1H, C=CH^2, *J* 5.8, *J* 2.8), 6.24 d.d (1H, C=CH^1, *J* 5.5, *J* 3.0), 6.80 s (1H, CH-q); *exo*-isomer (20%): 1.25 s and 1.33 s [9H each, both $C(CH_3)_3$], 1.8–2.0 m (H^4), 2.84 m and 2.90 m (1H, H^3 and H^7), 4.01 m and 8.4 d.d (1H each, OCH_2, ^2J 9.0, ^3J 9.0 and ^3J 7.0), 6.14 m (2H, CH^1=CH^2), 6.85 s (1H, CH-q); other signals of *exo*-isomer are eclipsed by intense signals of the *endo*-isomer. ^{13}C NMR spectrum, DEPT ($CDCl_3$), δ, ppm: *endo*-isomer, 29.0 (CH_3), 29.2 ($CH_2^{5,6}$), 30.5 (CH_3), 35.0 and 35.1 (CMe_3), 38.8 (CH^4), 42.3 (CH^7), 44.0 (CH^3), 49.6 ($CH_2^{8,9}$), 72.9 (CH_2O), 129.1 (C–Bu-*t*), 129.8 (CH-q), 131.8 (CH^2), 138.3 (CH^1), 149.4 (C–OCH_2), 162.8 (C–Bu-*t*), 181.7 and 182.1 (C=O).



endo-**I**

Polymerization. To a solution of **I** (0.18 g, 0.53 mmol) in 2 ml of CH_2Cl_2 was added at stirring the Grubbs catalyst of the third generation (8.9 mg, 0.01 mmol, 4.2 mol %) in 0.5 ml of CH_2Cl_2. The reaction mixture was stirred at room temperature. According to TLC, the reaction ended in 1 h. To the reaction mixture was added 0.1 ml of ethyl vinyl ether and the stirring was continued for 0.5 h. The reaction solution was poured into methanol (30 ml), the precipitated polymer was dissolved in 2 ml of methylene chloride and once again precipitated in methanol (30 ml). The precipitate was separated and dried in a vacuum to a constant weight. 0.174 g (97%) of the polymer was obtained, dark brown powdery substance. IR spectrum, ν, cm^{-1}: 1686 m, 1644 m (C=O), 1623, 1552, 1462, 1376, 1295, 1197, 1081, 1021, 960 (C–H at the *trans*-C=C), 801, 720 (C–H at the *cis*-C=C). ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 1.21 s and 1.29 s (9H, both $C(CH_3)_3$), 1.57 s (1H, NBE), 2.06 m (2H, NBE), 2.16 s (1H , NBE), 2.48 m (1H, NBE), 2.86 m (1H, NBE), 3.12 m (1H, NBE), 3.86 m and 4.04 m (1H each, both CH_2O), 5.38 m (2H, CH=CH) , 6.81 s (1H, CH-q). ^{13}C NMR spectrum, DEPT ($CDCl_3$) δ, ppm: 29.0 (CH_3), 29.7, 30.7 (CH_3), 30.9, 35.0 and 35.2 (both CMe_3), 71.3 (CH_2O), 129.6 (CH=), 129.7 (CH-q), 130.1 (CH=), 149.4 ($COCH_2$), 162.7 (CBu-*t*), 181.5 and 182.1 (both C=O).

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