Heterospin biradicals based on new piperidineoxyl-substituted 3,6-di-*tert*-butyl-*o*-benzoquinone*

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A nucleophilic addition reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (OH-TEMPO) to 3,6-di-*tert*-butyl-*o*-benzoquinone was used to obtain a new sterically hindered *o*-benzoquinone (**1**) containing 2,2,6,6-tetramethylpiperidineoxyl functional group, which was characterized by IR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction. A one-electron reduction of **1** with potassium and thallium is an efficient method for the generation of earlier unknown heterospin biradicals **5a** and **5b**, respectively, containing nitroxide and *o*-semiquinone radical centers. Analysis of the hyperfine structure of the ESR spectra of biradicals **5a** and **5b** in solution showed that they belong to the group of heterospin biradicals with strong ($J >> a$) and fast exchange interaction between the radical centers.

Key words: sterically hindered 2,2,6,6-tetramethylpiperidine-1-oxyl, synthesis, one-electron reduction, heterospin biradicals, generation.

One of the directions in the design of molecular magnets is the search for new bifunctional paramagnetic ligands to be used in the construction of multispin bi- and polynuclear metal complexes, as well as coordination polymers. Nitroxide (nitronyl-nitroxide) and *o*-semiquinone derivatives are two most representative classes of radical organic ligands. The works of the school of Academician G. A. Abakumov made a great contribution to the formation and development of the chemistry of metal complexes with these radical ligands.[1—4] To date, a large number of 2,2,6,6-tetramethylpiperidine-1-oxyl-derived paramagnetic ligands have been synthesized, which, in addition to the nitroxide magnetic center, also contain a functional group providing additional coordination with the metal.[5—8]

Biradical heterospin ligands simultaneously containing two magnetic centers of different nature are of particular interest as building blocks in the construction of molecular magnets. The most promising is a combination in this ligand of nitroxide and o-semiquinone radical centers, both capable to form strong coordination bonds with the metal center. There are known several examples of *o*-semiquinone ligands functionalized with a nitronyl-nitroxide substituents, in which the radical substituent is bonded to the aromatic system of the *o*-semiquinone fragment either directly or through a conjugated bridge.[9—15] The first examples of sterically hindered 3,5-di-*tert*-butylpyrocatechol and the corresponding *o*-benzoquinone functionalized with 2,2,6,6-tetramethylpiperidineoxyl fragment are described in the work.[16] No 3,6-di-*tert*-butyl-*o*-benzoquinone derivatives with piperidineoxyl substituents have been known to date.

The purpose of the present work is the synthesis of sterically hindered 3,6-di-*tert*-butyl-substituted *o*-benzoquinone with a radical 2,2,6,6-tetramethylpiperidine-1-oxyl fragment at position 4 of the aromatic ring, which is regarded as a starting reagent for obtaining heterospin (containing different in nature centers) biradicals, and study of their ESR spectra.

The functionalization of *o*-benzoquinones allowing variation of their redox properties can be accomplished by nucleophilic addition of organoelement compounds,[17,18] alcohols,[19] primary and secondary amines,[20,21] C—H acids.[22,23] The nucleophilic addition of alcohols to *o*-quinones is carried out in acetonitrile with a catalytic amount of potassium hydroxide and leads to the corresponding alkoxy-substituted *o*-benzoquinones as the final reaction products.

The reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-Q) with 2,2,6,6-tetramethyl-4-hydroxypiperidine-oxyl (OH-TEMPO) under such conditions leads to a mixture of unidentified products. The search for the conditions for the synthesis of the target alkoxyquinone showed that the optimal version is carrying out the reaction of 3,6-Q and OH-TEMPO in decane at 110 °C for two hours (Scheme 1).

* Dedicated to Academician of the Russian Academy of Sciences G. A. Abakumov on the occasion of his 80th birthday.

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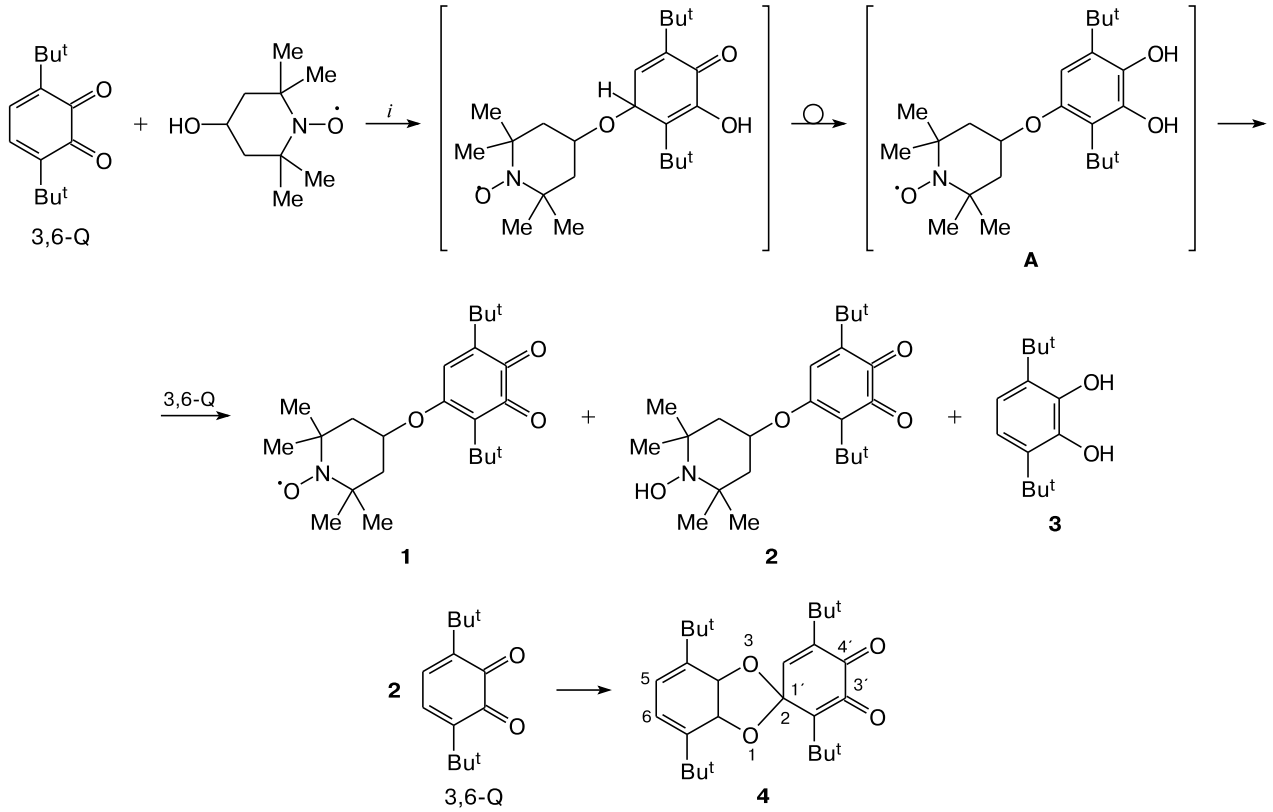
Scheme 1



i. Decane, 110 °C.

The target 4-(3,6-di-*tert*-butyl-1,2-dioxocyclohexa-3,5-dien-4-yloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (**1**) was isolated in the individual state as dark red crystals after separation of the reaction mixture by column chromatography (80% yield calculated on OH-TEMPO). Apart from that, some other reaction products were identified, namely, 3,6-di-*tert*-butyl-4-[(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)oxy]cyclohexa-3,5-dien-1,2-dione (**2**) (4-alkoxyquinone with the protonated nitroxide) in ~5% yield calculated on OH-TEMPO, 3,6-di-*tert*-butylpyrocatechol (**3**), and 2′,4,5′,7-tetra-*tert*-butyl-3′-hydroxy-3a,7a-dihydrospiro[benzodioxyl-2,1′-cyclohexa-[2,5]diene]-4′-one (**4**) (the coupling product of the starting 3,6-Q) in 8% yield calculated on OH-TEMPO. The formation of pyrocatechol **3** is explained by the oxidation of the primary product of nucleophilic addition (4-alkoxypyrocatechol **A**) with the starting quinone 3,6-Q, while the reduction of the TEMPO-containing quinone **1** to piperidinehydroxyquinone **2** becomes possible as any of the pyrocatechols appear in the reaction mixture. Note that product **2** readily undergoes oxidation to *o*-quinone **1** even with air oxygen. Running a solvent-free reaction of 3,6-Q with OH-TEMPO leads to the local overheating of the mixture, which results in the increase in the content of the side product **4** up to 15% calculated on the starting OH-TEMPO and in the decrease in the yield of the target (piperidineoxyl)oxyquinone **1**.

The structure of new alkoxyquinone **1** was confirmed by IR and ESR spectroscopy, as well as by mass spectrometry and X-ray crystallography.

The IR spectrum of compound **1** exhibits vibrations in the region of 1635 and 1678 cm^{-1} corresponding to the C=O carbonyl bonds of *o*-quinone, as well as a characteristic vibrational band of the N—O$^{\bullet}$ group (1365 cm^{-1}).[24] Apart from that, a band at 1236 cm^{-1} corresponding to the asymmetric stretching vibrations of the CH_2O—quinone ether group is present in the spectrum.

The isotropic ESR spectrum of functionalized *o*-quinone **1** is typical of 2,2,6,6-tetramethyl-4-hydroxypiperidineoxyl derivatives[25,26] and has a triplet pattern (1 : 1 : 1) with g_i = 2.0060 due to the hyperfine coupling (HFC) with one nitrogen nucleus (^{14}N, 99.64%, I = 1, g_N = 0.404), a_N = 1.535 mT (Fig. 1). The hyperfine structure (HFS) on the protons of the methyl and the methylene groups (^{1}H, 99.99%, I = 1/2, g_N=5.586) is not observed because of too broad line (~0.18 mT), considerably exceeding the value of the HFC constant (a_H < 0.05 mT).

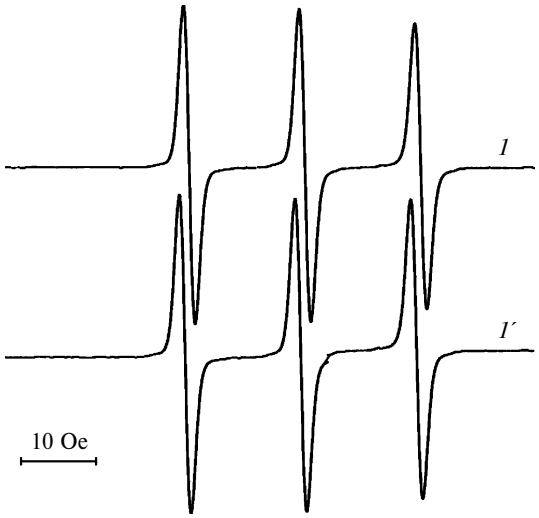


Fig. 1. Experimental (*1*)and simulated (*1′*) ESR spectra of *o*-benzoquinone **1** (THF, ~20 °C).

The mass spectrometry analysis showed that the mass spectrum of *o*-quinone **1** contained a peak attributed to the molecular ion with $m/z = 390$ (M^+) and a peak of the ion corresponding to the 4-hydroxypiperidineoxyl fragment with $m/z = 171$. A similar examination of *o*-quinone **2** showed the presence in its mass spectrum of a molecular ion peak with $m/z = 391$ (M^+).

The molecular and crystal structure of **1** was also confirmed by X-ray diffraction. An independent region of the crystal cell contains one molecule of *o*-quinone **1** and one THF molecule. The molecular structure of **1** is shown in Fig. 2. Selected bond distances and bond angles in the molecule are given in Table 1.

In molecule **1**, the carbonyl fragments and the *tert*-butyl substituent at atom C(6) are disordered over two

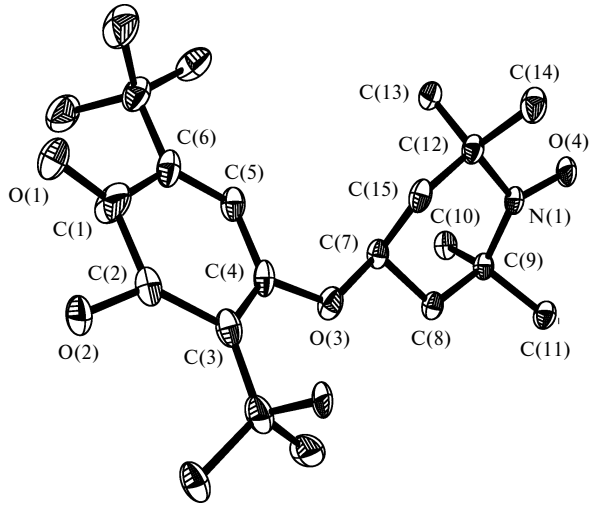


Fig. 2. Molecular structure of compound **1**. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted.

Table 1. Selected bond distances (*d*) and bond angles (ω) in compound **1**

Bond	*d*/Å	Angle	ω/deg
O(1)—C(1)	1.214(6)	O(1)—C(1)—C(2)	117.7(2)
	1.221(3)		118.0(5)
O(2)—C(2)	1.220(7)	C(1)—C(2)—O(2)	106.9(5)
	1.223(3)		117.6(2)
C(1)—C(2)	1.553(7)	C(4)—O(3)—C(7)	119.4(2)
	1.565(4)	C(8)—C(7)—C(15)	108.7(2)
C(4)—O(3)	1.357(2)	C(9)—N(1)—C(12)	124.8(2)
O(3)—C(7)	1.459(2)	C(9)—N(1)—O(4)	115.7(2)
C(7)—C(8)	1.514(2)	C(12)—N(1)—O(4)	115.6(2)
C(7)—C(15)	1.515(2)		
N(1)—O(4)	1.288(2)		
N(1)—C(9)	1.495(2)		
N(1)—C(12)	1.497(2)		

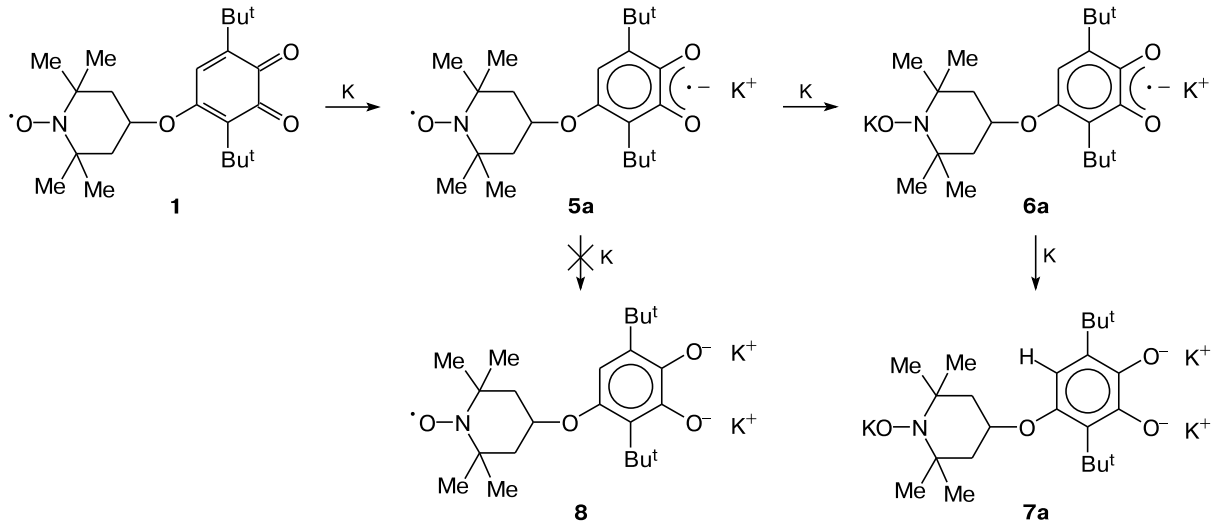
positions. The geometry of the OCCO dicarbonyl fragment is distorted, however, the C=O (1.214(6)—1.223(3) Å) and C—C bond distances (1.553(7)—1.565(4) Å) are comparable with the analogous values in similar *o*-quinones.[27] The O(1)—C(1)—C(2) and C(1)—C(2)—O(2) angles lie in a wide range of values 106.9(5)—118.0(5)°. The OCCO fragment in **1** is nonplanar (the O—C—C—O torsion angles lie within 3.9(9)—10.8(3)°), but is distorted considerably less than in other 3,6-*tert*-butyl-*o*-quinone derivatives with bulky substituents at positions 4 and 5 of the *o*-quinone ring.[28]

The tetramethylpiperidine-1-oxyl substituent in molecule **1** is in the *chair* conformation characteristic of such fragments[29] and is arranged at an angle to the *o*-quinone fragment (a dihedral angle between the mean planes of the six-membered rings is equal to 66.69(9)°). The N(1)...C(4) distance in **1** is 5.132(2) Å.

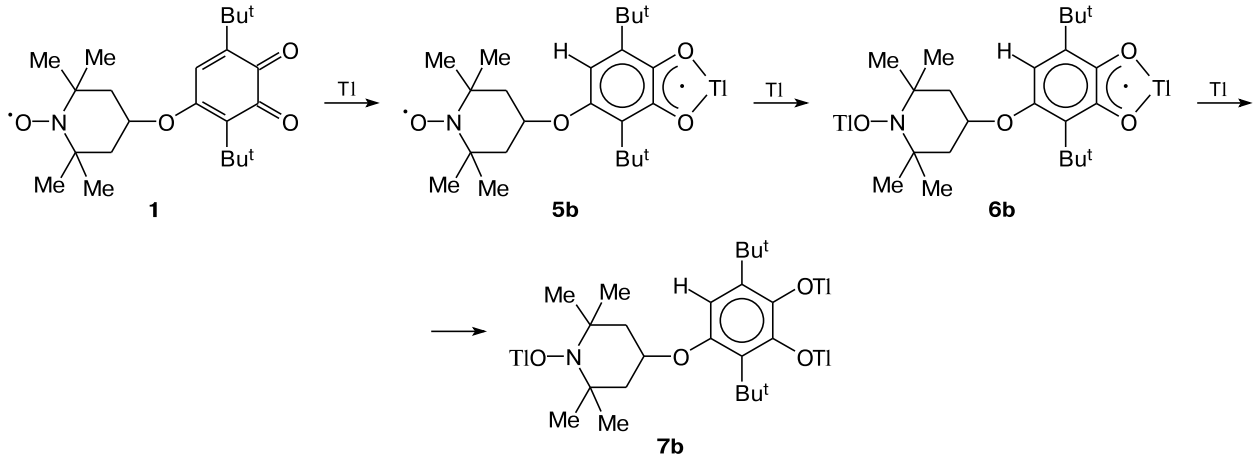
In order to obtain heterospin biradicals, we studied the reduction reaction of *o*-quinone **1** with metallic potassium (Scheme 2) and thallium (Scheme 3). The reaction of **1** with potassium metal in THF led to a gradual transformation of the initial signal of **1** to a new triplet (1 : 1 : 1) of doublets (1 : 1) with $g_i = 2.0055$ (Fig. 3). The hyperfine structure of the ESR spectrum is caused by the interaction of the unpaired electron with one nitrogen nucleus ^{14}N ($a_N = 0.78$ mT) and one hydrogen nucleus ($a_H = 0.18$ mT). The observed values of parameters of the isotropic ESR spectrum of **5** are equal to half the HFC constant values a_N and a_H in common nitroxide and *o*-semiquinone radicals, which corresponds to the case of heterospin biradical with strong and fast ($J >> a$) exchange interaction between different in nature magnetic centers.[33]

Similar heterospin biradicals are described in the literature, namely, tetramethylpiperidine-1-oxyl derivatives containing a phenoxyl or a diphenylpicrylhydrazyl fragment along with the nitroxide one.[33] Computer simula-

Scheme 2



Scheme 3



tion[34] was used to determine ESR parameters for the nitroxide and semiquinone radical centers in biradical **5a**: g_i = 2.00645, a_N = 1.555 mT and g_i = 2.00455, a_H = = 0.355 mT, respectively, at an exchange interaction energy $J > 3000$ MHz.

Thus, the reduction of *o*-quinone **1** with metallic potassium leads to the formation of the heterospin biradical **2**.

A further reduction of biradical **5** with metallic potassium led to almost complete disappearance of its ESR spectrum and the appearance of a new signal, a doublet HFS of which is associated with the HFC of the unpaired electron with one hydrogen nucleus. The parameters of the HFS of the observed ESR spectrum (Fig. 3, *c*) with g_i = 2.0047 and a_H = 0.37 mT are typical of the radical anions of 3,6-di-*tert*-butyl-*o*-benzoquinone 4-alkoxy derivatives and indicate the reduction in the second step of the process of the nitroxide center of biradical **5a** with the formation of a monoradical *o*-semiquinone derivative **6a**. Upon further reduction, the ESR signal of **6** gradually decreases until it completely disappears, which corresponds, most likely, to the formation of the final diamagnetic trianion **7a**. The signal corresponding to the nitroxyl-catecholate complex **8**, yet another possible reduction product of biradical **5a** (Scheme 2), is not observed in the ESR spectrum. From this, it can be concluded that the reduction of the nitroxide group in the heterospin biradical **5a** proceeds more easily than the reduction of the semiquinone one.

A reduction of *o*-quinone **1** with thallium gave similar results (Scheme 3).

Thus, the signal of the starting *o*-quinone **1** initially undergoes transformation into the signal of biradical **5b**, the ESR spectrum of which is a doublet (1 : 1) of triplets (1 : 1 : 1) of doublets (1 : 1) with g_i = 2.0017 and the HFS caused by the HFC with one thallium nucleus (^{205}Tl, 70.5%, I = 1/2, g_N = 3.275, ^{203}Tl, 29.5%, I = 1/2, g_N = 3.245) a_{Tl} = 2.59 mT, one nitrogen nucleus a_N = 0.775 mT, and one proton a_H = 0.18 mT (Fig. 4, *b*). The presence of an

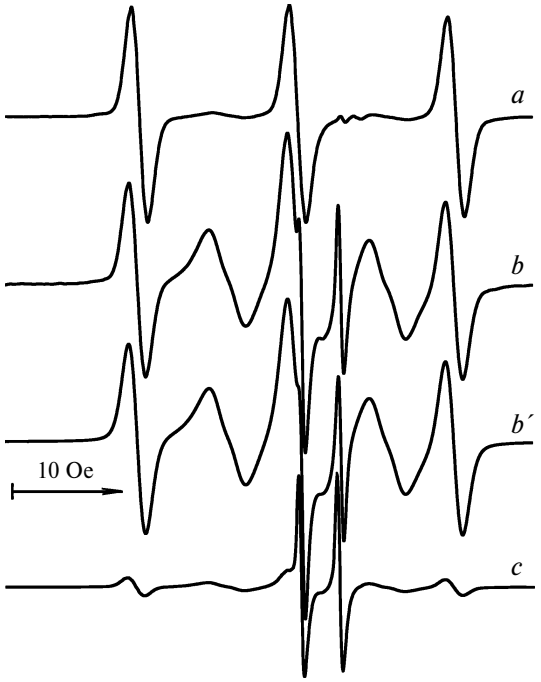


Fig. 3. The ESR spectra of the products of the reaction of *o*-quinone **1** with potassium (THF, ~20 °C) at the beginning of the reaction (*a*), 20 (*b, b´*) and 45 min after the beginning of the reaction (*c*); *b, b´* are the experimental and the simulated spectra, respectively.

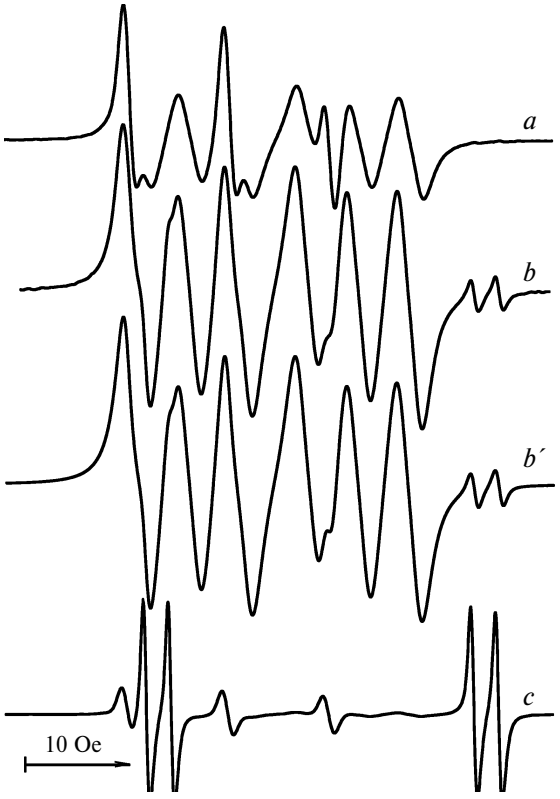


Fig. 4. The ESR spectra of the products of the reaction of *o*-quinone **1** with thallium amalgam (THF, ~20 °C) 5 (*a*), 10 (*b, b´*), and 50 min after the beginning of the reaction (*c*); *b, b´* are the experimental and the simulated spectra, respectively.

additional coupling on the magnetic isotopes of thallium is associated with the formation of a chelate semiquinone complex.[3] As in the previous case, the ESR signal indicates the biradical nature of **5b** with strong and fast exchange interaction ($J > 3500$ MHz) between two different in nature radical centers: the nitroxide ($g_i = 2.00625$, $a_N = 1.50$ mT) and the semiquinone ($g_i = 1.9975$, $a_{Tl} = 5.19$ mT, $a_H = 0.36$ mT).

Like in the case with potassium, further reaction leads to the reduction of the nitroxide radical center with the formation of thallium(I) *o*-semiquinolate **6b**. Its ESR spectrum is typical of the thallium(I) *o*-semiquinone derivatives and is a doublet (1 : 1) of doublets (1 : 1) with $g_i = 1.9974$ caused by the HFC of the unpaired electron with the magnetic isotopes of thallium ^{203}Tl and ^{205}Tl ($a_{Tl} = 5.03$ mT) and one proton ($a_H = 0.375$ mT) (see Fig. 4, *c*). More deep reduction leads to the formation of diamagnetic catecholate **7b** and, therefore, to the disappearance of the ESR signal.

In conclusion, we have developed and implemented a procedure for the synthesis of new sterically hindered 3,6-di-*tert*-butyl-*o*-benzoquinone functionalized with 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl **1**. We have shown that the one-electron reduction of compound **1** is an efficient method for the generation of earlier unknown heterospin biradicals **5a** and **5b** containing nitroxide and *o*-semiquinone radical centers. Analysis of the HFS of the ESR spectra of the biradicals in solution showed that they belong to the group of heterospin biradicals with strong ($J >> a$) and fast exchange interaction between the radical centers.

Experimental

IR spectra were recorded on a FSM 1201 IR Fourier-transform spectrometer (a suspension in Nujol), ESR spectra were recorded on a Bruker ER 200 DSRC spectrometer equipped with an ER 4105 DR double resonator and an ER 4111 VT thermocontroller, diphenylpicrylhydrazyl was used as a standard in the determination of the *g*-factor values. Mass spectra were recorded on a Polaris Q mass spectrometer. The energy of the ionizing electrons 70 eV.

X-ray diffraction study of compound 1 was carried out on an Agilent Xcalibur E diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, ω-scan technique, $T = 120$ K). The integration of experimental array of intensities and the correction for absorption were carried out using the *CrysAlis PRO* software package.[35] The structure was solved by a direct method and refined by the full-matrix least-squares method with respect to F^2_{hkl} in the anisotropic approximation for nonhydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions and refined isotropically. The calculations were made using the *SHELX* software package.[36]

Crystallographic data, parameters of X-ray diffraction experiment and refinement for compound **1** are as follows:

$C_{23}H_{36}NO_4 \cdot C_4H_8O$, molecular weight 462.63, *Pbca*, $a = 22.0737(4)$ Å, $b = 10.8741(2)$ Å, $c = 22.1030(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 5305.4(2)$ Å^3, $Z = 8$, $d_{calc} = 1.158$ mg m^{-3}, $\mu = 0.078$ mm^{-1}, range of scanning 3.21—27.10°, 74242 reflection were measured (5838 of them were independent, $R_{int} = 0.0481$), $GOOF(F^2) = 1.014$, $R_1 = 0.0604$ ($I > 2\sigma(I)$), $R_2 = 0.1806$ (on all the data), the maximum and the minimum of the residual electron density was 0.522/−0.546 e Å^{-3}. The structure was deposited with the Cambridge Crystallographic Data Center (CCDC 1557609) and is available at ccdc.cam.ac.uk/structures.

3,6-Di-*tert*-butyl-*o*-benzoquinone was synthesized according to the known procedure.[37] Solvents were dried and purified according to the standard procedures.[38] 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (OH-TEMPO) was commercially available from Aldrich. Column chromatography was performed on silokhrom C-120 (Reakhim), eluent light petroleum ether—THF (50 : 1).

Reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl. 3,6-Di-*tert*-butyl-*o*-benzoquinone (2.57 g, 11.6 mmol) was fused with 2,2,6,6-tetramethyl-4-hydroxypiperidineoxyl (1 g, 5.8 mmol) in the presence of decane (2 mL) with heating in an oil bath at 110 °C for 2 h. Then, the cake was washed with acetone and filtered from 2′,4,5′,7-tetra-*tert*-butyl-3′-hydroxy-3a,7a-dihydrospiro(benzo-1,3-dioxol-2,1′-cyclohexa[2,5]diene)-4′-one (**4**), a side product poorly soluble under these conditions. The mother liquor was concentrated and separated by column chromatography. Eluent light petroleum ether—THF (50 : 1).

According to the NMR spectroscopy data, the first yellow band contained 3,6-di-*tert*-butylpyrocatechol (**3**). Dark red crystals of 4-(3,6-di-*tert*-butyl-1,2-dioxocyclohexa-3,5-dien-4-yloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (**1**) were isolated from the second reddish brown band after removal of the eluent and crystallization from diethyl ether. M.p. 173 °C. Found (%): C, 70.92; H, 9.54. $C_{23}H_{36}NO_4$. Calculated (%): C, 70.74; H, 9.29. *m/z*: 390.26 (M^+). IR, ν/cm^{-1}: 480 w, 552 w, 587 w, 601 w, 650 w, 681 m, 721 m, 739 m, 809 w, 830 w, 844 w, 877 m, 888 m, 912 m, 921 m, 938 m, 964 s, 978 s, 999 w, 1024 m, 1083 s, 1185 s, 1202 s, 1236 s (CH_2O of quinone), 1300 s, 1314 s, 1365 s (N—O·), 1396 m, 1417 m, 1543 s, 1625 s, 1635 s (C=O), 1678 s (C=O).

The mass spectrometry data showed that the third light brown band contained 4-alkoxyquinone with a protonated nitroxyl, 3,6-di-*tert*-butyl-4-[(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)oxy]cyclohexa-3,5-diene-1,2-dione (**2**), which upon evaporation of the eluent in air slowly oxidized to the target *o*-quinone **1**. Found (%): C, 70.76; H, 9.89. $C_{23}H_{37}NO_4$. Calculated (%): C, 70.55; H, 9.52. *m/z*: 391.27 (M^+). ^{1}H NMR, δ: 1.25 (s, 12 H, Me); 1.31 (s, 18 H, Bu^t); 2.01 and 2.07 (both d, 2 H each, CH_2, $J = 3.60$ Hz). ^{13}C NMR, δ: 29,0 (Me); 30.6 (C($\underline{C}H_3)_3$); 35.1 ($\underline{C}(CH_3)_3$); 77 2 (C—$\underline{C}H_2$—C); 129.3; 149.2; 181,8 (C=O); 184.9 (C=O).

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References

1. G. A. Razuvayev, G. A. Abakumov, E. S. Klimov, *Dokl. Akad. Nauk SSSR*, 1971, **201**, 3, 624 [*Dokl. Chem.* (*Engl. Transl.*), 1971].
2. G. A. Razuvaev, V. D. Tikhonov, G. A. Abakumov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1970, **19**, 1634.
3. V. A. Muraev, G. A. Abakumov, G. A. Razuvayev, *Dokl. Akad. Nauk SSSR*, 1974, **217**, 5, 1083 [*Dokl. Chem.* (*Engl. Transl.*),1974].
4. G. A. Abakumov, *Zh. Ros. khim. o-va im. D. I. Mendeleyeva* [*Russ. Mendeleyev Chem. J.*], 1979, 156 (in Russian).
5. S. V. Larionov, *J. Struct. Chem.,* 1983, **23**, 594.
6. S. S. Eaton, *Coord. Chem. Rev.*, 1978, **26**, 20.
7. S. S. Eaton, G. R. Eaton, *Coord. Chem. Rev.*, 1988, **83**, 29.
8. A. V. Artem´ev, O. V. Vysotskaya, L. A. Oparina, A. S. Bogomyakov, S. S. Khutsishvili, I. V. Sterkhova, V. I. Ovcharenko, B.A. Trofimov, *Polyhedron*, 2016, **119**, 293.
9. D. A. Shultz, S. H. Bodnar, K. E. Vostrikova, J. W. Kampf, *Inorg. Chem.*, 2000, **39**, 6091.
10. E. Depperman, S. H. Bodnar, K. E. Vostrikova, D. A. Shultz, M. L. Kirk, *J. Am. Chem. Soc.*, 2001, **123**, 3133.
11. D. Shultz, K. Vostrikova, S. Bodnar, H. Koo, M. Whangbo, M. Kirk, E. Depperman, J. Kampf, *J. Am. Chem. Soc.*, 2003, **125**, 1607.
12. M. L. Kirk, D. A. Shultz, E. C. Depperman, *Polyhedron*, 2005, **24**, 2880.
13. D. A. Shultz, R. K. Kumar, S. Bin-Salamon, M. L. Kirk, *Polyhedron*, 2005, **24**, 2876.
14. D. E. Stasiw, J. Zhang, G. Wang, R. Dangi, B. W. Stein, D. A. Shultz, M. L. Kirk, L. Wojtas, R. D. Sommer, *J. Am. Chem. Soc.*, 2015, **137**, 9222.
15. E. V. Tretyakov, S. E. Tolstikov, G. V. Romanenko, A. S. Bogomyakov, V. K. Cherkasov, D. V. Stass, V. I. Ovcharenko, *Russ. Chem. Bull.*, 2011, **60**, 2325.
16. N. O. Druzhkov, E. N. Egorova, M. V. Arsen´ev, E. V. Baranov, V. K. Cherkasov, *Russ. Chem. Bull.*, 2016, **65**, 2855.
17. G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, N. O. Druzhkov, V. I. Nevodchikov, Yu. A. Kursky, N. P. Makarenko, *Metalloorgan. Khimiya*, 1991, 925 [*Organomet. Chem. USSR* (*Engl. Transl.*), 1991].
18. G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, V. I. Nevodchikov, N. O. Druzhkov, N. P. Makarenko, Yu. A. Kursky, *J. Organometallic. Chem.*, 1995, **491**, 127.
19. M. P. Shurygina, N. O. Druzhkov, M. V. Arsen´yev, M. P. Bubnov, G. K. Fukin, S. A. Chesnokov, V. K. Cherkasov, *Zh. Org. Khim*, 2011, **47**, 490 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2011, **47**].
20. G. A. Abakumov, V. K. Cherkasov, T. N. Kocherova, N. O. Druzhkov, Yu. A. Kurskii, L. G. Abakumova, *Russ. Chem. Bull.*, 2006, **55**, 1195.
21. G. A. Abakumov, V. K. Cherkasov, T. N. Kocherova, N. O. Druzhkov, Yu. A. Kurskii, M. P. Bubnov, G. K. Fukin, L. G. Abakumova, *Russ. Chem. Bull.,* 2007, **56**, 1849.
22. G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, V. K. Cherkasov, *Russ. Chem. Bull.*, 1997, **46**, 2093.
23. G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, V. K. Cherkasov, *Russ. Chem. Bull.*, 1997, **46**, 337.
24. V. T. Kasumov, I. Uзar, A. Bulut, Y. Yerli, *Solid State Sciences*, 2011, **13**, 1852.
25. C. C. Whisnant, S. Ferguson, D. B. Chesnut, *J. Phys. Chem.*, 1974, **78**, 1410.
26. J. J. Windle, *Magnetic Resonance,* 1981, **45**, 432.
27. C. G. Pierpont, R.M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.

28. G. K. Fukin, A. V. Cherkasov, M. P. Shurygina, N. O. Druzhkov, V. A. Kuropatov, S. A. Chesnokov, G. A. Abakumov, *Struct. Chem.*, 2010, **21**, 607.
29. O. L. Lebelev, S. N. Kazarnovskii, *J. Gen. Chem. USSR*, 1960, **30**, 1631.
30. E. G. Rozantsev, V. D. Sholle, *Synthesis*, 1971, 401.
31. W. R. Couet, *Tetrahedron*, 1985, **41**, 1165.
32. V. D. Sen, V. A. Golubev, N. N. Efimova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 53.
33. R. W. Kreilick, *Chem. Phys. Letters*, 1968, **2**, 277.
34. S. Stoll, A. Schweiger, *J. Magn. Res.*, 2006, 178, 42.
35. Agilent, *CrysAlis PRO*, 2014, Agilent Technologies Ltd, Yarnton, Oxfordshire, England.
36. G. M. Sheldrick, *Acta Cryst.*, 2015, C71, 3.
37. E. G. Rozantsev, V. D. Sholle, *Organicheskaya khimiya svobodnykh radikalov* [*Organic Chemistry of Free Radicals*], Khimiya, Moscow, 1973, 344 pp. (in Russian).
38. A. J. Gordon, R. A. Ford, *The Chemist´s Companion. A Handbook of Practical Data, Techniques, and References*, Wiley Interscience, New York, 1972.
39. M. P. Shurygina, N. O. Druzhkov, M. V. Arsen´ev, M. P. Bubnov, G. K. Fukin, S. A. Chesnokov, V. K. Cherkasov, *Russ. J. Org. Chem.*, 2011, **47**, 486.

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