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Reaction of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone with *N*,*N*-disubstituted dithiocarbamates*

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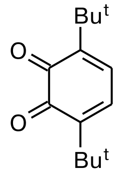
A reaction of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone with disubstituted *N*,*N*-dithiocarbamates leads to zwitterionic compounds containing 2-iminio-1,3-dithiole ring annulated to the quinone skeleton. These products reversibly add acids, giving salts of the corresponding catechols; they form complexes with copper involving oxygen atoms, as well.

Key words: dithiocarbamates, zwitterionic compounds, *o*-quinones, 1,3-dithiols, 1,3-benzodithiols, iminium compounds, copper complexes.

Sterically hindered *o*-benzoquinones and catechols are widely used as starting ligands in the chemistry of metal *o*-semiquinone complexes.[1] Functionalized sterically hindered *o*-benzoquinones are of special interest, since the presence of additional functional group in the skeleton of coordinated ligand will impose new physical and chemical properties onto the corresponding metal complexes, which opens new possibilities of exertion upon it chemical and physical action.[2—4]

Earlier, 3,6-di(*tert*-butyl)-1,2-benzoquinone (**1**) has been taken as an example to show that nucleophilic substitution at position 4 of the benzoquinone ring is an efficient approach for its functionalization.[5] Nucleophilic substitution for the chlorine atom in 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone (**2**) is yet another efficient method for modification of quinone **1**. If proper reagents are chosen, this method opens the way to the synthesis of annulated heterocyclic *o*-benzoquinones. Thus, we have shown earlier[6] that when potassium ethyl xanthate was used, the substitution product formed in the first step can easily cyclize giving 1,3-dithiol-2-one derivative **3**, whereas the reaction of sodium tetrathiooxalate with compound **2** is a new efficient method for the synthesis of di-*o*-quinone **4** annulated by the TTF-fragment.[3] There is also description[7] of the reaction of pyrrolidinedithiocarbamate with *p*-benzoquinone leading to the product **5**, whose oxidation gives the salt **6**.



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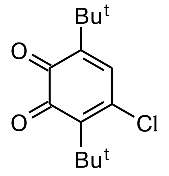

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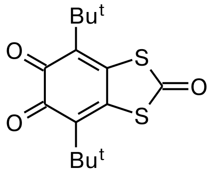

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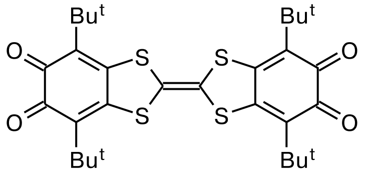

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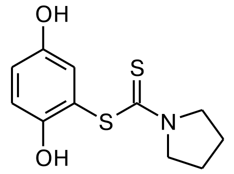

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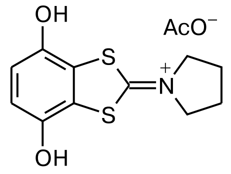

6

In the present work, we studied reactions of quinone **2** with *N*,*N*-disubstituted dithiocarbamates leading to 1,3-dithiole derivatives. In contrast to the case with ethyl xanthate,[6] we failed to isolate the product of initial substitution for the halogen atom by the dithiocarbamate fragment, and formation of the five-membered ring occured directly during the reaction. We assume that the process follows the Scheme 1.

After substitution for the halogen atom by dithiocarbamate fragment, the latter immediately attacks position 5 of the quinone ring. The higher reactivity of dithiocarbamate substituent as compared to ethyl xanthate one can be explained by the contribution of the mesomeric iminium form with the nitrogen—carbon double bond, whose

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* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 80th birthday.

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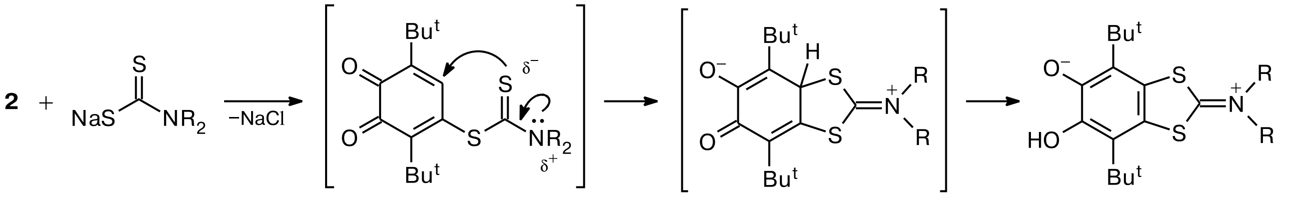
Scheme 1



7a—c

R = Et (**a**), Pr^i (**b**); R + R = —(CH$_2$)$_5$— (**c**)

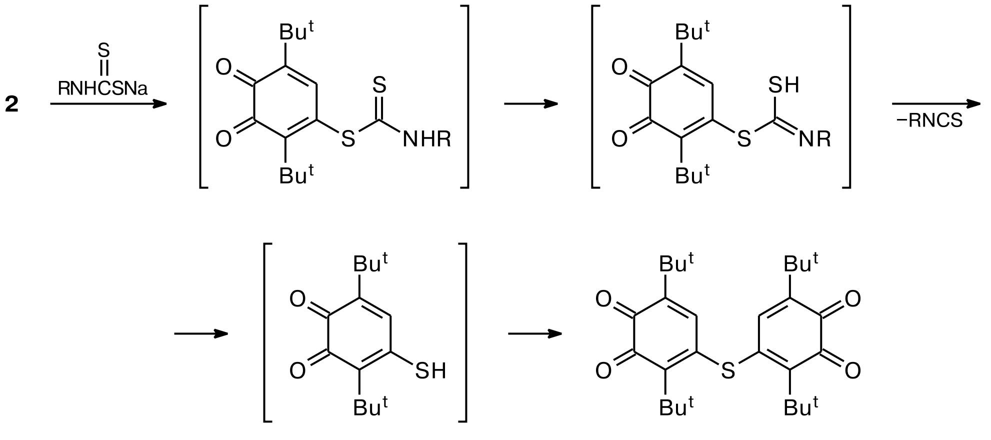
thiocarbonyl sulfur atom possesses increased nucleophilicity.

The reaction of compound **2** with *N*,*N*-disubstituted carbamates was carried out in acetone (Scheme 1). Dithiocarbamate dissolves upon stirring the mixture, sodium chloride precipitates, and the solution turns its color from dark red to orange, the color of the final product. The final products **7a**—**c** are orange or reddish orange crystalline compounds, soluble in polar organic solvents. It should be noted that compounds **7a**—**c** are zwitterionic structures with the positive charge localized on the iminium nitrogen atom.

The use of monosubstituted dithiocarbamates NaSC(S)NHR (R = *cyclo*-C_6H_{11} or —CH_2CH_2OH) in the reaction leads to diquinone **8** described by us earlier[3] (Scheme 2). We assume that due to a possibility of existence of an equilibrium mercapto-imine form, the initially formed quinone, substituted at position 4 with the dithiocarbamate fragment, is unstable and would decompose to give alkyl isothiocyanate and arenethiol **A**. The latter under the reaction conditions is converted to diquinone **8**.

The structures of compounds **7a**—**c** were established by standard methods of analysis. The structure of product **7a** was additionally confirmed by X-ray crystallography (Fig. 1). The X-ray diffraction studies showed that there are four independent molecules with close geometric parameters in the independent part of the cell. The fragment C(1—6, 15)O(1,2)S(1,2)N(1) in **7a** is virtually planar. The deviation from the mean plane is equal to 0.0298 Å. The distance O(1)...H(2X) is 1.43(5) Å, whereas the angle at the hydrogen atom is equal to 122.4(4)°, which is considerably lower than the geometrical criterion for the hydrogen bond to exist (2.1 Å).[8] It is necessary to note that the distance O(1)—C(5) is 1.269(12) Å, which is somewhat longer as compared to similar distances in 3,6-di(*tert*-butyl)-1,2-benzoquinones (1.207(1)—1.213(1) Å).[9] The bond distances in the six-membered ring have no clear alternation characteristic of quinones, and their values change within 1.373(14)—1.464(13) Å. The distances C=O and C—OH in compound **7a** differ by ~0.1 Å. Note that the distance N(1)—C(15) (1.314(12) Å) is within the range of values for the double C=N bonds (1.279—1.329 Å).[10] The distances C(15)—S(1, 2), equal to 1.717(10) and

Scheme 2



A

8

R = *cyclo*-C_6H_{11}, CH_2CH_2OH

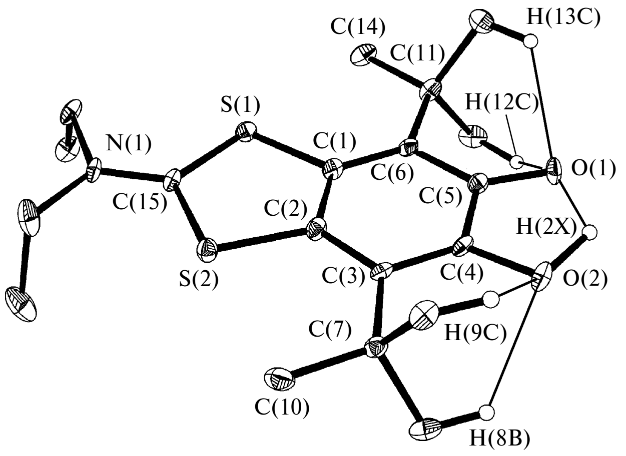


Fig. 1. Molecular structure of **7a**. Thermal ellipsoids are given with 30% probability.

1.717(9) Å, are considerably shorter than the distances S(1)—C(1) (1.774(9) Å) and S(2)—C(2) (1.768(10) Å). This allows us to suggest the presence of delocalization of electron density over the fragment N(1)C(15)S(1,2). Apparently, the charges in molecule **7a** are significantly separated.

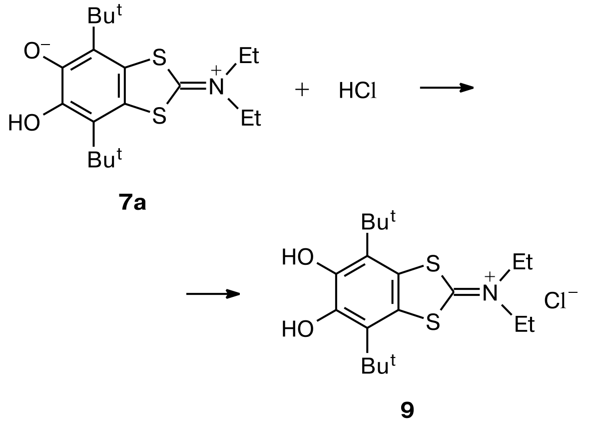
The ^{1}H NMR spectrum of **7a** adequately reflects its structure. The signal for the proton of the hydroxy group in $CDCl_3$ is not observed because of significant broadening of the line. The broadening results from a possibility for the proton migrate from one oxygen atom to another. When the spectrum is recorded in acetone-d_6, the signal for this proton becomes visible. In both acetone and chloroform, only one signal from the *tert*-butyl groups is observed. This fact also indicates a rapid (in the NMR time scale) prototropic tautomerism. The number of signals in the ^{13}C NMR spectrum of **7a** confirms symmetric structure of the molecule.

In the IR spectrum, the strong absorption bands corresponding to the C—O groups in the molecule **7a** are observed in the region 1550 cm^{-1}. Such an absorption is characteristic of one and a half the C—O bond and quite agrees with the bond distance values obtained by X-ray crystallography. The band characteristic of the OH groups are absent in the IR spectrum.

The zwitterionic nature of **7a** is displayed by its ability to add ionic compounds. It reacts with acids, turning the color from orange to colorless (Scheme 3). The reaction of salt **9** with bases leads to regeneration of **7a**.

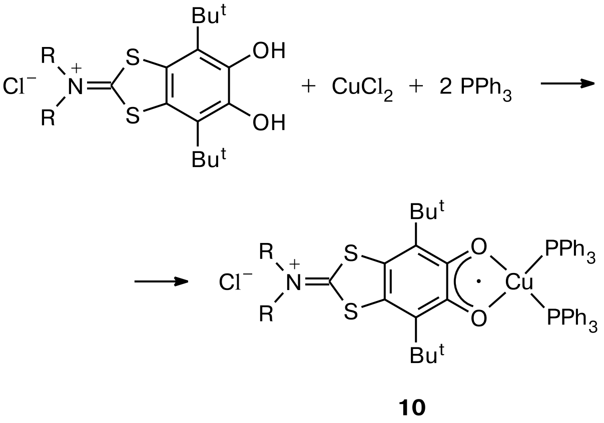
Compound **9** is a catechol derivative and an analog of hydroquinone **6** described by Watson.[7] The process of formation of catechol **9** was monitored by NMR spectroscopy. A weighed amount of compound **7a** dissolved in $CDCl_3$ was saturated with dry hydrogen chloride until it became colorless, after which a spectrum was recorded. Positions of all the lines in the spectrum were somewhat displaced with respect to the starting compound **7a**, in addition, it became possible to observe a signal at δ 5.98 with the integral intensity 2 H, which corresponds to the protons of the hydroxy groups. The ^{13}C NMR spectrum completely agrees with the structure **9**, as well.

Scheme 3



The zwitterionic compounds **7a—c** do not exhibit properties characteristic of the sterically hindered *o*-quinones. They do not react with metals to form semiquinone complexes. The hydrogen atom localized on the dioxolene fragment is prone to the displacement with alkali metals to yield the corresponding salts. Semiquinone and catecholate complexes can be obtained from catechol **9**. Thus, it oxidizes to the corresponding semiquinone complex **10** upon the action of divalent copper chloride in the presence of triphenylphosphine (Scheme 4).

Scheme 4



Formation of complex **10** was confirmed by EPR spectroscopy in THF solution at room temperature. The hyperfine splitting (HFS) constants on the copper nucleus (quartet, a^{63}Cu = 11.0 G, a^{65}Cu = 11.6 G) and on the two phosphorus nuclei (triplet 1 : 2 : 1, a^{31}P = 17.8 G), as well as the spectrum position (g = 2.0057) are characteristic of

Table 1. The absorption band maxima and the coefficients of molar extinction of compounds **7a—c** in different solvents

Compound	λ_{max}/nm (ε/mol^{-1} cm^{-1})		
	Toluene*	Chloroform	Methanol
7a	536	484 (6600)	414 (6000)
7b	544	486 (6800)	422 (6600)
7c	544	486 (4400)	416 (4700)

* The spectra in toluene were recorded for saturated solutions. Coefficients of molar extinction were not determined.

pseudotetrahedral complexes of copper (I) with phosphine ligands.[11] No splitting on the iminium nitrogen atom was detected in the spectrum.

The electron absorption spectra (Table 1) of compounds **7a—c** exhibit a broad band corresponding to the charge transfer. Position of this absorption band for all three compounds is virtually identical in different solvents and does not depend on the size of alkyl substituent at the nitrogen atom. At the same time, position of this band depends on polarity of the solvent. This band is blue shifted in more polar methanol. The values of molar extinction in toluene were not determined, since the spectra were recorded for the saturated solutions of compounds **7a—c** because of their limited solubility in toluene.

In conclusion, the reaction of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone with *N*,*N*-disubstituted dithiocarbamates furnished new zwitterionic compounds; a possibility of their use as ligands in coordination sphere of metals was demonstrated.

Experimental

3,6-Di(*tert*-butyl)-1,2-benzoquinone, obtained according to the known method,[12] was converted to 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone as described.[13] Solvents were purified according to the standard procedures.[14] Mono- and disubstituted dithiocarbamates were synthesized according to the procedure.[15] EPR spectra were recorded on Bruker ER 200D-SRC and Bruker EMX spectrometers. Diphenylpicrylhydrazyl (DPPH) was used as a standard in determination of *g*-factor. Samples of semiquinone and catecholate complexes for the EPR studies were prepared according to the known procedures.[11,16] IR spectra were recorded on a Specord M80 spectrometer. A SF-14 spectrometer was used for recording electron absorption spectra. NMR spectra were recorded on a Bruker Avance DPX-200 spectrometer (200 MHz for ^{1}H, 50 MHz for ^{13}C). Elemental analysis was performed on a Euro EA instrument.

4,7-Di(*tert*-butyl)-6-hydroxy-2-diethyliminio-1,3-benzodithiol-5-olate (7a). Potassium *N*,*N*-diethyldithiocarbamate (4.3 g, 0.023 mol) was added to a solution of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone (5.0 g, 0.020 mol) in acetone, and the mixture was stirred for 10 min. TLC was used to monitor the consumption of the starting quinone. Then, the organic layer was separated and concentrated. The product was isolated as deep orange crystals by crystallization from acetone. The yield was 5.17 g (71%). M.p. 199.0 °C. Found (%): C, 61.81; H, 7.72; N, 4.17; S, 16.44. $C_{19}H_{29}NO_2S_2$. Calculated (%): C, 62.08; H, 7.95; S, 17.45; N, 3.81. ^{1}H NMR (CDCl$_3$), δ: 1.64 (s, 18 H, Bu^t); 1.46 (t, 6 H, $NCH_2C\underline{H}_3$, J = 7.2 Hz); 3.77 (q, 4 H, $NC\underline{H}_2CH_3$, J = 7.2 Hz). ^{13}C NMR (CDCl$_3$), δ: 11.3 ($\underline{C}(CH_3)_3$); 31.2 ($C(\underline{C}H_3)_3$); 37.6 ($CH_2\underline{C}H_3$); 51.3 ($\underline{C}H_2CH_3$); 115.4, 122.9, 155.9, 181.3 ($S_2C{=}N$). IR, ν/cm^{-1}: 1550 m, 1530 m, 1640 m, 1460 s, 1440 s, 1385 s, 1360 s, 1340 m, 1290 m, 1240 w, 1220 w, 1160 w, 1000 w, 840 w.

X-ray diffraction studies of quinone 7a were performed on a Smart Apex I diffractometer at 100 K. Crystals ($C_{19}H_{29}NO_2S_2$, M = 367.55) are triclinic, the space group is $P\bar{1}$, a = 12.0801(9) Å, b = 15.9056(12) Å, c = 21.7606(16) Å, α = 73.851(2)°, β = 73.960(2)°, γ = 89.969(2)°, V = 3846.6(5) Å^3, Z = 8, d_{calc} = = 1.269 g cm^{-3}, μ = 0.288 mm^{-1}, F(000) = 1584, θ = 24°, 27500 reflections were collected, 11991 from them were independent (R_{int} = 0.0394), GOOF = 1.167, R_1 = 0.1380 ($I > 2\sigma$), wR_2 = = 0.3218 (all the data), residual electron density (e_{max}/e_{min}) 2.191/–0.654 e Å^{-3}. The structure was solved by the direct method and refined by the full-matrix least squares method on F^2_{hkl} in the anisotropic approximation for all the nonhydrogen atoms. The H atoms (except for carboxylic ones) were placed in the geometrically calculated positions and refined isotropically using the riding model. The carboxylic hydrogen atoms were found from the differential Fourier syntheses and refined isotropically. All the calculations were carried out using the SHELXTL v. 6.12 program package.[17]

4,7-Di(*tert*-butyl)-6-hydroxy-2-diisopropyliminio-1,3-benzodithiol-5-olate (7b). Potassium *N*,*N*-diisopropyldithiocarbamate (4.22 g, 0.020 mol) was added to a solution of 3,6-di(*tert*-butyl)-4-chloro-1,2-benzoquinone (**2**) (5.0 g, 0.020 mol) in acetone, and the mixture was stirred for 20—30 min. TLC was used to monitor the consumption of the starting quinone. The organic layer was separated and concentrated. The product was isolated as red crystals by crystallization from acetone. The yield was 6.5 g (83%). M.p. 228 °C. Found (%): C, 63.97; H, 7.59; N, 3.87; S, 16.62. $C_{21}H_{33}NO_2S_2$. Calculated (%): C, 63.75; H, 8.41; S, 16.21; N, 3.54. ^{1}H NMR (CDCl$_3$), δ: 1.66 (s, 18 H, ($C(C\underline{H}_3)_3$)); 1.54 (d, 12 H, $NC(H)(C\underline{H}_3)_2$, J = 6.0 Hz); 4.34 (q, 2 H, $NC(\underline{H})(CH_3)_2$, J = 6.0 Hz); 6.35 (s, 1 H, OH). IR, ν/cm^{-1}: 1525 m, 1530 m, 1360 s, 1280 m, 1240 m, 1200 m, 1170 m, 1150 s, 1130 m, 1060 m, 990 m, 980 m, 850 m, 780 w, 730 w.

4,7-Di(*tert*-butyl-6-hydroxy-2-(piperidinium-1-ylidene)-1,3-benzodithiol-5-olate (7c). Potassium piperidine-1-dithiocarboxylate was used instead of potassium *N*,*N*-diisopropyldithiocarbamate in the procedure similar to the preceding one. The product was isolated as fine orange crystals by crystallization from acetone. The yield was 6.0 g (79%). M.p. 210 °C. Found (%): C, 63.37; H, 7.44; N, 3.75; S, 16.60. $C_{20}H_{29}NO_2S_2$. Calculated (%): C, 63.28; H, 7.70; N, 3.69; S, 16.89. ^{1}H NMR (CDCl$_3$), δ: 1.63 (s, 18 H, ($C(C\underline{H}_3)_3$)); 1.85 (m, 6 H); 3.76 (m, 4 H). IR, ν/cm^{-1}: 1560 m, 1540 m, 1490 s, 1440 s, 1380 s, 1360 s, 1320 s, 1280 m, 1250 m, 1220 m, 1170 m, 1125 w, 1025 w, 1015 w, 990 w, 975 w, 895 w, 880 w, 845 m, 775 w, 745 w, 575 w, 550 w, 460 w.

***N*-[4,7-Di(*tert*-butyl)-5,6-dihydroxy-1,3-benzodithiol-2-ylidene]-*N*,*N*-diethylammonium chloride (9).** Dry gaseous HCl was bubbled through a solution of compound **7a** (0.5 g, 1.36 mmol) in chloroform (10 mL) until it turned colorless. The salt **9** was precipitated from chloroform by addition of acetone (5 mL).

The final product is a yellow finely crystalline compound. The yield was 0.52 g (70%). M.p. 241 °C (decomp.). Found (%): C, 56.21; H, 7.39; S, 16.07; N, 3.62. $C_{19}H_{30}NO_2S_2Cl$. Calculated (%): C, 56.48; H, 7.48; Cl, 8.25; Cl, 8.77; N, 3.47; S, 15.87. ^1H NMR ($CDCl_3$), δ: 1.60 (s, 18 H, ($C(C\underline{H}_3)_3$)); 1.52 (t, 6 H, $NCH_2C\underline{H}_3$, $J = 8.1$ Hz); 3.99 (q, 4 H, $NC\underline{H}_2CH_3$, $J = 8.1$ Hz); 5.98 (s, 2 H, OH). ^{13}C NMR ($CDCl_3$), δ: 11.5 ($\underline{C}(CH_3)_3$); 31.6 ($C(\underline{C}H_3)_3$); 38.7 ($CH_2\underline{C}H_3$); 53.2 ($\underline{C}H_2CH_3$); 122.9, 132.6, 148.0, 182.4 ($S_2C{=}N$).

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References

1. C. G. Pierpont, C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331.
2. M. Ruf, A. M. Lawrence, B. C. Noll, C. G. Pierpont, *Inorg. Chem.*, 1998, **37**, 1992.
3. V. Kuropatov, S. Klementieva, G. Fukin, A. Mitin, S. Ketkov, Yu. Budnikova, V. Cherkasov, G. Abakumov, *Tetrahedron*, 2010, **66**, 7605.
4. S. V. Klementieva, V. A. Kuropatov, G. K. Fukin, G. V. Romanenko, A. S. Bogomyakov, V. K. Cherkasov, G. A. Abakumov, *Z. Anorg. Allg. Chem.*, 2011, **637**, 232.
5. G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2206 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1997, **46**, 2093].
6. V. A. Kuropatov, V. K. Cherkasov, Yu. A. Kurskii, G. K. Fukin, L. G. Abakumova, G. A. Abakumov, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 683 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 708].
7. D. Sun, M. Krawiec, W. H. Watson, *J. Chem. Cryst.*, 1997, **27**, 515.
8. Yu. V. Zefirov, P. M. Zorkii, *Usp. Khim.*, 1995, **64**, 443 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1995, **65**].
9. 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.
10. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Trans. 2*, 1987, **12**, 1.
11. G. A. Abakumov, V. K. Cherkasov, A. V. Lobanov, G. A. Razuvaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1610 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1984, **33**, 1478].
12. N. S. Belostotskaya, N. L. Komissarova, E. V. Dzhuaryan, V. V. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 1380 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1973, 22].
13. V. A. Garnov, V. I. Nevodchikov, G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, Yu. A. Kurskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2793 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1985, **34**, 2589].
14. A. Weissberger, E. S. Proskauer, J. A. Riddick, E. E. Toops, *Organic Solvents. Physical Properties and Methods of Purification*, Interscience Publ., New York—London, 1955.
15. W. Walter, K. D. Bode, *Angew. Chem.*, 1967, **79**, 285.
16. V. A. Muraev, G. A. Abakumov, G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1974, **217**, 1083 [*Dokl. Chem.* (*Engl. Transl.*), 1974].
17. G. M. Sheldrick, SHELXTL *v. 6.12, Structure Determination Software Suite*, Bruker AXS: Madison, Wisconsin, USA, 2000.

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