Journal of Molecular Structure 1015 (2012) 173–180

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Persubstituted *p*-benzoquinone monoxime alkyl ethers and their molecular structure

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ARTICLE INFO

Article history:
Received 19 July 2011
Received in revised form 28 September 2011
Accepted 28 September 2011
Available online 20 October 2011

Keywords:
Hexasubstituted nitrosophenols
Alkylation
Nitroso phenols
Alkyl ethers of 1,4-benzoquinone-1-oximes
Polycrystalline X-ray diffraction analysis
Hartree–Fock quantum-chemical calculations

ABSTRACT

Theoretical and experimental approaches were applied for the investigation of the reactivity of persubstituted 4-nitrosophenols in the reaction with alkyl iodides, in particular the potassium salt of 2,6-di(alkoxycarbonyl)-3,5-dimethyl-4-nitrosophenol. Hartre–Fock calculations showed that the anion negative charge was located mostly on the oxygen of hydroxyl group, while estimation of the total energy of the alkylated products pointed out the benefit of alkylation on the oxygen atom of the nitroso group yielding *p*-benzoquinone monoxime alkyl ethers.

Methylation and ethylation of persubstituted nitrosophenols were carried out. The products obtained were investigated using X-ray diffraction, ^{1}H NMR spectroscopy and mass spectrometry. The crystal structure of the methyl ether of 2,6-di(alkoxycarbonyl)-3,5-dimethyl-1,4-benzoquinone-1-oxime ($\mathbf{C_{15}H_{19}NO_6}$) (I) was determined by the X-ray powder diffraction technique. The unit cell parameters were: a = 7.3322(6) Å, b = 10.5039(12) Å, c = 21.1520(20) Å, β = 93.742(6)°, V = 1625.58(2) Å^3 Z = 4, *Sp.Gr.* $P2_1/c$. The structure modeling was made in direct space by the Monte-Carlo approach using rigid and soft restrictions. The structure refinement was completed by the Rietveld method. It was established that the alkylation occurred on the oxygen atom of the nitroso group. The molecules (I) in the crystal structure were packed in columns along the axis a with pairwise convergence in a column up to the distance of 3.63 Å due to a 180° turn of every second molecule around the column axis. In the molecular structure the methyloxime group was oriented in the benzene plane and had π-conjugation with the ring. The ethoxycarbonyl groups were turned nearly perpendicular to the ring. Other compounds obtained had the structure of the alkyl ethers of 1.4-benzoquinone-1-oxime, which was proved by ^{1}H NMR spectroscopy and mass-spectrometry.

1. Introduction

A number of persubstituted nitrosophenols are known (Fig. 1), which exist as salts in the monomeric nitroso form. In the free nitrosophenol form these compounds are dimerized. [1–3]. Their hydrogenation results in the formation of *p*-aminophenols [4], some derivatives of which are applied in chemical and pharmaceutical industry as antiarrhythmic medical agents [5].

Recently, using polycrystalline X-ray diffraction analysis the crystal structure of the 2,6-diethoxycarbonyl-3,5-dimethyl-4-nitrosophenolate potassium salt (Fig. 2) belonging to the series under consideration has been determined [2,3]. In the crystal structure a potassium cation is located at a significant distance from the oxygen atom of a phenolate-ion; moreover, one of the ethoxycarbonyl groups is not located in the benzene ring plane but almost perpendicular to it due to the participation of both ethoxycarbonyl groups in the potassium coordination. The nitroso group in the plane of the benzene ring also coordinates potassium. The peculiarity of the structure is that both atoms of oxygen and nitrogen (d(K—O) = 2.50 Å and d(K—N) = 2.66 Å) participate in the potassium coordination sphere. The resulting orientation can be interpreted as a π-bond of the nitroso group to the potassium cation. The nitroso group turns out to be more active in the coordination of the potassium cation rather than the phenolate ion, which is likely due to the excessive negative charge being present in this group. Taking into account the structure peculiarities of the persubstituted nitroso phenol salts, it is of interest to determine the reactivity of the considered groups in reactions with other reagents. In particular, the question may be asked to how will the potassium salts of the persubstituted nitroso phenols be alkylated by alkyl halides: on the oxygen atom of the hydroxyl group or on the oxygen atom of

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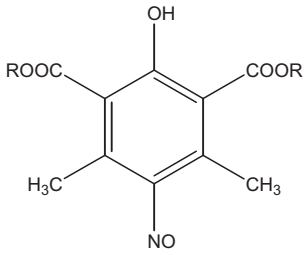
doi:10.1016/j.molstruc.2011.09.053



I (a-f)

R = Me (a), Et (b), Pr (c), Bu (d), i-Bu (e), i-Am (f)

Fig. 1. Molecular structure of persubstituted nitrosophenols.

the nitroso group? The scheme of possible reaction paths is given in Fig. 3.

The alkylation reactions of usual (non-hexasubstituted) nitrosophenols have long been known. Such nitroso phenols almost entirely exist as tautomeric *para*-benzoquinones monoximes (PQMO). When alkylating PQMO silver salt with methyl iodide a methyl ether of PQMO was obtained, and using ethyl iodide in the reaction resulted in an ethyl ether of PQMO [6]. The methyl ether of PQMO was also formed in the alkylation of quinone oxime by methyl tosylate in methanol in the presence of alkali [7] and using diazomethane in diethyl ether [8]. In [9] the ethyl ether of the oxime was obtained in the PQMO alkylation by ethanol in the presence of *p*-toluene sulfonic acid, however, here, it was shown that with methanol acting in the presence of sulfuric acid one obtained *p*-nitrosoanisole, i.e. alkylation could proceed on the phenolic hydroxyl, as well. The reaction of *p*-nitrosophenol with methanol occurred on the phenolic hydroxyl [10], forming *p*-nitrosoanisole. Thus, both possible courses of the reaction were experimentally confirmed. Therefore, it is difficult to foresee what the products of the alkylation of persubstituted *para*-nitrosophenols will be.

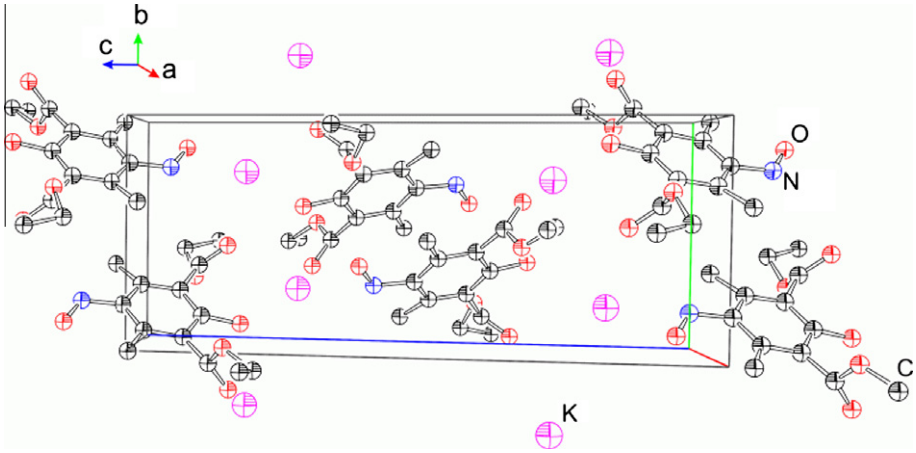
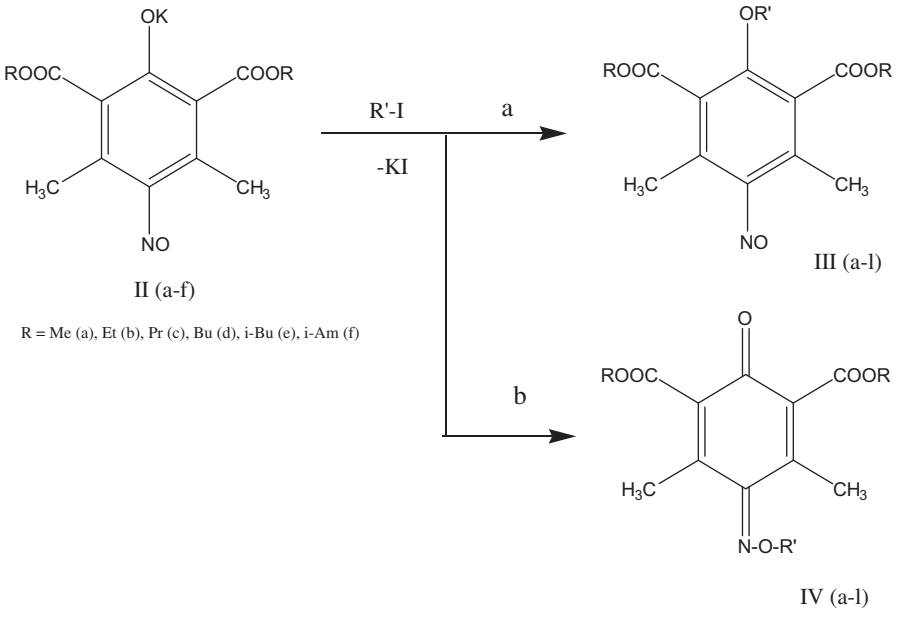


Fig. 2. Potassium salt of 2,6-ethoxycarbonyl-3,5-dimethyl-4-nitrosophenol structure projection along the *a* axis. Hydrogen atoms not shown [4].



II (a-f)

R = Me (a), Et (b), Pr (c), Bu (d), i-Bu (e), i-Am (f)

III (a-l)

IV (a-l)

a: R=R'=Me; b: R=Me, R'=Et; c: R=Et, R'=Me; d: R=R'=Et; e: R=Pr, R'=Me;
f: R=Pr, R'=Et; g: R=Bu, R'=Me; h: R=Bu, R'=Et; i: R=i-Bu, R'=Me;
j: R=i-Bu, R'=Et; k: R=i-Am, R'=Me; l: R=i-Am, R'=Et.

Fig. 3. The alkylation ways for persubstituted nitrosophenol salts.

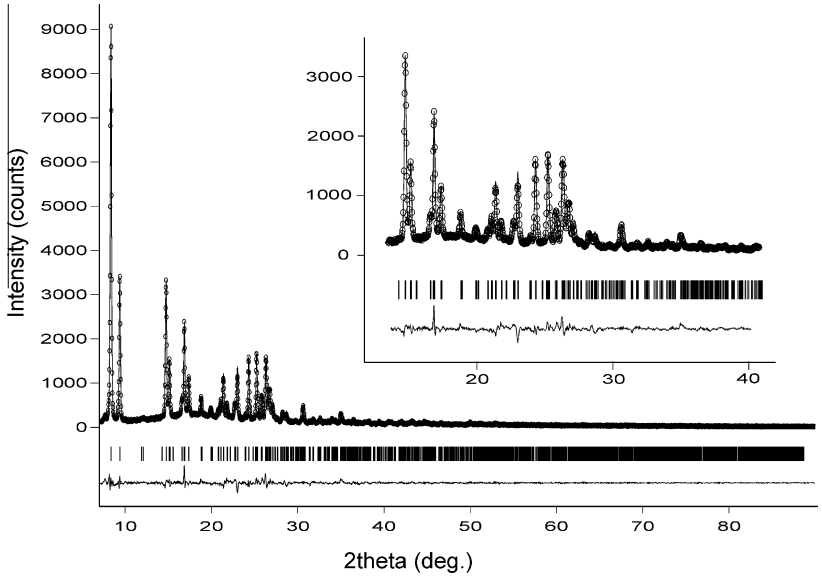


Fig. 4. Experimental (dots), calculated (solid line) and difference X-ray diffraction patterns corresponding to obtained solution for $C_{14}H_{16}KNO_6$. Location of the calculated reflections positions are indicated by the vertical strips. Giving in the insert is a zoomed high angle area of the X-ray diffraction patterns.

The most probable course of the alkylation reaction has been determined in the present work using two approaches. Theoretical quantum-chemical optimization of the nitrosophenolate-anion structure has been performed and the charge density on the reaction centers estimated. The alkylation of a number of the potassium salts of persubstituted nitrosophenols has experimentally been made. The structure of the alkylation products has been established using polycrystalline X-ray diffraction analysis, mass spectrometry and ^{1}H NMR spectroscopy.

2. Experimental

2.1. Synthesis

2.1.1. Alkylation of substituted 2,6-di(alkoxy carbonyl)-3,5-dimethyl-4-nitrosophenols

The potassium salt of hexasubstituted *para*-nitrosophenol (0,1 g) was suspended in absolute diethyl ether medium (2 ml) and excess of alkyl iodide was added. The mixture was refluxed on a water bath for 24 h at atmospheric pressure, with the mixture color changing from green to yellow. The reaction product was contained in the diethyl ether. The precipitate of potassium iodide form was filtered, and the filtrate was evaporated. The oily residue was porphyrized with hexane until solidification, followed by recrystallization from the petroleum ether. In all cases the powder obtained was yellow. The final product was additionally dried in vacuum at room temperature. Some physical–chemical properties and spectral data of the substances obtained are given below.

2.1.2. 3,5-Di(methoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, methyl ether (IVa)

Yellow crystals, yield 52%, m.p. 117–118 °C. NMR ^{1}H ($CDCl_3$): δ 2.24 (s, 3H, $PhCH_3$), 2.38 (s, 3H, $PhCH_3$), 3.902 (s, 3H, $COOCH_3$), 3.907 (s, 3H, $COOCH_3$), 4.25 (s, 3H, $NOCH_3$); mass spectrum M^+ 281.

Table 1
Crystallographic parameters of 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime methyl ether (I) and details of X-ray structure determination.

Chemical formula	$C_{15}H_{19}NO_6$
Molecular weight	309.31
Space group	$P2_1/c$
a, Å	7.3305(3)
b, Å	10.5034(8)
c, Å	21.1531(17)
α, (°)	90
β, (°)	93.785(5)
γ, (°)	90
$V_{\text{unit cell}}$, Å^3	1625.14(19)
Z	4
ρ_{cal}, g/sm^3	1.264
μ, mm^{-1}	0.827
T, K	295
Diffractometer	X'Pert PRO
Radiation	Cu Kα
λ, Å	λ_1 = 1.54056, λ_2 = 1.54439
Scan range, 2θ (°)	7.017–89.983
Number of points	3192
Number reflections	3369
Number of refinement parameters and coordinates	72
R_p, %	6.86
R_{wp}, %	9.42
R_{exp}, %	7.42
$S = R_{wp}/R_{exp}$	1,27

2.1.3. 3,5-Di(methoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, ethyl ether (IVb)

Yellow crystals, yield 17%, m.p. 86–87 °C. NMR ^{1}H ($CDCl_3$): δ 1.43 (t, 3H, NOC_2H_5), 2.25 (s, 3H, $PhCH_3$), 2.40 (s, 3H, $PhCH_3$), 3.902 (s, 3H, $COOCH_3$), 3.907 (s, 3H, $COOCH_3$), 4.50 (q, 2H, NOC_2H_5); mass spectrum M^+ 295.

2.1.4. 3,5-Di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, methyl ether (IVc)

Yellow crystals, yield 55%, m.p. 115–116 °C. NMR ^{1}H ($CDCl_3$): δ 1.371 (t, 3H, $COOC_2H_5$), 1.378 (t, 3H, $COOC_2H_5$), 2.24 (s, 3H, $PhCH_3$),

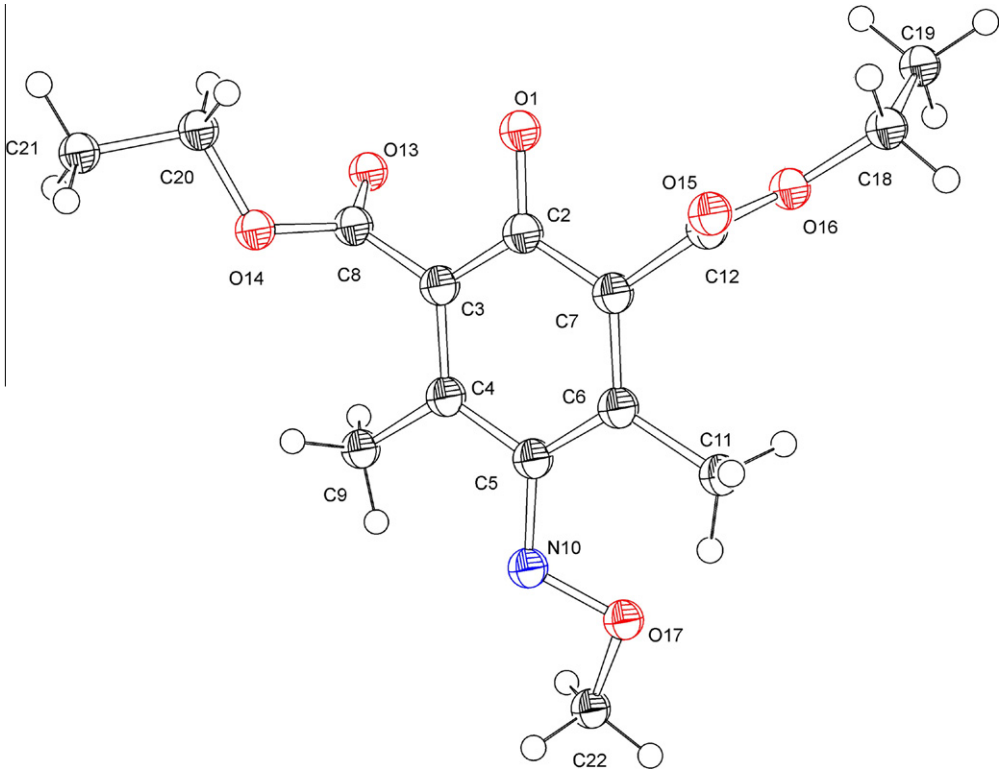


Fig. 5. Molecule 3,5-Di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime methyl ether ($C_{15}H_{19}NO_6$).

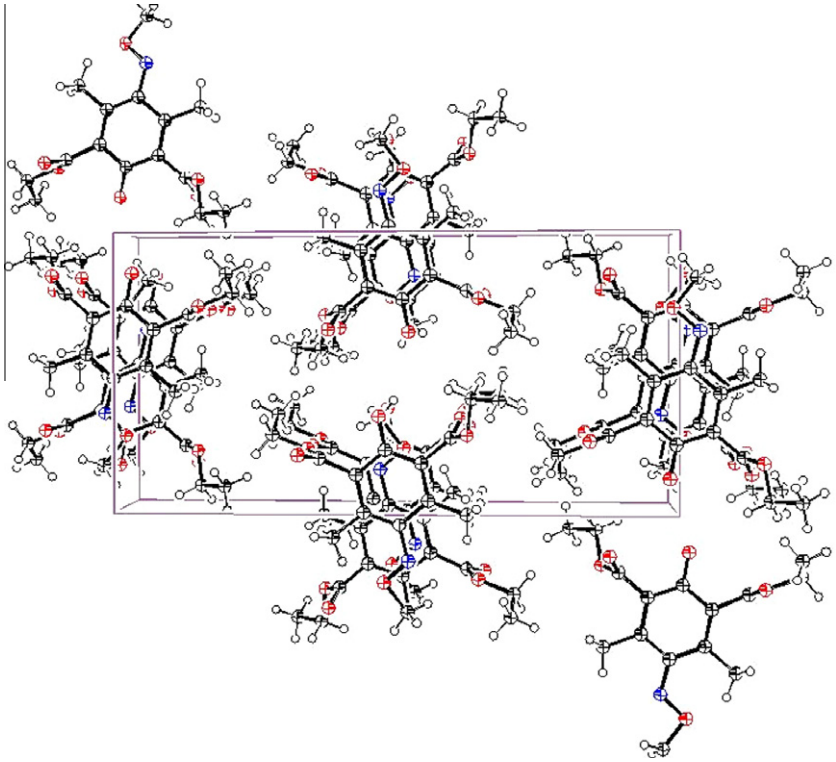


Fig. 6. Location of the molecules of 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime methyl ether within the unit cell.

Table 2
The effective charges of nucleophilic centers.

Anion	Oxygen of hydroxyl group	Oxygen of nitroso group
IIa	−0.545	−0.373
IIb	−0.539	−0.374
IIc	−0.539	−0.376
IId	−0.523	−0.389
IIe	−0.536	−0.372

Table 3
Persubstituted *para*-alkoxynitrosobenzenes and *para*-benzoquinonemonooximes alkyl ethers molecules total energy differences.

Molecules	Total energy differences, Hartree (E_{III}–E_{IV})
IIIa–IVa	0.0135
IIIb–IVb	0.0040
IIIc–IVc	0.0049
IIId–IVd	0.0062
IIIe–IVe	0.0047
IIIf–IVf	0.0061
IIIg–IVg	0.0010
IIIh–IVh	0.0063

2.38 (s, 3H, $PhCH_3$), 4.24 (s, 3H, $NOCH_3$), 4.379 (q, 2H, $COOC_2H_5$), 4.383 (q, 2H, $COOC_2H_5$); mass spectrum M^+ 309.

2.1.5. 3,5-Di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, ethyl ether (IVd)

Yellow crystals, yield 80%, m.p. 95–96 °C. NMR ^1H ($CDCl_3$): δ 1.367 (t, 3H, $COOC_2H_5$), 1.373 (t, 3H, $COOC_2H_5$), 1.42 (t, 3H, NOC_2H_5), 2.24 (s, 3H, $PhCH_3$), 2.40 (s, 3H, $PhCH_3$), 4.375 (q, 2H, $COOC_2H_5$), 4.378 (q, 2H, $COOC_2H_5$), 4.48 (t, 3H, NOC_2H_5); mass spectrum M^+ 323.

2.1.6. 3,5-Di(propoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, methyl ether (IVe)

Yellow crystals, yield 60%, m.p. 55–56 °C. NMR ^1H ($CDCl_3$): δ 1.01 (t, 6H, $2COOC_3H_7$), 1.75–1.77 (broad m, 4H, $2COOC_3H_7$), 2.24 (s, 3H, $PhCH_3$), 2.38 (s, 3H, $PhCH_3$), 4.24 (s, 3H, $NOCH_3$), 4.28 (t, 4H, $2COOC_3H_7$); mass spectrum M^+ 337.

2.1.7. 3,5-Di(propoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, ethyl ether (IVf)

Yellow crystals, yield 72%, m.p. 92–93 °C. NMR ^1H ($CDCl_3$): δ 0.99 (t, 6H, $2COOC_3H_7$), 1.43 (t, 3H, NOC_2H_5), 1.75–1.77 (broad m, 4H, $2COOC_3H_7$), 2.24 (s, 3H, $PhCH_3$), 2.40 (s, 3H, $PhCH_3$), 4.29 (t, 4H, 2 $COOC_3H_7$), 4.49 (q, 2H, NOC_2H_5); mass spectrum M^+ 351.

2.1.8. 3,5-Di(butoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, methyl ether (IVg)

Yellow crystals, yield 46%, m.p. 53–55 °C. NMR ^1H ($CDCl_3$): δ 0.960 (t, 3H, $COO\text{-}C_4H_9$), 0.964 (t, 3H, $COO\text{-}C_4H_9$), 1.40–1.44 (m, 4H, $2COOC_4H_9$), 1.65–1.71 (m, 4H, $2COOC_4H_9$), 2.23 (s, 3H, $PhCH_3$), 2.38 (s, 3H, $PhCH_3$), 4.23 (s, 3H, $NOCH_3$), 4.317 (t, 2H, $COOC_4H_9$), 4.320 (t, 2H, $COO—C_4H_9$); mass spectrum M^+ 365.

2.1.9. 3,5-Di(butoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, ethyl ether (IVh)

Yellow crystals, yield 47%, m.p. 68–70 °C. NMR ^1H ($CDCl_3$): δ 0.960 (t, 3H, $COOC_4H_9$), 0.965 (t, 3H, $COO—C_4H_9$), 1.41–1.42 (m, 4H, $2COOC_4H_9$), 1.43 (t, 3H, NOC_2H_5), 1.71–1.76 (m, 4H, $2COOC_4H_9$), 2.23 (s, 3H, $PhCH_3$), 2.39 (s, 3H, $PhCH_3$), 4.310 (t, 2H,

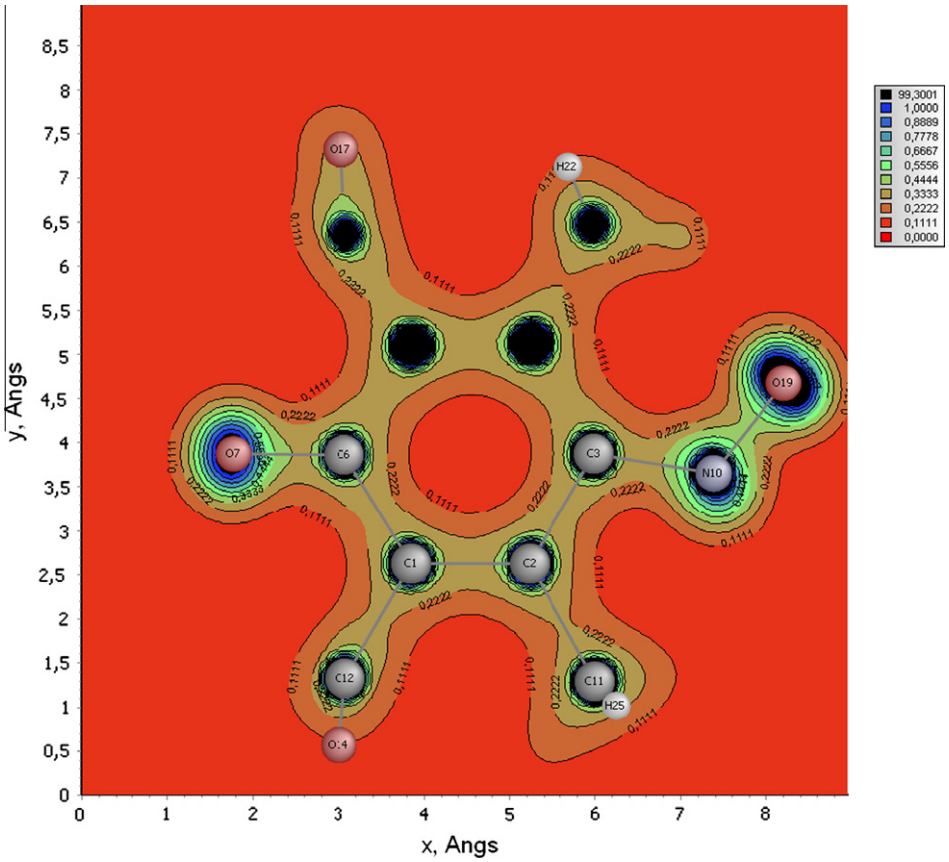


Fig. 7. The calculated electron density map of the 2,6-diethoxycarbonyl-3,5-dimethyl 4-nitrosophenolate anion.

Table 4
The most important interatomic distances in 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime methyl ether.

Atom A	Atom B	d(A–B), (Å)
O14	C8	1.338
O14	C20	1.464
O15	C12	1.220
O13	C8	1.211
O1	C2	1.199
O16	C12	1.342
O16	C18	1.451
O17	N10	1.399
O17	C22	1.430
C2	O1	1.199
C2	C3	1.445
C2	C7	1.451
C3	C4	1.351
C3	C2	1.445
C3	C8	1.497
C4	C3	1.351
C4	C5	1.452
C4	C9	1.506
C5	N10	1.300
C5	C6	1.446
C5	C4	1.452
C6	C7	1.355
C6	C5	1.446
C6	C11	1.514
C7	C6	1.355
C7	C2	1.451
C7	C12	1.502
C8	O13	1.211
C8	O14	1.338
C8	C3	1.497
C9	C4	1.506
C11	C6	1.514
C12	O15	1.220
C12	O16	1.342
C12	C7	1.502
C18	O16	1.451
C18	C19	1.476
C19	C18	1.476
C20	O14	1.464
C20	C21	1.481
C21	C20	1.481
C22	O17	1.430
N10	C5	1.300
N10	O17	1.399

$COOC_4H_9$), 4.317 (t, 2H, $COOC_4H_9$), 4.48 (q, 2H, NOC_2H_5); mass spectrum M^+ 379.

2.1.10. 3,5-Di(isobutoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, methyl ether (IV i)

Yellow crystals, yield 49%, m.p. 86–87 °C. NMR ^1H ($CDCl_3$): δ 0.988 (d, 6H, COO-i-C_4H_9), 0.995 (d, 6H, COO-i-C_4H_9), 2.043 (m, 2H, 2COO-i-C_4H_9), 2.24 (s, 3H, $PhCH_3$), 2.39 (s, 3H, $PhCH_3$), 4.106 (d, 2H, COO-i-C_4H_9), 4.110 (d, 2H, COO-i-C_4H_9), 4.24 (s, 3H, $NOCH_3$); mass spectrum M^+ 365.

2.1.11. 3,5-Di(isobutoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, ethyl ether (IV j)

Yellow crystals, yield 52%, m.p. 55–56 °C. NMR ^1H ($CDCl_3$): δ 0.986 (d, 6H, COO-i-C_4H_9), 0.992 (d, 6H, COO-i-C_4H_9), 1.43 (t, 3H, NOC_2H_5), 2.04 (m, 2H, 2COO-i-C_4H_9), 2.24 (s, 3H, $PhCH_3$), 2.40 (s, 3H, $PhCH_3$), 4.12 (d, 4H, 2COO-i-C_4H_9), 4.48 (q, 2H, NOC_2H_5); mass spectrum M^+ 379.

2.1.12. 3,5-Di(isoamoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, methyl ether (IV k)

Yellow crystals, yield 86%, m.p. 74–75 °C. NMR ^1H ($CDCl_3$): δ 0.953 (d, 6H, COO-i-C_5H_{11}), 0.958 (d, 6H, COO-i-C_5H_{11}), 1.63 (m, 4H, 2COO-i-C_5H_{11}), 1.74 (m, 2H, 2COO-i-C_5H_{11}), 2.23 (s, 3H, $PhCH_3$), 2.37 (s, 3H, $PhCH_3$), 4.346 (t, 2H, COO-i-C_5H_{11}), 4.349 (t, 2H, COO-i-C_5H_{11}), 4.23 (s, 3H, $NOCH_3$); mass spectrum M^+ 393.

Table 5
The most important angles between bonds in 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime methyl ether structure.

Atom **A**	Atom **B**	Atom **C**	Angle (**ABC**)
C8	O14	C20	121.06
C12	O16	C18	123.01
N10	O17	C22	107.43
O1	C2	C3	120.30
O1	C2	C7	119.96
C3	C2	C7	119.69
C4	C3	C2	120.52
C4	C3	C8	120.74
C2	C3	C8	118.69
C3	C4	C5	119.67
C3	C4	C9	116.09
C5	C4	C9	124.22
N10	C5	C6	124.11
N10	C5	C4	115.93
C6	C5	C4	119.94
C7	C6	C5	120.12
C7	C6	C11	121.87
C5	C6	C11	117.94
C6	C7	C2	119.90
C6	C7	C12	120.26
C2	C7	C12	119.64
O13	C8	O14	119.98
O13	C8	C3	121.45
O14	C8	C3	118.56
O15	C12	O16	119.89
O15	C12	C7	120.86
O16	C12	C7	119.23
O16	C18	C19	102.37
O14	C20	C21	107.59
C5	N10	O17	122.28

2.1.13. 3,5-Di(isoamoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, ethyl ether (IV l)

Yellow crystals, yield 83%, m.p. 60–61 °C. NMR ^1H ($CDCl_3$): δ 0.956 (d, 6H, COO-i-C_5H_{11}), 0.959 (d, 6H, COO-i-C_5H_{11}), 1.43 (t, 3H, NOC_2H_5), 1.63 (m, 4H, 2COO-i-C_5H_{11}), 1.75 (m, 2H, 2COO-i-C_5H_{11}), 2.23 (s, 3H, $PhCH_3$), 2.39 (s, 3H, $PhCH_3$), 4.35 (t, 4H, 2COO-i-C_5H_{11}), 4.48 (q, 2H, NOC_2H_5); mass spectrum M^+ 407.

2.2. Acquisition of ^1H NMR and mass spectra

The ^1H NMR spectra were obtained using Bruker Avance III 600 in deuterochloroform medium. The mass spectra were acquired with a Finnigan MAT 8200.

2.3. Methods of quantum-chemical calculations

The quantum chemical optimizations were made with the software package FireFly [11] using the Hartree–Fock method with the 6-31G basis set and Muller–Plesset second order electron correlation corrections [12–15].

2.4. X-ray diffraction method of determining the structure of the methyl ether of 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime

The X-ray powder diffraction data were obtained using Cu Kα radiation on a PANalytical X'Pert Pro diffractometer equipped with a PIXcel detector and a graphite monochromator.

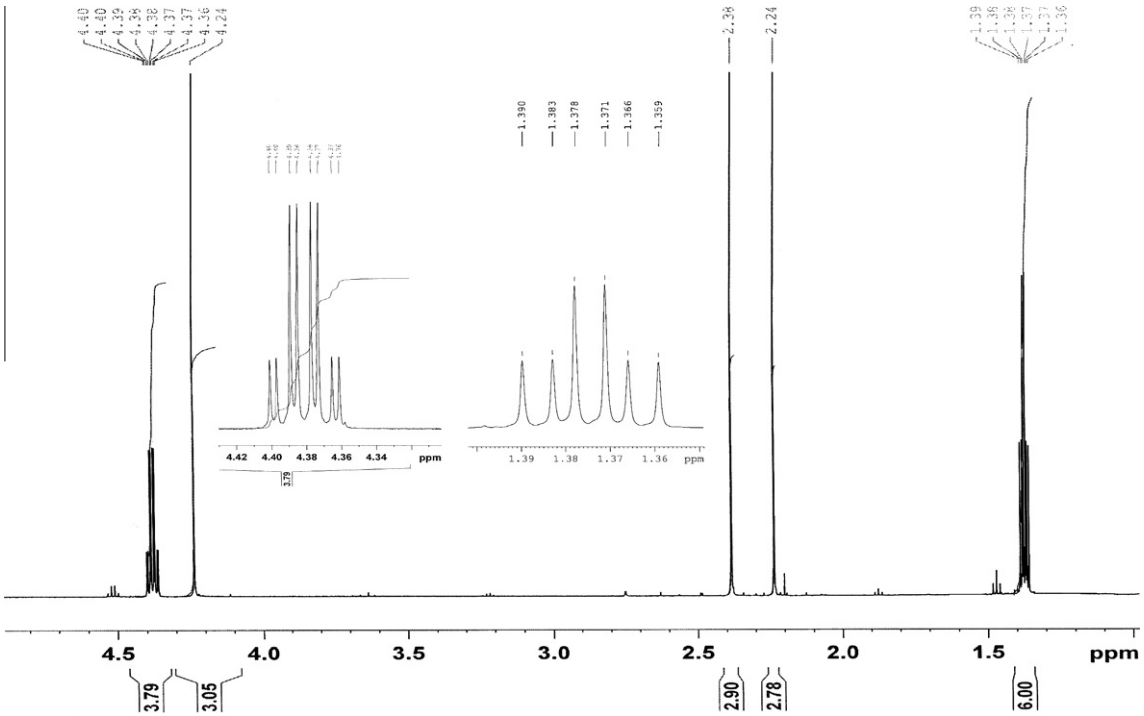


Fig. 8. NMR ^{1}H spectrum of 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime methyl ether. Duplication signals of Methyl and methylene groups of ester substituents are caused by syn- or anti-position with methyloxime group.

The sample was ground in an agate mortar and the holder was front loaded. The acquisition ranged from 3° to 90° in 2θ, with a step of 0.013°, Δt – 50 s.

The unit lattice parameters were determined and refined with the help of the software described in [16,17]. The search of the structure model was implemented by the Monte-Carlo method [22,23] using the software *FOX* [18]. The structure of the anion $C_{14}H_{17}NO_6$ was used as the initial model [2,3,20]. The refining procedure of the chosen structure variants was carried out with the help of the full-profile analysis using the program *FullProf* [19]. During refinement, both interatomic distances and angles were subjected to weighted restraints. The dihedral angles were not restrained. The restraints were relaxed gradually during refinement [21]. At the last stage of the refinement the hydrogen atoms rigidly attached to the corresponding carbon atoms were added into the structure model using the program *XP* [24]. The displacement coefficients of the atoms were specified in the isotropic approximation. Fig. 4 shows the result of the agreement between the simulated and experimental X-ray diffraction patterns for the final structure model. Table 1 presents the crystallographic structure characteristics of the methyl ether of 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime, while Figs. 5 and 6 show the crystal structure. More detailed data concerning present investigation can be found in [25]. Cif-file is deposited in CSD (#CCDC 846074).

3. Results and discussion

Taking into account the fact that in the anions of persubstituted nitrosophenols there are two nucleophilic centers – the oxygen atoms of the hydroxy group and nitroso group – quantum chemical optimizations of the nitrosophenolate anions were made to carry out an analysis of their reactivity.

Table 2 shows the charge density values on the oxygen atoms of the hydroxy and nitroso groups obtained as a result of the anion structure optimization. From the point of view of the charge values on the nucleophilic centers the course of the reaction on the oxygen atom of the hydroxyl group seems more preferable. On the average, the charge excess amounts to 0.17 e. The calculated electron density map of the 2,6-diethoxycarbonyl-3,5-dimethyl-4-nitrosophenolate anion presented in Fig. 7. The substitution of the alkoxycarbonyl groups in the series (Me, . . ., Am) leads only to a slight decrease of the charge difference in the considered groups which is apparently connected with the absence of the conjugation of their π-systems with the benzene ring. A possible obstacle for implementing the interaction on the oxygen atom of the hydroxyl group can be the increasing steric effect of the alkoxy groups.

Side by side with the difference in the charge density the HOMO's of oxygen of hydroxyl and nitroso groups have significant difference too. It means that the discussed chemical reaction may follows via different mechanisms: S_N1 and S_N2. The oxygen of hydroxyl group interacts with a carbocation via S_N1 while the oxygen of nitroso group follows S_N2 mechanism in the reaction with halogen alkane. The calculation carried out counts in favor of the second way. The difference HOMO of the oxygen hydroxyl group and LUMO of the carbocation is very large while HOMO of oxygen nitroso group and LUMO of halogenalkans are nearly equal.

On the other hand, the structure optimization of the possible nitrosophenol alkylation products and the comparison of the total energies of the molecules alkylated on the oxygen atoms of the hydroxyl or nitroso groups (Table 3) evidences a higher energy benefit of the alkylation products on nitroso groups which would result in the formation of the ethers of persubstituted *para*-benzoquinone monoximes.

The course of the alkylation reactions was experimentally revealed by the reaction of persubstituted nitrosophenol potassium salts with alkyl iodides in the absolute ether. In all the cases the crystalline alkylation products of yellow color were obtained. The product composition was confirmed by the mass-spectrometry measurements presented in the experimental part. In each mass-spectrum there was a molecular ion exactly corresponding to the molecular weight of the alkyl ether and the remaining molecule

fragments formed as a result of the electron impact. The crystal structure of the methyl ether of 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinon-1-oxime ($C_{15}H_{19}NO_6$) was determined by the X-ray structure analysis using a polycrystalline sample. The substance has a molecular structure (Fig. 4). In the unit cell there are 4 identical formula units, with the molecule being asymmetrical. The planes of the ethoxycarboxyl groups are turned almost perpendicular to the ring, forming dihedral angles of 79.89 ° and 76.84°. The ethoxy groups are oriented on different sides of the ring plane. Other substitutes (=O, —CH_3, —CH_3, =NO(CH_3)) are located in the ring plane. The methyloxime group is likely to have π-conjugation with the carbonyl group which is revealed by the presence of the quinoid distortion of the benzene ring, (d(C3—C2) = 1.44(1) Å, d(C3—C2) = 1.35(1) Å). The shortened distances C2—O1 (1.20(1) Å) and C5—N10 (1.30(1) Å) are also indicative of the appearance of double bonds with the oxygen atoms of the carbonyl and methyloxime groups. Other interatomic distances and angles are presented in Tables 4 and 5.

The crystal structure is a column packing of molecules along the axis *a*. (Fig. 6). In the column the molecules are located in pairs related by the symmetry center. The distance between the planes of the benzene rings in the pairs is about 3.63 Å. Hydrogen bonds are absent, thus, the observed packing is a result of the most dense molecule packing taking into account their own geometry.

Important information on the ether structure was obtained by analyzing the ^{1}H NMR spectra. The examination of the ^{1}H NMR spectra of the products showed that in all the cases the alkyl ethers of the hexasubstituted quinine-oximes were formed (Fig. 3, reaction course **b**). In the ^{1}H NMR spectra the protons of the ring methyl groups and the alkyl group protons of the ether substituents proved to be non-equivalent due to syn- or anti-location of these substituents with respect to the alkyloxime group, resulting in all the substitutes being in different environment. For this reason, the protons of all the indicated groups gave two signals of the same intensity with different chemical shifts. Since the alkyl groups of the oxime ether are not influenced by the asymmetrical group, thus, their protons give the usual signal. So, the methyl group of the oxime ether is revealed by one singlet in the weak field and the ethyl group – by one quartet in the weak field and one triplet in the strong one. Such a picture vividly confirms that the alkylation in all the cases occurred on the oxygen atom of the nitroso group.

The ^{1}H NMR spectrum of the methyl ether of 3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone-1-oxime is presented in Fig. 8. The methyl groups of the ring are non-equivalent due to syn- or anti-location with respect to the methyloxime group and give signals as singlets of the same intensity with the chemical shifts of 2.24 ppm and 2.38 ppm. Likewise, the signals of the ethyl ether groups for the same reason give «double» signals: triplets with the chemical shifts of 1371 ppm and 1378 ppm as well as quartets with 4379 ppm and 4383 ppm. The signal of the methyl group of oxime is a singlet with the chemical shift of 4.24 ppm.

Thus, it was established that (in spite of the high charge localization on the oxygen atom of the hydroxyl group) the alkylation reaction of persubstituted nitrosophenols occurred on the oxygen atom of the nitroso group with the formation of alkyl ethers of hexasubstituted quinine oximes which are more beneficial from the energy point of view.

The investigation was carried out at the financial support of the Ministry of Education and Science of the Russian Federation (State Contracts No. 02.740.11.0629 and No. П2263), and the International Center of Diffraction Data (ICDD, Grant No. 93-10).

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