Journal of Molecular Structure 1063 (2014) 341–350

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Structural study of the acylation products of persubstituted para-nitrosophenols

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HIGHLIGHTS

- Ten new acyl derivatives of persubstituted para-nitrosophenols were synthesized.
- The oxygen atom of nitroso group is subjected to acylation.
- Quinonoid structure was proved for all products by NMR and X-ray diffraction.
- The acylation products crystallize in molecular structure with stacking columns.

ARTICLE INFO

Article history:
Received 2 December 2013
Received in revised form 27 January 2014
Accepted 27 January 2014
Available online 2 February 2014

Keywords:
Persubstituted nitrosophenols
Quinonemonooximes
Acylation
X-ray powder diffraction crystal structure analysis
^{1}H NMR analysis

ABSTRACT

Acylation of potassium 2,6-di(alkoxycarbonyl)-3,5-dimethyl-4-nitrosophenolate with acetic anhydride and benzoyl chloride gave previously unknown 10 derived acyl compounds. ^{1}H NMR spectroscopy and X-ray diffraction data have been used to show that the oxygen atom of the nitroso group undergoes acylation to form the quinoid products. X-ray powder crystal structure analysis of 1-acetoxymino-3,5-di(methoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone, 1-acetoxymino-3,5-di(ethoxycarbonyl)-2,6-dimethyl-1,4-benzoquinone and 1-benzoyloxymino-3,5-di(propoxycarbonyl)-2,6-dimethyl-1,4-benzoquinon revealed a planar structure of the molecules with quinoid ring as the central moiety. Alkyloxycarbonyl groups rotate in the range 94–101° relative to the plane of the molecule. Typical hydrogen bonds are absent. Molecules fill the unit cell following the closest packing principle in the form of the columns. The ^{1}H NMR spectroscopic data indicates that the direction of acylation and type of structure for the other members of the series of the studied compounds are the same.

1. Introduction

There are known a number of persubstituted nitrosophenols existing as salts in monomeric nitrosoform [1]. Hydrogenation of persubstituted nitrosophenols gives corresponding para-aminophenols [2]. Their some derivatives have been used in the pharmaceutical industry as anti-arrhythmic drugs [3]. Despite the practical importance of these para-nitrosophenols, their chemical properties are poorly understood. It is only known that they dimerize in neutral and mildly acidic medium [4] and their oxidation by hydrogen peroxide in alkaline medium leads to the formation of nitrophenols [5]. Recently, on the example of a structure of the product of alkylation it have been shown that alkylation brought the alkylesters of para-benzoquinonemonooximes [6]. The acylation of persubstituted nitrosophenols is interesting to further study of their reactivity. For conventional nitrosophenols, existing in two tautomeric forms as p-nitrosophenol and p-benzoquinonemonooxime (PQMO), the acylation may proceed both onto the hydroxyl and onto the oxime group depending on the conditions. For example, p-nitrosophenol in the reaction with benzoyl chloride in dioxane gives the p-nitrosophenylbenzoat [7,8]. The reaction of the potassium salt of p-nitrosophenol with acetic anhydride in acetonitril in the presence of crown ether (18-crown-6) proceeds similarly, giving p-nitrosophenylacetate [9]. At the same time, the p-benzoquinonemonooxime acetate was obtained by action of acetic anhydride on PQMO or acetyl chloride on the silver salt of PQMO [10]. The same result was obtained at the acylation of the series of substituted PQMO by acetyl chloride [11]. Similarly, PQMO benzoylation with benzoyl chloride in pyridine occurs at the oxime group with forming an ester [12] and in diethyl ether in the presence of triethylamine [13]. Conclusion about the structure of the acylation products was made using the of electronic spectroscopy data. The nitroso group remains intact in the case of the

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http://dx.doi.org/10.1016/j.molstruc.2014.01.066
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acylation reaction following the oxygen atom of the hydroxy group. Nitroso group has a characteristic absorption at 680–760 nm (n → π transition), causing the substance to be green [14]. At the formation of the oxime type product similar absorption band in the spectrum is missing. These data indicate the reactivity of the two groups, which complicates the prediction of the acylation direction for persubstituted nitrosophenols: on the oxygen atom of the hydroxy or nitroso groups.

In order to clarify the prefer directions of the carbonyl group joining to the persubstituted nitrosophenols, we carried out the reactions of the five potassium salts of 2,6-dialkoxycarbonyl-3,5-dimethyl-4-nitrosophenols (Ia–Ie) with different alkyl groups: methyl, ethyl, propyl, buthyl, amyl and acetic anhydride or benzoyl chloride as the acylating agents. As the result 10 new compounds were obtained: 1-acetoxymino-3,5-di(alkoxycarbonyl)-3,5-dimethyl-1,4-benzoquinones (IIa–IIe) and 1-benzoiloxymino-3,5-di(alkoxycarbonyl)-2,6-dimethyl-1,4-benzoquinones (IIIa–IIIe). In this paper we present the results of syntheses, identification of the products and some structural results obtained by X-ray powder diffraction analysis. The individuality of the compounds is also confirmed by ^{1}H NMR spectroscopy and mass spectrometry.

2. Experimental

2.1. Synthesis

2.1.1. Acylation of the substituted 2,6-di(alkoxycarbonyl)-3,5-dimethyl-4-nitrosophenols

Acylation of 2,6-di(alkoxycarbonyl)-3,5-dimethyl-4-nitrosophenols (Ia–Ie) were carried out at atmospheric pressure, stirring and heating. Potassium salt of persubstituted p-nitrosophenol (0.2 g) was suspended in absolute diethyl ether (2 ml) with addition acetic anhydride or benzoyl chloride in 1.1 fold molar excess relative to the potassium salt of p-nitrosophenol. The reaction was conducted in the presence of sulfuric acid. The reaction mixture was heated in a round bottom flask with reflux condenser and drying tube with stirring for 1.5–3 h. The product was passed into the diethyl ether solution, the reaction mixture color changed from green to yellow. Then the mixture was cooled to room temperature, poured into 10–15 ml water and the aqueous layer was separated from the organic in a separatory funnel. The aqueous layer was extracted 3 times with 10 ml diethyl ether. The ether extracts were combined with the organic layer and washed with 10% sodium carbonate solution, then with water. Ether was evaporated and the solid residue was dried for 1 h under vacuum in a desiccator over anhydrous sodium sulfate. Those products are isolated as an oil, first had been triturated with hexane and then the resulting crystals were dried under vacuum. The substances were purified by recrystallization from petroleum ether. Some products were obtained as yellow oil. Some of the individual physico-chemical properties of the synthesized compounds are presented below.

2.1.2. (**IIa**) 1-Acetoxymino-3,5-di(methoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{14}H_{15}NO_7$ (Scheme 1)

Yield 60%, yellow crystals, mp 185–187 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, NO—$COCH_3$), 3.93 s (6H, COO—CH_3). Mass spectrum, *m/z* ($I_{rel.}$, %): 309 (7) $[M]^+$, 267 (8), 147 (5), 121 (7), 67 (16), 43 (100), 39 (9).

2.1.3. (**IIb**) 1-Acetoxymino-3,5-di(ethoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{16}H_{19}NO_7$

Yield 50%, yellow crystals, mp 123–125 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.371 t (3H, $COOC_2H_5$), 1.378 t (3H, $COOC_2H_5$), 2.34 t (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, $NOCOCH_3$), 4.397 q (2H, $COOC_2H_5$), 4.401 q (2H, $COOC_2H_5$). Mass spectrum, *m/z* ($I_{rel.}$, %): 337 (6) $[M]^+$, 295 (20), 249 (6), 204 (5), 67 (13), 43 (100), 39 (5).

2.1.4. (**IIc**) 1-Acetoxymino-3,5-di(propyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{18}H_{23}NO_7$

Yield 53%, yellow crystals, mp 63–65 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 t (3H, $COOC_3H_7$), 1.02 t (3H, $COOC_3H_7$), 1.75–1.79 m (4H, 2 $COOC_3H_7$), 2.34 s (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, $NOCOCH_3$), 4.30 t (2H, $COOC_3H_7$), 4.32 t (2H, $COOC_3H_7$). Mass spectrum, *m/z* ($I_{rel.}$, %): 365 (9) $[M]^+$, 323 (10), 203 (5), 121 (5), 67 (18), 43 (100), 41 (33), 39 (14).

2.1.5. (**IId**) 1-Acetoxymino-3,5-di(butyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{20}H_{27}NO_7$

Yield 40%, yellow oil, fp 0–5 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.974 t (3H, $COOC_4H_9$), 0.975 t (3H, $COOC_4H_9$), 1.417–1.480 m (4H, 2 $COOC_4H_9$), 1.702–1.750 m (4H, 2 $COOC_4H_9$), 2.33 s (3H, $PhCH_3$), 2.37 s (3H, $PhCH_3$), 2.47 s (3H, $NOCOCH_3$), 4.34 t (2H, $COOC_4H_9$), 4.35 t (2H, $COOC_4H_9$). Mass spectrum, *m/z* ($I_{rel.}$, %): 393 (2) $[M]^+$, 351 (7), 277 (23), 263 (11), 221 (20), 204 (11), 175 (7), 147 (13), 67 (21), 57 (59), 43 (83), 41 (100), 39 (22).

2.1.6. (**IIe**) 1-Acetoxymino-3,5-di(amyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{22}H_{31}NO_7$

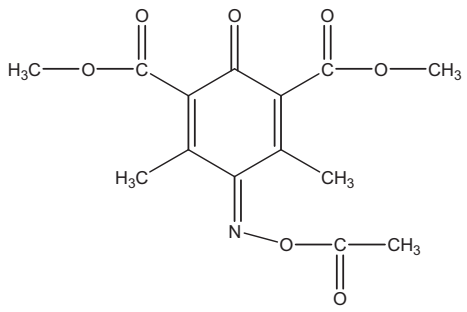
Yield 70%, yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (6H, 2 $COOC_5H_{11}$), 1.36–1.38 m (8H, 2 $COOC_5H_{11}$), 1.72–1.74 m (4H, 2 $COOC_5H_{11}$), 2.32 c (3H, $PhCH_3$), 2.36 c (3H, $PhCH_3$), 2.46 s (3H, $NOCOCH_3$), 4.32 t (4H, 2 $COOC_5H_{11}$). Mass spectrum, *m/z* ($I_{rel.}$, %): 421 (3) $[M]^+$, 379 (10), 291 (27), 277 (6), 221 (26), 205 (13), 202 (23), 189 (11), 175 (8), 147 (23), 67 (34), 55 (40), 43 (100), 41 (85), 39 (27).

2.1.7. (**IIIa**) 1-Benzoyloxymino-3,5-di(methoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{19}H_{19}NO_7$

Yield 55%, yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.44 s (3H, $PhCH_3$), 2.60 s (3H, $PhCH_3$), 3.95 s (3H, $COOCH_3$), 4.04 s (3H, $COOCH_3$), 7.57 m (2H, NOCOPh), 7.72 m (1H, NOCOPh), 8.11 m (2H, NOCOPh). Mass spectrum, *m/z* ($I_{rel.}$, %): 371 (15) $[M]^+$.

2.1.8. (**IIIb**) 1-Benzoyloxymino-3,5-di(ethoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_2{}^1H_{23}NO_7$

Yield 50%, yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (3H, $COOC_2H_5$), 1.39 t (3H, $COOC_2H_5$), 2.42 s (3H, $PhCH_3$), 2.59 s (3H, $PhCH_3$), 4.40 q (4H, 2 $COOC_2H_5$), 7.56 m (2H, NOCOPh), 7.71 m (1H, NOCOPh), 8.10 m (2H, NOCOPh). Mass spectrum, *m/z* ($I_{rel.}$, %): 399 (3) $[M]^+$, 354 (6), 295 (7), 249 (6), 234 (6), 219 (22), 205 (18), 202 (12), 175 (8), 147 (22), 122 (30), 105 (65), 67 (66), 51 (60), 43 (22), 39 (32).



Scheme 1. Structural formula for $C_{14}H_{15}NO_7$ (**IIa**).

*2.1.9. (**IIIc**) 1-Benzoyloxymino-3,5-di(propyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{23}H_{25}NO_7$*

Yield 86%, yellow cystals, mp 75–76 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 t (3H, $COOC_3H_7$), 1.02 t (3H, $COOC_3H_7$), 1.79 m (4H, 2 $COOC_3H_7$), 2.43 s (3H, $PhCH_3$), 2.60 s (3H, $PhCH_3$), 4.32 t (4H, 2 $COOC_3H_7$), 7.57 m (2H, NOCOPh), 7.70 m (1H, NOCOPh), 8.10 m (2H, NOCOPh). Mass spectrum, *m/z* ($I_{rel.}$, %): 427 (3) $[M]^+$, 205 (23), 147 (6), 122 (25), 105 (100), 67(32), 51 (47), 43 (96), 41 (70), 39 (32).

*2.1.10. (**IIId**) 1-Benzoyloxymino-3,5-di(butyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{25}H_{31}NO_7$*

Yield 55%, yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.98 t (3H, $COOC_4H_9$), 0.99 t (3H, $COOC_4H_9$), 1.45 m (4H, 2 $COOC_4H_9$), 1.74 m (4H, 2 $COOC_4H_9$), 2.43 s (3H, $PhCH_3$), 2.60 s (3H, $PhCH_3$), 4.36 t (4H, 2 $COOC_4H_9$), 7.55 m (2H, NOCOPh), 7.71 m (1H, NOCOPh), 8.11 m (2H, NOCOPh). Mass spectrum, *m/z* ($I_{rel.}$, %): 455 (10) $[M]^+$.

*2.1.11. (**IIIe**) 1-Benzoyloxymino-3,5-di(amyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone, $C_{27}H_{35}NO_7$*

Yield 50%, yellow crystals, mp 45–47 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.943 t (3H, 2 COO—C_5H_{11}), 0.953 t (3H, 2 COO—C_5H_{11}), 1.39 m (8H, 2 COO—C_5H_{11}), 1.76 m (4H, 2 COO—C_5H_{11}), 2.43 s (3H, $PhCH_3$), 2.60 s (3H, $PhCH_3$), 4.348 t (2H, 2 COO—C_5H_{11}), 4.359 t (2H, 2 COO—C_5H_{11}), 7.58 m (2H, NOCOPh), 7.72 m (1H, NOCOPh), 8.10 m (2H, NOCOPh). Mass spectrum, *m/z* ($I_{rel.}$, %): 483 (3) $[M]^+$, 105 (100), 77 (24), 51 (9), 43 (13).

2.2. Terms and conditions ^{1}H NMR and mass spectra

All NMR data were collected in $CDCl_3$ on Bruker Avance III 600 spectrometer system (14.1 T, Bruker) at 295 k. For proton NMR experiments single p/2-pulse was applied. For proton NMR analyses the relaxation delay were 3 s, 90° p/2-pulses of 13.7 μs, spectral width 5071 Hz.

Mass spectra were recorded on Finnigan MAT 8200 with double-focusing Nier-Johnson geometry and electron impact as ionization method. Range of recorded mass was set in the range of 5–2000 amu.

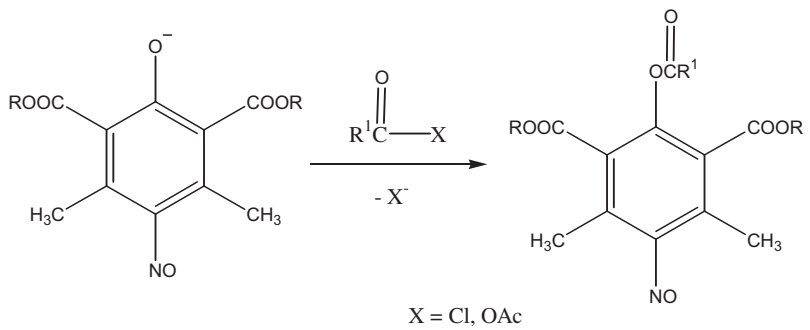
2.3. X-ray powder diffraction study

Solid state samples, were analyzed for crystallinity, monophase content and the possibility of crystal structure determination. For this purpose the X-ray powder diffraction data were obtained. X'Pert PRO diffractometer (PANalytical) with a PIXcel detector, equipped with a graphite monochromator, was used. Cu Kα radiation was applied. The sample for the survey was grinded up into an agate mortar and placed in a cuvettee of 25 mm in diameter by means of direct loading. The top of the excess was cut off with a razor to prevent preferential orientation of the particles on the surface. X-ray powder pattern registration was performed in range 3–90° 2θ with step 0.026°, $\Delta t - 50c$ at $T = 22$ °C. The angular limit for registration is caused by the lack of diffraction picks in the far angle region.

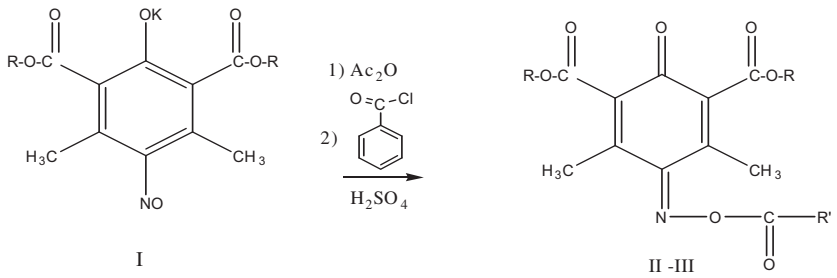
There were three suitable substances for structure research: (**IIa**) $C_{14}H_{15}NO_7$, (**IIb**) $C_{16}H_{19}NO_7$ and (**IIIc**) $C_{23}H_{25}NO_7$. The unit cell parameters were defined and refined using the programs described in [15,16]. The space groups were chosen according to regular reflection absence. The structural models were determined in the direct space applying the "simulated annealing" approach (the variety of Monte Carlo method) [17] with the program FOX [18]. In each case the complete molecule was taken as a molecular model with various substituents, in particular, with the addition of an acyl or benzoyl moiety by nitroso- or phenol centers. The search of a structure consisted in finding an optimal position of molecular gravity center and orientation of the molecule in a unit cell. More complete match of the calculated and experimental diffraction patterns achieved by removing the molecular constrains, including the substituents rotation regarding the plane of the benzene ring. The most optimal structural models were refined by full-profile analysis (Rietveld method) using the program FullProf [19]. Rigid and soft constraints were impose on refined atomic coordinates [20] using the weight coefficients and taking into account the average values of corresponding distances and angles [21]. Optimization of the structure was carried out by the gradual removal of restrictions and parallel refinement of the background and some of the profile parameters. Thermal parameters of the atoms were refined in the isotropic approximation. At the final refinement step hydrogen atoms were rigidly attached to the respective carbons [22]. The resulting structural data have been deposited on CSD #CCDC 974561, #CCDC 974562.

3. Results and discussion

The oxygen atoms of hydroxyl and nitroso group are two nucleophilic centers in the anions of persubstituted nitrosophenols. From the point of view of the of charge magnitude on the nucleophilic center the preferable direction for the attack of carbonyl group of acylating agent is oxygen atom of hydroxyl-group of the nitrosophenolate-ion (Scheme 2). Previously, we found that the alkylation of persubstituted nitrosophenols by alkyl halides in the diethyl ether went solely on the oxygen atom of the nitroso-group to form alkyl esters of p-benzoquinonemonooximes [6]. On this basis it was concluded that the reaction did not depend on the charge, but the orbital control, which was well described by the mechanism of nucleophilic substitution S_{N2}. There are evidences [14], that the acylation follows through the other two-stage mechanism by attaching the nucleophile towards the carbonyl



Scheme 2. The preferable reaction between nitrosophenolate-ion and the acylating agent.



I

R = Me (Ia), Et (Ib), Pr (Ic), Bu (Id) , Amyl (Ie)

II -III

R = Me (IIa), Et (IIb), Pr (IIc), Bu (IId) , Amy l (IIe), R'=Me

R = Me (IIIa), Et (IIIb), Pr (IIIc),Bu (IIId) , Amy l (IIIe), R'=Ph

Scheme 3. The reaction between persubstituted potassium para-nitrosophenolate and acetic anhydride or benzoyl chloride.

group, followed by elimination of the halogen anion for benzoyl chloride or acetate ion in the case of acetic anhydride. To clarify which of two nucleophilic centers the oxygen atom of the hydroxyl-group or nitroso-group of persubstituted nitrosophenols were active, the potassium salt was introduced in the reaction with acetic anhydride and benzoyl chloride in absolute ether in the presence of sulfuric acid.

Yellow crystalline or oily products were obtained in all conducted reactions of acylation. Supposed formation scheme of persubstituted para-nitrosophenols acyl derivatives is presented in Scheme 3. Important information about the structure of the acylation products was obtained by ^{1}H NMR spectroscopy. Fig. 1 shows the spectra of (**IIa**) $\mathbf{C_{14}H_{15}NO_7}$.

According to ^{1}H NMR data 1-acyloxymino-3,5-di(alcoxycarbonyl)-2,6-dimethyl-1,4-benzoquinones were formed in all cases. The protons of the methyl groups in the ring and the ester substituent's are not equal. ^{1}H NMR spectrum contains double bands with the same intensity of the components of the methyl groups protons corresponding syn- or anti-location of the substituents relative to acyloxime group. At the same time, the proton signals from of the acyl substituent at the oxime group is not doubled, that indicates their identical environment. In general, the ^{1}H NMR data in all cases consistent with the fact that the acylation goes on the oxygen atom of the nitroso-group.

Fig. 2 shows the ^{1}H NMR spectrum one of the benzoylation products $\mathbf{C_{27}H_{35}NO_7}$ (**IIIe**).

The spectrum shows signals of the aromatic ring protons of benzoyl substituent in a weak field with chemical shift δ = 8.1 ppm for two protons in the ortho-position, for one proton in the para-position with chemical shift δ = 7.72 ppm and for two protons in the meta-position with chemical shift δ = 7.58 ppm. The spectrum also contains signals of the ester group protons of benzoyl substituent's: four protons of methylene groups are close to the oxygen atom in the form of the triplet in the weaker field with the chemical shift δ = 4.34–4.36 ppm. The triplet splitting is due to the different environment of alkoxycarbonyl groups because of syn- or anti-location relative to the benzoyloxime group. Six protons of the methyl groups in a strong field are in the form of

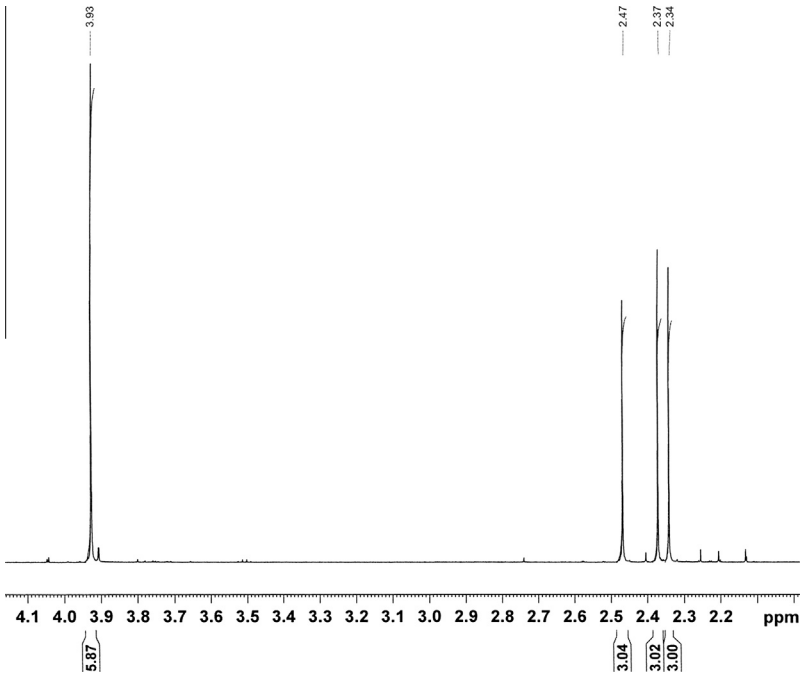


Fig. 1. ^{1}H NMR spectrum of 1-acetoxymino-3,5-di(methoxycarbonyl)-2,6-dimetyl-1,4-benzoquinone (**IIa**).

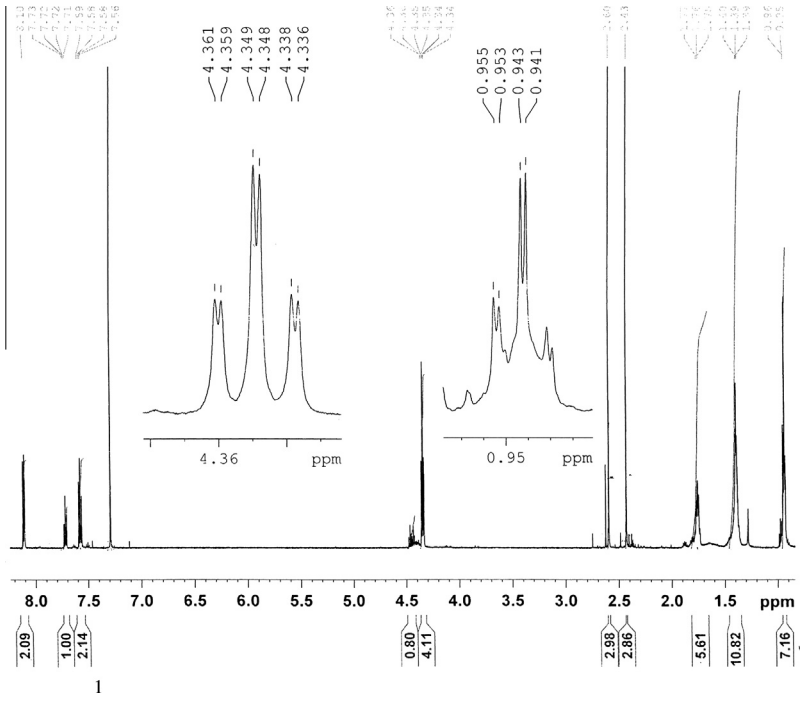


Fig. 2. ^{1}H NMR spectrum of 1-benzoyloxymino-3,5-di(amyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone (**IIIe**).

a "doubling" triplet with chemical shifts δ = 0.95–0.96 ppm. The other protons of the methylene groups are in the form of the multiplets (δ = 1.39–1.74 ppm). Six protons of the methyl groups of the ring give signals with chemical shifts δ = 2.43 ppm and δ = 2.60 ppm in the form of "doubling" singlets for the reason given above. A similar situation consistent with the quinoneoxime structure of the acylation products was observed in the spectra of all other acyl derivatives.

The crystal structures (**IIa**) $C_{14}H_{15}NO_7$, (**IIb**) $C_{16}H_{19}NO_7$ and the most likely structural model (**IIIc**) $C_{23}H_{25}NO_7$ were determined by X-ray powder diffraction analysis. Other substances had consistence unsuitable for X-ray diffraction analysis due to the low melting temperature. Their structure modeling was carried out using the initial knowledge about the structure of the original moieties, based on the method of synthesis, chemical analysis, mass spectrometry and NMR data. Orientation alkyloxycarbonyl groups to the ring were refined independently. Thus, overall orientation of the molecule in the unit cell, center of acylation and orientation of alkyloxycarbonyl groups were determined. Two molecular configurations of the acylation products on the hydroxyl or nitroso group were subsequently analyzed. It was found that the shift of the acylation center on the hydroxyl group leads to the significant difference between the experimental and calculated diffraction patterns with increasing R_{wp} of about 15.00% for (**IIa**). Crystal data and structure characteristics after verifying are presented in Table 1. Figs. 3 and 4 show final convergence of experimental and calculated X-ray diffraction patterns for (**IIa**) and (**IIb**) correspondently.

Table 1
Crystallographic parameters and details of powder X-ray diffraction structure determination for (**IIa**), (**IIb**) and (**IIIc**).

Chemical formula	$C_{14}H_{15}NO_7$	$C_{16}H_{19}NO_7$	$C_{23}H_{25}NO_7$
Molecular weight	309.27	337.32	440.32
Space group	$P-1$	$P-1$	$P2_1/a$
a, Å	11.896(1)	11.529(1)	17.459(1)
b, Å	9.080(1)	10.085(1)	16.795(1)
c, Å	8.245(1)	9.018(1)	7.671(1)
α, (°)	109.22(1)	105.87(1)	90
β, (°)	98.46(1)	111.28(1)	91.50(1)
γ, (°)	108.97(1)	102.44(1)	90
$V_{un,cell}$, Å^3	762.37	880.08	2248.27
Z	2	2	4
V/Z, Å^3	381.185	440.04	562.07
$\rho_{calc.}$, g/cm^3	1.347	1.273	
μ, mm^{-1}	0.936	0.853	
T, K	295	295	295
Diffractometer	X'Pert PRO	X'Pert PRO	X'Pert PRO
Radiation	Cu Kα	Cu Kα	Cu Kα
λ, Å	λ_1 = 1.54056, λ_2 = 1.54439	λ_1 = 1.54056, λ_2 = 1.54439	λ_1 = 1.54056, λ_2 = 1.54439
Scanning area, 2θ (°)	3.039–80.935	3.013–80.909	3.013–80.909
Number of points	2996	2996	
Number of reflections	1219	1102	
R_p, %	5.51	8.90	
R_{wp}, %	7.18	11.8	
R_{exp}, %	3.28	7.76	
$S = R_{wp}/R_{exp}$	2.19	1.52	

The crystal structures of investigated substances (**IIa**) $C_{14}H_{15}NO_7$, (**IIb**) $C_{16}H_{19}NO_7$ and (**IIIc**) $C_{23}H_{25}NO_7$ are of molecular type. The molecules of (**IIa**) and (**IIb**) are shown in Fig. 5, have a planar configuration. Non-hydrogen atoms of the molecules are substantially coplanar. The central fragment is the quinonoid ring. The difference between the lengths of C—C bonds in the ring, in particular, d(C2—C3) = 1.41(8) Å and d(C3—C4) = 1.34(4) Å, the short connections: d(C2—O1) = 1.17(0) Å and d(C5—N10) = 1.35(8) Å corresponding to the double bonds between the atoms, indicate the quinonoid structure with π-conjugation. Substituents: =O, —CH_3, =N are located in the plane of the benzene ring. Planes of alkyloxycarbonyl groups are substantially perpendicular to the quinonoid ring. The torsion angles of the opposite alkyloxycarbonyl groups relatively to plane of the quinonoid ring in (**IIa**) and (**IIb**) differ by 10°. The orientation of these groups relative to the plane of the ring is bilateral, which seems to be associated with the energy gain, realized at molecule packing in the unit cell volume. Acetoximine groups in both compounds are located in the plane of quinonoid ring. Some structural characteristics for the molecules

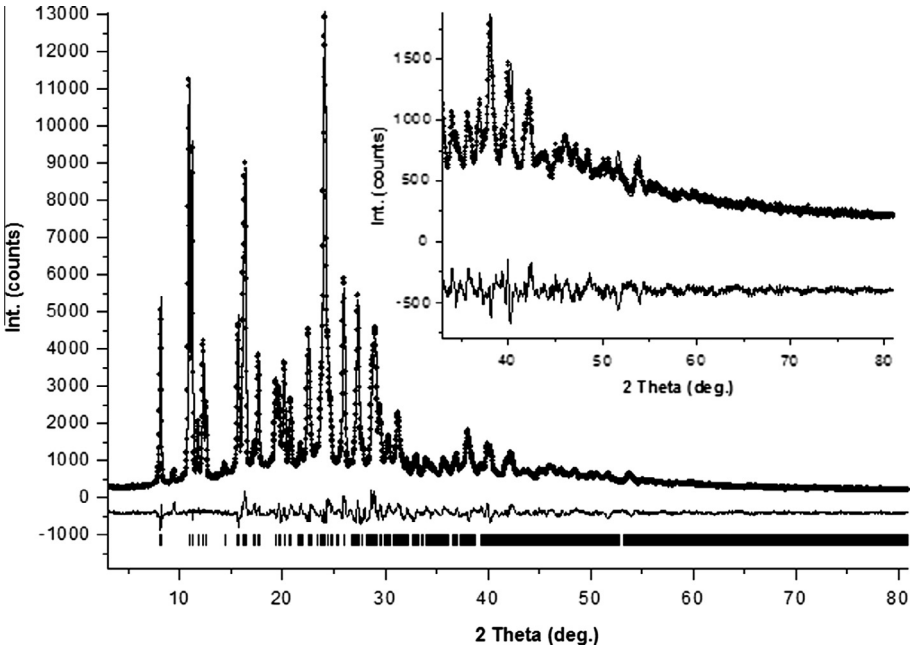


Fig. 3. X-ray diffraction patterns for (**IIa**) $C_{14}H_{15}NO_7$: the experimental (dots) and calculated (solid line), the difference (solid line), position of calculated reflections in bottom. The zoomed high angle part is shown in the insertion.

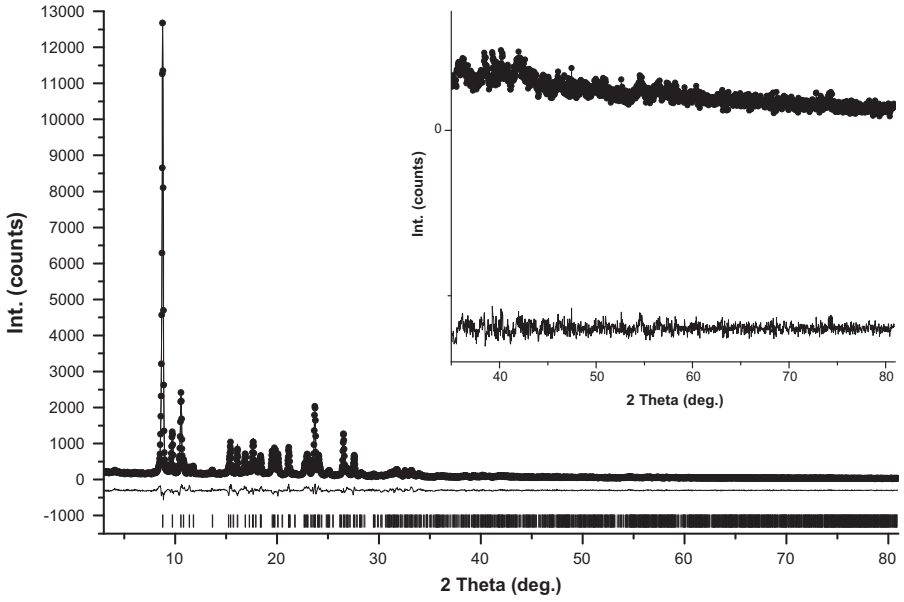


Fig. 4. X-ray diffraction patterns for (**IIb**) $C_{16}H_{19}NO_7$: the experimental (dots) and calculated (solid line), the difference (solid line), position of calculated reflections in bottom. The zoomed high angle part is shown in the insertion.

(**IIa**), (**IIb**) and (**IIIc**) are presented in Tables 2 and 3. Unit cells of (**IIa**) and (**IIb**) contain two asymmetrical molecules in parallel planes related via the symmetry center (Fig. 6). The pairs are stacked along translational vector at a distance of 3.71(9) and 3.59(2) Å between the planes of the rings. The centers of the quinonoid rings of each pair are spaced apart by distances 4.09(1) and 4.39(2) Å correspondently. Relative to each other pairs shifted by 6.07 and 3.01 Å. Formation of such pairs in the unit cell can be explained by steric effect of alkyloxycarbonyl substituent during the crystallization of compounds (**IIa**) and (**IIb**). Thus centrosymmetrical arrangement of the molecules is likely to lead to the achievement of the dense packing of the molecules in the crystals (Fig. 7).

The discussed compounds have no "classical" hydrogen bonds, so the supramolecular structure is regulated by the molecule forms and their packing. It results in formation of stacks of the planar molecules along the **c** axis. In the stacks centrosymmetrically related molecules arranged in pairs at angles of 60.2° and 86.9° to the column axis, respectively. There are no association of molecules from different columns in the layer (Fig. 8):

1-Benzoyloxymino-3,5-di(propyloxycarbonyl)-2,6-dimetyl-1,4-benzoquinone (**IIIc**) in contrast to the above-described compounds

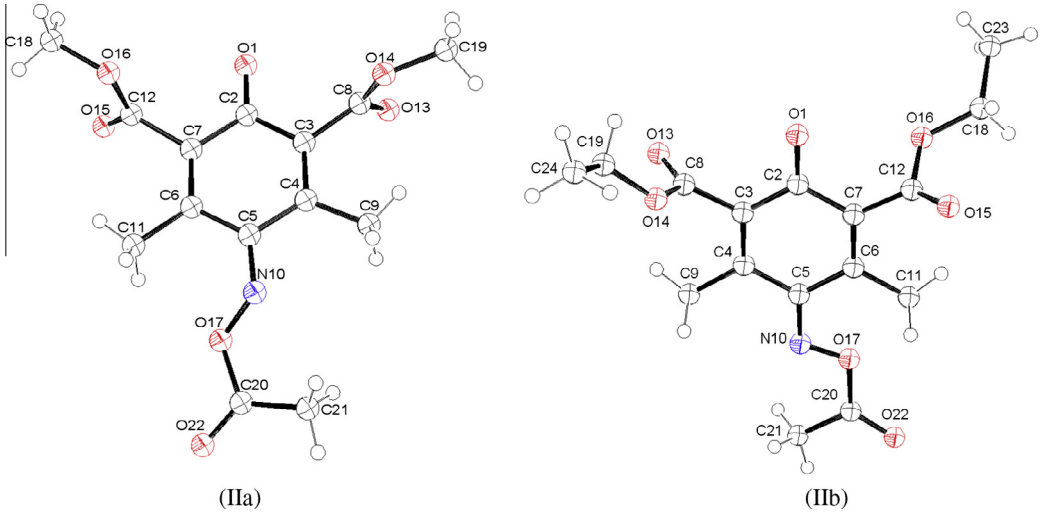


Fig. 5. Molecular structure of (**IIa**) $C_{14}H_{15}NO_7$ and (**IIb**) $C_{16}H_{19}NO_7$.

Table 2
The most important interatomic distances and angles for (**IIa**) $C_{14}H_{15}NO_7$.

Distance, Å		Angle, °		Torsion, °	
C2—C3	1.41(1)	O1—C2—C3	118.5(1)	O1—C2—C3—C4	−177.5(1)
C3—C4	1.34(1)	C2—C3—C4	121.2(1)	C2—C3—C8—O13	−91.4(1)
C6—C11	1.54(1)	C3—C4—C9	121.4(1)	C2—C7—C12—O15	101.3(1)
C5—N10	1.35(1)	C4—C5—N10	116.0(1)	O13—C8—O14—C19	−0.8(1)
N10—O17	1.40(1)	C5—N10—O17	125.0(1)	C2—C3—C4—C9	−179.1(0)
C20—C21	1.44(1)	N10—O17—C20	112.8(1)	C3—C4—C5—N10	−176.7(1)
C3—C8	1.47(1)	O13—C8—O14	120.1(1)	C4—C5—N10—O17	−173.2(1)
C8—O13	1.20(1)	C8—O14—C19	119.3(1)	C5—N10—O17—C20	179.9(1)
C8—O14	1.30(1)	C2—C3—C8	119.9(1)		
O14—C19	1.38(1)				
C2—O1	1.17(1)				

Table 3
The most important interatomic distances and angles for (**IIb**) $C_{16}H_{19}NO_7$.

Distance, Å		Angle, °		Torsion, °	
C2—C3	1.44(1)	O1—C2—C3	120.1(1)	O1—C2—C3—C4	−179.2(1)
C3—C4	1.34(1)	C2—C3—C4	120.4(1)	C2—C3—C8—O13	−94.0(1)
C6—C11	1.48(1)	C3—C4—C9	121.1(1)	C2—C7—C12—O15	110.8(1)
C5—N10	1.32(1)	C4—C5—N10	120.8(1)	O13—C8—O14—C19	−20.0(1)
C18—C23	1.50(1)	C5—N10—O17	125.0(1)	C2—C3—C4—C9	−179.6(1)
C20—C21	1.51(1)	N10—O17—C20	110.9(1)	C3—C4—C5—N10	−179.7(1)
C19—C24	1.52(1)	O13—C8—O14	121.4(1)	C4—C5—N10—O17	−176.8(1)
C8—O13	1.24(1)	O16—C18—C23	120.8(1)	C5—N10—O17—C20	174.8(1)
C8—O14	1.45(1)	O14—C19—C24	128.5(1)		
O14—C19	1.48(1)				
C2—O1	1.19(1)				

has two benzene rings which planes are tuned to each other on angle 18.6(1)°. It crystallizes in monoclinic lattice with Space group $P2_1/a$ that directly affects on mutual orientation of the molecules in the unit cell (Fig. 9). A proposed molecule arrangement in the unit cell is shown in Fig. 10. The crystal structure was only partially determined. However it allows to suggest the molecular parking scheme (Figs. 10 and 11). The calculated X-ray powder pattern demonstrates some differences with experimental one which at the moment are not explained. The estimation of the molecular and unit cell volume allows assumption the existence of solvent molecules in the unit cell. Taking into account non-hydrogen atom for $C_{23}H_{25}NO_7$. It is possible to get the difference in volume of about 100 Å^3. The solvent molecules may be present either between the base molecules or partially replace them. Fig. 11 shows a partially filled cell cavities which can hold solvent.

Thus, 10 new acetyl and benzoyl derivatives were obtained by the reaction of acetic anhydride and benzoyl chloride with persubstituted para-nitrosophenols. ^{1}H NMR data in all cases consistent with the fact that the acylation goes on the oxygen atom of the nitroso-group. The crystal structure investigation of several

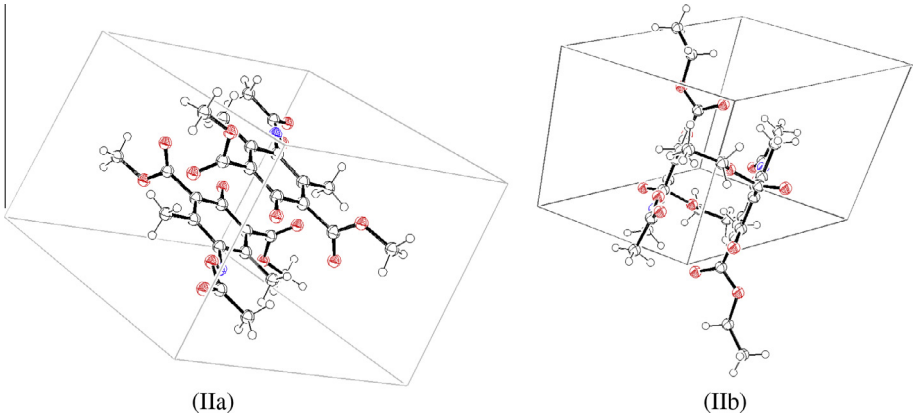


Fig. 6. The molecule orientation in the unit cell for (**IIa**) and (**IIb**).

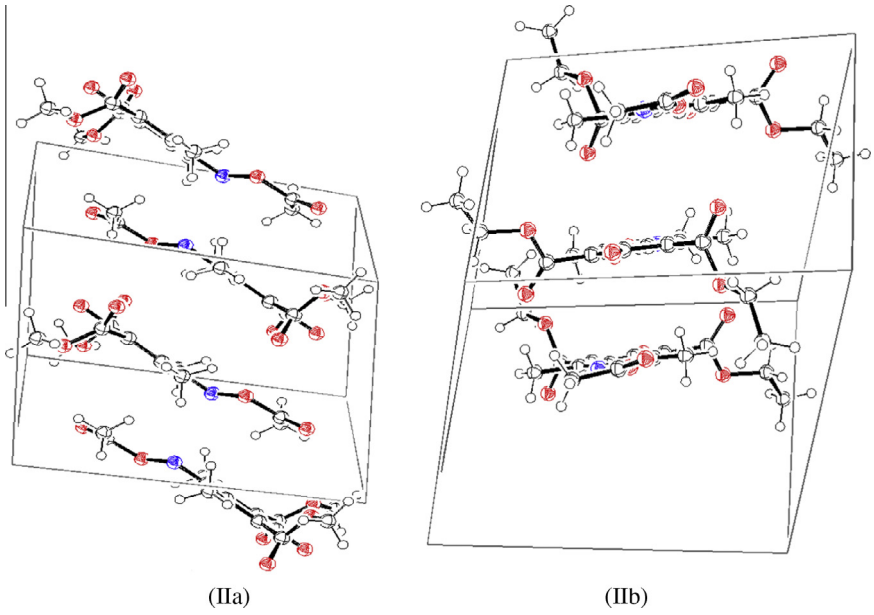


Fig. 7. The arrangement of the molecules (**IIa**) and (**IIb**) in the columns.

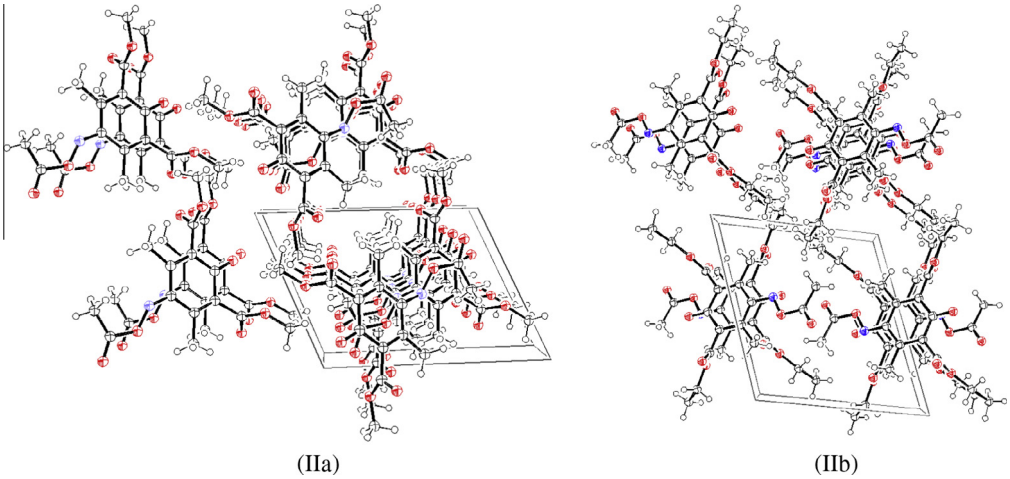


Fig. 8. The arrangement of columns in the crystal structures (**IIa**) and (**IIb**).

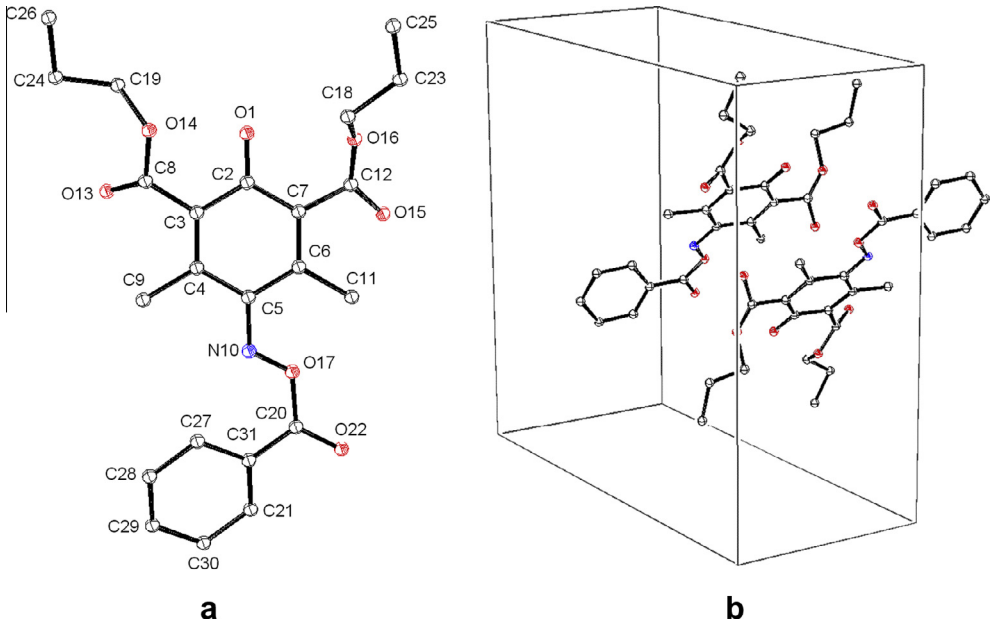


Fig. 9. Molecular structure (a) and orientation of the molecules in unit cell (b) for $C_{23}H_{25}NO_7$ (**IIIc**).

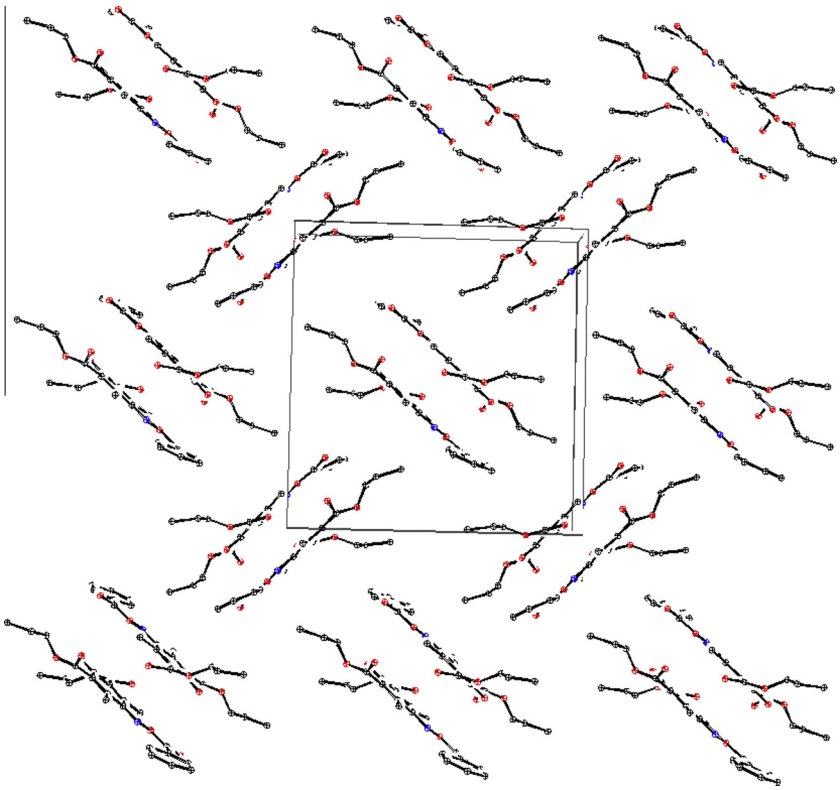


Fig. 10. Packing of molecules (**IIIc**) in plane (ab) in the unit cell volume.

products was carried out using X-Ray powder diffraction technique. The molecular crystal structure for (IIa), (IIb) and (IIIc) compounds shows that molecules have a generally planar configuration with the quinonoid ring as the central moiety. Alkyloxycarbonyl substituents are asymmetric and out of the ring plane. Arrangement of the molecules in the absence of hydrogen bonds obeys the principles of the closest packing, which is realized in the form of columns. The sectional shape of the column is different from the cylindrical and caused the presence of substituents. Voids, formed by stacking the columns can be filled with solvent.

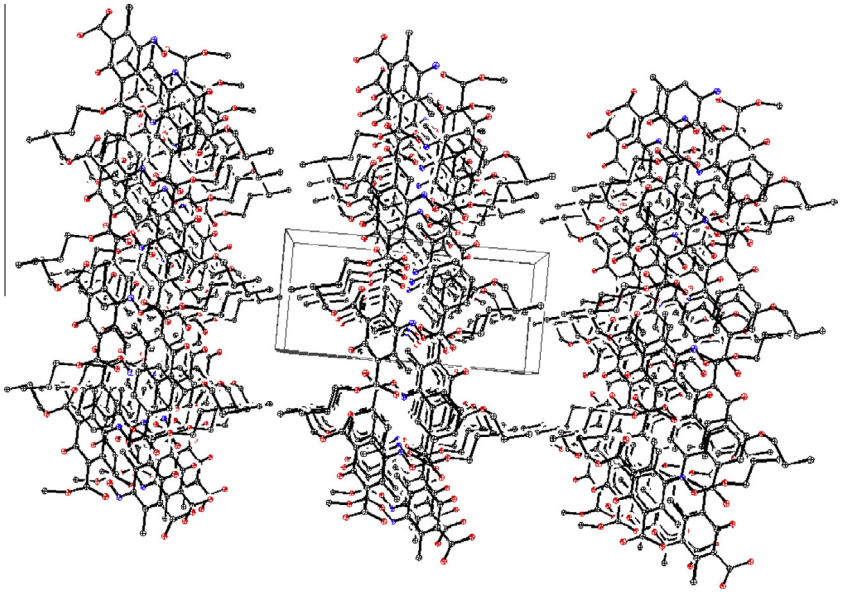


Fig. 11. Packing of molecules (**IIIc**) **along c-axis** with partial filling of the unit cell volume.

Acknowledgement

The investigation were carried out with financial support Ministry of Science and Education (State Contracts No 02.740.11.0629, Project 3.7970.2013), and ICDD (ICDD, Grant-in-Aid No 10-93).

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