Reactions of 9,10-phenanthrenequinone and its nitro derivatives with acetone in the presence of Al_2O_3

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The addition of acetone to 9,10-phenanthrenequinone and 2-nitro-, 2,7-dinitro-, and 2,4,7-trinitro-9,10-phenanthrenequinones in the presence of Al_2O_3 affords mono- and bisadducts. The crystal structures of 10-hydroxy-10-(2-oxopropyl)-2-nitro-9,10-dihydrophenanthren-9-one and 9,10″:10,9″-bishemiketal of 9,10-dihydroxy-2-nitro-9,10-bis(2-oxopropyl)-9,10-dihydrophenanthrene were determined.

Key words: 9,10-phenanthrenequinone; nitro-9,10-phenanthrenequinones, 10-hydroxy-10-(2-oxopropyl)-9,10-dihydrophenanthren-9-ones; (9,10-dihydroxy)nitro-9,10-bis(2-oxopropyl)-9,10-dihydrophenanthrenes, 9,10″:10,9″-bishemiketals; acetone; alumina; X-ray diffraction analysis; IR spectroscopy; ^1H NMR spectroscopy.

The nucleophilic addition products of CH acids (Me_2CO, $MeNO_2$, PhCOMe, acetylacetone, *etc.*) to the carbonyl groups of substituted 9,10-phenanthrenequinones can be of interest as intermediates for the synthesis of fused heterocyclic systems and ligands for the preparation of metal complexes. It is important to establish the influence of the character and position of substituents in 9,10-phenanthrenequinone, activities of CH acids, acid-base properties of the catalyst, and type of the solvent on the course of the reaction. This work is aimed at studying the reactions of 9,10-phenanthrenequinone (**1a**) and its mono-, di-, and trinitro derivatives with acetone in the presence of Al_2O_3.

Selection of 9,10-phenanthrenequinone (**1a**) and 2-nitro-, 2,7-dinitro-, and 2,4,7-trinitro-9,10-phenanthrenequinones (**1b—d**) makes it possible to assess the influence of the number of electron-withdrawing substituents on the reactivities of the carbonyl groups. It has previously been established[1] that 2,4,7-trinitro-9,10-phenanthrenequinone (**1d**) adds two molecules of nitromethane and 2,7-dinitro-9,10-phenanthrenequinone (**1c**) forms a mixture of mono- and bisadducts in a ratio of ~1 : 1 in HMPA. In addition, the formation of acetone monoaddition products was observed when 4-hydroxy-2,7-dinitro-9,10-phenanthrenequinone was chromatographed[2] on SiO_2 in a benzene—acetone system.

Although the adduct formation is known[3] for the reaction of quinone **1a** with acetone in the presence of KOH and its structure was determined,[4] monoaddition products have not been isolated and this reaction has not systematically been studied with different numbers of nitro groups and under different conditions. It is also known[5] that nitro derivatives of 9,10-phenanthrenequinone undergo a benzylic-type rearrangement in the presence of alkalis and, hence, the method mentioned[3] cannot be applied to them.

Results and Discussion

It is found that the addition of acetone to the carbonyl groups of phenanthrenequinones **1a—d** in the presence of Al_2O_3 at ~20 °C occurs stepwise, which allows the preparation of both mono- (**2a—d**) and bisadducts (**3a—d**) by varying the reaction time. In the case of nonsymmetrically substituted 9,10-phenanthrenequinones **1b** and **1d**, mixtures of isomeric ketols **2b** and **2b′**, as well as **2d** and **2d′**, respectively, are formed. Compounds **2d** and **2d′** were isolated in the individual form. The formation of compound **2b′** followed from TLC data. Elemental analysis data, m.p., and R_f of the compounds obtained are presented in Table 1.

The structure of compounds **2a—d** was proved by ^1H NMR and IR spectroscopy and X-ray diffraction analyysis. The IR spectra of compounds **2a—d** (Table 2) exhibit bands in the region of 3385—3485 cm^{-1} attributed to stretching vibrations of the OH groups, and bands at 1680—1735 cm^{-1} (stretching vibrations of C=O groups). The observed broadening of the C=O band in the spectrum of compounds **2a,b** or its doublet character for compounds **2c,d,d′** indicates the presence of two types of carbonyl groups, *viz.*, acetonyl and dihydro-

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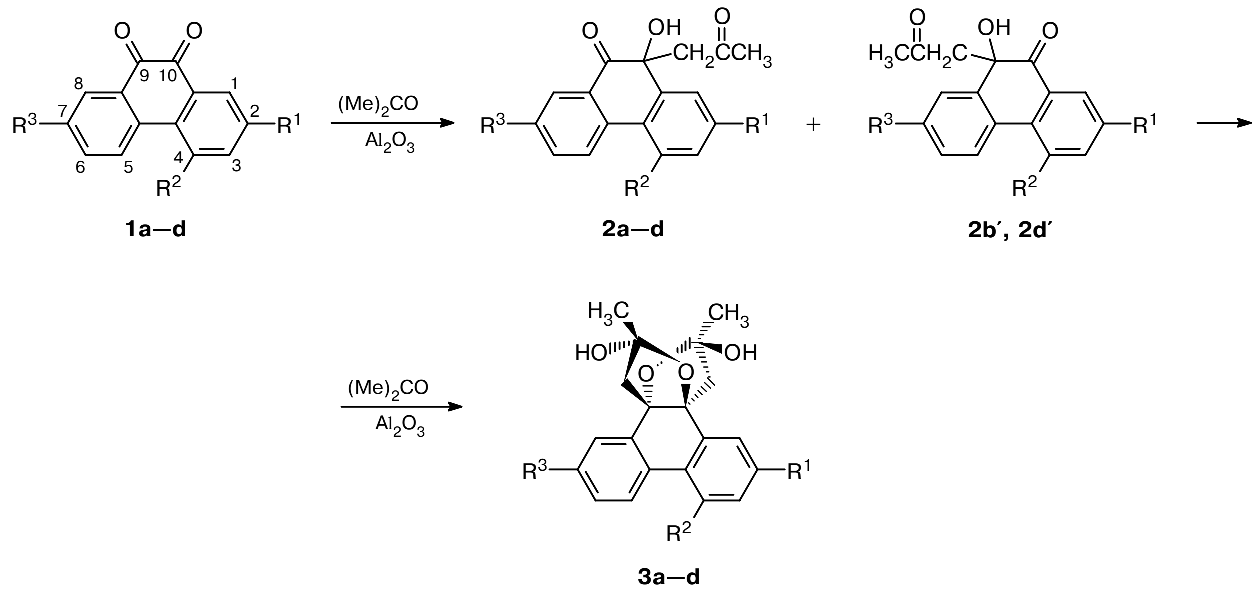
Scheme 1



$R^1 = R^2 = R^3 = H$ (**a**); $R^1 = NO_2$, $R^2 = R^3 = H$ (**b**,**b′**);
$R^1 = R^3 = NO_2$, $R^2 = H$ (**c**); $R^1 = R^2 = R^3 = NO_2$ (**d**,**d′**)

Table 1. Characteristics of compounds **2a—d, d′** and **3a—d**

Compound	Yield (%)	M.p. /°C	R_f	Found/Calculated (%) C	H	N	Molecular formula
2a	86	96—98	0.50	76.78 76.69	5.44 5.26	—	$C_{17}H_{14}O_3$
2b*	38	171—172	0.43	65.68 65.59	3.10 4.18	4.37 4.50	$C_{17}H_{13}NO_5$
2c	67	216—218	0.34	57.38 57.30	2.32 3.37	7.51 7.87	$C_{17}H_{12}N_2O_7$
2d	45	188—190	0.50	50.66 50.87	2.89 2.74	10.59 10.47	$C_{17}H_{11}N_3O_9$
2d′	34	197—199	0.42	51.06 50.87	3.03 2.74	10.51 10.47	$C_{17}H_{11}N_3O_9$
3a	53	179—180 179—181[3]	0.20	—	—	—	$C_{20}H_{20}O_4$
3b	59	181—182	0.19	64.15 65.04	5.44 5.14	3.57 3.79	$C_{20}H_{19}NO_6$
3c	82	225—227	0.22	57.66 57.97	4.58 4.35	6.79 6.76	$C_{20}H_{18}N_2O_8$
3d	30	188—190	0.23	51.40 52.29	3.77 3.70	8.90 9.15	$C_{20}H_{17}N_3O_{10}$

* See text for discussion of X-ray diffraction data.

phenanthrenone. Some difference in the half-widths, intensities, and positions of the ν(OH) and ν(C=O) bands can be explained by the involvement of the OH and C=O groups in the formation of intra- or intermolecular hydrogen bonds because the formation of these bonds shifts the OH band to the low-frequency region and sometimes decreases its intensity.[6] On going from the crystalline state to solution, the IR spectrum of compound **2a** exhibits the high-frequency shift of the ν(OH) and ν(C=O) bands by 95 and 15 cm^{-1}, respectively, which is due to the cleavage of the intermolecular hydrogen bond. It has previously been shown[1] by X-ray diffraction analysis that 10-hydroxy-2,7-dinitro-10-nitromethyl-9,10-dihydrophenanthren-9-one contains only a weak intermolecular bond. Therefore, the IR spectrum in the crystalline state exhibits bands ν(OH) 3392 cm^{-1}

Table 2. Positions of some bands in the IR spectra of compounds **2a—d, d′** and **3a—d** (ν/cm^{-1})

Compound	Conditions of spectrum recording	ν(O—H)	ν(C=O)
2a	KBr	3385 s	1695 s
	$C_2H_4Cl_2$	3475 w	1710 s
2b	Nujol	3485 w	1705 s
	KBr	3470 w	1710 s
2c	KBr	3450 s	1700 s, 1680 s
2d	KCl	3400 s, br	1735 s, 1702 m
2d′	KCl	3430 s, br	1725 s, 1700 m
3a	KBr	3440 v.s	—
3b	KBr	3250 s, br	—
	Nujol	3175 s, v.br	—
	$C_2H_4Cl_2$	3545 w	—
3c	KBr	3495 v.s	—
3d	KBr	3455 s, 3380 s	—

and ν(C=O) 1716 cm^{-1}. Similarly, the IR spectrum of compound **2b** contains a weak broad band ν(OH) due to the intermolecular hydrogen bond, which correlates well with X-ray data for this compound (see below).

The ^{1}H NMR spectra (Table 3) of monoacetonyl derivatives **2a—d** are characterized by a singlet signal of protons of the CH_3 group of the acetonyl substituent at δ 2.02—2.08. Methylene protons of this substituent give the spectrum of the AB type with a spin-spin coupling constant of 15.0—16.1 Hz at δ 2.97—3.37. The signal of the OH group is observed as a singlet at δ 6.13—6.90. The aromatic region of the ^{1}H NMR spectra contains signals of all aromatic protons, which are present in molecules of compounds **2a—d**, with multiplicities corresponding to their positions. The structures of isomeric monoacetonyl compounds **2d** and **2d′** were ascribed based on chemical shifts of the 3-H and 6-H protons in their ^{1}H NMR spectra. These protons must be most sensitive to the influence of the carbonyl group remaining in the molecule. The structure of **2d** was ascribed to the isomer with a more lowfield signal (δ 8.59) of the 6-H proton and a more highfield signal (δ 8.82) of the 3-H proton. According to the ^{1}H NMR data for the reaction mixture, compounds **2d** and **2d′** are formed in a ratio of ~1.6 : 1.

In the case of 2-nitro-9,10-phenanthrenequinone (**1b**), only compound **2b** was isolated in the individual

Table 3. ^{1}H NMR spectra of compounds **2a—d, d′** and **3a—d** (DMSO-d$_6$, δ (*J*/Hz))

Compound	CH_3	CH_2	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	OH
2a	2.02	2.99 3.12 (15.0)					7.39—8.17				6.13
2b	2.03	3.09 3.12 (15.3)	8.44 d (2.4)	— —	8.23 dd (2.4, 8.8)	8.37 d (8.8)	7.84 dd (7.3, 1.2)	7.93 td (7.3, 7.3, 1.2)	7.63 td (7.3, 7.3, 1.2)	8.28 d (7.3)	6.45
2c	2.05	3.30 3.37 (16.1)	8.50 d (1.5)	—	8.49 dd (7.5, 1.5)	8.28 dd (7.5, 1.5)	8.28 dd (7.5, 1.5)	8.50 dd (7.5,1.5)	— (1.5)	8.59 d	6.62
2d	2.05	2.97 3.16* (16.1)	8.72 d (2.2)	—	8.82 d (2.2)	—	7.77 d (8.8)	8.59 dd (8.8, 2.6)	—	8.47 d (2.6)	6.90
2d′	2.08	3.05 —*	8.72 d (2.2)	—	9.09 d (2.2)	— —	7.67 d (8.8)	8.30 dd (8.8, 2.6)	— —	8.53 d (2.6)	6.87
3a	1.15	1.85 2.50 (14.0)	7.53 m	7.32 m	7.32 m	7.91 m	7.91 m	7.32 m	7.32 m	7.53 m	6.26
3b	1.39 1.41	2.11 2.15 2.66 (14.3)					7.40—8.58				4.56 4.60
3c	1.55	1.91 2.61 (14.3)	8.42 d (2.8)	—	8.37 d (8.9)	8.23 dd (8.9, 2.8)	8.23 dd (8.9, 2.8)	8.37 d (8.9)	—	8.42 d (2.8)	6.76
3d	1.55	1.83 1.93 2.62 2.67 (14.3)	8.63 d (2.4)	—	8.78 d (2.4)	—	7.58 d (8.9)	8.25 dd (8.9, 2.5)	—	8.52 d (2.5)	5.98 6.03

* Overlapped with the band of water in DMSO.

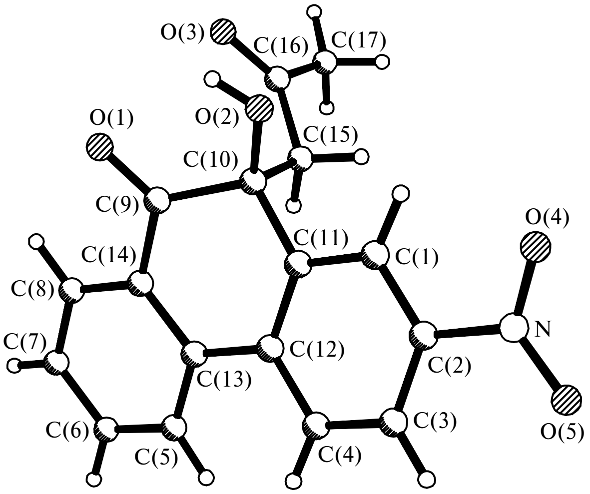


Fig. 1. Molecular structure of compound **2b**.

state, its structure was established by X-ray diffraction analysis (Fig. 1, Table 4). This compound is the addition product of acetone to the C(10) carbonyl of phenanthrenequinone **1b**. This molecule has structural characteristics close to those of previously studied addition products of water,[7,8] nitromethane,[1] and acetone[2] at the C(10)=O bond of some nitro derivatives of 9,10-phenanthrenequinone. The C(9)—O(1) and C(16)—O(3) bonds have equal lengths of 1.206(3) Å, which explains that the IR spectrum of this compound contains one ν(C=O) band. The O(1)...O(2) 2.66, O(1)...H(O2) 2.15, O(2)...O(3) 2.88, and O(3)...H(O2) 2.50 Å distances (the corresponding angles O(1)—H(O2)—O(2) 119.5 and O(2)—H(O2)—O(3) 108°) are shortened compared to the corresponding van der Waals nonvalent contacts,[9] which indicates the presence of intermolecular hydrogen bonds involving the OH group and both carbonyl groups. This affects, in turn, the position and intensity of the ν(OH) band in the IR spectrum.

Table 4. Main bond lengths (*d*/Å) and bond angles (ω/deg) of compounds **2b**

Bond	*d*/Å	Angle	ω/deg
O(1)—C(9)	1.206(3)	O(5)—N—O(4)	122.7(2)
O(3)—C(16)	1.206(3)	O(4)—N—C(2)	118.0(2)
O(5)—N	1.214(3)	O(1)—C(9)—C(10)	120.6(2)
C(9)—C(14)	1.475(3)	O(2)—C(10)—C(11)	109.19(17)
C(10)—C(11)	1.516(3)	C(11)—C(10)—C(9)	110.14(16)
C(15)—C(16)	1.506(3)	C(11)—C(10)—C(15)	106.91(15)
O(2)—C(10)	1.417(2)	O(3)—C(16)—C(15)	122.5(2)
O(4)—N	1.214(3)	C(17)—C(16)—C(15)	115.3(2)
N—C(2)	1.461(3)	O(5)—N—C(2)	119.3(2)
C(9)—C(10)	1.527(3)	O(1)—C(9)—C(14)	122.7(2)
C(10)—C(15)	1.545(3)	C(14)—C(9)—C(10)	116.75(17)
C(16)—C(17)	1.485(3)	O(2)—C(10)—C(9)	109.81(17)
		O(2)—C(10)—C(15)	110.81(17)
		C(9)—C(10)—C(15)	109.94(17)
		O(3)—C(16)—C(17)	122.1(2)

In nitrophenanthrenequinones **1b** and **1d**, the carbonyl at C(10) bound to a more electron-deficient fragment is more reactive, as follows from the predominant formation of compounds **2b** and **2d** and data obtained previously.[1,2,7,8]

The addition of the second acetone molecule to adducts **2a—d** occurs much more slowly than to the corresponding phenanthrenequinones **1a—d**. The intramolecular cyclization of the bisacetonyl derivatives that formed to bishemiketals **3a—d** occurs simultaneously.

The IR spectra of bishemiketals **3a—d** (see Table 2) contain the ν(OH) bands and no band in the region of stretching vibrations of the C=O groups. The ^{1}H NMR spectra (see Table 3) exhibit signals for all protons present in the molecules. The signals for methylene protons appear as the AB-type spectrum. The methylene groups are nonequivalent for compounds **3b** and **3d**, which are nonsymmetrically substituted at the phenanthrene fragment. The ^{1}H NMR spectrum of compound **3b** contains two signals each for protons of the CH_3 group and the OH group, which is most likely resulted from the different effects of the phenyl and nitrophenyl fragments of the molecule on the shifts of these protons due to anisotropy.

The structure of compound **3b** was confirmed by X-ray diffraction analysis (Fig. 2, Table 4). In molecule **3b**, the bond lengths and bond angles of the phenanthrene fragment and nitro group are close to those for the previously studied addition products of water[8] and nitromethane[1] to both carbonyl groups of compounds **1c** and **1d**. Both tetrahydrofuran rings, as in compound **3a**,[4] have the configuration of distorted envelopes with C(18) and C(13) deviated from the middle plane by 0.4261 and by 0.4463 Å, respectively. The methyl groups in compound **3b** are *trans*-arranged relatively to each other. A substantial distinction between compounds **3a**

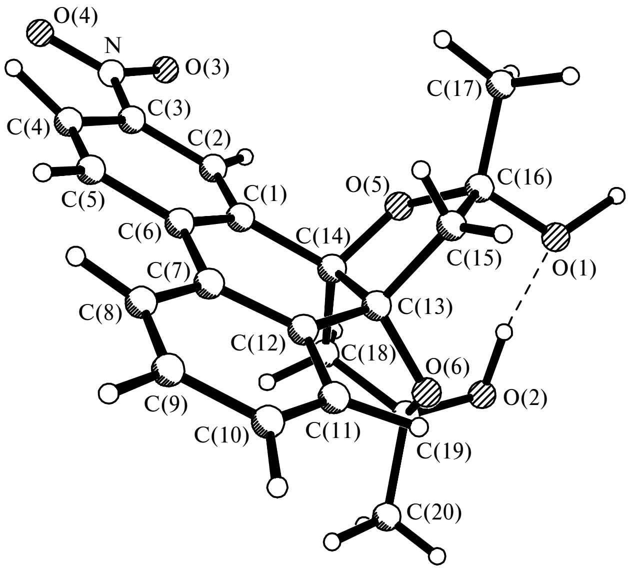


Fig. 2. Molecular structure of compound **3b**.

and **3b** is observed in the behavior of the OH groups. For example, it is established for compound **3a** that in crystal only one of the OH groups forms an intermolecular hydrogen bond with the oxygen atom of another tetrahydrofuran ring of the adjacent molecule (O(1)...O(4′) 2.838(3), O(1)...H(O4′) 2.07(3) Å, angle O(4′)—H(O4′)—O(1) 155(1)°, the numbering of atoms is the same[4]). In molecule **3b**, both OH groups are involved in hydrogen bond formation. One of them forms an intramolecular hydrogen bond with the oxygen atom of the second OH group (O(2)...O(1) 2.720, H(O2)...O(1) 1.666 Å, angle O(2)—H(O2)—O(1) 5.1°), and the second group forms an intermolecular hydrogen bond with oxygen of the similar group of the adjacent molecule (O(1)...O(1′) 2.748, O(1)...H(O1) 1.374, H(O1)...O(1′) 1.374 Å, angle O(1)H(O1)O(1′) 180°) losing one hydrogen atom, *i.e.*, compound **3b** in crystal is a dimer formed by the strong intermolecular hydrogen bond O(1)...H(O1)...O(1′).

Thus, it is shown that Al_2O_3 is an efficient catalyst of acetone addition to the carbonyl groups of 9,10-phenanthrenequinone and its nitro derivatives. Regioselective addition was established for nonsymmetrical phenanthrenequinones.

Experimental

IR spectra of samples in KBr, KCl, Nujol, and $C_2H_4Cl_2$ solutions were recorded on a Specord 75-IR spectrophotometer. ^1H NMR spectra were recorded on a WP-200 spectrometer (Bruker) with a working frequency of 200 MHz for ~3% solutions in DMSO-d_6 using Me_4Si as the internal standard. The course of the reaction and purity of compounds prepared were monitored by TLC on Silufol UV-366 plates in a benzene—acetone (10 : 1) system.

Compounds **1b** (m.p. 256—258 °C),[10] **1c** (m.p. 302—303 °C),[11] and **1d** (m.p. 213—214 °C)[12] were prepared according to the known procedures by nitration of 9,10-phenanthrenequinone (**1a**, m.p. 208—209 °C).

Acetone (analytically pure grade) and Al_2O_3 (neutral, Brockmann activity II, Reanal, Hungary) were used without any additional treatment.

Addition of acetone to phenanthrene-9,10-quinones 1a—d (general procedure). ***A.*** A suspension of 9,10-phenanthrenequinones (**1a—d**) (5.0 mmol) and Al_2O_3 (1.0 g) in acetone (50 mL) was stirred at ~20 °C (from 15 min to 2 h, TLC monitoring) and filtered, and Al_2O_3 was washed with acetone. Acetone was evaporated *in vacuo* without heating, and the residue was crystallized from CCl_4 (**2a**), acetone (**2c**), from chloroform and a 1,2-dichloroethane—CCl_4 mixture, 3 : 1 (**2b** and **2b′**) or a benzene—CCl_4 mixture, 1 : 1 (**2d**, **2d′**).

B. A suspension of 9,10-phenanthrenequinones (**1a—d**) (2.0 mmol) and Al_2O_3 (2.0 g) in acetone (25 mL) was stirred at ~20 °C for 1—6 weeks until compounds **2a—d** disappeared (TLC monitoring). The resulting mixture was filtered, Al_2O_3 was washed with acetone, acetone was evaporated, and the residue was crystallized from 1,2-dichloroethane (**3a,d**), chloroform (**3b**), and 1,4-dioxane (**3c**).

X-ray diffraction studies of compounds 2b and **3b** were carried out on samples with a size of 0.50×0.40×0.28 (from $CHCl_3$) and 0.18×0.09×0.06 mm (from $C_2H_4Cl_2$) on an Enraf-Nonius CAD-4 automated diffractometer using β-filtered Mo-Kα radiation. Crystals **2b** and **3b** are monoclinic, a = 9.110(2) and 27.284(5) Å, b = 16.423(3) and 9.488(2) Å, c = 10.094(2) and 14.229(3) Å, β = 112.44(3) and 106.30(3)°, V = 1395.8(3) and 3535.4(12) Å^3, ρ_{calc} = 1,481 and 1.388 g cm^{-3}, Z = 4 ($C_{17}H_{13}NO_5$) and Z = 8 ($C_{20}H_{19}NO_6$), space groups $P2_1/n$ and $C2/c$. As a whole, 1423 (**2b**) and 1136 (**3b**) reflections were collected from which 1345 and 1076 independent reflections (R_{int} = 0.016 and 0.052) with $I \geq 2\delta(I)$ were used in calculations. The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic (for nonhydrogen atoms) approximation to R = 0.030 (**2b**) and 0.068 (**3b**). The coordinates of H atoms were found from the difference Fourier synthesis, and their positional and isotropic thermal parameters were included into refinement. All calculations were carried out by the SHELX-97 program complex.[13] The bond lengths and bond angles of compounds **2b** and **3b** are presented in Table 4, and the coordinates of atoms and full tables of bond lengths and bond angles are sent to the Cambridge Bank of Structural Data.

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