Synthesis and structure investigations of *N*-arysulfinyl-1,4-benzoquinonemonoimines

Anatoly P. Avdeenko,*[1] Vladimir V. Pirozhenko,[2] Svetlana A. Konovalova,[1] Anna A. Santalova,[1] and Anatoliy V. Vakulenko[3]

[1] *Donbass State Machinery Academy, Shkadinova str., 72, Kramatorsk, Donetsk reg., Ukraine, 84313*
E-mail: chimist@dgma.donetsk.ua
[2] *Institute of Organic Chemistry of National Academy of Science of Ukraine, Murmanskaya str., 5, Kiev, Ukraine*
[3] *Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, FL 32611-7200*
E-mail: anatoliy@chem.ufl.edu

(received 27 Aug 05; accepted 14 Nov 05; published on the web 19 Nov 05)

Abstract

Stable *N*-arylsulfinyl-1,4-benzoquinonemonoimines have been obtained by oxidation of *N*-arylthio-1,4-benzoquinonemonoimines with *m*-chloroperbenzoic acid. The *N*-arylthio-1,4-benzoquinonemonoimines can be oxidized to *N*-arylsulfonyl-1,4-benzoquinonemonoimines. Comparative structural studies of various quinoneimines by X-ray analysis have shown that in molecule of *N*-arylsulfinyl-1,4-benzoquinonemonoimine an interaction of the π-orbital of the S=O bond with the π-electron cloud of the benzene ring is observed, similar to that found in *N*-aroyl-1,4-benzoquinonemonoimines.

Keywords: Oxidation, *N*-arylsulfinyl-1,4-benzoquinonemonoimines, X-ray, structure study

Introduction

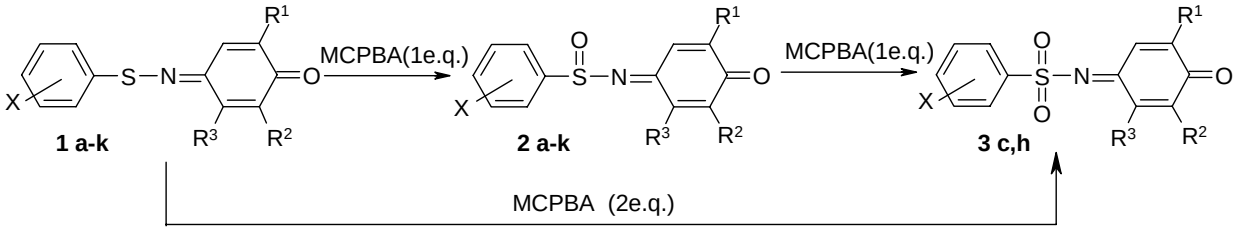
We have previously reported the first synthesis of stable *N*-arylsulfinyl-1,4-benzoquinonemonoimines by reaction of 1,4-benzoquinonemonooximes with arylsulfinyl chlorides.[1] The mechanism was postulated as occurring via the formation of *N*-arylsulfinyl-1,4-benzoquinonemonoimines by conversion of 1,4-benzoquinonemonooximes to 1,4-benzoquinonemonoimines accompanied by conversion of bivalent to a tetravalent sulfur . The major problem of this method was the formation of by-products, which were difficult to separate from the major product.

One example of an alternative preparative methods for quinone monoimines sulfonyl derivatives has been described. *N*-*tert*-Butylsulfinyl-1,4-benzoquinonemonoimine has been synthesized by oxidation of *N*-*tert*-butylthio-1,4-benzoquinonemonoimine with *m*-chloroperbenzoic acid (MCPBA). The quinone imine thus obtained was highly unstable and decomposed in one hour.[2]

N-Arylsulfinyl-1,4-benzoquinone monoimines are comparatively stable compounds.[1] The goal of the present work was to investigate a synthetic route towards new *N*-arylsulfinyl-1,4-benzoquinonemonoimines by oxidation of the corresponding *N*-arylthio-1,4-benzoquinonemonoimines followed by structural studies of the new *N*-arylsulfinyl-1,4-benzoquinonemonoimines.

Results and Discussion

Oxidation of *N*-arylthio-1,4-benzoquinonemonoimines **1a-k** with MCPBA in methylene chloride at room temperature gives *N*-arylsulfinyl-1,4-benzoquinonemonoimines **2a-k** in good yields (Scheme 1).



X= H (a), 4-Me (b,c), 4-MeO (d,e), 4-Cl (f-h), 4-NO_2 (i), 2-NO_2 (j,l); R^1= Me (a-h, k), i-Pr (j), t-Bu (i); R^2= H (a,b,d,f,g,j,k), Me (c,e,h), t-Bu (i); R^3= H (c,e,f,h,i), Me (a,b,d,g,j), i-Pr (k)

Scheme 1

The formation of *N*-arylsulfonyl-1,4-benzoquinonemonoimines as by-products was observed when excess of MCPBA was used for the oxidation of **1a-k**. Furthermore, *N*-arylsulfonyl-1,4-benzoquinonemonoimines **3c,h** were obtained as single products when a molar ratio of 1:2 (N-arylthio-1,4-benzoquinonemonoimine : MCPBA) was used. Oxidation of quinoneimines **2** by MCPBA with a molar ratio of 1:1 (**2** : MCPBA) also gave quinoneimines **3**.

Compounds **2a-k** were characterized by elemental analysis and ^{1}H NMR spectra.

It was shown earlier,[1] that the ^{1}H NMR spectra of *N*-arylsulfinyl-1,4-benzoquinonemonoimines have significant differences in the chemical shifts of the 3- and 5-protons of the quinone ring, relative to other quinone imines (N-arylthio-1,4-benzoquinonemonoimines, *N*-arylsulfonyl-1,4-benzoquinonemonoimines). Thus for benzoquinonemonoimines **2c,e,h** the differences are 1.35-1.38 ppm, whereas the differences are

0.21-0.38 ppm, for **1c,e,h** and 1.21-1.24 ppm for **3c,e,h**. Similar differences of chemical shifts in positions 3 and 6 for 2,5-dimethylsubstituted *N*-arylsulfinyl-1,4-benzoquinonemonoimines **2a,d,g** (Δδ 1.75-1.79 ppm) were observed relative to the corresponding *N*-arylsulfonyl-2,5-dimethyl-1,4-benzoquinonemonoimines (1.40-1.45 ppm), and *N*-arylthio-2,5-dimethyl-1,4-benzoquinonemonoimines – (0.80-0.90 ppm).

We continued the comparative structural study of *N*-arylsulfinyl-1,4-benzoquinonemonoimines by X-ray analyses of *N*-4-nitrophenylsulfinyl-2,6-di-t-butyl-1,4-benzoquinonemonoimine **2i** and *N*-4-nitrophenylthio-2,6-di-*tert*-butyl-1,4-benzoquinone-monoimine **1i**. We also considered published X-ray data for *N*-tosyl-2,6-dichlor-1,4-benzoquinonemonoimine **4**,[3] *N*-4-chlorobenzoyl-2,6-di-*t*-butyl-1,4-benzoquinone-monoimine **5**,[4] *N*-[*N*-phenylsulfonylbenzimidoyl]-2,6-dimethyl-1,4-benzoquinonemonoimine **6**,[4] 4-phenylsulfonyloximino-3-methyl-2,5-cyclohexadien-1-one **7**,[5] and 4-benzoyloximino-2,6-dimethyl-2,5-cyclohexadien-1-one **8**.[6]

The quinone ring of *N*-4-nitrophenylsulfinyl-2,6-di-*tert*-butyl-1,4-benzoquinonemonoimine **2i** (C^1-C^6) is planar within the limits of 0.047 Å (Figure 1). A deflection of atoms O^1, N^1, S^1, O^2 from the root-mean-square plane, formed by atoms C^1-C^6, are, respectively, -0.203, +0.016,-0.125, and +0.251 Å. The S=O group is located in a plane of the para-subsituted benzene ring (dihedral angle $C^8C^7S^1O^2$ is -178.30°). The C=O group in a molecule of N-aroyl-1,4-benzoquinonemonoimine **5** and the imidoyl C=N group in the molecule of N-[N-phenylsulfonylbenzimidoyl]-1,4-benzoquinonemonoimine **6** have similar locations.[4] Thus, the analysis of X-ray data proves, that in quinone imines **2**, **5**, and **6** identical interaction of the π-orbitals of the S=O, C=O and C=N groups, with the π-electronic cloud of benzene ring occurs.

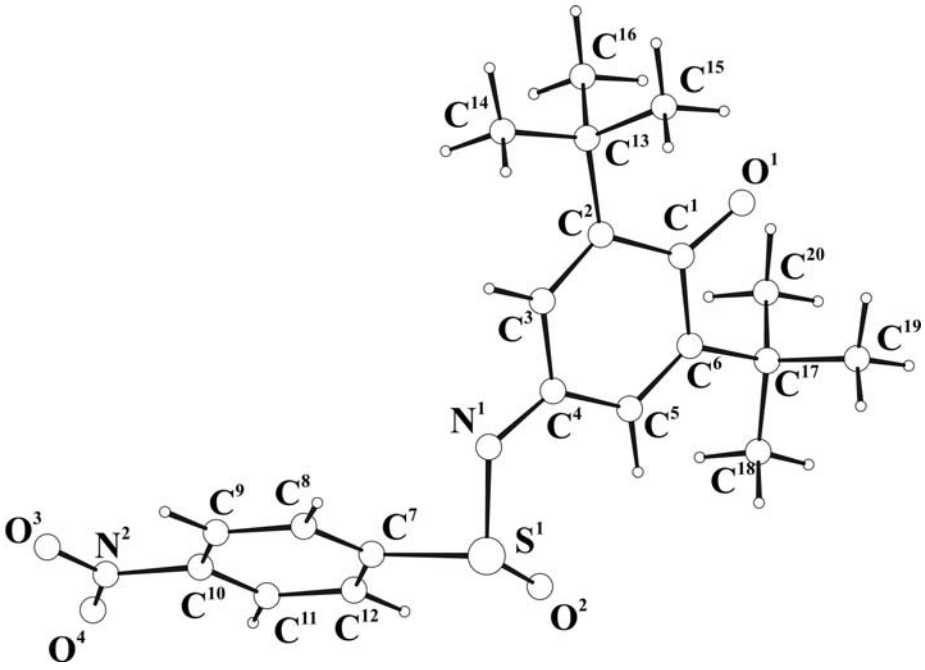


Figure 1. X-ray structure of **2i.**

Comparison of the angles between the quinone ring and the S=O, C=O, and C=N groups of the quinone imines shows, that in contrast to quinone imines **5**, **6**, having an orthogonal location of C=O (C=N) bond with the quinone ring, quinoneimine **2** has the S=O group located almost in plane with the quinone ring (dihedral angle $C^4N^1S^1O^2$ is -24.8°, and angle $C^5C^4N^1S^1$ – 8.59°).

N-4-Nitrophenylthio-2,6-di-t-butyl-1,4-benzoquinonemonoimine **1i** has a planar quinonoid ring (C^1-C^6) within the limits of 0.042 Å (Figure 2). Deflection of atoms O^1, N^1, S^1 from the root-mean-square plane, formed by atoms C^1-C^6, is 0.235, 0.106, and 0.240 Å, respectively. The molecule of **1i** is almost planar; with an angle between the planes of the aryl and quinonoid fragments of 12.09°. The angle between planes of aryl and quinonoid fragments for quinone imine **2i** is 57.31°, and for quinoneimines **5**, **6**, and **4** these planes are practically orthogonal with angles of 86.1,°[4] 86.4,°[4] and 87.4°, respectively.[3] Such an arrangement of planes in all the above-mentioned quinone imines is evidence of the absence of interaction between the π-electronic systems of aryl and quinone rings of these compounds.

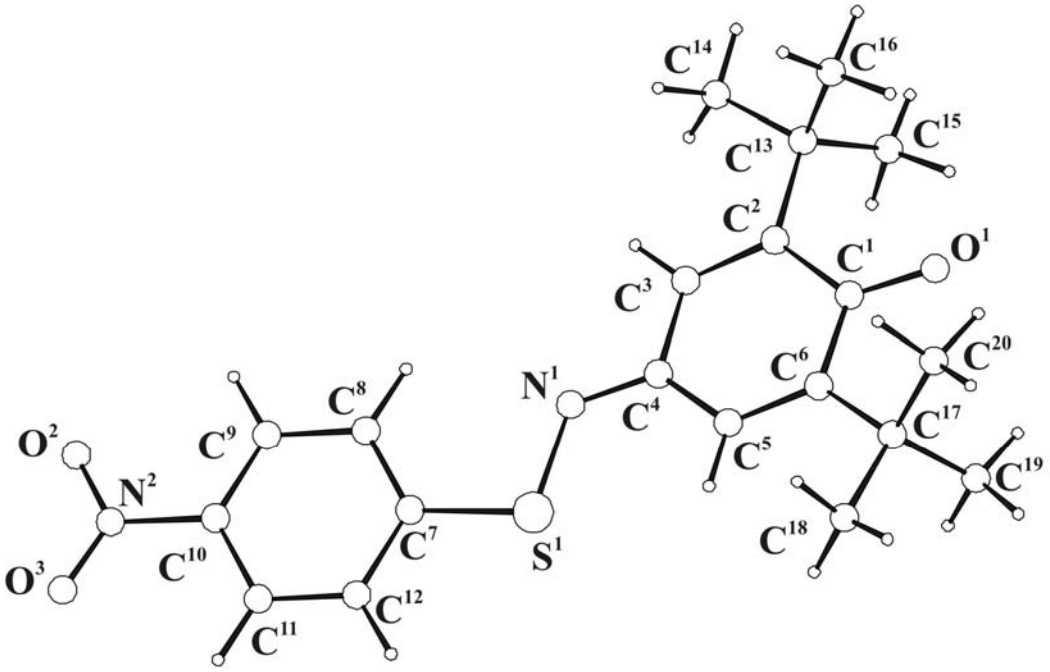


Figure 2. X-ray structure of **1i.**

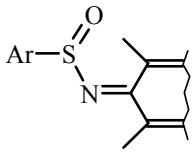
Angles N-S-C(Ar) for *N*-arylthio-1,4-benzoquinonemonoimine **1i** and *N*-arylsulfonyl-1,4-benzoquinonemonoimine **4** are close (100.1° and 99.8°, respectively).[3] Considerably smaller value of angle N-S-C(Ar) is observed for *N*-arylsulfinyl-1,4-benzoquinonemonoimine **2i** – 94.35°. Such value of an angle is typical for sulfoxide compounds.

From the data mentioned above the structure of *N*-arylsulfinyl-1,4-benzoquinonemonoimines **2** differs considerably from structures of quinoneimines with sulfur (II) and sulfur (VI), i.e. from *N*-arylthio-1,4-benzoquinonemonoimines **1** and *N*-arylsulfonyl-1,4-benzoquinonemonoimines **3**.

The only similarity is the interaction of the S=O (C=O) bond π-orbitals with the π-electronic cloud of benzene ring for **2i**, **5**, and **6** as mentioned above. The carbonyl of *N*-aroyl-1,4-benzoquinonemonoimine is perpendicular to the plane of the quinone ring,[5] which promotes interaction of the π-orbital of C=O group with lone pair on nitrogen (n_N) ($\pi_{C=O} \rightarrow n_N$). Consequently the energy of *E,Z*-isomerization in the quinone imine **5** is low at 43,0 kJ/mol.[7] In *N*-arylsulfinyl-1,4-benzoquinonemonoimine **2i** the S=O group lays almost in the plane of quinone ring, enabling S=O group π*-orbital interaction with the lone pair on nitrogen (n_N).

The C=N-X angle in the N-substituted *p*-quinone imines is one of the major structural characteristics which determines the energy of *E,Z*-isomerization and reactivity of quinoneimines.[8] *N*-Arylsulfonyl-1,4-benzoquinonemonoimines have the largest angle for C=N-S if positions 3 and 5 of quinone ring are unsubstituted. Thus, for quinone imine **4** this angle is 126.3°. From our X-ray data, the C=N-S angle in quinoneimine **2i** is 126.0°, but for **1i** is significant smaller at 119.6°. The high value of the C=N-C angle is observed for N-aroyl-1,4-benzoquinonemonoimines and *N*-[*N*-arylsulfonylbenzimidoyl]-1,4-benzoquinonemonoimines (124.1° for both compounds **5** and **6**).[4] The smallest value of C=N-X angle is observed for esters of 1,4-benzoquinonemonooximes. Hence, for 4-phenylsulfonyloximino-3-methyl-2,5-cyclohexadien-1-one **7** C=N-O angle is 111.1°,[5] and for 4-benzoyloximino-2,6-dimethyl-2,5-cyclohexadien-1-one **8** is 109.7°.[6] This is observed in spite of the steric strain in a molecule, caused by interactions of oxygen of oxiiminogroup and hydrogen atom in *orto*-position to imine group ($O^2 \ldots H^5$ – 2.37 Å (2.45 Å [9]) for compound **7** and $O^2 \ldots H^5$ – 2.34 Å (2.45 Å [9]) for compound **8**).

For quinone imine **2i** the shortened contacts are found for pairs of atoms: $N^1 \ldots C^8$ – 3.01 Å (3.20 Å [9]), $S^1 \ldots C^5$ – 3.15 Å (3.55 Å [9]), $S^1 \ldots H^5$ – 2.83 Å (2.92 Å [9]), $O^2 \ldots C^5$ – 2.86 Å (2.97 Å [9]), $O^2 \ldots H^5$ – 2.25 Å (2.64 Å [9]), which proves a significant steric strain in a fragment:



In a molecule of quinoneimine **1i** the shortened contacts are found for pairs atoms: $N^1 \ldots C^8$ – 2.87 Å (3.20 Å [9]), $N^1 \ldots H^8$ – 2.41 Å (2.64 Å [9]), $S^1 \ldots C^5$ – 2.99 Å (3.55 Å [9]), $S^1 \ldots H^5$ – 2.64 Å (2.92 Å [9]), *i.e.* the steric strain is also observed in fragment Ar-S-N.

The analysis of the shortened contacts shows, that the angle C=N-S for quinoneimines **2**, **4**, **5**, **6**, is close to 126°, due to significant steric strain between the atom of oxygen (nitrogen) of group S=O (C=O, C=N) and carbon and hydrogen atoms of the quinone ring. For quinone imine **1** and quinoneoximes **7**, **8** the steric strain of similar fragments is smaller, and a smaller value of the C=N-X angle is observed.

In spite of the significant differences of quinone imines and quinone oximes considered above, the length of C=N bond is practically constant within the limits of 1.29-1.30 Å. That can

be construed as evidence for the similar mode of conjugation in quinone imines and quinone oximes (C=N-C=C-C=O) and an insignificant influence of constituents at nitrogen atom on it.

Lengths of N-X and X-C_{Ar} bonds in some cases are different from average values reported for similar bonds[10] (these values for comparison are given in brackets). The length of N-S bond of quinone imine **1i** is 1.663 Å (1.656 Å), for quinone imine **2i** – 1.666 Å, and for quinoneimine **4** – 1.660 Å (1.642 Å). The length of N-C_{Ar} bond for quinone imine **5** is 1.398 Å (1.355 Å), for quinone imine **6** – 1.381 Å (1.355 Å). The length of N-O bond for quinone oxime **7** is 1.418 Å (1.416 Å), for quinone oxime **8** – 1.419 Å (1.416 Å). The length of S-C_{Ar} bond for quinoneimines **1i**, **2i**, and **4** is 1.761 Å (1.773 Å), 1.807 Å (1.790 Å), and 1.740 Å (1.788 Å), respectively. Thus, lengths of N-S bond are independent on sulfur state of oxidation for all three compounds **1i, 2i, 4**.

It is necessary to note, that for quinoneimines **5** and **6** the N-C_{Ar} bond is longer, than for similar compounds.[10] The length of C-C_{Ar} bond for quinoneimines **5** and **6** is 1.481 and 1.466 Å (1.500 Å), respectively. Longer N-C_{Ar} bond and shorter C-C_{Ar} bond additionally prove the π-interaction of C=O group with benzene ring [$\pi_{C=O} \rightarrow \pi(C_6H_6)$]. To the best of our knowledge bond lengths of N-S^{IV} and S^{IV}-C_{Ar} have been not reported. For this reason we were not able to perform similar structural comparison for quinone imine **2i**.

Conclusions

A new synthetic route to *N*-arylsulfinyl-1,4-benzoquinonemonoimines is described. Based on the X-ray results and comparisons with literature data for the *N*-aroyl-1,4-benzoquinonemonoimines there is π-interaction between the S=O bond and the π-electronic cloud of the benzene ring of *N*-arylsulfinyl-1,4-benzoquinonemonoimines. The angle at sulfur in *N*-arylsulfinyl-1,4-benzoquinonemonoimines is typical of sulfoxides.

Experimental Section

General Procedures. All melting points are uncorrected. ^{1}H-NMR spectra (300 MHz) were measured on a Varian VXR-300 spectrometer. Chemical shifts (δ) are given from TMS (0 ppm) as internal standard for ^{1}H-NMR; $CDCl_3$ was used as solvent. For thin-layer chromatography, Silufol UV-254 plates were used with – benzene-hexane (1:10) as eluent and development by UV light.

X-ray study of compound 1i. Analysis of monocrystal with linear sizes 0.22 x 0.43 x 0.49 mm was carried out at room temperature on automatic tetracircle diffractometer Enraf-Nonius CAD-4 (CuK_α - radiation, λ 1.54178 Å, the relation of speeds of scanning 2Θ/ω 1.2, Θ_{max} 70°, a segment of sphere $0 \le h \le 14$, $0 \le k \le 16$, $-15 \le l \le 15$). Altogether 3982 reflections were

collected from which 3656 were symmetry independent (R_{int} 0.052). Crystals of compound **1i** are monoclinic, *a* 12.171(8), *b* 13.626(8), *c* 12.941(8) Å, V 2003(2) Å^3, M 372.5, Z 4, d_{calc} 1.23 g/sm^3, μ 15.6 sm^{-1}, F (000) 795.3, space group $P2_1/n$ (N 14). The structure is deciphered by a direct method and specified by a method of the least squares in fullmatri anisotropic approximation using the CRYSTALS program package.[11] For specification the 1986 reflections with $I > 3\sigma(I)$ were used (235 adjustable parameters, number of reflections on parameter 7.2). All atoms of hydrogen were revealed from differed synthesis of electronic density and included in specification with the fixed position and thermal parameters. For specification the weight scheme of Chebushev[12] with four parameters was used: 0.65, -1.06, -0.09, and -0.64. Final values of factors of divergence R 0.059 and R_W 0.057, GOF 1.130 were obtained. The residual electron density from differed Fourier series is 0.26 and -0.29 e/Å^3. The calculation of absorption in a crystal was carried out by the method of azimuthal scanning.[13]

X-ray study of compound (2i). Analysis of a monocrystal with linear sizes 0.22 x 0.33 x 0.34 mm was carried out at room temperature on automatic tetracircle diffractometer Enraf-Nonius CAD-4 (CuK_α - radiation, λ 1.54178 Å, the relation of speeds of scanning 2Θ/ω 1.2, Θ_{max} 60°, and a segment of sphere $0 \le h \le 18$, $0 \le k \le 13$, $-11 \le l \le 11$). Altogether 3356 reflections were collected from which 3063 were symmetry independent (R_{int} 0.033). Crystals of compound **2i** are monoclinic, *a* 16.319(8), *b* 12.60(6), *c* 10.460(9) Å, V 2071(2) Å^3, M 388.5, Z 4, d_{calc} 1.25 g/sm^3, μ 16.1 sm^{-1}, F (000) 824.0, space group $P2_1/c$ (N 14). The structure is deciphered by a direct method and specified by a method of the least squares in fullmatri anisotropic approximation using the CRYSTALS program package.[11] For specification the 2280 reflections with $I > 3\sigma(I)$ were used (244 adjustable parameters, number of reflections on parameter 9.3). About 80% atoms of hydrogen were revealed from differed synthesis of electronic density; positions of other hydrogen atoms were calculated geometrically. All hydrogen atoms were included in specification with the fixed position and thermal parameters. For specification the weight scheme of Chebushev[12] with five parameters was used: 1.76, -0.77, 0.64, -0.74, and -0.24. Final values of factors of divergence R 0.062 and R_W 0.065, GOF 1.068 were obtained. The residual electron density from differed Fourier series is 0.43 and -0.24 e/Å^3. The calculation of absorption in a crystal was carried out by a method of azimuthal scanning.[13]

Initial quinoneimines 1a,b,d,f,g were obtained by a literature method [14] and crystallized from ethanol. Quinoneimines **1j,k** were obtained as described earlier[16]. The spectral characteristics of quinoneimines **1c,e,h**[15] and **1i**[1] are identical to those reported earlier.

***N*-Phenylsulfenyl-2,5-dimethyl-1,4-benzoquinonemonoimine (1a).** Yellow powder (yield 70%), mp 98-99°C; *Anal.* Calcd. $C_{14}H_{13}NOS$: C, 69.11; H, 5.39; N, 5.76; S, 13.18. Found: C, 69.25; H, 5.43; N, 5.72; S, 13.25. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.05 (3H, d, *J*=1.2 Hz), 2.24 (3H, d, *J*=1.2 Hz), 6.36 (1H, k, *J*=1.2 Hz), 7.22 (1H, k, *J*=1.2 Hz), 7.27-7.62 (5H, m). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.9 (C in CH_3^2), 17.5 (C in CH_3^5), 124.6 (C^6), 125.2 (C^2,C^6 in Ar), 127.3 (C^3), 129.1 (C^3,C^5 in Ar), 134.7 (C^4 in Ar), 137.9 (C^1 in Ar), 139.7 (C^5), 146.6 (C^2), 154.2 (C in C=N), 188.0 (C in C=O).

***N*-(4-Methylbenzene)sulfenyl-2,5-dimethyl-1,4-benzoquinonemonoimine (1b).** Yellow powder (yield 65%), mp 133-134°C; *Anal.* Calcd. $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44; S, 12.46. Found: C, 70.11; H, 5.85; N, 5.41; S, 12.49. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.05 (3H, d, *J*=0.9 Hz), 2.21 (3H, d, *J*=0.9 Hz), 2.38 (3H, s), 6.35 (1H, k, *J*=0.9 Hz), 7.22 (1H, k, *J*=0.9 Hz), 7.24 (2H, d, *J*=8.4 Hz), 7.49 (2H, d, *J*=8.4 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.9 (C in CH_3^2), 17.5 (C in CH_3^5), 21.1 (C in CH_3(Ar)), 124.5 (C^6), 125.1 (C^2,C^6 in Ar), 127.1 (C^3), 129.8 (C^3,C^5 in Ar), 134.6 (C^1 in Ar), 137.5 (C^4 in Ar), 139.5 (C^5), 146.6 (C^2), 153.9 (C in C=N), 188.0 (C in C=O).

***N*-(4-Methoxybenzene)sulfenyl-2,5-dimethyl-1,4-benzoquinonemonoimine (1d).** Yellow powder (yield 63%), mp 114-115°C; *Anal.* Calcd. $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12; S, 11.73. Found: C, 65.99; H, 5.51; N, 5.10; S, 11.70. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.05 (3H, d, *J*=1.2 Hz), 2.19 (3H, d, *J*=1.2 Hz), 3.85 (3H, s), 6.35 (1H, k, *J*=1.2 Hz), 6.99 (2H, d, *J*=9.0 Hz), 7.23 (1H, k, *J*=1.2 Hz), 7.53 (2H, d, *J*=9.0 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.9 (C in CH_3^2), 17.4 (C in CH_3^5), 55.4 (C in OCH_3), 114.7 (C^3,C^5 in Ar), 124.4 (C^6), 127.04 (C^3), 127.7 (C^2,C^6 in Ar), 128.8 (C^1 in Ar), 139.4 (C^5), 146.6 (C^2), 153.7 (C in C=N), 159.5 (C in OCH_3), 188.0 (C in C=O).

***N*-(4-Chlorbenzene)sulfenyl-2-methyl-1,4-benzoquinonemonoimine (1f).** Yellow powder (yield 70%), mp 88-89°C; *Anal.* Calcd. $C_{13}H_{10}ClNOS$: C, 59.20; H, 3.82; Cl, 13.44; N, 5.31; S, 12.16. Found: C, 59.25; H,3.85; Cl, 13.42; N, 5.28; S, 12.25. ^{1}H-NMR (300 MHz, $CDCl_3$) (E-isomer) δ 2.04 (3H, d, *J*=1.2 Hz), 6.58 (1H, d, *J*=10.2 Hz), 7.01 (1H, m), 7.37-7.40 (1H, dd, *J*=2.1 10.2 Hz), 7.42 (2H, d, *J*=8.4 Hz), 7.57 (2H, d, *J*=8.4 Hz); (Z-isomer) δ 2.10 (3H, d, *J*=1.5 Hz), 6.51 (1H, d, *J*=9.9 Hz), 7.06-7.09 (1H, dd, *J*=2.4 9.9 Hz), 8.28 (1H, m), 7.42 (2H, d, *J*=8.4 Hz), 7.57 (2H, d, *J*=8.4 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) (E-isomer) δ 16.5 (C in CH_3), 124.2 (C^2,C^6 in Ar), 126.6 (C^3), 128.6 (C^3,C^5 in Ar), 129.3 (C^6), 133.7 (C^4 in Ar), 135.9 (C^1 in Ar), 138.6 (C^2), 126.2 (C^5), 154.5 (C in C=N), 187.6 (C in C=O); (Z-isomer) δ 15.6 (C in CH_3), 124.2 (C^2,C^6 in Ar), 130.8 (C^6), 126.55 (C^3), 128.6 (C^3,C^5 in Ar), 129.3 (C^5), 133.7 (C^4 in Ar), 135.8 (C^1 in Ar), 137.0 (C^2), 154.6 (C in C=N), 187.6 (C in C=O).

***N*-(4-Chlorbenzene)sulfenyl-2,5-dimethyl-1,4-benzoquinonemonoimine (1g).** Yellow powder (yield 65%), mp 158-159°C; *Anal.* Calcd. $C_{14}H_{12}ClNOS$: C, 60.54; H, 4.35; Cl, 12.76; N, 5.04; S, 11.54. Found: C, 60.51; H, 4.33; Cl, 12.78; N, 5.01; S, 11.62. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.06 (3H, w.s), 2.23 (3H, w.s), 6.37 (1H, w.s), 7.18 (1H, w.s), 7.40 (2H, d, *J*=9.0 Hz), 7.53 (2H, d, *J*=9.0 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.9 (C in CH_3^2), 17.5 (C in CH_3^5), 124.6 (C^6), 125.8 (C^2,C^6 in Ar), 127.5 (C^3), 129.2 (C^3,C^5 in Ar), 133.1 (C^4 in Ar), 136.4 (C^1 in Ar), 140.0 (C^5), 146.5 (C^2), 154.4 (C in C=N), 187.9 (C in C=O).

***N*-(2-Nitrobenzene)sulfenyl-6-isopropyl-3-methyl-1,4-benzoquinonemonoimine (1j).** Yellow powder (yield 54%), mp 157-158°C; *Anal.* Calcd. $C_{16}H_{16}N_2O_3S$: C, 60.74; H, 5.10; N, 8.85; S, 10.13. Found: C, 60.78; H, 5.13; N, 8.90; S, 10.08. ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 17.8 (C in CH_3^3), 21.9 (C in $2CH_3^{i\text{-}Pr}$), 27.2 (C in $CH^{i\text{-}Pr}$), 121.6 (C^6 in Ar), 125.8 (C^2), 126.0 (C^5 in Ar), 126.5 (C^5), 129.2 (C^4 in Ar), 134.5 (C^3 in Ar), 138.4 (C^3), 143.3 (C^1 in Ar), 146.4 (C^2 in Ar), 150.4 (C^6), 156.6 (C in C=N), 187.2 (C in C=O).

***N*-(2-Nitrobenzene)sulfenyl-5-isopropyl-2-methyl-1,4-benzoquinonemonoimine (1k).** Yellow powder (yield 56%), mp 168-169°C; *Anal.* Calcd. $C_{16}H_{16}N_2O_3S$: C, 60.74; H, 5.10; N, 8.85; S, 10.13. Found: C, 60.75; H, 5.11; N, 8.88; S, 10.10. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.24 (6H, d, *J*=6.9 Hz), 2.11 (3H, s), 3.42-3.53 (1H, m), 6.42 (1H, s), 7.43 (1H, d, *J*=7.5 Hz), 7.47 (1H, w.s.), 7.77-7.82 (1H, m), 8.37 (1H, d, *J*=8.4 Hz), 8.50 (1H, d, *J*=8.4 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.9 (C in CH_3^2), 22.5 (C in $2CH_3^{i\text{-}Pr}$), 27.3 (C in $CH^{i\text{-}Pr}$), 125.3 (C^6 in Ar), 125.7 (C^5 in Ar), 125.86 (C^6), 126.5 (C^3), 134.5 (C^4 in Ar), 138.5 (C^5), 140.5 (C^3 in Ar), 143.5 (C^1 in Ar), 146.1 (C^2 in Ar), 155.0 (C^2), 156.3 (C in C=N), 188.5 (C in C=O).

General procedure for oxidation of *N*-arylthio-1,4-benzoquinonemonoimines 1a-k to *N*-arylsulfinyl-1,4-benzoquinonemonoimines 2a-k

MCPBA (460 mg, 2 mmol) (commercial, the content of the basic substance 70-75%) was added to a solution of corresponding N-arylthio-1,4-benzoquinonemonoimine **1a-k** (2 mmol) in 40 mL methylene chloride at room temperature with stirring. Stirring was continued within two hours. Completion of reaction was monitored by the TLC method. The solution was filtered, and the filtrate was evaporated under reduced pressure. The obtained mixture was washed with 10% solution of sodium bicarbonate, the solvent removed, the residue was dried and crystallized from petroleum-ether (boiling-point 40-70°C). Compounds **2j,k** were crystallized from octane. The quinoneimines **2j,k** are identical to those described earlier.[1]

***N*-Phenylsulfinyl-2,5-dimethyl-1,4-benzoquinonemonoimine (2a).** Yellow powder (yield 63%), mp 71-72°C; *Anal.* Calcd. $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40; S, 12.36. Found: C, 64.82; H, 5.08; N, 5.43; S, 12.43. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.04 (3H, d, *J*=1.5 Hz), 2.11 (3H, d, *J*=1.2 Hz), 6.45 (1H, k, *J*=1.5 Hz), 7.54-7.84 (5H, m), 8.24 (1H, k, *J*=1.2 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 16.0 (C in CH_3^2), 17.7 (C in CH_3^5), 125.3 (C^2,C^6 in Ar), 126.7 (C^6), 129.2 (C^3,C^5 in Ar), 131.0 (C^4 in Ar), 131.1 (C^3), 142.2 (C^5), 144.3 (C^1 in Ar), 147.5 (C^2), 161.1 (C in C=N), 186.5 (C in C=O).

***N*-(4-Methylbenzene)sulfinyl-2,5-dimethyl-1,4-benzoquinonemonoimine (2b).** Yellow powder (yield 65%), mp 101-102°C; *Anal.* Calcd. $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12; S, 11.73. Found: C, 65.89; H, 5.51; N, 5.15; S, 11.84. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.04 (3H, d, *J*=1.5 Hz), 2.11 (3H, d, *J*=1.2 Hz), 2.43 (3H, s), 6.43 (1H, k, *J*=1.5 Hz), 7.34 (2H, d, *J*=8.4 Hz), 7.71 (2H, d, *J*=8.4 Hz), 8.23 (1H, k, *J*=1.2 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 16.0 (C in CH_3^2), 17.7 (C in CH_3^5), 21.3 (C in CH_3(Ar)), 125.2 (C^2,C^6 in Ar), 126.7 (C^6), 129.9 (C^3,C^5 in Ar), 131.0 (C^3), 141.3 (C^1 in Ar), 141.6 (C^4 in Ar), 142.1 (C^5), 147.6 (C^2), 161.0 (C in C=N), 186.6 (C in C=O).

***N*-(4-Methylbenzene)sulfinyl-2,6-dimethyl-1,4-benzoquinonemonoimine (2c).** Yellow powder (yield 85%), mp 95-96°C; *Anal.* Calcd. $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12; S, 11.73. Found: C, 65.94; H, 5.55; N, 5.10; S, 11.66. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.02 (3H, w.s), 2.07 (3H, w.s), 2.42 (3H, s), 6.81 (1H, w.s), 7.34 (2H, d, *J*=8.7 Hz), 7.69 (2H, d, *J*=8.7 Hz), 8.19 (1H, w.s). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.8 (C in CH_3^2), 16.7 (C in CH_3^6), 21.4 (C in

CH_3(Ar)), 125.2 (C^2,C^6 in Ar), 126.2 (C^5), 130.0 (C^3,C^5 in Ar), 136.30 (C^3), 136.5 (C^1 in Ar), 141.7 (C^4 in Ar), 141.9 (C^2), 142.8 (C^6), 160.9 (C in C=N), 187.0 (C in C=O).

***N*-(4-Methoxybenzene)sulfinyl-2,5-dimethyl-1,4-benzoquinonemonoimine (2d).** Yellow powder (yield 63%), mp 112-113°C; *Anal.* Calcd. $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84; S, 11.08. Found: C, 62.28; H, 5.25; N, 4.81; S, 11.03. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.04 (3H, d, *J*=1.2 Hz), 2.11 (3H, d, *J*=1.2 Hz), 3.87 (3H, s), 6.44 (1H, k, *J*=1.2 Hz), 7.03 (2H, d, *J*=8.4 Hz), 7.75 (2H, d, *J*=8.4 Hz), 8.20 (1H, k, *J*=1.2 Hz). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 16.0 (C in $CH_3{}^2$), 17.7 (C in $CH_3{}^5$), 55.5 (C in OCH_3), 114.7 (C^3,C^5 in Ar), 126.7 (C^6), 127.1 (C^2,C^6 in Ar), 131.14 (C^3), 135.6 (C^1 in Ar), 142.2 (C^5), 147.7 (C^2), 161.0 (C in C=N), 162.0 (C^4 in Ar), 186.7 (C in C=O).

***N*-(4-Methoxybenzene)sulfinyl-2,6-dimethyl-1,4-benzoquinonemonoimine (2e).** Yellow powder (yield 62%), mp 86-87°C; *Anal.* Calcd. $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84; S, 11.08. Found: C, 62.24; H, 5.20; N, 4.86; S, 11.15. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.02 (3H, w.s), 2.04 (3H, w.s), 3.86 (3H, s), 6.81 (1H, w.s), 7.01 (2H, d, *J*=8.4 Hz), 7.73 (2H, d, *J*=8.4 Hz), 8.16 (1H, w.s). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.8 (C in $CH_3{}^2$), 16.7 (C in $CH_3{}^6$), 55.6 (C in OCH_3), 114.8 (C^3,C^5 in Ar), 126.2 (C^5), 127.1 (C^2,C^6 in Ar), 136.1 (C^3), 136.3 (C^1 in Ar), 141.8 (C^2), 142.9 (C^6), 160.9 (C in C=N), 162.2 (C^4 in Ar), 187.1 (C in C=O).

***N*-(4-Chlorbenzene)sulfinyl-2-methyl-1,4-benzoquinonemonoimine (2f).** Yellow powder (yield 75%), mp 88-89°C; *Anal.* Calcd. $C_{13}H_{10}ClNO_2S$: C, 55.82; H, 3.60; Cl, 12.67; N, 5.01; S, 11.46. Found: C, 55.86; H, 3.64; Cl, 12.64; N, 5.03; S, 11.41. ^{1}H-NMR (300 MHz, $CDCl_3$) (E-isomer) δ 2.04 (3H, w.s), 6.58 (1H, d, *J*=10.2 Hz), 6.87 (1H, w.s), 7.53 (2H, d, *J*=9.0 Hz), 7.76 (2H, d, *J*=9.0 Hz), 8.38-8.41 (1H, dd, *J*=2.1 10.2 Hz); (Z-isomer) δ 2.08 (3H, w.s), 6.58 (1H, d, *J*=10.2 Hz), 6.94-6.98 (1H, dd, *J*=2.4 10.2 Hz), 7.53 (2H, d, *J*=9.0 Hz), 7.76 (2H, d, *J*=9.0 Hz), 8.26 (1H, w.s). ^{13}C-NMR (75.4 MHz, $CDCl_3$) (E-isomer) δ 16.5 (C in $CH_3{}^2$), 126.7 (C^2,C^6 in Ar), 129.5 (C^3,C^5 in Ar), 129.8 (C^6), 128.3 (C^5), 133.9 (C^1 in Ar), 136.2 (C^4 in Ar), 136.8 (C^3), 142.6 (C^2), 161.0 (C in C=N), 186.6 (C in C=O); (Z-isomer) δ 15.5 (C in $CH_3{}^2$), 126.6 (C^3), 126.7 (C^2,C^6 in Ar), 129.5 (C^3,C^5 in Ar), 133.1 (C^1 in Ar), 136.2 (C^4 in Ar), 137.8 (C^5), 143.2 (C^2), 139.6 (C^6), 163.2 (C in C=N), 186.6 (C in C=O).

***N*-(4-Chlorbenzene)sulfinyl-2,5-dimethyl-1,4-benzoquinonemonoimine (2g).** Yellow powder (yield 67%), mp 124-125°C; *Anal.* Calcd. $C_{14}H_{12}ClNO_2S$: C, 57.24; H, 4.12; Cl, 12.07; N, 4.77; S, 10.91. Found: C, 57.26; H, 4.15; Cl, 12.10; N, 4.79; S, 11.05. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.04 (3H, w.s), 2.10 (3H, w.s), 6.45 (1H, w.s), 7.51 (2H, d, *J*=8.4 Hz), 7.77 (2H, d, *J*=8.4 Hz), 8.20 (1H, w.s). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 16.1 (C in $CH_3{}^2$), 17.7 (C in $CH_3{}^5$), 126.7 (C^6), 126.8 (C^2,C^6 in Ar), 129.6 (C^3,C^5 in Ar), 131.4 (C^3), 137.1 (C^4 in Ar), 142.6 (C^5), 146.0 (C^1 in Ar), 147.4 (C^2), 161.2 (C in C=N), 186.4 (C in C=O).

***N*-(4-Chlorbenzene)sulfinyl-2,6-dimethyl-1,4-benzoquinonemonoimine (2h).** Yellow powder (yield 61%), mp 109-110°C; *Anal.* Calcd. $C_{14}H_{12}ClNO_2S$: C, 57.24; H, 4.12; Cl, 12.07; N, 4.77; S, 10.91. Found: C, 57.21; H, 4.10; Cl, 12.09; N, 4.75; S, 10.85. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.03 (3H, w.s), 2.08 (3H, w.s), 6.81 (1H, w.s), 7.50 (2H, d, *J*=8.7 Hz), 7.76 (2H, d, *J*=8.7 Hz), 8.16 (1H, w.s). ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 15.8 (C in $CH_3{}^2$), 16.7 (C in $CH_3{}^6$), 126.1 (C^5),

126.8 (C^2,C^6 in Ar), 129.5 (C^3,C^5 in Ar), 136.1(C^3), 137.7 (C^4 in Ar), 142.0 (C^2), 143.2 (C^1 in Ar), 142.9 (C^6), 161.4 (C in C=N), 186.9 (C in C=O).

***N*-(4-Nitrobenzene)sulfinyl-2,6-di-*tert*-butyl-1,4-benzoquinonemonoimine (2i).** Yellow powder (yield 65%), mp 149-150°C; *Anal.* Calcd. $C_{20}H_{24}N_2O_4S$: S, 8.25. Found: S, 8.34. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.27 (9H, w.s), 1.31 (9H, w.s), 6.75 (1H, w.s), 8.03 (2H, d, *J*=9.0 Hz), 8.13 (1H, w.s), 8.42 (2H, d, *J*=9.0 Hz). The structure is uniquely proved by X-ray data (*vide supra*).

General procedure for oxidation of *N*-arylthio-1,4-benzoquinonemonoimines 1c,h to *N*-arylsulfonyl-1,4-benzoquinonemonoimines 3c,h

MCPBA (2.2 mmol) (commercial, the content of the basic substance 70-75%) was added to a solution of quinonemonoimine **1c,h** (2 mmol) in 20 mL methylene chloride at room temperature with stirring. Stirring was continued for one hour. The completion of the reaction was controlled by the TLC method. After evaporation of the methylene chloride the residue was washed with water and crystallized from glacial acetic acid. The obtained compounds **3c** (yield 55%) and **3h** (yield 60%) were identical with those previously described.[17]

General procedure for oxidation of *N*-arylsulfinyl-1,4-benzoquinonemonoimines 2c,h to *N*-arylsulfonyl-1,4-benzoquinonemonoimines 3c,h

MCPBA (1.2 mmol) (commercial, the content of the basic substance 70-75%) was added to a solution of quinonemonoimine **2c,h** (2 mmol) in 20 ml methylene chloride at room temperature while stirred. Stirring was continued for one hour. The completion of the reaction was controlled by the TLC method. After evaporation of the methylene chloride, the residue was washed with water, dried and crystallized from glacial acetic acid. The obtained compounds **3c** (yield 60%) and **3h** (yield 63%) were identical with those previously described.[17]

References

1. Avdeenko, A. P.; Pirozhenko, V. V.; Stanovskiy, M. V.; Konovalova, S. A.; Yusina, A. L. *Rus. J. Org. Chem. (Engl. Transl.)* **2004**, *40*, 1291.
2. Oue, S.; Shinhama, K.; Fujimori, K.; Kim, Y. H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 775.
3. Shvets, A. E.; Bleidelis, J.; Markava, E.; Freimanis, J.; Kanepe, D. V. *Zh. Strukturnoi Khim. (Russ. Ed.)* **1980**, *21*, 190; *Chem. Abstr*. **1980**, *93*, 248563.
4. Avdeenko, A. P.; Pirozhenko, V. V.; Yagupol'skii, L. M.; Marchenko, I. L. *Rus. J. Org. Chem. (Engl. Transl.)* **2001**, *37*, 991.
5. Avdeenko, A. P.; Konovalova, S. A.; Ilchenko, A. Ya.; Glinyanaya, N. M. Halogenation of *N*-substituted p-quinoneimines and esters of p-quinonemonooximes. III. Regioselectivity of halogenation of 4-aroyl(arylsulfonyl)oximino-2,5-cyclohexadien-1-ones *Rus. J. Org. Chem. (Engl. Transl.)* **2005**, *41*, in press.

6. Avdeenko, A. P.; Zhukova, S.A.; Glinyanaya, N. M.; Konovalova, S. A. *Rus. J. Org. Chem. (Engl. Transl.)* **1999**, *35*, 560.
7. Pirozhenko, V. V.; Avdeenko, A. P. *Rus. J. Org. Chem. (Engl. Transl.)* **1995**, *31*, 1514.
8. Avdeenko, A. P.; Yusina, A. L.; Menafova, Yu. V.; Pirozhenko, V. V. *Rus. J. Org. Chem. (Engl. Transl.)* **1995**, *31*, 1386.
9. (a) Zefirov, Yu. V. *Kristallografiya (Russ. Ed.)* **1997**, *42*, 936; *Chem. Abstr*. **1997**, *128*, 68627. (b) Zefirov, Yu. V.; Zorky, P. M. *Zh. Strukturnoi Khim. (Russ. Ed.)* **1976**, *17*, 994; *Chem. Abstr*. **1977**, *86*, 131510.
10. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.2* **1987**, 1.
11. Watkin D.J.; Prout C.K.; Carruthers J.R.; Betteridge P.W. *Crystals*, Issue 10, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1996.
12. Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr., Sect A* **1979**, *35*, 698.
13. North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect A* **1968**, *24*, 351.
14. Kramer, D. N.; Gamson, R. M. *J. Org. Chem.* **1959**, *24*, 1154.
15. Pirozhenko, V. V.; Avdeenko, A. P.; Yusina, A. L.; Konovalova, S. A. *Rus. J. Org. Chem. (Engl. Transl.)* **2004**, *40*, 1121.
16. Burmistrov, K. S. D.Sc. dissertation, USCTU, Ukraine, Dnepropetrovsk, 1990.
17. Avdeenko, A. P. *Rus. J. Org. Chem. (Engl. Transl.)* **2000**, *36*, 522.