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Activated Sterically Strained C=N bond in *N*-Substituted *p*-Quinone Mono- and Diimines: XIII.* Reactions of *N*-alkyl(aryl, trifluoromethyl)sulfonyl-, *N*-arylsulfinyl- and *N*-arylsulfanyl-1,4-benzoquinone Monoimines with Alcohols

A. P. Avdeenko[a], S. A. Konovalova[a], O. N. Mikhailichenko[a], A. A. Santalova[a], G. V. Palamarchuk[b], and O. V. Shishkin[b,c]

[a]*Donbass State Engineering Academy, Kramatorsk, 84313, Ukraine*
e-mail: chimist@dgma.donetsk.ua
[b]*Institute of single crystals, National Academy of Sciences of Ukraine, Kharkov, Ukraine*
[c]*Karazin Kharkov National University, Kharkov, Ukraine*

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Abstract—Steric strains arising between the substituent atoms at nitrogen (S, SO, or SO_2) and the methyl group located in positions *3* or *5* of the quinoid ring of 3,5-dimethyl-substituted quinone monoimines lead to the increased angle C=N–S. As a result in these quinone monoimines the reactions of 1,2-addition become thermodynamically possible since the formation of quinolide structures with the sp^3-hybridized carbon atom removes the steric strain.

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3,5-Disubstituted *N*-arylsulfonyl-1,4-quinone monoimines enter the 1,2-addition reactions at the C=N bond with alcohols, hydrazines, primary aromatic amines, dialkylphosphites, bis(*p*-dimethylaminophenyl)phosphinite [2–9]. The C=N bond exhibits a higher reactivity due to the increased bond angle C=N–X, and its activity starts to appear at the angle C=N–X exceeding 130 deg [3]. At the angle value over 145–150 deg the quinone imines get thermodynamically unstable, and their synthesis becomes impossible. These conclusions followed from the study of the structural features of quinone imines on the precision 3D atomic-molecular models «Tartu Models» and also from the XRD analysis of the 3,5-dimethyl-*N*-(4-chlorophenyl) sulfonyl-1,4-benzoquinone monoimine (angle C=N–X 132.7 deg) [3]. No XRD investigations of the other 3,5-disubstituted 1,4-quinone monoimines was performed.

The most studied among 1,2-addition reactions to 1,4-quinone monoimines are the reactions with alcohols [2–5]. Yet as a result of the reaction with alcohols of some 3,5-disubstituted *N*-arylsulfonyl-1,4-benzoquinone monoimines having a bulky alkyl group (*i*-PrOH, *t*-BuOH) previously mainly the hydrolysis products were isolated, and in the case of *N*-arylsulfanylperchloro-1,4-benzoquinone monoimines the initial quinone monoimines were recovered [3]. The reactions with alcohols of the other quinone imines containing a sulfur atom linked to nitrogen were not examined.

The characteristic feature of 3,5-disubstituted *N*-arylsulfonyl-1,4-benzoquinone monoimines is the existence of a fast in the NMR time scale *Z*,*E*-isomerization (topomerization) also due to the increased angle C=N–X as compared to the unsubstituted in the quinone ring 1,4-benzoquinone monoimines [2, 5, 10]. The structural and spectral features of *N*-arylsulfanyl- and *N*-arylsulfinyl-1,4-benzoquinone monoimine have not been studied before.

The goal of this research was revealing the structural features of 3,5-disubstituted 1,4-benzoquinone monoimines containing sulfur atoms of diverse oxidation state attached to the nitrogen atom, and establishing the rules governing the reactions of these quinone monoimines with alcohols. We selected as objects of the study 3,5-dimethyl-(2,3,5,6-tetrachloro)-substituted *N*-alkylsulfonyl- **Ia–Ic**, *N*-arylsulfonyl- **Id–If**, *N*-trifluoromethylsulfonyl- (**Ig**), *N*-arylsulfinyl- **IIa, IIb**,

*For communication XII, see [1].

and *N*-arylsulfanyl-1,4-benzoquinone monoimines **IIIa, IIIb**.

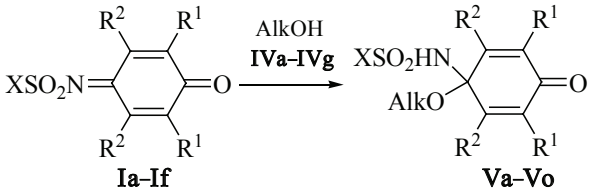
The syntheses and spectra were previously described for *N*-methyl(trifluoromethyl)sulfonyl- **Ia, Ig** [11], *N*-arylsulfonyl- **Id–If** [7, 12], 3,5-dimethyl-*N*-arylsulfanyl- **IIIa, IIIb** [Ar = Ph (a), Tol (b)] [13, 14] 1,4-benzoquinone monoimines. *N*-alkylsulfonyl- **Ib, Ic** and *N*-arylsulfinyl derivatives **IIa, IIb** are prepared for the first time.

The ^{1}H NMR spectra of quinone monoimines **Ib, Ic, IIa, IIb** similar to the spectra of formerly obtained 3,5-dimethyl derivatives **Ia, Id, If, IIIa, IIIb** [7, 11, 13] contain the signals of protons $H^{2,6}$ as singlets in the region 6.37–6.58 ppm which shows the existence of the fast in the NMR time scale *Z*,*E*-isomerization. In the ^{13}C NMR spectra of quinone imines **IIa, IIb** same as in the spectra of quinone monoimines **IIIa, IIIb** [14], the nuclei of atoms $C^{3,5}$ and $C^{2,6}$ are magnetically equivalent.

Formerly the reactions with alcohols were carried out at boiling [2–5] which sometimes might provoke the hydrolysis of initial quinone monoimine. In this study the reactions were performed under mild conditions, at room temperature. If the TLC monitoring showed that within 2 months the reaction failed to proceed, the reaction mixture was subjected to boiling for 12 h.

As a result of reactions of quinone imines **Ia–Ic** with methanol (**IVa**) and quinone imines **Id–If** with alcohols **IVa–IVg** we obtained products of 1,2-addition: quinolide structures **Va–Vo** (Scheme 1). Compound **Vd** was obtained for the first time; it could not be isolated before due to the competing hydrolysis of quinone monoimine in boiling alcohols [3]. We failed to obtain reaction products of quinone imines **Ia–Ic** with alcohols **IVb–IVg** and quinone imines **Ia–If** with *t*-BuOH **IVh**. The last reaction is evidently impossible due to steric hindrances.

Scheme 1.



I, X = Me (**a**), Et (**b**), Pr (**c**), Ph (**d**), 4-MeC_6H_4 (**e, f**); R^1 = H, R^2 = Me (**a–d, f**), R^1 = R^2 = Cl (**e**); **IV**, Alk = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), *i*-Bu (**e**), C_5H_{11} (f), cyclo-C_6H_{11} (**g**); **V**, X = Me (**a**), Et (**b**), Pr (**c**), Ph (**d–g**), 4-MeC_6H_4 (**h–o**); Alk = Me (**a–c**, k, **n**), Et (**l, o**), Pr (**m**), *i*-Pr (**d**), *t*-Bu (**e, h**), C_5H_{11} (**f, i**), cyclo-C_6H_{11} (**g, j**); R^1 = H, R^2 = Me (**a–g, n, o**), R^1 = R^2 = Cl (**h–m**).

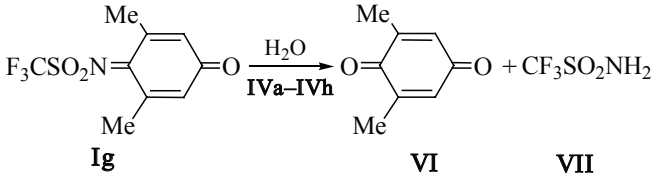
In the IR spectra of compounds **Va–Vo** the characteristic absorption band of the C=O group of the quinolide ring appears at 1690–1710 cm^{-1} in contrast to the C=O group absorption in initial 1,4-benzoquinone monoimines **Ia–If** (1635–1670 cm^{-1}), and the absorption band in the region 1545–1630 cm^{-1} corresponding to the C=N group is absent.

In the ^{1}H NMR spectra of compounds **Va–Vo** the singlet of protons $H^{2,6}$ of the quinoid ring is observed in the region 6.10–6.59 ppm, the signal of OMe group of compounds **Va–Vc, Vk, Vn**, at 3.02–3.04 ppm as is characteristic of quinolide structures [2–5], the signal of the NH group appears in the region 4.90–6.51 ppm.

The rate of reaction of quinone imines **Ia–If** with alcohols **IVa–IVg** depends on the volume of the substituent at the sulfo group of quinone imines **Ia–If** and of the alkyl group of the alcohols **IVa–IVg**. Thus the reaction of *N*-alkylsulfonyl-1,4-benzoquinone monoimines **Ia–Ic** with methanol (**IVa**) required 5–60 min, *N*-arylsulfonyl derivatives **Id–If** with alcohol **IVd** took 24 h, and with alcohols **IVe–IVg**, up to 1 month. Formerly the acceleration of the reaction with alcohols was observed for *N*-{arylsulfonylimino[phenyl(methyl)] methyl}-1,4-benzoquinone monoimines at replacement of the phenyl substituent at the nitrogen for the methyl group [15].

N-Trifluoromethylsulfonyl derivative **Ig** in the presence of alcohols **IVa–IVh** at room temperature in 2 months hydrolyzed into the corresponding quinone **VI** and trifluoromethanesulfonamide (**VII**) (Scheme 2). In the ^{19}F NMR spectrum the signal characteristic of quinone imine **Ig** at –79.33 ppm disappeared, but appeared a singlet at –79.85 ppm characteristic of amide **VII** [11].

Scheme 2.

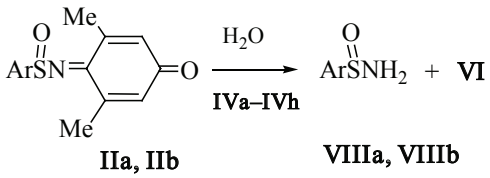


N-Aryl(alkyl)sulfonyl-1,4-benzoquinone monoimines with unoccupied position *3* and/or *5* of the quinoid ring do not react with alcohols. After the reaction of *N*-trifluoromethylsulfonyl analogs with alcohols only the corresponding quinones and trifluoromethanesulfonamide were isolated from the reaction mixture, apparently due to the low hydrolytic stability of the substrates [10].

In the reaction of *N*-arylsulfinyl-1,4-benzoquinone

monoimines **IIa, IIb** with alcohols **IVa–IVh** also only the products of the hydrolysis of the initial quinone imines were obtained (Scheme 3).

Scheme 3.



IIa, IIb **VIIIa, VIIIb**

Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**).

N-Arylsulfanyl derivatives **IIIa, IIIb** did not react with alcohols **IVa–IVh** even at boiling for 12 h (the initial reagents were recovered).

As known, the reactivity of quinone imines with respect to alcohols depends on the value of the angle C=N–X [2–5]. In order to establish the structural features of *N*-methyl(trifluoromethyl)sulfonyl-, *N*-arylsulfinyl-, and *N*-arylsulfanyl-1,4-benzoquinone imines and to compare them with the previously studied 3,5-dimethyl-*N*-(4-chlorophenyl)sulfonyl-1,4-benzoquinone monoimine (**Ih**) we subjected to XRD analysis compounds **Ia, IIb, IIIb** (Figs. 1–3). We failed to obtain crystals of compound **Ig** because of its low stability in air.

Aiming at comparing the geometric parameters of 3,5-dimethyl-substituted quinone imines containing sulfur of diverse valence with analogous quinone imines lacking substituents in the *ortho*-position to the nitrogen atom we performed the XRD analysis on a single crystal of 2,6-di-*tert*-butyl-*N*-arylsulfonyl derivative **Ii** (Fig. 4). The XRD study of sulfinyl- and sulfanyl analogs **IIc, IIIc** was carried out earlier [16].

In the series ArS (**IIIb**) → ArSO (**IIb**) → $MeSO_2$ (**Ia**) → $ArSO_2$ (**Ih**) [3] the value of the bond angle C=N–S increased from 127.9(2) in quinone imine **IIIb** to 132.7(3) deg in *N*-arylsulfonyl derivative **Ih** (Table 1).

The molecule of 3,5-dimethyl-*N*-(4-tolyl)sulfanyl-1,4-benzoquinone monoimine (**IIIb**) is virtually flat. The angle C^4=N^1–S^1 in this molecule is by 8.3 deg larger than in 2,6-di-*tert*-butyl derivative **IIIc** [16] but does not exceed the value of 130 deg that was formerly suggested as a criterion of the presence of a sterically strained C=N bond [3]. The increased angle originates from the steric strain between the sulfur atom and a methyl group in the position *3* or *5* of the quinoid ring: the shortened intramolecular contacts are observed between the atoms S^1… C^7 2.955 (sum of the van der Waals radii 3.55 [17]), S^1… H^{7A} 2.66 (3.00), S^1… H^{7B} 2.67 Å (3.00).

Table 1. Some geometric parameters of N-substituted 1,4-benzoquinone monoimines **Ia, Ih, Ii, IIb, IIc, IIIb, IIIc** according to XRD data

Compound no.	Angle C=N–S, deg	Bond length C=N, Å	Bond length N–S, Å
Ia	130.1	1.294	1.650
Ih	132.7	1.290	1.638
Ii	121.6	1.301	1.652
IIb	129.0	1.288	1.709
IIc	126.0	1.303	1.661
IIIb	127.9	1.303	1.653
IIIc	119.6	1.302	1.663

N-Arylsulfinyl derivatives **IIb, IIc** contain a chiral sulfur(IV) atom with a lone electron pair, and the group S=O may take different spatial positions with respect to the quinoid ring as is actually observed in quinone monoimines **IIb, IIc**. The S=O bond in both quinone monoimines **IIb, IIc** deviates from the plane of the quinoid ring: the torsion angle C^4=N^1–S^1=O^2 is 164.3(3) deg. However the group has different orientation with respect to the S–N bond. In quinone monoimine **IIc** this orientation is close to cisoid (torsion angle C^4=N^1–S^1=O^2 –24.8(3) deg [16]), and in **IIb**, to transoid. Namely, in the course of the synthesis that formed structure of the molecule of 3,5-dimethyl-1,4-quinone monoimine **IIb** is more favorable from the viewpoint of minimizing the steric strains where the SO group is spatially removed from the quinoid ring, and the intramolecular shortened contacts exist only between atoms S^1…C^8 3.074 (3.55), S^1… H^{8C} 2.77 (3.00), and S^1… H^{8B} 2.80 E (3.00). On the other hand, in 2,6-di-*tert*-butylquinone monoimine **IIc**, unlike *N*-arylsulfanyl **IIIc** and *N*-arylsulfonyl **Ii** derivatives the steric strain between the SO group and the atoms of the C^5–H^{51} bond of the quinoid ring led to the increase in the angle C^4=N^1–S^1 to 126.0 deg, and intramolecular shortened contacts are observed between atoms O^1…H^{51} 2.25 (2.45), O^1…C^5 2.985 (3.00), S^1… H^{51} 2.83 (3.00), S^1…C^5 3.154 E (3.55) [16]. As a result the angle C^4=N^1–S^1 in 3,5-dimethyl derivative **IIb** compared with 2,6-di-*tert*-butylquinone monoimine **IIc** is increased only by 3 deg.

The specific feature of quinone monoimines **Ia, Ih, Ii** is the location of SO_2 group symmetric with respect to the plane of the quinoid ring. In this event in 3,5-dimethyl-substituted quinone monoimines **Ia, Ih** a steric strain

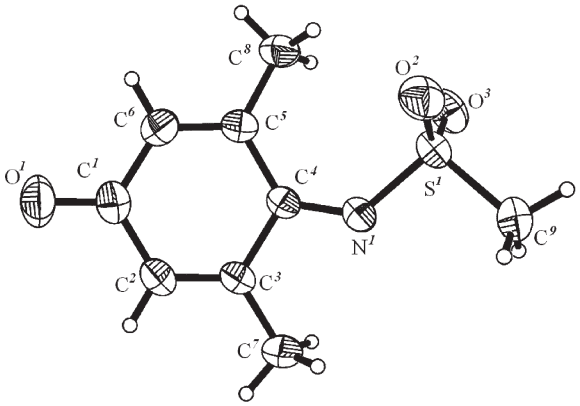


Fig. 1. Structure of *N*-mesyl-3,5-dimethyl-1,4-benzoquinone monoimine (**Ia**) according to XRD data.

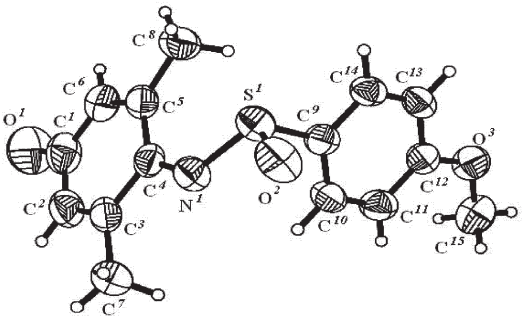


Fig. 2. Structure of 3,5-dimethyl-*N*-(4-methoxyphenyl)sulfinyl-1,4-benzoquinone monoimine (**IIb**) according to XRD data.

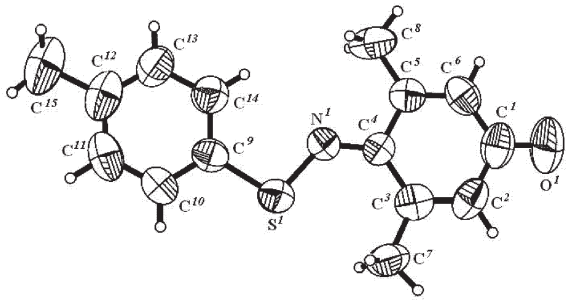


Fig. 3. Structure of 3,5-dimethyl-*N*-(4-tolyl)sulfanyl-1,4-benzoquinone monoimine (**IIIb**) according to XRD data.

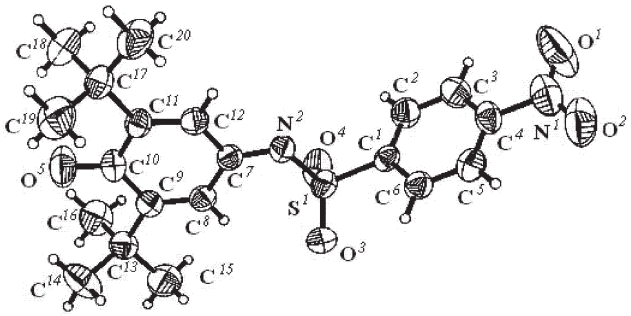


Fig. 4. Structure of 2,6-di-*tert*-butyl-*N*-(4-nitrophenyl)sulfonyl-1,4-benzoquinone monoimine (**Ii**) according to XRD data.

arises between the SO_2 and methyl group in the position *3* or *5* of the quinoid ring which results in intramolecular shortened contacts between atoms $S^1 \ldots C^8$ 3.198 (3.55) in quinone monoimine **Ia** and $S^1 \ldots C^8$ 3.160 (3.55), $O^3 \ldots H^{14A}$ 2.37 (2.45), $S^1 \ldots H^{14A}$ 2.73 A (3.00) in quinone monoimine **Ih** and leads to the increase in the angle $C^4{=}N^1{-}S^1$ in 3,5-dimethyl-1,4-quinone monoimines **Ia, Ih**. Consequently in these quinone monoimines containing a six-valent sulfur atom linked to the nitrogen the maximum increase in the angle $C^4{=}N^1{-}S^1$ is observed in 3,5-dimethyl derivative **Ih** amounting to 11.1 deg compared to 2,6-di-*tert*-butylquinone monoimine **Ii**.

The length of the bond C=N in the quinone monoimine series ArS → ArSO → $ArSO_2$ does not significantly change both in 2,6- and 3,5-disubstituted derivatives. Yet it should be noted that the bond lengths C=N in quinone monoimine **IIIb** and quinone monoimines **Ii, IIc, IIIc** lacking the sterically strained C=N bond at the nitrogen atom have close values unlike quinone imines **Ia, Ih**, **IIb** where the C=N bond is a little shorter (Table 1).

The introduction of substituents into the *ortho*-position to the imine carbon atom results in a slight decrease in the length of the N–S bond in *N*-arylsulfanyl **IIIb, IIIc** and *N*-arylsulfonyl derivatives **Ih, Ii**. The opposite trend is observed in *N*-arylsulfinylquinone monoimines **IIb, IIc:** the length of the N–S bond in 3,5-dimethyl derivative **IIb** increased to 1.709 Å. With increasing steric strain in the molecule in the series of quinone imines **IIIb–IIb–Ia** the bonds C^3–C^4 and C^4–C^5 regularly grow from 1.474(4) to 1.492(1) Å.

Thus the analysis of XRD data suggests a conclusion that the increased angle C=N–S in 3,5-dimethyl-substituted quinone monoimines **IIIb, IIb, Ia, Ih** containing at the nitrogen atom an atom of two-, four, and six-valent sulfur, as it has been concluded before, originates from the steric strain arising between the atoms of the substituent at the nitrogen (S, SO, or SO_2) and the methyl group in the position *3* or *5* of the quinoid ring.

In order to rationalize the difference in the reactivity of the considered quinone monoimines with respect to alcohols we carried out ab initio quantum-chemical calculations by the method B3LYP/6-31+G(d). The energy of the ground state of compounds **Ia, Id, Ig, Ij, Ik, IIa, IIIa, Va, Vp–Vw, IX** obtained by quantum-chemical

calculations and also the difference ΔE_{theor} between the energy of the end product (quinolide structure) and the sum of the energies of initial substances [the corresponding quinone monoimine and methanol, *E*(**IVa**) –115.725193 a.u.] are presented in Table 2.

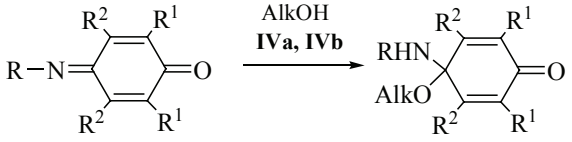
According to the calculated energy of quinolide structures **Vp, Vq** which should form in the reaction of unsubstituted and 2,6-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinone monoimines (**Ij, Ik**) with methanol **IVa**) is larger than the sum of the energy of initial reagents (ΔE_{theor} 9.54 and 3.52 kJ mol^{-1} respectively). In the case of 3,5-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinone monoimine (**Id**) the energy of the reaction product of quinolide structure **Vr** is less than the sum of the energies of the initial compounds **Id, IVa** (ΔE_{theor} –7.39 kJ mol^{-1}) (Table 2). This fact shows that the reaction of 3,5-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinone monoimine (**Id**) with methanol (**IVa**) is possible whereas the reactions with methanol of unsubstituted and 2,6-dimethyl-1,4-quinone monoimines (**Ij, Ik**) is impossible in total agreement with the experimental results.

Higher theoretical energies of reaction products **Vs**, **Vt** compared with the initial compounds were also observed in quinone imine **IIIa** and its oxygen analog, 3,5-dimethyl-4- phenyloximinocyclohexa-2,5-dion-1-ene (**IX**), full agreement with experiment : These compounds did not react with alcohols.

Quinone imine **Ig** in the reaction with alcohols **IVa**–**IVh** suffered a hydrolysis even at the room temperature, and quinone imine **Ia** was hydrolyzed at boiling with alcohols **IVb–IVh**. In keeping with calculations the energy difference between the final reaction product **Vu** and the energy sum of the initial reagents **Ig, IVa** was –1.72 kJ mol^{-1}, and for compounds **Vv** and **Ia, IVb** [*E*(**IVb**) –155.045511 a.u.] it was –1.94 kJ mol^{-1}. We presume that in these events beside the 1,2-addition of the alcohol molecule a competing hydrolysis takes place (1,2-addition–elimination) that becomes more favorable.

Proceeding from the quantum-chemical calculations the reaction between *N*-arylsulfinyl-1,4-benzoquinone monoimine **IIa** and methanol (**IVa**) should proceed to give a quinolide structure **Vw**, for the energy of the quinolide structure is less by 21.80 kJ mol^{-1} than the sum of the energies of the initial compounds. Yet compounds with vicinal SO and NH groups are unstable [18]. Therefore we presume that in this reaction first forms quinolide structure **Vw** which subsequently undergoes hydrolysis to compounds **VI** and **VIIIa**. This assumption was also confirmed by the investigation of the process by means of TLC: The formation of a product was detected

Table 2. Total energy of reagents and reaction products according to quantum-chemical calculations



Ia, Id, Ig, Ii, Ik
IIa, IIIa, IX

Va, Vp–Vw

R		E_{init},[a,b] a.u.		E_{end}, a.u.	ΔE_{theor}, kJ mol^{-1}
$MeSO_2$	**Ia**	–1028.121010	**Va**	–1143.847282	–2.83
$MeSO_2$	**Ia**	–1028.121010	**Vv**	–1183.167259	–1.94
CF_3SO_2	**Ig**	–1325.836011	**Vu**	–1441.56186	1.72
$PhSO_2$	**Id**	–1219.858931	**Vr**	–1335.586936	–7.39
$PhSO_2$	**Ij**	–1219.871946	**Vp**	–1335.593504	9.54
$PhSO_2$	**Ik**	–1141.226485	**Vq**	–1256.950338	3.52
PhSO	**IIa**	–1144.644101	**Vw**	–1260.377596	–21.80
PhS	**IIIa**	–1069.471307	**Vs**	–1185.186553	26.12
PhO	**IX**	–746.4719483	**Vt**	–862.1786274	48.61

[a] E_{init} = *E*(**I**–**IX**) + *E*(**IV**). [b]Energy of alcohols: *E*(**IVa**) –115.725193; *E*(**IVb**) –155.045511 a.u.

whose R_f was the value close to R_f of quinolide structures.

The analysis of the calculations data shows that from the thermodynamical viewpoint the reaction with alcohols is possible only for quinone monoimines with the CNS angle exceeding 130 deg. The presence of substituents in the positions *3* and *5* of the quinoid ring results in a steric strain in the node C=N–S and, consequently, in the activation of the C=N bond. Then the 1,2-addition becomes thermodynamically probable since this removes the steric strain: the C^4 atom in the product is sp^3-hybridized.

EXPERIMENTAL

Quantum-chemical calculations were performed using GAUSSIAN 03 software [19]. The molecular structure of compounds under study was calculated in the framework of the density functional theory applying functional B3LYP [20–25]. The standard basis set 6-31+G(d) [26, 27] was used in the calculations. The XRD data were taken as the initial parameters of the optimization. The geometrical parameters of quinone imines **Ia, Id, IIa, IIIa** after the optimization are well consistent with the XRD data.

IR spectra were taken on a spectrophotometer Vertex-70 from solutions in $CHCl_3$ (compounds **Ia–Ig, IIa**, **IIb, IIIa, IIIb, Va–Vf, Vh, Vi, Vk–Vo**) and in acetone (compounds **Vg, Vj**). ^{1}H NMR spectra were recorded on a spectrometer Varian VXR-300 (300 MHz) relative to TMS in $CDCl_3$ solution for compounds **Ib, Ic, IIa**, **IIb, Va–Vf, Vh, Vi** and in acetone-d_6 for compounds **Vg, Vj**. ^{13}C NMR spectra were recorded on a spectrometer Varian VXR-300 (75.4 MHz) in $CDCl_3$. The purity of quinone imines and the products of their reactions was checked

Table 3. Main crystallographic parameters of quinone imines **Ia, Ii, IIb, IIIb**

Characteristics	**Ia**	**Ii**	**IIb**	**IIIb**
Unit cell parameters, Å, deg	*a* 7.6940(5) *b* 8.6599(7) *c* 8.7955(6) α 65.159(7) *β* 72.246(6) γ 74.865(7)	*a* 6.0953(14) *b* 17.7251(19) *c* 19.188(9) β 91.14(3)	*a* 18.5040(7) *b* 8.7800(2) *c* 8.8490(3) β 98.780(3)	*a* 13.5844(12) *b* 11.8108(13) *c* 16.8848(16)
V, Å^3	500.46(6)	2072.7(11)	1420.81(8)	2709.0(5)
Crystal system	triclinic	monoclinic	monoclinic	rhombic
Space group	P-1	$P2_1/c$	$P2_1/c$	*P*bca
Z	2	4	4	8
F(000)	224	856	608	1088
D_{calc} g/cm^3	1.415	1.296	1.353	1.262
μ(MoK_α), mm^{-1}	0.304	0.189	0.234	0.226
$2\theta_{max}$, deg	60	50	50	50
Reflections measured	10253	8673	11009	9073
Number of independent reflections	2856	3598	2424	2342
R_{int}	0.017	0.026	0.043	0.055
Reflections with $F > 4\sigma(F)$	2317	2101	1586	880
Number of parameters	130	259	181	166
wR_2	0.085	0.071	0.155	0.113
R_1 [$F > 4\sigma(F)$]	0.030	0.036	0.053	0.049
S	1.017	0.980	1.011	0.776
CCDC number	848554	851690	848553	848552

by TLC on Silufol UV-254 plates. Chloroform, acetone, THF were used as solvents, eluents ethanol–chloroform, 1 : 10, benzene–hexane, 10:1, hexane–ethyl acetate, 1 : 2, development under UV radiation.

The XRD investigation of compounds **Ia** ($C_9H_{11}NO_3S$, *M* 213.25), **IIb** ($C_{15}H_{15}NO_3S$, *M* 289.34), **IIIb** ($C_{15}H_{15}NOS$, *M* 257.34), and **Ii** ($C_{20}H_{24}N_2O_5S$, *M* 404.47) was carried out at 293K on an automatic four-circle diffractometer Xcalibur 3 (MoK_α, graphite monochromator, CCD detector, ω-scanning). The structure was solved by the direct method applying SHELXTL software [28]. The refinement was carried out in an anisotropic approximation for the nonhydrogen atoms. The position of hydrogen atoms were found from the difference synthesis of the electron density and were refined in the *rider* model with $U_{iso} = nU_{eq}$ of the nonhydrogen atom linked to this hydrogen (n = 1.5 for methyl group, 1.2 for the other hydrogen atoms) with a fixed parameter of the thermal vibrations. The main crystallographic parameters are given in Table 3. The final atomic coordinates, geometric parameters of molecules and the crystallographic data are deposited in the Cambridge Crystallographic Data Center (e-mail: deposit@ccdc.cam.ac.uk).

Quinone imines were synthesized by known procedures: **Ia–Ic, Ig** [11], **Id, If** [7], **Ie** [12], **IIa, IIb** [29], **IIIa, IIIb** [14]. The characteristics of compounds are consistent with published data: **Ia, Ig** [11], **Id, If** [7], **Ie** [12], **IIIa, IIIb** [13, 14], **Vk–Vm** [2], **Vn, Vo** [3].

3,5-Dimethyl-*N*-ethylsulfonyl-1,4-benzoquinone monoimine (Ib). Yield 75%, mp 119–120°C. ^{1}H NMR spectrum, δ, ppm: 1.52 t (3H, $CH_2\underline{Me}$, *J* 7.8 Hz), 2.36 s (6H, 3,5-Me), 3.34–3.41 m (2H, $C\underline{H}_2Me$), 6.50 s (2H, H^{2,6}). Found, %: N 6.10, 6.29. $C_{10}H_{13}NO_3S$. Calculated, %: N 6.16.

3,5-Dimethyl-*N*-propylsulfonyl-1,4-benzoquinone monoimine (Ic). Yield 61%, mp 91–93°C. ^{1}H NMR spectrum, δ, ppm: 1.10–3.36 m (7H, Pr), 2.35 s (6H, 3,5-Me), 6.50 s (2H, H^{2,6}). Found, %: N 5.65, 5.88. $C_{11}H_{15}NO_3S$. Calculated, %: N 5.80.

3,5-Dimethyl-*N*-phenylsulfinyl-1,4-benzoquinone monoimine (IIa). Yield 82%, mp 79–81°C. ^{1}H NMR spectrum, δ, ppm: 2.34 s (6H, 3,5-Me), 6.42 s (2H, H^{2,6}), 7.55–7.83 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 21.50 (3,5-Me), 125.51 (C$^{2',6'}$), 129.39 (C$^{3',5'}$), 131.92 (C$^{4'}$), 132.26 (C^{2,6}), 145.95 (C$^{1'}$), 146.22 (C^{3,5}), 161.99 (C=N), 186.20 (C=O). Found, %: N 5.21, 5.45. $C_{14}H_{13}NO_2S$. Calculated, %: N 5.40.

3,5-Dimethyl-*N*-(4-methoxyphenyl)sulfinyl-1,4-benzoquinone monoimine (IIb). Yield 80%, mp 82–84°C. ^{1}H NMR spectrum, δ, ppm: 2.33 s (6H, 3,5-Me), 3.87 s (3H, 4-$\underline{Me}OC_6H_4$), 6.41 s (2H, H^{2,6}), 7.04 d (2H, H$^{3',5'}$, 4-$MeOC_6H_4$, *J* 8.7 Hz), 7.77 d (2H, H$^{2',6'}$, 4-$MeOC_6H_4$, *J* 8.7 Hz). ^{13}C NMR spectrum, δ, ppm: 21.53 (3,5-Me), 55.61 (MeO), 114.91 (C$^{3',5'}$), 127.38 (C$^{2',6'}$), 132.17 (C^{2,6}), 137.39 (C$^{1'}$), 146.23 (C^{3,5}), 160.98 (C=N), 162.64 (C$^{4'}$), 186.16 (C=O). Found, %: N 4.59, 4.83. $C_{15}H_{15}NO_3S$. Calculated, %: N 4.84.

Reactions of *N*-substituted 1,4-benzoquinone imines Ia–Ig, IIa, IIb, IIIa, IIIb with alcohols IVa–IVh. To a slurry of 1.4 mmol of benzoquinone monoimine **Ia–Ig, IIa, IIb, IIIa, IIIb** in ethyl ether at room temperature in a flow of argon was added 4 ml of anhydrous alcohol **IVa–IVh**. The yellow color of the initial quinone imines **Ia–If** gradually disappeared, and a colorless precipitate separated of compounds **Va–Vo** that were isolated and washed with hexane or petroleum ether. The reactions of quinone imines **Ia–Ic** with alcohols **IVb–IVh**, quinone imines **Ig, IIa, IIb** with alcohols **IVa–IVh**, and quinone imines **Id–If** with *t*-BuOH (**IVh**) were monitored by TLC over 2 months, then the solvent was distilled off in a vacuum to obtain the products of hydrolysis of initial quinone imines **Ia–Ig**. Mixtures of quinone imines **IIIa, IIIb** and alcohols **IVa–IVh** were maintained over 2 months at room temperature without air access, then the mixtures were boiled for 12 h and evaporated in a vacuum to recover initial quinone imines **IIIa, IIIb**.

***N*-(2,6-Dimethyl-1-methoxy-4-oxocyclohexa-2,5-dien-1-yl)methanesulfonamide (Va).** Yield 78%, mp 172–173°C. ^{1}H NMR spectrum, δ, ppm: 2.07 s (6H, 2,6-Me), 2.99 s (3H, $MeSO_2$), 3.04 s (3H, MeO), 5.28 br.s (1H, NH), 6.31 s (2H, H^{3,5}). Found, %: N 5.65, 5.87. $C_{10}H_{15}NO_4S$. Calculated, %: N 5.71.

***N*-(2,6-Dimethyl-4-oxo-1-ethoxycyclohexa-2,5-dien-1-yl)methanesulfonamide (Vb).** Yield 59%, mp 138–140°C. ^{1}H NMR spectrum, δ, ppm: 1.38 t (3H, $CH_2\underline{Me}$, *J* 7.8 Hz), 2.07 s (6H, 2,6-Me), 2.99–3.07 m (2H, $C\underline{H}_2Me$), 3.03 s (3H, MeO), 5.19 br.s (1H, NH), 6.30 s (2H, H^{3,5}). Found, %: N 5.34, 5.55. $C_{11}H_{17}NO_4S$. Calculated, %: N 5.40.

***N*-(2,6-Dimethyl-4-oxo-1-propoxycyclo-hexa-2,5-dien-1-yl)methanesulfonamide (Vc).** Yield 45%, mp 106–109°C. ^{1}H NMR spectrum, δ, ppm: 1.02–3.00 m (7H, Pr), 2.06 s (6H, 2,6-Me), 3.02 s (3H, MeO), 5.01 br.s (1H, NH), 6.30 s (2H, H^{3,5}). Found, %: N 5.01, 5.20. $C_{12}H_{19}NO_4S$. Calculated, %: N 5.12.

***N*-[2,6-Dimethyl-4-oxo-1-(propan-2-yloxy)-**

cyclohexa-2,5-dien-1-yl]benzenesulfonamide (Vd). Yield 66%, mp 122–123°C. ^{1}H NMR spectrum, δ, ppm: 1.08 d (6H, CH$\underline{Me}_2$, *J* 6.3 Hz), 1.76 s (6H, 2,6-Me), 3.52–3.60 m (1H, C$\underline{H}Me_2$), 5.53 br.s (1H, NH), 6.11 s (2H, H^{3,5}), 7.45–7.79 m (5H, Ph). Found, %: N 4.07, 4.21. $C_{17}H_{21}NO_4S$. Calculated, %: N 4.18.

***N*-(1-*tert*-Butoxy-2,6-dimethyl-4-oxo-cyclohexa-2,5-dien-1-yl)benzenesulfonamide (Ve).** Yield 47%, mp 135–137°C. ^{1}H NMR spectrum, δ, ppm: 0.88 d (6H, $CH_2CH\underline{Me}_2$, *J* 6.6 Hz), 1.72 s (6H, 2,6-Me), 1.72–1.82 m (1H, $CH_2C\underline{H}Me_2$), 2.74 d (2H, $C\underline{H}_2CHMe_2$, *J* 6.6 Hz), 5.44 br.s (1H, NH), 6.11 s (2H, H^{3,5}), 7.46–7.79 m (5H, Ph). Found, %: N 3.95, 4.15. $C_{18}H_{23}NO_4S$. Calculated, %: N 4.01.

***N*-(2,6-Dimethyl-4-oxo-1-pentyloxycyclohexa-2,5-dien-1-yl)benzenesulfonamide (Vf).** Yield 45%, mp 109–111°C. ^{1}H NMR spectrum, δ, ppm: 0.85– 2.98 m [11H, $(CH_2)_4Me$], 1.71 s (6H, 2,6-Me), 5.25 br.s (1H, NH), 6.10 s (2H, H^{3,5}), 7.45–7.76 m (5H, Ph). Found, %: N 3.81, 4.06. $C_{19}H_{25}NO_4S$. Calculated, %: N 3.85.

***N*-(2,6-Dimethyl-4-oxo-1-cyclohexyloxycyclohexa-2,5-dien-1-yl)benzenesulfonamide (Vg).** Yield 71%, mp 85–88°C. ^{1}H NMR spectrum, δ, ppm: 1.21–3.59 m (11H, Cy), 1.93 s (6H, 2,6-Me), 6.50 s (1H, NH), 6.59 s (2H, H^{3,5}), 7.51–7.92 m (5H, Ph). Found, %: N 3.60, 3.76. $C_{20}H_{25}NO_4S$. Calculated, %: N 3.73.

***N*-(1-*tert*-Butoxy-4-oxo-2,3,5,6-tetrachlorocyclohexa-2,5-dien-1-yl)-toluene-4-sulfonamide (Vh).** Yield 84%, mp 177–179°C. ^{1}H NMR spectrum, δ, ppm: 0.90 d (6H, $CH_2CH\underline{Me}_2$, *J* 6.3 Hz), 1.81–1.91 m (1H, $CH_2C\underline{H}Me_2$), 2.44 s (3H, 4-$\underline{Me}C_6H_4$), 2.88 d (2H, $C\underline{H}_2CHMe_2$, *J* 6.3 Hz), 4.90 br.s (1H, NH), 7.32 d (2H, H$^{3',5'}$, 4-MeC_6H_4, *J* 7.8 Hz), 7.82 d (2H, H$^{2',6'}$, 4-MeC_6H_4, *J* 7.8 Hz). Found, %: N 2.75, 3.00. $C_{17}H_{17}Cl_4NO_4S$. Calculated, %: N 2.96.

4-Methyl-*N*-(4-oxo-1-pentoxy-2,3,5,6-tetrachlorocyclohexa-2,5-dien-1-yl)benzenesulfonamide (Vi). Yield 82%, mp 160–162°C. ^{1}H NMR spectrum, δ, ppm: 0.85–3.14 m [11H, $(CH_2)_4Me$], 2.44 s (3H, 4-$\underline{Me}C_6H_4$), 5.65 br.s (1H, NH), 7.28 d (2H, H$^{3',5'}$, 4-MeC_6H_4, *J* 8.8 Hz), 7.56 d (2H, H$^{2',6'}$, 4-MeC_6H_4, *J* 8.8 Hz). Found, %: N 2.70, 2.98. $C_{18}H_{19}Cl_4NO_4S$. Calculated, %: N 2.87.

4-Methyl-*N*-(4-oxo-2,3,5,6-tetrachloro-1-cyclopentoxy-cyclohexa-2,5-dien-1-yl)benzene-sulfonamide (Vj). Yield 48%, mp 109–110°C. ^{1}H NMR spectrum, δ, ppm: 1.21–3.76 m (11H, Cy), 2.42 s (3H, 4-$\underline{Me}C_6H_4$), 6.51 br.s (1H, NH), 7.37 d (2H, H$^{3',5'}$, 4-MeC_6H_4, *J* 8.2 Hz), 7.78 d (2H, H$^{2',6'}$, 4-MeC_6H_4, *J* 8.2 Hz). Found, %: N 2.80, 2.98. $C_{19}H_{19}Cl_4NO_4S$. Calculated, %: N 2.81.

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