

Synthesis and ^{13}C NMR Spectra of N-Substituted *p*-Quinonimines: III.* N-Arylthio- and N-Arylsulfonyl-1,4-benzoquinonimines with Enhanced Electron-donor Character of Quinoid Ring

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Abstract—Incorporation of alkyl substituents into quinonimine fragments of N-arylthio- and N-arylsulfonyl-1,4-benzoquinonimines results in virtually equal changes in the chemical shifts of the carbon atoms from this fragment compared to those of unsubstituted and chloroderivatives. The substituents in the benzene ring also similarly affect the spectra of both groups of alkyl-substituted compounds. The pattern observed is due to the lack of a unique conjugation system, and the alterations revealed in the spectra might be caused by the changes in the geometry of the molecules.

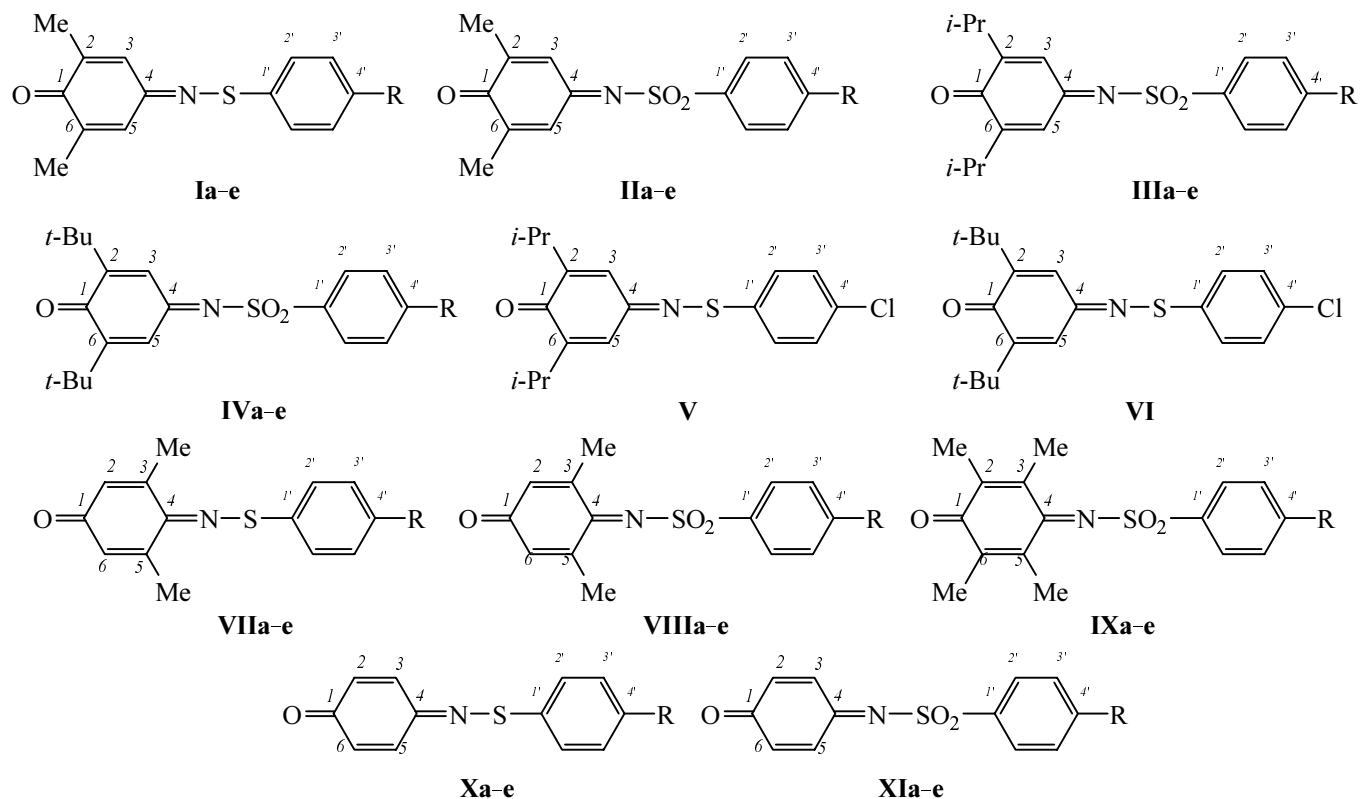
We formerly carried out a comparative investigation of ^{13}C NMR spectra of N-arylsulfonyl- and N-arylthio-1,4-benzoquinonimines substituted by chlorine in the quinonimine fragment. The study demonstrated that both the substituents in the benzene ring and chlorine atoms in the quinonimine moiety affected virtually in the same manner the chemical shifts of carbon atoms in the spectra of both groups of compounds [1]. Moreover, the changes in the chemical shifts proved to be similar when compared with those in the spectra of unsubstituted quinonimines [2] suggesting a conclusion on insignificant conjugation of the sulfur atom with the π -system of the quinonimine fragment.

Chlorosubstituted compounds were chosen in order to increase the electron-withdrawing character of the quinonimine fragment since in this case it was presumable that the interaction of the thioaryl part of the molecule with the quinonimine moiety would be enhanced. However it is still probable that the results obtained may mean the attainment of the maximum possible conjugation of the bivalent sulfur already in the unsubstituted N-arylthio-1,4-benzoquinonimines. Therefore further increase in the electron-withdrawing character of the quinonimine fragment did not provide

any significant changes in the chemical shifts of carbon atoms at variation of substituents in the benzene ring. To check the validity of this assumption we synthesized several series of N-arylthio- and N-aryl-sulfonyl-1,4-benzoquinonimines with electron-donor substituents in the quinonimine fragment, and their ^{13}C NMR spectra were measured. We chose as electron-donor substituents alkyl groups Me, *i*-Pr, and *t*-Bu. To facilitate the assignment of signals in the NMR spectra compounds **I–IX** were synthesized symmetrically substituted in the quinonimine fragment.

The data obtained by analysis of ^{13}C NMR spectra are presented in Table 1. Introduction of methyls into 2 and 6 positions of the quinonimine fragment affected virtually in the same manner the chemical shifts of carbon atoms in the spectra of both types of compounds [*N*-arylthio- (**I**) and *N*-arylsulfonyl- (**II**)-2,6-dimethyl-1,4-benzoquinonimines]: The signals from C³ and C⁵ were displaced upfield whereas the other carbon signals shifted downfield. The displacement in both cases also proved to be equal. Moreover, in the spectra of both groups compounds the changes in the chemical shifts of carbons belonging to the benzene ring also were the same: the introduction of methyl groups into the 2 and 6 positions shifted downfield the signal from atom C¹, and the degree

* For Communication II see [1].



R = MeO (a), Me (b), H (c), Cl (d), NO₂ (e).

of the shift was virtually independent of the character of substituents in the benzene ring. The identical transmission of electronic effects from one part of the molecule to another is also clear from the similar character of changes in the chemical shifts of carbon signals belonging to the quinonimine fragment on variation of substituents in the benzene ring. For instance, on going from the electron-donor substituents (R = OMe) to electron-withdrawing ones (R = NO₂) the chemical shift of C⁴ carbon changed in both groups of compounds by 1.7 ppm. Note that this value altered by virtually the same amount at varying the substituents character in the benzene ring both of unsubstituted [2] and 2,6-dichloro-substituted compounds [1].

The increase in donor properties of substituents attached to positions 2, 6 of the quinonimine fragment [N-arylsulfonyl-2,6-diisopropyl-1,4-benzoquinonimines (**IIIa-e**) and N-arylsulfonyl-2,6-di-*tert*-butyl-1,4-benzoquinonimines (**IVa-e**)] does not result in considerably different changes of the chemical shifts of the benzene ring carbons as compared with 2,6-dimethyl derivatives. The effect of the properties of substituents at the benzene ring on the chemical shifts of carbons belonging to the quinonimine fragment also is similar to

that observed in the other types of 2,6-disubstituted benzoquinonimines [1, 3]. As expected the largest shift of signals from atoms C¹, C², C⁴, and C⁶ in the series Me, *i*-Pr, *t*-Bu as compared to the spectra of unsubstituted compounds was observed for quinonimines **IVa-e** with *tert*-butyl substituents whereas for atoms C³ and C⁵ the maximal displacement occurred in quinonimine **V** with isopropyl substituents (cf. ¹³C NMR spectra of compounds **II**d, **III**, and **IV**d, Table 1). The same relations were observed also in the *N*-arylthio derivatives: *N*-4-chlorophenylthio-2,6-diisopropyl-1,4-benzoquinonimine (**V**), *N*-4-chlorophenylthio-2,6-di-*tert*-butyl-1,4-benzoquinonimine (**VI**) [cf. ¹³C NMR spectra of compounds **II**d, **V**, and **VI**, Table 1].

The observed pattern of changes in the carbon chemical shifts in going from unsubstituted and chlorine-containing 1,4-benzoquinonimines to the alkyl-substituted compounds, and also the similarity in transmission of the electronic effects from the benzene ring to the quinonimine part of the molecule for all types of 2,6-disubstituted benzoquinonimines in both groups of compounds confirms the former conclusion [1] on the lack of conjugation between the π-systems of quinonimine and benzene fragments in *N*-arylthio derivatives.

Table 1. Chemical shifts of carbon atoms (δ_c , ppm) in the ¹³C NMR spectra of N-arylthio- (**I**, **V**, **VI**, **VII**, **X**) and N-arylsulfonyl- (**II–IV**, **VIII**, **IX**, **XI**)-1,4-benzoquinonimines^a

Compd. no.	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ^{1'}	C ^{2'}	C ^{3'}	C ^{4'}	Alk	R
Ia	188.00 (+0.29)*	136.41 (+8.04)	135.83 (−3.37)	154.35 (+0.77)	123.51 (−2.97)	140.35 (+8.78)	128.69 (+0.91)	129.35 (−0.09)	115.06 (+0.11)	160.25 (−0.13)	16.53, 15.66	55.56
Ib	188.04 (+0.49)	136.38 (+8.01)	135.82 (−3.21)	154.37 (+0.73)	123.62 (−2.91)	140.42 (+8.85)	134.32 (+0.66)	126.29 (+0.05)	129.91 (−0.06)	137.96 (−0.50)	16.61, 15.73	21.17
Ic	187.95 (+0.34)	136.62 (+8.03)	135.80 (−3.38)	154.65 (+0.77)	123.70 (−2.98)	140.55 (+8.80)	137.81 (+0.84)	125.68 (+0.03)	129.16 (−0.09)	127.60 (−0.48)	15.69, 16.56	–
Id	187.85 (+0.38)	136.91 (+8.07)	135.66 (−3.40)	154.94 (+0.77)	123.73 (−3.05)	140.86 (+8.88)	136.34 (+0.87)	126.76 (−0.02)	129.34 (−0.10)	133.57 (−0.42)	16.57, 15.69	–
Ie	187.65 (+0.44)	137.81 (+8.22)	135.48 (−3.49)	156.03 (+0.68)	123.91 (−3.09)	141.65 (+8.96)	146.63 (+1.30)	124.16 (−0.20)	124.26 (−0.10)	146.29 (−0.49)	16.64, 15.75	–
IIa	186.63 (+0.74)	144.87 (+9.75)	136.53 (−4.01)	164.21 (+0.94)	126.70 (−3.42)	145.18 (+9.66)	131.93 (+0.79)	129.63 (−0.35)	114.25 (−0.15)	163.51 (−0.38)	16.01, 16.84	55.69
IIb	186.62 (+0.81)	145.00 (+9.84)	136.55 (−3.70)	164.56 (+0.92)	126.91 (−3.25)	145.30 (+9.75)	137.70 (+0.98)	127.47 (−0.17)	129.67 (−0.11)	144.36 (−0.05)	15.94, 16.78	21.61
IIc	186.56 (+0.83)	145.47 (+10.21)	136.45 (−3.87)	164.84 (+0.94)	126.96 (−3.28)	145.80 (+10.18)	140.59 (+0.89)	127.38 (−0.26)	129.05 (−0.10)	133.68 (−0.07)	15.96, 16.78	–
IIId	186.31 (+0.68)	145.32 (+9.82)	136.21 (−4.00)	164.98 (+0.74)	126.84 (−3.44)	145.62 (+9.75)	139.14 (+0.92)	128.81 (−0.30)	129.24 (−0.31)	139.87 (−0.66)	15.83, 16.66	–
IIe	186.32 (+0.90)	145.90 (+10.11)	135.88 (−3.89)	165.92 (+0.88)	127.04 (−3.32)	145.94 (+9.78)	146.32 (+1.14)	128.73 (−0.22)	124.27 (−0.07)	150.40 (+0.22)	16.16, 16.95	–
IIIa	185.28 (−0.61)	154.64 (+19.52)	133.27 (−7.27)	165.13 (+1.86)	123.42 (−6.70)	154.61 (+19.09)	132.11 (+0.97)	129.68 (−0.30)	114.29 (−0.11)	163.55 (−0.34)	21.53, 27.11, 27.84	55.68
IIIb	185.24 (−0.57)	154.71 (+19.55)	133.21 (−7.04)	165.45 (+1.81)	123.52 (−6.64)	154.68 (+19.13)	137.58 (+0.86)	127.45 (−0.19)	129.68 (−0.10)	144.37 (−0.54)	21.53, 27.09, 27.85	21.53
IIIc	185.21 (−0.52)	154.89 (+19.63)	133.12 (−7.20)	165.76 (+1.86)	123.63 (−6.61)	154.85 (+19.23)	140.53 (+0.83)	127.41 (−0.23)	129.09 (−0.06)	133.38 (−0.37)	21.56, 27.15, 27.88	–
IIId	185.15 (−0.48)	155.22 (+19.72)	132.98 (−7.23)	166.06 (+1.82)	123.62 (−6.66)	155.18 (+19.31)	139.09 (+0.87)	128.95 (−0.16)	129.39 (−0.16)	140.01 (−0.52)	21.55, 27.22, 27.94	–
IIIe	184.98 (−0.44)	155.83 (+20.04)	132.62 (−7.15)	166.84 (+1.80)	123.79 (−6.57)	155.79 (+19.63)	146.12 (+0.94)	128.78 (−0.17)	124.26 (−0.08)	150.48 (+0.30)	21.56, 27.34, 28.06	–
IVa	186.35 (+0.46)	157.24 (+22.12)	133.46 (−7.08)	165.47 (+2.20)	123.76 (−6.36)	157.24 (+21.72)	132.25 (+1.11)	127.68 (−2.30)	114.29 (−0.11)	163.52 (−0.37)	29.46, 30.88, 35.91, 36.44	55.67
IVb	186.39 (+0.58)	157.33 (+22.17)	133.41 (−6.84)	165.82 (+2.18)	123.91 (−6.25)	157.33 (+21.78)	137.73 (+1.01)	127.45 (−0.19)	129.73 (−0.05)	114.33 (−0.58)	29.50, 35.91, 36.49	21.65
IVc	186.27 (+0.54)	157.43 (+22.17)	133.27 (−7.05)	166.01 (+2.11)	123.93 (−6.31)	157.43 (+21.81)	140.62 (+0.92)	127.38 (−0.26)	129.02 (−0.13)	133.27 (−0.48)	29.43, 29.50, 35.96, 36.49	–
IVd	186.14 (+0.51)	157.67 (+22.17)	133.08 (−7.13)	166.26 (+2.02)	123.91 (+6.37)	157.67 (+21.80)	139.04 (+0.82)	128.85 (−0.26)	129.34 (−0.21)	139.96 (−0.57)	29.46, 35.96, 36.54	–
IVe	186.00 (+0.58)	158.35 (+22.56)	132.76 (−7.01)	167.00 (+1.96)	124.08 (−6.28)	158.35 (+22.19)	146.17 (+0.99)	128.71 (−0.24)	124.22 (−0.12)	150.42 (+0.24)	29.46, 36.10, 36.61	–
V	186.14 (−1.33)	150.45 (+21.60)	132.13 (−6.93)	155.37 (+1.20)	119.98 (−6.80)	146.67 (+14.69)	136.17 (+0.70)	126.67 (−0.11)	129.29 (−0.15)	133.37 (−0.62)	21.87, 26.35, 26.59	–
VI	187.24 (−0.23)	152.83 (+23.99)	132.43 (−6.63)	155.64 (+1.47)	120.62 (−6.16)	149.02 (+17.04)	136.36 (+0.89)	126.86 (+0.08)	129.31 (−0.13)	133.40 (−0.59)	29.52, 35.93	–

Table 1. (Contd).

Compd. no.	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ^{1'}	C ^{2'}	C ^{3'}	C ^{4'}	Alk	R
VIIa	187.16 (-0.55)	~129	~145 sh	152.39 (-1.19)	~145 sh	~129	131.76 (+3.98)	127.20 (-2.24)	114.99 (+0.04)	159.99 (-0.39)	21.8 sh	55.54
VIIb	187.17 (-0.38)	~129	141-145 sh	152.49 (-1.15)	141-145 sh	~129	137.24 (+3.58)	124.76 (-1.48)	129.94 (-0.03)	137.99 (-0.47)	21.3 sh	21.16
VIIc	187.06 (-0.55)	~129	141-145 sh	(-1.00)	141-145 sh	~129	140.48 (+3.51)	124.51 (-1.14)	129.24 (-0.01)	127.77 (-0.31)	21.7 sh	-
VIIId	187.02 (-0.45)	~131	148 sh	153.14 (-1.03)	142 sh	~127	138.84 (+3.37)	125.63 (-1.15)	129.41 (-0.03)	133.71 (-0.28)	20.0 sh, 22.0 sh	-
VIIe	186.82 (-0.39)	127.8 (-1.79)	148.2 (+8.4)	154.64 (-0.71)	142.2	132.2 (-0.5)	148.17 (+2.84)	123.90 (-0.46)	124.45 (+0.09)	147.00 (+0.22)	20.0 sh, 23.0 sh	-
VIIIa	186.10 (+0.21)	133.51 (-1.81)	146.96 (+11.63)	164.39 (+1.12)	146.96 (+11.63)	133.51 (-1.81)	134.41 (+3.27)	128.72 (-1.26)	114.07 (-0.33)	163.03 (-0.86)	20.48	55.55
VIIIb	186.07 (+0.26)	133.60 (-1.76)	147.02 (+11.81)	164.72 (+1.08)	147.02 (+11.81)	133.60 (-1.76)	139.44 (+2.72)	126.56 (-1.08)	129.53 (-0.25)	143.69 (-1.22)	20.68	21.57
VIIIc	186.11 (+0.38)	133.68 (-1.76)	146.89 (+11.61)	164.99 (+1.09)	146.89 (+11.61)	133.68 (-1.76)	142.58 (+2.88)	126.52 (-1.12)	128.89 (-0.26)	132.72 (-1.03)	20.48	-
VIIIId	185.95 (+0.32)	133.74 (-1.95)	146.62 (+11.37)	165.27 (+1.03)	146.62 (+11.37)	133.74 (-1.95)	141.00 (+2.78)	127.96 (-1.15)	129.15 (-0.40)	139.19 (-1.34)	20.34	-
VIIIe	185.97 (+0.55)	134.24 (-1.74)	146.46 (+11.39)	166.41 (+1.37)	146.46 (+11.39)	134.24 (-1.74)	147.89 (+2.71)	127.94 (-1.01)	124.32 (-0.02)	150.31 (+0.13)	20.41	-
IXa	185.48 (-0.41)	140.02 (+4.70)	142.18 (+6.85)	167.56 (+4.29)	142.18 (+6.85)	140.02 (+4.70)	134.79 (+3.65)	128.80 (-1.18)	114.00 (-0.40)	162.82 (-1.07)	12.80, 16.86	55.61
IXb	185.44 -0.37)	140.06 (+4.70)	142.11 (+6.90)	167.85 (+4.21)	142.11 (+6.90)	140.06 (+4.70)	140.02 (+3.30)	126.59 (-1.05)	129.40 (+0.25)	143.26 (-1.65)	12.80, 16.83	21.52
IXc	185.45 (-0.28)	140.23 (+4.79)	142.07 (+6.79)	168.19 (+4.29)	142.07 (+6.79)	140.23 (+4.79)	142.85 (+3.15)	126.56 (-1.07)	128.84 (-0.31)	132.52 (-1.23)	12.86, 16.83	-
IXd	185.33 (-0.30)	140.47 (+4.78)	141.86 (+6.61)	168.48 (+4.24)	141.86 (+6.61)	140.47 (+4.78)	141.36 (+3.14)	128.06 (-1.05)	129.12 (-0.43)	138.94 (-1.59)	12.87, 16.77	-
IXe	185.19 (-0.23)	141.05 (+5.07)	141.53 (+6.46)	169.40 (+4.36)	141.53 (+6.46)	141.05 (+5.07)	148.26 (+3.08)	127.84 (-1.11)	124.20 (-0.14)	149.91 (-0.27)	13.00, 16.70	-
Xa	187.71	128.37	139.20	153.58	126.48	131.57	127.78	129.44	114.95	160.38	-	-
Xb	187.55	128.37	139.03	153.64	126.53	131.57	133.66	126.24	129.97	138.46	-	-
Xc	187.61	128.59	139.18	153.88	126.68	131.75	136.97	125.65	129.25	128.08	-	-
Xd	187.47	128.84	139.06	154.17	126.78	131.98	135.47	126.78	129.44	133.99	-	-
Xe	187.21	129.59	138.97	155.35	127.00	132.69	145.33	124.36	124.36	146.78	-	-
XIa	185.89	135.12	140.54	163.27	130.12	135.52	131.14	129.98	114.40	163.89	-	-
XIb	185.81	135.16	140.25	163.64	130.16	135.55	136.72	127.64	129.78	144.91	-	-
XIc	185.73	135.26	140.32	163.90	130.24	135.62	139.70	127.64	129.15	133.75	-	-
XId	185.63	135.50	140.21	164.24	130.28	135.87	138.22	129.11	129.55	140.53	-	-
XIe	185.42	135.79	139.77	165.04	130.36	136.16	145.18	128.95	124.34	150.18	-	-

^a The changes in the chemical shift values of carbons compared to those of the respective atoms in the spectra of quinoneimines unsubstituted in the ring are given in parentheses. For compounds **VIIIa-e** and **IXa-e** chemical shifts of atoms C², C⁶ and C³, C⁵ are compared with the corresponding averaged chemical shifts of atoms C², C⁶ and C³, C⁵ of quinoneimines unsubstituted in the ring.

In the preceding study [1] we demonstrated that at incorporation of chlorine atoms into positions 3 and 5 of the quinoid ring the changes in carbon chemical shifts differ from those observed in the 2,6-dichloro-1,4-benzoquinonimines. This effect we attributed to the specific structural features of 3,5-disubstituted 1,4-benzoquinonimines (at two substituents in the *ortho*-position in respect to the imino group the bond angle-C=N-S increased [4]). It was interesting to establish what difference in the chemical shifts would arise on introducing alkyl substituents into positions 3 and 5 instead positions 2 and 6. It should be noted that introduction of substituents into the 3 and 5 positions of the quinonimine fragment results in decreasing the barrier to the *Z,E*-isomerization of the studied benzoquinonimine*. Consequently the signals from atoms C², C³, C⁵, C⁶ in the ¹³C NMR spectra of *N*-arylthiobenzoquinonimines are notably broadened, and the barrier for *N*-arylsulfonylbenzoquinonimine is decreased still stronger resulting in magnetic equivalence of atoms C², C⁶ and C⁵, C³ whose resonances appear as singlets.

The incorporation of methyl groups into positions 3 and 5 (quinonimines VIIa–e and VIIIa–e) differently affects the chemical shifts of C¹ and C⁴ in *N*-arylthio (VIIa–e) and *N*-arylsulfonyl (VIIIa–e) derivatives. Whereas in the spectra of the latter the changes are similar to those observed in the 2,6-dimethyl-substituted compounds, in the spectra of the *N*-arylthio derivatives the signals of C¹ and C⁴ are strongly shifted upfield. The changes in the chemical shifts of C², C³, C⁵, and C⁶ atoms occur in the same fashion. In the 3,5-dimethyl derivatives of the *N*-arylthio-1,4-benzoquinonimines the magnetic nonequivalence of atoms C³ and C⁵ is considerably reduced leading to closer chemical shift values of the corresponding signals compared to the spectra of unsubstituted and 2,6-dichloro-substituted compounds. Analogous effect was observed in 3,5-dichloro-substituted *N*-arylthiobenzoquinonimines [1]. Note that alkyl substituents introduced into positions 3 and 5 produce a considerable downfield shift of the signal from C¹ atom of the benzene ring as is also observed in the chloroderivatives of 1,4-benzoquinonimines [1]. In all likelihood the changes in chemical shifts here also are caused primarily by the altered geometry of molecules at incorporation of substituents into the *ortho*-position with respect to the imine carbon: The observed effect is due to increase in the CNS angle and not to electronic

effects of substituents. These changes in geometry are also responsible for the already mentioned reduced magnetic nonequivalence of C³ and C⁵ atoms in the 3,5-disubstituted compounds.

It should also be pointed out that like the case of 3,5-dichloro-substituted 1,4-benzoquinonimines the largest shift of the C¹ atom was observed in the *para*-methoxy derivatives and the smallest shift occurred in the *para*-nitro compounds. Similar changes in the chemical shifts of the benzene ring carbon signals of compounds substituted by chlorine as well as methyl group in the quinonimine fragment confirm the conclusion on the lack of conjugation between the π -systems of the quinonimine and benzene fragments.

We also investigated *N*-arylsulfonyl-2,3,5,6-tetramethyl-1,4-benzoquinonimines (IXa–e). The presence of four methyl groups resulted in the downfield shift of signals from atoms C²–C⁶ as was observed also in the other types of alkyl-substituted benzoquinonimines. At the same time the carbonyl carbon peak shifted upfield. The alterations in the chemical shifts of the benzene ring in this series of compounds are similar to those observed in the 3,5-dimethyl-substituted benzoquinonimines. Furthermore, the pattern of these changes is like that observed in the spectra of 3,5- and 2,3,5,6-chloro derivatives of arylsulfonyl-1,4-benzoquinonimines [1] testifying again to the conclusion on the origin of this changes lying in the geometrical and not electronic reasons. This statement is also supported by comparison of parameters of correlation equations that we calculated analogously to [1]:

$$\delta_{C^1} = a + b\delta_C.$$

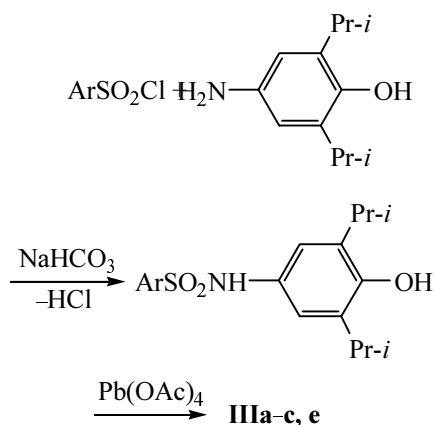
Here δ_{C^1} is the chemical shift of atom C¹ in benzoquinonimines under study, δ_C is the chemical shift of a

Table 2. Parameters of correlation equations of chemical shift values of C¹ atom in relation to the nature of substituent *R* in *N*-substituted 1,4-benzoquinonimines (*n* = 5)

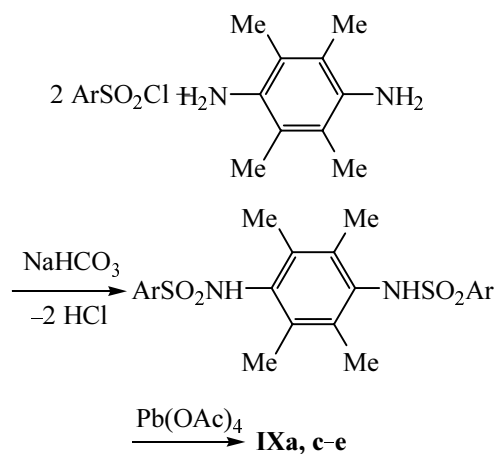
Compd. no.	<i>a</i>	<i>b</i>	<i>R</i>
I	138.42	1.29 (0.04)	0.998
II	140.46	1.02 (0.06)	0.994
III	140.39	1.00 (0.06)	0.995
IV	140.56	0.94 (0.04)	0.984
VII	140.82	1.18 (0.02)	0.999
VIII	142.31	0.97 (0.05)	0.996
IX	142.70	0.96 (0.05)	0.996

* The results of the study on conformational stability of substituted benzoquinonimines will be published elsewhere.

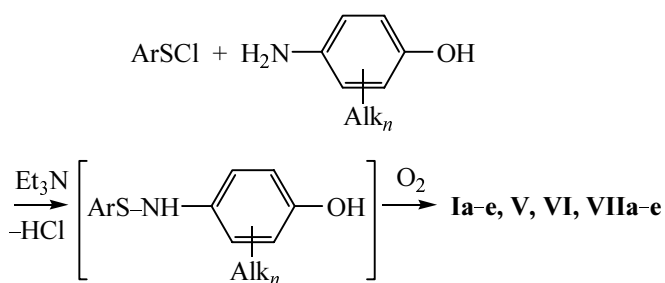
Scheme 1.



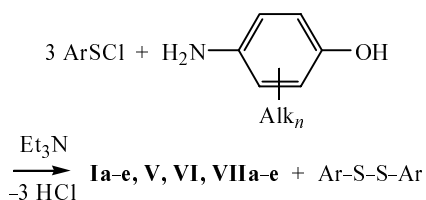
Scheme 2.



Scheme 3.



Scheme 4.



carbon atom in the *para*-position of a monosubstituted benzene $\text{C}_6\text{H}_5\text{R}$ (Table 2).

As seen from the data in Table 2 in the case of *N*-arylthio-1,4-benzoquinonimines in going from unsubstituted to 2,6-disubstituted compounds the character of variations in the *b* factor is nearly independent of the substituent nature and is the same for quinonimines substituted in the quinonimine fragment both by chlorine and methyl group. Analogous similarity in alterations of this factor is also observed for 3,5-disubstituted *N*-arylthio-1,4-benzoquinonimines. Therewith we believe that the significant decrease in the factor in the latter case is due to the change in the interaction character between the sulfur atom and the benzene ring originating first of all from structural reasons caused by the presence of substituents in the *ortho*-position with respect to nitrogen, i.e., by increased bond angle CNS. Note that whereas for arylthio derivatives of benzoquinonimines the value of the *b* factor depends on the presence of substituents at the quinonimine fragment, for arylsulfonyl derivatives, as seen from Table 2, the corresponding value is practically constant and notwithstanding the substituents nature and their location is equal to unity within the error limits thus revealing the barrier character of the SO_2 group. The dependence of the *b* factor in *N*-arylthio-1,4-benzoquinonimines on the presence of substituents at the quinonimine fragment although confirms the absence of a unique conjugation system in these compounds yet as we guess indicates that the bivalent sulfur somehow interacts with the quinonimine and aryl fragments.

In conclusion we present here refined assignments of the carbon chemical shifts for *N*-arylthio- (**Xa-e**) and *N*-arylsulfonyl- (**XIa-e**) -1,4-benzoquinonimine unsubstituted in the quinonimine fragment previously published in [2]. These data were used here in calculating the changes in the chemical shifts of carbons in compounds **I-IX** substituted in the quinonimine fragment. The data for *N*-4-methoxyphenylsulfonyl-1,4-benzoquinonimine (**XIa**) were obtained for the first time.

N-Arylsulfonyl-2,6-diisopropyl-1,4-benzoquinonimines (**IIIa-c, e**) were prepared for the first time from the corresponding *N*-arylsulfonyl-2,6-diisopropyl-1,4-aminophenols by oxidation with lead tetraacetate in acetic acid along procedure described in [5]. Initial *N*-arylsulfonyl-2,6-diisopropyl-1,4-aminophenols were obtained from 2,6-diisopropyl-1,4-aminophenol and appropriate arenesulfonyl chlorides in water in the presence of sodium hydrogen carbonate (Scheme 1) by procedure [6].

Table 3. Yields, melting point, and elemental analyses of *N*-arylthio-1,4-benzoquinonimines **Ia–e**, **V**, **VI**, **VIIa–e** and *N*-arylsulfonyl-1,4-benzoquinonimines **IIIa–e**, **IXa**, **c–e** alkyl-substituted in quinonimine ring

Compd. no.	Yield, %	mp, °C (solvent for crystallization)	Found S, %	Formula	Calculated S, %
Ia	34	85–86 (C ₇ H ₁₆)	11.68, 11.72	C ₁₅ H ₁₅ NO ₂ S	11.72
Ib	30	111–112 (C ₇ H ₁₆)	12.37, 12.42	C ₁₅ H ₁₅ NOS	12.45
Ic	29	147–148 (CH ₃ CO ₂ H)	13.20, 13.24	C ₁₄ H ₁₃ NOS	13.17
Id	21	137–138 (C ₇ H ₁₆)	11.55, 11.59	C ₁₄ H ₁₂ CINOS	11.53
Ie	30	155–156 (CH ₃ CO ₂ H)	11.04, 11.11	C ₁₄ H ₁₂ N ₂ O ₃ S	11.07
IIIa	34	78–79 (C ₇ H ₁₆)	8.80, 8.82	C ₁₉ H ₂₃ NO ₄ S	8.86
IIIb	29	80–81 (C ₇ H ₁₆)	9.15, 9.24	C ₁₉ H ₂₃ NO ₃ S	9.28
IIIc	25	70–71 (C ₇ H ₁₆)	9.64, 9.70	C ₁₈ H ₂₁ NO ₃ S	9.67
IIId	27	108–109 (C ₇ H ₁₆)	8.77, 8.94	C ₁₈ H ₂₀ CINO ₃ S	8.75
IIIe	31	146–147 (C ₇ H ₁₆)	8.17, 8.19	C ₁₈ H ₂₀ N ₂ O ₃ S	8.21
V	28	121–122 (CH ₃ CO ₂ H)	9.68, 9.74	C ₁₈ H ₂₀ CINOS	9.59
VI	22	112–113 (CH ₃ CO ₂ H)	8.79, 8.84	C ₂₀ H ₂₄ CINOS	8.85
VIIa	29	135–136 (CH ₃ CO ₂ H)	11.69, 11.75	C ₁₅ H ₁₅ NO ₂ S	11.72
VIIb	39	125–126 (C ₇ H ₁₆)	12.30, 12.44	C ₁₅ H ₁₅ NOS	12.45
VIIc	23	178–179 (C ₇ H ₁₆)	13.20, 13.25	C ₁₄ H ₁₃ NOS	13.17
VIIId	34	186–187 (C ₇ H ₁₆)	11.54, 11.57	C ₁₄ H ₁₂ CINOS	11.53
VIIe	22	227–228 (C ₆ H ₆)	11.00, 11.03	C ₁₄ H ₁₂ N ₂ O ₃ S	11.07
IXa	20	116–117 (C ₇ H ₁₆)	9.56, 9.63	C ₁₇ H ₁₈ NO ₄ S	9.64
IXc	27	99–100 (C ₇ H ₁₆)	10.47, 10.52	C ₁₆ H ₁₇ NO ₃ S	10.56
IXd	35	118–119 (C ₇ H ₁₆)	9.40, 9.45	C ₁₆ H ₁₆ CINO ₃ S	9.48
IXe	25	152–153 (C ₇ H ₁₆)	9.09, 9.14	C ₁₆ H ₁₆ N ₂ O ₃ S	9.17

N-Arylsulfonyl-2,3,5,6-tetramethyl-1,4-benzoquinonimines (**IXa**, **c–e**) were synthesized for the first time along procedure described in [7] for quinonimine **IXb** (Scheme 2).

N-arylthio-1,4-benzoquinonimines alkyl-substituted in the quinoid ring (**Ia–e**, **V**, **VI**, **VIIa–e**) were prepared for the first time by acylation of alkyl-substituted *para*-aminophenols with appropriate arenesulfonyl chlorides in the presence of triethylamine. In the course of the reaction the intermediate *N*-arylthio-1,4-aminophenols were oxidized by the air oxygen to the corresponding *N*-arylthio-1,4-benzoquinonimines (Scheme 3).

The yield of products was very low, and besides a lot of diaryldisulfides was found in the reaction mixture, apparently due to the competing reaction along Scheme 4.

EXPERIMENTAL

^{13}C and ^1H NMR spectra were registered on spectrometers Varian VXR-300 and GEMINI-200

(300 MHz and 200 MHz respectively) from solutions in CDCl₃. Chemical shifts are presented relative to TMS with accuracy for ^{13}C NMR spectra ± 0.05 and for ^1H NMR spectra ± 0.005 ppm.

N-Arylsulfonyl-1,4-benzoquinonimines **IIa–e**, **IVa–e**, and **VIIIa–e** were first described in [8, 9] and were prepared along these procedures.

***N*-arylthio-1,4-benzoquinonimines alkyl-substituted in the quinoid ring Ia–e, V, VI, VIIa–e.** To a suspension of 2 mmol of alkyl-substituted *p*-aminophenol in 20 ml of anhydrous ethyl ether were added equimolar amounts of an appropriate arenesulfonyl chloride and triethylamine. The separated precipitate of triethylamine hydrochloride was filtered off, the filtrate was evaporated under the reduced pressure of a water-jet pump. The formed precipitate of *N*-arylthio-1,4-benzoquinonimine was washed with methanol and acetic acid. Inasmuch as the product contained a considerable quantity of diaryldisulfide impurity, it was purified by several recrystallizations from a suitable solvent. The characteristics of *N*-arylthio-1,4-benzoquinonimines **Ia–e**, **V**, **VI**, **VIIa–e** are given in Table 3.

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