

# Synthesis and $^{13}\text{C}$ NMR Spectra of N-Substituted *para*-Quinone Imines: II.\* N-Arylthio- and N-Arylsulfonyl-1,4-benzoquinone Imines with Enhanced Electron-withdrawing Character of the Quinoid Ring

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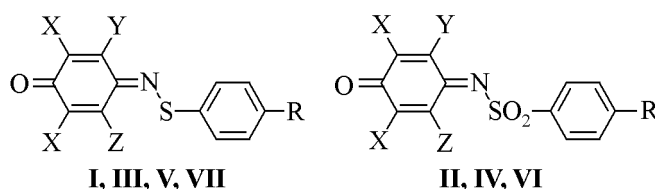
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**Abstract**—Introduction of chlorine substituents into quinone imine fragment results in virtually the same variations in the chemical shifts of the quinoid ring carbons both in *N*-arylthio and *N*-arylsulfonyl-1,4-benzoquinone imines as compared to the unsubstituted analogs. In both classes of chloro-substituted compounds the effect of substituents in the benzene ring on the character and the range of chemical shifts variations for the carbon signals from the quinoid ring also turned out to be identical. Any differences observed may be due to the change in the geometry of the molecules, in particular, to the increase in the bond angle C=N–S.

Previous investigations of  $^{13}\text{C}$  NMR spectra of unsubstituted *N*-arylthio and *N*-arylsulfonyl-1,4-benzoquinone imines [1] demonstrated that the electronic effects of substituents in the benzene ring were transmitted to the quinoid part of the molecule similarly both through the sulfur(II) atom and through  $\text{SO}_2$  group. This fact was unexpected for according to UV spectral data the bivalent sulfur atom in contrast to  $\text{SO}_2$  group was capable of conjugation with the quinone imine moiety [2]. We carried out investigation in more detail of the specific features of electron effects transmission in both types of compounds. To this end we synthesized and measured  $^{13}\text{C}$  NMR spectra of several series of *N*-arylthio and *N*-arylsulfonyl-1,4-benzoquinone imines substituted by chlorine in the quinoid ring. The choice of chlorine as a substituent was determined by its electron-withdrawing character since at the growing electron-acceptor quality of the quinoid ring the degree of the assumed conjugation between the thioaryl fragment and the quinone imine part should have increased. To avoid difficulties in the assignment of signals in  $^{13}\text{C}$  NMR spectra in case of the presence of *Z*-*E*-isomers we synthesized and investigated symmetrically substituted benzoquinone imines and 2,3,6-trichlorobenzoquinone imines that existed in a single conformation.\*\*



R =  $\text{CH}_3\text{O}$  (a),  $\text{CH}_3$  (b), H (c), Cl (d),  $\text{NO}_2$  (e); X = Cl (I–VI), (VII); Y = Cl (III–VII), H (I, II); Z = Cl (V–VII), H (I–IV).

Note that this study is also of independent interest for as far as we know this class of compound has not been subjected to systematic investigation by NMR spectroscopy.

The results of NMR spectra analysis are presented in Table 1.

As seen from Table 1, the replacement of hydrogens by chlorine in positions 2, 6 (compounds I and II) in both series of compounds results in virtually equal displacement of carbon signals in the quinone imine as well as in the aryl fragments compared to their position in the spectra of compounds unsubstituted in the quinoid ring. Therewith the character of these changes in the chemical shift values is nearly insensitive to the nature of the substituents in the benzene ring. The latter, as seen from the data obtained, affect the range of changes insignificantly.

\* For communication I, see [1].

\*\* The results of the study on conformational stability of substituted benzoquinone imines will be published elsewhere.

**Table 1.** Chemical shift values in  $^{13}\text{C}$  NMR spectra of *N*-arylthio- (**I**, **III**, **V**, **VII**) and *N*-arylsulfonyl- **II**, **IV**, **VI** 1,4-benzoquinone imines,  $\text{CDCl}_3$ , TMS,  $\delta_{\text{C}}$ , ppm

Compd.	$\text{C}^1$	$\text{C}^2$	$\text{C}^3$	$\text{C}^4$	$\text{C}^5$	$\text{C}^6$	$\text{C}^{1'}$	$\text{C}^{2'}$	$\text{C}^{3'}$	$\text{C}^{4'}$	R
<b>Ia</b>	173.42 (-14.29) <sup>a</sup>	133.52 (+5.15)	136.17 (-3.03)	150.19 (-3.39)	123.60 (-2.88)	138.10 (+6.53)	127.36 (-0.42)	129.21 (-0.23)	115.15 (+0.20)	160.83 (+0.45)	55.54
<b>Ib</b>	173.49 (-14.06)	133.44 (+4.77)	136.20 (-2.83)	150.22 (-3.42)	123.75 (-2.78)	138.01 (+6.44)	133.09 (-0.57)	126.09 (-0.15)	130.12 (+0.15)	139.24 (+0.78)	21.26
<b>Ic</b>	173.46 (-14.15)	133.68 (+5.09)	136.21 (-2.97)	150.49 (-3.39)	123.87 (-2.81)	138.23 (+6.48)	136.41 (-0.56)	125.58 (-0.07)	129.39 (+0.14)	128.68 (+0.60)	
<b>Id</b>	173.44 (-14.03)	133.95 (+5.11)	136.13 (-2.93)	150.78 (-3.39)	123.98 (-2.80)	138.50 (+6.52)	134.86 (-0.61)	126.75 (-0.03)	129.60 (+0.16)	134.71 (+0.72)	
<b>Ie</b>	173.24 (-13.97)	134.94 (+5.35)	136.05 (-2.92)	152.02 (-3.33)	124.26 (-2.74)	139.35 (+6.66)	144.40 (-0.93)	124.58, (+0.22)	124.52 (+0.16)	147.36 (+0.58)	
<b>IIa</b>	172.10 (-13.79)	141.00 (+5.88)	137.75 (-2.79)	159.66 (-3.61)	127.43 (-2.69)	142.45 (+6.93)	130.59 (-0.55)	130.20 (+0.22)	114.58 (+0.18)	164.24 (+0.35)	55.82
<b>IIb</b>	172.04 (-13.77)	141.11 (+5.95)	137.65 (-2.60)	160.03 (-3.61)	127.54 (-2.62)	142.55 (+7.00)	136.31 (-0.41)	127.84 (+0.20)	129.93 (+0.15)	145.35 (+0.44)	21.71
<b>IIc</b>	172.00 (-13.73)	141.26 (+6.00)	137.55 (-2.77)	160.38 (-3.52)	127.64 (-2.60)	142.68 (+7.06)	139.29 (-0.41)	127.76 (+0.12)	129.29 (+0.14)	134.10 (+0.35)	
<b>IId</b>	171.92 (-13.71)	141.49 (+5.99)	137.39 (-2.82)	160.62 (-3.62)	127.61 (-2.67)	142.90 (+7.03)	137.74 (-0.48)	129.23 (+0.12)	129.63 (+0.08)	140.92 (+0.39)	
<b>IIe</b>	171.76 (-13.66)	142.01 (+6.22)	137.00 (-2.77)	161.48 (-3.56)	127.75 (-2.61)	143.38 (+7.22)	144.68 (-0.50)	129.11 (+0.16)	124.47 (+0.13)	150.83 (+0.65)	
<b>IIIa</b>	172.17 (-15.54)	133.1 br (+4.73)	141.49 (+2.29)	144.77 (-8.81)	123.64 (-2.84)	136.40 (+4.83)	127.77 (-0.01)	127.81 (-1.63)	115.23 (+0.28)	160.66 (+0.28)	55.57
<b>IIIb</b>	172.22 (-15.33)	133.19 (+4.82)	141.7 (+2.67)	144.97 (-8.67)	123.78 (-2.75)	136.64 (+5.07)	133.57 (-0.09)	125.30 (-0.94)	130.25 (+0.38)	139.17 (+0.71)	21.25
<b>IIIc</b>	172.16 (-15.45)	133.32 (+4.73)	141.60 (+2.42)	145.23 (-8.65)	123.89 (-2.79)	136.82 (+5.07)	136.78 (-0.19)	124.91 (-0.74)	129.51 (+0.26)	128.65 (+0.57)	-
<b>IIId</b>	172.04 (-15.43)	133.60 (+4.76)	141.55 (+2.49)	145.53 (-8.64)	123.97 (-2.81)	137.13 (+5.15)	134.75 (-0.78)	126.18 (-0.60)	129.74 (+0.30)	135.17 (+1.18)	-
<b>IIIe</b>	171.90 (-15.31)	133.16 (+3.57)	141.62 (+2.65)	146.71 (-8.64)	124.16 (-2.84)	137.99 (+5.30)	144.48 (-0.85)	124.61, (+0.25)	124.43 (+0.07)	147.35 (+0.57)	
<b>IVa</b>	170.59 (-15.30)	139.21 (+4.09)	143.10 (+2.56)	155.54 (-7.73)	127.11 (-3.01)	141.39 (+5.87)	130.36 (-0.78)	130.11 (+0.13)	114.50 (+0.10)	164.11 (+0.22)	55.77
<b>IVb</b>	170.59 (-15.22)	139.35 (+4.19)	143.08 (+2.83)	156.03 (-7.61)	127.28 (-2.88)	141.54 (+5.99)	136.12 (-0.60)	127.75 (+0.11)	129.94 (+0.16)	145.42 (+0.51)	21.79
<b>IVc</b>	170.54 (-15.19)	139.47 (+4.21)	143.00 (+2.68)	156.39 (-7.51)	127.35 (-2.89)	141.71 (+6.09)	139.14 (-0.56)	127.64 (0.0)	129.32 (+0.17)	134.18 (+0.43)	

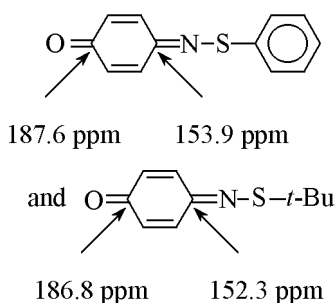
Table 1. Contd.

Compd.	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>	C <sup>1'</sup>	C <sup>2'</sup>	C <sup>3'</sup>	C <sup>4'</sup>	R
<b>IVd</b>	170.45 (-15.18)	139.69 (+4.19)	142.83 (+2.62)	156.67 (-7.57)	127.31 (-2.97)	141.97 (+6.10)	137.65 (-0.57)	129.14 (+0.03)	129.68 (+0.13)	140.93 (+0.40)	
<b>IVe</b>	170.20 (-15.22)	140.08 (+4.29)	142.44 (+2.67)	157.54 (-7.50)	127.33 (-3.03)	142.48 (+6.32)	144.60 (-0.58)	128.93 (-0.02)	124.50 (+0.16)	150.75 (+0.57)	
<b>Va</b>	169.90 (-17.81)	136.95 (+8.19)	141.64 (+2.44)	137.20 (-16.38)	132.03 (+5.55)	135.38 (+3.81)	131.97 (+4.19)	126.41 (-3.03)	115.15 (+0.20)	160.68 (+0.30)	55.59
<b>Vb</b>	169.90 (-17.65)	136.06 (+7.69)	141.80 (+2.77)	137.43 (-16.21)	132.20 (+5.67)	135.55 (+3.98)	137.43 (+3.77)	124.42 (-1.82)	130.20 (+0.23)	139.41 (+0.95)	21.31
<b>Vc</b>	169.92 (-17.69)	136.09 (+7.50)	141.89 (+2.71)	137.70 (-16.18)	132.39 (+5.71)	135.79 (+4.04)	140.37 (+3.40)	124.27 (-1.38)	129.50 (+0.25)	128.92 (+0.84)	-
<b>Vd</b>	169.81 (-17.66)	136.03 (+7.19)	141.75 (+2.69)	138.04 (-16.13)	132.67 (+5.89)	136.10 (+4.12)	138.79 (+3.32)	125.55 (-1.23)	129.69 (+0.25)	135.01 (+1.02)	-
<b>Ve</b>	169.70 (-17.51)	136.13 (+6.54)	141.83 (+2.86)	139.24 (-16.11)	133.45 (+6.45)	136.87 (+4.18)	147.45 (+2.12)	124.38, (+0.02),	124.64 (+0.28)	147.66 (+0.88)	-
<b>VIa</b>	169.27 (-16.62)	139.73 (+4.61)	140.10 (-0.44)	149.62 (-13.65)	140.10 (+9.98)	139.73 (+4.21)	133.87 (+2.73)	129.36 (-0.62)	114.30 (-0.10)	163.65 (-0.24)	55.75
<b>VIb</b>	169.21 (-16.60)	139.91 (+4.75)	139.69 (-0.56)	149.83 (-13.81)	139.69 (+9.53)	139.91 (+4.36)	138.88 (+2.16)	126.93 (-0.71)	129.69 (-0.09)	144.37 (-0.54)	21.68
<b>VIc</b>	169.16 (-16.57)	139.88 (+4.62)	139.84 (-0.48)	150.11 (-13.79)	139.84 (+9.60)	139.88 (+4.26)	141.78 (+2.08)	126.87 (-0.77)	129.10 (-0.05)	133.38 (-0.37)	
<b>VIId</b>	169.07 (-16.56)	140.05 (+4.55)	139.69 (-0.52)	150.42 (-13.82)	139.69 (+9.41)	140.05 (+4.18)	140.27 (+2.05)	128.35 (-0.76)	129.42 (-0.13)	139.93 (-0.60)	
<b>VIe</b>	168.89 (-16.53)	140.64 (+4.85)	139.53 (-0.24)	151.31 (-13.73)	139.53 (+9.17)	140.64 (+4.48)	147.41 (+2.23)	124.43 (+0.09)	128.24 (-0.71)	150.57 (-0.39)	
<b>VIIa</b>	182.61 (-5.10)	130.28 (+1.91)	145.22 (+6.02)	139.41 (-14.17)	139.30 (+12.82)	126.58 (-4.99)	132.15 (+4.37)	126.37 (-3.07)	115.06 (+0.11)	160.41 (+0.03)	55.52
<b>VIIb</b>	182.73 (-4.82)	130.44 (+2.07)	145.47 (+6.44)	139.69 (-13.95)	139.45 (+12.92)	126.71 (-4.86)	137.62 (+3.96)	124.49 (-1.75)	130.09 (+0.12)	138.89 (+0.43)	21.20
<b>VIIc</b>	182.51 (-5.10)	130.79 (+2.20)	145.3 in (+6.12)	140.25 (-13.63)	139.4 m (+12.72)	127.06 (-4.69)	140.25 (+3.28)	125.51 (-0.14)	129.59 (+0.34)	128.47 (+0.39)	-
<b>VIIId</b>	182.50 (-4.97)	130.84 (+2.00)	145.0 in (+5.94)	140.31 (-13.86)	139.4 m (+12.62)	127.11 (-4.87)	139.10 (+3.63)	125.57 (-1.21)	129.61 (+0.17)	134.68 (+0.69)	-
<b>VIIe</b>	182.35 (-4.86)	131.28 (+1.69)	145.28 (+6.31)	141.34 (-14.01)	139.37 (+12.37)	127.62 (-5.05)	147.87 (+2.54)	124.12 (-0.24)	124.52 (+0.16)	147.40 (+0.62)	-

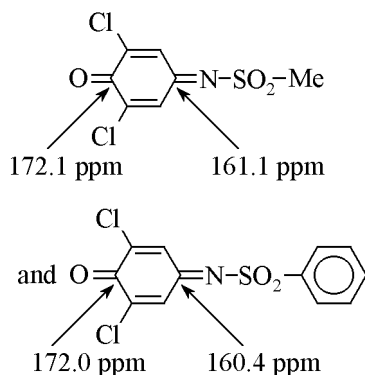
<sup>a</sup> The changes in chemical shift values occurring on substitution of quinone imines with chlorine in the quinone ring are given in parentheses

Note that whereas for  $\text{C}^3$  and  $\text{C}^5$  atoms the changes in the chemical shifts values at introduction of a chlorine atom are virtually the same, for both atoms and in both series of compounds ( $\text{ArS}$  and  $\text{ArSO}_2$ ), the variation of chemical shift  $\delta_{\text{C}^6}$  is in both series of compounds more significant than  $\delta_{\text{C}^2}$ . Variation of substituents in the benzene ring in both series of compounds (*N*-arylthio and *N*-arylsulfonyl derivatives) affects the chemical shifts of carbons in the quinone imine moiety to the same extent as in the unsubstituted benzoquinone imines. This fact is an evidence of insignificant conjugation of the bivalent sulfur with the  $\pi$ -system of the quinoid ring. In the reverse case the changes in the chemical shift values for *N*-arylthio derivatives should be larger than for *N*-arylsulfonyl derivatives. This conclusion is also supported by analysis of  $^{13}\text{C}$  NMR spectra of trichloro-substituted benzoquinone imines (compounds **III** and **IV**).

As show the data in Table 1, the introduction of one more chlorine into the quinone imine fragment does not bring significant additional change in the chemical shifts of carbon atoms in the compound series under investigation. Note that the lack of considerable conjugation between bivalent sulfur and quinone imine fragment follows also from comparison of carbon chemical shifts in quinone imine fragments of *N*-phenylthio-1,4-benzoquinone imine [1] and of *N*-*tert*-butylthio-1,4-benzoquinone imine [3].



The observed upfield shift of the signal from imino group  $\text{C}=\text{N}$  carbon when the benzene ring is replaced

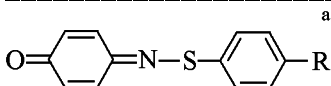
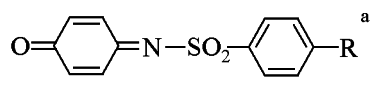


by *tert*-butyl group might be ascribed to increased transfer of the electron density from the sulfur atom to the quinoid ring. However we performed a similar comparison for *N*-methylsulfonyl-2,6-dichloro-1,4-benzoquinone imine and quinone imine **IIc** where no conjugation was possible, and the change in the chemical shift values was similar.

It should be noted that introduction of chlorine atoms into the quinoid ring differently affects the chemical shifts of carbon atoms in the benzene ring of arylsulfonyl and arylthio derivatives. For instance, in the dichloro- and trichloro-substituted arylsulfonyl derivatives the largest displacement of signal from  $\text{C}^{1'}$  atom suffers the compound with  $\text{R} = \text{OMe}$ , whereas in the arylthio derivatives the largest shift occurs in the compound with  $\text{R} = \text{NO}_2$ .

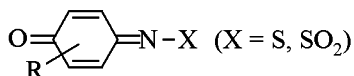
In derivatives with four chlorine atoms in the quinone imine fragment (compounds **V** and **VI**) the chemical shifts of carbons suffer great changes both in quinoid and aryl parts of the molecules. As seen from Table 1, in contrast to arylsulfonyl compounds in the spectra of the arylthio derivatives occur considerably larger changes in the  $\delta_{\text{C}^4}$  values as compared to quinone imines unsubstituted in the ring. Thus whereas in sulfonyl derivatives **VI** this value alters by  $\sim 13.7$  ppm, in the thiocompounds **V** this change exceeds 16 ppm. Even larger alterations are observed in the chemical shifts of  $\text{C}^{1'}$  atom. Therewith the character of the changes is opposite to that observed in 2,6- and 2,3,6-substituted compounds. For instance, whereas in the latter the signal of  $\text{C}^{1'}$  atom is shifted upfield, this signal in the tetrachloro derivatives is displaced downfield as compared to compounds unsubstituted in the ring. It may be assumed that the presence of four chlorine atoms in the quinoid part of the  $\text{ArS}$  derivatives resulted in decreased interaction of sulfur with the benzene ring and consequently its enhanced interaction with the quinone imine fragment. However the data in Table 1 show that analogous changes in the chemical shift of  $\text{C}^{1'}$  atom are observed also in tetrachlorosulfonyl derivatives **VI**. Apparently the difference observed is caused mostly by the changes in the geometry of the molecules at introduction of substituents into positions 3 and 5 (namely, by increase in the angle  $\text{C}=\text{N}-\text{S}$  [4]) and not by electronic effects due to the presence of four chlorine atoms. This assumption is also supported by the analysis of  $^{13}\text{C}$  NMR spectra of 3,5-dichlorosubstituted *N*-arylthio-1,4-benzoquinone imines **VII**. As seen from Table 3, the presence of only two chlorine atoms results in virtually identical shift of the signal from  $\text{C}^{1'}$  atom as is observed in the spectra of tetrachloro derivatives.

**Table 2.** Parameters of correlation equations

Compounds	<i>a</i>	<i>b</i>	Correlation factor, <i>r</i>	Number of points, <i>n</i>
	137.89	1.36 (0.06)	0.997	5
	139.28	0.99 (0.07)	0.992	6
<b>I</b>	136.80	1.22 (0.03)	0.999	5
<b>II</b>	138.92	1.03 (0.07)	0.993	5
<b>III</b>	137.03	1.20 (0.02)	0.999	5
<b>IV</b>	138.88	1.01 (0.07)	0.993	5
<b>V</b>	140.63	1.11 (0.02)	0.999	5
<b>VI</b>	141.62	0.97 (0.03)	0.999	5
<b>VII</b>	140.84	1.12 (0.04)	0.998	5

<sup>a</sup> Data from [1].

To reveal the specific features of interaction between the fragment



and benzene ring we calculated correlations suggested in [5] of the following kind:

$$\delta_{C^{I'}} = a + b\delta_C,$$

where  $\delta_{C^{I'}}$  is chemical shift value of  $C^{I'}$  atom in the benzoquinone imines under study,  $\delta_C$  are the corresponding chemical shifts of carbons in the *para*-position of monosubstituted benzenes  $C_6H_5R$ .

Parameters of the correlation equations obtained are given in Table 2.

The presented data show that for all N-arylsulfonyl derivatives under study the factor *b* practically equals unity thus giving an evidence of a barrier character of  $SO_2$  group in transmission of electronic effects along a  $\pi$ -system. The pattern is quite different with *N*-arylthio-1,4-benzoquinone imines. The deviation of the *b* factor from unity demonstrates the nonadditive character of the interaction between the moiety neighboring to the benzene ring and the  $\pi$ -electron orbitals of the  $C^{I'}$  atom. We believe that the increase in this factor means the less efficient interaction of the sulfur atom with the benzene ring. The least values of the *b* factor observed for tetrachloro and 3,5-dichloro derivatives **VI**, **VII** evidence that the change in the

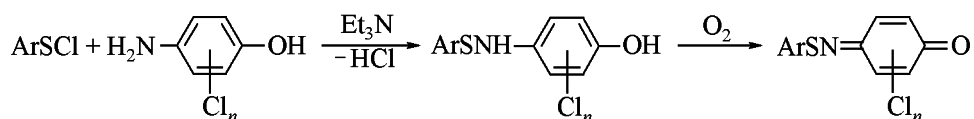
character of interaction between the sulfur and benzene ring is first of all caused by the altered geometry of molecules due to the presence of bulky substituents in the *ortho*-position with respect to nitrogen [4].

The use of  $\sigma_p$  constants permitted [1] quantitative estimation of transfer of electronic effect from substituent R on the quinoid fragment in the molecules of unsubstituted benzoquinone imines. As indicator center there was chosen  $C^4$  atom. We also calculated analogous correlations in order to establish the extent of substituents influence on the transmission of the electronic effects. As a result the equations given below were obtained describing the variation of chemical shift of  $C^4$  atom as a function of substituent R character.

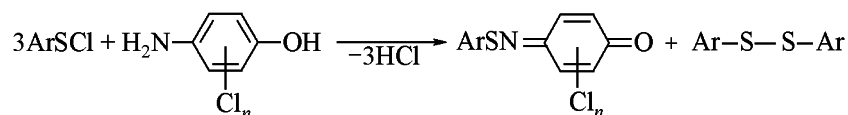
The equations obtained revealed some increase in transmission of the electronic effects of the R substituents through the bivalent sulfur but this increase is comparable with that observed for arylsulfonyl derivatives. This fact confirms the absence of a unified conjugation system in the *N*-arylthio-1,4-benzoquinone imines.

Apparently in both compounds classes the increase in sensitivity of  $\delta_{C^4}$  value to the nature of the character of R substituent as compared to the substances unsubstituted in the quinoid ring is due to stronger polarization of  $\pi$ -bond  $C=N$  to the carbon; as a result the range of chemical shifts variation increases. The decrease of the factor for tetrachloro-sulfonyl derivatives **VI** may be caused by structural changes.

## Scheme 1.



## Scheme 2.



Thus the analysis of chemical shift values in chloro-substituted 1,4-benzoquinone imines **I-VII** testifies to the absence of the conjugation between the bivalent sulfur atom and  $\pi$ -system of the quinone imine moiety.

The assignment of carbon signals in the  $^{13}\text{C}$  NMR spectra was carried out basing on the data of [1]. To perform more exact attribution of carbon signals in the spectra of *N*-arythio-3,5-dichloro-1,4-benzoquinone imines (**VIIa-e**) and *N*-arythio-2,3,5,6-tetrachloro-1,4-benzoquinone imines (**Va-e**) we measured  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of *N*-4-chlorophenylthio-2,3,5-trichloro-1,4-benzoquinone imine [2]. According to  $^1\text{H}$  NMR spectrum the compound exists as a mixture of *Z,E*-isomers in 0.37:0.63 ratio. In the  $^{13}\text{C}$  NMR spectrum of the compound the signal of  $\text{C}^6$  atom attached to a proton appears as two signals at 129.4 ppm (less intensive) and at 126.0 ppm (more intensive). Our quantum-chemical calculations by PM3 method revealed that as expected the more favored was *E*-isomer. Therefore its signal in the  $^{13}\text{C}$  NMR spectrum should be that at 126.0 ppm. Consequently the signal of  $\text{C}^6$  atom in the *Z*-isomer is located at 129.4 ppm.

*N*-Arylsulfonyl-2,6-dichloro-1,4-benzoquinone imines **IIa, e**, and *N*-arylsulfonyl-2,3,6-trichloro-1,4-benzoquinone imines **IVa, e** were prepared for the first time from the corresponding *N*-arylsulfonyl-1,4-aminophenols by successive oxidation with lead tetraacetate and hydrochlorination with gaseous hydrogen chloride in chloroform or dimethylformamide by procedures similar to those described in [6, 7].

*N*-4-Nitrophenylsulfonyl-2,3,5,6-tetrachloro-1,4-benzoquinone imine **VIId** was obtained for the first time by chlorination of *N*-4-nitrophenylsulfonyl-1,4-aminophenol by procedure similar to that published in [8].

Chloro-substituted in the quinoid ring *N*-arythio-1,4-benzoquinone imines **Ia, b, d, e, IIIa-c, e, VIIa-e** were first synthesized by acylation of chloro-

substituted *p*-aminophenols with the corresponding arylsulfonyl chlorides in the presence of triethylamine. Here the intermediate *N*-arythio-1,4-aminophenols were oxidized by air oxygen into the corresponding quinone imines (Scheme 1).

The yield of the target products was very low, and besides in the reaction mixture arise considerable amounts of diaryl disulfides presumably formed by a parallel reaction along Scheme 2.

The concurrent characteristics of the newly obtained quinone imines are presented in Table 3.

## EXPERIMENTAL

$^{13}\text{C}$  NMR spectra were registered on spectrometers Varian VXR-300 and Gemini-200 from solutions in  $\text{CDCl}_3$ . The chemical shifts were measured relative to TMS with an accuracy  $\pm 0.05$  ppm.

Compound **Ic** was prepared by procedure described in [9], compounds **IIb, c, IVb, c** by procedure from [10], compounds **IIId, IVd, VIb-d** by that from [8], compounds **IIIId, Va, b, d, e** by that from [11], preparation of compound **Vc** was published in [12], that of compound **VIa** in [13].

***N*-4-Nitrophenylsulfonyl-2,3,5,6-tetrachloro-1,4-benzoquinone imine (VIe)**. Through a suspension of 1 g of *N*-4-nitrophenylsulfonyl-1,4-aminophenol in 6 ml of a mixture DMF- $\text{CH}_3\text{COOH}$  (1:5) at room temperature was passed a stream of chlorine at a rate 15–20 ml  $\text{min}^{-1}$  till separated a colorless precipitate of 4-(4-nitrophenyl)sulfonylimino-2,3,5,6,6-pentachloro-2-cyclohexen-1-one. The precipitate was filtered off and washed with small portions of acetic acid. In air within 24 h the 4-(4-nitrophenyl)sulfonylimino-2,3,5,6,6-pentachloro-2-cyclohexen-1-one underwent dehydrochlorination to furnish orange *N*-4-nitrophenylsulfonyl-2,3,5,6-tetrachloro-1,4-benzoquinone imine (**VIId**).

**Table 3.** Yields, melting points, and elemental analyses of *N*-arylthio-1,4-benzoquinone imines **Ia-e**, **IIIa-c, e**, **VIIa-e** and *N*-arylsulfonyl-1,4-benzoquinone imines **IIa, e**, **IVa, e**, **VIe** substituted with chlorine in the quinoid ring

Compd. no.	Yield, %	mp, °C (solvent for crystallization)	Found S, %	Formula	Calculated S, %
<b>Ia</b>	25	153 (CH <sub>3</sub> CO <sub>2</sub> H)	9.98, 10.07	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>2</sub> S	10.19
<b>Ib</b>	21	184 (CH <sub>3</sub> CO <sub>2</sub> H)	10.71, 10.80	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> NOS	10.74
<b>Ic</b> [10]	28	186 (CH <sub>3</sub> CO <sub>2</sub> H)	11.07, 11.21	C <sub>12</sub> H <sub>7</sub> Cl <sub>2</sub> NOS	11.27
<b>Id</b>	32	168 (CH <sub>3</sub> CO <sub>2</sub> H)	10.06, 10.11	C <sub>12</sub> H <sub>6</sub> Cl <sub>3</sub> NOS	10.05
<b>Ie</b>	37	262 (CH <sub>3</sub> CO <sub>2</sub> H)	9.68, 9.75	C <sub>12</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub> S	9.73
<b>IIa</b>	76	123 (CH <sub>3</sub> CO <sub>2</sub> H)	9.51, 9.64	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>4</sub> S	9.68
<b>IIe</b>	64	135 (CH <sub>3</sub> CO <sub>2</sub> H)	8.91, 8.99	C <sub>12</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub> S	8.88
<b>IIIa</b>	23	169 (CH <sub>3</sub> CO <sub>2</sub> H)	9.22, 9.31	C <sub>13</sub> H <sub>8</sub> Cl <sub>3</sub> NO <sub>2</sub> S	9.20
<b>IIIb</b>	29	220 (CH <sub>3</sub> CO <sub>2</sub> H)	9.53, 9.60	C <sub>13</sub> H <sub>8</sub> Cl <sub>3</sub> NOS	9.64
<b>IIIc</b>	16	203 (CH <sub>3</sub> CO <sub>2</sub> H)	9.99, 10.04	C <sub>12</sub> H <sub>6</sub> Cl <sub>3</sub> NOS	10.06
<b>IIIe</b>	26	256 (decomp.) (CH <sub>3</sub> CO <sub>2</sub> H)	8.79, 8.84	C <sub>12</sub> H <sub>5</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>3</sub> S	8.82
<b>IVa</b>	73	(CH <sub>3</sub> CO <sub>2</sub> H)	8.39, 8.45	C <sub>13</sub> H <sub>8</sub> Cl <sub>3</sub> NO <sub>4</sub> S	8.42
<b>IVe</b>	68	(CH <sub>3</sub> CO <sub>2</sub> H)	7.98, 8.08	C <sub>12</sub> H <sub>5</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>5</sub> S	8.11
<b>VIe</b>	64	194 (CH <sub>3</sub> CO <sub>2</sub> H)	7.22, 7.36	C <sub>12</sub> H <sub>4</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>5</sub> S	7.46
<b>VIIa</b>	30	167 (CH <sub>3</sub> CO <sub>2</sub> H)	10.20, 10.22	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> NO <sub>2</sub> S	10.19
<b>VIIb</b>	23	109 (CH <sub>3</sub> CO <sub>2</sub> H)	10.66, 10.73	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> NOS	10.74
<b>VIIc</b>	25	213 ( <i>n</i> -C <sub>7</sub> H <sub>16</sub> )	11.15, 11.24	C <sub>12</sub> H <sub>7</sub> Cl <sub>2</sub> NOS	11.27
<b>VIIId</b>	27	217 ( <i>n</i> -C <sub>7</sub> H <sub>16</sub> )	10.02, 10.08	C <sub>12</sub> H <sub>6</sub> Cl <sub>3</sub> NOS	10.05
<b>VIIe</b>	23	171 (CH <sub>3</sub> CO <sub>2</sub> H)	9.71, 9.75	C <sub>12</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub> S	9.73

*N*-Arylthio-1,4-benzoquinone imines **Ia-e**, **IIIa-e**, **VIIa-e** substituted with chlorine in the quinone ring. To suspension of 2 mmol of chloro-substituted *p*-aminophenol in 20 ml of anhydrous ethyl ether were added equimolar amounts of an appropriate arylsulfonyl chloride and triethylamine. The arising precipitate of triethylamine hydrochloride was filtered off, the filtrate was evaporated in a vacuum of a water-jet pump. The precipitate of *N*-arylthio-1,4-benzoquinone imine formed was washed with methanol and acetic acid.

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