

Synthesis, X-Ray Diffraction Data, and ^1H and ^{13}C NMR Spectra of N -(N -Arylsulfonylimidoyl)-1,4-benzoquinonimines Derived from N -Aroyl(acetyl)-1,4-benzoquinonimines

A. P. Avdeenko¹, V. V. Pirozhenko², L. M. Yagupol'skii², and I. L. Marchenko¹

¹ Donbass State Machine-Building Academy, ul. Shkadinova 72, Kramatorsk, 84313 Ukraine

² Institute of Organic Chemistry, National Academy of Sciences of Ukraine

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Abstract—Oxidation of N -(N -arylsulfonylimidoyl)-4-aminophenols gave the corresponding N -(N -arylsulfonylimidoyl)-1,4-benzoquinonimines, derivatives of N -aroyl- and N -acetyl-1,4-benzoquinonimines. The structure of the products was studied by the X-ray diffraction method and ^1H and ^{13}C NMR spectroscopy. N -(N -Arylsulfonylimidoyl)-1,4-benzoquinonimines were found to undergo fast (on the NMR time scale) Z,E isomerization about the $\text{C}=\text{N}$ bond in the quinonimine fragment. N -(N -Arylsulfonylacetyl)-1,4-benzoquinonimines in solution give rise to dynamic Z,E -isomerization with respect to the $\text{C}=\text{N}$ bond in the N -arylsulfonylacetyl fragment.

We previously studied the ^1H and ^{13}C NMR spectra of N -aroyl-1,4-benzoquinonimines [1]. The results showed a considerable reduction of the barriers to Z,E isomerization of these compounds ($\Delta G_k^\ddagger = 44\text{--}46$ kJ/mol) relative to those found for the other N -substituted p -benzoquinonimines (e.g., for N -arylsulfonyl-1,4-benzoquinonimines, $\Delta G_k^\ddagger = 65\text{--}80$ kJ/mol [2]; for N -arylthio-1,4-benzoquinonimines, $\Delta G_k^\ddagger = 75\text{--}80$ kJ/mol [3]; for N -aryl-1,4-benzoquinonimines, $\Delta G_k^\ddagger = 75\text{--}95$ kJ/mol [4]) and the absence of conjugation between π -electron systems of the quinoid and aroyl fragments. We presumed that molecules of N -aroyl-1,4-benzoquinonimines have nonplanar structure, so that the π -electron systems of the quinoid and aroyl fragments are orthogonal. According to the results of quantum-chemical calculations, just in this case the interaction between the lone electron pair on the nitrogen atom and π^* orbital of the $\text{C}=\text{O}$ bond could lead to considerable reduction of the barrier to Z,E isomerization. In order to prove this assumption, we performed X-ray analysis of 2,6-di-*tert*-butyl- N -(4-chlorobenzoyl)-1,4-benzoquinonimine (**I**).

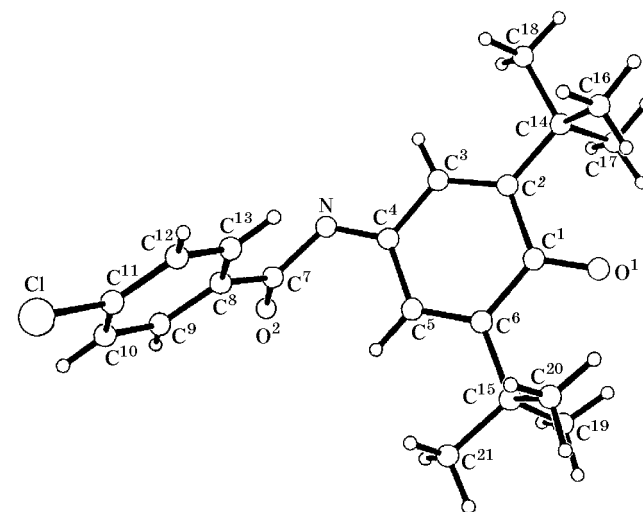
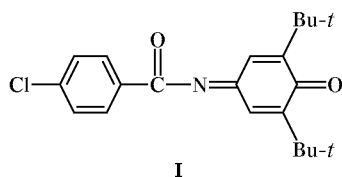


Fig. 1. Absolute configuration of the molecule of N -(4-chlorobenzoyl)-2,6-di-*tert*-butyl-1,4-benzoquinonimine (**I**) according to the X-ray diffraction data.

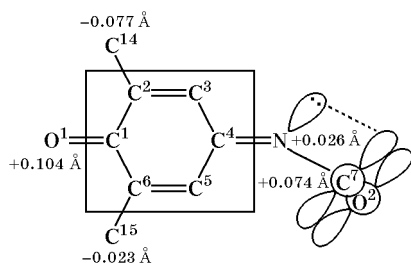


Fig. 2. Quinonimine fragment in the molecule of *N*-(4-chlorobenzoyl)-2,6-di-*tert*-butyl-1,4-benzoquinonimine (**I**) according to the X-ray diffraction data.

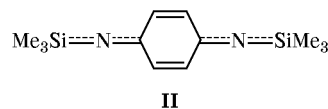
quinonimines in crystal is much greater than 120° ; then, these compounds should be characterized by a low energy of activation for *Z,E* isomerization.

According to the results of X-ray diffraction study, the bond angle $C=N-C(O)$ in molecule **I** is 124.6° . This value approaches those found for the corresponding *N*-aryl derivatives [6]. Therefore, reduction of the barrier to topomerization of *N*-aryl-2,6-di-*tert*-butyl-1,4-benzoquinonimines does not correlate with the $C=N-C$ bond angle. The $C=N$ bond length (1.29 \AA) is typical for the other benzoquinonimine derivatives [6, 7], which excludes the possibility for change of the isomerization mechanism from inversion to rotational in going to *N*-aryl-1,4-benzoquinonimines.

The absolute configuration of molecule **I** is shown in Fig. 1. It supports the assumption made in [1] to explain reduction of the barriers to *Z,E* isomerization. In fact, the planes of the *p*-chlorophenyl substituent and the quinoid fragment are almost orthogonal: the corresponding dihedral angle is 86.1° which excludes conjugation between π -electron systems of the aryl and quinoid fragments. The quinoid ring (C^1-C^6) is planar within 0.024 \AA ; the deviations of the O^1 , N , C^7 , C^{14} , and C^{15} atoms from the mean-square plane (C^1-C^6) are given in Fig. 2. The C^7 carbonyl carbon atom lies in the quinoid ring plane; this also follows from the torsion angles $C^7NC^4C^3$ (178.2°) and $C^7NC^4C^5$ (-2.6°). The aryl carbonyl group is orthogonal to the quinoid ring plane, and the π^* orbital of the $C=O$ bond is parallel to the orbital occupied by the lone electron pair on the nitrogen (n_N); such arrangement favors interaction between $\pi^*(C=O)$ and n_N and reduces the energy of the latter; hence the energy of the linear structure is also reduced.

Thus, the results of X-ray diffraction study of compound **I** are fully consistent with our previous assumption [1] on the reasons for reduced barrier to *Z,E* isomerization in *N*-aryl derivatives of 1,4-benzoquinonimines.

N,N'-Bis(trimethylsilyl)-1,4-benzoquinonediimine (**II**) was assigned [8] a linear structure with *sp*-hybridized nitrogen atoms, which is stabilized through the exchange interaction $n_N \rightarrow d_{Si}$, i.e., via donation of the nitrogen lone electron pair to the silicon *d* orbital. This conclusion was drawn on the basis of spectral data, including the 1H NMR spectra which showed magnetic equivalence of all quinoid ring protons.



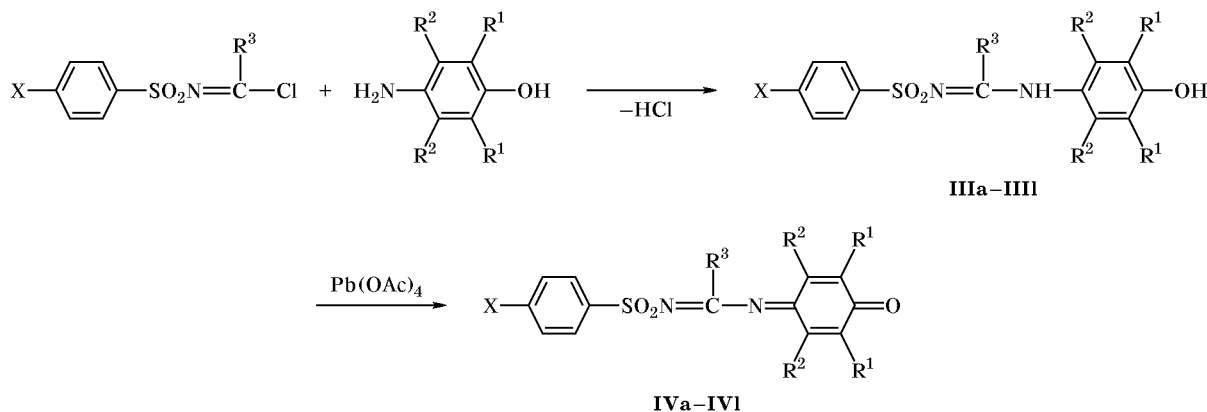
We believe that in this case very fast (on the NMR time scale) *Z,E* isomerization about the $C=N$ double bond occurs; also, a considerable contribution of the linear structure with *sp*-hybridized nitrogen atoms is conceivable. Presumably, a significant contribution of the linear structure exists in the case of *N*-aryl-1,4-benzoquinonimines.

N-(*N*-Arylsulfonylimidoyl)-1,4-benzoquinonimines **IV**, some representatives of which were synthesized by us previously [9], are derivatives of *N*-aryl-(acetyl)-1,4-benzoquinonimines in which the carbonyl oxygen atom in the aryl or acetyl moiety is replaced by arylsulfonylimino group ($ArSO_2N=$). We expected that the structure and hence the 1H and ^{13}C NMR spectra of compounds **IV** should be similar to those of *N*-aryl(acetyl)-1,4-benzoquinonimines.

In the 1H NMR spectra of quinonimines **IV** signals from the 2-H/6-H and 3-H/5-H protons appear as two doublets, indicating that they are magnetically equivalent in pairs (Table 1). Compounds **IVa**, **IVb**, and **IVf-IVi** show in the ^{13}C NMR spectra two singlets from C^2/C^6 and C^3/C^5 ; this means that C^2/C^6 and C^3/C^5 are also equivalent (Table 2). Therefore, the *E,Z* isomerization of *N*-(*N*-arylsulfonylimidoyl)-1,4-benzoquinonimines **IV** with respect to the quinonimine $C=N$ bond in solution is very fast on the NMR time scale and there is a considerable contribution of the linear structure (linear transition state) in which the quinonimine nitrogen atom has *sp* hybridization.

N-(*N*-Arylsulfonylimidoyl)-1,4-benzoquinonimines **IVa-IVi** were synthesized by oxidation of the corresponding *N*-substituted 4-aminophenols **IIIa-IIIi** with lead tetraacetate in acetic acid. *N*-(*N*-Arylsulfonylimidoyl)-4-aminophenols **IIIa-IIIi** were prepared by acylation of 4-aminophenols with appropriate *N*-arylsulfonylbenz(or acet)imidoyl chlorides in a mixture of DMF with acetic acid (1:3) in the presence of anhydrous sodium acetate, following the procedure reported in [9] (Scheme 1). The yields, melting points,

Scheme 1.



X = H (**a**, **c–e**), CH_3 (**b**, **f**, **j**, **l**), Cl (**k**), Br (**g–i**); R^1 = H (**a**, **b**, **d**, **f**, **g**, **i**, **k**), CH_3 (**c**, **h**, **j**), Cl (**e**, **l**); R^2 = H (**a–c**, **e–h**, **j**, **l**), CH_3 (**g**, **i**, **k**); R^3 = C_6H_5 (**a–e**, **g–i**), $4\text{-ClC}_6\text{H}_4$ (**f**), CH_3 (**j–l**).

and elemental analyses of compounds **IIIc–IIIi** and **IVc–IVi** are given in Table 3. Compounds **IIIa**, **IIIb**, **IVa**, and **IVb** were described in [9].

X-Ray analysis of a single crystal of 2,6-dimethyl-*N*-(*N*-phenylsulfonylbenzimidoyl)-1,4-benzoquinonimine (**IVc**) showed that the $\text{C}=\text{N}-\text{C}$ bond angle in the quinonimine fragment is 124.1° (cf. X-ray diffraction data for compound **I**). The absolute configuration of molecule **IVc** is shown in Fig. 3. As in molecule **I**, quinonimine derivative **IVc** lacks conjugation between π -electron systems of the aryl and quinoid fragments

which are almost orthogonal to each other (the corresponding dihedral angle is 86.4°). The quinoid fragment and the aryl group in the ArSO_2 moiety are coplanar, i.e., they lie in parallel planes which form a dihedral angle of 3.6° . The quinoid ring C^1-C^6 in **IVc** is planar within 0.027 \AA ; the deviations of the O^1 , N^1 , C^7 , C^{20} , and C^{21} atoms from the mean-square plane are given in Fig. 4. In keeping with these data, the C^7 atom lies almost in the quinoid ring plane: the torsion angles $\text{C}^7\text{N}^1\text{C}^4\text{C}^3$ and $\text{C}^7\text{N}^1\text{C}^4\text{C}^5$ are -3.1 and 176.5° , respectively. The $\text{C}^7=\text{N}^2$ group in the

Table 1. ^1H NMR spectra (δ , ppm) of *N*-(*N*-arylsulfonylimidoyl)-1,4-benzoquinonimines **IVa–IVi** in CDCl_3

Compound no. ^a	Quinoid ring		R^3	4- XC_6H_4
	R^1	R^2		
IVa ^b	6.66–6.70 d (2H)	7.00–7.03 d (2H)	7.43–7.81 m (5H)	7.51–7.99 m (5H)
IVb ^c	6.65–6.68 d (2H)	6.99–7.02 d (2H)	7.42–7.80 m (5H)	7.31–7.86 d.d (4H), 2.44 s (3H, CH_3)
IVc	2.06 s (6H, CH_3)	6.74 br.s (2H)	7.41–7.82 m (5H)	7.49–8.00 m (5H)
IVd	6.49 br.s (2H)	2.07 s (6H, CH_3)	7.44–7.80 m (5H)	7.52–7.99 m (5H)
IVe	–	7.22 br.s (2H)	7.44–7.80 m (5H)	7.53–8.00 m (5H)
IVf ^b	6.65–6.69 d (2H)	6.97–7.00 d (2H)	7.40–7.74 d.d (4H)	7.31–7.85 d.d (4H), 2.44 s (3H, CH_3)
IVg ^b	6.68–6.71 d (2H)	7.00–7.04 d (2H)	7.43–7.80 m (5H)	7.66–7.86 d.d (4H)
IVh	2.07 s (6H, CH_3)	6.73 br.s (2H)	7.42–7.81 m (5H)	7.64–7.86 d.d (4H)
IVi	6.51 s (2H)	2.10 s (6H, CH_3)	7.45–7.78 m (5H)	7.65–7.87 d.d (4H)
IVj (Z, 25)	2.07 s (6H, CH_3)	6.76 br.s (2H)	2.68 br.s (3H, CH_3)	7.30–7.88 d.d (4H), 2.43 s (3H, CH_3)
IVj (E, 75)	2.07 s (6H, CH_3)	6.68 br.s (2H)	2.26 br.s (3H, CH_3)	7.29–7.80 d.d (4H), 2.43 s (3H, CH_3)
IVk (Z, 7)	6.48 br.s (2H)	2.14 s (6H, CH_3)	2.40 br.s (3H, CH_3)	7.28–7.79 d.d (4H), 2.38 s (3H, CH_3)
IVk (E, 93)	6.48 br.s (2H)	2.14 s (6H, CH_3)	2.13 br.s (3H, CH_3)	7.47–7.86 d.d (4H), 2.38 s (3H, CH_3)
IVl (Z, 34)	–	7.25 br.s (2H)	2.71 br.s (3H, CH_3)	7.33–7.87 d.d (4H), 2.44 s (3H, CH_3)
IVl (E, 66)	–	7.51 br.s (2H)	2.29 br.s (3H, CH_3)	7.31–7.80 d.d (4H), 2.44 s (3H, CH_3)

^a In parentheses is given the fraction (%) of the corresponding isomer. ^b $J_{2,3} = 10.2 \text{ Hz}$. ^c $J_{2,3} = 9.9 \text{ Hz}$.

Table 2. ^{13}C NMR spectra (δ_{C} , ppm) of *N*-(*N*-arylsulfonylimidoyl)-1,4-benzoquinonimines **IVa**, **IVb**, and **IVf–IVk** in CDCl_3

Comp. no.	Quinonimine fragment	$\text{R}^3\text{-C=N}$	$4\text{-XC}_6\text{H}_4\text{SO}_2$
IVa	185.84 (C^1), 135.02 (C^2 , C^6), 129.10 (C^3 , C^5), 156.92 (C^4)	168.28 (C=N), 131.71 (C^1), 129.08 (C^2 , C^6), 128.84 (C^3 , C^5), 134.28 (C^4)	141.14 (C^1), 127.43 (C^2 , C^6), 135.20 (C^3 , C^5), 132.89 (C^4)
IVb	185.80 (C^1), 135.02 (C^2 , C^6), 129.03 (C^3 , C^5), 156.89 (C^4)	167.94 (C=N), 131.87 (C^1), 129.42 (C^2 , C^6), 129.01 (C^3 , C^5), 134.12 (C^4)	138.33 (C^1), 127.53 (C^2 , C^6), 135.09 (C^3 , C^5), 143.74 (C^4), 21.52 (CH_3)
IVf	185.71 (C^1), 134.89 (C^2 , C^6), 129.51 (C^3 , C^5), 157.29 (C^4)	166.84 (C=N), 131.87 (C^1), 129.45 (C^2 , C^6), 130.29 (C^3 , C^5), 140.97 (C^4)	138.15 (C^1), 127.56 (C^2 , C^6), 135.27 (C^3 , C^5), 143.94 (C^4), 21.56 (CH_3)
IVg	185.77 (C^1), 134.88 (C^2 , C^6), 132.09 (C^3 , C^5), 156.91 (C^4)	168.61 (C=N), 131.26 (C^1), 129.09 (C^2 , C^6), 129.04 (C^3 , C^5), 134.49 (C^4)	139.85 (C^1), 128.92 (C^2 , C^6), 135.29 (C^3 , C^5), 127.99 (C^4)
IVh	186.62 (C^1), 144.70 (C^2 , C^6), 131.22 (C^3 , C^5), 156.99 (C^4), 16.27 (2- CH_3 , 6- CH_3)	169.05 (C=N), 131.21 (C^1), 129.17 (C^2 , C^6), 129.02 (C^3 , C^5), 134.16 (C^4)	140.46 (C^1), 129.05 (C^2 , C^6), 132.05 (C^3 , C^5), 127.78 (C^4)
IVi	186.29 (C^1), 133.42 (C^2 , C^6), 145.21 (C^3 , C^5), 155.84 (C^4), 18.89 (3- CH_3 , 5- CH_3)	164.84 (C=N), 131.25 (C^1), 129.24 (C^2 , C^6), 128.38 (C^3 , C^5), 133.97 (C^4)	140.71 (C^1), 128.60 (C^2 , C^6), 132.15 (C^3 , C^5), 127.59 (C^4)
IVj	186.60 (C^1), 144.30 (C^2 , C^6), 129.72 and 129.43 (C^3 , C^5), 153.38 and 153.34 (C^4), 16.26 (2- CH_3 , 6- CH_3)	173.03 (C=N), 25.94 and 25.90 (CH_3)	137.98 (C^1), 127.65 (C^2 , C^6), 131.13 (C^3 , C^5), 143.75 (C^4), 21.57 (CH_3)
IVk	186.10 (C^1), 133.30 and 133.14 (C^2 , C^6), 145.14 and 145.03 (C^3 , C^5), 152.03 (C^4), 18.78 and 18.66 (3- CH_3 , 5- CH_3)	168.00 (C=N), 25.55 and 25.50 (CH_3)	139.29 (C^1), 128.54 (C^2 , C^6), 129.16 (C^3 , C^5), 139.29 (C^4), 21.55 (CH_3)

N-phenylsulfonylbenzimidoyl fragment is orthogonal to the quinoid ring plane, and the antibonding π^* orbital of the $\text{C}^7=\text{N}^2$ bond is parallel to the non-bonding n_{N} orbital of the nitrogen. Such arrangement favors interaction between the orbitals and reduction of the energy of n_{N} . The greatest decrease in energy, as with compound **I**, could be expected for the transition state where the bond angle $\text{C}^4=\text{N}^1-\text{C}^7$ is 180° ;

as a result, the barrier to isomerization about the C=N bond in the quinonimine fragment should be reduced considerably.

In the case of *N*-(*N*-arylsulfonylimidoyl)-1,4-benzoquinonimines **IVa–IVi** having one more C=N group in the imidoyl fragment, *Z,E* isomerization about that group could be expected. However, our ^1H NMR study of 1,4-benzoquinonimines **IVa–IVi** at various

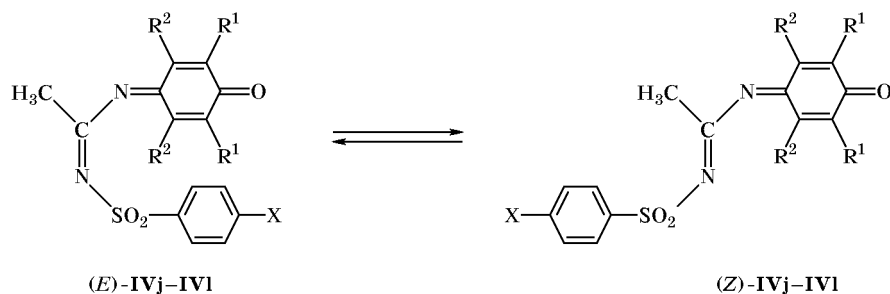
Scheme 2.

Table 3. Yields, melting points, and elemental analyses of *N*-(*N*-arylsulfonylimidoyl)-4-aminophenols **IIIc–IIIk** and 1,4-benzoquinonimines **IVc–IVl**

Comp. no.	Yield, %	mp, °C	Found N, %	Formula	Calculated N, %
IIIc	76	190	7.12, 7.26	C ₂₁ H ₂₀ N ₂ O ₃ S	7.37
III d	86	252	7.05, 7.31	C ₂₁ H ₂₀ N ₂ O ₃ S	7.37
III e	90	182	6.39, 6.58	C ₁₉ H ₁₄ Cl ₂ N ₂ O ₃ S	6.65
III f	86	255	7.37, 7.45	C ₂₀ H ₁₇ ClN ₂ O ₃ S	6.99
III g	93	258	6.22, 6.29	C ₁₉ H ₁₅ BrN ₂ O ₃ S	6.50
III h	65	125	5.93, 6.07	C ₂₁ H ₁₉ BrN ₂ O ₃ S	6.10
III i	89	263	5.84, 5.89	C ₂₁ H ₁₉ BrN ₂ O ₃ S	6.10
III j	79	220	8.05, 8.31	C ₁₇ H ₂₀ N ₂ O ₃ S	8.43
III k	57	195	8.09, 8.15	C ₁₆ H ₁₇ ClN ₂ O ₃ S	7.94
III l	47	175	7.82, 7.97	C ₁₅ H ₁₄ Cl ₂ N ₂ O ₃ S	7.84
IV c	88	175	7.16, 7.22	C ₂₁ H ₁₈ N ₂ O ₃ S	7.41
IV d	61	142	7.07, 7.39	C ₂₁ H ₁₈ N ₂ O ₃ S	7.41
IV e	75	181	6.68, 6.83	C ₁₉ H ₁₂ Cl ₂ N ₂ O ₃ S	6.67
IV f	85	130	7.42, 7.48	C ₂₀ H ₁₅ ClN ₂ O ₃ S	7.02
IV g	88	163	6.39, 6.52	C ₁₉ H ₁₃ BrN ₂ O ₃ S	6.53
IV h	66	173	6.07, 6.22	C ₂₁ H ₁₇ BrN ₂ O ₃ S	6.13
IV i	87	160	6.02, 6.16	C ₂₁ H ₁₇ BrN ₂ O ₃ S	6.13
IV j	86	189	8.33, 8.42	C ₁₇ H ₁₈ N ₂ O ₃ S	8.48
IV k	83	170	7.78, 7.96	C ₁₆ H ₁₅ ClN ₂ O ₃ S	7.99
IV l	62	160	7.72, 7.77	C ₁₅ H ₁₂ Cl ₂ N ₂ O ₃ S	7.88

Table 4. Crystallographic parameters, conditions of X-ray diffraction experiment, and divergence factors for compounds **I** and **IVc**

Parameter	I	IVc	Parameter	I	IVc
Formula	C ₂₁ H ₂₄ ClNO ₂	C ₂₁ H ₁₈ N ₂ O ₃ S	Number of reflections:		
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	total	3320	2461
Unit cell parameters:			independent	2677	2271
<i>a</i> , Å	5.9113 (6)	8.281 (2)	with <i>I</i> > 2σ(<i>I</i>)	2230	1392
<i>b</i> , Å	30.765 (2)	10.212 (2)	<i>R</i> (int)	0.0305	0.0272
<i>c</i> , Å	10.805 (1)	11.363 (2)	Number of refined parameters	323	244
α, deg	90	76.16 (3)	Number of reflections per parameter	6.90	5.70
β, deg	103.051 (8)	87.08 (3)	Divergence factors:		
γ, deg	90	85.32 (3)	<i>R</i> ₁ (<i>F</i>)	0.0392	0.0664
<i>V</i> , Å ³	1914.2 (4)	929.4 (3)	<i>R</i> _w (<i>F</i> ²)	0.0991	0.1519
<i>Z</i>	4	2	GOF	1.033	0.995
Temperature, °C	20	20	Ratio of the maximal (average) shift to the error	0.150 (0.010)	0.007 (0.001)
<i>d</i> _{calc} , g/cm ³	1.24	1.35	Residual electron density from the difference Fourier series, \bar{e} Å ³	0.13	0.30
μ, mm ⁻¹	1.865	0.198		-0.17	-0.28
<i>F</i> (000)	760	396			
Crystal habit, mm	0.46 × 0.27 × 0.22	0.31 × 0.25 × 0.19			
Spherical segment	-6 ≤ <i>h</i> ≤ 6 -24 ≤ <i>k</i> ≤ 34 -12 ≤ <i>l</i> ≤ 11	0 ≤ <i>h</i> ≤ 8 -10 ≤ <i>k</i> ≤ 10 -11 ≤ <i>l</i> ≤ 11			
Limiting diffraction angle θ, deg	60	22			

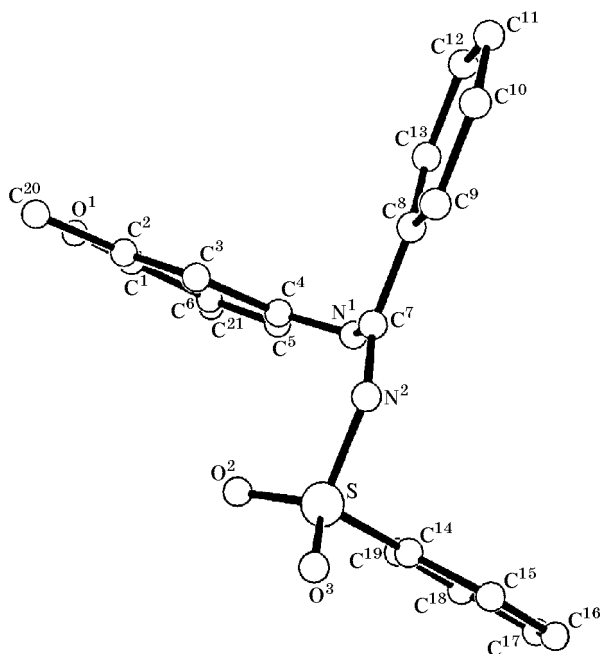


Fig. 3. Absolute configuration of the molecule of 2,6-dimethyl-*N*-(*N*-phenylsulfonylbenzimidoyl)-1,4-benzoquinonimine (**IVc**) according to the X-ray diffraction data.

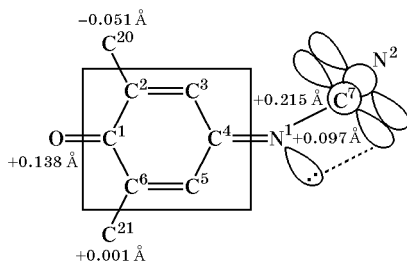


Fig. 4. Structure of the quinonimine fragment in the molecule of 2,6-dimethyl-*N*-(*N*-phenylsulfonylbenzimidoyl)-1,4-benzoquinonimine (**IVc**) according to the X-ray diffraction data.

temperatures revealed no dynamic *Z,E* isomerization process. These compounds exist in solution as a single *E* isomer with more favorable *trans* arrangement of the ArSO_2 group with respect to the benzimidoyl fragment. According to the X-ray diffraction data, compound **IVc** in crystal also exists as a single *E* isomer (Fig. 3).

Dynamic *Z,E* isomerization was observed for *N*-(*N*-arylsulfonylacetimidoyl)-1,4-benzoquinonimines **IVj–IVI** in solution (Scheme 2). Compounds **IVj–IVI** showed in the ^1H NMR spectra two broadened singlets from the quinoid ring protons and $\text{CH}_3\text{—C=N}$ group, which indicates the presence of two isomers occurring in a dynamic equilibrium. In all cases, the *E* isomer

was the major one (Table 1). In the ^1H NMR spectrum of compound **IVj** recorded in CDCl_3 or $\text{DMSO-}d_6$ at 45°C we observed coalescence of signals from the CH_3 protons and signals from 3-H and 5-H of the quinoid ring (coalescence temperature $T_c = 318\text{ K}$). On further raising the temperature to 80°C (solution in $\text{DMSO-}d_6$) the broadened signals become narrower. This pattern is typical of a dynamic process which is likely to involve *Z,E* isomerization.

The ^{13}C NMR spectra of compounds **IVj** and **IVk** contain separate signals from C^3 and C^5 of the quinoid ring ($\Delta\delta_{\text{C}} 0.1\text{--}0.3\text{ ppm}$), indicating a weak magnetic nonequivalence of the corresponding nuclei. The CH_3 carbon atom of the $\text{R}^3\text{—C=N}$ group also gives two signals. Slightly nonequivalent signals from C^2 and C^6 of the quinoid fragment ($\Delta\delta_{\text{C}} 0.16\text{ ppm}$) were also observed in the ^{13}C NMR spectrum of compound **IVk**. The C^4 atom in the quinoid ring of **IVj** gives two signals in the spectrum (Table 2).

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz for ^1H and 75.4 MHz for ^{13}C . The chemical shifts were measured relative to TMS.

X-ray analysis of single crystals of compounds **I** and **IVc** was performed at room temperature using an Enraf–Nonius CAD-4 automatic four-circle diffractometer (λMoK_α irradiation, graphite monochromator, scan rate ratio $\omega/2\theta = 1.2$). The unit cell parameters and crystal orientation matrices were determined from 22 reflections with $28^\circ < \theta < 30^\circ$ for compound **I** and $12^\circ < \theta < 13^\circ$ for compound **IVc**. The structure was solved by the direct method and was refined by the least-squares procedure in full-matrix anisotropic approximation using SHELXS and SHELXSL-93 programs [10, 11]. All hydrogen atoms were visualized from the difference synthesis of electron density and were included in the calculations with fixed positional and thermal parameters $U_{\text{iso}} = 0.08\text{ \AA}^2$. The calculations were carried out on a PC-AT/486. The principal crystallographic data for compounds **I** and **IVc** and conditions for the X-ray diffraction experiments are given in Table 4. The coordinates of atoms in molecules **I** and **IVc** are listed in Tables 5 and 6, respectively; the bond lengths and bond angles, in Tables 7 and 8; and Tables 9 and 10 contain principal torsion angles in molecules **I** and **IVc**, respectively.

***N*-(*N*-Arylsulfonylimidoyl)-4-aminophenols IIIc–IIIh.** To a solution of 0.01 mol of appropriate *p*-aminophenol and 0.011 mol of anhydrous sodium

Table 5. Coordinates of atoms ($\times 10^4$) in molecule **I**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cl	1331(1)	70(1)	7208(1)	C ¹⁰	5651(5)	199(1)	8626(2)
O ¹	4522(4)	1998(1)	15 117(1)	C ¹¹	3426(5)	360(1)	8263(2)
O ²	10 438(3)	899(1)	11 354(2)	C ¹²	2831(5)	750(1)	8728(2)
N	8010(4)	1477(1)	11 226(2)	C ¹³	4476(5)	979(1)	9576(2)
C ¹	5217(4)	1873(1)	14 199(2)	C ¹⁴	5381(4)	2676(1)	13 480(2)
C ²	5826(3)	2197(1)	13 292(2)	C ¹⁵	4751(4)	1075(1)	14 904(2)
C ³	6759(4)	2045(1)	12 360(2)	C ¹⁶	2792(4)	2751(1)	13 420(2)
C ⁴	7109(4)	1584(1)	12 164(2)	C ¹⁷	6835(5)	2835(1)	14 757(2)
C ⁵	6404(4)	1273(1)	13 017(2)	C ¹⁸	6028(5)	2953(1)	12 434(2)
C ⁶	5490(3)	1397(1)	13 989(2)	C ¹⁹	6242(6)	1147(1)	16 243(2)
C ⁷	8518(5)	1051(1)	10 929(2)	C ²⁰	2183(5)	1141(1)	14 899(3)
C ⁸	6724(4)	823(1)	9972(2)	C ²¹	5077(8)	610(1)	14 517(3)
C ⁹	7285(5)	430(1)	9482(2)				

Table 6. Coordinates of atoms ($\times 10^4$) in molecule **IVc**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
S	1190(2)	-186(2)	2681(1)	C ⁹	2774(8)	-4024(6)	5251(5)
O ¹	4219(6)	-3661(5)	-1729(4)	C ¹⁰	3248(9)	-5235(7)	6047(5)
O ²	1863(5)	-116(4)	1470(3)	C ¹¹	3039(10)	-6442(7)	5807(6)
O ³	1634(5)	803(4)	3280(4)	C ¹²	2359(10)	-6489(7)	4739(7)
N ¹	956(6)	-2888(5)	2239(4)	C ¹³	1872(9)	-5284(6)	3929(6)
N ²	1684(5)	-1650(5)	3609(4)	C ¹⁴	-911(7)	-98(5)	2638(4)
C ¹	3456(8)	-3385(6)	-867(6)	C ¹⁵	-1817(8)	220(6)	3607(6)
C ²	4356(7)	-3105(6)	145(6)	C ¹⁶	-3436(10)	360(8)	3602(8)
C ³	3546(7)	-2933(6)	1147(6)	C ¹⁷	-4224(10)	196(8)	2584(12)
C ⁴	1812(7)	-2986(5)	1279(5)	C ¹⁸	-3352(11)	-121(7)	1639(9)
C ⁵	909(7)	-3175(5)	259(5)	C ¹⁹	-1698(8)	-263(6)	1638(5)
C ⁶	1694(7)	-3370(5)	-755(5)	C ²⁰	6161(8)	-3052(7)	-1(6)
C ⁷	1601(7)	-2779(6)	3306(5)	C ²¹	805(9)	-3618(6)	-1797(5)
C ⁸	2082(7)	-4054(6)	4162(5)				

Table 7. Bond lengths *d* and bond angles ω in molecule **I**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cl-C ¹¹	1.730(3)	C ² -C ³	1.337(3)	C ⁸ -C ¹³	1.387(3)	C ¹⁴ -C ¹⁸	1.531(3)
O ¹ -C ¹	1.218(2)	C ² -C ¹⁴	1.520(3)	C ⁸ -C ⁹	1.389(3)	C ¹⁴ -C ¹⁶	1.534(3)
O ² -C ⁷	1.217(3)	C ³ -C ⁴	1.455(3)	C ⁹ -C ¹⁰	1.376(4)	C ¹⁴ -C ¹⁷	1.532(3)
N-C ⁴	1.289(2)	C ⁴ -C ⁵	1.453(3)	C ¹⁰ -C ¹¹	1.377(4)	C ¹⁵ -C ²¹	1.516(3)
N-C ⁷	1.398(3)	C ⁵ -C ⁶	1.342(3)	C ¹¹ -C ¹²	1.377(3)	C ¹⁵ -C ¹⁹	1.531(3)
C ¹ -C ⁶	1.494(3)	C ⁶ -C ¹⁵	1.531(3)	C ¹² -C ¹³	1.371(4)	C ¹⁵ -C ²⁰	1.531(3)
C ¹ -C ²	1.498(3)	C ⁷ -C ⁸	1.481(3)				

Table 7. (Contd.)

Angle	ω , deg	Angle	ω , deg	Angle	ω , deg	Angle	ω , deg
C ⁴ NC ⁷	124.6(2)	C ⁵ C ⁴ C ³	118.6(2)	C ⁹ C ⁸ C ⁷	118.9(2)	C ¹⁸ C ¹⁴ C ¹⁶	107.4(2)
O ¹ C ¹ C ⁶	120.1(2)	C ⁶ C ⁵ C ⁴	122.2(2)	C ¹⁰ C ⁹ C ⁸	121.0(3)	C ² C ¹⁴ C ¹⁷	110.6(2)
O ¹ C ¹ C ²	119.8(2)	C ⁵ C ⁶ C ¹	118.3(2)	C ¹¹ C ¹⁰ C ⁹	119.0(2)	C ¹⁸ C ¹⁴ C ¹⁷	107.7(2)
C ⁶ C ¹ C ²	120.1(2)	C ⁵ C ⁶ C ¹⁵	123.0(2)	C ¹⁰ C ¹¹ C ¹²	121.1(3)	C ¹⁶ C ¹⁴ C ¹⁷	110.0(2)
C ³ C ² C ¹	117.5(2)	C ¹ C ⁶ C ¹⁵	118.6(2)	C ¹⁰ C ¹¹ Cl	119.8(2)	C ²¹ C ¹⁵ C ⁶	111.2(2)
C ³ C ² C ¹⁴	123.6(2)	O ² C ⁷ N	120.3(2)	C ¹² C ¹¹ Cl	119.1(2)	C ²¹ C ¹⁵ C ¹⁹	108.4(2)
C ¹ C ² C ¹⁴	118.9(2)	O ² C ⁷ C ⁸	122.7(2)	C ¹³ C ¹² C ¹¹	119.4(3)	C ⁶ C ¹⁵ C ¹⁹	109.2(2)
C ² C ³ C ⁴	123.2(2)	NC ⁷ C ⁸	116.6(2)	C ¹² C ¹³ C ⁸	120.9(2)	C ²¹ C ¹⁵ C ²⁰	108.2(2)
NC ⁴ C ⁵	124.0(2)	C ¹³ C ⁸ C ⁹	118.6(2)	C ² C ¹⁴ C ¹⁸	111.1(2)	C ⁶ C ¹⁵ C ²⁰	109.8(2)
NC ⁴ C ³	117.4(2)	C ¹³ C ⁸ C ⁷	122.4(2)	C ² C ¹⁴ C ¹⁶	109.9(2)	C ¹⁹ C ¹⁵ C ²⁰	110.1(2)

Table 8. Bond lengths d and bond angles ω in molecule **IVc**

Bond	d , Å	Bond	d , Å	Bond	d , Å	Bond	d , Å
S–O ²	1.445(4)	C ¹ –C ⁶	1.457(9)	C ⁷ –C ⁸	1.466(8)	C ¹⁴ –C ¹⁵	1.388(8)
S–O ³	1.426(4)	C ¹ –C ²	1.497(8)	C ⁸ –C ¹³	1.371(8)	C ¹⁵ –C ¹⁶	1.344(10)
S–N ²	1.645(5)	C ² –C ³	1.333(8)	C ⁸ –C ⁹	1.397(7)	C ¹⁶ –C ¹⁷	1.403(12)
S–C ¹⁴	1.737(6)	C ² –C ²⁰	1.500(9)	C ⁹ –C ¹⁰	1.387(9)	C ¹⁷ –C ¹⁸	1.352(12)
O ¹ –C ¹	1.216(7)	C ³ –C ⁴	1.440(8)	C ¹⁰ –C ¹¹	1.350(9)	C ¹⁸ –C ¹⁹	1.366(10)
N ¹ –C ⁴	1.290(7)	C ⁴ –C ⁵	1.469(7)	C ¹¹ –C ¹²	1.376(9)		
N ¹ –C ⁷	1.381(7)	C ⁵ –C ⁶	1.342(8)	C ¹² –C ¹³	1.393(9)		
N ² –C ⁷	1.287(7)	C ⁶ –C ²¹	1.507(8)	C ¹⁴ –C ¹⁹	1.389(8)		
Angle	ω , deg	Angle	ω , deg	Angle	ω , deg	Angle	ω , deg
O ³ SO ²	117.0(3)	C ³ C ² C ¹	119.6(6)	N ² C ⁷ N ¹	123.9(5)	C ¹⁹ C ¹⁴ C ¹⁵	119.5(6)
O ³ SN ²	105.0(2)	C ³ C ² C ²⁰	122.2(6)	N ² C ⁷ C ⁸	119.7(5)	C ¹⁹ C ¹⁴ S	121.8(5)
O ² SN ²	111.9(2)	C ¹ C ² C ²⁰	118.2(6)	N ¹ C ⁷ C ⁸	116.2(5)	C ¹⁵ C ¹⁴ S	118.6(5)
O ³ SC ¹⁴	108.4(3)	C ² C ³ C ⁴	121.8(6)	C ¹³ C ⁸ C ⁹	118.6(5)	C ¹⁶ C ¹⁵ C ¹⁴	121.3(7)
O ² SC ¹⁴	108.9(3)	N ¹ C ⁴ C ³	125.2(5)	C ¹³ C ⁸ C ⁷	121.9(5)	C ¹⁵ C ¹⁶ C ¹⁷	118.6(8)
N ² SC ¹⁴	105.0(2)	N ¹ C ⁴ C ⁵	115.9(5)	C ⁹ C ⁸ C ⁷	119.5(5)	C ¹⁸ C ¹⁷ C ¹⁶	120.5(8)
C ⁴ N ¹ C ⁷	124.1(5)	C ³ C ⁴ C ⁵	118.9(5)	C ¹⁰ C ⁹ C ⁸	119.1(6)	C ¹⁹ C ¹⁸ C ¹⁷	121.1(8)
C ⁷ N ² S	122.0(4)	C ⁶ C ⁵ C ⁴	120.6(6)	C ¹¹ C ¹⁰ C ⁹	121.8(6)	C ¹⁸ C ¹⁹ C ¹⁴	118.9(7)
O ¹ C ¹ C ⁶	122.5(6)	C ⁵ C ⁶ C ¹	120.6(5)	C ¹⁰ C ¹¹ C ¹²	119.9(6)		
O ¹ C ¹ C ²	119.1(6)	C ⁵ C ⁶ C ²¹	121.8(6)	C ¹¹ C ¹² C ¹³	119.2(6)		
C ⁶ C ¹ C ²	118.4(5)	C ¹ C ⁶ C ²¹	117.6(5)	C ⁸ C ¹³ C ¹²	121.4(6)		

Table 9. Principal torsion angles φ in molecule **I**

Angle	φ , deg	Angle	φ , deg	Angle	φ , deg
O ¹ C ¹ C ² C ³	174.64(0.21)	NC ⁷ C ⁸ C ⁹	169.17(0.18)	O ¹ C ¹ C ⁶ C ¹⁵	3.40(0.31)
C ⁶ C ¹ C ² C ³	–4.58(0.28)	C ¹³ C ⁸ C ⁹ C ¹⁰	–0.23(0.33)	C ¹ C ² C ¹⁴ C ¹⁷	62.52(0.25)
O ¹ C ¹ C ² C ¹⁴	–4.79(0.30)	C ⁷ C ⁸ C ⁹ C ¹⁰	177.65(0.20)	C ² C ¹ C ⁶ C ¹⁵	–177.39(0.18)
C ⁶ C ¹ C ² C ¹⁴	175.99(0.18)	C ⁸ C ⁹ C ¹⁰ C ¹¹	–0.54(0.34)	C ⁵ C ⁶ C ¹⁵ C ²¹	–2.94(0.33)

Table 9. (Contd.)

Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
C ¹ C ² C ³ C ⁴	2.65 (0.30)	C ⁹ C ¹⁰ C ¹¹ C ¹²	1.03 (0.35)	C ⁴ NC ⁷ O ²	-92.47 (0.29)
C ¹⁴ C ² C ³ C ⁴	-177.95 (0.19)	C ⁹ C ¹⁰ C ¹¹ Cl	-178.89 (0.17)	C ¹ C ⁶ C ¹⁵ C ²¹	178.07 (0.24)
C ⁷ NC ⁴ C ⁵	-2.61 (0.36)	C ¹⁰ C ¹¹ C ¹² C ¹³	-0.72 (0.36)	C ⁴ NC ⁷ C ⁸	94.44 (0.26)
C ⁷ NC ⁴ C ³	178.17 (0.22)	ClC ¹¹ C ¹² C ¹³	179.20 (0.18)	C ⁵ C ⁶ C ¹⁵ C ¹⁹	116.61 (0.24)
C ² C ³ C ⁴ N	179.51 (0.20)	C ¹¹ C ¹² C ¹³ C ⁸	-0.08 (0.36)	O ² C ⁷ C ⁸ C ¹³	174.06 (0.22)
C ² C ³ C ⁴ C ⁵	0.25 (0.31)	C ⁹ C ⁸ C ¹³ C ¹²	0.54 (0.33)	C ¹ C ⁶ C ¹⁵ C ¹⁹	-62.38 (0.26)
NC ⁴ C ⁵ C ⁶	179.42 (0.21)	C ⁷ C ⁸ C ¹³ C ¹²	-177.26 (0.21)	NC ⁷ C ⁸ C ¹³	-13.03 (0.29)
C ³ C ⁴ C ⁵ C ⁶	-1.37 (0.31)	C ³ C ² C ¹⁴ C ¹⁸	2.73 (0.28)	C ⁵ C ⁶ C ¹⁵ C ²⁰	-122.62 (0.24)
C ⁴ C ⁵ C ⁶ C ¹	-0.59 (0.30)	C ¹ C ² C ¹⁴ C ¹⁸	-177.88 (0.19)	O ² C ⁷ C ⁸ C ⁹	-3.73 (0.31)
C ⁴ C ⁵ C ⁶ C ¹⁵	-179.59 (0.19)	C ³ C ² C ¹⁴ C ¹⁶	121.46 (0.22)	C ¹ C ⁶ C ¹⁵ C ²⁰	58.39 (0.26)
O ¹ C ¹ C ⁶ C ⁵	-175.64 (0.21)	C ¹ C ² C ¹⁴ C ¹⁶	-59.15 (0.24)		
C ² C ¹ C ⁶ C ⁵	3.57 (0.29)	C ³ C ² C ¹⁴ C ¹⁷	-116.88 (0.24)		

Table 10. Principal torsion angles φ in molecule IVc

Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
O ³ SN ² C ⁷	-172.95 (0.45)	O ¹ C ¹ C ⁶ C ⁵	174.22 (0.55)	C ⁹ C ⁸ C ¹³ C ¹²	-1.23 (0.99)
O ² SN ² C ⁷	-45.04 (0.51)	C ² C ¹ C ⁶ C ⁵	-3.21 (0.81)	C ⁷ C ⁸ C ¹³ C ¹²	178.89 (0.63)
C ¹⁴ SN ² C ⁷	72.92 (0.49)	O ¹ C ¹ C ⁶ C ²¹	-4.14 (0.87)	C ¹¹ C ¹² C ¹³ C ⁸	1.22 (1.15)
O ¹ C ¹ C ² C ³	-173.43 (0.58)	C ² C ¹ C ⁶ C ²¹	178.43 (0.47)	O ³ SC ¹⁴ C ¹⁸	142.06 (0.46)
C ⁶ C ¹ C ² C ³	4.09 (0.80)	SN ² C ⁷ N ¹	-6.31 (0.76)	O ² SC ¹⁴ C ¹⁹	13.75 (0.54)
O ¹ C ¹ C ² C ²⁰	5.52 (0.84)	SN ² C ⁷ C ⁸	178.98 (0.40)	N ² SC ¹⁴ C ¹⁹	-106.21 (0.47)
C ⁶ C ¹ C ² C ²⁰	-176.97 (0.54)	C ⁴ N ¹ C ⁷ N ²	97.95 (0.69)	O ³ SC ¹⁴ C ¹⁵	-34.43 (0.52)
C ¹ C ² C ³ C ⁴	-1.04 (0.85)	C ⁴ N ¹ C ⁷ C ⁸	-87.16 (0.66)	O ² SC ¹⁴ C ¹⁵	-162.74 (0.43)
C ²⁰ C ² C ³ C ⁴	-179.94 (0.53)	N ² C ⁷ C ⁸ C ¹³	173.72 (0.57)	N ² SC ¹⁴ C ¹⁵	77.31 (0.49)
C ⁷ N ¹ C ⁴ C ³	-3.12 (0.88)	N ¹ C ⁷ C ⁸ C ¹³	-1.40 (0.82)	C ¹⁹ C ¹⁴ C ¹⁵ C ¹⁶	0.55 (0.91)
C ⁷ N ¹ C ⁴ C ⁵	176.50 (0.48)	N ² C ⁷ C ⁸ C ⁹	-6.16 (0.81)	SC ¹⁴ C ¹⁵ C ¹⁶	177.12 (0.52)
C ² C ³ C ⁴ N ¹	176.79 (0.53)	N ¹ C ⁷ C ⁸ C ⁹	178.72 (0.50)	C ¹⁴ C ¹⁵ C ¹⁶ C ¹⁷	-0.83 (1.04)
C ² C ³ C ⁴ C ⁵	-2.82 (0.84)	C ¹³ C ⁸ C ⁹ C ¹⁰	1.07 (0.90)	C ¹⁵ C ¹⁶ C ¹⁷ C ¹⁸	1.20 (1.17)
N ¹ C ⁴ C ⁵ C ⁶	-175.93 (0.51)	C ⁷ C ⁸ C ⁹ C ¹⁰	-179.05 (0.56)	C ¹⁶ C ¹⁷ C ¹⁸ C ¹⁹	-1.30 (1.21)
C ³ C ⁴ C ⁵ C ⁶	3.72 (0.77)	C ⁸ C ⁹ C ¹⁰ C ¹¹	-0.96 (1.03)	C ¹⁷ C ¹⁸ C ¹⁹ C ¹⁴	0.99 (1.03)
C ⁴ C ⁵ C ⁶ C ¹	-0.63 (0.81)	C ⁹ C ¹⁰ C ¹¹ C ¹²	0.95 (1.16)	C ¹⁵ C ¹⁴ C ¹⁹ C ¹⁸	-0.60 (0.84)
C ⁴ C ⁵ C ⁶ C ²¹	177.66 (0.49)	C ¹⁰ C ¹¹ C ¹² C ¹³	-1.06 (1.18)	SC ¹⁴ C ¹⁹ C ¹⁸	-177.06 (0.49)

acetate in 10 ml of a 1:3 dimethylformamide–acetic acid mixture, cooled in an ice bath, we added with stirring a solution of 0.01 mol of the corresponding *N*-arylsulfonylbenzimidoyl chloride. The mixture was stirred for 30 min and diluted with 100 ml of ice water. The precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. The yields, melting points, and elemental analyses of compounds **IIIc–III** are given in Table 3.

***N*-(*N*-Arylsulfonylimidoyl)-1,4-benzoquinonimines IVc–IVl.** Lead tetraacetate, 0.013 mol, was

added to a mixture of 0.01 mol of *N*-(*N*-arylsulfonylimidoyl)-4-aminophenol **IIIc–III** in 15 ml of acetic acid, and the mixture was vigorously stirred. The reaction was exothermic. In the synthesis of compounds **IVf–IVi**, the mixture was additionally heated to 50–60°C. When a solid separated, the mixture was cooled, and 1 ml of ethylene glycol was added. The yellow precipitate was filtered off, washed with acetic acid and methanol, dried, and recrystallized from acetic acid. The yields, melting points, and elemental analyses of compounds **IVc–IVl** are given in Table 3.

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