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Reaction of *N*,*N*′-Disubstituted 1,4-Benzoquinone Diimines with Sodium Arenesulfinates

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Abstract—Radical anion 1,6-addition path in the reactions of *N*,*N*′-disubstituted 1,4-benzoquinone diimines with sodium arenesulfinates is favored by increase of the electron-donating power of the substituent in the *para* position of arenesulfinate ion and redox potential of the initial 1,4-benzoquinone diimine.

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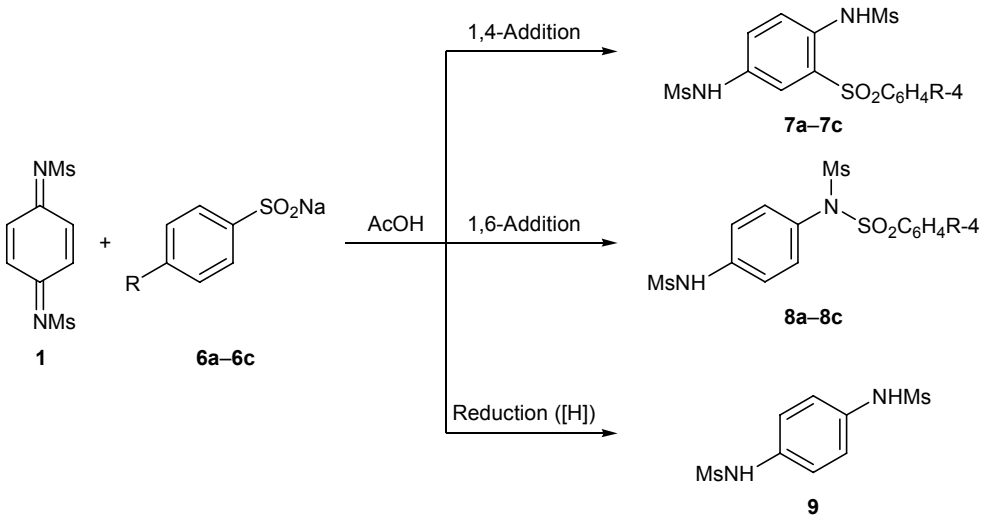
Adams and co-workers [1–7] previously isolated only 1,4-addition products, 2-arenesulfonylbenzene-1,4-diamines, in the reactions of symmetrical *N*,*N*′-dimesyl-, *N*,*N*′-bis(benzenesulfonyl)-, and *N*,*N*′-dibenzoyl-1,4-benzoquinone diimines with sodium arenesulfinates. The product structure was determined only on the basis of their IR spectra, whereas ^{1}H NMR data were not given. *N*-Substituted 1,4-benzoquinone diimines are characterized by considerably higher redox potentials than 1,4-benzoquinone monoimines. According to [8], this should favor formation of 1,6-addition products and reduction of the initial diimines.

The goal of the present study was to compare the reactivity of several classes of *N*-substituted 1,4-quinone diimines containing substituents with different donor–acceptor properties toward sodium arenesulfinates. The reactions of *N*,*N*′-dimesyl- (**1**) *N*,*N*′-bis(arenesulfonyl)- (**2a**, **2b**), *N*,*N*′-bis[4-chlorobenzene-

Scheme 1.



R = Me (**a**), MeO (**b**), F (**c**).

sulfonylimino(phenyl)methyl]- (**3**), *N*-(4-methylbenzoyl)-*N*′-tosyl- (**4**), and *N*,*N*′-diaroyl-1,4-benzoquinone diimines (**5a**–**5c**) with sodium arenesulfinates **6a**–**6e** were carried out at a reactant ratio of 1:2 in acetic acid. In order to facilitate signal assignment in the ^{1}H NMR spectra of the products, the aryl fragments in the initial compounds contained mainly methyl or methoxy group in the *para* position.

N,*N*′-Dimesyl-1,4-benzoquinone diimine (**1**) reacted with sodium arenesulfinates **6a**–**6c** to give mixtures of 1,4- and 1,6-addition products **7a**–**7c** and **8a**–**8c** and reduction product **9** of the initial quinone diimine (Scheme 1). Characteristically, increase of the electron-withdrawing power of the *para*-substituent in sodium arenesulfinate in the series Me < MeO < F was accompanied by increase of the yield of 1,4-addition product **7a**–**7c** and decrease of the fraction of 1,6-addition product **8a**–**8c** (see table). This is consistent with our assumption [9] that the 1,6-addition path follows radical anion mechanism and that 1,4-addition products are formed via nucleophilic ionic mechanism.

The ^{1}H NMR spectra of **7a**–**7c** displayed singlets from two NH protons at δ 8.86–8.95 and 10.13–10.20 ppm, a doublet from 3-H at δ 7.87–7.93 ppm (*meta* coupling), a doublet of doublets from 5-H at δ 7.46–7.54 ppm, and a doublet from 6-H at δ 7.47–7.54 ppm (*ortho* coupling). In the ^{1}H NMR spectra of 1,6-addition products **8a**–**8c** we observed one NH singlet at δ 10.18–10.20 ppm and doublets due to 2-H/6-H and 3-H/5-H at δ 7.16–7.18 and 7.20–7.22 ppm, respectively.

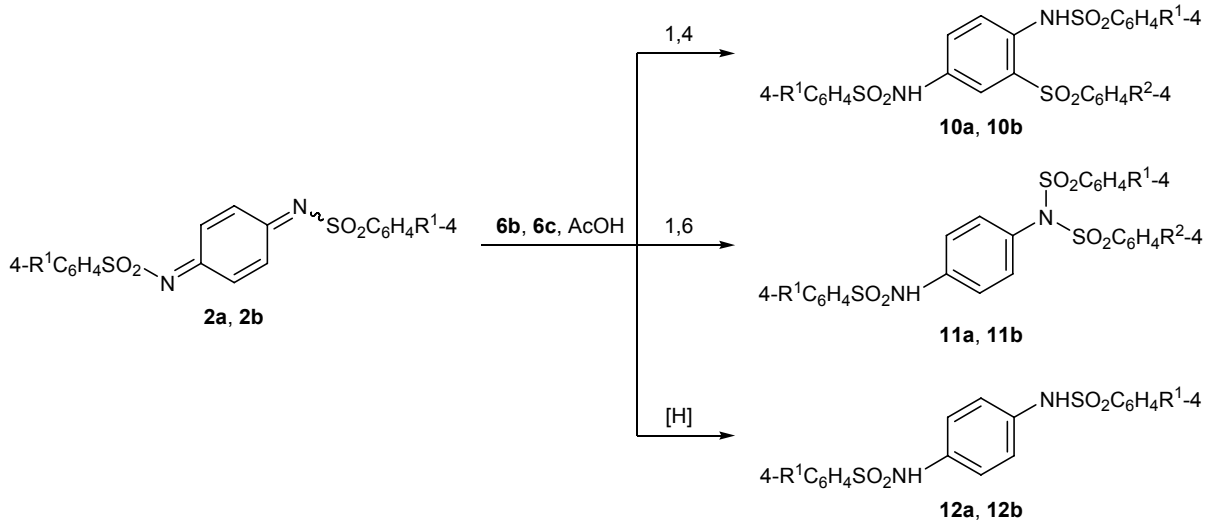
Product composition in the reactions of quinone diimines **1**–**4** with sodium arenesulfinates **6a**–**6c** (Schemes 1–4)

Reactant nos.	Product composition, %				
	1,4	1,6	6,1	6,3	[H]
1 + **6a**	60	20	–	–	20
1 + **6b**	56	26	–	–	18
1 + **6c**	65	8	–	–	27
2a + **6c**	63	15	–	–	22
2b + **6b**	41	26	–	–	33
3 + **6a**	73	–	–	–	27
3 + **6b**	70	–	–	–	30
4 + **6b**	28	20	20	15	17

Like quinone diimine **1**, symmetrical *N*,*N*′-bis-(arenesulfonyl)-1,4-benzoquinone diimines **2a** and **2b** reacted with sodium arenesulfinates **6b** and **6c** to afford mixtures of 1,4- and 1,6-addition products **10** and **11** and benzenediamines **12a** (Scheme 2). In the reaction with 4-methoxybenzenesulfinate **6b**, the fraction of the corresponding 1,4-addition product **10a** was larger (see table).

The reactions of quinone diimine **3** with sodium arenesulfinates **6a** and **6b** were highly regioselective, and only 1,4-addition products **13a** and **13b** were obtained. The reaction mixtures also contained some amount of reduction product **14** (Scheme 3). According to published data, increased fraction of 1,6-addition products would be expected, taking into account higher redox potential of quinone diimine **3** relative to **1** and **2** [10]. Presumably, steric hindrances created by

Scheme 2.

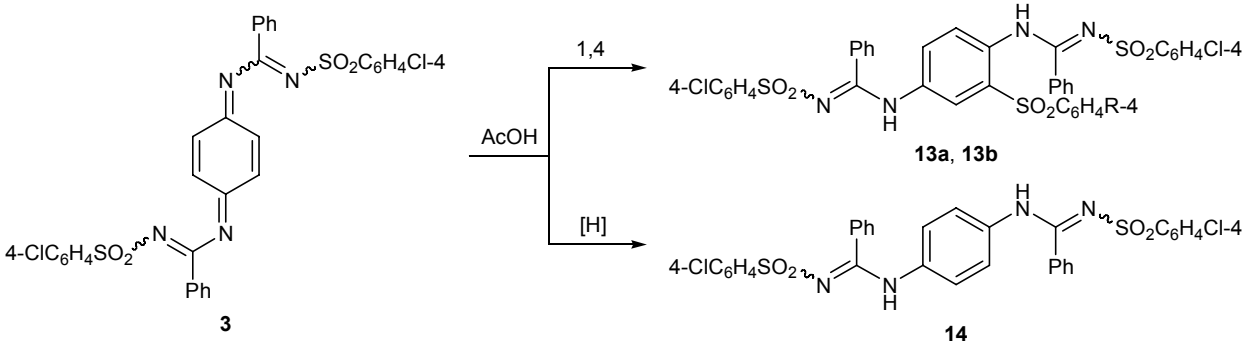


2, **12**, R^1 = H (**a**), Me (**b**); **10**, **11**, R^1 = H, R^2 = F (**a**), R^1 = Me, R^2 = MeO (**b**).

the bulky C(Ph)NSO_2Ar group prevented the 1,6-addition path.

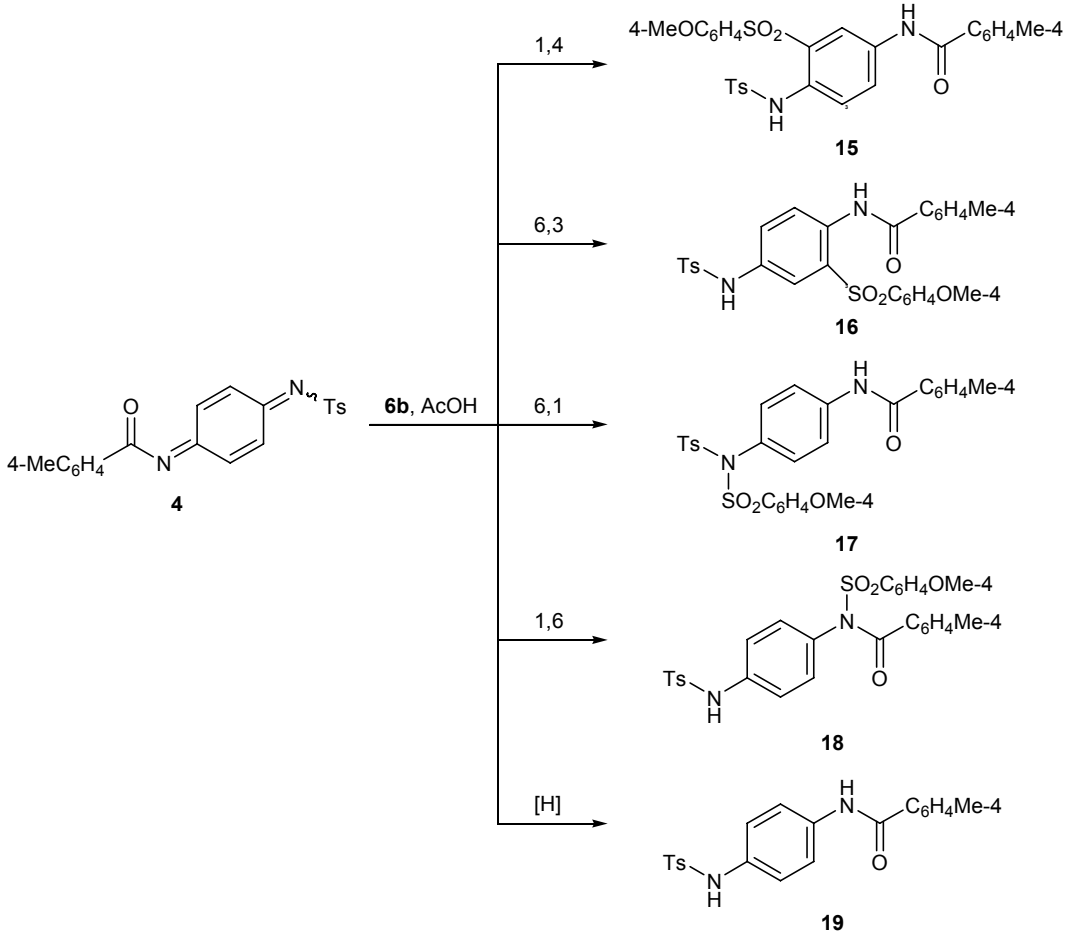
The reaction of unsymmetrical *N*-(4-methylbenzenesulfonyl)-*N*′-(4-methylbenzoyl)-1,4-benzoquinone diimine (**4**) with sodium 4-methoxybenzenesulfinate (**6b**) led to the formation of a mixture of 1,4- (**15**), 6,3- (**16**), 6,1- (**17**), and 1,6-adducts (**18**) and reduction product **19** (Scheme 4). It should be noted that introduction of an ArCO group into the initial quinone diimine essentially changes the product composition, both qualitative and quantitative. In particular, the fraction of the 1,4-addition product considerably decreases, while the amount of 1,6- and 6,1-addition products (radical ion mechanism [9]) increases (see

Scheme 3.

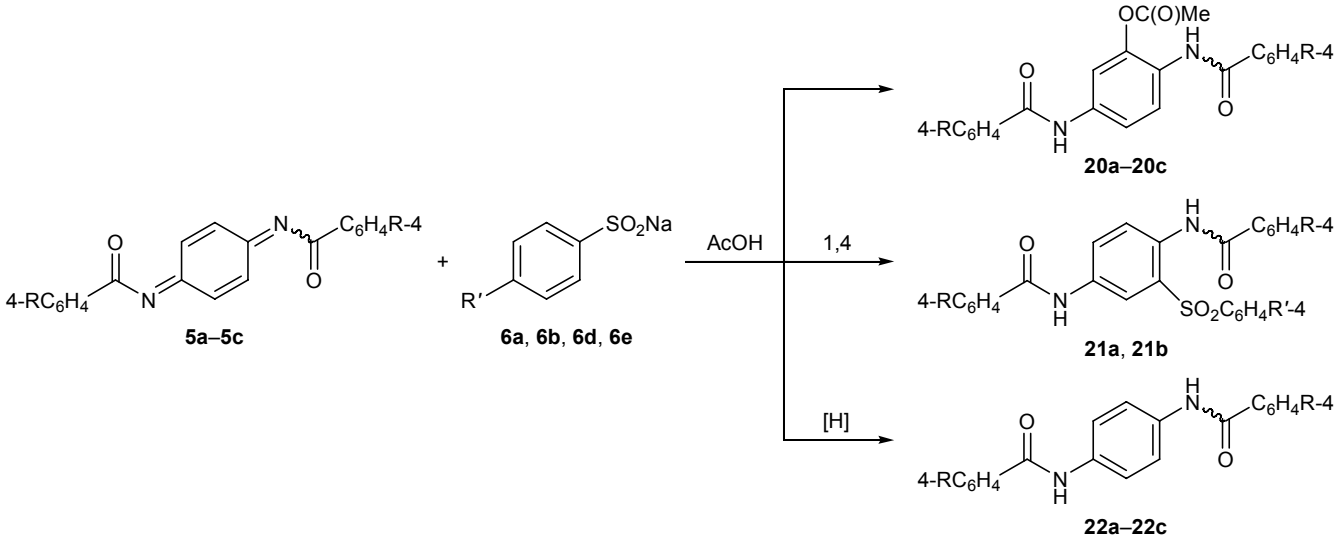


R = Me (**a**), MeO (**b**).

Scheme 4.



Scheme 5.



6, R′ = Me (**a**), MeO (**b**), Cl (**d**), H (**e**); **5**, **20**, **22**, R = H (**a**), Me (**b**), MeO (**c**); **21**, R = R′ = H (**a**), MeO (**b**).

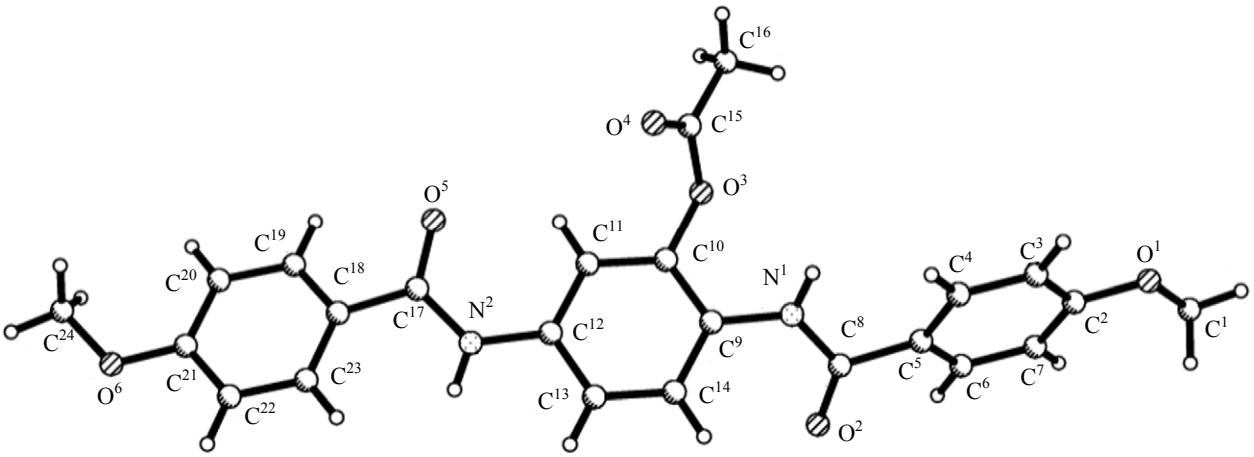
table). The most probable reason is higher redox potential of the initial quinone diimine due to the presence of ArCO group [11].

The spectral parameters of compounds **15** and **16** unambiguously identify them as 1,4- and 6,3-addition products, respectively; i.e., the arenesulfonyl group enters the *meta* (**15**) and *ortho* positions (**16**) with respect to the ArCO group. The ^{1}H NMR spectrum of **15** contained a doublet at δ 8.48 ppm (*meta* coupling, 2-H), a doublet of doublets at 7.98–8.01 ppm (6-H), and a doublet at δ 7.38 ppm (*ortho* coupling, 5-H). In the downfield region of the spectrum of **16**, the doublet at δ 7.98 ppm (*ortho* coupling) was assigned to 6-H, and the 3-H and 5-H protons resonated as a doublet at δ 7.79 ppm (*meta* coupling) and a doublet of doublets at δ 7.38 ppm, respectively.

Scheme 5 shows the results of the reactions of *N*,*N*′-diaroyl derivatives **5a**–**5c** with sodium arenesulfinates **6a**, **6b**, **6d**, and **6e**. Among the examined *N*,*N*′-disubstituted benzoquinone diimines, compounds **5a**–**5c** are characterized by the highest redox potentials [12], so that increased fraction of radical anion addition products (1,6-addition path) should be expected. However, the reactions of **5a** with **6b** and **6e** at room temperature gave 1,4-addition products **21a** and **21b**, whereas compounds **20a**–**20c** (products of 1,4-addition of acetate ion) were obtained from **5a**–**5c** in boiling acetic acid. Also, the corresponding reduction products, bis-amides **22a**–**22c** were detected. The observed pattern may be rationalized taking into account that increase of the redox potential favors reduction of the initial quinone diimine to a larger extent than radical anion 1,6-addition.

It was quite difficult to determine the structure of **20a**–**20c** on the basis of spectral data. Therefore, their structure was finally confirmed by X-ray analysis of 2,5-bis(4-methoxybenzamido)phenyl acetate (**20c**). According to the X-ray diffraction data (see figure), the substituent on C^{12} is almost coplanar to the C^9–C^{14} benzene ring [torsion angles $C^{17}N^2C^{12}C^{11}$ –13.4(2)° and $C^{23}C^{18}C^{17}N^2$ 27.0(2)°]. The methoxy group on C^{21} slightly deviates from the aromatic ring plane [torsion angle $C^{24}O^6C^{21}C^{20}$ –10.6(3)°]. Analogous substituent on C^9 is less planar [torsion angles $C^{14}C^9N^1C^8$ and $N^1C^8C^5C^4$ are 43.1(2) and 31.3(2)°, respectively]. The nonplanar conformation of the substituents is determined by steric repulsion between the NH and aromatic hydrogen atoms (shortened contacts N^1–H···H–C^4 2.12 and N^2–H···H–C^{23} 2.11 Å; sum of the van der Waals radii 2.34 Å [13]). The acetoxy group on C^{10} adopts +*sc*-conformation with respect to the C^9–C^{14} benzene ring [torsion angle $C^{10}O^3C^{15}O^4$ 65.3(2)°].

Thus, the results of our study provide further support to the ionic mechanism of 1,4-addition of arenesulfinates to quinone imines and radical ion mechanism of the 1,6-addition. Increased electron-donating power of the substituent in the *para* position of arenesulfinate ion favors the radical anion addition path, while increased redox potential of 1,4-benzoquinone diimine favors formation of 1,6-addition products (radical anion mechanism) and reduction of the initial quinone diimine.



Structure of the molecule of 2,5-bis(4-methoxybenzamido)phenyl acetate (**20c**) according to the X-ray diffraction data.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz using TMS as internal reference. The purity of initial quinone imines **1**, **2a**, **2b**, **3**, **4**, and **5a**–**5c** was checked by TLC on Silufol UV-254 plates; samples were applied from solutions in chloroform, benzene–hexane (10:1) was used as eluent, and spots were detected under UV light.

The unit cell parameters and intensities of 12519 reflections (3860 independent reflections, R_{int} = 0.123) for compound **20c** were measured on an Xcalibur-3 diffractometer (MoK_α irradiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 50°). Triclinic crystal system; unit cell parameters (21°C): a = 6.115(3), b = 11.459(4), c = 15.983(3) Å; α = 106.18(2), β = 92.92(3), γ = 94.94(3)°; V = 1068.3(7) Å^3; M 434.45; Z = 2; space group $P\bar{1}$; d_{calc} = 1.351 g/cm^3; μ(MoK_a) = 0.098 mm^{-1}; $F(000)$ = 456. The structure was solved by the direct method using SHELXTL [14]. Hydrogen atoms were localized by difference synthesis of electron density maps, and their positions were refined according to the riding model ($U_{iso} = nU_{eq}$; n = 1.5 for methyl groups, n = 1.2 for other hydrogen atoms). The structure was refined against F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms to wR_2 = 0.051 (for 3860 reflections) and R_1 = 0.042 [for 935 reflections with $F > 4\sigma(F)$]; goodness of fit S = 0.565. The coordinates of atoms and complete set of tabulated bond lengths and bond angles were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 993760).

N,*N*′-Disubstituted 1,4-quinone diimines **1**, **2a**, and **2b** were synthesized according to the procedure described in [15]. Compound **3** was synthesized by acylation of benzene-1,4-diamine with the corresponding *N*-arenesulfonyl(aryl)imidoyl chloride in DMF–AcOH (1:3) in the presence of anhydrous sodium acetate as reported in [10] and subsequent oxidation of the resulting *N*-substituted benzene-1,4-diamine with lead tetraacetate in acetic acid. Compounds **4** [16] and **5a**–**5c** [17] were prepared by known methods. The properties of quinone diimine **4** were consistent with published data [18]. Sodium arenesulfinates **6a**–**6e** were synthesized according to [19].

***N*,*N*′-(Cyclohexa-2,5-diene-1,4-diylidene)dimethanesulfonamide (1).** Yield 85%, mp 200–201°C. ^{1}H NMR spectrum* ($CDCl_3$), δ, ppm: *E* isomer: 3.29 s (6H, Me), 6.90–6.93 d.d (2H, 2-H, 5-H, J = 9.0, 2.1 Hz), 7.86–7.90 d.d (2H, 3-H, 6-H, J = 10.2 Hz); *Z* isomer: 3.28 s (6H, Me), 6.96–6.98 m (2H, 5-H, 6-H), 7.83–7.84 m (2H, 2-H, 3-H). Found, %: N 10.32, 10.91; S 24.18, 24.57. $C_8H_{10}N_2O_4S_2$. Calculated, %: N 10.68; S 24.45.

***N*,*N*′-(Cyclohexa-2,5-diene-1,4-diylidene)dibenzenesulfonamide (2a).** Yield 85%, mp 187–188°C; published data [15]: mp 188°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 7.54–8.05 m (10H, Ph), 6.92 d (2H, 2-H, 5-H, J = 2.7 Hz), 8.13–8.14 m (2H, 3-H, 6-H); *Z* isomer: 7.54–8.05 m (10H, Ph), 6.97 d (2H, 5-H, 6-H, J = 3.0 Hz), 8.09 d (2H, 2-H, 3-H, J = 3.0 Hz).

* Hereinafter, unprimed locants refer to protons in the former quinone ring, primed locants refer to protons in the aromatic rings of the substituents on the nitrogen atoms (if two nonequivalent aromatic rings are present, protons in one of them are denoted with primed locants, and those in the other, with triple primed locants), and double primed locants refer to protons formerly belonging to arenesulfinate.

***N*,*N*′-(Cyclohexa-2,5-diene-1,4-diylidene)bis-(4-methylbenzenesulfonamide) (2b).** Yield 90%, mp 204–205°C; published data [15]: mp 206.5–207.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 3.05 s (6H, Me), 6.89 m (2H, 2-H, 5-H), 7.37 d (4H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.89 d (4H, 3′-H, 5′-H, *J* = 8.1 Hz), 8.12–8.14 m (2H, 3-H, 6-H); *Z* isomer: 3.05 s (6H, Me), 6.93 d (2H, 5-H, 6-H, *J* = 7.2 Hz), 7.37 d (4H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.89 d (4H, 3′-H, 5′-H, *J* = 8.1 Hz), 8.05 d (2H, 2-H, 3-H, *J* = 7.2 Hz).

***N*,*N*′-(Cyclohexa-2,5-diene-1,4-diylidene)bis-[*N*′-(4-chlorobenzenesulfonyl)benzenecarboximidamide] (3).** Yield 85%, mp 201–202°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.88 br.s (4H), 7.43–7.82 m (10H, Ph), 7.48 d (4H, 2′-H, 6′-H, *J* = 9.0 Hz), 7.93 d (4H, 3′-H, 5′-H, *J* = 9.0 Hz). Found, %: N 8.25, 8.61; S 9.44, 9.65. $C_{32}H_{22}Cl_2N_4O_4S_2$. Calculated, %: N 8.47; S 9.69.

***N*,*N*′-(Cyclohexa-2,5-diene-1,4-diylidene)dibenzamide (5a).** Yield 87%, mp 140–141°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.92 s (4H), 7.46–7.93 m (10H, Ph). Found, %: N 8.78, 8.99. $C_{20}H_{14}N_4O_2$. Calculated, %: N 8.91.

***N*,*N*′-(Cyclohexa-2,5-diene-1,4-diylidene)bis-(4-methylbenzamide) (5b).** Yield 83%, mp 155–157°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s (6H, Me), 6.86 s (4H), 7.31 d (4H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.84 d (4H, 3′-H, 5′-H, *J* = 8.1 Hz). Found, %: N 8.03, 8.31. $C_{22}H_{18}N_2O_2$. Calculated, %: N 8.18.

***N*,*N*′-(Cyclohexa-2,5-diene-1,4-diylidene)bis-(4-methoxybenzamide) (5c).** Yield 68%, mp 128–129°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 s (6H, Me), 6.88 s (4H), 6.97 d (4H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.70 d (4H, 3′-H, 5′-H, *J* = 8.1 Hz). Found, %: N 7.32, 7.55. $C_{22}H_{18}N_2O_4$. Calculated, %: N 7.48.

Reaction of quinone diimines 1, 2a, 2b, 3, 4, and 5a–5c with sodium arenesulfinates 6a–6e (*general procedure*). A solution of 2 mmol of quinone imine **1**–**5** in 20 mL of glacial acetic acid was heated to 70°C, 4 mmol of the corresponding sodium arenesulfinate **6a–6e** was added in one portion, and the mixture was stirred until it became colorless. The mixture was cooled, water was added until complete precipitation, and the colorless residue was filtered off and washed first with cold and then with warm water. A part of the crude product was recrystallized from acetic acid. The mother liquor was diluted with water, and the precipitate was filtered off. The three crystalline samples were analyzed by ^{1}H NMR. Compounds **7b**, **7c**, **8a**, **10a**, **10b**, **15**, **16**, **20b**, and **20c** were isolated in the pure state by successive crystallizations.

***N*,*N*′-[2-(4-Methylbenzenesulfonyl)benzene-1,4-diyl]dimethanesulfonamide (7a).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 s (3H, 4″-Me), 3.05 s and 3.11 s (3H each, $MeSO_2$), 7.46 d (2H, 2″-H, 6″-H, *J* = 8.1 Hz), 7.47–7.50 d.d (1H, 5-H, *J* = 2.1, 9.0 Hz), 7.54 d (1H, 6-H, *J* = 8.7 Hz), 7.81 d (2H, 3″-H, 5″-H, *J* = 8.1 Hz), 7.89 d (1H, 3-H, *J* = 2.7 Hz), 8.87 s and 10.14 s (1H each, NH).

***N*,*N*′-[2-(4-Methoxybenzenesulfonyl)benzene-1,4-diyl]dimethanesulfonamide (7b).** Yield 16%, mp 163–164°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.05 s and 3.14 s (3H each, Me), 3.84 s (3H, MeO), 7.17 d (2H, 2″-H, 6″-H, *J* = 9.0 Hz), 7.46–7.49 d.d (1H, 5-H, *J* = 2.1, 9.0 Hz), 7.54 d (1H, 6-H, *J* = 9.0 Hz), 7.86 d (2H, 3″-H, 5″-H, *J* = 9.0 Hz), 7.87 d (1H, 3-H, *J* = 2.7 Hz), 8.86 s and 10.13 s (1H each, NH). Found, %: N 6.64, 6.27; S 21.75, 22.34. $C_{15}H_{18}N_2O_7S_3$. Calculated, %: N 6.45; S 22.14.

***N*,*N*′-[2-(4-Fluorobenzenesulfonyl)benzene-1,4-diyl]dimethanesulfonamide (7c).** Yield 38%, mp 183–184°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.08 s and 3.14 s (3H each, Me), 7.47 d (1H, 6-H, *J* = 8.7 Hz), 7.51–7.54 d.d (1H, 5-H, *J* = 2.1, 9.0 Hz), 7.51 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.93 d (1H, 3-H, *J* = 2.1 Hz), 8.00 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 8.95 s and 10.20 s (1H each, NH). Found, %: N 6.11, 6.52; S 22.58, 23.13. $C_{14}H_{15}FN_2O_6S_3$. Calculated, %: N 6.63; S 22.77.

***N*-(4-Methylbenzenesulfonyl)-*N*,*N*′-(benzene-1,4-diyl)dimethanesulfonamide (8a).** Yield 12%, mp 205–207°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.43 s (3H, 4″-Me), 3.10 s and 3.58 s (3H each, $MeSO_2$), 7.16 d (2H, 2-H, 6-H, *J* = 8.7 Hz), 7.21 d (2H, 3-H, 5-H, *J* = 8.7 Hz), 7.47 d (2H, 2″-H, 6″-H, *J* = 8.1 Hz), 7.71 d (2H, 3″-H, 5″-H, *J* = 8.1 Hz), 10.18 s (1H, NH). Found, %: N 6.85, 6.54; S 23.14, 22.86. $C_{15}H_{18}N_2O_6S_3$. Calculated, %: N 6.69; S 22.99.

***N*-(4-Methoxybenzenesulfonyl)-*N*,*N*′-(benzene-1,4-diyl)dimethanesulfonamide (8b).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.10 s and 3.59 s (3H each, Me), 3.88 s (3H, MeO), 7.16 d (2H, 2-H, 6-H, *J* = 9.0 Hz), 7.20 d (2H, 3-H, 5-H, *J* = 9.0 Hz), 7.41 d (2H, 2″-H, 6″-H, *J* = 9.0 Hz), 7.75 d (2H, 3″-H, 5″-H, *J* = 9.0 Hz), 10.18 s (1H, NH).

***N*-(4-Fluorobenzenesulfonyl)-*N*,*N*′-(benzene-1,4-diyl)dimethanesulfonamide (8c).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.10 s and 3.61 s (3H each, Me),

7.18 d (2H, 2-H, 6-H, J = 9.0 Hz), 7.22 d (2H, 3-H, 5-H, J = 9.0 Hz), 7.54 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.89 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 10.20 s (1H, NH).

***N*,*N*′-(Benzene-1,4-diyl)dimethanesulfonamide (9).** Yield 89%, mp 263–264°C; published data [2]: mp 263–265°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.95 s (6H, Me), 7.18 s (4H), 9.63 s (2H, NH). Found, %: N 20.41, 20.63. $C_8H_{12}N_2$. Calculated, %: N 20.57.

***N*,*N*′-[2-(4-Fluorobenzenesulfonyl)benzene-1,4-diyl]dibenzenesulfonamide (10a).** Yield 48%, mp 118–120°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.99 d (1H, 6-H, J = 8.7 Hz), 7.24−7.27 d.d (1H, 5-H, J = 2.4, 8.7 Hz), 7.42−7.79 m (10H, Ph), 7.56 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.70 d (1H, 3-H, J = 2.1 Hz), 7.72 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 9.54 br.s and 10.71 s (1H each, NH). Found, %: N 5.26, 5.40; S 17.41, 17.80. $C_{24}H_{19}FN_2O_6S_3$. Calculated, %: N 5.12; S 17.60.

***N*,*N*′-[2-(4-Methoxybenzenesulfonyl)benzene-1,4-diyl]bis(4-methylbenzenesulfonamide) (10b).** Yield 27%, mp 159–160°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.34 s and 2.35 s (3H each, 4′-Me), 3.87 s (3H, MeO), 7.11 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.19 d (1H, 6-H, J = 9.0 Hz), 7.24–7.27 d.d (1H, 5-H, J = 2.1, 8.7 Hz), 7.33 d (4H, 2′-H, 6′-H, J = 8.4 Hz), 7.59 d and 7.67 d (2H each, 3′-H, 5′-H, J = 8.4 Hz), 7.60 d (1H, 3-H, J = 2.1 Hz), 7.65 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 9.33 br.s and 10.62 s (1H each, NH). Found, %: N 4.59, 4.80; S 16.05, 16.56. $C_{27}H_{26}N_2O_7S_3$. Calculated, %: N 4.77; S 16.40.

***N*-[4-(Benzenesulfonamido)phenyl]-*N*-(benzenesulfonyl)-4-fluorobenzenesulfonamide (11a).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.90 d (2H, 2-H, 6-H, J = 8.7 Hz), 7.11 d (2H, 3-H, 5-H, J = 8.7 Hz), 7.50–7.84 m (10H, Ph), 7.56 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.75 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 10.76 s (1H, NH).

4-Methoxy-*N*-[4-(4-methylbenzenesulfonamido)-phenyl]-*N*-(4-methylbenzenesulfonyl)benzenesulfonamide (11b). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s and 2.44 s (3H each, 4-**Me**C_6H_4), 3.89 s (3H, MeO), 6.85 d (2H, 2-H, 6-H, J = 8.7 Hz), 7.09 d (2H, 3-H, 5-H, J = 8.7 Hz), 7.39 d (2H, 2′-H, 6′-H, J = 8.7 Hz), 7.43 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.47 d (2H, 2‴-H, 6‴-H, J = 8.7 Hz), 7.63 d (2H, 3‴-H, 5‴-H, J = 8.7 Hz), 7.71 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.71 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 10.68 s (1H, NH).

***N*,*N*′-(Benzene-1,4-diyl)dibenzenesulfonamide (12a).** Yield 82%, mp 247–248°C; published data [15]: mp 247°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.92 s (4H), 7.48–7.67 m (10H, Ph), 10.13 s (2H, NH). Found, %: N 7.03, 7.38; S 16.35, 16.72. $C_{18}H_{16}N_2O_4S_2$. Calculated, %: N 7.21; S 16.51.

***N*,*N*′-(Benzene-1,4-diyl)bis(4-methylbenzenesulfonamide) (12b).** Yield 89%, mp 265–266°C; published data [20]: mp 266°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (6H, Me), 6.90 s (4H), 7.29 d (4H, 2′-H, 6′-H, J = 8.1 Hz), 7.54 d (4H, 3′-H, 5′-H, J = 8.1 Hz), 10.04 s (2H, NH). Found, %: N 6.64, 6.80; S 15.15, 15.62. $C_{20}H_{20}N_2O_4S_2$. Calculated, %: N 6.73; S 15.40.

***N*,*N*′-[2-(4-Methylbenzenesulfonyl)benzene-1,4-diyl]bis[*N*′-(4-chlorobenzenesulfonyl)benzenecarboximidamide] (13a).** Yield 56%, mp 211–212°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, Me), 7.34 d (2H, 2″-H, 6″-H, J = 8.1 Hz), 7.46 d (1H, 5-H, J = 8.1 Hz), 7.49–7.65 m (10H, Ph), 7.50 d (4H, 2′-H, 6′-H, J = 8.7 Hz), 7.50–7.54 d.d (1H, 6-H, J = 2.1, 8.7 Hz), 7.57 d (2H, 3″-H, 5″-H, J = 8.1 Hz), 7.75 d (4H, 3′-H, 5′-H, J = 8.7 Hz), 8.58 d (1H, 3-H, J = 2.7 Hz), 10.44 d and 10.95 s (1H each, NH). Found, %: N 7.11, 6.83; S 11.98, 11.48. $C_{39}H_{30}Cl_2N_4O_6S_3$. Calculated, %: N 6.85; S 11.76.

***N*,*N*′-[2-(4-Methoxybenzenesulfonyl)benzene-1,4-diyl]bis[*N*′-(4-chlorobenzenesulfonyl)benzenecarboximidamide] (13b).** Yield 52%, mp 178–180°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.80 s (3H, MeO), 7.04 d (2H, 2″-H, 6″-H, J = 8.7 Hz), 7.27–7.60 m (10H, Ph), 7.48 d (1H, 5-H, J = 8.1 Hz), 7.50 d (4H, 2′-H, 6′-H, J = 8.7 Hz), 7.52–7.56 d.d (1H, 6-H, J = 2.1, 8.7 Hz), 7.62 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 7.75 d (4H, 3′-H, 5′-H, J = 8.7 Hz), 8.56 d (1H, 3-H, J = 2.4 Hz), 10.43 d and 10.94 s (1H each, NH). Found, %: N 6.62, 6.38; S 11.28, 11.73. $C_{39}H_{30}Cl_2N_4O_7S_3$. Calculated, %: N 6.72; S 11.54.

***N*,*N*′-(Benzene-1,4-diyl)bis[*N*′-(4-chlorobenzenesulfonyl)benzenecarboximidamide] (14).** Yield 93%, mp 288–289°C; published data [10]: mp 289°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.45–7.59 m (10H, Ph), 7.54 s (4H), 7.54 d (4H, 2′-H, 6′-H, J = 9.0 Hz), 7.65 d (4H, 3′-H, 5′-H, J = 9.0 Hz), 10.71 s (2H, NH).

***N*-[3-(4-Methoxybenzenesulfonyl)-4-(4-methylbenzenesulfonamido)phenyl]-4-methylbenzamide (15).** Yield 16%, mp 188–190°C. ^{1}H NMR spectrum** (DMSO-d_6), δ, ppm: 2.36 s (3H, 4′-Me), 2.39 s (3H,

** In the ^{1}H NMR spectra of **15**–**19**, triple primed locants refer to the 4-Me$C_6H_4SO_2$ substituent.

4‴-Me), 3.86 s (3H, MeO), 7.13 d (2H, 2″-H, 6″-H, *J* = 9.0 Hz), 7.34 d (2H, 2‴-H, 6‴-H, *J* = 8.1 Hz), 7.34 d (2H, 2′-H, 6′-H, *J* = 7.8 Hz), 7.38 d (1H, 5-H, *J* = 9.0 Hz), 7.71 d (2H, 3′-H, 5′-H, *J* = 7.8 Hz), 7.76 d (2H, 3″-H, 5″-H, *J* = 9.0 Hz), 7.87 d (2H, 3‴-H, 5‴-H, *J* = 8.1 Hz), 7.98–8.01 d.d (1H, 6-H, *J* = 2.7, 9.0 Hz), 8.48 d (1H, 2-H, *J* = 2.7 Hz), 9.38 s and 10.47 s (1H each, NH). Found, %: N 5.24, 4.96; S 11.60, 11.72. $C_{28}H_{26}N_2O_6S_2$. Calculated, %: N 5.09; S 11.65.

***N*-[2-(4-Methoxybenzenesulfonyl)-4-(4-methylbenzenesulfonamido)phenyl]-4-methylbenzamide (16).** Yield 9%, mp 243–244°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, 4′-Me), 2.41 s (3H, 4‴-Me), 3.80 s (3H, MeO), 7.01 d (2H, 2″-H, 6″-H, *J* = 8.4 Hz), 7.37 d (2H, 2‴-H, 6‴-H, *J* = 8.4 Hz), 7.38 d.d (1H, 5-H, *J* = 2.1, 9.0 Hz), 7.40 d (2H, 2′-H, 6′-H, *J* = 7.5 Hz), 7.55 d (2H, 3‴-H, 5‴-H, *J* = 8.4 Hz), 7.64 d (2H, 3′-H, 5′-H, *J* = 7.5 Hz), 7.79 d (1H, 3-H, *J* = 2.4 Hz), 7.81 d (2H, 3″-H, 5″-H, *J* = 8.4 Hz), 7.98 d (1H, 6-H, *J* = 9.0 Hz), 10.03 s and 10.59 br.s (1H, NH). Found, %: N 5.10, 5.22; S 11.48, 11.54. $C_{28}H_{26}N_2O_6S_2$. Calculated, %: N 5.09; S 11.65.

***N*-{4-[*N*-(4-Methoxybenzenesulfonyl)-4-methylbenzenesulfonamido]phenyl}-4-methylbenzamide (17).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.21 s (3H, 4′-Me), 2.35 s (3H, 4‴-Me), 3.87 s (3H, MeO), 7.26 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.33 d (2H, 2′-H, 6′-H, *J* = 7.8 Hz), 7.33 d (2H, 2‴-H, 6‴-H, *J* = 8.1 Hz), 7.59 d (2H, 2-H, 6-H, *J* = 8.1 Hz), 7.61 d (2H, 3-H, 5-H, *J* = 8.1 Hz), 7.75 d (2H, 3′-H, 5′-H, *J* = 7.8 Hz), 7.83 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 7.89 d (2H, 3‴-H, 5‴-H, *J* = 8.1 Hz), 10.25 s (1H, NH).

***N*-(4-Methoxybenzenesulfonyl)-4-methyl-*N*-[4-(4-methylbenzenesulfonamido)phenyl]benzamide (18).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.23 s (3H, 4′-Me), 2.37 s (3H, 4‴-Me), 3.88 s (3H, MeO), 6.99 d (2H, 2″-H, 6″-H, *J* = 9.0 Hz), 7.09 d (2H, 2‴-H, 6‴-H, *J* = 8.1 Hz), 7.20 d (2H, 2′-H, 6′-H, *J* = 7.8 Hz), 7.49 d (2H, 2-H, 6-H, *J* = 8.7 Hz), 7.52 d (2H, 3-H, 5-H, *J* = 8.7 Hz), 7.65 d (2H, 3″-H, 5″-H, *J* = 9.0 Hz), 7.73 d (2H, 3′-H, 5′-H, *J* = 7.8 Hz), 7.79 d (2H, 3‴-H, 5‴-H, *J* = 8.1 Hz), 9.83 s (1H, NH).

4-Methyl-*N*-[4-(4-methylbenzenesulfonamido)-phenyl]benzamide (19). Yield 83%, mp 240–241°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, 4′-Me), 2.37 s (3H, 4‴-Me), 7.04 d (2H, 2-H, 6-H, *J* = 8.7 Hz), 7.31 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.34 d (2H, 2‴-H, 6‴-H, *J* = 8.1 Hz), 7.60 d (2H, 3‴-H, 5‴-H, *J* = 8.1 Hz), 7.62 d (2H, 3-H, 5-H, *J* = 8.7 Hz), 7.82 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 10.08 s (2H, NH). Found, %: N 7.17, 7.48; S 8.26, 8.45. $C_{21}H_{20}N_2O_3S$. Calculated, %: N 7.36; S 8.43.

2,5-Bis(benzamido)phenyl acetate (20a). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.23 s (3H, Me), 7.51–7.98 m (10H, Ph), 7.61 d (1H, 3-H, *J* = 8.4 Hz), 7.63–7.66 d.d (1H, 4-H, *J* = 2.7, 8.4 Hz), 7.80 d (1H, 6-H, *J* = 1.8 Hz), 9.96 s and 10.43 s (1H each, NH).

2,5-Bis(4-methylbenzamido)phenyl acetate (20b). Yield 70%, mp 223–225°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.21 s (3H, Me), 2.39 s (6H, 4′-Me), 7.33 d (2H, 2′-H, 6′-H, *J* = 8.1 Hz), 7.35 d (2H, 2‴-H, 6‴-H, *J* = 8.1 Hz), 7.59 d (1H, 3-H, *J* = 9.0 Hz), 7.62–7.65 d.d (1H, 4-H, *J* = 2.4, 9.0 Hz), 7.78 d (1H, 6-H, *J* = 1.8 Hz), 7.86 d (2H, 3′-H, 5′-H, *J* = 8.1 Hz), 7.89 d (2H, 3‴-H, 5‴-H, *J* = 8.1 Hz), 9.85 s and 10.32 s (1H each, NH). Found, %: N 6.80, 7.18. $C_{24}H_{22}N_2O_4$. Calculated, %: N 6.96.

2,5-Bis(4-methoxybenzamido)phenyl acetate (20c). Yield 64%, mp 236–237.5°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.22 s (3H, Me), 3.84 s (6H, MeO), 7.06 d (2H, 2′-H, 6′-H, *J* = 8.4 Hz), 7.08 d (2H, 2‴-H, 6‴-H, *J* = 8.4 Hz), 7.59 d (1H, 3-H, *J* = 8.7 Hz), 7.62–7.65 d.d (1H, 4-H, *J* = 2.1, 9.0 Hz), 7.77 d (1H, 6-H, *J* = 2.1 Hz), 7.95 d (2H, 3′-H, 5′-H, *J* = 8.4 Hz), 7.98 d (2H, 3‴-H, 5‴-H, *J* = 8.4 Hz), 9.78 s and 10.25 s (1H each, NH). Found, %: N 6.35, 6.91. $C_{24}H_{22}N_2O_6$. Calculated, %: N 6.45.

***N*,*N*′-[2-(Benzenesulfonyl)benzene-1,4-diyl]dibenzamide (21a).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.49–8.04 m (15H, Ph), 7.77 d (1H, 5-H, *J* = 8.1 Hz), 8.14–8.17 d.d (1H, 6-H, *J* = 2.1, 8.4 Hz), 8.67 d (1H, 3-H, *J* = 2.4 Hz), 10.15 s and 10.64 s (1H each, NH).

***N*,*N*′-[2-(4-Methoxybenzenesulfonyl)benzene-1,4-diyl]bis(4-methoxybenzamide) (21b).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.78 s, 3.86 s, and 3.88 s (3H each, MeO); 7.04 d (2H, 2′-H, 6′-H, *J* = 9.0 Hz), 7.09 d (2H, 2‴-H, 6‴-H, *J* = 8.7 Hz), 7.16 d (2H, 2″-H, 6″-H, *J* = 8.7 Hz), 7.71 d (2H, 3″-H, 5″-H, *J* = 8.7 Hz), 7.79 d (1H, 5-H, *J* = 8.4 Hz), 7.93 d (2H, 3′-H, 5′-H, *J* = 9.0 Hz), 8.01 d (2H, 3‴-H, 5‴-H, *J* = 8.7 Hz), 8.13–8.17 d.d (1H, 6-H, *J* = 2.1, 7.8 Hz), 8.60 d (1H, 3-H, *J* = 2.4 Hz), 10.11 s and 10.43 s (1H each, NH).

***N*,*N*′-(Benzene-1,4-diyl)dibenzamide (22a).** Yield 91%, mp 336–338°C; published data [21]: mp 337–340°C. ^{1}H NMR spectrum (DMSO-d_6), δ,

ppm: 7.52–7.99 m (10H, Ph), 7.78 s (4H), 10.27 s (2H, NH).

***N*,*N*′-(Benzene-1,4-diyl)bis(4-methylbenzamide) (22b).** Yield 82%, mp 340°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 s (6H, Me), 7.33 d (4H, 2′-H, 6′-H, J = 7.5 Hz), 7.74 s (4H), 7.88 d (4H, 3′-H, 5′-H, J = 7.5 Hz), 10.12 s (2H, NH). Found, %: N 7.87, 8.28. $C_{22}H_{20}N_2O_2$. Calculated, %: N 8.13.

***N*,*N*′-(Benzene-1,4-diyl)bis(4-methoxybenzamide) (22c).** Yield 35%, mp 336–337°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.84 s (6H, MeO), 7.07 d (4H, 2′-H, 6′-H, J = 8.7 Hz), 7.74 s (4H), 7.98 d (4H, 3′-H, 5′-H, J = 8.7 Hz), 10.08 s (2H, NH). Found, %: N 7.74, 7.49. $C_{22}H_{20}N_2O_4$. Calculated, %: N 7.44.

REFERENCES

1. Adams, R. and Moje, W., *J. Am. Chem. Soc*., 1952, vol. 74, p. 5560.
2. Adams, R. and Samuels, W.P., *J. Am. Chem. Soc*., 1955, vol. 77, p. 5383.
3. Adams, R., Young, T.E., and Short, R.W.P., *J. Am. Chem. Soc*., 1954, vol. 76, p. 1114.
4. Adams, R. and Acker, D.S., *J. Am. Chem. Soc*., 1952, vol. 74, p. 3657.
5. Adams, R. and Nair, M.D., *J. Am. Chem. Soc*., 1956, vol. 78, p. 5927.
6. Adams, R. and Young, T.E., *J. Am. Chem. Soc*., 1953, vol. 75, p. 3235.
7. Adams, R. and Nair, M.D., *J. Am. Chem. Soc*., 1956, vol. 78, p. 5932.
8. Burmistrov, K.S. and Burmistrov, S.I., *Vopr. Khim. Khim. Technol*., 1981, no. 65, p. 42.
9. Konovalova, S.A., Avdeenko, A.P., Pirozhenko, V.V., Ledeneva, O.P., and Santalova, A.A., *Russ. J. Org. Chem*. 2014, vol. 50, p. 1283.
10. Avdeenko, A.P., Burmistrov, K.S., Dubina, V.L., and Skripets, V.I., *Ukr. Khim. Zh*., 1980, vol. 46, p. 1081.
11. Burmistrov, K.S. and Burmistrov, S.I., *Zh. Org. Khim*., 1980, vol. 16, p. 1487.
12. Burmistrov, K.S., *Doctoral (Chem.) Dissertation*, Dnepropetrovsk, 1990.
13. Zefirov, Yu.V., *Kristallografiya*, 1997, vol. 42, p. 936.
14. Sheldrick, G.M., *SHELXTL PLUS. PC Version. A System of Computer Programs for the Determination of Crystal Structure from X-Ray Diffraction Data. Rev.5.1*, 1998.
15. Adams, R. and Nagarkatti, A.S., *J. Am. Chem. Soc*., 1950, vol. 72, p. 4601.
16. Boger, D.L. and Zarrinmayeh, H., *J. Org. Chem*., 1990, vol. 55, p. 1379.
17. Adams, R. and Reifschneider, W., *Bull. Soc. Chim. Fr*., 1958, vol. 25, p. 23.
18. Konovalova, S.A., Avdeenko, A.P., Pirozhenko, V.V., Goncharova, S.A., Shishkin, O.V., and Palamarchuk, G.V., *Russ. J. Org. Chem*., 2014, vol. 50, p. 1465.
19. Whitmore, F.C. and Hamilton, F.H., *Org. Synth*., 1922, vol. 2, p. 89.
20. Willstatter, R. and Pfannenstiel, A., *Ber*., 1905, vol. 38, p. 2244.
21. Adams, R. and Anderson, J., *J. Am. Chem. Soc*., 1950, vol. 72, p. 5154.