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Halogenation of *N*-Substituted *p*-Quinone Monoimines and *p*-Quinone Monooxime Ethers: XIV.* Halogenation of *N*-[Arylsulfonylimino(phenyl)methyl]-2,5-dialkyl-1,4-benzoquinone Monoimines and Their Reduction Products

A. P. Avdeenko[a], S. A. Konovalova[a], O. P. Ledeneva[a], A. A. Santalova[a], V. V. Pirozhenko[b], G. V. Palamarchuk[c], and O. V. Shishkin[c, d]

[a] *Donbass State Engineering Academy, ul. Shkadinova 72, Kramatorsk, 84313 Ukraine*
e-mail: chimist@dgma.donetsk.ua

[b] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 5, Kiev, 02660 Ukraine*

[c] *Institute of Single Crystals, National Academy of Sciences of Ukraine, Kharkiv, Ukraine*

[d] *Karazin Kharkiv National University, Kharkiv, Ukraine*

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Abstract—Despite steric hindrances created by the bulky substituent on the nitrogen atom, halogenation of 2,5-dialkyl-*N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines fairly readily gives their derivatives having two halogen atoms in the quinoid ring.

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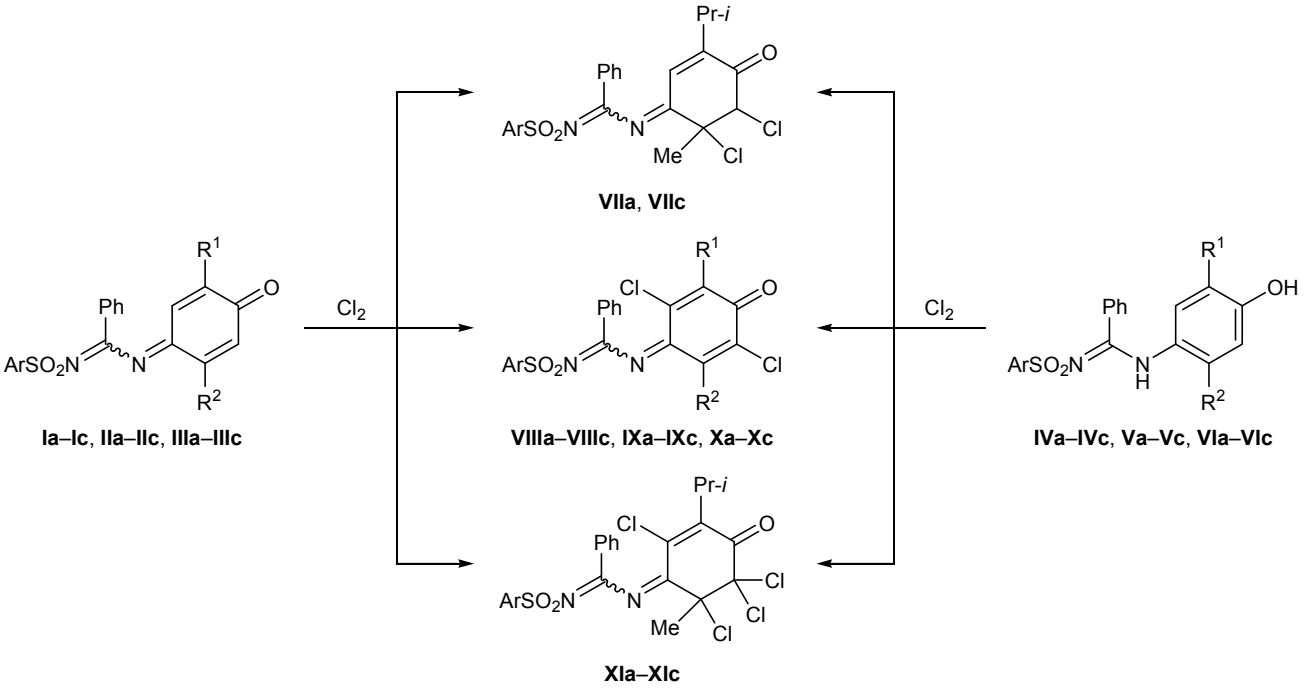
Halogenation of *N*-arylsulfonyl- [2–6] and *N*-aroyl-1,4-benzoquinone monoimines [1, 5–8] has been studied in sufficient detail. Differences in the behavior of these compounds under halogenation conditions reflect different electronic properties of substituents on the nitrogen atom; therefore, they may be related to the redox potentials [9]. *N*-Aroyl derivatives contain a π-electron-acceptor substituent on the nitrogen atom and are characterized by high redox potentials, which largely determines the results of their halogenation. Unlike analogous *N*-arylsulfonyl-1,4-benzoquinone monoimines [3], halogenation of *N*-aroyl-2,5-dialkyl-1,4-benzoquinone monoimines involves methyl groups in the quinoid ring and is accompanied by formation of cyclohex-2-ene-1,4-dione derivatives having an aroyloxy group in the 5-position [8] and 1,3-benzoxazoles [1]. Cyclohexene (semiquinoid) compounds were isolated only in a few cases [1, 5–8], though (as in the halogenation of *N*-arylsulfonyl analogs) cyclohexene compounds are stable and fairly readily isolable [3].

N-[Arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines rank between *N*-arylsulfonyl- and *N*-aroyl-1,4-benzoquinone monoimines with respect to their redox potentials [10–12]. For example, in some cases *N*-arylsulfonylimino(phenyl)methyl derivatives react with sodium arenesulfinates like *N*-arylsulfonyl derivatives, while in other cases, like *N*-aroyl analogs [13, 14]. On the other hand, the presence of a considerably bulkier substituent on the nitrogen atom in *N*-arylsulfonylimino(phenyl)methyl derivatives could affect their behavior in reactions with halogens. Therefore, it seemed reasonable to elucidate how the above two factors (intermediate redox potential and large substituent on the nitrogen) could affect halogenation of *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines.

We previously demonstrated similarity in the chlorination of *N*-[arylsulfonylimino(phenyl)methyl]- [15] and *N*-arylsulfonyl-1,4-benzoquinone monoimines [16] having no substituents in the quinoid ring. In both cases, compounds containing different numbers of chlorine atoms in the quinoid ring were obtained. On

* For communication XIII, see [1].

Scheme 1.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**); **I**, **IV**, **VIII**, $R^1 = R^2 = Me$; **II**, **V**, **IX**, $R^1 = i$-Pr, $R^2 = Me$; **III**, **VI**, **X**, $R^1 = Me$, $R^2 = i$-Pr.

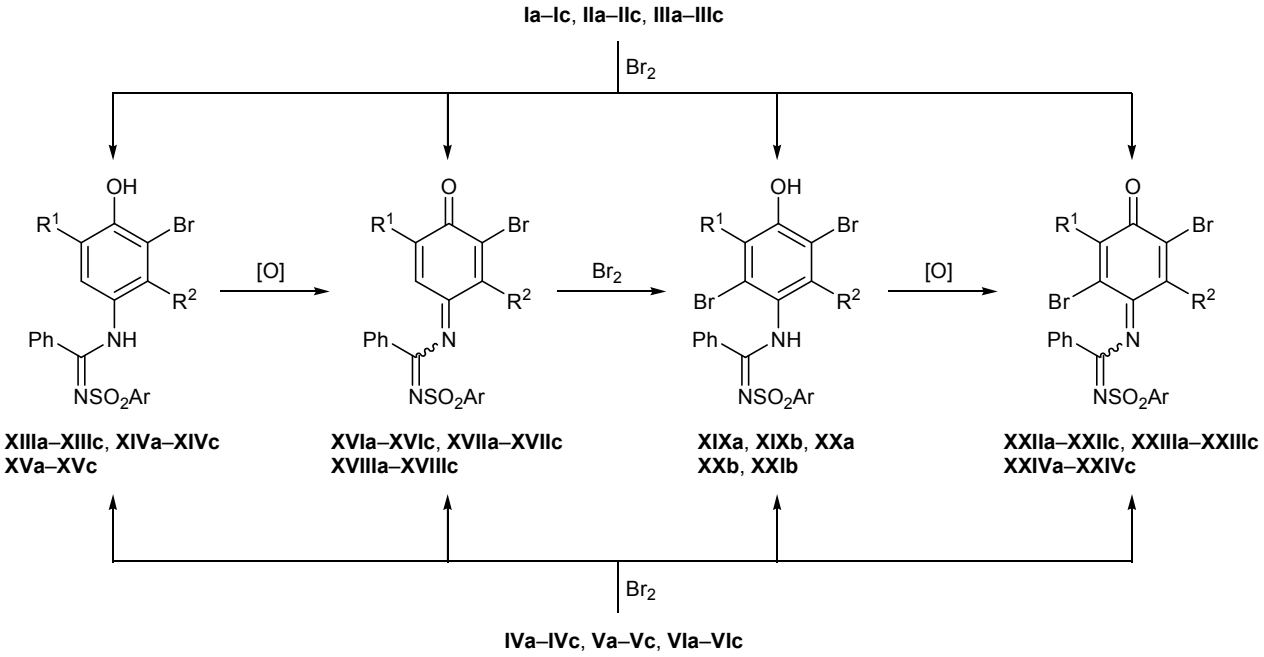
the other hand, in the chlorination of unsubstituted *N*-aroyl derivatives we succeeded in isolating only aminophenols and quinone imines with three and four halogen atoms in the quinoid ring [17]. Halogenation of alkyl-substituted *N*-[arylsulfonylimino(phenyl)-methyl]-1,4-benzoquinone monoimines was not studied previously, though the presence of alkyl substituents in the quinoid ring is known to considerably affect the reaction course and the possibility for isolating intermediate products [1–8].

The goal of the present work was to reveal general relations holding in the halogenation of alkyl-substituted *N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines. As substrates we selected benzoquinone imine derivatives **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc** with methyl and isopropyl groups in positions *2* and *5* of the quinoid ring, as well as their reduction products, the corresponding aminophenols **IVa**–**IVc**, **Va**–**Vc**, and **VIa**–**VIc**. Compounds **I**–**III** were synthesized by oxidation of aminophenols **IV**–**VI** with lead tetraacetate in acetic acid. It is characteristic that quinone imines **I**–**III** do not undergo *Z*/*E* isomerization with respect to the quinone imine C=N bond [18], i.e., they exist in solution as a single isomer.

The halogenation of all quinone imines **I**–**III** and aminophenols **IV**–**VI** was performed using gaseous chlorine or molecular bromine (substrate-to-bromine ratio 1:3 or 1:5) in chloroform, acetic acid, or DMF–AcOH (1:5). The chlorination of **Ia**–**Ic**, **IIIa**–**IIIc**, **IVa**–**IVc**, and **VIa**–**VIc** gave the corresponding 3,6-dichloro derivatives **VIIIa**–**VIIIc** and **Xa**–**Xc** (Scheme 1) whose structure was determined on the basis of ^{1}H NMR data. By chlorination of **IIa** and **IIc** in chloroform we obtained 5,6-dichlorocyclohex-2-en-1-ones **VIIa** and **VIIc**, while the chlorination of **IIb** and **Va**–**Vc** in chloroform and DMF–AcOH (1:5) led to the formation of mixtures of 2,5-dichlorocyclohexa-2,5-dien-1-ones **IXa**–**IXc** and 3,5,6,6-tetrachlorocyclohex-2-en-1-ones **XIa**–**XIc**, which we failed to separate. Compound **VIIc** was also obtained only as a mixture with **IXc**.

Compounds **VIIa** and **VIIc** displayed in the ^{1}H NMR spectra a broadened singlet from the 6-H proton (δ 4.62 ppm), and the 3-H proton and 5-Me or 5-*i*-Pr group gave rise to double sets of strongly broadened signals (δ 6.28, 2.13–2.15, 0.96 and 6.37–6.39, 1.97–2.02, 1.08 ppm, respectively). Presumably, the presence of two sets of signals results from *Z*/*E*-isomerization with respect to the quinone imine C=N bond. No signals assignable to protons in the quinoid ring were observed in the ^{1}H NMR spectra of **IXa**–**IXc** and **XIa**–**XIc**. Quinone imines **IXa**–**IXc** were characterized by signals from the C**H**Me_2 proton (δ 3.31–3.42 ppm) and methyl protons (δ 2.36–2.37 ppm),

Scheme 2.



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**); **XIII**, **XVI**, **XIX**, **XXII**, $R^1 = R^2 = Me$; **XIV**, **XVII**, **XX**, **XXIII**, $R^1 = i$-Pr, $R^2 = Me$; **XV**, **XVIII**, **XXI**, **XXIV**, $R^1 = Me$, $R^2 = i$-Pr.

which were displaced downfield relative to the corresponding signals of initial quinone imines **IIa**–**IIc** (δ 2.92–3.03 and 2.19–2.22 ppm, respectively) [18]; the downfield shift is induced by the neighboring chlorine atoms. In the ^1H NMR spectra of **XIa**–**XIc**, the methyl proton signal appeared as a singlet at δ 2.21–2.24 ppm, which is typical of methyl group attached to an sp^3-carbon atom.

Quinone imines **IXa**–**IXc** and **Xa**–**Xc** and cyclohexenones **XIa**–**XIc** characteristically displayed doubling of the doublet signals from methyl protons in the isopropyl group. Analogous signal splitting was observed previously only in the spectra of halogen-containing cyclohexene (semiquinoid) structures obtained by halogrnation of *N*-arylsulfonyl- [2–6] and *N*-aroyl-1,4-benzoquinone monoimines [5–8]. The observed pattern may be rationalized assuming that methyl groups in the isopropyl fragment are diastereotopic due to the presence of bulky substituents in positions *3* and *5*, which restrict free rotation about the C(Ph)–N single bond, thus giving rise to internal axial chirality. Conformational behavior of imidoyl derivatives will be the subject of our separate study. Compounds **XIa**–**XIc** possess an asymmetric carbon atom, which may also be responsible for diastereotopicity of isopropyl methyl groups. The magnitude of splitting of the CH**Me**$_2$ doublets in the ^1H NMR spectra of **XIa**–**XIc** is much greater than in the spectra of other cyclohexene compounds. Such splitting is typical of semiquinoid structures with two halogen atoms attached to sp^3-carbon atom [8].

The bromination of **I**–**III** and **IV**–**VI** in chloroform with 3 equiv of bromine afforded 2-bromophenols **XIII**–**XV**, while 2,5-dibromophenols **XIXa**, **XIXb**, **XXa**, **XXb**, and **XXIb** were formed in the reaction of the same substrates with 5 equiv of Br_2 (Scheme 2) or via bromination of **XVI**–**XVIII** in chloroform. Quinone imines **XVI**–**XVIII** were synthesized by oxidation of aminophenols **XIII**–**XV** with lead tetraacetate in acetic acid, as well as by bromination of **I**–**III** or **IV**–**VI** in acetic acid. Quinone imines **XXII**–**XXIV** were obtained by bromination of **I**–**III** and **IV**–**VI** in DMF–AcOH (1 : 5) using 5 equiv of bromine and by oxidation of **XIXa**, **XIXb**, **XXa**, **XXb**, and **XXIb** with lead tetraacetate in acetic acid. We failed to isolate compounds **XXIIc** and **XXIVa** as individual substances, and they were isolated only as mixtures with quinone imines **XVIc** and **XVIIIa**, respectively.

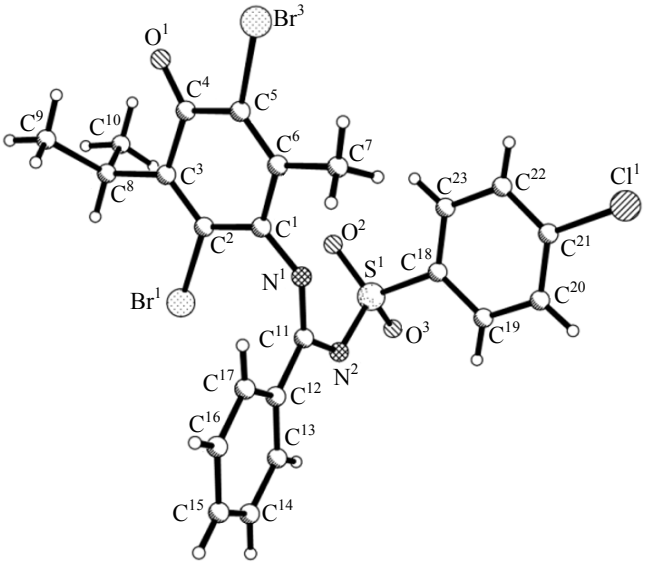
Aminophenols **XIII**–**XV** and quinone imines **XVI**–**XVIII** were identical to those synthesized previously by hydrobromination of 2,5-dialkyl-*N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines [18]. The structure of aminophenols **XXa** and **XXb** and quinone imines **XXII**–**XXIV** was confirmed by

their ^{1}H and ^{13}C NMR spectra. It should be noted that compounds **XXIIIa**–**XXIIIc** and **XXIVa**–**XXIVc**, like **IXa**–**IXc** and **Xa**–**Xc**, displayed in the ^{1}H NMR spectra doublets of doublets due to methyl groups in the isopropyl fragment. As noted above, this is the result of restricted rotation about the C(Ph)–N bond, which endows their molecules with internal chirality and makes the methyl groups diastereotopic. In the spectra of **XVIIa**–**XVIIc** and **XVIIIa**–**XVIIIc** having no substituent in one *ortho* position with respect to the C=N group, such signal doubling is observed only at reduced temperature. This indicates that the rotation about the C(Ph)–N bond becomes possible as the size of the *ortho*-substituent decreases.

The structure of quinone imines **XXII**–**XXIV** was also confirmed by the X-ray diffraction data for 2,5-dibromo derivative **XXIIIc** (see figure). The quinoid ring C^1–C^6 in molecule **XXIIIc** has a flattened *twist-boat* conformation with the following puckering parameters [19]: $S = 0.15$, $\Theta = 65.04$, $\Psi = 13.80$; the C^1, C^6, C^5, and C^4 atoms lie in one plane [the torsion angle $C^1C^6C^5C^4$ is –0.9(3)°], and the C^2 and C^3 atoms deviate from that plane by 0.145(3) and 0.205(3) Å, respectively. Presumably, nonplanar structure of the C^1–C^6 ring is determined by repulsion of spatially close substituents (shortened contacts $Br^1\cdots C^{11}$ 3.011 and $O^1\cdots C^9$ 2.923 Å; sum of the van der Waals radii 3.67 and 2.99 Å [20], respectively). Taking into account high conformational flexibility of the quinoid ring, such mode of steric strain relaxation seems to be one of the most favorable [21, 22].

The substituent on C^3 is oriented in such a way that the H^8 atom appears almost in the C^1–C^6 ring plane (torsion angle $H^8C^8C^3C^2$ 15°). The presence of a bulky substituent on N^1 causes it to rotate about the N^1–C^{11} bond [torsion angle $N^2C^{11}N^1C^1$ 100.5(9)°], so that conjugation between the double C=N bonds is disrupted. In addition, the bond angles at C^1 deviate from the trigonal configuration [$C^6C^1N^1$ 116.2(6), $C^2C^1N^1$ 124.5(6)°]. The $N^1C^{11}N^2S^1$ fragment is almost planar and coplanar to the C^{12}–C^{17} benzene ring [torsion angles $N^1C^{11}N^2S^1$ 12(9) and $N^1C^{11}C^{12}C^{17}$ 1.1(9)°]. The N^2–S^1 bond is +*synclinal* relative to the C^{18}–C^{19} bond in the chlorophenyl substituent, the torsion angle $N^2S^1C^{18}C^{19}$ being 56.6(6)°.

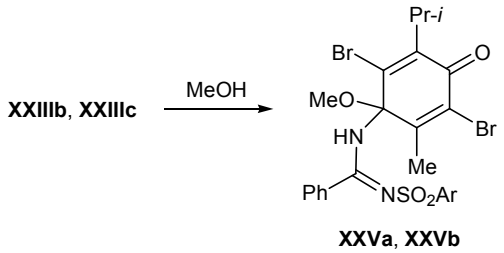
Molecule **XXIIIc** is characterized by considerable increase of the C=N–C angle [135.4(6)°] due to effect of substituents in positions *3* and *5* of the quinoid ring. Therefore, we presumed that quinone imines **VIII**–**X** and **XXII**–**XXIV** possess an activated sterically strained C=N bond, which inevitably should affect their reactivity, e.g., toward alcohols [23]. In fact, quinone imines **XXIIIb** and **XXIIIc** reacted with methanol to give compounds **XXVa** and **XXVb** as a result of 1,2-addition (Scheme 3).



Structure of the molecule of *N*′-(4-chlorophenylsulfonyl)-*N*-[2,5-dibromo-6-methyl-4-oxo-3-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene]benzimidamide (**XXIIIc**) according to the X-ray diffraction data.

Thus, reactions of 2,5-dialkyl-*N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines with halogens give mainly products with maximal degree of halogenation. Semiquinoid structures were obtained only in a few cases, which indicates their instability, in keeping with our previous data on the halogenation of *N*-aroyl-1,4-benzoquinone monoimines. Facile formation of quinone imines having two halogen atoms in the quinoid ring should also be noted. No such compounds were obtained by halogenation of *N*-arylsulfonyl- [2–6] and *N*-aroyl-1,4-benzoquinone monoimines [5–8] or by hydrohalogenation of 2,5-dialkyl-*N*-[arylsulfonylimino(phenyl)methyl]-1,4-benzoquinone monoimines [18].

Scheme 3.



Ar = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**).

As shown previously [4, 7, 8], halogenation of quinone imines involves a series of consecutive reactions. Depending on the reaction conditions and substrate structure, the results are determined by the order of the following processes: halogen addition, dehydrohalogenation, oxidation, reduction, hydrohalogenation, electrophilic substitution. On the basis of our previous data and those obtained in the present work, we believe that aminophenols **XIX**–**XXI** are formed via addition of halogen molecule to quinone imines **XVI**–**XVIII** through intermediate unstable semiquinoid structures. The latter undergo dehydrohalogenation, followed by reduction of quinone imines thus formed. Semiquinoid structures formed by addition of halogen molecule at the C=C bond of *N*-arylsulfonyl- and *N*-aroyl-1,4-benzoquinone monoimines are more stable, and they do not undergo dehydrohalogenation [2–8]. Another possible way of formation of aminophenols **XIX**–**XXI** is electrophilic replacement of 3-H in aminophenols **XIII**–**XV** by bromine atom.

The formation of quinone imines **VIII**–**X** and **XXII**–**XXIV** in DMF–AcOH (1:5) is the result of either oxidation of the corresponding aminophenols or addition of halogen to quinone imines already containing one halogen atom and subsequent dehydrohalogenation.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively, using tetramethylsilane as internal reference. The IR spectra of aminophenols **XIXa**, **XIXb**, **XXa**, **XXb**, and **XXIb** contained absorption bands at 3430–3440 (OH), 3310–3330 (NH), 1620–1640 (C=N), and 1150, 1290 cm^{-1} (SO_2), and quinone imines **XXIIa**, **XXIIb**, **XXIIIa**–**XXIIIc**, **XXIVb**, and **XXIVc** displayed absorption bands at 1670 (C=O), 1580 (C=N), and 1180, 1320 cm^{-1} (SO_2).

The reaction mixtures were analyzed by TLC on Silufol UV-254 plates; samples were applied from solutions in chloroform, and benzene–hexane (10:1) was used as eluent; spots were visualized under UV light.

The X-ray diffraction data for compound **XXIIIc** were acquired on an Xcalibur-3 diffractometer (MoK_α irradiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ = 50°). Triclinic crystals, $C_{23}H_{19}Br_2ClN_2O_3S$, with the following unit cell parameters (293 K): a = 7.825(2), b = 13.115(6), c = 13.1256(7) Å; α = 75.419(7), β = 73.97(3), γ = 74.073(7)°; V = 1222.2(6) Å^3; M_r = 598.73; Z = 2; space group P-1; d_{calc} = 1.627 g/cm^3; μ(MoK_α) = 3.538 mm^{-1}; F(000) = 596. Total of 7989 reflection intensities were measured; 3972 reflections were independent (R_{int} = 0.031). The structure was solved by the direct method using SHELXTL software package [24]. The positions of hydrogen atoms were determined by the difference synthesis of electron density and were refined according to the riding model ($U_{iso} = nU_{eq}$ for a non-hydrogen atom linked to the given hydrogen atom; n = 1.5 for methyl groups and 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 = 0.179 (3947 reflections), R_1 = 0.066 [2342 reflections with $F > 4\sigma(F)$, S = 1.007]. The final coordinates of atoms, geometric parameters of the molecule, and crystallographic data were deposited to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +441223336033; e-mail: *deposit@ccdc.cam.ac.uk*); entry no. CCDC 827793.

Compounds **IV**–**VI** were synthesized by reaction of the corresponding 4-amino-2,5-dialkylphenols with *N*-arylsulfonylbenzimidoyl chlorides in DMF–AcOH (1:3) in the presence of anhydrous sodium acetate; oxidation of **IV**–**VI** with lead tetraacetate in acetic acid according to [12] gave compounds **I**–**III**. Compounds **Ia** [25], **Ib**, **IIIb** [14], **Ic**, **IIa**–**IIc**, **IIIa**, **IIIc**, **VIII**–**X**, and **XIII**–**XVIII** [18] were reported previously; the spectra of **I**–**III**, **XVIa**–**XVIc**, and **XVIIa**–**XVIIc** were given in [18].

***N*-(4-Hydroxy-2,5-dimethylphenyl)-*N′*-(phenylsulfonyl)benzimidamide (IVa).** Yield 69%, mp 174–175°C. Found, %: N 7.30, 7.45; S 8.40, 8.58. $C_{21}H_{20}N_2O_3S$. Calculated, %: N 7.36; S 8.43.

***N*-(4-Hydroxy-2,5-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzimidamide (IVb).** Yield 62%, mp 175.5–176°C. Found, %: N 7.03, 7.24; S 8.11, 8.38. $C_{22}H_{22}N_2O_3S$. Calculated, %: N 7.10; S 8.13.

***N′*-(4-Chlorophenylsulfonyl)-*N*-(4-hydroxy-2,5-dimethylphenyl)benzimidamide (IVc).** Yield 54%, mp 196–197°C. Found, %: N 6.78, 6.91; S 7.61, 7.83. $C_{21}H_{19}ClN_2O_3S$. Calculated, %: N 6.75; S 7.73.

***N*-[4-Hydroxy-2-methyl-5-(propan-2-yl)phenyl]-*N′*-(phenylsulfonyl)benzimidamide (Va).** Yield 94%, mp 181–182°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.08 d (6H, 5-CH**Me**$_2$, J = 8.7 Hz), 2.07 s (3H, 2-Me), 3.07–3.13 m (1H, 5-CH), 6.63 s (1H, 6-H), 6.98 s (1H, 3-H), 7.38–7.57 m (10H, Ph), 9.32 s (1H,

NH), 9.96 s (1H, OH). Found, %: N 6.80, 6.95; S 7.51, 7.78. $C_{23}H_{24}N_2O_3S$. Calculated, %: N 6.86; S 7.85.

***N*-[4-Hydroxy-2-methyl-5-(propan-2-yl)phenyl]-*N′*-(4-methylphenylsulfonyl)benzimidamide (Vb).** Yield 96%, mp 166.5–167°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.08 d (6H, 5-CH**Me**$_2$, J = 9.0 Hz), 2.07 s (3H, 2-Me), 2.31 s (3H, **Me**C$_6$H$_4$), 3.07–3.13 m (1H, 5-CH), 6.62 s (1H, 6-H), 6.95 s (1H, 3-H), 7.17 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.37 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 7.45–7.58 m (5H, Ph), 9.32 s (1H, NH), 9.91 s (1H, OH). Found, %: N 6.34, 6.49; S 7.60, 7.82. $C_{24}H_{26}N_2O_3S$. Calculated, %: N 6.63; S 7.59.

***N′*-(4-Chlorophenylsulfonyl)-*N*-[4-hydroxy-2-methyl-5-(propan-2-yl)phenyl]benzimidamide (Vc).** Yield 71%, mp 163–164°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.04 d (6H, 5-CH**Me**$_2$, J = 8.7 Hz), 2.06 s (3H, 2-Me), 3.06–3.13 m (1H, 5-CH), 6.63 s (1H, 6-H), 6.94 s (1H, 3-H), 7.39–7.58 m (5H, Ph), 7.49 d (2H, 3′-H, 5′-H, J = 6.3 Hz), 7.60 d (2H, 2′-H, 6′-H, J = 6.3 Hz), 9.32 s (1H, NH), 10.05 s (1H, OH). Found, %: N 6.30, 6.45; S 7.40, 7.58. $C_{23}H_{23}ClN_2O_3S$. Calculated, %: N 6.32; S 7.24.

***N*-[4-Hydroxy-5-methyl-2-(propan-2-yl)phenyl]-*N′*-(phenylsulfonyl)benzimidamide (VIa).** Yield 65%, mp 180–181°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.08 d (6H, 2-CH**Me**$_2$, J = 8.7 Hz), 2.06 s (3H, 5-Me), 2.96–3.07 m (1H, 2-CH), 6.70 s (1H, 3-H), 6.87 s (1H, 6-H), 7.37–7.53 m (10H, Ph), 9.32 s (1H, NH), 10.04 br.s (1H, OH). Found, %: N 6.90, 7.25; S 7.56, 7.81. $C_{23}H_{24}N_2O_3S$. Calculated, %: N 6.86; S 7.85.

***N*-[4-Hydroxy-5-methyl-2-(propan-2-yl)phenyl]-*N′*-(4-methylphenylsulfonyl)benzimidamide (VIb).** Yield 62%, mp 177.5–178.5°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.08 d (6H, 2-CH**Me**$_2$, J = 8.7 Hz), 2.06 s (3H, 5-Me), 2.93–2.99 m (1H, 2-CH), 6.71 s (1H, 3-H), 6.87 s (1H, 6-H), 7.33 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.40–7.56 m (5H, Ph), 7.59 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 9.32 s (1H, NH), 10.12 br.s (1H, OH). Found, %: N 6.49, 6.62; S 7.36, 7.58. $C_{24}H_{26}N_2O_3S$. Calculated, %: N 6.63; S 7.55.

***N′*-(4-Chlorophenylsulfonyl)-*N*-[4-hydroxy-5-methyl-2-(propan-2-yl)phenyl]benzimidamide (VIc).** Yield 63%, mp 196–197°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.08 d (6H, 2-CH**Me**$_2$, J = 9.0 Hz), 2.06 s (3H, 5-Me), 2.91–2.99 m (1H, 2-CH), 6.71 s (1H, 3-H), 6.86 s (1H, 6-H), 7.32 d (2H, 3′-H, 5′-H, J = 7.8 Hz), 7.43–7.59 m (5H, Ph), 7.57 d (2H, 2′-H, 6′-H, J = 7.8 Hz), 9.33 s (1H, NH), 10.14 br.s (1H, OH). Found, %: N 6.18, 6.35; S 7.32, 7.48. $C_{23}H_{23}ClN_2O_3S$. Calculated, %: N 6.32; S 7.24.

Chlorination of substituted *N*-(arylsulfonyl)-benzimidamides I–III and IV–VI (*general procedure*). Gaseous chlorine was passed at a flow rate of 15–20 ml/min through a solution of 2 mmol of compound **I–VI** in 3 ml of chloroform or dimethylformamide–acetic acid (1:5) until saturation. The mixture was kept for 24 h, and the precipitate was filtered off and recrystallized from acetic acid.

***N*-[5,6-Dichloro-6-methyl-4-oxo-3-(propan-2-yl)-cyclohex-2-en-1-ylidene]-*N′*-(phenylsulfonyl)benzimidamide (VIIa).** Yield 75%, mp 134–135°C. ^{1}H NMR spectrum ($CDCl_3$), isomer mixture, δ, ppm: 0.96 br.d (3H, 3-CH**Me**$_2$, J = 2.4 Hz), 1.1 br.s (3H, 3-CH**Me**$_2$), 2.02 br.s and 2.15 br.s (3H, 6-Me), 2.91–3.01 m (1H, 3-CH), 4.62 br.s (1H, 5-H), 6.28 br.s and 6.39 br.s (1H, 2-H), 7.42–8.06 m (10H, Ph). Found, %: Cl 14.61, 14.89; N 5.70, 5.93; S 6.70, 7.01. $C_{23}H_{22}Cl_2N_2O_3S$. Calculated, %: Cl 14.85; N 5.87; S 6.72.

***N′*-(4-Chlorophenylsulfonyl)-*N*-[5,6-dichloro-6-methyl-4-oxo-3-(propan-2-yl)cyclohex-2-en-1-ylidene]benzimidamide (VIIc).** ^{1}H NMR spectrum ($CDCl_3$), isomer mixture, δ, ppm: 1.0 br.d (3H, 3-CH**Me**$_2$, J = 2.4 Hz), 1.08 br.s (3H, 3-CH**Me**$_2$), 2.02 br.s and 2.15 br.s (3H, 6-Me), 2.92–3.02 m (1H, 3-CH), 4.63 br.s (1H, 5-H), 6.28 br.s and 6.37 br.s (1H, 2-H), 7.43–7.86 m (5H, Ph), 7.51 d (2H, 3′-H, 5′-H, J = 7.5 Hz), 7.99 d (2H, 2′-H, 6′-H, J = 7.5 Hz).

***N*-(2,5-Dichloro-3,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(phenylsulfonyl)benzimidamide (VIIIa).** Yield 85%, mp 126–128°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.08 s (6H, 3-Me, 6-Me), 7.43–8.07 m (10H, Ph). Found, %: Cl 15.47, 15.62; N 6.04, 6.38; S 7.19, 7.32. $C_{21}H_{16}Cl_2N_2O_3S$. Calculated, %: Cl 15.85; N 6.26; S 7.17.

***N*-(2,5-Dichloro-3,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-methylphenylsulfonyl)-benzimidamide (VIIIb).** Yield 60%, mp 147–149°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.08 s (6H, 3-Me, 6-Me), 2.45 s (3H, **Me**C$_6$H$_4$), 7.34 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.42–7.93 m (5H, Ph), 7.93 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Cl 15.06, 15.32; N 6.14, 6.37; S 6.88, 6.98. $C_{22}H_{18}Cl_2N_2O_3S$. Calculated, %: Cl 15.37; N 6.07; S 6.95.

***N′*-(4-Chlorophenylsulfonyl)-*N*-(2,5-dichloro-3,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzimidamide (VIIIc).** Yield 84%, mp 135–136°C.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.06 s (6H, 3-Me, 6-Me), 7.42–7.83 m (5H, Ph), 7.52 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 8.00 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Cl 21.88, 22.07; N 5.62, 5.73; S 6.29, 6.41. $C_{21}H_{15}Cl_3N_2O_3S$. Calculated, %: Cl 22.08; N 5.81; S 6.66.

***N*-[2,5-Dichloro-6-methyl-4-oxo-3-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N*′-(phenylsulfonyl)-benzimidamide (IXa).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 d.d (6H, 3-CH**Me**$_2$, J = 6.9, 12 Hz), 2.36 s (3H, 6-Me), 3.31–3.42 m (1H, 3-CH), 7.43–8.07 m (10H, Ph).

***N*-[2,5-Dichloro-6-methyl-4-oxo-3-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N*′-(4-methylphenylsulfonyl)benzimidamide (IXb).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 d.d (6H, 3-CH**Me**$_2$, J = 6.9, 12 Hz), 2.36 s (3H, 6-Me), 2.44 s (3H, **Me**C_6H_4), 3.31–3.42 m (1H, 3-CH), 7.33 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.43–7.81 m (5H, Ph), 7.90 d (2H, 2′-H, 6′-H, J = 8.4 Hz).

***N*′-(4-Chlorophenylsulfonyl)-*N*-[2,5-dichloro-6-methyl-4-oxo-3-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene]benzimidamide (IXc).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 d.d (6H, 3-CH**Me**$_2$, J = 6.9, 12.6 Hz), 2.37 s (3H, 6-Me), 3.31–3.42 m (1H, 3-CH), 7.42–7.79 m (5H, Ph), 7.47 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.96 d (2H, 2′-H, 6′-H, J = 8.7 Hz).

***N*-[2,5-Dichloro-3-methyl-4-oxo-6-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N*′-(phenylsulfonyl)-benzimidamide (Xa).** Yield 54%, mp 137–139°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.49 d.d (6H, 6-CH**Me**$_2$, J = 6.9, 12.9 Hz), 2.07 s (3H, 3-Me), 3.72–3.81 m (1H, 6-CH), 7.38–8.08 m (10H, Ph). Found, %: Cl 14.38, 14.50; N 5.27, 5.39; S 6.81, 6.92. $C_{23}H_{20}Cl_2N_2O_3S$. Calculated, %: Cl 14.92; N 5.89; S 6.75.

***N*-[2,5-Dichloro-3-methyl-4-oxo-6-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N*′-(4-methylphenylsulfonyl)benzimidamide (Xb).** Yield 71%, mp 170–172°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.49 d.d (6H, 6-CH**Me**$_2$, J = 6.9, 13.2 Hz), 2.07 s (3H, 3-Me), 2.44 s (3H, **Me**C_6H_4), 3.71–3.81 m (1H, 6-CH), 7.32–7.57 m (5H, Ph), 7.76 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.95 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Cl 14.05, 14.27; N 5.63, 5.82; S 6.19, 6.33. $C_{24}H_{22}Cl_2N_2O_3S$. Calculated, %: Cl 14.49; N 5.72; S 6.55.

***N*′-(4-Chlorophenylsulfonyl)-*N*-[2,5-dichloro-3-methyl-4-oxo-6-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene]benzimidamide (Xc).** Yield 86%, mp 160–161°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.49 d.d (6H, 6-CH**Me**$_2$, J = 7.2, 12.6 Hz), 2.07 s (3H, 3-Me), 3.71–3.80 m (1H, 6-CH), 7.39–7.76 m (5H, Ph), 7.52 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 8.01 d (2H, 2′-H, 6′-H, J = 8.7 Hz). Found, %: Cl 20.49, 20.61; N 5.37, 5.68; S 6.02, 6.31. $C_{23}H_{19}Cl_3N_2O_3S$. Calculated, %: Cl 20.86; N 5.49; S 6.29.

***N*′-(Phenylsulfonyl)-*N*-[2,5,5,6-tetrachloro-6-methyl-4-oxo-3-(propan-2-yl)cyclohex-2-en-1-ylidene]benzimidamide (XIa).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 d and 1.35 d (3H each, 3-CH**Me**$_2$, J = 6.9 Hz), 2.21 s (3H, 6-Me), 3.29–3.40 m (1H, 3-CH), 7.43–8.07 m (10H, Ph).

***N*′-(4-Methylphenylsulfonyl)-*N*-[2,5,5,6-tetrachloro-6-methyl-4-oxo-3-(propan-2-yl)cyclohex-2-en-1-ylidene]benzimidamide (XIb).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 d and 1.35 d (3H each, 3-CH**Me**$_2$, J = 6.9 Hz), 2.22 s (3H, 6-Me), 3.29–3.40 m (1H, 3-CH), 7.35 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.41–7.81 m (5H, Ph), 7.94 d (2H, 2′-H, 6′-H, J = 8.1 Hz).

***N*′-(4-Chlorophenylsulfonyl)-*N*-[2,5,5,6-tetrachloro-6-methyl-4-oxo-3-(propan-2-yl)cyclohex-2-en-1-ylidene]benzimidamide (XIc).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23 d and 1.36 d (3H each, 3-CH**Me**$_2$, J = 6.9 Hz), 2.24 s (3H, 6-Me), 3.28–3.39 m (1H, 3-CH), 7.42–7.79 m (5H, Ph), 7.50 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.99 d (2H, 2′-H, 6′-H, J = 8.7 Hz).

Bromination of *N*-substituted *N*′-(arylsulfonyl)-benzimidamides I–VI (*general procedure***).** A solution of 6 or 10 mmol of bromine in the corresponding solvent was added dropwise under stirring to a solution of 2 mmol of quinone imine **I**–**VI** in 3 ml of chloroform, acetic acid, or a 1:5 mixture of dimethylformamide with acetic acid heated to 40–50°C. The mixture was kept for 24 h, and the precipitate was filtered off and recrystallized from acetic acid.

***N*-[3-Bromo-2-methyl-4-oxo-5-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene]-*N*′-(4-methylphenylsulfonyl)benzimidamide (XVIIb).** ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 18.54 (2-Me), 21.24 (CH**Me**$_2$), 21.47 (**Me**C_6H_4), 28.28 (5-CH), 125.85 (C^6), 127.25 ($C^{2'}$), 128.83 ($C^{3'}$), 128.94 ($C^{2''}$), 129.38 ($C^{3''}$), 131.59 ($C^{1'}$), 133.99 ($C^{4'}$), 134.69 (C^3), 138.21 ($C^{1''}$), 145.57 (C^2), 143.59 ($C^{4''}$), 152.36 (C^5), 155.96 (C=N^1), 167.72 (C=N^2), 178.16 (C=O).

***N*-(2,5-Dibromo-4-hydroxy-3,6-dimethylphenyl)-*N*′-(phenylsulfonyl)benzimidamide (XIXa).** Yield 76%, mp 256.5–258°C. Found, %: Br 29.43, 29.66;

N 4.87, 5.12; S 5.63, 5.80. $C_{21}H_{18}Br_2N_2O_3S$. Calculated, %: Br 29.69; N 5.20; S 5.96.

***N*-(2,5-Dibromo-4-hydroxy-3,6-dimethylphenyl)-*N′*-(4-methylphenylsulfonyl)benzimidamide (XIXb).** Yield 59%, mp 267–268°C. Found, %: Br 28.91, 29.24; N 5.16, 5.39; S 5.40, 5.67. $C_{22}H_{20}Br_2N_2O_3S$. Calculated, %: Br 28.94; N 5.07; S 5.81.

***N*-[2,5-Dibromo-4-hydroxy-6-methyl-3-(propan-2-yl)phenyl]-*N′*-(phenylsulfonyl)benzimidamide (XXa).** Yield 84%, mp 206–208°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.31 d.d (6H, 3-CH**Me**$_2$, J = 6.0, 6.9 Hz), 2.26 s (3H, 6-Me), 3.56–3.71 m (1H, 3-CH), 7.32–7.58 m (10H, Ph), 9.30 br.s (1H, NH), 10.42 br.s (1H, OH). Found, %: Br 28.01, 28.27; N 4.93, 5.33; S 5.48, 5.72. $C_{23}H_{22}Br_2N_2O_3S$. Calculated, %: Br 28.22; N 4.95; S 5.66.

***N*-[2,5-Dibromo-4-hydroxy-6-methyl-3-(propan-2-yl)phenyl]-*N′*-(4-methylphenylsulfonyl)benzimidamide (XXb).** Yield 79%, mp 246–247.5°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.31 d.d (6H, 3-CH**Me**$_2$, J = 6.0, 6.9 Hz), 2.26 s (3H, 6-Me), 2.30 s (3H, **Me**C$_6$H$_4$), 3.57–3.72 m (1H, 3-CH), 7.14 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.27 d (2H, 2′-H, 6′-H, J = 8.1 Hz), 7.46–7.58 m (5H, Ph), 9.28 br.s (1H, NH), 10.35 br.s (1H, OH). Found, %: Br 27.55, 27.69; N 4.40, 4.67; S 5.13, 5.55. $C_{24}H_{24}Br_2N_2O_3S$. Calculated, %: Br 27.54; N 4.83; S 5.53.

***N*-[2,5-Dibromo-4-hydroxy-3-methyl-6-(propan-2-yl)phenyl]-*N′*-(4-methylphenylsulfonyl)benzimidamide (XXIb).** Yield 80%, mp 260–262°C. Found, %: Br 27.48, 27.66; N 4.73, 4.95; S 5.66, 5.91. $C_{24}H_{24}Br_2N_2O_3S$. Calculated, %: Br 27.54; N 4.83; S 5.53.

***N*-(2,5-Dibromo-3,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(phenylsulfonyl)benzimidamide (XXIIa).** Yield 91%, mp 185–186°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, 3-Me), 2.40 s (3H, 6-Me), 7.43–7.97 m (10H, Ph). Found, %: Br 29.61, 29.87; N 5.14, 5.36; S 5.70, 5.83. $C_{21}H_{16}Br_2N_2O_3S$. Calculated, %: Br 29.80; N 5.22; S 5.98.

***N*-(2,5-Dibromo-3,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*N′*-(4-methylphenylsulfonyl)-benzimidamide (XXIIb).** Yield 73%, mp 197–199°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 s (3H, 3-Me), 2.40 s (3H, 6-Me), 2.42 s (3H, **Me**C$_6$H$_4$), 7.30 d (2H, 3′-H, 5′-H, J = 9.0 Hz), 7.42–7.78 m (5H, Ph), 7.85 d (2H, 2′-H, 6′-H, J = 9.0 Hz). Found, %: Br 28.91, 29.07; N 4.88, 5.02; S 5.63, 5.77. $C_{22}H_{18}Br_2N_2O_3S$. Calculated, %: Br 29.04; N 5.09; S 5.83.

***N′*-(4-Chlorophenylsulfonyl)-*N*-(2,5-dibromo-3,6-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)-benzimidamide (XXIIc).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 s (3H, 3-Me), 2.40 s (3H, 6-Me), 7.43–7.79 m (5H, Ph), 7.49 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.91 d (2H, 2′-H, 6′-H, J = 8.7 Hz).

***N*-[2,5-Dibromo-6-methyl-4-oxo-3-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N′*-(phenylsulfonyl)-benzimidamide (XXIIIa).** Yield 74%, mp 160.5–162°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 d.d (6H, 3-CH**Me**$_2$, J = 7.2, 18 Hz), 2.35 s (3H, 6-Me), 3.39–3.49 m (1H, 3-CH), 7.43–7.96 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.88 and 20.02 (CH**Me**$_2$), 20.64 (6-Me), 35.84 (3-CH), 127.06 (C$^{3'}$), 128.43 (C$^{2'}$), 128.84 (C$^{2''}$), 129.01 (C$^{3''}$), 131.64 (C$^{1'}$), 131.75 (C^2), 132.68 (C$^{4''}$), 133.67 (C$^{4'}$), 134.77 (C^5), 141.08 (C$^{1''}$), 144.04 (C^6), 149.30 (C^3), 151.82 (C=N^1), 163.18 (C=N^2), 175.58 (C=O). Found, %: Br 28.14, 28.37; N 4.56, 4.81; S 5.62, 5.79. $C_{23}H_{20}Br_2N_2O_3S$. Calculated, %: Br 28.32; N 4.96; S 5.68.

***N*-[2,5-Dibromo-6-methyl-4-oxo-3-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N′*-(4-methylphenylsulfonyl)benzimidamide (XXIIIb).** Yield 72%, mp 159–160°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 d.d (6H, 3-CH**Me**$_2$, J = 6.9, 18 Hz), 2.35 s (3H, 6-Me), 2.42 s (3H, **Me**C$_6$H$_4$), 3.40–3.49 m (1H, 3-CH), 7.29 d (2H, 3′-H, 5′-H, J = 8.4 Hz), 7.43–7.79 m (5H, Ph), 7.83 d (2H, 2′-H, 6′-H, J = 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.83 and 19.96 (CH**Me**$_2$), 20.56 (6-Me), 21.49 (**Me**C$_6$H$_4$), 35.65 (3-CH), 126.91 (C$^{3'}$), 128.16 (C$^{2'}$), 128.68 (C$^{2''}$), 129.13 (C$^{3''}$), 131.57 (C$^{1'}$), 131.72 (C^2), 134.38 (C^5), 134.38 (C$^{4'}$), 138.26 (C$^{1''}$), 143.07 (C$^{4''}$), 144.15 (C^6), 149.10 (C^3), 151.49 (C=N^1), 162.39 (C=N^2), 175.20 (C=O). Found, %: Br 27.40, 27.53; N 4.81, 4.99; S 5.06, 5.26. $C_{24}H_{22}Br_2N_2O_3S$. Calculated, %: Br 27.63; N 4.84; S 5.54.

***N′*-(4-Chlorophenylsulfonyl)-*N*-[2,5-dibromo-6-methyl-4-oxo-3-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene]benzimidamide (XXIIIc).** Yield 83%, mp 187–188°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 d.d (6H, 3-CH**Me**$_2$, J = 7.2, 15 Hz), 2.38 s (3H, 6-Me), 3.40–3.49 m (1H, 3-CH), 7.43–7.79 m (5H, Ph), 7.49 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 7.91 d (2H, 2′-H, 6′-H, J = 8.7 Hz). Found, %: Br+Cl 32.41, 32.79; N 4.38, 4.60; S 5.13, 5.29. $C_{23}H_{19}Br_2ClN_2O_3S$. Calculated, %: Br+Cl 32.61; N 4.68; S 5.36.

***N*-[2,5-Dibromo-3-methyl-4-oxo-6-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N*′-(phenylsulfonyl)-benzimidamide (XXIVa).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.48 d.d (6H, 6-CH**Me**$_2$, J = 7.2, 18 Hz), 2.24 s (3H, 3-Me), 3.76–3.85 m (1H, 6-CH), 7.43–7.96 m (10H, Ph).

***N*-[2,5-Dibromo-3-methyl-4-oxo-6-(propan-2-yl)-cyclohexa-2,5-dien-1-ylidene]-*N*′-(4-methylphenyl-sulfonyl)benzimidamide (XXIVb).** Yield 68%, mp 117–118°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.47 d.d (6H, 6-CH**Me**$_2$, J = 7.2, 18 Hz), 2.24 s (3H, 3-Me), 2.42 s (3H, **Me**C_6H_4), 3.76–3.85 m (1H, 6-CH), 7.29 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.43–7.78 m (5H, Ph), 7.88 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Br 27.64, 27.80; N 4.53, 4.69; S 5.16, 5.31. $C_{24}H_{22}Br_2N_2O_3S$. Calculated, %: Br 27.63; N 4.84; S 5.54.

***N*′-(4-Chlorophenylsulfonyl)-*N*-[2,5-dibromo-3-methyl-4-oxo-6-(propan-2-yl)cyclohexa-2,5-dien-1-ylidene]benzimidamide (XXIVc).** Yield 71%, mp 131–133°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.47 d.d (6H, 6-CH**Me**$_2$, J = 7.2, 18 Hz), 2.26 s (3H, 3-Me), 3.76–3.84 m (1H, 6-CH), 7.44–7.77 m (5H, Ph), 7.49 d (2H, 3′-H, 5′-H, J = 8.1 Hz), 7.94 d (2H, 2′-H, 6′-H, J = 8.1 Hz). Found, %: Br+Cl 32.30, 32.51; N 4.72, 4.88; S 5.19, 5.39. $C_{23}H_{19}Br_2ClN_2O_3S$. Calculated, %: Br+Cl 32.61; N 4.68; S 5.36.

Reaction of quinone imines XXIIIb and XXIIIc with methanol (*general procedure*). A solution of 1.1 mmol of compound **XXIIIb** and **XXIIIc** in 4 ml of methanol was heated under reflux with protection from atmospheric moisture until the initial quinone imine disappeared according to the TLC data (reaction time 36 and 30 h, respectively). The mixture was cooled, and the colorless crystalline product was filtered off, washed with methanol, and dried.

***N*-[2,5-Dibromo-1-methoxy-6-methyl-4-oxo-3-(propan-2-yl)cyclohexa-2,5-dien-1-yl]-*N*′-(4-methylphenylsulfonyl)benzimidamide (XXVa).** Yield 80%, mp 164–167°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.98 d and 1.18 d (3H each, 3-CH**Me**$_2$, J = 6.9 Hz), 2.18 s (3H, 6-Me), 2.38 s (3H, **Me**C_6H_4), 3.01 s (3H, MeO), 3.20–3.30 m (1H, 3-CH), 5.90 br.s (1H, NH), 7.17 d (2H, 3′-H, 5′-H, J = 8.2 Hz), 7.47–7.75 m (5H, Ph), 7.48 d (2H, 2′-H, 6′-H, J = 8.2 Hz). Found, %: Br 26.30, 26.25; N 4.40, 4.52; S 5.20, 5.10. $C_{25}H_{26}Br_2N_2O_4S$. Calculated, %: Br 26.18; N 4.59; S 5.25.

***N*′-(4-Chlorophenylsulfonyl)-*N*-[2,5-dibromo-1-methoxy-6-methyl-4-oxo-3-(propan-2-yl)cyclohexa-2,5-dien-1-yl]benzimidamide (XXVb).** Yield 75%, mp 155–157°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.98 d and 1.20 d (3H each, 3-CH**Me**$_2$, J = 6.9 Hz), 2.17 s (3H, 6-Me), 3.03 s (3H, MeO), 3.21–3.29 m (1H, 3-CH), 5.97 s (1H, NH), 7.35 d (2H, 3′-H, 5′-H, J = 8.9 Hz), 7.49–7.73 m (5H, Ph), 7.53 d (2H, 2′-H, 6′-H, J = 8.9 Hz). Found, %: Br+Cl 30.78, 30.89; N 4.40, 4.52; S 5.00, 5.10. $C_{24}H_{23}Br_2ClN_2O_4S$. Calculated, %: Br+Cl 30.95; N 4.44; S 5.08.

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