ISSN 1070-4280, Russian Journal of Organic Chemistry, 2016, Vol. 52, No. 5, pp. 644–649. © Pleiades Publishing, Ltd., 2016.
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Reaction of *N*-Sulfonyl Derivatives of 1,4-Benzoquinone Monoimine with Substituted Hydrazines

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Received February 10, 2016

Abstract—Reaction direction of *N*-sulfonyl derivatives of 1,4-benzoquinone monoimine with substituted hydrazines depends on the redox potential of the quinone imine and on the basicity of the hydrazine. Aryl (alkyl)hydrazines of high basicity favor the reduction of quinone monoimine. In reactions with less basic aroylhydrazones *N*'-(4-oxocyclohexa-2,5-dienylidene)aroylhydrazides were obtained only from the alkyl-substituted in the quinoid ring *N*-sulfonyl derivatives possessing a lower redox potential.

DOI: 10.1134/S1070428016050055

Reactions of quinoid compounds with substituted hydrazine were extensively studies for their products may be used as acid-base indicators [1], pharmaceuticals [2, 3], insecticides, fungicides, pesticides, plant growth regulators, dyes, antioxidants [2], rubber modifyers [4].

Lately in reaction of 1,4-benzoquinone derivatives with substituted hydrazine the corresponding 1,4-benzoquinone hydrazones were isolated [5–7]. In the case of *N*-substituted derivatives of 1,4-benzoquinone monoimine the corresponding hydrazones were obtained only from 2,6-diisopropyl derivatives [8] having lower redox potential than the other *N*-sulfonyl derivatives [9], whose reactions with hydrazines provided only reduction products [10].

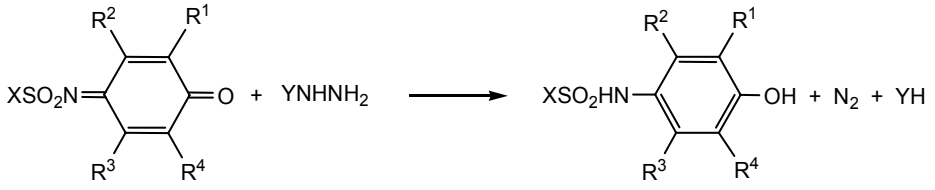
In case of 1,4-naphthoquinone imine derivatives possessing a lower redox potential than the 1,4-benzoquinone monoimines [9] reactions with aroylhydrazines along with 1,4-naphthoquinone aroylhydrazones afforded also 1,4-addition products [11].

It was concluded in [8, 10] that the direction of reaction between *N*-arylsulfonyl-1,4-quinone monoimines and hydrazines depends on the basicity of the hydrazine and the ratio of the redox potentials of the initial and final products: the reaction proceeds in the direction of formation of compounds possessing lower redox potential. Yet the reactions were carried out under different conditions that might affect their course: the aroylhydrazones of 1,4-benzoquinones were obtained at room temperature, and the reduction of the initial quinone monoimines occurred at boiling in ethanol. Reactions of *N*-arylsulfonyl-1,4-benzoquinone monoimines having alkyl substituents in the ring (beside the 2,6-diisopropyl derivative) with substituted hydrazines were not explored up till now.

This study was aimed at exploring the regularities in reactions of different *N*-sulfonyl derivatives of 1,4-benzoquinone monoamine with aryl-, alkyl-, and aroylhydrazines.

As a result of reactions of *N*-aryl(methyl, trifluoromethyl)sulfonyl-1,4-benzoquinone monoimines **1a**–**1p** with phenyl-, 2,4-dinitrophenyl-, and ethylhydrazines **2a**–**2c** in ethanol, acetonitrile, and acetic acid both at boiling and at room temperature we obtained the corresponding *N*-aryl(methyl, trifluoromethyl)sulfonyl-4-aminophenols **3a**–**3p** (Scheme 1) that were reduced forms of initial quinone monoimines, therefore a common redox process occurred.

Scheme 1.



1a–1p **2a–2c** **3a–3p**

1, **3**, X = Ph (**a**, **d**, **e**, **g**), 4-MeC_6H_4 (**f**, **j**, **m**, **p**), Me (**b**, **h**, **k**, **n**), CF_3 (**c**, **i**, **l**, **o**); $R^1 = R^2 = R^3 = R^4 = H$ (**a–c**), $R^2 = R^3 = R^4 = H$, R^1 = Me (**d**), $R^1 = R^3 = R^4 = H$, R^2 = Me (**e**), $R^3 = R^4 = H$, $R^1 = R^2$ = Me (**f**), $R^2 = R^4 = H$, $R^1 = R^3$ = Me (**g–i**), $R^2 = R^3 = H$, $R^1 = R^4$ = Me (**j–l**), $R^1 = R^4 = H$, $R^2 = R^3$ = Me (**m–o**), $R^2 = R^3 = H$, $R^1 = R^4$ = *i*-Pr (**p**); **2**, Y = Et (**a**), Ph (**b**), 2,4-$(NO_2)_2C_6H_3$ (**c**).

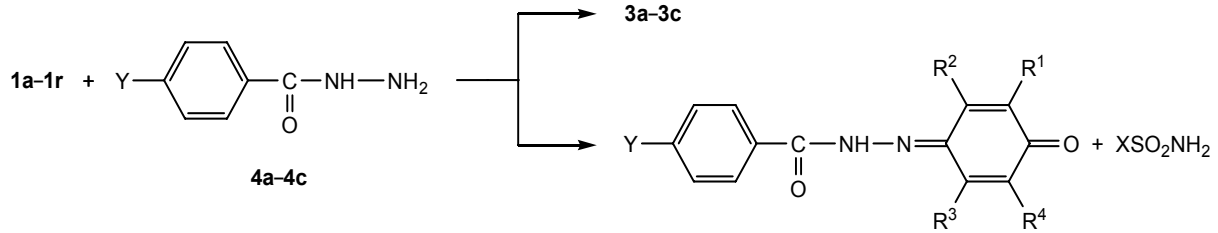
The reaction of unsubstituted in the ring 1,4-benzoquinone monoimines **1a–1c** with aroylhydrazines **4a–4c** in ethanol or chloroform at room temperature also resulted in their reduction to the corresponding aminophenols **3a–3c** (Scheme 2) in agreement with the findings of [10]. 1,4-Benzoquinone monoimines with alkyl substituents in the ring **1d–1r** reacted with aroylhydrazines **4a–4c** in ethanol, chloroform, or acetonitrile affording the corresponding aroylhydrazones of 1,4-benzoquinone monoimine **5a–5l** (Scheme 2). Along with compounds **5a–5l** also arylsulfamides **6a–6d** were isolated, and we failed to separate the mixture of compounds **5b** and **6b**.

We obtained for the first time the aroylhydrazone of 3,5-dimethyl-1,4-benzoquinone **5f** containing substituents in both *ortho*-positions with respect to the imine carbon atom. Previous attempts to obtain such compounds proceeding from alkyl-substituted 1,4-benzoquinones were unsuccessful due to the steric hindrances from the alkyl groups.

Compounds **5c–5h** containing two methyl groups in the quinoid ring are better soluble in aprotic solvents (chloroform, dichloromethane, acetone) compared to compounds **5a** and **5b** with a single methyl group. Introducing isopropyl or *tert*-butyl groups in the positions *2* and *6* of the quinoid ring of compounds **5i–5l** even more increases their solubility. Besides the acceptor substituents in the *para*-position of the aromatic ring decrease the solubility in aprotic solvents. We presume that this behavior is due to the *azo*-hydrazone tautomerism of these compounds in solutions [12].

To confirm this assumption we performed a complete geometry optimization for quinonehydrazone form (**A**) and azoform (**B**) of aroylhydrazones of 1,4-benzoquinones **5g**, **5h**, **5m**, and **5n** (Scheme 3). According to obtained data in all compounds the quinonehydrazone forms **A** possess a lower energy [–1044.492978 (**5g**), –839.984944 (**5h**), –761.341322 (**5m**), –997.239054 (**5n**) a.u.] than azaforms **B** [–1044.484833 (**5g**), –839.976010 (**5h**), –761.337894 (**5m**), –997.228628 (**5n**) a.u.], and the introduction of alkyl groups in the quinoid ring of compounds **5g**, **5h**, and **5n** leads to the increase in the energy difference

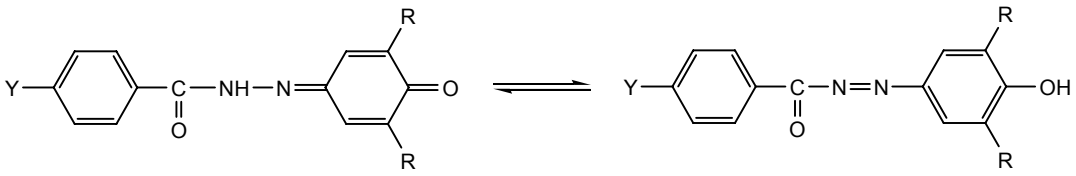
Scheme 2.



4a–4c **5a–5l** **6a–6d**

1, X = Ph, $R^2 = R^3 = H$, $R^1 = R^4$ = *t*-Bu (**q**); X = 4-MeC_6H_4, $R^2 = R^4 = H$, R^3 = Me, R^1 = *i*-Pr, (**r**); **4**, Y = H (**a**), Cl (**b**), NO_2 (**c**); **5**, Y = H (**c**, **h**), Cl (**e**, **j**), NO_2 (**a**, **b**, **d**, **f**, **g**, **i**, **k**, **l**); $R^2 = R^3 = R^4 = H$, R^1 = Me (**a**); $R^1 = R^3 = R^4 = H$, R^2 = Me (**b**); $R^3 = R^4 = H$, $R^1 = R^2$ = Me (**c**); $R^2 = R^4 = H$, $R^1 = R^3$ = Me (**d**, **e**), $R^1 = R^4 = H$, $R^2 = R^3$ = Me (**f**); $R^2 = R^3 = H$, $R^1 = R^4$ = Me (**g**, **h**); $R^2 = R^3 = H$, $R^1 = R^4$ = *i*-Pr (**i**, **j**); $R^2 = R^3 = H$, $R^1 = R^4$ = *t*-Bu (**k**); $R^2 = R^4 = H$, R^3 = Me, R^1 = *i*-Pr (**l**); **6**, X = Ph (**a**), 4-MeC_6H_4 (**b**), Me (**c**), CF_3 (**d**).

Scheme 3.

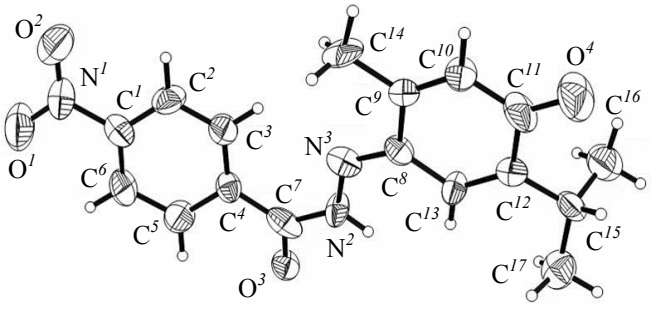


A **5g, 5h, 5m, 5n** **B**

Y = NO_2, R = Me (**g**); Y = H, R = Me (**h**); Y = R = H (**m**); Y = H, R = *i*-Pr (**n**).

between these forms [ΔE = E(B) – E(A) 21.39 (**5g**), 23.46 (**5h**), 27.38 (**5n**) kJ mol^{-1}], namely, quinine-hydrazone form **A** becomes even more feasible by energy, and its prevalence favors the solubility of compounds in aprotic solvents. The results obtained are well consistent with the data of [12] where it has been found that the content of the quinonehydrazone form in compounds **5m** and **5n** equals 87.5 ± 2.5 and 98.1 ± 0.2%. The introduction of acceptor substituents in the *para*-position of the aromatic ring affects the difference in these energies significantly weaker that the introduction of alkyl substituents in the quinoid ring. The obtained data confirm our assumption on the growth of the solubility of 1,4-benzoquinones aroyl-hydrazones **5a–5l** in aprotic solvents at increasing content of the quinonehydrazone form.

The obtained results are also confirmed by ^{1}H NMR spectra of compounds **5a–5l**. In the ^{1}H NMR spectra of compounds **5a** and **5b** containing one alkyl substituent in the quinoid ring the majority of peaks appear as very broadened singlets showing that in solutions of these compounds a dynamic process occurs of mutual transformation of forms **A** and **B**. The relative content of these forms may be evaluated only from the integral intensities of the peaks of protons from NH and OH groups: the broadened singlet of the NH group proton corresponding to quinonehydrazone form **A** is observed in the region δ 12.21–12.31 ppm, the singlet of the proton of the OH group belonging to azoform **B** appears in the region δ 11.03–11.96 ppm**.** In the spectra of compounds **5c–5l** containing two alkyl substituents in the ring only the singlet from NH group is present corresponding to form **A**. IR spectra of compounds **5a–5l** contain an absorption band in the region 3367–3435 cm^{-1} characteristic of the NH group.



Structure of *N*'-(5-isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide **5l** according to XRD data.

Since the ^{1}H NMR spectra were of complicated pattern the unambiguous proof of the structure of the prepared hydrazones **5** was obtained from X-ray diffraction (XRD) analysis of the single crystal of compound **5l** (see the figure).

The carbamide group is present in the *ap*-conformation with respect to the endocyclic C^8–C^{13} bond of the benzoquinone fragment [torsion angle $C^{13}C^8N^3N^2$–1.7(2) deg]. *para*-Nitrophenyl substituent is present in the *sp*-conformation with respect to the N^2–N^3 bond [torsion angle $C^4C^7N^2N^3$ –1.9(1) deg] and slightly deviates from the plane of the amide fragment [torsion angle $C^3C^4C^7N^2$ –19.8(1) deg], apparently due to the presence of an intramolecular hydrogen bond C^3–H^3···N^3 (H···N 2.26 Å, CHN angle 122 deg) and of a shortened intramolecular contact O^3···H^5 2.38 Å (sum of van der Waals radii 2.46 Å [13]). The isopropyl substituent is turned with respect to the plane of the benzene ring at a torsion angle $C^{11}C^{12}C^{15}H^{15}$ of 47 deg.

In the crystal the molecules **5l** form double columns along the crystallographic direction [100]. The molecules are bound in the column by stacking interactions (the distance between the contiguous molecules is 3.6 Å), the neighbor columns are bound by intermolecular hydrogen bonds N^2–H^2···$O^{3'}$ (–1/2 + x, –1,5 –y, –z) (H···O 2.13 Å, NHO angle 156.8 deg).

Hence, the hydrazones of 1,4-benzoquinone mono-amine may be obtained by reaction of alkyl-substituted in the quinoid ring *N*-sulfonyl derivatives of 1,4-benzoquinone monoamine with aroylhydrazines. This is due to the lower redox potential of these quinone

monoimines compared to the unsubstituted in the ring *N*-sulfonyl derivatives and to the lower basicity of aroylhydrazine than that of aryl- and alkylhydrazines. Therewith the nature of the solvent and the temperature conditions do not significantly affect the course of the reaction. The results obtained agree well with the data of [10], which has shown that the increase in the redox potential of the initial quinone monoamine and in the basicity of the hydrazine favor the proceeding of the redox process.

EXPERIMENTAL

IR spectra of synthesized compounds were recorded on a spectrophotometer Vertex–70 from pellets with KBr (**5a–5h**) or solution in $CHCl_3$ (**5i–5l**). ^{1}H NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequency 300 MHz, reference TMS. ^{13}C NMR spectrum of compound **5i** was taken on a spectrometer Varian VXR-300 at operating frequency 75.4 MHz. The purity of quinone imines and their reaction products was checked by TLC on Silufol UV-254 plates using as solvents chloroform, acetone, THF, as eluents, ethanol–chloroform, 1 : 10, benzene–hexane, 10 : 1, hexane–ethyl acetate, 1 : 2, spots visualized under UV irradiation.

Quantum-chemical calculations were carried out using FireflyQC software [14] based partially on the initial code of program package GAMESS (US) [15]. The optimization of quinonehydrazone form (**A**) and azoform (**B**) of aroylhydrazones of 1,4-benzoquinones **5g**, **5h**, **5m**, and **5n** was performed along all geometry parameters by DFT (B3LYP) method using basis set 6-31+G(d).

Characteristics of compounds **1a**, **3a** [16], **1b**, **1c**, **1h**, **1i**, **1k**, **1l**, **1n**, **1o**, **3b**, **3c**, **3h**, **3i**, **3k**, **3l**, **3n**, **3o** [17], **1d**, **1e**, **3d**, **3e** [18], **1f**, **3f** [19], **1g**, **1r**, **3g**, 3**r** [20], **1j**, **1m**, **3j**, **3m** [21], **1p**, **3p** [22], **1q**, and **3q** [23] are in agreement with the data published in the mentioned references.

Reaction of quinone monoimines (1a–1r) with hydrazines 2a–2c and 4a–4c. *a*. To a solution of 2 mmol of quinone imine **1a–1p** in 10 mL of ethanol or acetonitrile, glacial acetic acid, a mixture of acetic acid with chloroform was added dropwise a solution of 4 mmol of hydrazine **2a–2c** in appropriate solvent at room temperature or at the boiling point of the solvent (**1a**, **1b**, **1d–1h**, **1j**, **1k**, **1m**, **1n**, and **1p**), or at cooling to –10°C (**1a–1c**, **1h**, **1i**, **1k**, **1l**, **1n**, and **1o**). The reaction mixture was stirred for 12 h, the separated precipitate of compounds **3a–3p** was filtered off. When the precipitate did not form, the solution was poured on ice or the solvent was partially evaporated in a vacuum. The product was recrystallized from ethanol, or from benzene–hexane mixture, 1 : 2, or from acetic acid.

b. To a solution of 2 mmol of quinone imine **1a–1r** in 10 mL of ethanol, chloroform, or acetonitrile was added dropwise a solution of 2 mmol of hydrazine **4a–4c** in appropriate solvent at room temperature (**1a**, **1b**, **1d–1h**, **1j**, **1k**, **1m**, **1n**, and **1p–1r**) or at cooling to –10°C (**1c**, **1i**, **1l**, and **1o**). The reaction mixture was stirred for 2 h, the separated precipitate was filtered off. When the precipitate did not form the solvent was partially evaporated in a vacuum. The product was recrystallized from ethanol.

***N*'-(3-Methyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5a).** Yield 51%, mp 245–247°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.02 br.s (3H, 3-Me), 6.59 br.s (1H, H^5), 7.30 br.s (1H, H^2), 8.01 br.s (1H, H^6), 8.18 br.s (2H, 4-$NO_2C_6H_4$), 8.37 d (2H, 4-$NO_2C_6H_4$, *J* 8.7 Hz), 11.96 br.s [1H, OH, 22% (**B**)], 12.31 br.s [1H, NH, 78% (**A**)]. Found, %: N 14.65, 14.74. $C_{14}H_{11}N_3O_4$. Calculated, %: N 14.73.

***N*'-(2-Methyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5b).** ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.02 s (3H, 2-Me), 7.08–7.11 d.d (1H, H^5, *J* 1.2, 8.4 Hz), 7.15 d (1H, H^3, *J* 1.2 Hz), 8.14 d (1H, H^6, *J* 8.4 Hz), 8.32 d (2H, 4-$NO_2C_6H_4$, *J* 9.3 Hz), 8.41 d (2H, 4-$NO_2C_6H_4$, *J* 9.3 Hz), 11.03 br.s [1H, OH, 25% (**B**)], 12.21 br.s [1H, NH, 75% (**A**)].

***N*'-(2,3-Dimethyl-4-oxocyclohexa-2,5-dienylidene)benzohydrazide (5c).** Yield 64%, mp 203–204°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.93 s (3H, 3-Me), 2.17 br.s (3H, 2-Me), 6.47 d (1H, H^5, *J* 9.9 Hz), 7.54–7.91 m (5H, Ph), 8.07 d (1H, H^6, *J* 9.9 Hz), 12.13 br.s (1H, NH). Found, %: N 11.00, 11.10. $C_{15}H_{14}N_2O_2$. Calculated, %: N 11.02.

***N*'-(2,5-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5d).** Yield 78%, mp 259–260°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (3H, 5-Me), 2.10 br.s (3H, 2-Me), 6.41 s (1H, H^3), 7.94 s (1H, H^6), 8.12 d (2H, 4-$NO_2C_6H_4$, *J* 7.2 Hz), 8.37 d (2H, 4-$NO_2C_6H_4$, *J* 7.2 Hz), 12.30 br.s (1H, NH). Found, %: N 13.90, 13.98. $C_{15}H_{13}N_3O_4$. Calculated, %: N 14.04.

***N*'-(2,5-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-4-chlorobenzohydrazide (5e).** Yield 75%, mp 258–260°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.97 s (3H, 5-Me), 2.11 s (3H, 2-Me), 6.42 s (1H, H^3), 7.63 d (2H, 4-ClC_6H_4, *J* 8.1 Hz), 7.94 d (2H, 4-ClC_6H_4, *J* 8.1 Hz), 7.94 s (1H, H^6), 12.04 br.s (1H, NH). Found, %: N 9.60, 9.69. $C_{15}H_{13}ClN_2O_2$. Calculated, %: N 9.70.

***N*'-(2,6-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5f).** Yield 52%, mp 268–270°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.88 s (6H, 2-Me), 1.89 s (6H, 6-Me), 6.82 s (1H, H^5), 7.92 s (1H, H^3), 8.16 d (2H, 4-$NO_2C_6H_4$, *J* 8.2 Hz), 8.44 d (2H, 4-$NO_2C_6H_4$, *J* 8.2 Hz), 11.98 br.s (1H, NH). Found, %: N 13.99, 14.00. $C_{15}H_{13}N_3O_4$. Calculated, %: N 14.04.

***N*'-(3,5-Dimethyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5g).** Yield 81%, mp 267–268°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.98 s (3H, 3-Me), 2.00 s (3H, 5-Me), 7.15 s (1H, H^2), 7.97 s (1H, H^6), 8.15 d (4H, 4-$NO_2C_6H_4$, *J* 7.2 Hz), 8.36 d (4H, 4-$NO_2C_6H_4$, *J* 7.2 Hz), 12.20 br.s (1H, NH). Found, %: N 14.00, 14.09. $C_{15}H_{13}N_3O_4$. Calculated, %: N 14.04.

***N*'-(3,5-Dimethyl-4-oxocyclohexa-2,5-dienylidene)benzohydrazide (5h).** Yield 85%, mp 219–220°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.96 s (3H, 3-Me), 2.00 s (3H, 5-Me), 7.18 s (1H, H^2), 7.52–7.93 m (5H, Ph), 8.01 s (1H, H^6), 11.96 br.s (1H, NH). Found, %: N 10.90, 10.99. $C_{15}H_{14}N_2O_2$. Calculated, %: N 11.02.

***N*'-(3,5-Diisopropyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5i).** Yield 89%, mp 199–200°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 d (6H, 3-Pr-*i*, *J* 8.4 Hz), 1.15 d (6H, 5-Pr-*i*, *J* 8.4 Hz), 3.05–3.16 m (1H, 3-Pr-*i*), 3.13–3.26 m (1H, 5-Pr-*i*), 6.79 br.s (1H, H^2),7.59 br.s (1H, H^6), 8.09 d (2H, 4-$NO_2C_6H_4$, *J* 8.4 Hz), 8.35 d (2H, 4-$NO_2C_6H_4$, *J* 8.4 Hz), 11.48 br.s (1H, NH). ^{13}C ($CDCl_3$), δ, ppm: 21.75 (2Me, 3-Pr-*i*), 21.96 (2Me, 5-Pr-*i*), 26.79 (CH, 3-Pr-*i*), 27.50 (CH, 5-Pr-*i*), 115.61 (C$^{3',5'}$), 123.18 (C$^{2',6'}$), 132.38 (C^{3,5}), 138.12 (C$^{1'}$), 148.97 (C$^{4'}$), 149.71 (C=N), 152.18 (C^{2,6}), 183.15 (NHC=O), 185.66 (C=O). Found, %: N 11.70, 11.80. $C_{19}H_{21}N_3O_4$. Calculated, %: N 11.82.

***N*'-(3,5-Diisopropyl-4-oxocyclohexa-2,5-dienylidene)-4-chlorobenzohydrazide (5j).** Yield 95%, mp 174–177°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 d (6H, 3-Pr-*i*, *J* 6.0 Hz), 1.16 d (6H, 5-Pr-*i*, *J* 6.9 Hz), 3.01–3.13 m (1H, 3-Pr-*i*), 3.13–3.26 m (1H, 5-Pr-*i*), 6.93 br.s (1H, H^2), 7.41 br.s (1H, H^6), 7.48 d (2H, 4-ClC_6H_4, *J* 7.5 Hz), 7.88 d (2H, 4-ClC_6H_4, *J* 7.5 Hz), 11.51 br.s (1H, NH). Found, %: N 8.00, 8.15. $C_{19}H_{21}ClN_2O_2$. Calculated, %: N 8.12.

***N*'-(3,5-Di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5k).** Yield 96%, mp 222–224°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 s (9H, 3-*t*-Bu), 1.33 s (9H, 5-*t*-Bu), 6.80 br.s (1H, H^2), 7.42 br.s (1H, H^6), 8.04 d (2H, 4-$NO_2C_6H_4$, *J* 9.0 Hz), 8.36 d (2H, 4-$NO_2C_6H_4$, *J* 9.0 Hz), 11.03 br.s (1H, NH). Found, %: N 10.90, 10.93. $C_{21}H_{25}N_3O_4$. Calculated, %: N 10.96.

***N*′-(5-Isopropyl-2-methyl-4-oxocyclohexa-2,5-dienylidene)-4-nitrobenzohydrazide (5l).** Yield 88%, mp 191–192°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 d (6H, *i*-Pr, *J* 6.6 Hz), 2.04 br.s (3H, 2-Me), 3.08–3.21 m (1H, *i*-Pr), 6.40 s (1H, H^6),7.54 s (1H, H^3), 8.06 d (2H, 4-$NO_2C_6H_4$, *J* 8.7 Hz), 8.34 d (2H, 4-$NO_2C_6H_4$, *J* 8.7 Hz), 11.48 br.s (1H, NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.11 d (6H, *i*-Pr, *J* 5.7 Hz), 2.04 br.s (3H, 2-Me), 2.95–3.12 m (1H, *i*-Pr), 6.39 s (1H, H^6), 7.81 s (1H, H^3), 8.08 d (2H, 4-$NO_2C_6H_4$, *J* 6.9 Hz), 8.36 d (2H, 4-$NO_2C_6H_4$, *J* 6.9 Hz), 12.55 br.s (1H, NH). Found, %: N 12.78, 12.80. $C_{17}H_{17}N_3O_4$. Calculated, %: N 12.84.

XRD analysis. Crystals of compound **5l** rhombic, at 21°C *a* 4.989(3), *b* 12.313(5), *c* 25.566(6) Å, α = β = γ = 90 deg, *V* 1570.4(9) Å^3, *M* 327.33, *Z* 4, space group $P2_12_12_1$, d_{calc} 1.384 g/cm^3, μ(MoK_α) 0.101 mm^{-1}, *F*(000) 688. The parameters of the unit cell and intensities of 9677 reflections (2859 independent, R_{int} 0.183) were measured on a diffractometer Xcalibur-3 (MoK_α radiation CCD-detector, graphite monochromator, ω-scanning, $2\theta_{max}$ 50 deg).

The structure was solved by the direct method using program package SHELXTL [24]. Positions of hydrogen atoms were found from the difference synthesis of electron density and refined in the *rider* model with $U_{iso} = nU_{eq}$ (n = 1.5 for methyl groups, 1.2 for the other hydrogen atoms) of the nonhydrogen atom bound to this hydrogen. The structure was refined with respect to F^2 by the full-matrix least-squares method in anisotropic approximation for nonhydrogen atoms till wR_2 0.062 for 2859 reflections [R_1 0.039 for 660 reflections with $F > 4\sigma(F)$, *S* 0.438]. Atomic coordinates and full tables of bond lengths and bond angles are deposited in the Cambridge Crystallographic Data Center (CCDC 1443421).

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