

Quinoxaline based derivatives from the reaction of 2-azabicyclo-[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxide with *o*-phenylenediamines

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Dedicated to Prof. Alexander F. Pozharskii on the occasion of his 70th Birthday in recognition of his outstanding contribution to the chemistry of heterocyclic compounds and physical organic chemistry

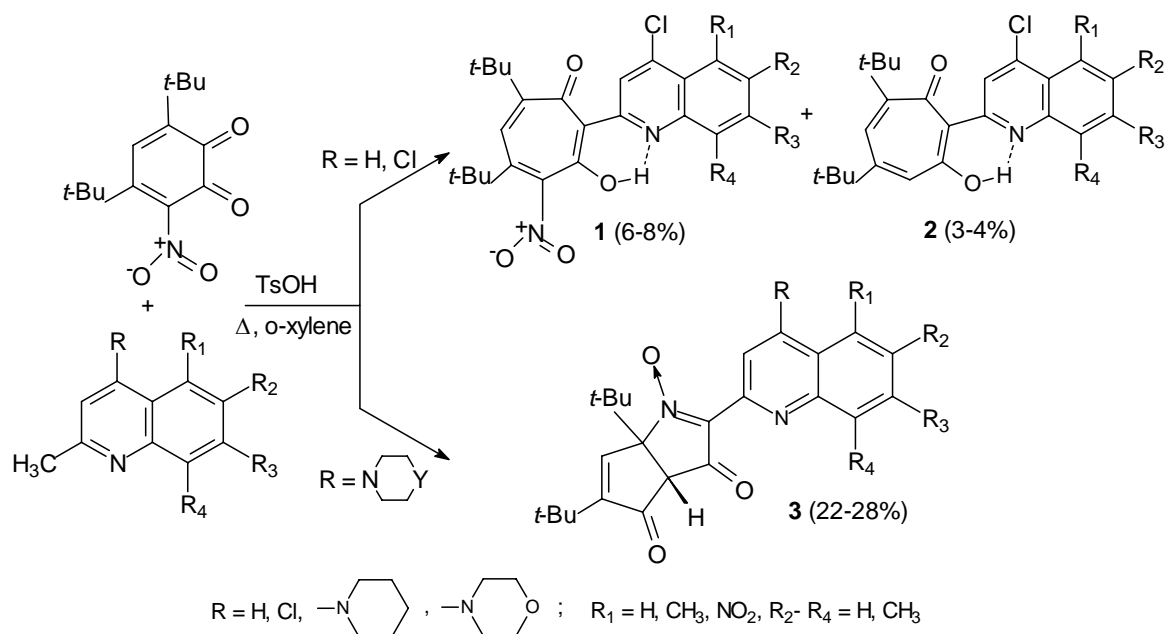
Abstract

Novel hetaryl substituted quinoxalines have been prepared by the acid-catalyzed condensation of 2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxide with derivatives of *o*-phenylenediamine. The mechanism of the reaction has been considered and the molecular structure of one of the prepared quinoxalines determined by X-ray crystallography.

Keywords: 3,5-Di-(*tert*-butyl)-1,2-benzo-quinone, *o*-phenylenediamines, quinoxalines, crystal structure

Introduction

We have recently reported that the reaction of 3-nitro-4,6-di(*tert*-butyl)-1,2-benzoquinone with 2-methylquinolines occurring upon heating under reflux of their *o*-xylene solution for 1 h leads to the expansion of the six-membered *o*-quinone ring resulting in the formation of 2-quinolinyl derivatives of 4-nitro- β -tropolones **1** and 2-quinolinyl- β -tropolones **2** as the minor products (Scheme 1).¹

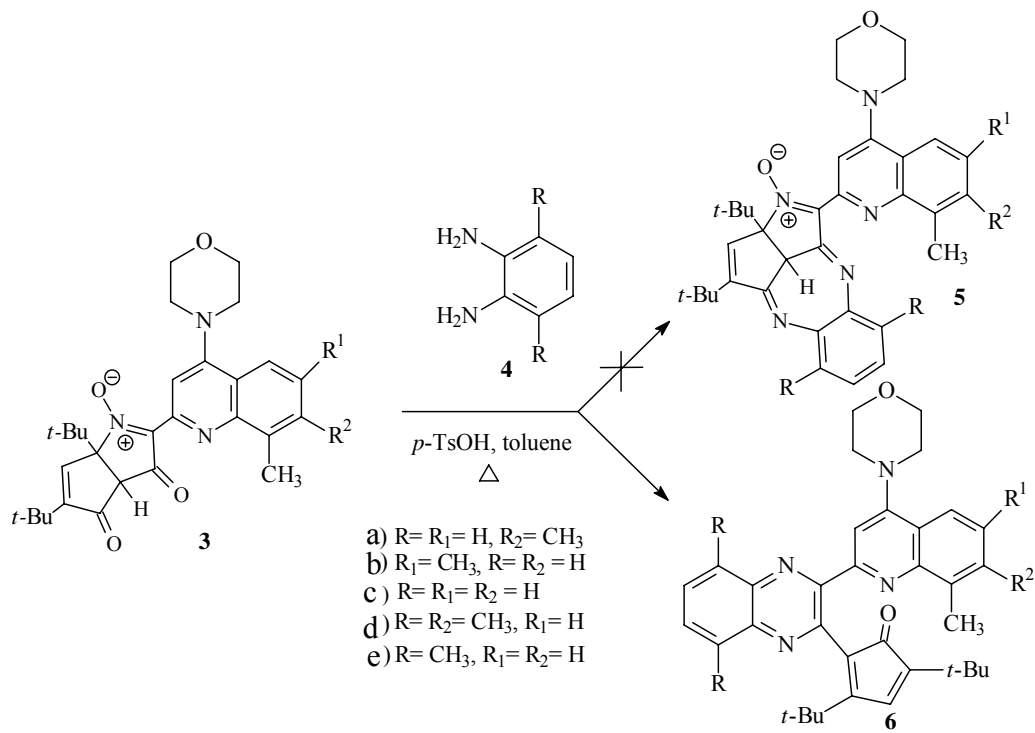
**Scheme 1**

Under the same conditions 2-methylquinolines containing a strong electron-releasing group ($\text{N(CH}_2\text{)}_4\text{O}$, $\text{N(CH}_2\text{)}_5$) in the position 4 react differently affording readily isolated crystal products, the structure of which was identified with the use of X-ray crystallography as 3-(2-quinolyl)-2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxides **3**.¹⁻³ Since the molecular framework of compounds **3** contains a 1,3-diketone moiety one may expect that these will be prone to some of the reactions characteristic of 1,3-diketones⁴. In the hope of preparing new derivatives of 1,5-benzodiazepines we have studied the condensation of compounds **3** with *o*-phenylenediamines.

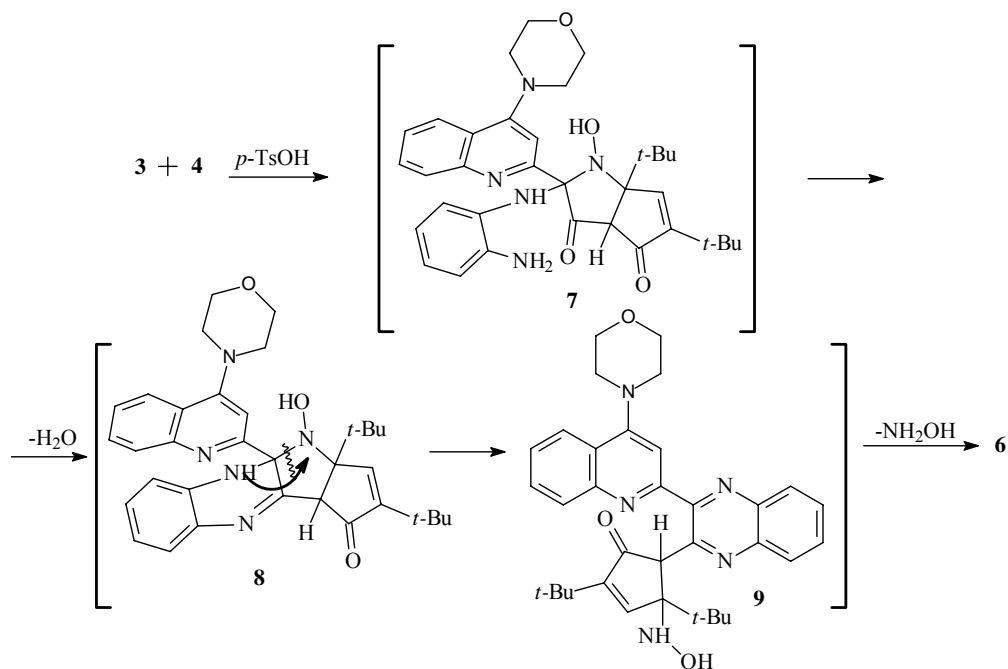
Results and Discussion

Contrary to expectations the acid-catalyzed reaction of 3-(2-quinolyl)-2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxides **3** with *o*-phenylenediamines gives rise not to 1,5-benzodiazepines **5**, but to previously unknown hetaryl derivatives of quinoxaline **6**, obtained in 57-74 % yields (Scheme 2).

The conjectural mechanism of the reaction is shown in Scheme 3. At the initial stage a molecule of *o*-phenylenediamine adds to the electrophilic C(3) center of **3** that is activated by the adjacent *N*-oxide group.^{5,6} The subsequent intramolecular cyclization of **7** proceeding with elimination of a molecule of water affords the dihydroquinoxaline **8**, which undergoes 1,3-sigmatropic shift of a hydrogen **8**→**9**. The elimination of a molecule of hydroxylamine then results in **6**.

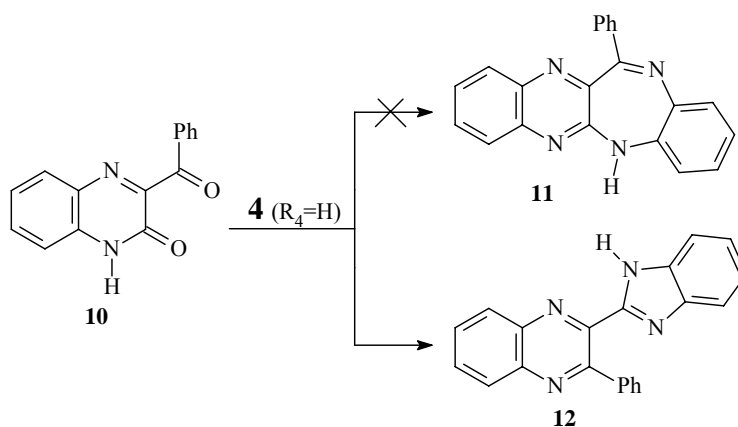


Scheme 2



Scheme 3

A previous attempt⁷ to synthesize derivatives of 1,5-benzodiazepine by coupling *o*-phenylenediamine with 3-benzoyl-1,2-dihydro-2-oxoquinoxaline **10** containing an 1,3-dicarbonyl fragment has also failed. The prolonged heating of an acetic acid solution of the components gave rise not to the expected quinoxalinobenzodiazepine **11**, but to its isomer, 2-benzimidazolyl-3-phenylquinoxaline **12** (Scheme 4). The mechanism of this reaction is assumed to involve a complicated transformation of the quinoxaline ring of **10** into the 2-benzimidazolyl substituent, whereas the 3-phenylquinoxaliny fragment of **12** is formed from *o*-phenylenediamine.



Scheme 4

The majority of currently known methods for the synthesis of quinoxalines are based on the reactions of *o*-phenylenediamines with 1,2-dicarbonyl compounds or their oximes.^{7,8} Therefore, the method for the preparation of compounds **6** using 1,3-dicarbonyl-containing compounds **3** can be regarded as a new approach to the derivatives of quinoxaline. The molecular structure of the compound, **6a** (R⁴ = R² = H, R³ = CH₃) has been proved by X-ray analysis (Figure 1). The values of important bond lengths and valence angles are given in Table 1.

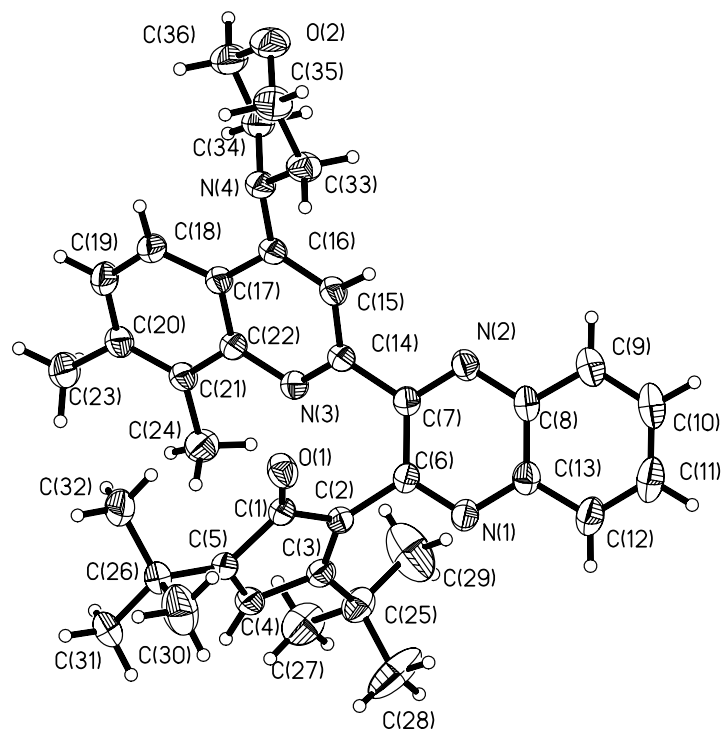


Figure 1. Molecular structure of 3,5-di(*tert*-butyl)-2-[3-(7,8-dimethyl-4-morpholino-2-quinolyl)-2-quinoxaliny]-2,4-cyclopentadien-1-one (**6a**).

Table 1. Bond lengths [Å] and angles [deg] for (**6a**)

N(1)-C(6)	1.323(3)	N(1)-C(13)	1.366(4)
N(2)-C(7)	1.317(3)	N(2)-C(8)	1.377(3)
N(3)-C(14)	1.322(3)	N(3)-C(22)	1.381(3)
N(4)-C(16)	1.409(3)	N(4)-C(33)	1.452(3)
N(4)-C(34)	1.470(4)	O(1)-C(1)	1.217(3)
O(2)-C(36)	1.415(4)	O(2)-C(35)	1.419(4)
C(1)-C(2)	1.498(4)	C(1)-C(5)	1.510(4)
C(2)-C(3)	1.341(4)	C(2)-C(6)	1.475(4)
C(3)-C(4)	1.502(4)	C(3)-C(25)	1.510(4)
C(4)-C(5)	1.326(4)	C(5)-C(26)	1.508(4)
C(6)-C(7)	1.434(4)	C(7)-C(14)	1.494(4)
C(8)-C(13)	1.392(4)	C(8)-C(9)	1.411(4)
C(9)-C(10)	1.379(4)	C(10)-C(11)	1.384(5)
C(11)-C(12)	1.354(5)	C(12)-C(13)	1.416(4)
C(14)-C(15)	1.404(4)	C(15)-C(16)	1.376(3)

Table 1. Continued

C(17)-C(18)	1.415(4)	C(18)-C(19)	1.360(4)
C(19)-C(20)	1.407(4)	C(20)-C(21)	1.377(4)
C(20)-C(23)	1.510(4)	C(21)-C(22)	1.429(4)
C(21)-C(24)	1.500(4)	C(25)-C(28)	1.519(5)
C(25)-C(27)	1.521(5)	C(25)-C(29)	1.531(4)
C(26)-C(32)	1.514(4)	C(26)-C(31)	1.517(4)
C(26)-C(30)	1.541(5)	C(33)-C(35)	1.496(4)
C(34)-C(36)	1.506(4)	C(6)-N(1)-C(13)	117.7(3)
C(7)-N(2)-C(8)	117.3(2)	C(14)-N(3)-C(22)	117.7(2)
C(16)-N(4)-C(33)	117.3(2)	C(16)-N(4)-C(34)	115.3(2)
C(33)-N(4)-C(34)	109.3(2)	C(36)-O(2)-C(35)	109.6(3)
O(1)-C(1)-C(2)	126.1(3)	O(1)-C(1)-C(5)	126.7(3)
C(2)-C(1)-C(5)	107.2(2)	C(3)-C(2)-C(6)	133.0(3)
C(3)-C(2)-C(1)	107.7(2)	C(6)-C(2)-C(1)	118.9(2)
C(2)-C(3)-C(4)	107.5(3)	C(2)-C(3)-C(25)	131.2(3)
C(4)-C(3)-C(25)	121.3(3)	C(5)-C(4)-C(3)	112.9(3)
C(4)-C(5)-C(26)	130.5(3)	C(4)-C(5)-C(1)	104.7(2)
C(26)-C(5)-C(1)	124.6(3)	N(1)-C(6)-C(7)	121.1(3)
N(1)-C(6)-C(2)	115.4(3)	C(7)-C(6)-C(2)	123.2(2)
N(2)-C(7)-C(6)	121.7(2)	N(2)-C(7)-C(14)	116.2(3)
C(6)-C(7)-C(14)	122.1(2)	N(2)-C(8)-C(13)	121.0(3)
N(2)-C(8)-C(9)	118.9(3)	C(13)-C(8)-C(9)	120.0(3)
C(10)-C(9)-C(8)	118.8(3)	C(9)-C(10)-C(11)	120.6(3)
C(12)-C(11)-C(10)	121.7(3)	C(11)-C(12)-C(13)	119.2(3)
N(1)-C(13)-C(8)	121.1(2)	N(1)-C(13)-C(12)	119.1(3)
C(8)-C(13)-C(12)	119.7(3)	N(3)-C(14)-C(15)	123.7(2)
N(3)-C(14)-C(7)	117.0(2)	C(15)-C(14)-C(7)	119.3(3)
C(16)-C(15)-C(14)	120.2(3)	C(15)-C(16)-N(4)	122.9(2)
C(15)-C(16)-C(17)	117.7(2)	N(4)-C(16)-C(17)	119.3(2)
C(22)-C(17)-C(18)	117.9(2)	C(22)-C(17)-C(16)	118.4(2)
C(18)-C(17)-C(16)	123.7(3)	C(19)-C(18)-C(17)	119.8(3)
C(18)-C(19)-C(20)	123.1(3)	C(21)-C(20)-C(19)	118.7(3)
C(21)-C(20)-C(23)	122.3(3)	C(19)-C(20)-C(23)	119.0(3)
C(20)-C(21)-C(22)	119.3(3)	C(20)-C(21)-C(24)	121.9(3)
C(22)-C(21)-C(24)	118.7(2)	N(3)-C(22)-C(17)	122.2(2)
N(3)-C(22)-C(21)	116.8(2)	C(17)-C(22)-C(21)	121.0(2)
C(3)-C(25)-C(28)	107.8(3)	C(3)-C(25)-C(27)	111.6(3)
C(28)-C(25)-C(27)	112.0(4)	C(3)-C(25)-C(29)	110.3(3)
C(28)-C(25)-C(29)	107.8(3)	C(27)-C(25)-C(29)	107.4(3)

Table 1. Continued

C(5)-C(26)-C(32)	109.8(3)	C(5)-C(26)-C(31)	110.9(3)
C(32)-C(26)-C(31)	109.2(3)	C(5)-C(26)-C(30)	108.0(2)
C(32)-C(26)-C(30)	110.1(3)	C(31)-C(26)-C(30)	108.8(3)
N(4)-C(33)-C(35)	109.3(3)	N(4)-C(34)-C(36)	109.0(3)
O(2)-C(35)-C(33)	112.0(3)	O(2)-C(36)-C(34)	112.3(3)
O(1)-C(1)-C(2)-C(3)	176.2(3)	C(5)-C(1)-C(2)-C(3)	-0.2(3)
O(1)-C(1)-C(2)-C(6)	1.8(4)	C(5)-C(1)-C(2)-C(6)	-174.7(2)
C(6)-C(2)-C(3)-C(4)	172.6(3)	C(1)-C(2)-C(3)-C(4)	-0.7(3)
C(6)-C(2)-C(3)-C(25)	6.7(5)	C(1)-C(2)-C(3)-C(25)	179.9(3)
C(2)-C(3)-C(4)-C(5)	1.6(3)	C(25)-C(3)-C(4)-C(5)	-179.0(3)
C(3)-C(4)-C(5)-C(26)	-177.6(3)	C(3)-C(4)-C(5)-C(1)	-1.7(3)
O(1)-C(1)-C(5)-C(4)	-175.2(3)	C(2)-C(1)-C(5)-C(4)	1.2(3)
O(1)-C(1)-C(5)-C(26)	1.0(4)	C(2)-C(1)-C(5)-C(26)	177.4(2)
C(13)-N(1)-C(6)-C(7)	-0.6(4)	C(13)-N(1)-C(6)-C(2)	-174.3(2)
C(3)-C(2)-C(6)-N(1)	-58.0(4)	C(1)-C(2)-C(6)-N(1)	114.8(3)
C(3)-C(2)-C(6)-C(7)	128.4(3)	C(1)-C(2)-C(6)-C(7)	-58.8(3)
C(8)-N(2)-C(7)-C(6)	0.5(4)	C(8)-N(2)-C(7)-C(14)	-179.4(2)
N(1)-C(6)-C(7)-N(2)	-0.5(4)	C(2)-C(6)-C(7)-N(2)	172.7(3)
N(1)-C(6)-C(7)-C(14)	179.4(3)	C(2)-C(6)-C(7)-C(14)	-7.4(4)
C(7)-N(2)-C(8)-C(13)	0.5(4)	C(7)-N(2)-C(8)-C(9)	-179.2(3)
N(2)-C(8)-C(9)-C(10)	179.7(3)	C(13)-C(8)-C(9)-C(10)	-0.1(4)
C(8)-C(9)-C(10)-C(11)	-0.7(5)	C(9)-C(10)-C(11)-C(12)	0.7(5)
C(10)-C(11)-C(12)-C(13)	0.2(5)	C(6)-N(1)-C(13)-C(8)	1.6(4)
C(6)-N(1)-C(13)-C(12)	178.8(3)	N(2)-C(8)-C(13)-N(1)	-1.6(4)
C(9)-C(8)-C(13)-N(1)	178.2(3)	N(2)-C(8)-C(13)-C(12)	-178.8(3)
C(9)-C(8)-C(13)-C(12)	1.0(4)	C(11)-C(12)-C(13)-N(1)	-178.2(3)
C(11)-C(12)-C(13)-C(8)	-1.0(5)	C(22)-N(3)-C(14)-C(15)	-2.4(4)
C(22)-N(3)-C(14)-C(7)	179.2(2)	N(2)-C(7)-C(14)-N(3)	148.2(3)
C(6)-C(7)-C(14)-N(3)	-31.7(4)	N(2)-C(7)-C(14)-C(15)	-30.2(4)
C(6)-C(7)-C(14)-C(15)	149.9(3)	N(3)-C(14)-C(15)-C(16)	2.7(4)
C(7)-C(14)-C(15)-C(16)	-179.0(2)	C(14)-C(15)-C(16)-N(4)	178.0(3)
C(14)-C(15)-C(16)-C(17)	0.6(4)	C(33)-N(4)-C(16)-C(15)	-15.8(4)
C(34)-N(4)-C(16)-C(15)	115.1(3)	C(33)-N(4)-C(16)-C(17)	161.6(3)
C(34)-N(4)-C(16)-C(17)	-67.5(3)	C(15)-C(16)-C(17)-C(22)	-3.8(4)
N(4)-C(16)-C(17)-C(22)	178.7(2)	C(15)-C(16)-C(17)-C(18)	173.9(3)
N(4)-C(16)-C(17)-C(18)	-3.6(4)	C(22)-C(17)-C(18)-C(19)	-3.8(4)
C(16)-C(17)-C(18)-C(19)	178.4(3)	C(17)-C(18)-C(19)-C(20)	-0.1(5)
C(18)-C(19)-C(20)-C(21)	3.3(5)	C(18)-C(19)-C(20)-C(23)	-178.1(3)
C(19)-C(20)-C(21)-C(22)	-2.4(4)	C(23)-C(20)-C(21)-C(22)	179.0(3)

Table 1. Continued

C(19)-C(20)-C(21)-C(24)	177.7(3)	C(23)-C(20)-C(21)-C(24)	-0.8(5)
C(14)-N(3)-C(22)-C(17)	-1.1(4)	C(14)-N(3)-C(22)-C(21)	-179.5(2)
C(18)-C(17)-C(22)-N(3)	-173.7(3)	C(16)-C(17)-C(22)-N(3)	4.2(4)
C(18)-C(17)-C(22)-C(21)	4.6(4)	C(16)-C(17)-C(22)-C(21)	-177.5(3)
C(20)-C(21)-C(22)-N(3)	176.9(3)	C(24)-C(21)-C(22)-N(3)	-3.3(4)
C(20)-C(21)-C(22)-C(17)	-1.5(4)	C(24)-C(21)-C(22)-C(17)	178.4(3)
C(2)-C(3)-C(25)-C(28)	99.8(4)	C(4)-C(3)-C(25)-C(28)	-79.5(4)
C(2)-C(3)-C(25)-C(27)	-23.6(5)	C(4)-C(3)-C(25)-C(27)	157.1(3)
C(2)-C(3)-C(25)-C(29)	-142.8(3)	C(4)-C(3)-C(25)-C(29)	37.9(4)
C(4)-C(5)-C(26)-C(32)	-132.8(3)	C(1)-C(5)-C(26)-C(32)	52.0(4)
C(4)-C(5)-C(26)-C(31)	-12.1(4)	C(1)-C(5)-C(26)-C(31)	172.8(3)
C(4)-C(5)-C(26)-C(30)	107.1(4)	C(1)-C(5)-C(26)-C(30)	-68.1(4)
C(16)-N(4)-C(33)-C(35)	-167.9(3)	C(34)-N(4)-C(33)-C(35)	58.5(3)
C(16)-N(4)-C(34)-C(36)	167.8(2)	C(33)-N(4)-C(34)-C(36)	-57.5(3)
C(36)-O(2)-C(35)-C(33)	57.9(4)	N(4)-C(33)-C(35)-O(2)	-59.3(4)
C(35)-O(2)-C(36)-C(34)	-57.3(4)	N(4)-C(34)-C(36)-O(2)	57.7(4)

The quinoline ring of **6a** is virtually planar. Deviations of C(14)-C(22) and N(3) atoms from the mean-square plane are in the limits of 0.063(2) to -0.053(2) Å, whereas those of C(23) and C(24) atoms are 0.069(4) and 0.075(4) Å, respectively. The largest deviations from the mean-square plane found for atoms C(7) and N(4) are equal to 0.137(4) and 0.094(4) Å, respectively. A morpholine ring in **6a** having the chair conformation is turned around the N(4)-C(16) bond in such a way that the dihedral angles C(33)-N(4)-C(16)-C(17) and C(34)-N(4)-C(16)-C(17) are equal to 119.3(3)° and -67.5(3)°, respectively. The sum of the valence angles at the tetrahedral N(4) centre is equal to 342.8°. The N(1), N(2), C(6)-C(12) atoms of the quinoxaline moiety of **6a** deviate from the common mean-square plane in the range of -0.010(2) - 0.022(3) Å. This plane contains also the C(4) atom. The torsion angle N(2)-C(7)-C(9)-N(3) is equal to 148.2°. Deviations of atoms O(1), C(25), C(25) and C(6) from the mean-square plane of the cyclopentadienyl ring are -0.075(4), 0.014(5), -0.047(5) and -0.132(4) Å, respectively. The dihedral angles C(1)-C(5)-C(26)-C(31), C(4)-C(3)-C(25)-C(27) and C(1)-C(2)-C(6)-C(7) are 172.8(3)°, 157.1(3)° and -58.8(4)°, respectively. The crystal structure of **6a** is characterized by a shortened contact (2.83 Å) between N(1) atom of one molecule and a hydrogen atom of an adjacent molecule.

Experimental Section

General Procedures. The elemental analyses were carried out by the laboratory of microanalysis of the Institute of Physical and Organic Chemistry. The ¹H NMR spectra were recorded on a Varian Unity-300 spectrometer. The mass spectra were run on a Finnigan MAT

INCOS-50 instrument. The IR spectra were measured on a Specord IR-75 spectrometer from samples dispersed in nujol mulls. The chromatography was performed using standard aluminium oxide columns. Melting temperatures (uncorrected) were measured in glass capillaries with the use of a PTP instrument.

X-Ray analysis

The unit cell parameters and reflection intensities (a three-dimensional set) were measured on a Bruker P-4 autodiffractometer (λ MoK $_{\alpha}$ irradiation, graphite monochromator). Monoclinic crystals; molecular formula C₃₆H₄₀O₂N₄, M = 560.72; *a* 16.721(2), *b* 12.109(2), *c* 17.019(2) Å, β = 111.850(10) $^{\circ}$, *V* 3198.4(8) Å³, *Z* 4, *d*_{calc} 1.164 g cm³, P2₁/n space group. Intensities of 6156 reflections were measured in the reciprocal space ($2\Theta \leq 50$) using $\omega/2\Theta$ scanning. After exclusion of systematically cancelled reflections and averaging intensities of equivalent reflections, the working array of measured $F^2(hkl)$ and $\sigma(F^2)$ reflections contained 4660 independent reflections, 2745 of which with $F^2 \geq 4\sigma(F^2)$. The structure was solved with the direct method and was refined by the full-matrix least-squares procedure with respect to F^2 in anisotropic approximation for non-hydrogen atoms using SHELXL-97 program.⁹ All hydrogen atoms were localized in the Fourier synthesis of the difference electronic density. The coordinates and isotropic thermal parameters were computed using the least-square "rider" model.⁹ In the final cycle of the full-matrix refinement, the absolute values of shifts of all variable 380 parameters of the structure of **6a** were less than 0.001 σ . The final refined parameters were: $R_1 = 0.057$, $wr_2 = 0.13$ for the reflections observed with $I \geq 2\sigma(I)$ and ; $R_1 = 0.107$, $wr_2 = 0.15$ for all measured reflections, GOF = 1.012. The maximum and minimum values of the difference electronic densities are 0.250 and -0.116258 e/Å³. Atomic coordinates, full tables of bond lengths, bond angles and thermal parameters of **6a** have been deposited at the Cambridge Crystallographic Data Center (deposition numbers: CCDC 669813).

3,5-Di(*tert*-butyl)-2-[3-(7,8-dimethyl-4-morpholino-2-quinolyl)-2-quinoxaliny]l-2,4-cyclopentadien-1-one (6a). A solution of 0.4 mmol of 1,7-di(*tert*-butyl)-3-(7,8-dimethyl-4-morpholino-2-quinolyl)-2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxide (**3a**)³, 1.2 mmol of *o*-phenylenediamine and 50 mg of *p*-toluenesulfonic acid in 5 ml of toluene was heated for 4 h under reflux. The solution was cooled, the solvent evaporated and the residue was dissolved in 5 ml of chloroform. The chloroform solution was passed through an aluminium oxide column and the column was eluted with chloroform. A bright orange fraction was collected to give after evaporation of the solvent and recrystallization from 2-propanol **6a** in 67% yield. Orange crystals, m.p. 194-196 °C (from 2-propanol). IR-spectrum, ν , cm⁻¹: 1700, 1607, 1513, 1473, 1367, 1287, 1247. Mass spectrum, *m/z* (*I*_{rel.}, %): 561 (45), 546 (35), 503 (65), 243 (15), 83 (30), 57 (40), 45 (100). ¹H NMR spectrum (CDCl₃): δ 0.89 (s, 9H, C(CH₃)₃), 1.21 (s, 9H, C(CH₃)₃), 2.46 (s, 3H, CH₃), 2.69 (s, 3H, CH₃), 3.20 - 3.45 (m, 4H), 3.90 - 4.10 (m, 4H), 6.80 (s, 1H), 7.28 (m, 1H), 7.79 (m, 4H), 8.13 (m, 1H), 8.21 (m, 1H). Anal. calcd. for C₃₆H₄₀N₄O₂ (560.73): C 77.11; H 7.19; N 9.99; O 5.71. Found: C 77.04; H 7.12; N 9.82.

3,5-Di(*tert*-butyl)-2-[3-(6,8-dimethyl-4-morpholino-2-quinolyl)-2-quinoxaliny]-2,4-cyclopentadien-1-one (6b). It was obtained by coupling of 0.6 mmol 1,7-di(*tert*-butyl)-3-(6,8-dimethyl-4-morpholino-2-quinolyl)-2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxide (**3b**), 1.2 mmol of *o*-phenylenediamine and 50 mg of *p*-toluenesulfonic acid as described for **6a**. Yield 74%, orange crystals, m.p. 182-184 °C. IR-spectrum, ν , cm^{-1} : 1700, 1580, 1513, 1473, 1380, 1233. Mass spectrum, m/z (I_{rel} , %): 561 (15), 546 (20), 503 (38), 243 (23), 77 (23), 57 (100), 41 (97). ^1H NMR spectrum (CDCl_3): δ 0.91 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.20 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.45 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 3.20 - 3.40 (m, 4H), 3.90 - 4.10 (m, 4H), 6.80 (s, 1H), 7.24 (m, 1H), 7.60 - 7.90 (m, 4H), 8.15 (m, 1H), 8.23 (m, 1H). Anal. calcd. for $\text{C}_{36}\text{H}_{40}\text{N}_4\text{O}_2$ (560.73): C 77.11; H 7.19; N 9.99; O 5.71. Found: C 77.02; H 7.15; N 9.73.

3,5-Di(*tert*-butyl)-2-[3-(8-methyl-4-morpholino-2-quinolyl)-2-quinoxaliny]-2,4-cyclopentadien-1-one (6c). It was obtained by coupling 0.6 mmol 1,7-di(*tert*-butyl)-3-(8-methyl-4-morpholino-2-quinolyl)-2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxide (**3c**), 1.2 mmol of *o*-phenylenediamine and 50 mg of *p*-toluenesulfonic acid as described for **6a**. Yield 61%, orange crystals, m.p. 184-186 °C. IR-spectrum, ν cm^{-1} : 1700, 1580, 1500, 1460, 1367. Mass spectrum, m/z (I_{rel} , %): 547 (13), 531 (17), 489 (23), 229 (17), 115 (28), 91 (17), 77 (25), 65 (15), 57 (96), 41 (100). ^1H NMR spectrum (CDCl_3): δ 0.90 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.19 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.74 (s, 3H, CH_3), 3.20 - 3.40 (m, 4H), 3.90- 4.10 (m, 4H), 6.80 (c, 1H), 7.30 - 7.50 (m, 2H), 7.70 - 7.90 (m, 4H), 8.12 (m, 1H), 8.21 (m, 1H). Anal. calcd. for $\text{C}_{35}\text{H}_{38}\text{N}_4\text{O}_2$ (546.71): C 76.89; H 7.01; N 10.25; O 5.85. Found: C 76.62; H 7.04; N 10.02.

3,5-Di(*tert*-butyl)-2-[3-(7,8-dimethyl-4-morpholino-2-quinolyl)-5,8-dimethyl-2-quinoxaliny]-2,4-cyclopentadien-1-one (6d). It was obtained by coupling 0.6 mmol 1,7-di(*tert*-butyl)-3-(7,8-dimethyl-4-morpholino-2-quinolyl)-2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxide (**3a**), 1.2 mmol of 3,6-dimethyl-*o*-phenylenediamine and 50 mg of *p*-toluenesulfonic acid as described for **6a**. Yield 57%, orange crystals, mp 253-255 °C. Mass spectrum, m/z (I_{rel} , %): 589 (3), 532 (10), 243 (18), 103 (12), 91 (15), 77 (25), 57 (100), 41 (89). ^1H NMR spectrum (CDCl_3): δ 0.82 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.36 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.45 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 3.20 - 3.40 (m, 4H), 3.90 - 4.10 (m, 4H), 6.89 (s, 1H), 7.40 - 7.60 (m, 2H), 7.70 - 7.85 (m, 2H), 8.12 (m, 1H), 8.08 (s, 1H). Anal. calcd. for $\text{C}_{38}\text{H}_{44}\text{N}_4\text{O}_2$ (588.79): C 77.52; H 7.53; N 9.52; O 5.43. Found: C 77.38; H 7.44; N 9.42.

3,5-Di(*tert*-butyl)-2-[3-(8-methyl-4-morpholino-2-quinolyl)-5,8-dimethyl-2-quinoxaliny]-2,4-cyclopentadien-1-one (6e). It was obtained by coupling 0.4 mmol 1,7-di(*tert*-butyl)-3-(8-methyl-4-morpholino-2-quinolyl)-2-azabicyclo[3.3.0]octa-2,7-dien-4,6-dione-*N*-oxide (**3c**), 0.8 mmol of 3,6-dimethyl-*o*-phenylenediamine and 50 mg of *p*-toluenesulfonic acid as described for **6a**. Yield 65%, orange crystals, m.p. 247-249 °C. IR-spectrum, ν , cm^{-1} : 1700, 1580, 1527, 1500, 1460, 1233. Mass spectrum, m/z (I_{rel} , %): 575 (10), 560 (11), 517 (27), 229 (23), 115 (19), 91 (16), 77 (25), 65 (10), 57 (100), 41 (87). ^1H NMR spectrum (CDCl_3): δ 0.84 [s, 9H, $\text{C}(\text{CH}_3)_3$], 1.35 [s, 9H, $\text{C}(\text{CH}_3)_3$], 2.75 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 3.20 - 3.40 (m, 4H), 3.90 - 4.10 (m, 4H), 6.88 (s, 1H), 7.30 - 7.50 (m, 4H), 7.88 (m, 1H), 8.12 (s, 1H). Anal.

calcd. for $C_{37}H_{42}N_4O_2$ (574.76): C 77.32; H 7.37; N 9.75; O 5.57. Found: C 77.16; H 7.24; N 9.48.

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