Quinone imines and aminophenols as precursors of new heterocycles

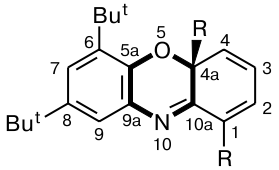
G. A. Abakumov, N. O. Druzhkov, Yu. A. Kurskii, L. G. Abakumova, A. S. Shavyrin, G. K. Fukin, A. I. Poddel´skii, V. K. Cherkasov, and L. S. Okhlopkova*

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation. Fax: +7 (831 2) 62 7497. E-mail: kursk@iomc.ras.ru

Cyclization of substituted quinone imines and diazabutadiene derivatives of aminophenols affords 4a*H*-phenoxazine or 4*H*-1,4-benzoxazine derivatives, which are finally transformed into the following fused heterocycles: the stable 1,4,6,8-tetra(*tert*-butyl)phenoxazin-10-yl radical and 7a,14a,15a,15b-tetrahydro-14,16-dioxa-5,9-diaza-8,15-ethenohexaphene and 5a,6,11a,12-tetrahydro[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine derivatives. The influence of the substituents on the pathways of the reactions of intermediate benzoxazines and phenoxazines, such as oxidation, [2+4] dimerization, and the closure of the second ring, was studied. The structures of the fused heterocycles were determined by X-ray diffraction, NMR spectroscopy, and ESR.

Key words: cyclization, 4*H*-1,4-benzoxazine, 4a*H*-phenoxazine, 14,16-dioxa-5,9-diaza-8,15-ethenohexaphene, [1,4]benzoxazino[3,2-*b*][1,4]benzoxazine, stable radical, X-ray diffraction, NMR, ESR.

The range of heterocyclic compounds is being gradually extended due to the involvement of new synthons capable of undergoing cyclization.[1] The recently described[2] cyclization of *N*-aryl-*o*-quinoneimines affords chiral 4a*H*-phenoxazine derivatives (**1**). In molecule **1**, the 2*H*-1,4-oxazine fragment, in which the double bond is located at the nitrogen atom, is indicated by thick solid lines. This compound is an isomer of 4*H*-1,4-oxazine containing a substituent at the nitrogen atom. New isomers of phenoxazine appeared to be highly reactive. In 1,4a-dialkyl-4a*H*-phenoxazines **1**, the double bonds at positions 1 and 3 are activated by the 2*H*-1,4-oxazine fragment. Hence, compounds **1** readily undergo Diels—Alder dimerization (thermal [2+4] dimerization), and the formation of 6,8-di(*tert*-butyl)-1,4a-diisopropyl-4a*H*-phenoxazine was detected only in solution by NMR spectroscopy.[2] Condensation of *o*-aminophenols with ninhydrin affords stable 5a-hydroxy-5a*H*-indeno[2,1-*b*]benzo-1,4-oxazin-5-one derivatives[3] (in the fragment of **1**, R = OH). The 4a-unsubstituted 4a*H*-phenoxazine derivatives, which are apparently generated as intermediates, are readily subjected to oxidation[4] or oxidative aromatization.[5] The reaction of 2-propyn-1-ol with an excess of *o*-aminophenols or 2-amino alcohol in the presence of $HgCl_2$ produces only *cis*-[1,4]oxazino[3,2-*b*][1,4]oxazine derivatives.[6] In the study,[6] it was hypothesized that the reaction affords substituted 1,4-diazabutadiene as an intermediate, in which the intramolecular addition of two hydroxy groups at the C=N double bonds occur. All the above-mentioned reactions give (or supposedly give) heterocycles containing the 2*H*-1,4-oxazine fragment as intermediate products. The aim of the present study was to examine the influence of the substituents on the pathways of the reactions of heterocycles containing this isomeric oxazine fragment.



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Oxidation of Mn^{III} complex (**2**) containing two *N*-(2,6-diisopropylphenyl)-3,5-di(*tert*-butyl)-*o*-benzoquinone imine ligands in air afforded 1,3,11,13-tetra(*tert*-butyl)-6,8,14a,15b-tetraisopropyl-7a,14a,15a,15b-tetrahydro-14,16-dioxa-5,9-diaza-8,15-ethenohexaphene (**3**) (Scheme 1).

Analogous products were prepared by heating *N*-aryl-*o*-quinoneimines in solution as a result of cyclization giving rise to substituted 4a*H*-phenoxazines **1** followed by Diels—Alder dimerization of **1**.[2] The dimerization occurs stereoselectively to give only 7a*R*,8*R*,14a*R*,15*S*,15a*S*,15b*R* isomer **3** and its 7a*S*,8*S*,14a*S*,15*R*,15a*R*,15b*S* enantiomer, although the formation of eight diastereomers (a total of 16 isomers) is theoretically possible for cyclic compound **3** containing six chiral carbon atoms. Slow crystallization of compound **3** prepared from complex **2** gave crystals suitable for X-ray diffraction study. The structure of **3** was established by X-ray diffraction (Fig. 1). In compound **3**, two 4,6-di*(tert*-butyl)phenyloxyimine fragments are linked by the 1,4-etheno-1,3,5,7-tetraisopropyl-1,2,3,4,4a,5,6,7a-octahydronaphthalene fragments, and

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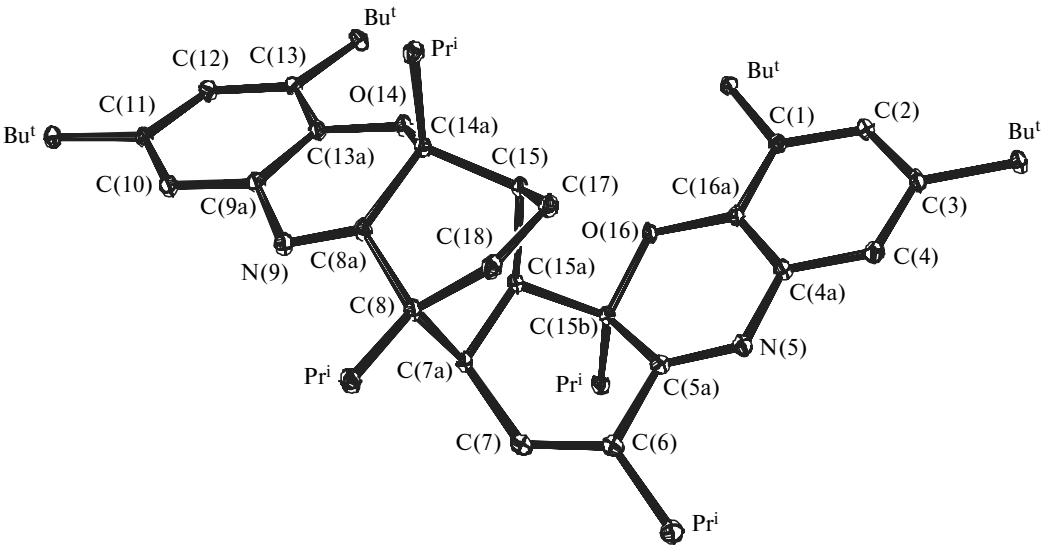
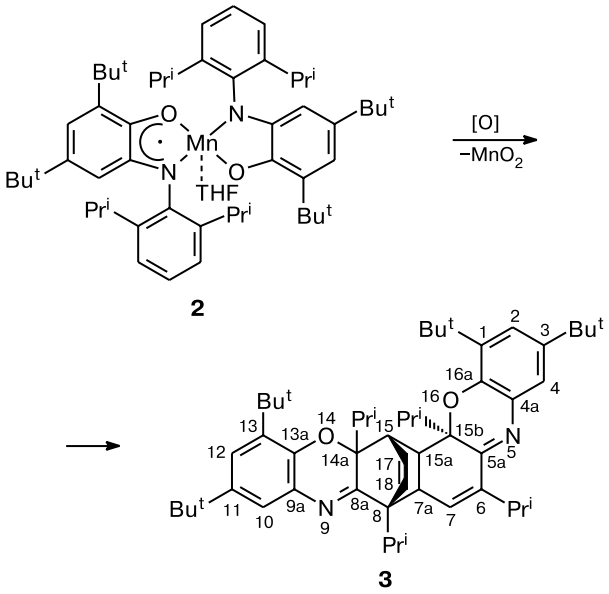


Fig. 1. Molecular structure of **3**. The terminal carbon atoms of the *tert*-butyl and isopropyl groups are omitted. Here and in Figs 2 and 4, the atoms are represented by anisotropic displacement ellipsoids at the 30% probability level.

Scheme 1



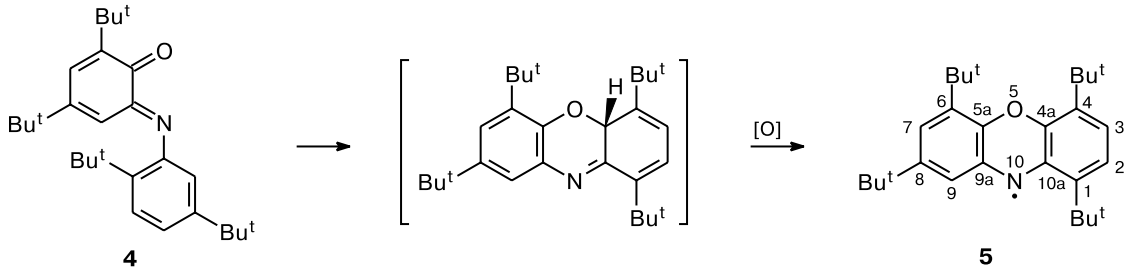
the molecule, as a whole, adopts a *Z* configuration. The lengths of the single bonds (except for C(7a)—C(8)) and double bonds in the 1,4-ethenooctahydronaphthalene fragment are in the ranges typical of the C—C and C=C bonds (1.447(2)—1.563(2) and 1.328(2)—1.337(2) Å, respectively) and agree with the tabulated values.[7] The C(7a)—C(8) distance is 1.603(2) Å, which is, apparently, attributed to steric hindrance caused by the isopropyl group at position 8. The C(17)...C(14a), C(17)...C(15a), C(18)...C(8a), and C(18)...C(7a) distances are in the range of 2.454(2)—2.512(2) Å. An analogous situation was observed also for other compounds containing the 1,4-ethenooctahydronaphthalene fragment.[8]

Heating of *N*-[2,5-di(*tert*-butyl)phenyl]-3,5-(di-*tert*-butyl)-*o*-benzoquinone imine (**4**) also leads to intramolecular cyclization. This reaction is most probable for the *Z* isomer. The barrier to the interconversion between the *E* and *Z* isomers relative to the C=N bond is low (102±15 kJ mol^{-1}).[9] Unlike 4a-alkyl-substituted phenoxazines,[2] intermediate 4a*H*-phenoxazine is easily oxidized. In this reaction, both atmospheric oxygen and the starting quinone imine can serve as an oxidizer, the latter being reduced to aminophenol. Diels—Alder dimerization of this 4a*H*-phenoxazine derivative is hindered, because both conjugated double bonds at positions 1 and 3 are shielded by the bulky *tert*-butyl groups. Oxidation affords the stable radical, *viz.*, 1,4,6,8-tetra(*tert*-butyl)phenoxazin-10-yl (**5**) (Scheme 2). The structure of **5** was established by X-ray diffraction (Fig. 2) and ESR spectroscopy (Fig. 3).

X-ray diffraction study demonstrated that molecule **5** is planar, and the Me groups of the *tert*-butyl substituents are in an eclipsed configuration relative to each other. The N(10)—C(9a) and N(10)—C(10a) distances are 1.364(4) and 1.369(4) Å, respectively. The N—C distances in radical **5** are somewhat shorter than those in analogous phenoxazines (for example, 1.375—1.425 Å in 10-(3′-chlorobutyl)phenoxazine[10] and 1.397—1.411 Å in 10-(3′-chloropropyl)-2-chlorophenoxazine[11]) and are longer than the analogous distances in pyridine (1.337 Å).[7] This is a consequence of delocalization the unpaired electron over the C(9a)—N(10)—C(10a) fragment.

This radical is highly stable. For example, it remains intact in solutions of concentrated strong organic and mineral acids and captures a proton to form the radical cation of 1,4,6,8-tetra(*tert*-butyl)-10*H*-phenoxazine. The

Scheme 2



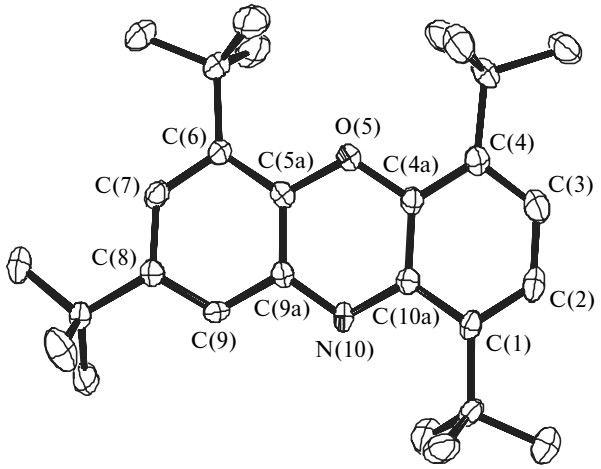


Fig. 2. Molecular structure of stable radical **5**.

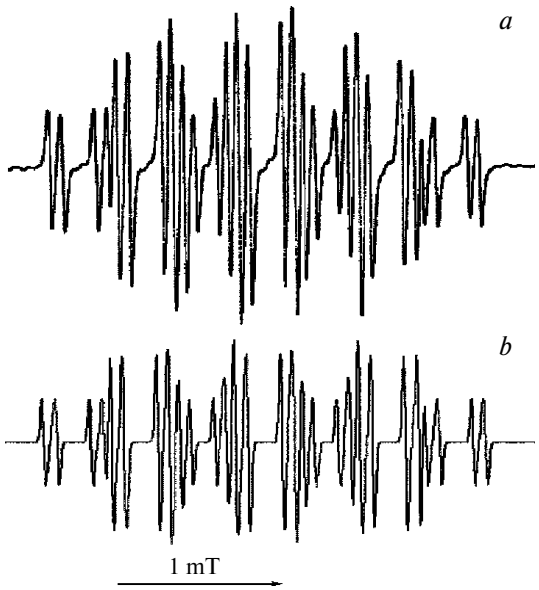


Fig. 3. Experimental (*a*) and calculated (*b*) ESR spectra of stable radical **5**.

structure of radical **5** was chemically confirmed by the fact that it is reduced with hydrazine hydrate to give 1,4,6,8-tetra(*tert*-butyl)-10*H*-phenoxazine (**6**).

In the presence of acids, *N*,*N*′-bis(hydroxyphenyl)-substituted diazabutadienes (**7a,b**) easily undergo rearrangements. An attempt to synthesize dimethyl-substituted (R = Me) diazadiene **7b** failed. The product is unstable and was rearranged to give 2,4,8,10-tetra(*tert*-butyl)-5a,11a-dimethyl-5a,6,11a,12-tetrahydro[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine (**8b**) already during the synthesis (Scheme 3).

Apparently, the formation of the heterocycle started with protonation of the nitrogen atom. The positive charge in the cation is localized not on the nitrogen atom but predominantly on the adjacent carbon atom. The subsequent nucleophilic intramolecular cyclization affords 2*H*-1,4-benzoxazine, in which the oxazine ring includes the chiral carbon atom.

The replacement of the hydrogen atoms of the azadiene fragment in **7a** with the methyl substituents increases stability of the cation. As a result, the rearrangement of dimethyl-substituted diazadiene **7b** occurs more easily. The direction of the approach of the oxygen atom to the carbon atom in the course of second cyclization is controlled by the configuration of the first chiral center. That is why only a racemic mixture of the *RR* and *SS* isomers is produced.

X-ray diffraction study of tetracyclic compound **8b** (Fig. 4) demonstrated that the methyl substituents

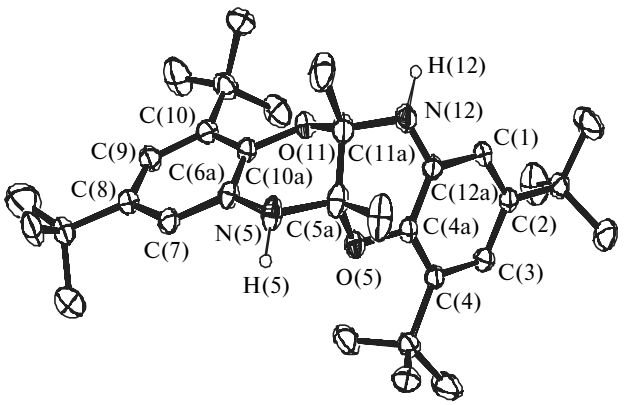
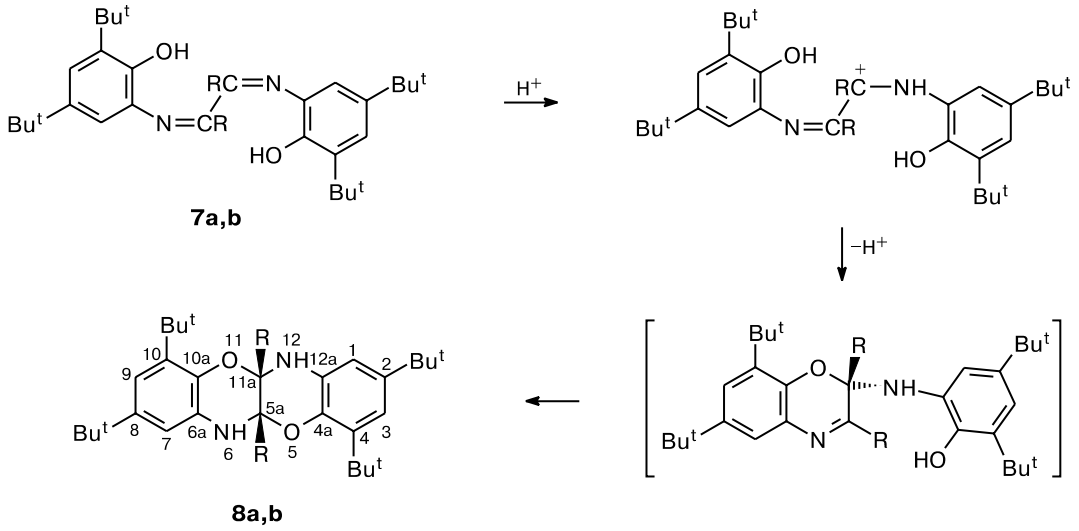


Fig. 4. Molecular structure of **8b**. The structure of one independent molecule is shown; only the H atoms at the N atoms are displayed.

Scheme 3



are in *cis* positions with respect to each other. The Me—C(5a)—C(11a)—Me dihedral angle is 62°. The configuration and geometry of product **8b** are similar to the corresponding characteristics of (5a*R*,11a*R*)-5a,6,11a,12-tetrahydro-5a-methyl-11a-phenyl-[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine.[6]

The NMR spectroscopic data confirm that the *cis* isomer containing the chiral C(5a) and C(11a) centers in the *RR* or *SS* configuration is formed both in the case of **8a** and **8b**. The ^{13}C NMR spectra of products **8a** and **8b** each show six peaks corresponding to the carbon atoms of two aromatic rings, one signal for the C(5a) and C(11a) atoms, and signals for two nonequivalent *tert*-butyl groups. Additional signals, which could belong to the *trans* isomers of **8a** or **8b** containing chiral centers in the *RS* configuration, were not observed.

To summarize, *o*-quinone imines and *o*-aminophenols are convenient starting compounds serving as precursors of new heterocycles. Cyclization of substituted *o*-quinone imines or diazadiene derivatives of *o*-aminophenols affords unstable intermediate 4a*H*-phenoxazine or 4*H*-1,4-benzoxazine derivatives. Then unsubstituted 4a*H*-phenoxazine derivatives are easily oxidized, 4a-alkyl-substituted 4a*H*-phenoxazine derivatives spontaneously undergo Diels—Alder dimerization, and *N*-*o*-aminophenol derivatives of 4*H*-1,4-benzoxazine close the second heterocycle. The reactions proceed stereoselectively to give fused heterocycles in high yields.

Experimental

One- and two-dimensional NMR spectra were recorded on a Bruker Avance DPX-200 instrument (200 MHz for ^{1}H and 50 MHz for ^{13}C) with Me_4Si as the internal standard. The data were processed using the XwinNMR 2.1 program. The ESR spectra were measured on a Bruker ER200D-SRC instrument operating at 9.5 GHz. The IR spectra were recorded on a Perkin—Elmer 577 instrument in Nujol mulls. X-ray diffraction data sets for complexes **3** and **8b** were collected on an automated Smart APEX diffractometer. X-ray diffraction data for complex **5** were measured on a Siemens P3/PC diffractometer. The principal crystallographic characteristics, details of X-ray data collection, and parameters of structure refinement are given in Table 1. All structures were solved by direct methods and refined by the least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The H atoms in complexes **3** and **5** were located from difference Fourier maps and refined isotropically. The H atoms in complex **8b** were placed in geometrically calculated positions and refined using a riding model. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[12] Absorption corrections were applied using the SADABS program.[13]

[4,6-Di(*tert*-butyl)-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinono]-[4,6-di(*tert*-butyl)-*N*-(2,6-diisopropylphenyl)-*o*-amidophenolato]manganese(III) tetrahydrofuranate (2) was prepared according to a known procedure.[14]

1,3,11,13-Tetra(*tert*-butyl)-6,8,14a,15b-tetraisopropyl-7a,14a,15a,15b-tetrahydro-14,16-dioxa-5,9-diaza-8,15-ethenohexaphene (3). Compound **2** (0.225 mmol, 0.2 g) was dissolved in toluene (30 mL) and the mixture was refluxed in air for 30 min. After recrystallization at −12 °C for 2 days, dark semitransparent rhombic crystals of **3** with m.p. 152—154 °C (with decomp.) were obtained in a yield of 0.05 g (29.2%). The X-ray diffraction data are given in Tables 1 and 2. The structure is completely identical to that established earlier by two-dimensional NMR.[2]

2,4-Di(*tert*-butyl)-6-[2′,5′-di(*tert*-butyl)phenyl]iminocyclohexa-2,4-dien-1-one (4). 3,5-Di(*tert*-butyl)-*o*-benzoquinone (10 mmol, 2.2 g) was dissolved in methanol (20 mL), and 2,5-di(*tert*-butyl)aniline (2.05 mL) was added. The reaction

Table 1. Principal crystallographic characteristics, details of X-ray diffraction study, and parameters of structure refinement for **3**, **5**, and **8b**

Parameter		**3**	**5**	**8b**
Formula	$C_{52}H_{74}N_2O_2$	$C_{28}H_{40}NO$	$C_{32}H_{48}N_2O_2$	
Molecular weight		759.13	406.61	492.73
Temperature/K		100(2)	293(2)	293(2)
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	
a/Å	21.5738(9)	20.792(4)	15.5889(7)	
b/Å	9.9610(4)	10.602(2)	10.5861(5)	
c/Å	22.2183(10)	11.342(2)	36.9007(17)	
β/deg	109.663(1)	98.74(3)	94.774(1)	
V/Å^3	4496.2(3)	2471.0(9)	6068.4(5)	
Z		4	4	8
ρ_{calc}/g cm^{-3}	1.121	1.093	1.079	
μ/mm^{-1}	0.067	0.065	0.066	
$2\theta_{max}$/deg	58	56	50	
Number of measured reflections		46263	2770	33008
Number of reflections with $I > 2\sigma$		10300 (R_{int} = 0.0286)	1505 (R_{int} = 0.1023)	10686 (R_{int} = 0.0438)
Number of parameters in refinement		789	431	721
R_1 ($I > 2\sigma(I)$)		0.0568	0.0569	0.0713
wR_2 (based on F^2 for all reflections)		0.1468	0.1163	0.1978
Weighting scheme		$w^{-1} = \sigma^2(F_0^2) + (\alpha P)^2 + \beta P$, where $P = 1/3(F_0^2 + 2F_c^2)$		
	α	0.0765	0.0494	0.0895
	β	1.8421	0.1254	1.8676
Residual electron density peaks, max/min, e Å^{-3}		1.520/−0.216	0.112/−0.173	0.487/−0.230
Transmission factors, T_{min}/T_{max}		0.9734/0.9934		0.9489/0.9969

mixture was stirred without heating for 10 h (until the color of the starting quinone disappeared). The precipitate that formed was filtered off and dissolved in diethyl ether. After recrystallization from diethyl ether, dark-brown crystals of **4** precipitated. The product with m.p. 121—123 °C was isolated in a yield of 1.9 g (49.6%). Found (%): C, 82.35; H, 10.29. $C_{28}H_{41}NO$. Calculated (%): C, 82.50; H, 10.14. IR (Nujol mulls), ν/cm^{-1}: 1670 (C=O); 1630 (C=N). ^{1}H NMR ($CDCl_3$), δ: 1.12, 1.27, 1.34, and 1.35 (all s, 9 H each, Bu^t); 6.25 (d, 1 H, C(5)H, J = 2.4 Hz); 6.42 (d, 1 H, C(6′)H, J = 2.2 Hz); 7.04 (d, 1 H, C(3)H, J = 2.4 Hz); 7.15 (dd, 1 H, C(4′)H, J = 2.2 and 8.2 Hz); 7.34 (d, 1 H, C(3′)H, J = 8.2 Hz).

1,4,6,8-Tetra(*tert*-butyl)phenoxazin-10-yl (5). Formic acid (1—2 drops) was added to a solution of **4** (10 mmol, 4.07 g) in methanol (70 mL), and the reaction mixture was heated for 2 h. The precipitate that formed was filtered off and dissolved in hexane. After recrystallization from hexane, bright-red crystals of **5** precipitated. The product with m.p. 158—160 °C was isolated in a yield of 3.2 g (78.9%). Found (%): C, 82.79; H, 10.09. $C_{28}H_{40}NO$. Calculated (%): C, 82.76; H, 9.92. ESR (a/mT): g = 2.0037, a_N = 0.747, a_H(1 H, C(2)H) = 0.076, a_H(1 H, C(3)H) = 0.406, a_H(1 H, C(7)H) = 0.406, a_H(1 H, C(9)H) = 0.283. The X-ray diffraction data are given in Tables 1 and 2. After dissolution of **5** in a mixture of trifluoroacetic and sulfuric acid, the radical cation was obtained. ESR of the protonated form (a/mT): g = 2.0035, a_N = 0.720, a_H(1 H, C(2)H) = 0.055 a_H(1 H, C(3)H) = 0.330, a_H(1 H, C(7)H) = 0.330, a_H(1 H, C(9)H) = 0.125, a_H(1 H, NH) = 0.84. The theoretical spectrum was calculated using the WinEPR Simfonia v.1.25 program.

1,4,6,8-Tetra(*tert*-butyl)-10*H*-phenoxazine (6). A solution of hydrazine hydrate was added dropwise to a suspension of **5** (10 mmol, 4.06 g) in methanol (50 mL) under argon until the precipitate was completely dissolved and the reaction mixture turned colorless. After cooling, colorless crystals of **6** precipitated. The product was isolated in a yield of 2.76 g (64.2%). Found (%): C, 82.45; H, 9.87. $C_{28}H_{41}NO$. Calculated (%): C, 82.50; H, 10.14. IR (Nujol mulls), ν/cm^{-1}: 1205 (C—O—C), 3600 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.26, 1.40, 1.43, and 1.46 (all s, 9 H each, Bu^t); 5.32 (s, 1 H, NH); 6.25 (d, 1 H, C(7)H, J = 2.5 Hz); 6.63 (d, 1 H, C(3)H, J = 8.6 Hz); 6.72 (d, 1 H, C(9)H, J = 2.5 Hz); 6.74 (d, 1H, C(2), J = 8.6 Hz). ^{13}C NMR ($CDCl_3$): 30.2, 30.7, 30.9, and 31.3 ($C(\underline{C}H_3)_3$); 33.5, 34.33, 34.4, and 34.8 ($\underline{C}(CH_3)_3$); 109.0 (C(9)H); 116.5 (C(C(7)H); 118.1 (C(3)H); 120.2 (C(2)H); 130.3, 130.6, 131.0, 135.0, 136.3, 140.0, 143.4 (C(1), C(4), C(4a), C(5a), C(6), C(9a), C(10a)); 145.4 (C(8)).

***N*,*N*′-Ethane-1,2-diylidenedi(2-amino-4,6-di-*tert*-butylphenol) (7a).** A 40% glyoxal solution (0.23 mL, 2 mmol) in methanol (5 mL) was added with stirring to a solution of 2-amino-4,6-di(*tert*-butyl)phenol (4 mmol, 0.89 g) in methanol (25 mL). After 1 h, yellow crystals of **7a** that precipitated were filtered off and washed with cold methanol. The product was isolated in a yield of 0.52 g (55%). Found (%): C, 77.27; H, 9.69. $C_{30}H_{44}N_2O_2$. Calculated (%): C, 77.59; H, 9.48. IR (Nujol mulls), ν/cm^{-1}: 3360 (OH); 1625 (C=N). ^{1}H NMR ($CDCl_3$), δ: 1.34 and 1.45 (both s, 18 H each, Bu^t); 7.27 (d, 2 H, C(5)H, J = 2.3 Hz); 7.35 (d, 2 H, C(3)H, J = 2.3 Hz); 7.85 (br.s, 2 H, OH); 8.6 (s, 2 H, CH=N). ^{13}C NMR ($CDCl_3$), δ: 29.3, 31.5 ($C(\underline{C}H_3)_3$); 34.6, 35.1 ($\underline{C}(CH_3)_3$); 109.8 (C(3)H); 125.9

Table 2. Selected bond lengths (*d*) and bond angles (ω) in compounds **3**, **5**, and **8b**

Parameter	Value	Parameter	Value	Parameter	Value
		Compound **3**			
Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
N(5)—C(4a)	1.412(2)	C(14a)—C(15)	1.549(2)	C(17)—C(15)—C(14a)	107.0(1)
N(5)—C(5a)	1.282(2)	C(14a)—C(8a)	1.523(2)	C(17)—C(15)—C(15a)	109.6(1)
C(5a)—C(6)	1.477(2)	C(15)—C(15a)	1.558(2)	C(14a)—C(15)—C(15a)	107.23(9)
C(6)—C(7)	1.337(2)	C(15a)—C(15b)	1.547(2)	C(18)—C(8)—C(7a)	104.3(1)
C(7)—C(7a)	1.501(2)	C(15a)—C(7a)	1.563(2)	C(8a)—C(8)—C(7a)	100.37(9)
C(7a)—C(8)	1.603(2)	C(15b)—C(5a)	1.518(2)	C(18)—C(8)—C(8a)	110.9(1)
C(8)—C(8a)	1.531(2)	C(15)—C(17)	1.503(2)		
N(9)—C(8a)	1.278(2)	C(17)—C(18)	1.328(2)		
N(9)—C(9a)	1.418(2)	C(18)—C(8)	1.518(2)		
		Compound **5**			
Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
O(5)—C(5a)	1.402(4)	N(10)—C(10a)	1.369(4)	C(4a)—O(5)—C(5a)	119.7(3)
O(5)—C(4a)	1.400(4)	C(5a)—C(9a)	1.399(5)	C(9a)—N(10)—C(10a)	118.9(3)
N(10)—C(9a)	1.364(4)	C(4a)—C(10a)	1.416(5)		
		Compound **8b***			
Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
O(5)—C(4a)	1.379(2)/1.387(2)	C(4a)—O(5)—C(5a)	117.0(1)/117.0(1)	O(5)—C(5a)—C(11a)	107.6(2)/107.8(1)
O(5)—C(5a)	1.451(2)/1.444(2)	C(10a)—O(11)—C(11a)	117.5(1)/117.3(1)	C(21)—C(5a)—C(11a)	114.2(2)/114.2(2)
O(11)—C(10a)	1.382(2)/1.384(2)	C(6a)—N(6)—C(5a)	117.2(2)/118.0(2)	N(12)—C(11a)—O(11)	107.6(2)/107.8(1)
O(11)—C(11a)	1.444(2)/1.448(2)	C(12a)—N(12)—C(11a)	117.4(2)/116.9(1)	N(12)—C(11a)—C(30)	109.9(2)/110.1(2)
C(5a)—C(11a)	1.534(3)/1.539(3)	N(6)—C(5a)—O(5)	107.6(2)/107.3(1)	O(11)—C(11a)—C(30)	108.5(2)/109.2(2)
N(6)—C(5a)	1.422(2)/1.427(2)	N(6)—C(5a)—C(21)	110.4(2)/110.2(2)	N(12)—C(11a)—C(5a)	108.3(2)/108.0(2)
N(6)—C(6a)	1.413(2)/1.408(2)	O(5)—C(5a)—C(21)	108.6(2)/109.3(2)	C(30)—C(11a)—C(5a)	114.5(2)/114.0(2)
N(12)—C(11a)	1.424(3)/1.424(2)	N(6)—C(5a)—C(11a)	108.1(2)/107.8(2)		
N(12)—C(12a)	1.406(2)/1.416(2)				

* The geometric characteristics for the second independent molecule are also given.

(C(5)H); 133.4 and 136.0 (C(6), C(2)); 147.7 (CH=N); 150.1 and 150.4 (C(4), C(1)).

2,4,8,10-Tetra(*tert*-butyl)-5a,6,11a,12-tetrahydro[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine (8a). Compound **7a** (1 mmol, 0.47 g) was dissolved in methanol (30 mL) and two drops of formic acid were added. The reaction mixture was refluxed for 2 h. Then methanol was removed, and the reaction mixture was dissolved in hexane, from which colorless crystals of **8a** precipitated upon cooling. The product was isolated in a yield of 0.35 g (75%). Found (%): C, 77.18; H, 9.30. $C_{30}H_{44}N_2O_2$. Calculated (%): C, 77.59; H, 9.48. IR (Nujol mulls), ν/cm^{-1}: 3440, 3390 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.28 and 1.33 (s, 9 H each, Bu^t); 4.70 (br.d, 2 H, NH, J = 3.8 Hz); 5.23 (s, 2 H, CH—N); 6.57 (d, 2 H, C(3)H and C(9)H, J = 2.3 Hz); 6.77 (d, 2 H, C(1)H and C(7)H, J = 2.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 29.9, 31.6 (C($\underline{C}H_3)_3$); 34.4, 34.9 ($\underline{C}(CH_3)_3$); 76.3 (CH—NH); 110.1 (C(1)H and C(7)H); 114.7 (C(3)H and C(9)H); 128.9, 137.6, 138.0, 143.6 (C(2) and C(8), C(6a) and C(12a), C(4a) and C(10a), C(4) and C(10)).

2,4,8,10-Tetra(*tert*-butyl)-5a,11a-dimethyl-5a,6,11a,12-tetrahydro[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine (8b). Diacetyl (2 mmol) and formic acid (2 drops) were added to a solution of 2-amino-4,6-di(*tert*-butyl)phenol (4 mmol, 0.89 g) in methanol (30 mL). The reaction mixture was heated and refluxed for 2 h. Then methanol was removed, and the reaction mixture was dissolved in isooctane, from which colorless crystals of **8b** precipitated upon cooling. The product was isolated in a yield of 0.69 g (65%). Found (%): C, 77.91; H, 9.59. $C_{32}H_{48}N_2O_2$. Calculated (%): C, 78.05; H, 9.76. IR (Nujol mulls), ν/cm^{-1}: 3420 (OH), 3400 (NH). ^{1}H NMR ($CDCl_3$), δ: 1.19 and 1.26 (both s, 9 H each, Bu^t); 1.56 (s, 6 H, Me); 4.2 (br.s, 2 H, NH); 6.54 (d, 2 H, C(1)H, C(7)H, J = 2.4 Hz); 6.71 (d, 2 H, C(3)H, C(9)H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 22.5 (Me); 29.8, 31.8 (C($\underline{C}H_3)_3$); 34.4, 34.9 ($\underline{C}(CH_3)_3$); 82.5 (C(5a), C(11a)); 110.5 (C(1)H, C(7)H); 115.0 (C(3)H, C(9)H); 128.6, 136.6, 138.9, 142.4 (C(2) and C(8), C(4) and C(10), C(4a) and C(10a), C(6a) and C(12a)). The X-ray diffraction data are given in Tables 1 and 2. There are two molecules per asymmetric unit cell. The independent molecules have similar geometric parameters.

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