Synthesis, chemical properties, and crystal structure of 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one

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The reaction of di(*tert*-butyl) derivatives of pyrocatechol with 2,6-dihydroxyaniline afforded 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one. The chemical properties of the reaction product and its ability to form complexes with metal salts as the tridentate ligand were investigated. The structure of hydroxyphenoxazinone was established by X-ray diffraction.

Key words: 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one, tautomerism, metal chelates, tridentate ligands, ESR spectroscopy, X-ray diffraction study, quantum chemical calculations.

Phenoxazine systems and their sterically hindered structural analogs can be involved in reversible one-electron redox reactions to form paramagnetic intermediates, the presence of the *tert*-butyl groups leading to a substantial increase in the stability of such free-radical species.[1]

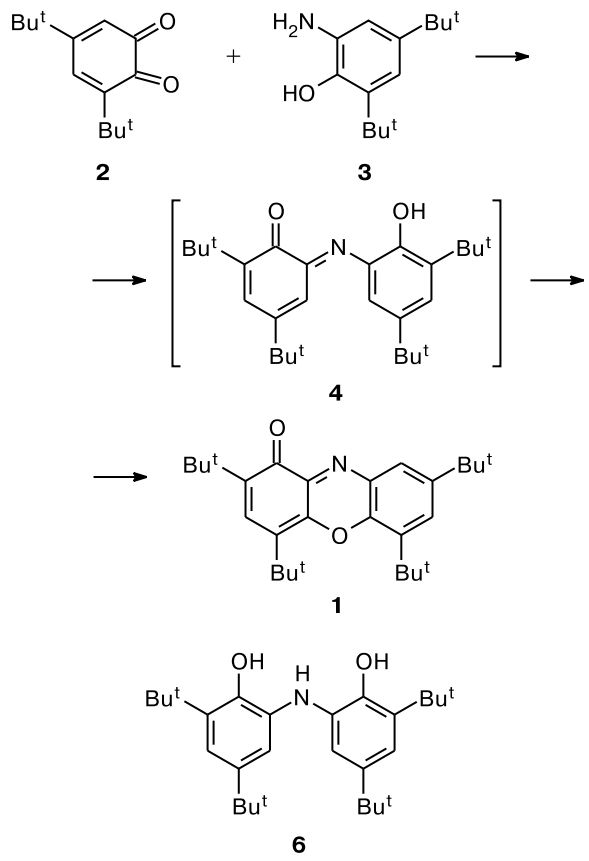
The development of methods for the synthesis of sterically hindered quinoneimine systems[2,3] made it possible to prepare 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one (**1**).[4—6] It appeared that the reaction of 3,5-di(*tert*-butyl)-1,2-benzoquinone (**2**) with 3,5-di(*tert*-butyl)-2-hydroxyaniline **3** gives sterically hindered tricyclic system **1** (see Ref. 6) instead of the expected hydroxyphenyliminobenzoquinone **4** (see Ref. 7) (Scheme 1).

It was shown[5] that the reaction of 3,5-di(*tert*-butyl)-*o*-benzoquinone (**2**) with 3,5-di(*tert*-butyl)pyrocatechol (**5**) in aqueous ethanolic ammonia (under anaerobic conditions) gives the diamagnetic crystalline adduct **A**. According to the X-ray diffraction data, the adduct **A** consists of two phenoxazinone molecules **1** linked to the molecule of bis[3,5-di(*tert*-butyl)-2-hydroxyphenyl]amine (**6**) by hydrogen bonds.

The oxidation of benzene solutions of the adduct **A** with atmospheric oxygen affords 2,4,6,8-tetra(*tert*-butyl)-phenoxazin-1-one (**1**) in quantitative yield. This confirms the instability of compound **6** in oxidation reactions, which are accompanied by the intramolecular homolytic cyclization giving phenoxazinone **1**.[5]

Previously, it has been shown that compound **6** can serve as the paramagnetic tridentate ligand stabilized by

Scheme 1



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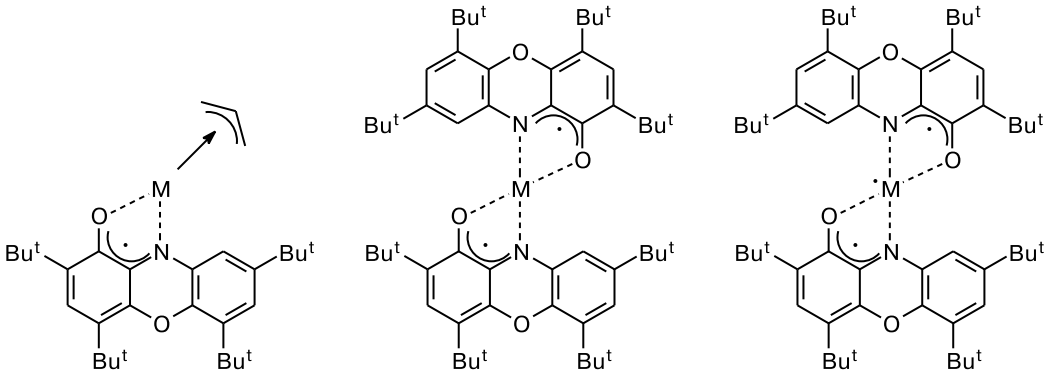


7 **8** **9**

the metal chelation in complexes prepared by the template synthesis.[7]

The chemistry of sterically hindered phenoxazinones has attracted interest primarily due to the ability of phenoxazinone **1** to be involved in reversible one-electron redox processes to form a radical anion, whose reactions with metal salts give paramagnetic bidentate metal complexes **7**—**9** with different chemical structures.[8]

Based on the structures of compounds **7**—**9** established by X-ray diffraction and the character of the intramolecular spin exchange in these metal complexes studied by ESR spectroscopy, such compounds can be divided into three main groups.[8,9]

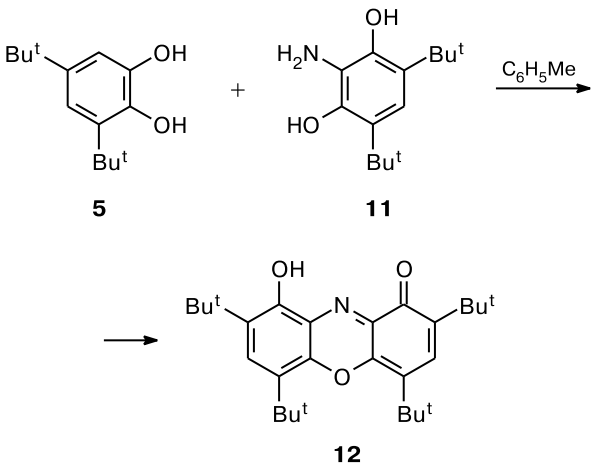
One group includes free-radical allyl-type organometallic compounds (monoradicals) **7**. Two other groups include compounds **8** and **9**, which are biradical systems that differ in the type of the electron shell (closed (**8**) or open (**9**)) of the central metal atom in the bidentate chelate unit of the metal complexes.

Results and Discussion

The aim of the present study was to synthesize the sterically hindered phenoxazine system capable of forming the tridentate metal chelate unit upon the coordination.

For this purpose, we studied the reaction of sterically hindered pyrogallol with ammonia. It was found that 4,6-di(*tert*-butyl)pyrogallol (**10**) (which was prepared by the alkylation of pyrogallol with *tert*-butyl alcohol in sulfuric acid)[2] easily undergoes amination under the action of aqueous ammonia. However, the reaction gives the symmetric product 3,5-di(*tert*-butyl)-2,6-dihydroxyaniline (**11**) instead of the expected 3,5-di(*tert*-butyl)-2,3-dihydroxyaniline. This result suggests that, as opposed to pyrogallol, the central hydroxy group is involved in the amination in the sterically hindered analog. The condensation of 3,5-di(*tert*-butyl)-2,6-dihydroxyaniline **11** with 3,5-di(*tert*-butyl)pyrocatechol (**5**) in toluene in the presence of catalytic amounts of *p*-toluenesulfonic acid affords 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one (**12**) (Scheme 2).

Scheme 2



5 **11** **12**

Product **12** is a violet crystalline compound readily soluble in low-polarity aprotic solvents (hexane and benzene) and poorly soluble in alcohols. The UV spectrum of compound **12** is shown in Fig. 1.

The intramolecular character of the $O^1 \leftrightarrows N \leftrightarrows O^2$ prototropy (Scheme 3) in molecule **12** is confirmed by the fact that the polarity of the solvent has no effect on the character of the UV spectrum of compound **12** (see Fig. 1, curves *1* and *2*). Thus the spectra recorded in hexane and ethanol are identical in the short-wavelength region and are only slightly different in the long-wavelength region. The addition of an equimolar amount of an ethanolic NaOH solution to an ethanolic solution of compound **12** resulted in the appearance of an additional absorption band at $\lambda_{max} = 695$ cm^{-1} (see Fig. 1, curve *3*), which is apparently associated with the formation of symmetric mesomeric anion **12a**. The subsequent addition of an equimolar amount of MeCOOH to the ethanolic solution of anion **12a** results in the regeneration of the starting 2,4,6,8-tetra-

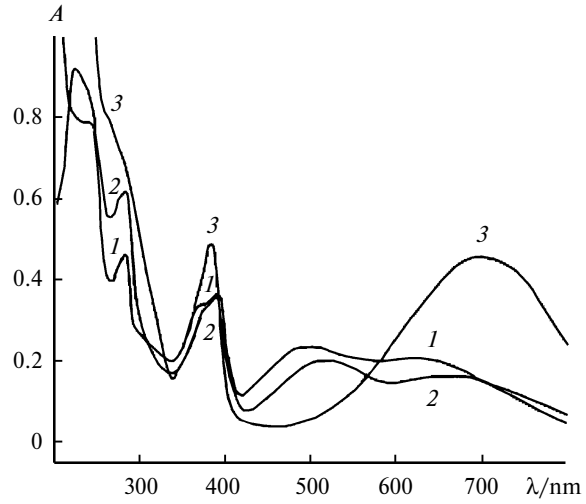
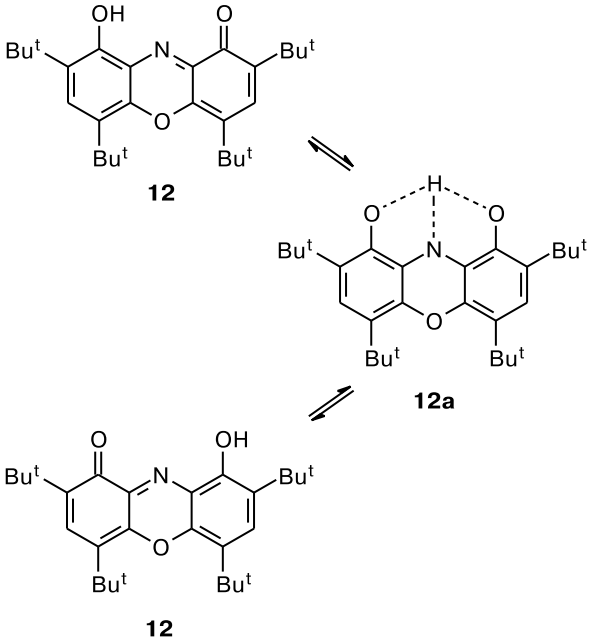


Fig. 1. UV-Vis spectra of compound **12** in hexane (*1*) and ethanol (*2*, *3*) before (*2*) and after the addition of NaOH (*3*); $C = 4 \cdot 10^{-5}$ mol L^{-1}).

(*tert*-butyl)-9-hydroxyphenoxazin-1-one (**12**). This is indicative of the reversibility of the reaction under consideration. As opposed to 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one (**1**),[6] the low basicity of the nitrogen atom in the phenoxazine ring of compound **12** makes it impossible to prepare protonated derivatives by the treatment with mineral acids or free HCl in solvents of different polarity (benzene or ethanol).

Scheme 3



The X-ray diffraction study showed that compound **12** crystallizes as the solvate with ethanol. Molecule **12** is a tautomer with the hydrogen atom located at one of the oxygen atoms (O(2)) (Fig. 2). The ethanol molecule forms relatively strong hydrogen bonds with the C=O (O(1S)...O(3), 2.761(2) Å; O(1S)H(1S)O(3), 169.8°) and OH (O(2)...O(1S), 2.680(2) Å; O(2)H(102)O(1S), 161°) groups serving both as the hydrogen atom donor and acceptor. Based on the N(1)...O(2) distance (2.714(2) Å), the formation of the intramolecular O(2)H(2)...N(1)H hydrogen bond cannot be ruled out as well, although the O(2)H(102)N(1) angle (110.2°) essentially deviates from 180°. It should also be mentioned that there is the forced shortened O(1S)...N(1) contact (2.876(2) Å), which, among other factors, can stabilize this solvate.

An analysis of the molecular geometry of compound **12** (Table 1) showed that the bond length distribution in the quinone ring C(7)—C(12) (1.365(2)—1.488(2) Å) is virtually identical to that found previously[10] in 2,4,6,8-tetra-(*tert*-butyl)phenoxazin-1-one (**1**). In the second hydroxy-substituted ring, the bond lengths are more equalized (1.389(2)—1.427(2) Å) (see Table 1). The fused ring in compound **12** is planar (the average deviation of the atoms is no larger than 0.0158 Å); the deviations of the central C(13), C(17), C(21), and C(25) atoms of the *tert*-butyl groups from this plane are in the range of 0.029—0.09 Å. All *tert*-butyl groups deviate in the same direction, whereas the C(25) atom deviates in the opposite direction, which is apparently attributed to the steric crowding of the molecule. Actually, the presence of four bulky *tert*-butyl substituents results in the formation of numerous shortened intermolecular contacts, such as two C—H...O(2) contacts (H(20C)...O(2), 2.24 Å; H(18A)...O(2), 2.33 Å), two C—H...O(3) contacts (H(23B)...O(3), 2.36 Å; H(22c)...O(3), 2.33 Å), and four C—H...O(2) contacts (the H...O distances vary in the range of 2.34—2.47 Å). In addition to the C—H...O interactions, there are also abnormally short intramolecular H...H contacts H(15B)...H(26A) and H(14B)...H(26A) (1.83 and 1.89 Å, respectively). In all *tert*-butyl groups, the CCC bond angles at the central atom are distorted in the same manner, *viz.*, the CCC angles at the carbon atom of the methyl groups (C(16), C(19), C(28), or C(24), respectively), which is involved in none of the above-mentioned intramolecular contacts, are decreased.

To estimate whether the tautomer that is found in the crystal corresponds to the energy minimum or results from the stabilization by specific solvation and to investigate the character of the above-mentioned intramolecular interactions, we carried out quantum chemical calculations (B3LYP/6-31G**).

The geometry optimization of two tautomers containing the hydroxy group (**A**) and the protonated nitrogen atom (**B**) showed that the tautomer **A** in the gas phase also corresponds to the global minimum and is 4.33 kcal mol^{-1} more stable. A comparison of the experimental and calculated geometry reveals that the chosen level of theory and

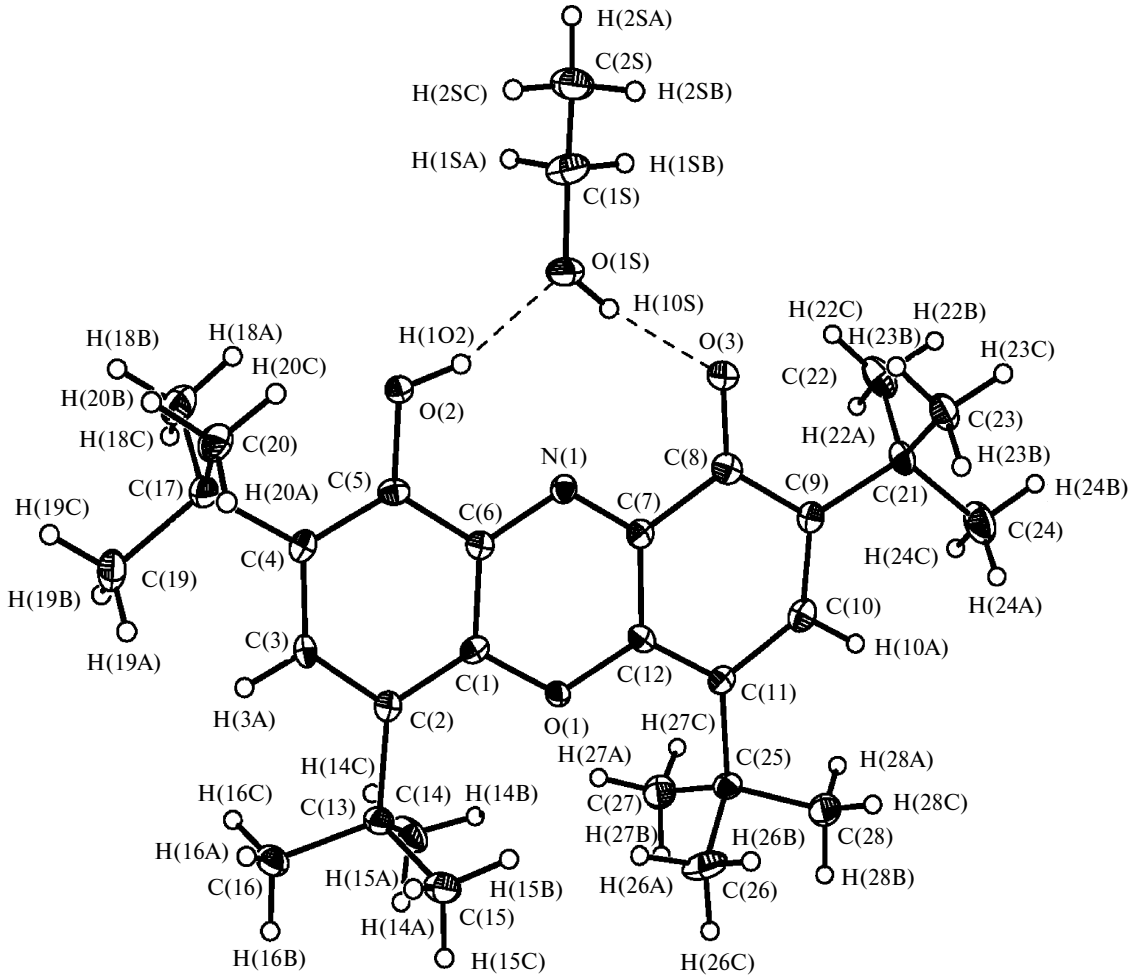


Fig. 2. Molecular structure of compound **12** represented by displacement ellipsoids (p = 50%).

the basis set adequately reproduce the main structural features of compound **12** (see Table 1). Apparently, the tautomer **A** is additionally stabilized due to the essential alternation of the bonds in two quinonoid rings in the tautomer **B** (C—C, 1.373—1.474 Å) resulting in the loss of aromaticity compared to the hydroxy-substituted tautomer **A**. In addition, the intramolecular N—H...O hydrogen bond can occur in the tautomer **A**, whereas the presence of intramolecular hydrogen bonds in the tautomer **B** is unlikely. To study the character of interactions in detail, we carried out the topological analysis of the electron density distribution $\rho(r)$ for the tautomers **A** and **B**. According to the results of the analysis, the degree of aromaticity in the cyclic system of the tautomer **B** is, on the whole, lower. This can be illustrated, for example, with the use of the absolute value of the negative eigenvector of the Hessian ($|\lambda_1|$) at the critical points (3, +1) of the rings as the quantitative criterion. This value characterizes the curvature $\rho(r)$ in the direction perpendicular to the plane of the ring and, consequently, reflects the degree of π-density delocalization.[11]

Actually, the $|\lambda_1|$ values for the tautomer **B** are 0.3277 and 0.4338 e Å^{-5} in the quinonoid and central rings, respectively, whereas the $|\lambda_1|$ values for both the hydroxy-substituted and central rings in the tautomer **A** are somewhat larger (0.34463 and 0.4579 e Å^{-5}, respectively), and a slight decrease in $|\lambda_1|$ (0.328 e Å^{-5}) is observed only for the quinonoid ring. In addition, there is the intramolecular H(1O2)...N(1) hydrogen bond in the tautomer **A**. The energy of this bond estimated based on Espinosa´s correlation scheme[12] is 7.25 kcal mol^{-1}. The topological analysis of $\rho(r)$ also showed that all the above-mentioned intramolecular C—H...O and H...H contacts do correspond to bonding interactions, their number and strength in both tautomers being virtually identical (Fig. 3). Thus the energy of the C—H...O interactions evaluated according to the same correlation scheme for the hydroxy and C=O groups is 2.9—3.0 kcal mol^{-1}, and this energy for the endocyclic oxygen atom is 2 kcal mol^{-1}. The energy of the H...H interactions is substantially lower (0.76 kcal mol^{-1}). As can be seen from the molecular graphs of the tautomers **A** and **B**, there are not only the above-mentioned H...H

Table 1. Selected bond lengths (d) and bond angles (ω) in the crystal of compound **12** and in the isolated tautomers **A** and **B** calculated at the B3LYP/6-31G* level of theory

Parameter	**12**	**12A**	**12B***
Bond		d/Å	
O(1)—C(12)	1.386(2)	1.380	1.396
O(1)—C(1)	1.388(2)	1.386	—
O(2)—C(5)	1.336(2)	1.335	—
O(3)—C(8)	1.255(2)	1.246	1.246
N(1)—C(6)	1.364(2)	1.355	1.355
N(1)—C(7)	1.303(2)	1.305	—
C(1)—C(2)	1.389(2)	1.398	—
C(1)—C(6)	1.412(2)	1.413	—
C(2)—C(3)	1.408(2)	1.413	—
C(3)—C(4)	1.395(2)	1.399	—
C(4)—C(5)	1.397(2)	1.399	—
C(5)—C(6)	1.427(2)	1.429	—
C(7)—C(12)	1.444(2)	1.449	1.422
C(7)—C(8)	1.488(3)	1.498	1.474
C(8)—C(9)	1.444(3)	1.453	1.457
C(9)—C(10)	1.365(2)	1.373	1.373
C(10)—C(11)	1.439(2)	1.447	1.449
C(11)—C(12)	1.365(2)	1.376	1.380
Angle		ω/deg	
C(12)—O(1)—C(1)	120.6(2)	121.5	121.1
C(7)—N(1)—C(6)	118.8(2)	120.4	125.0
O(1)—C(1)—C(2)	120.8(2)	121.5	—
O(1)—C(1)—C(6)	117.9(2)	117.5	—
C(2)—C(1)—C(6)	121.3(2)	121.0	—
C(1)—C(2)—C(3)	114.8(2)	114.6	—
C(4)—C(3)—C(2)	127.3(2)	127.6	—
C(3)—C(4)—C(5)	116.1(2)	116.3	—
O(2)—C(5)—C(4)	120.2(2)	120.6	—

Parameter	**12**	**12A**	**12B***
Angle		ω/deg	
O(2)—C(5)—C(6)	120.2(2)	120.6	—
C(4)—C(5)—C(6)	119.6(2)	118.8	—
N(1)—C(6)—C(1)	122.4(2)	121.6	—
N(1)—C(6)—C(5)	116.8(2)	116.8	—
C(1)—C(6)—C(5)	120.9(2)	121.6	—
N(1)—C(7)—C(12)	123.3(2)	124.7	118.7
N(1)—C(7)—C(8)	115.7(2)	114.6	115.9
C(12)—C(7)—C(8)	121.0(2)	120.7	125.3
O(3)—C(8)—C(9)	123.7(2)	124.6	127.3
O(3)—C(8)—C(7)	119.5(2)	119.5	118.1
C(9)—C(8)—C(7)	116.7(2)	116.0	114.6
C(10)—C(9)—C(8)	116.8(2)	117.1	117.0
C(9)—C(10)—C(11	128.6(2)	128.8	128.5
C(12)—C(11)—C(10)	115.5(2)	115.5	115.6
C(11)—C(12)—O(1	121.8(2)	122.3	122.9
C(11)—C(12)—C(7)	121.2(2)	120.9	118.9
O(1)—C(12)—C(7)	117.0(2)	116.8	118.2
C(15)—C(13)—C(14)	111.3(2)	110.7	—
C(15)—C(13)—C(16)	107.2(2)	107.1	—
C(14)—C(13)—C(16)	106.5(2)	106.8	—
C(20)—C(17)—C(18)	110.1(2)	109.9	—
C(20)—C(17)—C(19)	107.4(2)	107.5	—
C(18)—C(17)—C(19)	107.9(2)	107.6	—
C(23)—C(21)—C(22)	110.1(2)	109.5	109.4
C(23)—C(21)—C(24)	107.6(2)	107.8	108.1
C(22)—C(21)—C(24)	107.9(2)	107.9	108.2
C(26)—C(25)—C(27)	110.7(2)	110.7	110.5
C(26)—C(25)—C(28)	107.0(2)	106.6	106.8
C(27)—C(25)—C(28)	107.4(2)	107.0	107.2

* The atomic numbering scheme for the tautomers **A** and **B** is identical to that given in Fig. 2. For the tautomer **B**, only the independent parameters are given (the molecule has the symmetry C_2).

and C—H...O contacts in the structure, but also unusual C—H...C interactions between the hydrogen atoms of the aromatic system and the aliphatic carbon atoms of the *tert*-butyl groups. These contacts are characterized by a relatively high energy (3—3.4 kcal mol^{-1}) compared to the H...H interactions. However, unlike the above-mentioned contacts, these contacts are not stable because the distance between the critical points (CP) (3, −1) and (3, +1) is relatively small and, consequently, even a slight change in the distance between the interacting atoms will lead to the disappearance of the bond path. It should be noted that the presence of H...H bonding interactions is manifested not only in the topological parameters but also in the geometric parameters of the C—H bonds. Thus the distances for the pair of the interacting hydrogen atoms are 0.006—0.008 Å shorter than the corresponding distances with noninteracting atoms.

The results of the calculations for the complex of compound **12** with an ethanol molecule are in good agreement with the experimental parameters of the hydrogen bonds. Thus, the O(1S)...O(3) distance (2.655 Å) is slightly shorter, whereas the O(2)...O(1) distance (2.799 Å) is, on the contrary, elongated. The topological analysis of ρ(r) of the solvate showed that the ethanol molecule forms, in addition to the expected O—H...O bonds, the shortened N(1)...O(1S) contact at which the CP (3, −1) is also located. It should be noted that the intramolecular hydrogen bond that is observed in the isolated tautomer **A** is absent in the associate. Taking into account that the N(1)...O(1S) distance in the associate is somewhat longer (2.919 Å) compared to that in the crystal, it can be concluded that this distance is retained in the crystal. The estimation of the interaction energy according to the above-mentioned scheme gave the energies of 9.09 and 13.45 kcal mol^{-1} for the O—H...O bonds with the C=O and COH groups, respectively, and the energy of 3.13 kcal mol^{-1} for the O...N interactions. The validity of the estimation of the energy of the hydrogen bonds in the

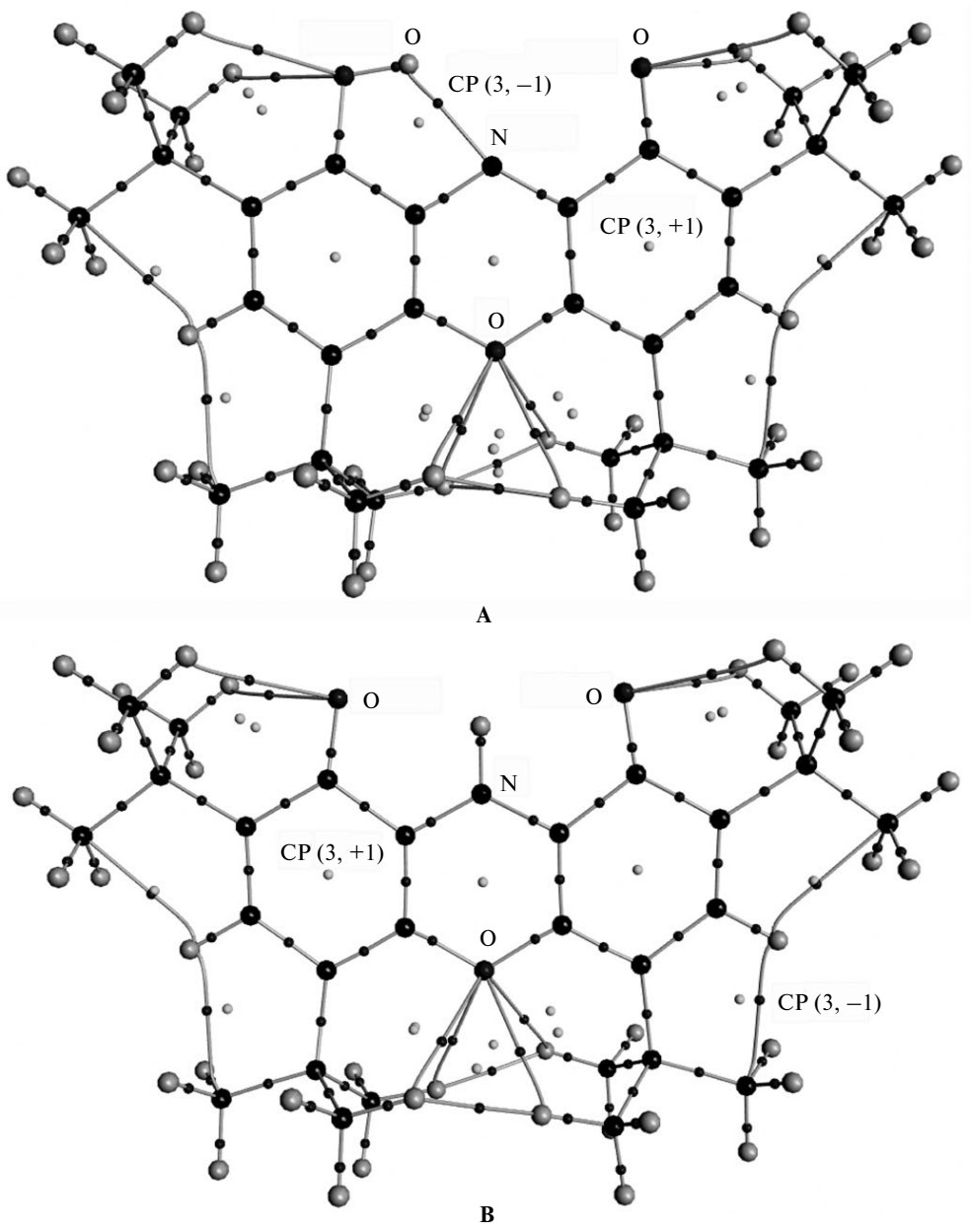


Fig. 3. Molecular graphs of the tautomers **A** and **B** (compound **12**) calculated at the B3LYP/6-31G* level of theory.

associate is additionally confirmed by the comparison of the total energy of the interaction between the methanol molecule and compound **12** (25.67 kcal mol^{-1}) with the difference between the energy of the associate and the sum of the energies of the noninteracting tautomer **A** and the ethanol molecule (17.83 kcal mol^{-1}). Actually, the formation of the associate is accompanied by the disappearance of the intramolecular N—H...O bond and, consequently, the energy of the complex is 18.4 kcal mol^{-1}, which is in good agreement with the above-mentioned value.

Taking into account the high energy of the O—H...O interactions with the ethanol molecule, it can be suggested that this is favorable for the proton transfer from the hydroxy group to the carbonyl group, thus lowering the barrier to tautomeric transformations.

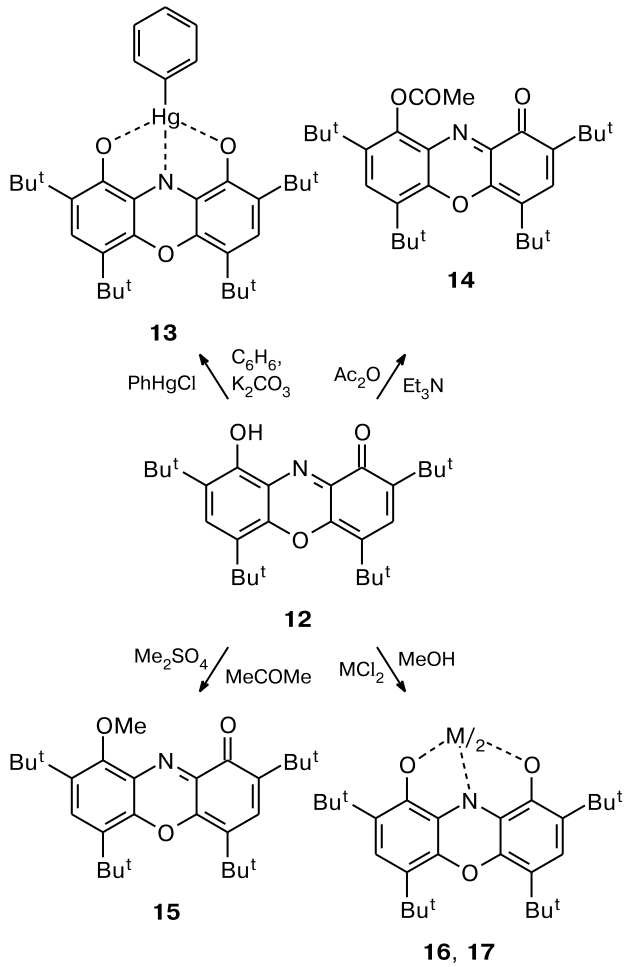
Product **12** is, on the one hand, a close structural analog of 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one **1** (see Ref. 10) and, on the other hand, a tricyclic analog of the well-known tridentate free-radical ligand, which is formed by the oxidation of metastable bis[3,5-di(*tert*-butyl)-2-hydroxydiphenyl]amine.[4]

The ^{1}H NMR spectra of compound **12** in solvents of different polarity ($CDCl_3$, DMSO-d_6, and toluene-d_8) show signals for the *tert*-butyl groups and the hydrogen

atoms at the carbocycles pairwise averaged due to the three-center prototropy $O^1 \leftrightarrows N \leftrightarrows O^2$ (δ 7.45 (2 H), 1.44 (18 H), 1.39 (18 H), $CDCl_3$). A decrease in the temperature to 207 K does not lead to a change in the spectral pattern, which indicates that this tautomeric process is fast on the ^{1}H NMR time scale.

Since 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one (**12**) is the first representative of the three-center tautomeric system ($O^1 \leftrightarrows N \leftrightarrows O^2$) (Scheme 4) in the series of sterically hindered phenoxazinones, we investigated the dependence of the character of the tautomeric process on the nature of the substituent at position 9 of the phenoxazine ring.

Scheme 4



Due to the high lability of the hydrogen atom of the hydroxy group in compound **12** associated with the three-center prototropic tautomerism ($O^1 \leftrightarrows N \leftrightarrows O^2$), it can be replaced by substituents with different chemical properties (HgPh, COMe, or Me) (see Scheme 4).

The reaction of 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one (**12**) with phenylmercury chloride in benzene affords the phenylmercury derivative of phenoxazine **13**. The ^{1}H NMR spectrum of the latter compound ($CDCl_3$, toluene-d_8) shows pairwise-averaged signals of the *tert*-butyl groups (δ 1.47 (18 H), 1.38 (18 H), $CDCl_3$) and the aromatic protons of the phenoxazine ring (δ 7.45 (2 H), $CDCl_3$), which is indicative of the $O^1 \leftrightarrows N \leftrightarrows O^2$ migration of the phenylmercury moiety in compound **13** fast on the NMR time scale.

The substantially different spectral patterns are observed for compounds **14** and **15**. The NMR spectra of these compounds are indicative of the absence of the tautomeric process. The acylation of phenoxazin-1-one **12** with acetic anhydride affords 9-acetoxy-2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one (**14**) in high yield. *O*-Methyl derivative **15** of phenoxazinone **12** was synthesized by the reaction of compound **12** with a threefold excess of dimethyl sulfate in acetone in the presence of anhydrous potassium carbonate.

As opposed to 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one (**1**),[9,13] the reaction of phenoxazin-1-one **12** with a powder of zinc metal in benzene gives diamagnetic coordination compound **16** instead of the expected Zn^{II} *o*-iminobenzosemiquinone complex. The symmetrical ^{1}H NMR spectral pattern (δ 7.41 (2 H), 1.45 (18 H), 1.24 (18 H), $CDCl_3$) of compound **16** corresponds to the tridentate ligand stabilized due to the metal chelation. The structurally identical six-coordinate Zn^{II} complex **16** was obtained by the reaction of compound **12** with Zn^{II} acetate in methanol.

The reaction of 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one **12** with $CuCl_2$ in methanol gave complex **17**, which was studied by ESR spectroscopy. We investigated powders and toluene solutions of compound **17** at room temperature and in low-temperature glasses (60% of toluene and 40% of chloroform) at liquid nitrogen temperature.

The most informative spectra in low-temperature glasses have a set of lines characteristic of the chelate unit, in which the nearest environment of the central atom has a nearly axial symmetry. In the $g_\parallel$ region, there are hyperfine lines assigned to the interaction between the unpaired electron spin and the spin of the $^{63.65}$Cu nucleus with the g factor $g_\parallel = 2.0035$ and the hyperfine coupling constant $A_\parallel = 145 \cdot 10^{-4}$ cm^{-1}. The intense line in the $g_\perp$ region is split into two components, which is attributed to a small deviation of the structure of the chelate unit in compound **17** from the axial symmetry ($g_2 = 2.224$, $g_3 = 2.260$). The $g_\parallel$ value is similar to the g factor of the free electron ($g_0 = 2.0023$) and the g_2 and g_3 values are larger than $g_\parallel$. These facts provide evidence that the orbital of the unpaired electron in compound **17** is close to the $3d_z^2$ orbital. This is characteristic of six-coordinate chelate units, in which the nearest environment of the copper atom can be described as a flattened octahedron. The coefficients k_1^2 and k_0

were evaluated from the spectral parameters according to the equations

$$A_{\parallel} = k_1^2 P_0(-k_0 + 4/7) + P_0(g_{\parallel} - g_0) - 1/7 P_0(g_{\perp} - g_0),$$

$$A_{\perp} = k_1^2 P_0(-k_0 - 2/7) + 15/14[P_0(g_{\perp} - g_0),$$

suitable for the $3d_{z^2}$ ground state.[14] In these equations, the coefficient k_1^2 characterizes the degree of delocalization of the unpaired electron orbital, the coefficient k_0 determines the isotropic component of the hyperfine coupling, $P_0 = 360 \cdot 10^{-4}$ cm^{-1}, and $g_{\perp} = 1/2(g_2 + g_3)$. It was assumed that $A_{\perp} = 0$ because of the absence of the hyperfine splitting of the spectral lines in the g region. The evaluated $k_1 = 0.81$ is indicative of the 80% localization of the unpaired electron on the Cu^{II} atom. The lower $k_0 = 0.033$ compared to $k_0 = 0.43$ for the planar complexes with the $3d_{x^2y^2}$ ground state can be attributed to an admixture of the 4s state in the $3d_{z^2}$ ground state.[15]

The spectra of powders of compound **17** are similar to those measured in low-temperature glasses. The $g_{\parallel}$ region shows the hyperfine coupling with $g_{\parallel} = 2.012$, $A_{\parallel} = 139 \cdot 10^{-4}$ cm^{-1}; the $g_{\perp}$ region has a broad line with $g_{\perp} = 2.23$. The hyperfine coupling observed in powders is apparently associated with the large size of the molecules of complex **17**, resulting in an increase in the distances and, consequently, in a weakening of the dipole-dipole interaction between the spins of Cu^{II} of the adjacent molecules in the crystal lattice, which hinders the observation of the hyperfine coupling. In toluene solutions, the hyperfine coupling is not observed. The spectrum consists of a single asymmetric line with $g = 2.19$. Apparently. the rate of the random rotation of the bulky molecules in toluene solutions is insufficient to average the anisotropic spectrum, which is observed in the spectra of free radicals or copper complexes with small ligands characterized by isotropic spectra with the average parameters $g_{aver} = 1/3g_{\parallel} + g_{\perp}$, $A_{aver} = 1/3A_{\parallel} + 2/3A_{\perp}$.

To conclude, we found the route to the synthesis of the first representative of the three-center tautomeric systems in the series of sterically hindered phenoxazines, which are widely used as ligands in studies of intramolecular redox reactions in metal complexes. A comparison of the chemical behavior of 2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one (**1**) and 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one (**12**) in the complex formation with metal salts leads to the conclusion that the presence of the hydroxy group in position 9 of the sterically hindered phenoxazine ring results in a change in the coordination mode from bidentate (iminobenzosemiquinolate) for compound **1** to tridentate (diamagnetic) for compound **12**.

Experimental

The UV-Vis spectra were measured on an APEL PD-303 UV spectrometer in polar (ethanol) and nonpolar (hexane) solvents. The ^{1}H NMR spectra were recorded in $CDCl_3$, toluene-d_8, and DMSO-d_6 on a Varian Unity-300 instrument (300 MHz) with the accuracy of 0.1 ppm; the signals of the residual protons of these solvents were used as the internal standard. The ESR spectra were measured on a Bruker EMX 10/12 spectrometer. The IR spectra were recorded on a Specord-75IR spectrometer in Nujol mulls. Column chromatography was performed on alumina (Reakhim). The course of the reactions was monitored and the purity of the reaction products was checked by TLC on plates coated with alumina (Brockman activity IV).

4,6-Di(*tert*-butyl)pyrogallol (10). Concentrated H_2SO_4 (5 mL) was added with stirring to a solution of pyrogallol (12 g, 0.093 mol) in *tert*-butyl alcohol (35 mL, 0.367 mol) at 50 °C. The reaction mixture was stirred for 0.5 h. Then the organic layer was separated and washed with hot water (3×15 mL). The solidified substance was recrystallized from hexane and dried under reduced pressure. White crystals of compound **10**, which turned pink in air, were obtained in a yield of 12.28 g (55%), m.p. 110 °C. ^{1}H NMR ($CDCl_3$), δ: 6.72 (s, 1 H, arom.); 5.12 (br.s, 3 H, OH); 1.3 (s, 18 H, Bu^t). Found (%): C, 90.31; H, 9.30. $C_{14}H_{22}O_3$. Calculated (%): C, 90.72; H, 9.24.

2,6-Dihydroxy-3,5-di(*tert*-butyl)aniline (11). Compound **10** (10 g, 0.042 mol) was stirred with aqueous ammonia (300 mL) for 3 h. The precipitate that formed was filtered off, washed with hexane, and dried under reduced pressure. White crystals of compound **11**, which rapidly turned dark in air, were obtained, m.p. 147 °C. The yield was 9.66 g (97%). ^{1}H NMR ($CDCl_3$), δ: 6.95 (s, 1 H, arom.); 1.4 (s, 18 H, Bu^t). Found (%): C, 90.50; H, 9.62; N, 5.99. $C_{14}H_{23}NO_2$. Calculated (%): C, 91.10; H, 9.71; N, 5.91.

2,4,6,8-Tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one (12). A catalytic amount of TsOH was added to a solution of 3,5-di(*tert*-butyl)pyrocatechol (**5**) (6.3 g, 0.028 mol) and compound **11** (8 g, 0.034 mol) in benzene (200 mL). The reaction mixture was refluxed with a Dean—Stark trap for 7 h until 0.5 mL of water was distilled off. Then the mixture was concentrated to dryness and chromatographed on alumina using chloroform as the eluent, and the violet fraction with $R_f = 0.35$ was collected. The solvent was evaporated and the product was washed with methanol. Violet crystals of compound **12** were obtained, m.p. 190 °C. The yield was 4.66 g (38%). ^{1}H NMR ($CDCl_3$), δ: 7.45 (s, 2 H, arom.); 1.44 (s, 18 H, Bu^t); 1,39 (s, 18 H, Bu^t). IR, ν/cm^{-1}: 3430 (OH), 1640 (C=O), 1630 (C=N). Found (%): C, 76.78; H, 8.90; N, 3.25. $C_{28}H_{39}NO_3$. Calculated (%): C, 76.89; H, 8.92; N, 3.20.

2,4,6,8-Tetra(*tert*-butyl)-9-phenylmercuroxyphenoxazin-1-one (13). Phenylmercury chloride (0.22 g, 0.6 mmol) and an excess of K_2CO_3 were added to a solution of phenoxazin-1-one **12** (0.2 g, 0.4 mmol) in benzene (15 mL). The reaction mixture was refluxed for 10 h and then chromatographed on alumina using benzene as the eluent. The solvent was evaporated. Dark-green crystals of compound **13** were obtained, m.p. 130 °C. The yield was 0.23 g (82%). ^{1}H NMR ($CDCl_3$), δ: 7.64—7.36 (m, 7 H, arom.); 1.47 (s, 18 H, Bu^t); 1.38 (s, 18 H, Bu^t). Found (%): C, 57.09; H, 5.97; N, 1,99. $C_{34}H_{43}NO_3Hg$. Calculated (%): C, 57.22; H, 6.03; N, 1.96.

9-Acetoxy-2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one (14). Triethylamine (2 mL) was added to a solution of compound **12** (1 g, 0.002 mol) in acetic anhydride (20 mL). The reaction mixture was kept for 1 h. Then water (20 mL) was added, and the reaction mixture was kept for 12 h. The blue precipitate that

formed was filtered off and washed with water. Blue needle-like crystals of compound **14** were obtained, m.p. (decomp.) 151 °C. The yield was 1.07 g (97%). ^{1}H NMR ($CDCl_3$), δ: 7.57 (s, 1 H, arom.); 7.38 (s, 1 H, arom.); 2.58 (s, 3 H, Ac); 1.49 (s, 9 H, Bu^t); 1.44 (s, 9 H, Bu^t); 1.39 (s, 9 H, Bu^t); 1.30 (s, 9 H, Bu^t). IR, ν/cm^{-1}: 1780 (w ether), 1640 (C=O), 1620 (C=N). Found (%): C, 72.69; H, 8.19; N, 2.85. $C_{30}H_{41}NO_4$. Calculated (%): C, 72.73; H, 8.28; N, 2.83.

2,4,6,8-Tetra(*tert*-butyl)-9-methoxyphenoxazin-1-one (15). Dimethyl sulfate (0.75 mL, 0.006 mol) and an excess of dry K_2CO_3 were added to a solution of compound **12** (1 g, 0.002 mol) in acetone (20 mL). The reaction mixture was refluxed for 3 h. Then the solvent was evaporated and the residue was dried at room temperature. The mixture was chromatographed on alumina using benzene as the eluent, and the fraction with $R_f = 0.55$ was collected. The solvent was evaporated. Black crystals of compound **15** were obtained, m.p. 178 °C. The yield was 0.72 g (80%). ^{1}H NMR ($CDCl_3$), δ: 7.44 (s, 1 H, arom.); 7.40 (s, 1 H, arom.); 4.22 (s, 3 H, OMe); 1.49 (s, 9 H, Bu^t); 1.47 (s, 9 H, Bu^t); 1.40 (s, 9 H, Bu^t); 1.33 (s, 9 H, Bu^t). IR, ν/cm^{-1}: 1640 (C=O), 1620 (C=N). Found (%): C, 82.35; H, 8.97; N, 3.11. $C_{29}H_{41}NO_3$. Calculated (%): C, 82.48; H, 9.09; N, 3.10.

Zinc complex of 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one (16). Zinc chloride (54.4 mg, 0.4 mmol) was added with heating to a solution of phenoxazin-1-one **12** (0.4 g, 0.8 mmol) in methanol. The reaction mixture was kept for 12 h. Then the solvent was evaporated. The reaction product was twice washed with methanol. Blue-green crystals of compound **16** were obtained, m.p. 295 °C. The yield was 0.28 g (77%). ^{1}H NMR ($CDCl_3$), δ: 7.41 (s, 2 H, arom.); 1.45 (s, 18 H, Bu^t); 1.24 (s, 18 H, Bu^t). Found (%): C, 71.63; H, 8.05; N, 3.07. $C_{56}H_{76}N_2O_6Zn$. Calculated (%): C, 71.72; H, 8.11; N, 2.99.

Copper complex of 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one (17). Copper(II) chloride (53.8 mg, 0.4 mmol) was added with heating to a solution of phenoxazin-1-one **12** (0.4 g, 0.8 mmol) in methanol. The reaction mixture was kept for 12 h. Then the solvent was evaporated. The reaction product was twice washed with methanol. Dark-green crystals of compound **17** were obtained, m.p. 290 °C. The yield was 0.26 g (72%). $C_{56}H_{76}N_2O_6Cu$. Found (%): C, 74.25; H, 8.40; N, 3.17. Calculated (%): C, 74.66; H, 8.44; N, 3.11.

Crystals of compound **12** were grown by recrystallization from ethanol. At 100 K, the crystals of ($C_{30}H_{45}NO_4$) **12** are monoclinic, space group $P2_1/n$, a = 13.8821(19) Å, b = = 9.1178(13) Å, c = 22.450(3) Å, β = 96.869(3)°, V = 2821.2(7) Å^3, Z = 4, d_{calc} = 1.139 g cm^{-3}, μ(MoKα) = 0.74 cm^{-1}, $F(000)$ = = 1056. The intensities of 23237 reflections were measured at 110 K on a Smart APEX II CCD diffractometer (λ(MoKα) = = 0.71072 Å, ω-scanning technique, 2θ < 60°), and 8081 independent reflections were used in the structure refinement. The data were processed and merged with the use of the SAINT Plus and SADABS program packages.[16]

The structure was solved by direct methods with the use of successive electron density maps. All hydrogen atoms were located in difference electron desnisty maps. The structure was refined based on F^2_{hkl} with anisotropic displacement parameters for nonhydrogen atoms and isotropic displacement parameters (using a riding model) for hydrogen atoms.

The final R factors for compound **12** were as follows: R_1 = = 0.0618 (calculated based on F_{hkl} for 3350 reflections with $I > 2\sigma(I)$), wR_2 = 0.1883, 329 refined parameters, GOOF 0.993. The calculations were carried out with the use of the SHELXTL 5.10 program package.[17]

Quantum chemical calculations were performed by the density functional theory with the use of the B3LYP hybrid functional and the 6-311G(d,p) basis set using the Gaussian 03W program.[18] The topological analysis of the theoretical electron density distribution was performed with the MORPHY98 program.[19]

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