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Binuclear and polynuclear transition metal complexes with macrocyclic ligands

2.* New macrocyclic Schiff's base in the reaction of 4-*tert*-butyl-2,6-diformylphenol with 1,2-diaminobenzene. Synthesis and structural, spectroscopic, and theoretical study

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Condensation of 4-*tert*-butyl-2,6-diformylphenol with 1,2-diaminobenzene in ethanol is accompanied by partial reduction of the azomethine double bonds to form symmetrical macrocyclic Schiff's base containing the alternating >C=N and >CH—NH fragments. In solution, this compound exists as the only isomer in which two endocyclic hydrogen atoms are bound to the oxygen atoms of the phenol groups and two other endocyclic H atoms are attached to the nitrogen atoms of the CH_2—NH fragments. All endocyclic protons are involved in hydrogen bonding and undergo rapid exchange with each other at room temperature. In the crystal, the planar macrocyclic molecules are arranged in closely packed stacks. The steric hindrances resulting from overlapping of the bulky *tert*-butyl groups are eliminated through rotation of the molecules with respect to each other in the adjacent layers. Study of the potential energy surface for the Schiff's base under consideration by the DFT method demonstrated that the structure corresponding to the global minimum is similar to that found in solution. However, the isolated molecule is nonplanar, its macrocycle adopting a ladder conformation. The local minimum on the potential energy surface whose energy is 2.6 kcal mol^{-1} higher than that of the global minimum corresponds to the zwitterionic structure in which all four endocyclic hydrogen atoms are attached to the nitrogen atoms and the macrocycle adopts a tub conformation. Flattening of the ring is considered as a consequence of stacking interactions between the molecules in the crystal.

Key words: macrocyclic ligands, Schiff's bases, X-ray diffraction analysis, NMR spectroscopy, quantum chemistry, density functional method.

Considerable recent attention has been given to homo- and heteronuclear transition metal complexes, which contain two or several metal ions in the cavity of one macrocyclic ligand in the immediate proximity to each other. Complexes of this type are of interest as models of active sites of metal-containing proteins and also as molecular magnetics and potential components of homogeneous catalytic systems.[2—5] Expanded porphyrins[6] and macrocyclic Schiff's bases of type **1**, which can be prepared by the reactions of α,α´-dicarbonyl derivatives of pyrroles, pyridines, α,α´-dipyrroles, and phenols with aromatic and aliphatic diamines, are particularly promising as macroligands for these complexes. In complexes with such ligands, their π-electron systems (π_1 and π_2) serve as an electron reservoir with respect to transition metal ions, which is of great importance for the manifestation of catalytic activity. The type of the donor centers $\mathbf{d_1}$ and $\mathbf{d_2}$ and the character of the bridging groups $\mathbf{l_1}$ and $\mathbf{l_2}$, which link the π systems, can be varied, thus changing both the distances between the metal centers and the degree of conjugation between the π systems. Homo- and heterobinuclear transition metal complexes with macrocyclic ligands based on 4-substituted 2,6-diformylphenols have been studied in sufficient detail.[7] These complexes are generally syn-

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[*] For Part 1, see Ref. 1.

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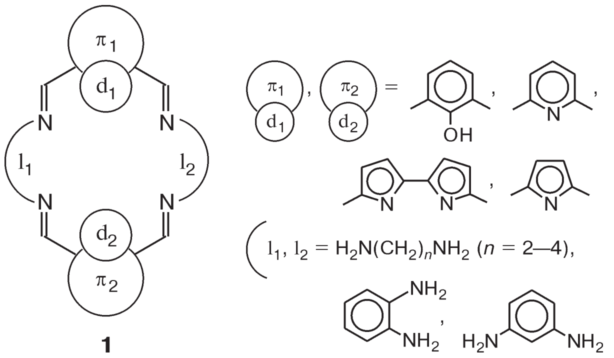
thesized by the template method based on the reactions of diamines with dicarbonyl derivatives of phenol in the presence of metal ions.



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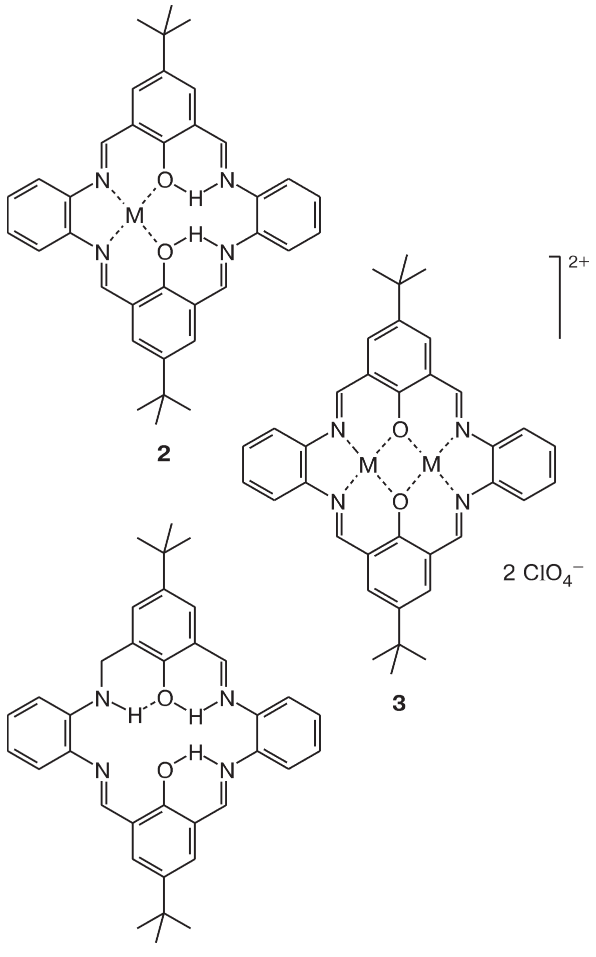
The reactions of 4-alkyl-2,6-diformylphenols with 1,2-diaminobenzene and its derivatives containing substituents in the aromatic ring exemplify this method.



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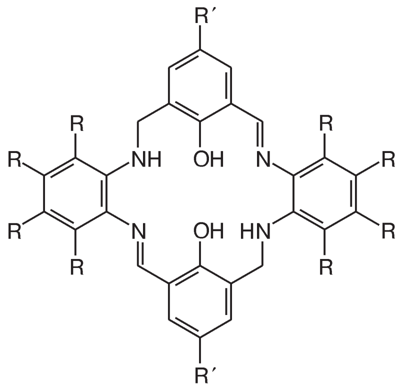
3

4

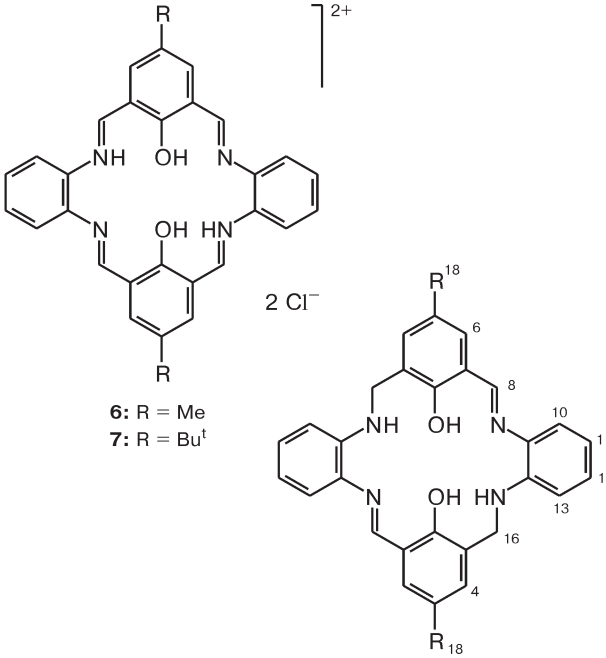
At 50 °C, the reactions with 4-*tert*-butyl-2,6-diformylphenol in the presence of Mn^{II}, Co^{II}, Fe^{II}, or Ni^{II} salts in methanol afforded mononuclear complexes **2** in yields from 37% to 80%.[8] In addition, binuclear complexes **3** and free macrocyclic ligand **4** in which one of the double C=N bonds was reduced were obtained in low yields as by-products. However, the reaction with 1,2-diamino-3,4,5,6-tetrafluorobenzene performed under the same conditions in the presence of Mn^{II}, Co^{II}, or Ni^{II} salts gave rise to free symmetrical macrocycle **5** (R′ = Bu^t) in which two double C=N bonds were reduced. The latter compound has been characterized by X-ray diffraction analysis. The reactions of 4-*tert*-butyl-2,6-diformylphenol and 2,6-diformyl-4-methylphenol with 1,2-diaminobenzene and 1,2-diamino-4,5-dimethylbenzene were studied in detail.[9] In the absence of a templating agent at room temperature, the reaction in ethanol or in ethanol—diethyl ether mixtures produced only a complex mixture of oligomeric condensation products irrespective of the ratio and concentrations of the starting reagents.



5: R = F, R′ = Bu^t

The reactions with the use of the reactants taken in a ratio of 1 : 1 in the presence of two moles of concentrated HCl or with the use of diamine dichlorohydrate as the amine component afforded completely conjugated macrocyclic Schiff's bases **6** and **7** as their dihydrochlorides in ~70% yields. The structures of perchlorates **6** and **7** were studied by X-ray diffraction analysis. The reaction of 2,6-diformyl-4-methylphenol with 1,2-diaminobenzene in the presence of catalytic amounts of HCl gave rise to partially hydrogenated macrocycle **8** (R = Me) in ~70% yield. The authors[9] believed that 1,2-diaminobenzene was a reducing agent in this reaction. Compound **8** was first synthesized[10] by the reaction of 2,6-diformyl-4-methylphenol with 1,2-diaminobenzene on refluxing in methanol in the absence of HC1. The structure of compound **8** has been established[10] by X-ray diffraction analysis, but its yield was not reported.[10]

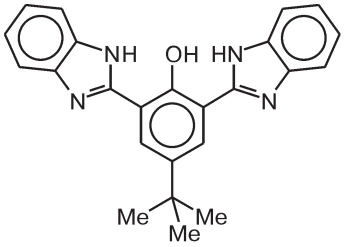
As part of our continuing studies of binuclear and polynuclear transition metal complexes with macrocyclic Schiff's bases, we examined the reaction of 4-*tert*-butyl-2,6-diformylphenol with 1,2-diaminobenzene in boiling anhydrous ethanol in the absence of a templating agent, the reagents being taken in a ratio of 1 : 1 at low concen-



6: R = Me
7: R = Bu^t

8: R = Me
9: R = Bu^t

trations. In this case, we obtained a new macrocyclic Schiff's base (**9**, R = Bu^t) in 44% yield. In addition, the reaction afforded bis-benzimidazole derivative **10** in 32% yield. The use of the reagents in other ratios, including an excess of 1,2-diaminobenzene, variations in the nature of the solvent, and additives of reducing agents, such as hydroquinone, had no substantial effect on the ratio of the reaction products, which always remained close to 1 : 1. This fact suggests that redox disproportionation of Schiff's base **11**, which was generated in the first step of the reaction, to form compounds **12** and **13** proceeded more rapidly than condensation of **11** with the second diamine molecule. Most likely, symmetrical macrocycle **9** is generated through condensation of two molecules **13**.



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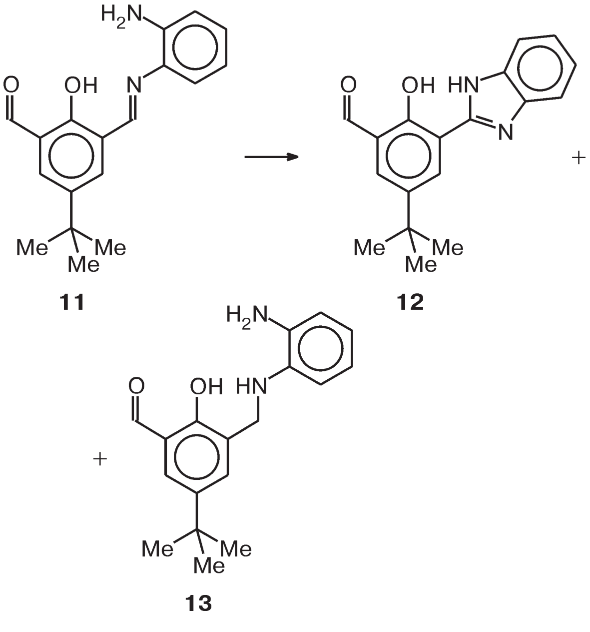


11 **12** **13**

The structure of macrocycle **9** in solution was established by ^{1}H and ^{13}C NMR spectroscopy and 2D heteronuclear correlation experiments. The unambiguous assignment of the resonance signals was made based on the results of a series of the NOE experiments.[11,12] The spectroscopic parameters and the results of the NOE experiments are given in Table 1.

Analysis of the NOE data revealed the following chains of the spatially close protons (see the atomic numbering schemes in the formulas of compound **8** and **9**):

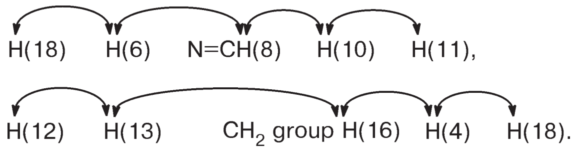


Table 1. Parameters of the ^{1}H NMR spectra for compound **9** and the results of the NOE experiments[a]

Atom	$\delta_{^1H}$ ($J_{H,H}$/Hz)	NOE data	
		Irradiated nucleus	NOE (%) (observed proton)[b]
2 (OH)	13.56 s	H(2)	−8.0 (H(15))[c]
4	7.43 d (2.35)		
6	7.35 d (2.35)	H(6)	13.8 (H(8)); 9.2 (H(18))
8	8.63 s	H(8)	18.0 (H(6)); 14.3 (H(10))
10	7.07 d[d]	H(10)	12.8 (H(8)); 11.8 (H(11)); −1.6 (H(6))[e]
11	6.79 t[d]		
12	7.25 t[d]		
13	6.96 d[d]	H(13)	7.3 (H(16)); 11.0 (H(12))
15 (NH)	6.33 t (5.49)	H(15)	6.3 (H(16)); −11.2 (H(2))
16 (CH_2)	4.47 d (5.49)	H(16)	10.0 (H(4)); 9.9 (H(13)); 2.1 (H(15))
18	1.34 s	H(18)	~1.9 (H(4)); ~2.1 (H(6))

[a] The numbering scheme of the hydrogen atoms is given in the text.

[b] NOE (%) was calculated with respect to the irradiated signal (−100%).

[c] NOE caused by exchange.

[d] For the H(10), H(11), H(12), and H(13) protons, ^3J = 7.5—7.7 Hz.

[e] Secondary NOE.

At room temperature, the ^{1}H NMR spectrum has two separated signals with equal intensities for the NH and OH protons at δ 6.33 and 13.56, respectively. This is unambiguous evidence for the fact that in solution of compound **9**, two of four endocyclic protons are bound to the O atoms and the other two protons are attached to the N atoms. Irradiation of the the NH proton led not only to NOE on the protons of the CH_2 group but also to a large negative effect for the OH proton (−11.2%). In the independent experiment, saturation of the signal of the OH group was also accompanied by negative NOE on the NH proton. These results indicate that rather rapid exchange occurs between the NH and OH protons in solution at room temperature. The rate constant of the exchange, which was estimated from additional exchange broadening of the signal for the OH protons at 303 K, was ~1 s^{-1}. The occurrence of such rapid exchange between the NH and OH protons in solution is, undoubtedly, accompanied by the formation of a series of tautomeric forms.

The results of X-ray diffraction analysis of compound **9** allow the comparison of the structure of molecule **9** in the crystalline state (Fig. 1) with its structure in solution. The crystallographic and geometric parameters of compound **9** are given in Tables 2 and 3, respectively.

Table 2. Crystallographic parameters of compounds **9** and **10**

Compound	**9**	**10**
Molecular formula	$C_{36}H_{40}N_4O_2$	$C_{26}H_{28}N_4O_2$
Space group	*Pbam*	*P*2(1)/*n*
a/Å	28.582(6)	8.952(3)
b/Å	15.326(3)	17.229(6)
c/Å	6.900(2)	15.131(6)
V/Å^3	3022.5(12)	2291.1(15)
Z	4*	4
ρ_{calc}/g cm^{-3}	1.232	1.242
μ/cm^{-1}	0.077	0.080
Radiation	Mo-Kα (λ = 0.71073 Å)	
2θ Scan range/deg	3—48	3.6—60.0
Number of independent reflections	1726	7393
Number of reflections with $I > 4\sigma$	974	4682
R_1	0.081	0.069
wR_2	0.189	0.161

* Two independent molecules occupy the crystallographic inversion centers on the *m* plane.

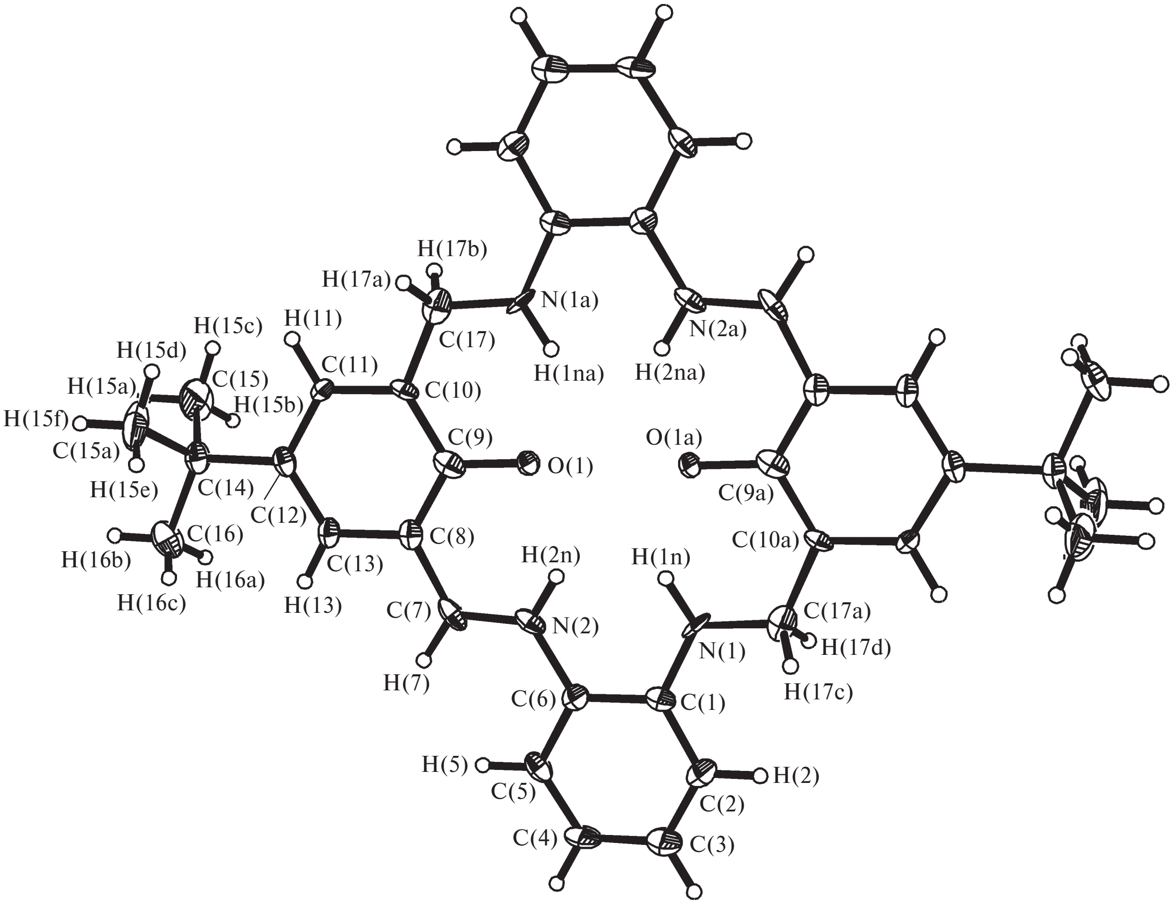


Fig. 1. Structure of one of independent molecules **9** in the crystal.

Table 3. Principal geometric parameters of compound **9***

Parameter	Molecule A	Molecule B
Bond	d/Å	
O(1)—C(9)	1.34(1)	1.33(1)
N(1)—C(1)	1.41(1)	1.41(1)
N(1)—C(17)$^{\#1}$	1.35(1)	1.35(1)
N(2)—C(6)	1.43(1)	1.41(1)
N(2)—C(7)	1.39(1)	1.39(1)
C(1)—C(2)	1.37(1)	1.39(1)
C(1)—C(6)	1.45(1)	1.43(1)
C(2)—C(3)	1.37(2)	1.35(1)
C(3)—C(4)	1.38(2)	1.34(2)
C(4)—C(5)	1.33(2)	1.35(1)
C(5)—C(6)	1.40(1)	1.38(1)
C(7)—C(8)	1.48(1)	1.49(1)
C(8)—C(9)	1.40(1)	1.39(1)
C(8)—C(13)	1.37(1)	1.44(1)
C(9)—C(10)	1.42(1)	1.37(1)
C(10)—C(11)	1.43(1)	1.42(1)
C(10)—C(17)	1.49(1)	1.50(1)
C(11)—C(12)	1.41(1)	1.40(1)
C(12)—C(13)	1.40(1)	1.40(1)
C(12)—C(14)	1.52(1)	1.53(1)
C(14)—C(15)	1.53(1)	1.50(1)
C(14)—C(16)	1.53(1)	1.52(1)
Angle	ω/deg	
C(6)—N(2)—C(7)	117.1(6)	119.5(6)
C(1)—N(1)—C(17)$^{\#1}$	119.8(8)	119.5(8)
N(1)—C(1)—C(2)	123.3(7)	123.8(6)
N(1)$^{\#1}$—C(17)—C(10)	115.5(8)	115.4(8)
Angle	ω/deg	
N(1)—C(1)—C(6)	117.7(6)	118.0(6)
C(2)—C(1)—C(6)	118.9(7)	118.2(6)
C(1)—C(2)—C(3)	121.3(8)	121.0(7)
C(2)—C(3)—C(4)	120.8(9)	120.3(8)
C(3)—C(4)—C(5)	119.1(9)	121.7(8)
C(4)—C(5)—C(6)	124.1(8)	120.6(7)
N(2)—C(6)—C(1)	117.6(6)	117.3(6)
N(2)—C(6)—C(5)	126.7(7)	124.6(7)
C(1)—C(6)—C(5)	115.7(7)	118.1(7)
N(2)—C(7)—C(8)	115.5(6)	114.8(6)
C(7)—C(8)—C(9)	125.0(6)	128.4(6)
C(7)—C(8)—C(13)	117.0(6)	112.9(6)
C(9)—C(8)—C(13)	118.0(6)	118.7(6)
O(1)—C(9)—C(8)	120.4(6)	118.2(6)
O(1)—C(9)—C(10)	118.6(6)	120.7(6)
C(8)—C(9)—C(10)	121.1(6)	121.2(6)
C(9)—C(10)—C(11)	117.7(6)	119.6(6)
C(9)—C(10)—C(17)	126.6(6)	126.4(6)
C(11)—C(10)—C(17)	115.7(6)	114.0(6)
C(10)—C(11)—C(12)	122.2(7)	121.4(6)
C(11)—C(12)—C(13)	115.9(7)	117.9(6)
C(11)—C(12)—C(14)	121.6(7)	123.6(6)
C(13)—C(12)—C(14)	122.6(7)	118.5(6)
C(8)—C(13)—C(12)	125.2(7)	121.1(6)
C(12)—C(14)—C(15)	109.4(6)	110.0(6)
C(12)—C(14)—C(16)	113.2(6)	112.6(6)
C(15)—C(14)—C(16)	107.8(6)	107.2(6)

* The atoms marked with #1 are generated from the basis atoms by the symmetry operations $1-x$, $1-y$, $-z$.

In the crystal, the independent planar molecules (Fig. 2) with the symmetry C_{2h} located at the heights $z = 0$ (A) and $z = 0.5$ (B) are packed in stacks consisting of the alternating A and B molecules. In the adjacent layers (distance between the layers is $c/2 = 3.45$ Å), the molecules are rotated with respect to each other about the crystallographic twofold axis, which minimizes steric interactions between the *tert*-butyl groups of the adjacent molecules in the stack. The C—N bond lengths in both fragments of two crystallographically independent molecules vary in the very narrow range from 1.35 to 1.41(1) Å (see Table 3). The C(Ph)—C(7,17,27,37)—N bond angles also differ only slightly (close to 116°). In the crystal structure of compound **8**, the CH=N and CH_2—N bond lengths are 1.303 and 1.460 Å, respectively. The corresponding bond angles at the C(7) atom are 110° and 120°. The model in which the —CH_2—NH— and —CH=N— fragments statistically replace each other seems to offer the most reasonable explanation for equalization of the C—N bonds in molecule **9**. Hence, we actually observed an averaged pattern due to superposition of the —CH_2—NH—C(Ph) and —CH=N—C(Ph) fragments in the structure of **9**, which hinders the correct determination of the coordinates of the H atoms in these fragments. Formally, the crystal structure can be described as a superposition of several tautomeric forms: 1) molecular species in which the H atom is attached to different N atoms and 2) zwitterionic forms in which three or four N atoms are protonated and the negative charges are located on one or two O atoms (in the crystal structure, the C—O bond lengths are 1.33(1) and 1.34(1) Å, *i.e.*, these values are close (to within the 3σ error) to the standard C(sp^2)—OH and C(sp^2)—O^- bond lengths).[13] The last-mentioned tautomer can be considered as a double zwitterion. One of the possible tautomers with the localized —CH_2—NH—C(Ph) and —CH=NH—C(Ph) fragments in the molecules A and B is shown in Fig. 1. The proposed model adequately explains the planarity of the macrocycles in the crystal and accounts for the difficulties associated with location of the positions of the H atoms in the structure of **9**. Apparently, the flattened structures of the macrocycles are to some extent stabilized through stacking interactions between the macrocycles in the crystal structure.

The differences in the molecular structures of **8** and **9** are remarkable. In the crystal, molecule **8** in which the

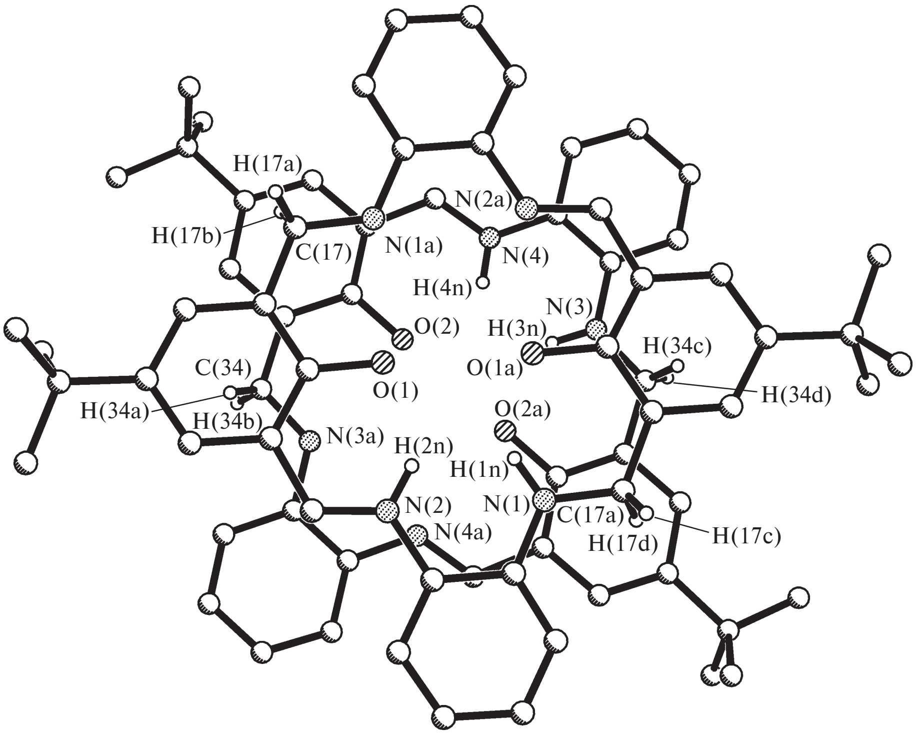


Fig. 2. Arrangement of two independent molecules **9** (one of several possible tautomers with the localized —CH_2—NH—C(Ph) and —CH=NH—C(Ph) fragments in the molecules A and B) in the unit cell. The distance between the molecular planes in the crystal is 3.450 Å.

arrangement of the endocyclic H atoms is identical with that observed in solution adopts a ladder conformation. This conformation is very similar to that of **9a**, which we established in a DTF study of isolated molecule **9**.

The structure of another product formed in the same reaction is equally interesting. The structure of 2,6-bis(benzimidazol-2-yl)-4-*tert*-butylphenol, $C_{24}H_{22}N_4O$ (**10**), which crystallized as a 1 : 1 solvate with ethanol, $C_{24}H_{22}N_4O \cdot EtOH$, was established by X-ray diffraction analysis and confirmed by IR and NMR spectroscopy and mass spectrometry.

The principal crystallographic data for compound **10** are given in Table 2. The bond lengths and bond angles of **10** are listed in Table 4. The geometric parameters of the hydrogen bonds are given in Table 5. The structure of **10** · EtOH is shown in Fig. 3. The geometry of molecules **10** is adequately described by the dihedral angles between three planar fragments. The dihedral angle between the planes of the benzimidazole fragments is 4.7°. The dihedral angles between the plane of the phenol ring and the planes of the benzimidazole rings are 4.2 and 7.5°. Apparently, this coplanar arrangement of the fragments results from conjugation. The molecule contains two intramolecular hydrogen bonds (see Fig. 3 and Table 5), which are also favorable for retention of the coplanarity of the benzimidazole and phenol groups. In addition, these bonds stabilize the unsymmetrical arrangement of both heterocycles in the molecule. It can readily be seen that the protonated nitrogen atoms of the benzimidazole fragments point in the opposite directions with respect to the C(13) atom of the phenol ring bound to the O(1) atom. The corresponding C(13)C(12)C(14)N(4) and C(13)C(8)C(7)N(1) torsion angles are 3.6 and 176.4°, respectively. As a result, the N(4) atom is involved in the formation of the N(4)—H...O(1) hydrogen bond, whereas the N(1) atom of another benzimidazole fragment does not participate in an analogous hydrogen bond. Instead, the deprotonated N(2) atom of the latter fragment is involved in O—H...N hydrogen bonding with the O(1) atom. Hence, two of four active protons participate in the formation of an intramolecular hydrogen bond. The third active proton at the N(1) atom in molecule **10** forms a hydrogen bond with the ethanol molecule of solvation. In the crystal structure, the molecules are linked in the hydrogen-bonded ...EtO—H...**10**...H—OEt chains *via* the hydrogen bond between the N(3) atom and the fourth active proton belonging to the second ethanol molecule (it is omitted in Fig. 3).

We carried out the theoretical study of isolated molecule **9** (which corresponds to the conditions of the gas phase) using DFT calculations. Nonplanar structure **9a** corresponds to the global minimum on the potential energy surface (two projections of structure **9a** are shown in Fig. 4). This structure is characterized by distinct local-

Table 4. Principal geometric parameters of compound **10**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
O(1)—C(13)	1.366(2)	C(7)—N(1)—C(1)	107.08(17)	C(13)—C(12)—C(11)	119.11(17)
N(1)—C(1)	1.390(3)	C(7)—N(2)—C(6)	105.40(17)	C(13)—C(12)—C(14)	122.96(16)
N(1)—C(7)	1.366(3)	C(14)—N(3)—C(15)	105.56(17)	O(1)—C(13)—C(8)	120.87(18)
N(2)—C(6)	1.392(3)	C(14)—N(4)—C(20)	107.08(17)	O(1)—C(13)—C(12)	119.52(17)
N(2)—C(7)	1.339(2)	N(1)—C(1)—C(2)	132.14(19)	C(12)—C(13)—C(8)	119.60(16)
N(3)—C(14)	1.334(3)	N(1)—C(1)—C(6)	105.70(18)	N(3)—C(14)—N(4)	111.97(17)
N(3)—C(15)	1.394(3)	C(2)—C(1)—C(6)	122.15(19)	N(3)—C(14)—C(12)	124.65(17)
N(4)—C(14)	1.379(2)	C(3)—C(2)—C(1)	116.8(2)	N(4)—C(14)—C(12)	123.31(18)
N(4)—C(20)	1.389(3)	C(2)—C(3)—C(4)	121.6(2)	N(3)—C(15)—C(16)	129.8(2)
C(1)—C(2)	1.396(3)	C(5)—C(4)—C(3)	121.6(2)	N(3)—C(15)—C(20)	109.73(19)
C(1)—C(6)	1.407(3)	C(4)—C(5)—C(6)	117.5(2)	C(16)—C(15)—C(20)	120.49(19)
C(2)—C(3)	1.381(3)	N(2)—C(6)—C(5)	130.24(19)	C(17)—C(16)—C(15)	117.6(2)
C(3)—C(4)	1.407(3)	N(2)—C(6)—C(1)	109.47(17)	C(16)—C(17)—C(18)	121.4(2)
C(4)—C(5)	1.382(3)	C(5)—C(6)—C(1)	120.3(2)	C(19)—C(18)—C(17)	121.8(2)
C(5)—C(6)	1.402(3)	N(2)—C(7)—N(1)	112.34(18)	C(18)—C(19)—C(20)	116.7(2)
C(7)—C(8)	1.465(3)	N(1)—C(7)—C(8)	125.28(16)	N(4)—C(20)—C(15)	105.64(17)
C(8)—C(9)	1.403(3)	N(2)—C(7)—C(8)	122.38(18)	N(4)—C(20)—C(19)	132.4(2)
C(8)—C(13)	1.419(3)	C(9)—C(8)—C(7)	121.23(18)	C(19)—C(20)—C(15)	121.9(2)
C(9)—C(10)	1.402(3)	C(9)—C(8)—C(13)	119.32(18)	C(10)—C(21)—C(23)	108.54(18)
C(10)—C(11)	1.395(3)	C(13)—C(8)—C(7)	119.42(16)	C(22)—C(21)—C(24)	108.4(2)
C(10)—C(21)	1.540(3)	C(10)—C(9)—C(8)	122.05(18)	C(22)—C(21)—C(10)	111.70(17)
C(11)—C(12)	1.409(3)	C(11)—C(10)—C(9)	117.39(17)	C(22)—C(21)—C(23)	108.5(2)
C(12)—C(13)	1.402(3)	C(9)—C(10)—C(21)	120.87(18)	C(24)—C(21)—C(10)	110.54(17)
C(12)—C(14)	1.467(3)	C(11)—C(10)—C(21)	121.68(19)	C(24)—C(21)—C(23)	109.11(19)
C(15)—C(16)	1.401(3)	C(10)—C(11)—C(12)	122.53(19)	O(1s)—C(1s)—C(2s)	109.00(17)
C(15)—C(20)	1.404(3)	C(11)—C(12)—C(14)	117.85(18)		
C(16)—C(17)	1.384(3)				
C(17)—C(18)	1.403(3)				
C(18)—C(19)	1.386(3)				
C(19)—C(20)	1.399(3)				
C(21)—C(22)	1.528(3)				
C(21)—C(24)	1.529(3)				
C(21)—C(23)	1.544(3)				
O(1s)—C(1s)	1.431(3)				
C(1s)—C(2s)	1.508(3)				

ization of two endocyclic protons at the O atoms of the phenol groups, which are involved in hydrogen bonding with the N atoms of the azomethine CH=N fragments. Hence, according to the results of the DFT calculations, the structure of the isolated molecule is identical with that observed in solution. The CH=N and CH$_2$—NH bond lengths are substantially different (1.303 and 1.460 Å, respectively) and are close to those found[10] in the crystal structure of compound **8**. The macrocycle adopts a ladder conformation. Two planar fragments consisting of the phenol rings and the CH=N and CH$_2$—NH groups are parallel to one another and form an angle of 147.4° with the plane in which both the phenyl rings and the N atoms of the *o*-phenylenediamine fragments are located. Previously, an analogous conformation was found for molecule **8** and also for hexafluorophosphate of doubly protonated macrocyclic Schiff's base **14**, which was prepared by condensation of 2,6-diacetyl-4-methylphenol with ethylenediamine.[14]

The local minimum on the potential energy surface whose energy is 2.63 kcal mol^{-1} higher than that of the

Table 5. Geometric parameters of the D—H...A hydrogen bonds in the structure of **10**·EtOH, the H...A distances are smaller than *r*(A) + 2.000 Å and the D—H—A angles are larger than 110°

D	A	*d*/Å			Angle/deg D—H—A
		D—H	H...A	D...A	
O(1)	N(2)	0.981	1.633	2.554	154.39
N(1)	O(1s)	0.945	1.880	2.810	167.22
N(4)	O(1)	0.926	1.969	2.662	130.14
O(1s)	N(3)	0.905	1.847	2.748	173.47

Note: *r* is the radius.

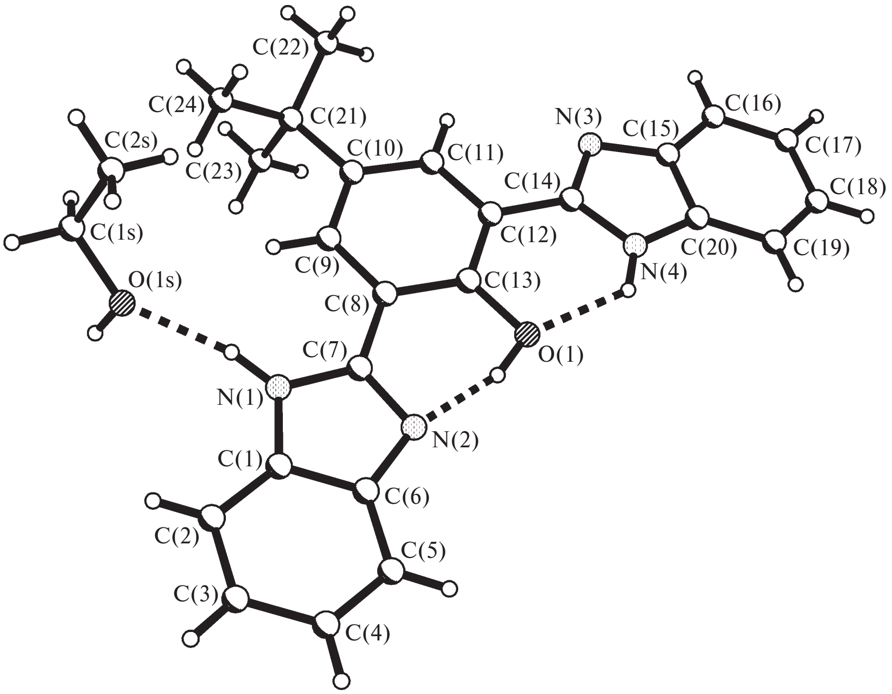
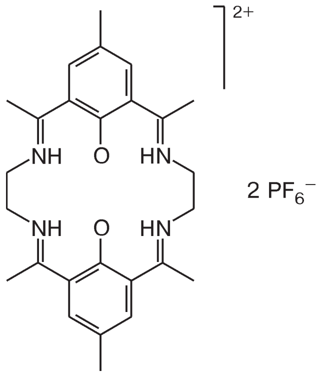


Fig. 3. Molecular structure of **10** in the crystal.



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global minimum corresponds to structure **9b** (Fig. 5), which is close to the zwitterionic structure found for this compound in the crystal structure. All four endocyclic protons in this structure are located at the N atoms. The CH=N and CH_2—NH bond lengths are somewhat equalized compared to those in structure **9a** (1.329 Å and 1.463 Å, respectively). However, the macrocycle in molecule **9b** is nonplanar and adopts a tub conformation as distinct from the conformation in the crystalline state. The bottom of the tub is formed by the plane in which the phenyl rings and the N atoms of the *o*-phenylenediamine fragments are located. Two planar fragments involving the phenol rings and the CH=N and CH_2—NH fragments form angles of 150° with the tub bottom. The principal geometric parameters of structures **9a** and **9b** are given in Table 6. The zwitterionic character of structure **9b** is clearly manifested in the changes in the electron density distribution and the dipole moment as compared to structure **9a** (Table 7). The negative charges on the O atoms are substantially increased, and the negative charges on the N atoms of the CH_2—NH fragments are also somewhat increased, whereas the negative charges on the azomethine N atoms are sharply decreased. The small difference in the energies of structures **9a** and **9b** suggests that migration of the endocyclic protons, which was observed in solution of compound **9** by NMR spectroscopy, proceeded through an intermediate possessing structure **9b**.

Table 6. Bond lengths (Å) in structures **9a** and **9b** from DFT calculations

Bond	**9a**	**9b**
O(1)—C(9); O(1a)—C(9a)	1.351	1.292
O(1)—H(2na); O(1a)—H(2n)	1.027	1.958
O(1)—H(1na); O(1a)—H(1n)	2.143	1.542
N(2)—H(2n); N(2a)—H(2na)	1.628—1.635	1.085
N(1)—H(1na); N(1)—H(1n)	—	1.025
N(1a)—C(17); N(1)—C(17a)	1.460	1.463
N(2)—C(7); N(2a)—C(7a)	1.303	1.329
N(2)—C(11); N(2a)—C(11a)	1.405	1.411
N(1a)—C(10a); N(1)—C(10)	1.376	1.376
N(2)—H(2na); N(2a)—H(1n)	2.320	—

Note. The atomic numbering schemes are given in Figs. 4 and 5.

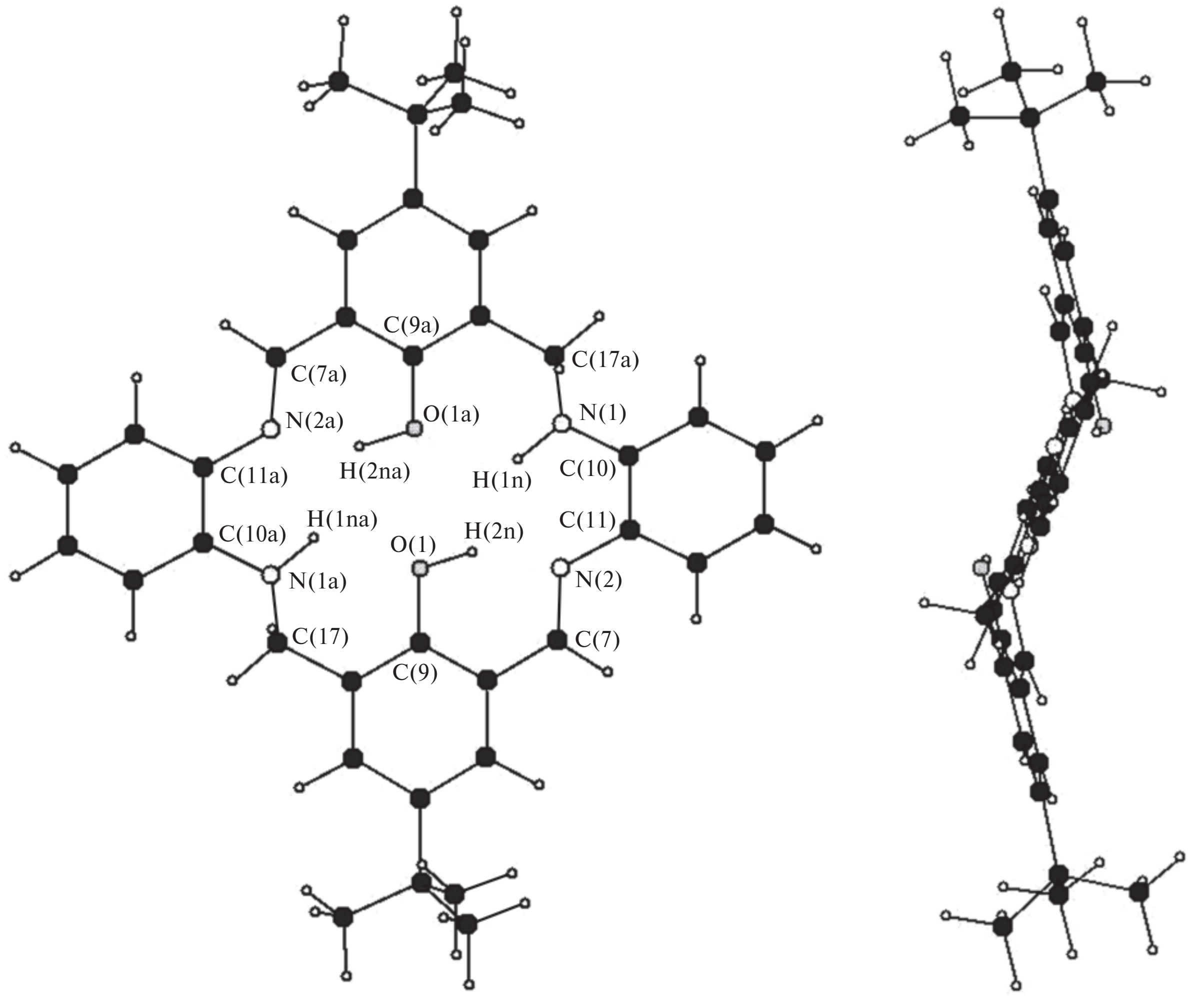

Fig. 4. Molecular structure of **9a** according to the DFT calculations.

Table 7. Charges on the atoms from the Hirschfeld analysis and the dipole moments* in structures **9a** and **9b****

Atom	**9a**	**9b**	Atom	**9a**	**9b**
O(1)	−0.1550	−0.2173	C(17)	−0.0163	−0.0180
O(1a)	−0.1553	−0.2175	C(7)	0.0386	0.0535
N(1)	−0.1082	−0.1098	C(10a)	0.0464	0.0482
N(2)	−0.0949	−0.0380	C(11a)	0.0177	0.0269
N(1a)	−0.1082	−0.1097	C(11)	0.0175	0.0268
N(2a)	−0.0943	−0.0380	C(10)	0.0646	0.0482
C(9a)	0.0784	0.0797	H(1na)	0.0887	0.0874
C(7a)	0.0393	0.0534	H(2na)	0.0977	0.0881
C(17a)	−0.0164	−0.0180	H(1n)	0.0886	0.0873
C(9)	0.0793	0.0796	H(2n)	0.0973	0.0881

* The dipole moments are 0.102 D (**9a**) and 1.765 D (**9b**).

** The atomic numbering schemes are given in Figs. 4 and 5.

In conclusion, it should be noted that the above-considered differences in structures **9** in the crystalline state and in the gas phase are reasonable. It is quite possible that the effects of the crystal packing, which are pronounced for porphyrin-like macrocycles due to stacking interactions, are responsible for flattening of the very labile macrocycle. New macrocyclic Schiff's base **9** synthesized in the present study can serve as a hexadentate ligand to form binuclear complexes with various transition metals. The structures and properties of these complexes will be described in the following parts of this series of papers.

Experimental

4-*tert*-Butyl-2,6-diformylphenol was prepared according to a procedure described previously.[15] The NMR spectra were recorded on a Bruker DPX-300 instrument at 24 °C. The IR spectra were measured on a Specord M80 spectrometer in KBr pellets. The mass spectra were obtained on a Finnigan MAT 212 instrument; the energy of ionizing electrons was 70 eV; the temperature of the ionization chamber was 230 °C.

Synthesis of compounds 9 and 10. Weighed samples of the starting reagents, *viz.*, 4-*tert*-butyl-2,6-diformylphenol (175 mg, 0.83 mmol) and 1,2-diaminobenzene (91 mg, 0.83 mmol), were

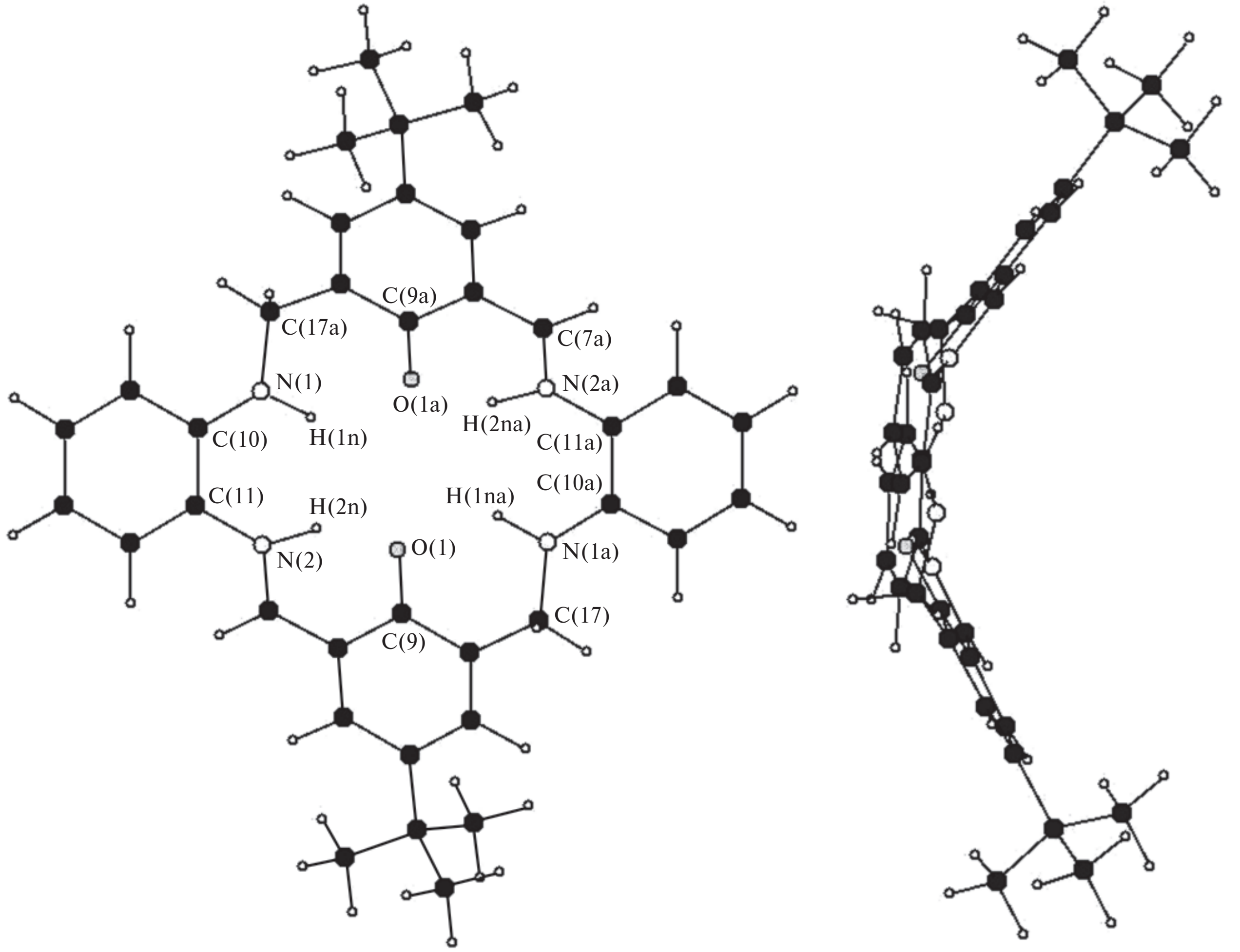

Fig. 5. Molecular structure of **9b** according to the DFT calculations.

dissolved in anhydrous ethanol (25 mL) and refluxed for 3 h. After completion of refluxing, the dark solution was slowly cooled to ~20 °C. The pale-brown needle-like crystals of **9** that precipitated were filtered off. The mother liquor was concentrated to obtain an additional amount of crystals of **9**. Compound **10** was isolated by concentrating the mother liquor to dryness and washing off the starting reagents and compound **9** with chloroform (~1 mL). Compound **9** was isolated in the pure form after evaporation of chloroform and recrystallization from ethanol. Air-stable compounds **9** and **10** are insoluble in water. Schiff's base **9** is readily soluble in chloroform and poorly soluble in aromatic and saturated hydrocarbons. Compound **10** is poorly soluble in organic solvents, except for ethanol and DMSO. The melting point of **9** was 272—273 °C (from ethanol). At 250 °C, the crystals of **9** turned dark. Compound **10** did not melt up to 350 °C.

Compound 9. Found (%): C, 76.75, 76.89; H, 7.07, 7.16; N, 9.75, 9.67. $C_{36}H_{40}N_4O_2$. Calculated (%): C, 77.11; H, 7.19; N, 9.99. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 560 $[M]^+$ (13); 453 $[M - 107]^+$ (2), 383 $[M - 177]^+$ (16), 281 $[0.5M + 1]^+$ (100), 265 $[0.5M - 15]^+$ (30), 119 $[C_7H_5N_2]^+$ (50). ^{13}C NMR ($CDCl_3$), δ^1: 31.38 (C(18), $^1J_{CH}$ = 125.8); 34.01 (C(17)); 47.24 (C(16), J = 137.3); 111.70 (C(13), $^1J_{CH}$ = 154.5 Hz); 117.38 (C(11), $^1J_{CH}$ = 161.1 Hz); 117.94 (C(10), $^1J_{CH}$ = 155 Hz); 119.15; 124.98; 127.98 (C(6), $^1J_{CH}$ = 152.5 Hz); 128.19 (C(12), $^1J_{CH}$ = 157 Hz); 130.81 (C(4), $^1J_{CH}$ = 153.8 Hz); 136.11; 141.79; 143.43 (C(5)); 157.22 (C(2)); 162.07 (C(8), $^1J_{CH}$ = 161.9 Hz). IR (KBr), ν/cm^{-1}: 3424 (N—H); 2960, 2920, 2872 (C—H); 1664, 1600, 1568, 1512, 1456, 1368, 1288, 1232, 1184, 736, 464. The ^1H NMR spectrum is given in Table 1.

Compound 10. Found (%): C, 74.79, 74.06; H, 6.58, 6.49; N, 14.03, 13.91. $C_{24}H_{22}N_4O$. Calculated (%): C, 75.37; H, 5.80; N, 14.65. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 382 $[M]^+$ (195); 367 $[M - CH_3]^+$ (100); 43 $[(H_3C)_2CH]^+$ (31). ^1H NMR (DMSO-d_6), δ: 1.47 (s, 9 H, $-C(CH_3)_3$); 7.48 and 7.84 (both m, 8 H, AA´BB´); 8.50 (s, 2 H); 15.00 (br.s, 3 H, O—H and N—H). ^{13}C NMR (DMSO-d_6), δ: 31.19, 34.70, 111.79, 114.41, 124.61, 128.47, 133.69, 141.80, 148.76, 156.66. IR (KBr), ν/cm^{-1}: 3394, 3367, 2964, 2919, 2869, 1625, 1556, 1515, 1461, 1313, 1047, 750.

X-ray diffraction study of compounds 9 and 10. The X-ray diffraction data for the crystal of **9** were collected on a four-circle automated Siemens R3v/m diffractometer (λ(Mo-Kα) radiation, λ = 0.71074 Å, 22 °C). The unit cell parameters were determined and refined using 24 equivalent reflections with $2\theta < 24—28°$. Three strong reflections with $0 < \chi < 65°$ used as standard reflections were monitored after each 1000 reflections. The semiempirical absorption correction[16] was ignored because of the low absorption coefficient. The calculations were carried out using the SHELX97 program package.[17] The crystallographic parameters of **9** and **10** and details of their structure refinement are given in Table 2.

The structure of compound **9** was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and refined using the riding model. The principal geometric parameters of **9** are listed in Table 3.

The structure of **10** was solved by direct methods and refined by the least-squares method with anisotropic thermal parameters (isotropic thermal parameters for the H atoms) using the SHELXS97 [17] and SHELXL97 [18] program packages to $R = 0.069$ ($wR_2 = 0.161$) for 4682 reflections with $F^2 > 2\sigma(I)$; the goodness-of-fit GOF = 1.007. The X-ray diffraction data were collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λ(Mo) radiation, graphite monochromator, 140 K, ω scanning technique, scan step was 0.3°, frames were exposed for 10 s, $2\theta_{max} = 60°$) using a standard procedure.[19]

Theoretical study. The potential energy surfaces for molecule **9** were calculated by the DFT method using the PRIRODA program.[20]

The PBE functional, which involves the electron density gradient, was used.[21] The Kohn—Sham equations were solved using the TZ3p atomic basis sets of the grouped Gaussian functions. The orbital basis sets included the contraction sets (5s1p)/[3s1p] for H and (11s6p2d)/[6s3p2d] for C, N, and O. The matrix elements of the Coulomb and exchange-correlation potentials were calculated using expansion of the electron density in the auxiliary basis set consisting of the atom-centered nongrouped Gaussian functions (*4s*1*p*) for H and (3*s2d*1*f*) for C, N, and O.[22] The geometry was optimized without restrictions imposed on the molecular symmetry. The character of the stationary points was determined based on analytical calculations of the second derivatives of the energy. Previously, we have successfully used this method and the PRIRODA program in the study of the structures and reactivities of silicon-containing organophosphorus betaines[23] and in examination of the mechanism of activation of alkanes with cationic titanium and zirconium complexes.[24,25]

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