Properties and structures of porphyrexides

E. V. Tretyakov,[a] A. S. Bogomyakov,[b] E. Yu. Fursova,[a] G. V. Romanenko,[a] V. N. Ikorskii,[a] and V. I. Ovcharenko[a,b]★

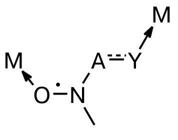
[a]International Tomography Center, Siberian Branch of the Russian Academy of Sciences,
3a ul. Institutskaya, 630090 Novosibirsk, Russian Federation
Fax: +7 (383) 333 1399. E-mail: Victor.Ovcharenko@tomo.nsc.ru
[b]Novosibirsk State University,
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation

The molecular and crystal structures of porphyrexides, *viz.*, 4-amino-2-imino- (**1**) and (*Z*)-2-amino-4-bromoimino-5,5-dimethyl-4,5-dihydro-1*H*-imidazole 1-oxyls (**7**), and their diamagnetic precursors were determined. Compound **1** is kinetically unstable because it is oxidized with atmospheric oxygen to form (*E*)-1,2-bis[1-amino-1-(cyanoimino)-2-methylpropan-2-yl]diazene 1,2-dioxide.

Key words: nitroxides, porphyrexide, X-ray diffraction study.

The synthesis of new types of magnetically active compounds is based on the development of methods for the construction of highly efficient exchange-coupled ensembles. The use of complexes of paramagnetic transition metal ions with paramagnetic organic ligands is one of approaches that have gained wide acceptance in the design of such ensembles.[1—5] Nowadays, at the early stage of investigation, *i.e.*, at the molecular level, researchers try to endow the structure of a paramagnetic ligand with parameters, which would be expected to be favorable for the desired physical characteristics at the macrolevel. First, a paramagnetic ligand should be polyfunctional to induce self-assembly of polymeric structures, *i.e.*, the ligand should serve as a bridge. Second, the ligand should provide efficient exchange interactions between the unpaired electrons of the paramagnetic centers, between which this ligand is located, and, what is extremely important, the occurrence of cooperative magnetic interactions at the macrolevel. Third, the ligand should possess high kinetic stability, which is necessary for growing single crystals required for the subsequent structure solution and construction of reliable magnetic-structure relationships. In addition, kinetic stability of ligands allows one to perform desired transformations without the introduction and removal of protective groups.

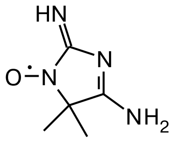
These requirements can be simultaneously satisfied only by introducing a particular combination of functional fragments. Nitroxide bound to the α,β-unsaturated heteroatomic fragment or its vinylog can serve as such a construction, which allows also bridging coordination.



Y = N, O

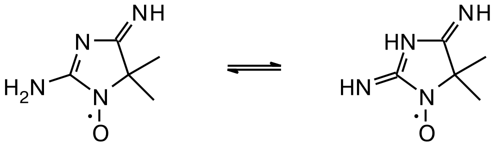
Spin density delocalization in the bridging fragment provides conditions for the formation of an efficient exchange interaction channel between the unpaired electrons of paramagnetic metal ions.

Classical porphyrexide (**1**) has attracted our attention because it satisfies all the above-mentioned requirements. A procedure for the synthesis of this compound has been described many years ago.[6] Much more recently, radiospectroscopic studies of solutions of isotopically labelled porphyrexide derivatives by ESR have demonstrated that porphyrexide **1** exists in dioxane as a mixture of tautomeric forms **1A** and **1B** (Scheme 1), form **1B** being the major one.[7] The representation of the porphyrexide molecule as tautomer **1B** is commonly accepted and was cited in reviews and monographs for more than three decades.[8,9]



1

Scheme 1



1A **1B**

Porphyrexide has attracted our attention as a potent paramagnetic ligand. This has stimulated the need for a more detailed analysis of its structural characteristics. Since the data on its structure were absent in the Cambridge Structural Database,[10] we studied the structure of this compound by X-ray diffraction. It was unexpectedly

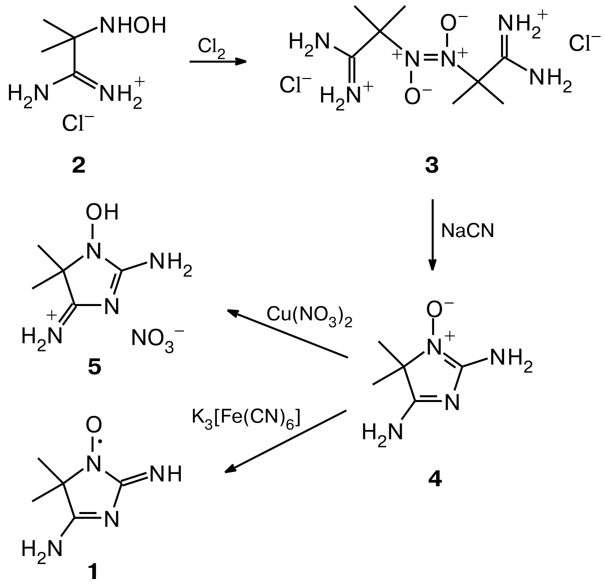
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 441—447, March, 2006.

1066-5285/06/5503-0457 © 2006 Springer Science+Business Media, Inc.

found that, in the solid state, **1** exists in the form different from **1B**. Since the molecular structure of the diamagnetic precursor of porphyrexide in the solid state also differs from the commonly accepted structure, we report here the X-ray diffraction data for compound **1** and its diamagnetic precursors.

For each compound (Scheme 2), it was necessary to find a procedure for the growth of single crystals suitable for X-ray diffraction. For example, we succeeded in growing well-faceted crystals of hydroxylamine **2** only from the mother liquor obtained after a twofold dilution of a methanolic solution of **2** with a diethyl ether—hexane mixture (1 : 1, v/v).

Scheme 2



In the solid state, the C(6)—N(3) and C(6)—N(2) bonds involving both N atoms of the protonated amidine fragment in compound **2** have similar lengths (1.313(3) and 1.305(3) Å, respectively), which are intermediate between single and double bond lengths (Fig. 1). The *p*-π conjugation in the amidine fragment of molecule **2** is also evidenced by the arrangement of the N(2), C(6), N(3), H(21), H(22), H(31), and H(32) atoms in a single plane. The C—C (1.524(4)—1.531(4) Å), O(4)—N(5) (1.452(3) Å), and N(5)—C(8) (1.477(3) Å) distances are typical of single bonds. It should also be noted that the organic cations and chloride anions in the solid state of **2** are linked to each other by a hydrogen bond network to form a three-dimensional framework.

Single crystals of (*E*)-1,2-bis(1-amino-1-iminio-2-methylpropan-2-yl)diazene 1,2-dioxide dichloride (**3**, see Scheme 2) suitable for X-ray diffraction were isolated directly from the reaction mixture upon oxidation of an aqueous solution of **2** with chlorine. Dimeric nitrosoamidine **3**, like compound **2**, is protonated at both amidine groups, all atoms of the latter being located virtually in a single plane. The dication is centrosymmetric with respect to the midpoint of the N—N bond (Fig. 2). The bond lengths in this fragment are as follows: C(1)—N(1), 1.288(2) Å; C(1)—N(2), 1.301(2) Å; N(3)—O(1), 1.265(2) Å; and N(3)—N(3′), 1.310(3) Å. As a whole, the structure of **3** consists of layers in which all organic dications and chloride anions are linked to each other by numerous hydrogen bonds.

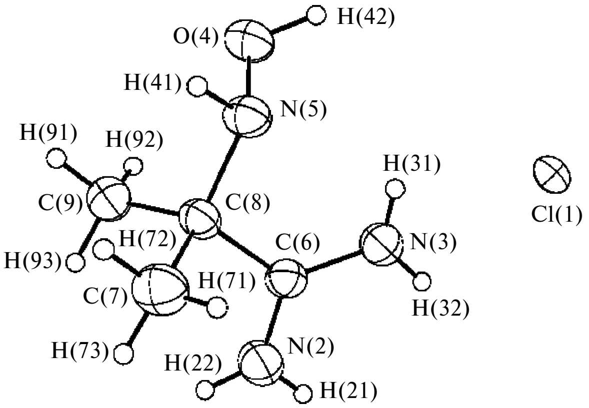


Fig. 1. Molecular structure **2**.

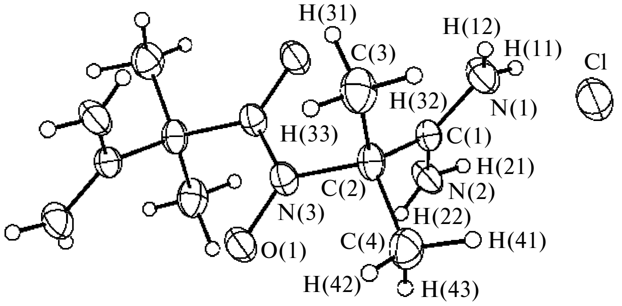
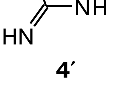


Fig. 2. Molecular structure of dimer **3**.

Polar aqueous-alcoholic media proved to be solutions of choice for the crystal growth of **4** (see Scheme 2). Crystallization of the reaction product of nitroso derivative **3** with NaCN from a MeOH—water mixture afforded crystals of dihydrate **4**$\cdot$2H_2O, whereas crystallization from water gave crystals of the corresponding trihydrate **4**$\cdot$3H_2O. X-ray diffraction study demonstrated that molecules **4** in both hydrates exist in the amino-nitronic form, *i.e.*, as 2,5-diamino-4,4-dimethyl-4*H*-imidazole 3-oxide (Fig. 3, *a*).

Earlier,[13] the structure of hydroxyamino-imine tautomer **4′** has been assigned to the cyclic product formed by the reaction of **3** with NaCN, whereas the results of investigation of the structures of **4**$\cdot$2H_2O and **4**$\cdot$3H_2O correspond to the structure of nitrone **4** (see



4′

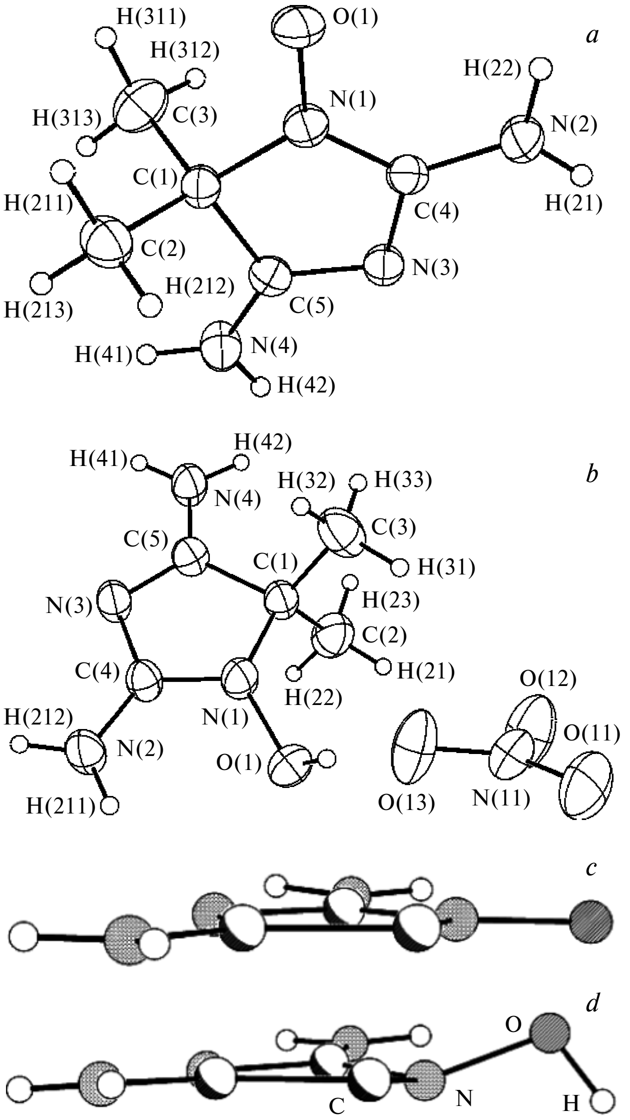


Fig. 3. Structure and geometry of 2,4-diamino-5,5-dimethyl-5*H*-imidazole 1-oxide **4** (*a*, *c*); the molecular structure of **5** (*b*) and the geometry of the cation in molecule **5** (*d*).

Scheme 2). The nitrone form is also evidenced by the fact that all atoms of molecule **4**, except for the atoms of the *gem*-methyl groups, are in a single plane. Their maximum deviation from the mean plane is at most 0.054 Å (see Fig. 3, *c*). This is a fundamental difference between the structure of nitrone **4** and the structure of hydroxyamine derivative **5** (Fig. 3, *b*), in which the O atom substantially deviates from the plane of the heterocycle (Fig. 3, *d*). The rearrangement of the nitrone fragment into the hydroxyamine group is also evidenced by the fact that the N(1)—C(4), C(4)—N(2), and C(4)—N(3) bond lengths in hydrates $\mathbf{4}\cdot 2H_2O$ and $\mathbf{4}\cdot 3H_2O$ differ from those in compound **5** (Table 1).

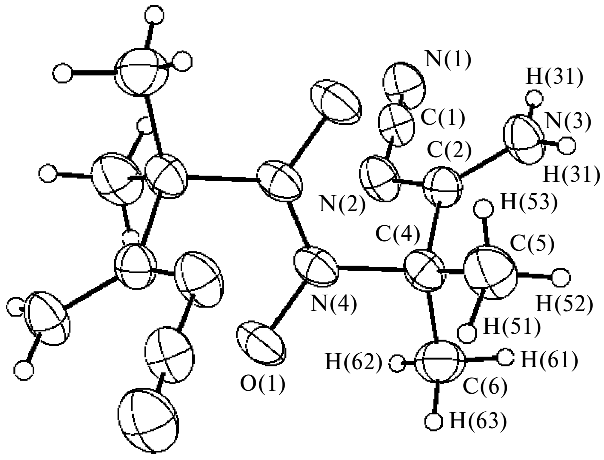


Fig. 4. Structure of dimer **6**.

Using the classical procedure[6,13] for the preparation of porphyrexide, we oxidized compound **4** with $K_3[Fe(CN)_6]$. As a result, we prepared porphyrexide **1** in ~40% yield as a finely dispersed crystalline red precipitate. Attempts to grow larger single crystals of **1** from acetone, MeOH, THF, or water gave similar results. Upon storage in an open vessel for several hours either at room or low temperature, the color of the mother liquor changed from red to orange, and compound **1** was absent from the resulting precipitate (IR spectroscopic data). Hence, we attempted to grow crystals of **1** directly from the reaction mixture formed in the course of the synthesis of porphyrexide. Slow cooling and storage of the reaction mixture at 5—6 °C for 14 h afforded three types of rather large partially intergrown crystals. X-ray diffraction study demonstrated that red prisms were porphyrexide **1**, pale-brown prisms were (*E*)-1,2-bis[1-amino-1-(cyanoimino)-2-methylpropan-2-yl]diazene 1,2-dioxide (**6**), and pale-yellow plates were $K_4[Fe(CN)_6]$. In dimer **6**, whose structure is shown in Fig. 4, the C(2)—N(2) and C(2)—N(3) distances are 1.306(2) and 1.307(2) Å, respectively, the N(4)—O(1) distance is 1.265(1) Å, the N(4)—N(4′) distance is 1.310(2) Å, and the N(1)—C(1) distance is 1.153(2) Å, which correspond to the structural formula of **6** presented in Scheme 3.

Scheme 3

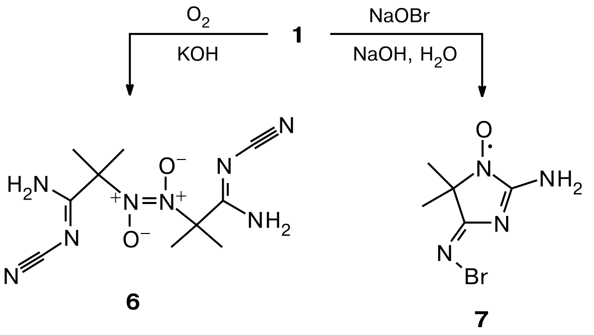


Table 1. Selected bond lengths in the structures of **1**, **4**$\cdot$2H_2O, **4**$\cdot$3H_2O, **5**, and **7**

Bond	*d*/Å							
	4$\cdot$3H_2O	**4**$\cdot$2H_2O	**5**	**7**	**1**			
					A	**B**	**C**	**D**
C(5)—N(4)	1.311(3)	1.310(2)	1.303(2)	1.284(4)	1.364(7)	1.331(7)	1.307(7)	1.303(8)
N(3)—C(5)	1.317(3)	1.324(2)	1.318(2)	1.381(3)	1.369(7)	1.420(6)	1.274(7)	1.279(7)
C(4)—N(3)	1.382(2)	1.386(2)	1.365(2)	1.315(4)	1.361(8)	1.341(7)	1.416(8)	1.405(7)
C(4)—N(2)	1.318(3)	1.317(2)	1.298(2)	1.310(4)	1.278(6)	1.266(6)	1.296(6)	1.300(6)
N(1)—C(4)	1.302(2)	1.310(2)	1.330(2)	1.401(4)	1.449(6)	1.446(6)	1.443(6)	1.419(6)
N(1)—O(1)	1.364(2)	1.374(2)	1.388(2)	1.260(3)	1.267(6)	1.279(6)	1.249(6)	1.258(6)
C(1)—N(1)	1.466(2)	1.463(2)	1.475(2)	1.483(3)	1.483(6)	1.481(6)	1.483(6)	1.490(7)
C(1)—C(2)	1.521(3)	1.521(2)	1.508(3)	1.514(4)	1.514(6)	1.570(7)	1.553(7)	1.507(8)
C(1)—C(3)	1.520(3)	1.527(3)	1.518(3)	1.515(4)	1.573(8)	1.574(8)	1.579(7)	1.566(7)
C(1)—C(5)	1.512(3)	1.518(2)	1.511(3)	1.528(4)	1.447(7)	1.447(8)	1.468(8)	1.486(6)
N(4)—Br				1.895(2)				

An increase in the time of storage of the reaction mixture to several days led to the complete disappearance of crystals of **1**, and the precipitate contained only crystals of **6** and $K_4[Fe(CN)_6]$. Therefore, not only recrystallization of **1** but also the synthesis of porphyrexide is accompanied by its gradual decomposition.

Hence, we decided to synthesize porphyrexide under argon with the use of pre-deaerated solutions of the reagents. Under these conditions, the reaction afforded only porphyrexide **1** in the solid state. The magnetic moment of **1** (μ_{eff} = 1.71 μ_B at 293 K) is virtually equal to the theoretical value for the monoradical (1.73 μ_B), which is indicative of high purity of the resulting sample. Unfortunately, porphyrexide crystallized from the reaction mixture as crystal intergrowths. However, we succeeded in separating rather homogeneous crystalline fragments from these intergrowths and studied them by X-ray diffraction. The quality of crystals of **1** was lower than that of the other compounds under study (Table 2). We failed to locate hydrogen atoms, and their positions were calculated geometrically and then refined using a riding model. The satisfactory *R* factor for compound **1** was obtained only taking into account a twin model (1 0 0 / 0 1 0 / 0 0 –1; BASF = 0.4168). For the corresponding brominated derivative **7**, whose solid phase consisted only of the tautomeric form, the quality of the crystals appeared to be much higher. Hence, it was reasonable to consider the structure of **1** in comparison with the structure of bromoporphyrexide **7**, which we also synthesized.

In four crystallographically independent molecules comprising the structure of **1** (Fig. 5), like in molecules **4**, all atoms are in a single plane, except for the *gem*-methyl groups. The bond lengths (see Table 1) allowed us to unambiguously distinguish the double bond in the C(4)—N(2) fragments in molecules **1A—D**. The C(5)—N(3) double bond is clearly seen also in the amidine group of molecules **1C** and **1D**. On the contrary, the N(3)—C(4)—N(2) amidine fragment and the C(5)—N(4) bromoimine group are clearly distinguished in the structure of molecules **7** based on X-ray diffraction data (Table 1). According to these data, the amidine fragment in **7** involves the N(3)—C(4)—N(2) atoms, whereas the amidine fragment in molecule **1** is formed by the N(3)—C(5)—N(4) atoms. This is confirmed by the fact that pairs of molecules **A—D** and **B—C** are present in the structure of **1** (see Fig. 5). These pairs are formed by two H bonds between the above-mentioned amidine fragments. It was unambiguously established that the amidine fragments in the structure of **7** are linked to each other through hydrogen bonds in the same fashion. In addition, there are hydrogen bonds between the Br atoms and the O atoms of the adjacent nitroxides and the hydrogen atoms of the amino groups in the structure of **7**, resulting in the formation of ribbons (Fig. 6, *b*).

In the ribbons, pairs of nitroxide fragments face each other. Hence, the structure of **7** is formed by exchange-coupled pairs of paramagnetic centers, within which the O...O distances are short (3.485 Å). In complete agreement with these data, the experimental temperature dependences of the effective magnetic moment μ_{eff} and the magnetic susceptibility χ (Fig. 7) for **7** are well processed according to the model of exchange-coupled dimers[11] with the exchange interaction energy $J/k = -19.7$ K.

To summarize, we established the earlier unknown structures of porphyrexide, its bromo derivative, and diamagnetic precursors of porphyrexide. The results of our study confirmed the assignment of the structural formulas presented in Schemes 2 and 3 to compounds **1** and **7**, respectively.

Table 2. Principal crystallographic data and details of X-ray diffraction study

Parameter	**1**	**2**	**3**	**4**$\cdot$3H_2O	**4**$\cdot$2H_2O	**5**	**6**	**7**
Molecular formula	$C_5H_9N_4O$	$C_4H_{12}ClN_3O$	$C_8H_{20}Cl_2N_6O_2$	$C_5H_{16}N_4O_4$	$C_5H_{14}N_4O_3$	$C_5H_{11}N_5O_4$	$C_{10}H_{16}N_8O_2$	$C_5H_8BrN_4O$
T/K	240	240	240	240	295	295	295	240
FW	141.16	153.62	303.20	196.22	178.20	205.19	280.30	220.06
Space group	$P2_1$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	C2/c	$P2_1/c$
a/Å	5.946(2)	5.9701(9)	6.5586(14)	11.246(4)	11.603(3)	6.1563(10)	13.932(2)	8.411(4)
b/Å	18.471(7)	7.7732(12)	10.264(2)	7.125(2)	6.5529(14)	9.4328(15)	10.4588(16)	7.932(4)
c/Å	13.204(5)	16.904(3)	10.658(2)	13.563(4)	13.321(3)	16.439(3)	11.0347(17)	13.316(6)
β/deg	90.123(6)		102.472(4)	109.525(6)	106.923(3)	95.852(3)	120.990(2)	106.753(6)
V/Å^3	1450.1(10)	784.5(2)	700.5(3)	1024.2(6)	968.9(4)	949.6(3)	1378.3(4)	850.6(7)
Z	8	4	2	4	4	4	4	4
D_c/g cm^{-3}	1.293	1.301	1.437	1.273	1.222	1.435	1.351	1.718
μ(Mo-Kα) /mm^{-1}	0.096	0.420	0.469	0.108	0.100	0.123	0.101	4.784
θ/deg	1.10—29.05	2.41—23.32	2.79—23.28	1.92—23.27	2.05—23.34	2.49—23.32	3.41—23.26	2.53—23.24
I_{nkl}*	12513/6558	3291/1117	2919/1007	4227/1467	6776/1401	7098/1373	5095/981	5985/1215
R_{int}	0.0632	0.0248	0.0194	0.0540	0.0376	0.0632	0.0213	0.0433
N	495	131	123	182	170	172	124	133
GOOF	0.969	0.481	0.823	0.965	0.496	0.905	1.053	1.047
R_1	0.0579	0.0300	0.0281	0.0350	0.0370	0.0386	0.0325	0.0266
wR_2 ($I > 2\sigma_I$)	0.1081	0.0866	0.0926	0.0813	0.1167	0.1109	0.0957	0.0726
R_1	0.0990	0.0322	0.0305	0.0440	0.0420	0.0451	0.0348	0.0293
wR_2	0.1336	0.0918	0.0954	0.0855	0.1253	0.1170	0.0981	0.0745

* Number of reflections, measured/independent.

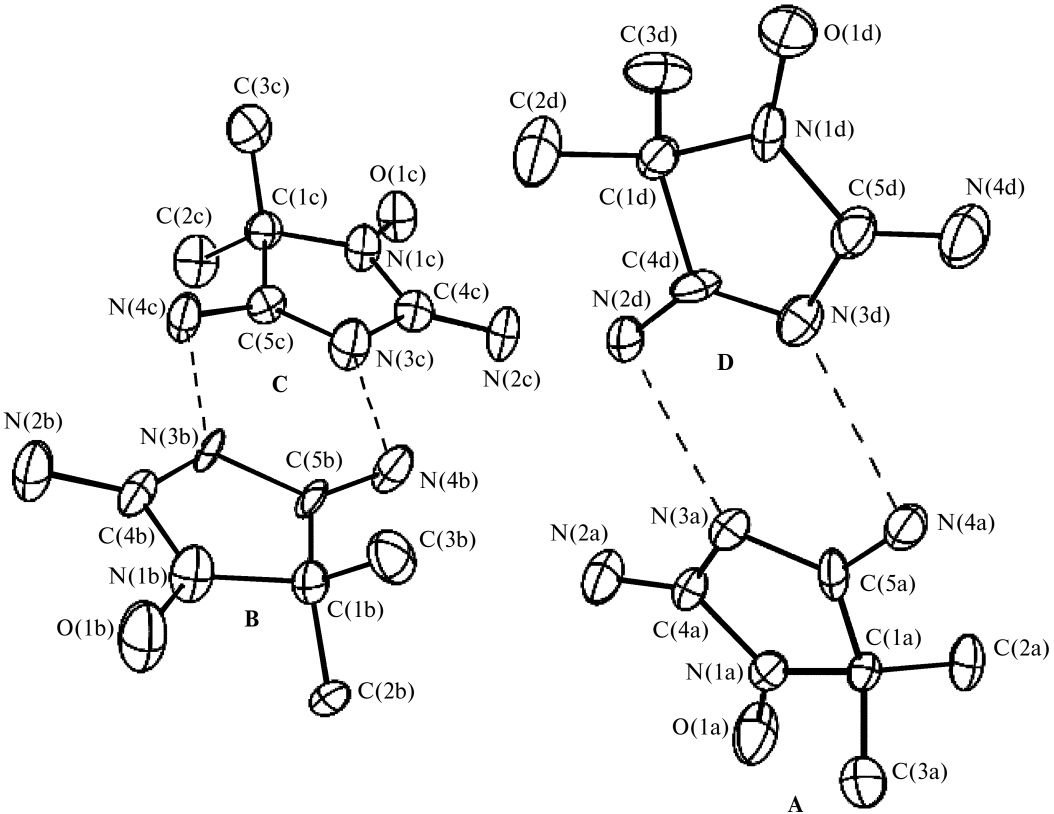


Fig. 5. Dimerization of molecules **1**.

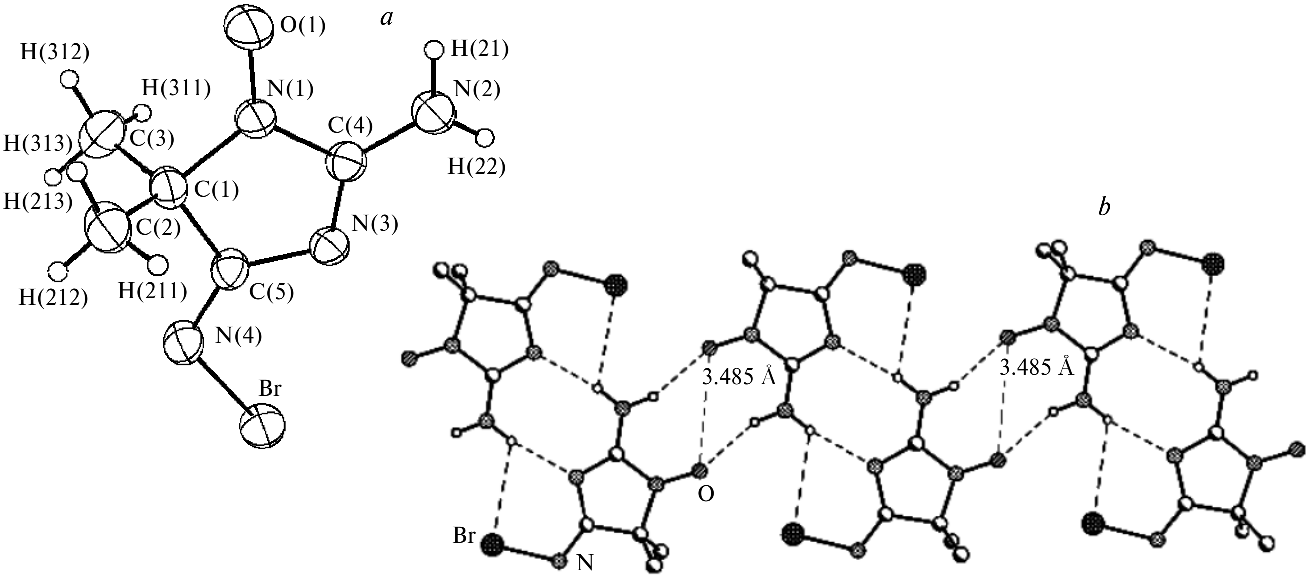


Fig. 6. Molecular structure of bromoporphyrexide **7** (*a*) and an H-bond system giving rise to polymeric ribbons (*b*) (hydrogen atoms of the methyl groups are omitted).

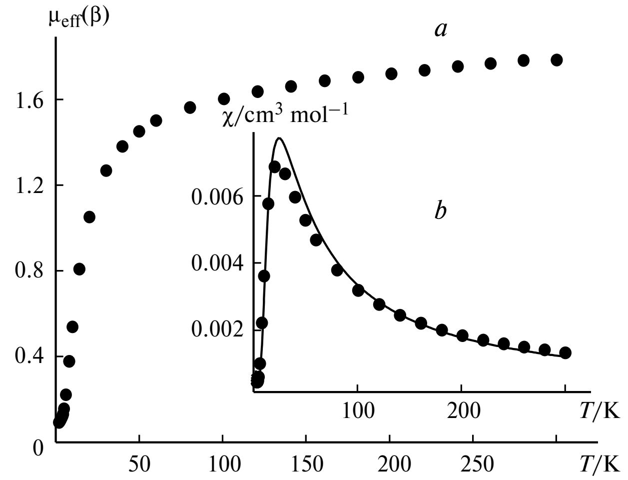


Fig. 7. Plots $\mu_{eff}(T)$ (*a*) and $\chi(T)$ (*b*) for compound **7** (experimental data are indicated by dotted lines and the calculated data are shown by a solid line).

Experimental

The IR spectra were recorded on a Bruker VECTOR-22 spectrophotometer (KBr pellets) in the 400—4000 cm^{-1} region. The melting points were determined on a Boetius hot-stage apparatus. Microanalyses were carried out on a Carlo Erba 1106 analyzer at the Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The mass spectra were obtained on a Finnigan MAT-8200 instrument (electron impact, 70 eV). The magnetic measurements were performed on a SQUID MPMS-5S (Quantum Desing) magnetometer in the temperature range of 2—300 K in magnetic field of 5 kOe.

1-Amino-2-(hydroxyamino)-2-methylpropylideneimidinium chloride (2) was prepared according to a known procedure.[12] Crystals of **2** suitable for X-ray diffraction study were grown as follows. Finely crystalline hydroxyamine **2** was dissolved in MeOH. The solution was diluted with a diethyl ether—hexane mixture (1 : 1, v/v). After 10 h, the growth of colorless well-faceted prismatic crystals started. IR, ν/cm^{-1}: 451, 568, 654, 740, 845, 916, 970, 1031, 1071, 1113, 1193, 1250, 1373, 1429, 1511, 1658, 1689, 2789, 3062, 3269 br.

(*E*)-1,2-Bis(1-amino-1-iminio-2-methylpropan-2-yl)diazene 1,2-dioxide dichloride (3) was synthesized according to a procedure described earlier.[13] Nitrosoamidine **3** was crystallized directly from a mixture as well-faceted colorless crystals. IR, ν/cm^{-1}: 420, 456, 565, 688, 757, 859, 960, 1071, 1152, 1189, 1213, 1301, 1372, 1468, 1516, 1685, 3051, 3370 br.

2,4-Diamino-5,5-dimethyl-5*H*-imidazole 1-oxide (4) was prepared by the reaction of **3** with NaCN in 80—90% yields.[13] Crystallization of **4** from a MeOH—water mixture afforded high-quality crystals of its dihydrate, **4**$\cdot$2H$_2$O, whereas crystallization from water gave colorless crystals of trihydrate **4**$\cdot$3H$_2$O. IR, ν/cm^{-1}: 498, 580, 706, 787, 944, 1047, 1110, 1154, 1176, 1216, 1251, 1367, 1381, 1448, 1590, 1686, 3245, 3441 br.

2-Amino-1-hydroxy-5,5-dimethyl-1*H*-imidazole-4(5*H*)-iminium nitrate (5). A solution of **4**$\cdot$3H$_2$O (140 mg, 0.07 mmol) in water (1 mL) was added to a solution of Cu(NO$_3$)$_2\cdot$3H$_2$O (85 mg, 0.35 mmol) in water (1 mL). The reaction mixture was stored for 3 days in an open flask. Colorless crystals of the same shape appeared on the bottom. One crystal was taken and used for X-ray diffraction study.

4-Amino-2-imino-5,5-dimethyl-2,5-dihydro-1*H*-imidazole 1-oxyl (1).[6] A solution of **4**$\cdot$3H$_2$O (0.1 g, 0.51 mmol) in water (0.1 mL) was added to a solution of K$_3$[Fe(CN)$_6$] (0.17 g, 0.52 mmol) in water (0.3 mL). An aqueous KOH solution (30 mg in 50 μL) was added to the resulting red solution, which was accompanied by a sharp intensification of the color and the appearance of the brown tint. Then the reaction mixture was cooled.

A. After fast cooling of the reaction mixture to ~0 °C, a finely crystalline red precipitate was obtained. The precipitate was filtered off and dried in air. Study by IR spectroscopy and magetochemical measurements demonstrated that the precipitate was an individual phase of nitroxide **1**. The yield was 41 mg (57%).

B. Slow cooling and storage of the reaction mixture at 5—6 °C for 14 h afforded rather large individual crystals and three types of crystal intergrowths. The total weight was 42 mg. X-ray diffraction study demonstrated that nitroxide **1** was obtained as red prisms, (*E*)-1,2-bis[1-amino-1-(cyanoimino)-2-methylpropan-2-yl]diazene 1,2-dioxide (**6**) was obtained as pale-brown prisms, and $K_4[Fe(CN)_6]$ was obtained as pale-yellow plates. After storage of the reaction mixture at 5—6 °C for one week, the initially formed crystals of nitroxide **1** completely disappeared. The precipitate contained only crystals of **6** and $K_4[Fe(CN)_6]$.

C. Before the synthesis, argon was bubbled through the solutions of the reagents. The synthesis and subsequent storage of the reaction mixture at 5—6 °C for 14 h were also performed under argon. The large red crystals of nitroxide **1** that formed were filtered off, washed with ice water (2×1 mL), and dried in air. The yield was 30 mg (42%). IR, ν/cm^{-1}: 409, 570, 649, 760, 815, 841, 1067, 1105, 1181, 1242, 1338, 1366, 1480, 1554, 1662, 3022, 3222, 3270. High-resolution MS. Found: m/z 141.0762 [M^+]. $C_5H_9N_4O$. Calculated: M = 141.0776. MS, m/z (I_{rel} (%)): 141 (19), 125 (7), 111 (31), 83 (39), 74 (42), 69 (100), 68 (52). $\mu = 1.71\ \mu_B$ (293 K).

(*Z*)-2-Amino-4-(bromoimino)-5,5-dimethyl-4,5-dihydro-1*H*-imidazole 1-oxyl (7). Compound **1** (100 mg, 0.7 mmol) was added to a stirred solution of NaBrO (0.68 g, 0.7 mmol), which was prepared by the addition of Br_2 (0.67 g, 4.2 mmol) to a solution of NaOH (0.5 g, 12.5 mmol) in water (3 mL). Argon was bubbled through the resulting dark-brown solution for 15 min. Then the reaction mixture was neutralized with a 25% aqueous AcOH solution (340 mg, 1.4 mmol). The dark-brown precipitate that formed was filtered off and dried in air. The yield was 125 mg (80%). Crystals suitable for X-ray diffraction study were grown from ethyl acetate. IR, ν/cm^{-1}: 554, 607, 693, 718, 757, 853, 933, 1096, 1155, 1191, 1277, 1375, 1475, 1549, 1611, 1699, 3107, 3379. $\mu = 1.73\ \mu_B$ (293 K). Found (%): C, 26.8; H, 3.6; N, 24.8. $C_5H_8BrN_4O$. Calculated (%): C, 27.3; H, 3.7; N, 25.5.

X-ray diffraction study. X-ray diffraction data sets were collected on a Smart Apex diffractometer (λMo-Kα, graphite monochromator, SMART V5.625, SAINT+ V6.0, SADABS, and Bruker AXS programs). The structures were solved by direct methods and refined by the full-matrix least-squares method using the SHELXTL program package.* The positions of the H atoms in the structures of **2—7** were located from difference electron density maps and refined isotropically along with the nonhydrogen atoms. The positions of the H atoms in the structure of **1** were calculated geometrically and refined using a riding model. The principal crystallographic characteristics and details of X-ray data study are given in Table 2.

For compound **1**, R_1 was 0.0579, which was due to poor quality of the crystals. Individual crystals of **1** were visually transparent. However, internal cracks were observed under a light transmission microscope. These cracks decreased the quality of the crystals and, consequently, X-ray diffraction data sets gave the higher *R* factors for the calculated structure. The crystal, from which X-ray data were collected, was obtained by cleaving from an intergrowth, which, apparently, gave rise to internal stresses, although visible defects were unobservable even under a microscope. In addition, all crystals of **1** were twins, and the structure was solved taking into account the twin model (1 0 0 / 0 1 0 / 0 0 –1; BASF = 0.4168), which made it possible to reduce the *R* factor by more than half.

This study was financially supported by the Russian Science Support Foundation, the Russian Academy of Sciences, the Siberian Branch of the Russian Academy of Sciences, the Russian Foundation for Basic Research (Project No. 05-03-32305), and the US Civilian Research and Development Foundation (CRDF, Grant Y2-C-08-01).

References

1. K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizumi, and Y. Ohashi, *J. Am. Chem. Soc.*, 1996, **118**, 1803.
2. K. Fegy, D. Luneau, T. Ohm, C. Paulsen, and P. Rey, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1270.
3. K. Fegy, N. Sanz, D. Luneau, E. Belorizky, and P. Rey, *Inorg. Chem.*, 1998, **37**, 4518.
4. V. I. Ovcharenko and R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Rev.*, 1999, **68**, 345].
5. S. J. Blundell and F. L. Pratt, *J. Phys.: Condens. Matter.*, 2004, **16**, R771.
6. O. Piloty and B. Graf Schwerin, *Ber. Deutsch. Chem. Ges.*, 1901, **34**, 1870.
7. H. G. Aurich and J. Trösken, *Tetrahedron*, 1974, **30**, 2515.
8. J. F. W. Keana, *Chem. Rev.*, 1978, **78**, 37.
9. L. B. Volodarsky, V. A. Reznikov, and V. I. Ovcharenko, *Synthetic Chemistry of Stable Nitroxides*, CRC Press, Florida, 1994.
10. Cambridge Structural Database, Version 5.26, November 2004 (Updates August 2005).
11. V. T. Kalinnikov and Yu. V. Rakitin, *Vvedenie v magnetokhimiyu* [*Introduction to Magnetochemistry*], Nauka, Moscow, 1980, 302 pp. (in Russian).
12. O. Piloty and B. Graf Schwerin, *Ber. Deutsch. Chem. Ges.*, 1901, **34**, 1863.
13. H. A. Lillevik and R. L. Hossfeld, *J. Org. Chem.*, 1942, **7**, 164.

---

* SHELXTL, V6.14, August 10, 2003.

Received February 22, 2006