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CONFORMATIONAL AND STRUCTURAL ANALYSIS OF bis(4-CHLOROQUINOLINE-N-OXIDE)HYDROGEN TRIBROMIDE

V. V. Romanov[1], Ya. P. Nizhnik[2], and A. D. Fofanov[1]

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The X-ray diffraction and conformational study of bis(4-chloroquinoline-N-oxide)hydrogen tribromide is performed. Two conformations corresponding to the minima on the energy curve are found by DFT using the ABINIT software. The model of one of the conformers generally matches with the structure determined experimentally for this compound using X-ray diffraction. In both instances, the structure with the dihedral angle (quinoline – N–O–H) close to 90° is most favorable, which is explained in terms of resonance theory and steric factors. It is concluded that oxygen atoms in the complex are in the *sp*^{3} hybridization state and the *sp*^{2} hybrid state of the oxygen atom is not possible here due to steric factors.

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Keywords: conformation, conformer, N-oxide, hybridization, X-ray diffraction study.

INTRODUCTION

In this article, we propose to use the conformational analysis of the salts of heteroaromatic N-oxides to estimate the possible occurrence of the *sp*^{2} hybridization state of the oxygen atom in these compounds.

Heteroaromatic N-oxides contain an oxygen atom bound to an endocyclic nitrogen atom of the aromatic heterocycle via a semipolar bond. Due to the features of the electronic structure of these molecules, the N–O group can exhibit both electron-donor and electron-acceptor properties depending on the structure [1, 2], which can be demonstrated by the example of mesomeric structures of pyridine N-oxide (Fig. 1).

It has recently been shown that in a range of heteroaromatic N-oxides, the rates of the reactions proceeding through the S_N mechanism are significantly accelerated by the complex formation of N-oxides with Lewis and Brønsted–Lowry acids [3-6]; therewith, the oxygen atom of the N-oxide group acts as a donor center. It was assumed [7, 8] that in different molecular complexes of heteroaromatic N-oxides the oxygen atom could be either in the *sp*^{3} hybridization state (Fig. 1, structure **1**; Fig. 2*A*), or in the *sp*^{2} hybridization state (Fig. 1, structure **2**; Fig. 2*B*).

To verify this hypothesis, it is necessary to analyze the energy of different conformations of adducts because a specific adduct structure can be associated solely with steric factors rather than the type of the oxygen atom hybridization (*sp*^{2} and *sp*^{3}). Given possible free rotation around the single N–O bond in the structure with the *sp*^{3} hybridized oxygen atom, we can use structure *A*, which predominantly occurs in the solid state in these adducts, for evaluating the energy of structure *B* in terms of steric factors. To this end, we should construct a dependence of the adduct energy on the dihedral angle between the aromatic ring plane and the N–O–A plane (A is the Lewis or Brønsted–Lowry acid). If the energy of the

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[1] Petrozavodsk State University, Petrozavodsk, Russia; vvromanov09@mail.ru. [2] Bioo Scientific Corp. Austin, Texas, USA; yakov_nizhnik@mail.ru. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 56, No. 2, pp. 381-386, March-April, 2015. Original article submitted December 19, 2013; revised August 25, 2014.

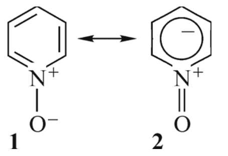

Fig. 1. Mesomeric structures of pyridine N-oxide.

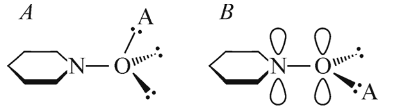

Fig. 2. Structure of the adducts of pyridine N-oxide with the oxygen atom in the sp^3 (*A*) and sp^2 hybridization (*B*) states.

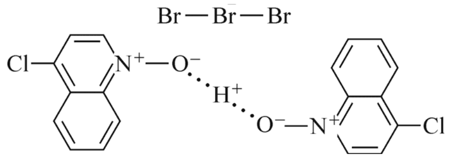

Fig. 3. Structural formula of bis(4-chloroquinoline-N-oxide)hydrogen tribromide.

structure corresponding to structure *B* corresponds to a maximum on energy dependence, then the possible existence of the complexes of N-oxides with the sp^2 hybridized oxygen atom could be brought into doubt.

Here, in order to study the above mentioned structural feature we the chose semi-salt of 4-chloroquinoline N-oxide, since, according to [7], it is the weak interaction between the oxygen atom in N-oxides and the acid center that should favor the sp^2 hybridized oxygen atom. Moreover, the symmetric ligand$\cdots H^+ \cdots$ligand structure makes the calculation of the energy dependence much easier, and a weak-base Br_3^- anion in the obtained semi-salt (Figs. 3 and 4) should not strongly interact with a weak Brønsted acid (the bis(4-chloroquinoline-N-oxide)hydrogen cation), in which the positive charge is mostly distributed between two ligands. Therefore, in the crystal structure, the anion should be located entirely in the outer coordination sphere of the complex and should not have a considerable effect on the cation structure.

RESULTS AND DISCUSSION

Synthesis of bis(4-chloroquinoline-N-oxide)hydrogen tribromide. Bis(4-chloroquinoline-N-oxide)hydrogen tribromide was synthesized from 4-chloroquinoline N-oxide (1), which in turn was obtained from quinoline (Fig. 4). Brown crystals of salt (5) form after the addition of bromine to the solution of 4-chloroquinoline N-oxide in acetonitrile (see Experimental).

The reaction of the product formation from 4-chloroquinoline N-oxide and molecular bromine is likely to proceed in three stages: (1) the formation of the molecular complex of N-oxide with bromine in the solution [10]; (2) the formation of bis(4-chloroquinoline-N-oxide)bromine tribromide [11]; (3) the transformation of bis(4-chloroquinoline-N-oxide)bromine tribromide into bis(4-chloroquinoline-N-oxide)hydrogen tribromide.

It seems that in the latter case, a redox reaction involving the solvent occurs, during which, in the excess of bromine, hydrogen tribromide (HBr_3) forms. A similar formation of hydrogen tribromide salts is not unusual and described in the literature [11, 12].

X-ray diffraction study of bis(4-chloroquinoline-N-oxide)hydrogen tribromide. Main crystallographic parameters are listed in Table 1; the ORTEP structure of the bis(4-chloroquinoline-N-oxide)hydrogen cation and ion packing in the crystal are shown in Fig. 5.

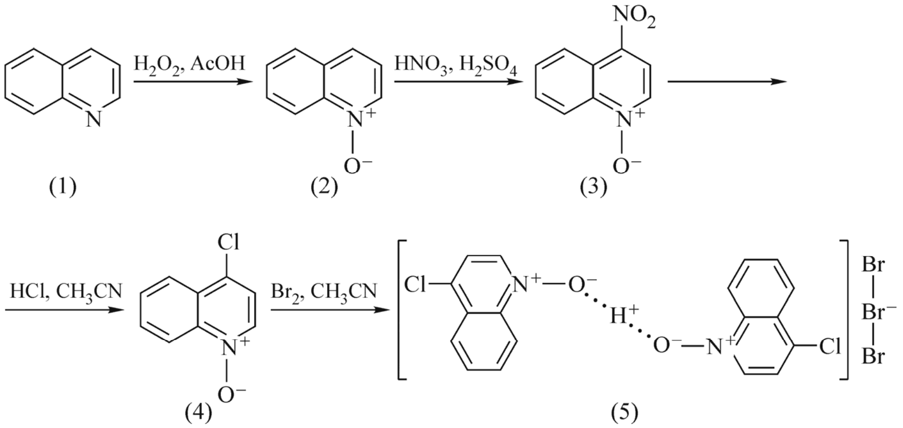

Fig. 4. Synthesis of bis(4-chloroquinoline-N-oxide)hydrogen tribromide.

TABLE 1. Crystallographic Parameters of bis(4-Chloroquinoline-N-oxide)hydrogen Tribromide

Chemical formula	$C_{18}H_{13}N_2O_2Cl_2Br_3$
M_r	599.93
X-ray wavelength, Å	0.71073
T, K	173(2)
Crystal system	Triclinic
Space group	P-1
a, b, c, Å	7.055(6), 7.877(7), 10.299(8)
α, β, γ, deg	94.23(3), 100.02(4), 114.04(2)
V, Å^3	508.0(7)
Z	1
R factor, %	3.52

The bond lengths, bond and torsion angles (Table 2) in the molecule of bis(4-chloroquinoline-N-oxide)hydrogen tribromide do not differ considerably from those for the analogous structures described in the literature. The dihedral angle between the planes drawn through the quinoline ring atoms and the N–O···H···O–N atoms is 87.5°, which apparently suggests the sp^3 hybridization state of the oxygen atom of the N$\rightarrow$O group (Fig. 2*A*).

Quantum mechanical simulation of conformational transitions in the bis(4-chloroquinoline-N-oxide)hydrogen ion. In order to construct the potential curve (Fig. 6), we rotated one of the quinoline planes around the N$\rightarrow$O bond with a step of 1°. Conventionally, it was assumed that a turning angle of zero corresponded to the parallel arrangement of the planes, as shown in Fig. 5*a* (the planes are parallel to and distant from each other). With a clockwise rotation of the upper quinoline plane (looking from O_1 to N_1) by 90°, the quinoline planes would be perpendicular and close to each other; with a rotation by 180°, they would be parallel and close to each other; with 270° rotation, they would be perpendicular to and distant from each other.

The obtained energy dependence is presented in Fig. 6. As can be seen from this dependence, the least favorable is the conformation in which the planes are mutually perpendicular and close to each other (a dihedral angle of 90°). It is this conformation that is characterized by the approach of the oxygen atom of the second ligand to one of the hydrogen atoms of the first ligand, which is accompanied by a significant increase in the energy (129 kJ/mol). When the dihedral angle is 270°, the oxygen atom of the second ligand and the hydrogen atom at the C1 carbon atom appear to be close to each other, which causes a relatively minor energy increase (11.3 kJ/mol). Thus, there are two minima at 0° and 180° on the graph corresponding to the antiparallel (↑↓, as with the structure determined by XRD) and parallel (↑↑) arrangement of quinoline

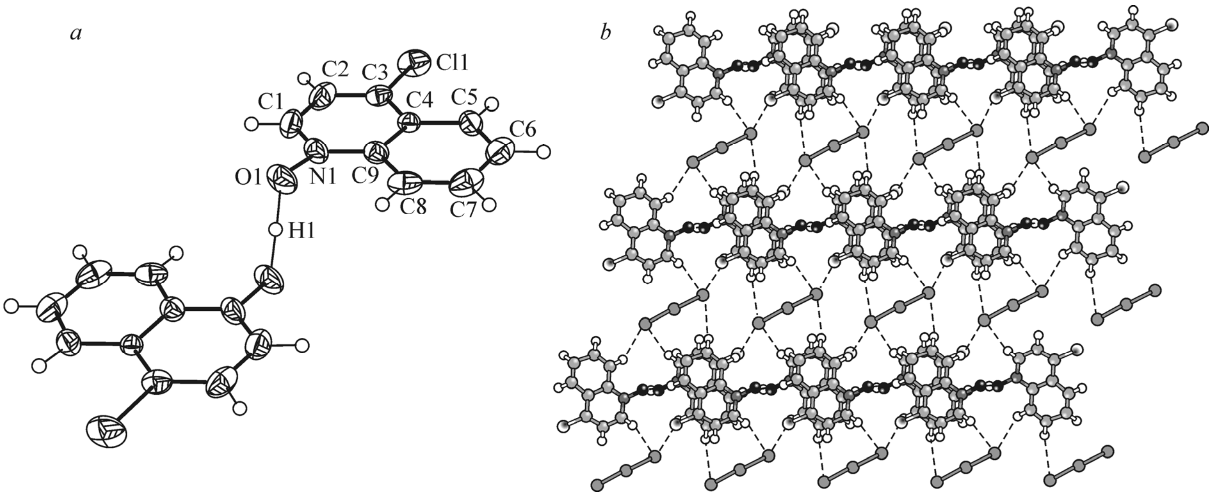

Fig. 5. Structure of the bis(4-chloroquinoline-N-oxide)hydrogen cation (*a*), ion packing in the crystal lattice of the salt along the *b* axis (*b*).

TABLE 2. Selected Interatomic Distances and Bond Angles in bis(4-Chloroquinoline-N-oxide)hydrogen Tribromide According to the XRD Data

Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Br1–Br2	2.5445(16)	N1–O1	1.360(3)	Br1–Br2–Br3	180.000(18)	O1–N1–C9	119.0(3)
Br2–Br3	2.5445(16)	O1–H1	1.216(2)	C1–N1–O1	118.9(3)	N1–O1–H1	109.45(19)
Cl1–C3	1.722(3)			C1–N1–C9	122.1(2)		

rings, and hence, under certain conditions, a metastable conformational polymorph with the parallel (↑↑) arrangement of quinoline rings can exist.

It is evident that the oxygen atom in the (4-chloroquinoline N-oxide) ligand is in the sp^3 hybridization state because the experimental and calculated dihedral angle between the quinoline ring plane and the plane of the N–O···H···O–N moiety is about 90° (corresponds to the 0° angle on the graph in Fig. 6). In the case of the sp^2 hybridization state of the oxygen atom, this dihedral angle should be 0° (corresponds to 90° and 270° angle, Fig. 6). However, if we assume the possible occurrence of the sp^2 hybridization state of the oxygen atom in this complex, then it is obvious that the geometric parameters of this complex will correspond to the maxima on the energy dependence. Hence, we do not preclude that the sp^2 hybridization state of the oxygen atom of the N→O group does not occur at all in rather stable complexes. The O(sp^2) geometry of such complexes (the dihedral pyridine – N–O–A angle is 0°, where A is the acid center in a Brønsted–Lowry or Lewis acid) can be typical of compounds with a weak orbital interaction or for adducts with a low rotation barrier relative to the N→O bond.

EXPERIMENTAL

Synthesis and characterization of the compounds. N-oxides of quinoline (dihydrate) [9], 4-nitroquinoline [9], 4-chloroquinoline [4, 9] were synthesized by the known procedures according to the scheme presented in Fig. 4.

Synthesis of bis(4-chloroquinoline-N-oxide)hydrogen tribromide. To a solution of 144 mg (0.8 mmol) 4-chloroquinoline N-oxide in 1 ml of absolute acetonitrile 0.05 ml (≈1 mmol) of bromide were added. The solution was kept for 1 h at room temperature and for 2 days at –20 °C. Yellow-orange crystals formed were washed with acetonitrile, ether and dried in the air. Yield: 143 mg (59 %). T_{melt} is 144-145 °C.

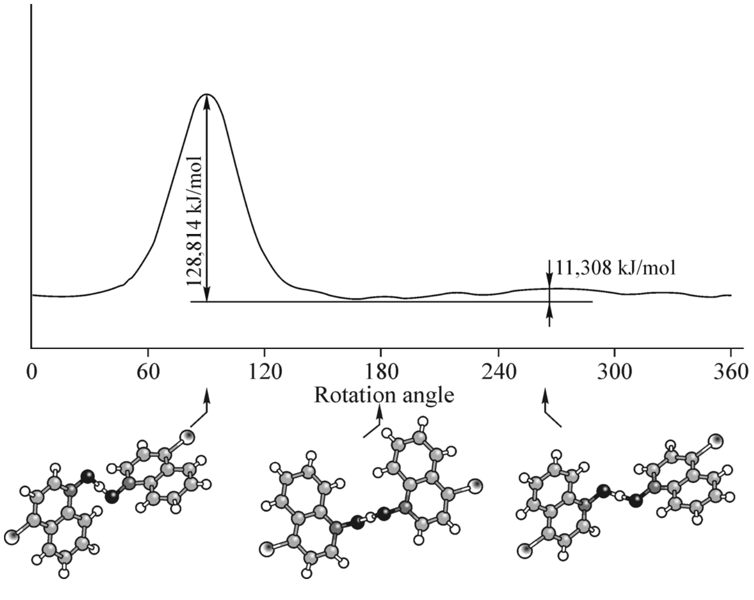

Fig. 6. Dependence of the bis(4-chloroquinoline-N-oxide)hydrogen ion energy on the rotation angle of one of the chloroquinoline planes around the respective N→O bond.

Single crystal XRD. The crystal structure of bis(4-chloroquinoline-N-oxide)hydrogen tribromide was determined by single crystal XRD on a Bruker SMART Apex diffractometer equipped with a CCD detector (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by a direct method, then all characteristics were refined by the least squares technique [13-15]. The structures were drawn using the ORTEP-3 [16] and Mercury 3.0 software.

The CIF file containing full information on the studied structure was deposited with CCDC under number 973663, from where it can be obtained on request via the following website: www.ccdc.cam.ac.uk/data_request/cif.

Quantum mechanical calculation technique. The energies of the conformations were calculated using the ABINIT software, in which the density functional procedure is implemented [17]. The calculation was performed in the local density approximation using the Troullier–Martins (TM) pseudopotentials and the plane-wave basis. In addition to ABINIT, we wrote a utility to vary the conformational parameters of the molecule according to the predetermined rules and generate the input data for ABINIT (corresponding to each particular conformation).

CONCLUSIONS

Based on the data of single crystal XRD and quantum mechanical calculations of the energy of bis(4-chloroquinoline-N-oxide)hydrogen tribromide conformations, we concluded that, in this case, the oxygen atom is in the sp^3 hybridization state. We assume that the sp^2 hybridization state of the oxygen atom of the N→O group does not occur at all in rather stable complexes.

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