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# Molecular Complexes of Heteroaromatic *N*-Oxides with Boron Trifluoride

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**Abstract—**Study of crystalline and molecular structure of complexes of 4-methyl-and 4-methoxypyridine *N*-oxides with boron trifluoride by the X-ray structural method and literature data analysis have shown that the donor-acceptor properties of substituents in aromatic rings do not influence the hybridization state ($sp^3$) of the oxygen atom.

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It is widely accepted that oxygen in the *N*-oxide group of heteroaromatic *N*-oxides is in the $sp^2$ hybridization state [1–3] and is conjugated to the heteroaromatic nucleus. However, it is not improbable that in the molecular complexes of *N*-oxides of pyridines with $BF_3$ the hybridization state of the oxygen atom can depend on the nature of substituents in the aromatic ring. We have found that all protons of pyridine rings in fluoroborides of 4-chloropyridine, pyridine, and 4-methylpyridine *N*-oxides have different chemical shifts in $^1$H NMR spectra in $CDCl_3$ and DMSO-$d_6$, but in the complexes of more basic 4-methoxypyridine and pyridine 4-(4-di-methylaminostyryl) *N*-oxides $H^{2,6}$ and $H^{3,5}$ protons are pairwise equivalent. It would be possible to understand this phenomenon from the viewpoint of different hybridizations of oxygen atoms bound to boron atoms in these complexes: $sp^2$ in the first three cases and $sp^3$ in the other two cases [4].

It is obvious that fast (in the NMR spectroscopy timescale) conformation ($OBF_3$ fragment rotation) changes of a molecule during the formation of a single bond between the pyridine ring nitrogen atom and the oxygen atom in the $sp^3$ hybrid state will lead to averaging chemical shifts of the $H^{2,6}$ and $H^{3,5}$ protons {as is the case with tetraphenylborate of 1-(dimethylcarbamoyloxy)-4-(4-methoxystyryl)pyridinium [5]}.

Data of X-ray structural analysis might be an important argument in favor of the oxygen atom rehybridization ($sp^2 \rightarrow sp^3$) in the reaction of heteroaromatic *N*-oxides with boron trifluoride.

We have studied crystal and molecular structure of complexes of 4-methyl- and 4-methoxypyridine *N*-oxides with $BF_3$ [4-MePyO·$BF_3$ (**I**) and 4-MeOPyO·$BF_3$ (**II**) (Figs. 1 and 2, Tables 1 and 2)] [6] by the X-ray single-crystal method, assuming that, according to the NMR data, in the first case the boron atom will be

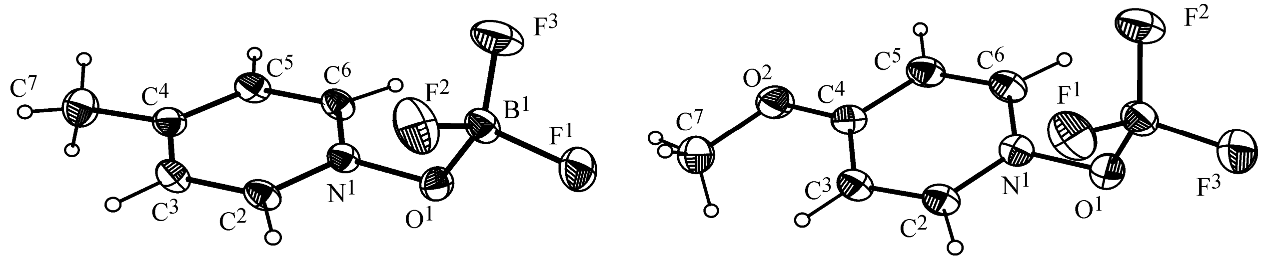

**Fig. 1.** General view of molecules of complexes of 4-methylpyridine (**I**) and 4-methoxypyridine (**II**) *N*-oxides with $BF_3$ (displacement ellipsoids are represented with a 50% probability).

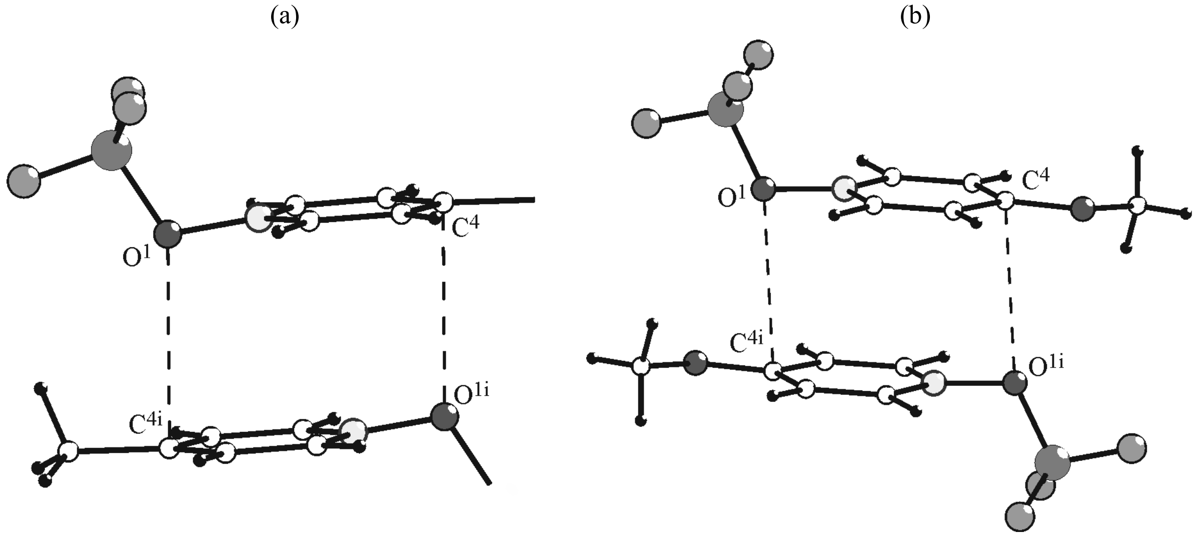

**Fig. 2.** General view of centrosymmetric dimers in crystal structures of molecular complexes of (a) 4-methylpyridine and (b) 4-methoxypyridine *N*-oxides with $BF_3$.

in the pyridine ring plane while in the second case it will not. However, it has turned out (Fig. 1, Table 1) that in crystals of adducts **I** and **II** valence angles N–O–B [113.95(15)° and 113.26(16)°], and also dihedral angles between the plane passing through N–O–B atoms and the pyridine ring plane (87.81° and 87.63°, respectively) are equal. Similar dispositions of the O–B bonds (Fig. 1) unambiguously point to the absence of conjugation between the oxygen atom of the *N*-oxide group and the heteroaromatic ring, i.e. the $sp^3$-hybrid state of this atom in crystals of both compounds.

**Table 1.** Bond lengths and angles in molecules of complexes of heteroaromatic *N*-oxides **I** and **II** with $BF_3$

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| | | **I** | |
| $O^1$–$N^1$ | 1.372(2) | $N^1O^1B^1$ | 113.95(15) |
| $O^1$–$B^1$ | 1.496(3) | $F^1B^1F^2$ | 110.88(17) |
| $O^2$–$C^4$ | 1.331(3) | $F^1B^1F^3$ | 111.13(18) |
| $O^2$–$C^7$ | 1.445(3) | $F^2B^1F^3$ | 110.6(2) |
| $F^1$–$B^1$ | 1.366(3) | $F^1B^1O^1$ | 104.05(19) |
| $F^2$–$B^1$ | 1.364(3) | $F^2B^1O^1$ | 109.63(17) |
| $F^3$–$B^1$ | 1.359(3) | $F^3B^1O^1$ | 110.38(16) |
| | | **II** | |
| $O^1$–$N^1$ | 1.370(2) | $N^1O^1B^1$ | 113.26(16) |
| $O^1$–$B^1$ | 1.502(3) | $C^4O^2C^7$ | 118.0(2) |
| $O^2$–$C^4$ | 1.331(3) | $F^1B^1F^2$ | 110.2(2) |
| $O^2$–$C^7$ | 1.445(3) | $F^1B^1F^3$ | 113.4(2) |
| $F^1$–$B^1$ | 1.359(3) | $F^2B^1F^3$ | 111.2(2) |
| $F^2$–$B^1$ | 1.367(3) | $F^1B^1O^1$ | 108.94(19) |
| $F^3$–$B^1$ | 1.368(3) | $F^2B^1O^1$ | 109.8(2) |
| | | $F^3B^1O^1$ | 103.0(2) |

This fact is in agreement with the $^1H$ NMR data for the complex 4-MeOPyO·$BF_3$ in $CDCl_3$ and DMSO-$d_6$ (pairwise equivalence of $H^{2,6}$ and $H^{3,5}$ protons) and does not agree with the presence of four types of protons in the pyridine ring of 4-MePyO·$BF_3$. It can result from special features of intermolecular interactions in a solution and in a crystal state.

In our complexes **I** and **II** the N–O and O–B bond lengths (Table 1) are comparable with published data for adducts of 4-nitropyridine and quinoline *N*-oxides with boron trifluoride {1.368(3) and 1.370(3) (N–O), 1.524(5) and 1.513(3) Å (O–B); dihedral angles between the plane passing through N–O–B atoms and the heterocycle plane are equal to 78.4(3)° and 81.6(3)° [7]}. Therefore, in the solid phase donor-acceptor properties of substituents ($NO_2$, Me, and OMe) in pyridine and quinoline rings do not influence the hybridization state ($sp^3$) of the oxygen atom in complexes of *N*-oxides with $BF_3$.

The tetracoordinated ($sp^3$ hybridized) boron atom in complexes **I** and **II** forms FBF valence angles of 110°–113°. Other Lewis acids ($FeCl_3$, $TlCl_3$, $TlBr_3$, $TLI_3$, etc.) unlike $BF_3$ are capable to form complexes with two pyridine *N*-oxide molecules (CSD refcode: IJIYIJ, CYPOTL10, DEPHAH, COHMIV [8]), in which molecules of acceptors are planar, and the coordination bond is formed by means of an oxygen atom in the $sp^3$-hybridized state ($C_5$NOmetal dihedral angle is 50°–82°).

A characteristic feature of the crystal structure of compounds **I** and **II** is the presence of a centrosymmetric dimer in both structures resulted from π-π and dipole-dipole interactions (Fig. 2). Distances between mean square planes (drawn through six atoms of a heterocycle) in dimers **I** and **II** are equal to 3.355 and 3.389(2) Å, respectively, and the shortest distances between atoms of two adjacent molecules in a dimer $O^1\cdots C^{4i}$ are 3.239(2) and 3.365(2) Å where $i = 0.5 - x$, $1.5 - y$, $1 - z$ for compound **I** (Fig. 2a) and $i = 1 - x$, $1 - y$, and $1 - z$ for compound **II** (Fig. 2b).

Deviations of $O^1$, $B^1$ and $C^7$ atoms (structure **I**) or $O^1$, $B^1$, and $O^2$ (structure **II**) from the above-mentioned planes are –0.135(1), 1.169(2), –0.086(4) and –0.111(2), 1.217(3), 0.032(2) Å, respectively.

Thus, at the moment the problem on a possibility of the $sp^2 \rightarrow sp^3$ rehybridization of oxygen atoms during the formation of molecular complexes of heteroaromatic *N*-oxides with boron trifluoride remains open. Further we are going to attract the gas electron diffraction in order to obtain additional information on the influence of intermolecular interactions on the structure of such adducts.

## EXPERIMENTAL

The $^1$H NMR spectra [4] were recorded in $CDCl_3$ and DMSO-$d_6$ on a Bruker WM 400 (400 MHz) spectrometer.

*N*-Oxides of 4-methylpyridine and 4-methoxypyridine were obtained as described in [9, 10]. Their molecular complexes **I** and **II** with boron trifluoride were prepared by adding equimolar amounts of $BF_3{\cdot}Et_2O$ to saturated solutions of corresponding *N*-oxides in acetone. Precipitated colorless crystals were dried in air. 4-MePyO·$BF_3$ (**I**), mp 125–127°C; 4-MeOPyO·$BF_3$ (**II**), mp 116–117°C.

Sets of diffraction reflections for crystals of compounds **I** and **II** were obtained on a CAD-4 single-crystal diffractometer using copper radiation (λ 1.54184 Å, a graphitic monochromator, ω-scanning) at room temperature. Crystal structures were determined by the direct method realized in program package SHELXS-97 [11, 12]. Position and heat parameters of non-hydrogen atoms were refined by the LS method in a full-matrix approximation (SHELXL97). Positions of hydrogen atoms were determined by Fourier differential synthesis and refined in an isotropic approximation without constraints. Interatomic distances C-H lie within the range of 0.87(3)–1.03(3) Å for structure **I** and 0.90(4)–1.02(5) Å for structure **II**. Isotropic heat parameters lie in the range of 0.05–0.14 (**I**) and 0.07–0.11 Å$^2$ (**II**). The main crystallographic data of compounds **I** and **II** are given in Tables 1 and 2.

**Table 2.** Crystallographic data of compounds **I** and **II**

| Compound | **I** | **II** |
|---|---|---|
| Formula | $C_6H_7BF_3NO$ | $C_6H_7BF_3NO_2$ |
| *M* | 176.94 | 192.94 |
| Crystal size | 0.1×0.1×0.4 | 0.1×0.1×0.1 |
| *T*, K | 296 | 296 |
| Crystal system | Monoclinic | Triclinic |
| Space group | *C*2/*c* | *P*-1 |
| *a*, Å | 10.907(1) | 6.9618(1) |
| *b*, Å | 11.910(1) | 7.9689(1) |
| *c*, Å | 12.222(2) | 8.1012(1) |
| α, deg | 90.00 | 80.37(2) |
| β, deg | 98.78(1) | 82.33(2) |
| γ, deg | 90.00 | 66.49(2) |
| *V*, Å$^3$ | 1569.2(3) | 405.21(9) |
| *Z* | 8 | 2 |
| $d_{calc}$, g/cm$^3$ | 1.498 | 1.581 |
| μ | 1.303 | 1.412 |
| θ, deg | 5.54–69.53 | 5.55–64.92 |
| Variation limits *h*, *k*, *l* | –13.12, 0.14, 0.14 | –8.8, –9.9, 0.9 |
| Total number of reflects | 1540 | 1489 |
| Number of independent reflects | 1469 | 1380 |
| Number of reflects with $I > 2\sigma s(I)$ | 1279 | 1173 |
| Number of refined parameters | 138 | 147 |
| $R(F^2)$ | 0.046 | 0.049 |
| $Rw\ (F^2)$ | 0.132 | 0.137 |
| Quality factor | 1.051 | 1.086 |

Structural data are deposited in the Cambridge Crystallographic Data Centre (CCDC 848664, 848665).

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