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Change in the Hybridization of the N→O Group Oxygen Atom upon Complex Formation of Pyridine and Quinoline *N*-Oxides with ν-Acceptors

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Abstract—It was shown on the basis of X-ray structural and NMR data that the ($sp^2 \rightarrow sp^3$) rehybridization of the oxygen atom of the N→O group can take place in reactions of heteroaromatic *N*-oxides with Lewis and Bronsted-Lowry acids. The hybridization type depends on the ligand and acceptor natures, composition of a complex, and spatial stresses arising during the complex formation.

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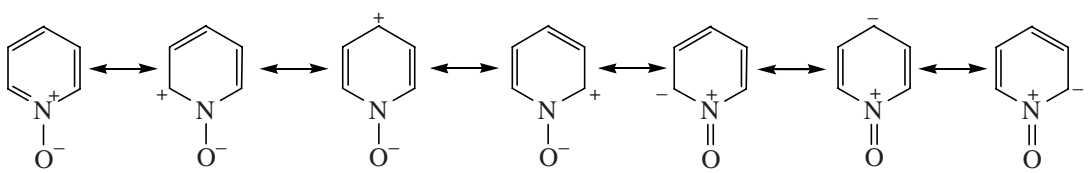
It is commonly accepted to consider that oxygen in the *N*-oxide group of heteroaromatic *N*-oxide is in the state of the sp^2-hybridization [1] in conjugation with a heteroaromatic ring. A low basicity of heteroaromatic *N*-oxides compared to their non-oxidized forms is normally caused by the presence of conjugation and a high electronegativity of the oxygen atom [2]. However a number of processes are known in which *N*-oxides possessing a lower basic capacity than the corresponding pyridine derivatives exhibit higher nucleophilic properties [3]. This circumstance served as the basis for systematic comparative study of the nucleophilic reactivity of *N*-oxides in relation to various electrophilic substrates (benzoyl chloride, diphenyl chlorophosphate, 4-toluene sulfobromide, and methyl iodide in acetonitrile and methyl chloroformiate in ethanol [4]), and also of the transfer of acetyl [5] and dimethyl carbomoyl [6] groups.

Heteroaromatic *N*-oxides are often named supernucleophilic reagents, and their "anomalous" behavior in relation to electrophilic reagents is referred to the accessibility of the reactive center. However, such low basic capacity of the *N*-oxides, apparently, cannot be compensated by steric accessibility of oxygen atom when its high electronegativity is taken into consideration. To account for unusually high nucleophilic properties of *N*-oxides, it is necessary to take into consuderation the fact that the order of the N→O bond in resonance structures of pyridine *N*-oxide (**1–7**) increases upon conjugation with an aromatic ring and in structures **5–7** this bond becomes double (Scheme 1).

A high polarizability is known to be one of special features of double bonds. Therefore, an electrophilic agent can cause the polarization of the N→O bond in the initial stage of the reaction with heteroaromatic *N*-oxides, during which (by analogy to mechanisms of reactions involving double bonds) the formation of a π-complex and then of a chemical bond with the oxygen atom is not ruled out.

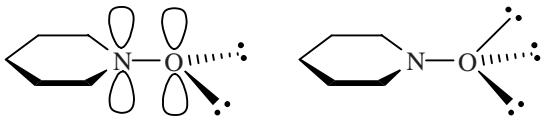
Scheme 1.



1 **2** **3** **4** **5** **6** **7**

In this case it is of fundamental importance to find out which of oxygen atomic orbitals is overlapped with the orbital of the electrophilic center. If the attack of the oxygen atom by an electrophilic agent is considered, one of its sp^2-hybrid orbitals can take part in the chemical bonding. At the same time the initial polarization of the N→O-group bond can result in oxygen atom ruling out from the conjugation with the aromatic ring and in its subsequent sp^2 (A)→sp^3 (B) rehybridization (Scheme 2).

Scheme 2.



A **B**

According to the proton magnetic resonance data for molecular complexes of *N*-oxides of pyridines with BF_3, their spatial structure and the hybridization of the oxygen atom can depend on the nucleophile basic capacity. We have found that all pyridine ring protons in the ^{1}H NMR spectra of boron fluorides of pyridine and 4-methylpyridine *N*-oxides, as expected, have different chemical shifts, but in complexes of more basic *N*-oxides of 4-methoxypyridine and 4-(4-dimethylaminostyryl)pyridine $H^{2,6}$ and $H^{3,5}$ protons are pairwise equivalent (Table 1). In our opinion this phenomenon appears well explicable from the viewpoint of different hybridization of oxygen atoms forming bonds with the boron atom in these complexes: sp^2 in the first two cases and sp^3 in the remaining [7]. It is obvious that fast (in the time scale of the NMR spectroscopy) conformational changes of a molecule upon the formation of a single bond between the nitrogen atom of the pyridine ring and the oxygen atom in the sp^3-hybridization state shall lead to averaging chemical shifts of $H^{2,6}$ and $H^{3,5}$ protons, as is the case with 1-dimethylcarbamoyloxy-4-(4-methoxystyryl)pyridinium tetraphenylborate [6]. However a possibility must not be completely ruled out for the existence of some complexes of heteroaromatic *N*-oxides [for example, in presence of substituents in positions **2** and **6** (Scheme 2)] in the form of one stable conformation where the oxygen sp^3-hybrid orbital forming bond with the boron atom is in the plane perpendicular to the pyridine ring and passing through N, O, and C^4 atoms.

The possibility of the oxygen atom rehybridization in heteroaromatic *N*-oxides can be either confirmed or disproved by the X-ray analysis of the products of reactions in which a bond involving oxygen is formed, for example, of complexes with Brønsted–Lowry and Lewis acids.

Table 1. ^{1}H NMR spectra of *N*-oxides of pyridine derivatives and of their molecular complexes with BF_3 in DMSO-d_6, δ, ppm

Compound	H^2	H^6	H^3	H^5	H^4	R
4-Chloropyridine *N*-oxide	8.20 d		7.50 d		–	–
4-Chloropyridine·*N*-oxide · BF_3	8.71 d	8.83 d	7.95 d	8.09 d	–	–
Pyridine *N*-oxide	8.17 d		7.36 t		7.27 t	
Pyridine *N*-oxide · BF_3	8.53 d	8.86 d	8.01 t	8.38 t	7.70 t	–
4-Methylpyridine *N*-oxide	8.29 d		7.42 d		–	2.47 s (CH_3)
4-Methylpyridine *N*-oxide · BF_3	8.46 d	8.98 d	7.60 d	8.07 d	–	2.59 s (CH_3)
4-Methoxypyridine *N*-oxide	8.01 d		6.97 d		–	3.82 s (OCH_3)
4-Methoxypyridine *N*-oxide · BF_3	8.68 d		7.45 d		–	4.05 s (OCH_3)
4-(4-Dimethylaminostyryl)pyridine *N*-oxide	8.04 d		7.48 d		–	7.20 d, 6.84 d (CH=CH), 7.39 d ($H^{2'}$, $H^{6'}$), 6.67 d ($H^{3'}$, $H^{5'}$), 3.00 s [$N(CH_3)_2$]
4-(4-Dimethylaminostyryl)pyridine *N*-oxide · BF_3	8.22 d		7.66 d		–	7.39 d, 6.98 d (CH=CH), 7.50 d ($H^{2'}$, $H^{6'}$), 6.78 d ($H^{3'}$, $H^{5'}$), 2.94 s [$N(CH_3)_2$]

In this respect the comparison of N→O-bond lengths and valence angles in a corresponding complex and in an initial *N*-oxide would be rather informative. However, according to the published data (Table 2), the formation of a chemical bond involving oxygen causes an elongation of the N→O bond not only in heteroaromatic *N*-oxides, but also in their non-aromatic analogs (nitrons and aliphatic *N*-oxides), and the values of NOA valence angles can deviate considerably from expected values owing to a steric repulsion between donor and acceptor molecules. In the case of trimethylamine *N*-oxide complexes the angle close to 109.5° is observed only when the electron acceptor is very small (Table 2, nos. **2–4**). Therefore, to clear up the hybridization type of the oxygen atom, we first of all should examine dihedral angles in molecular complexes of certain heteroaromatic *N*-oxides (and their analogs) with boron trifluoride, zinc and copper chlorides, and other ν-acceptors.

In the case of the only known [8] complex of BF_3 with a nitron—2-phenyl-1-oxa-3-azaspiro[4.5]decane *N*-oxide (Fig. 1) a pattern characteristic for the sp^3-hybrid state of the oxygen atom of the N→O group is observed: the $N^1O^2B^1$ angle is 112.9(1)°, and the dihedral angle between the plane passing through the $N^1O^2B^1$ atoms and the plane of the dihydrooxazole ring is 89.7(3)°.

The X-ray data suggest that the rehybridization of the oxygen atom in the N→O group can occur upon the formation of molecular complexes of hetero-aromatic *N*-oxides of pyridine derivatives with Brønsted–Lowry and Lewis acids. It follows from Table 3 that a considerable dihedral angle between the pyridine ring and NOA planes is observed in most cases. It points to the fact that the sp^3-hybrid orbital of the oxygen atom is involved in the complex formation. If the sp^2-hybrid orbital participates in the complex formation, such geometry would be impossible or the principle of the greatest orbital overlapping would be broken. The analogous situation is also traced for alkoxypyridine salts (Table 3, nos. **41** and **45**), which can be considered as complexes of *N*-oxides with carbo cations.

The N→O bond is elongated in all complexes presented in Table 3, that could point to a decrease in the order of this bond and, correspondingly, to an increase in contributions of resonance structures (Scheme 1, **1–4**) with a dominating sp^3-hybrid state of the oxygen atom. However, as it was noted above, this bond is elongated also in the case of the complex formation of *N*-oxides of aliphatic amines containing the sp^3-hybridized oxygen atom both in a free state and in complexes. Therefore, most likely, it cannot be a reliable proof of the hybridization change. For the same reasons the NOA valence angle in the case of

Table 2. X-ray data for *N*-oxides of trimethylamine and its complexes

Comp. no.	Electron acceptor	CSD refcode[a]	N–O bond length, Å	NOA angle, deg
1	–	TMEAMO	1.388	–
2	HCl	TMOHCL	1.424	109.88[b]
		TMOHCL01	1.421	110.40[b]
3	Pentachlorophenol	WOLZUS	1.415	104.26[c]
4	Pentachlorophenol ·H_2O	WOMBAB	1.414	107.79[c]
5	$Al(CH_3)_3$	WAWKEK	1.410	127.21
6	$ZnCl_2$	TAPHAT	1.402	124.56
			1.412	122.06
7	$ZnBr_2$	TAPHEX	1.410	124.75
8	ZnI_2	FIQBIQ	1.400	124.99
9	CoI_2	TAPGUM	1.420	125.25

[a] Hereinafter CSD refcode is a compound code in the Cambridge structural database. [b] NOCl angle. [c] NOH angle.

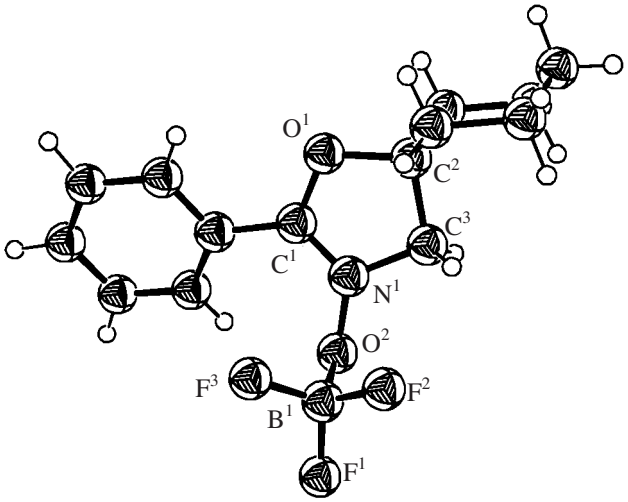


Fig. 1. Structure of the complex of boron trifluoride with 2-phenyl-1-oxa-3-aзaspiro[4.5]decane *N*-oxide [8].

complexes of heteroaromatic *N*-oxides cannot be a measure for the determination of hybridization state either. It is necessary to note that, as well as in the case of *N*-oxides of aliphatic amines, the NOA angle is close to the theoretically expected for the sp^3-hybrid state in the case of complexes with proton donors, for which the steric repulsion of components of a complex should be minimal owing to a small size of proton donors (Table 3, nos. **2–7, 19–21, 30–33, 53**, and **75**). However in adducts with bulk electron acceptors this angle is naturally increased up to 120°–130° and can reach 136° in the case of complexes with a high stoichiometric ratio (Table 3, no. **28**).

Let us consider the foregoing regularities in more detail using as an example complexes for which we have determined structure by the powder and single-crystal X-ray analyses.

The complex of 2-methylquinoline *N*-oxide with $CuCl_2$ (2 : 1) [10] can be considered as a trans-isomer (Fig. 2) with planar aromatic cycles almost parallel to each other to a first approximation. The dihedral angle between planes containing methylquinoline fragments is 10.88(8)°, and the coordination polyhedron formed by oxygen and chlorine atoms around the copper cation is not plane: oxygen atoms are arranged at 0.252 Å above the plane traced by the least-squares method through coordination polyhedron center, whereas the chlorine atoms are arranged at 0.265 Å under it. At the same time ClCuCl [164.97(7)°] and OCuO [166.80(16)°] angles slightly differ from 180°, and OCuCl valence angles are 94.83(10) ($O^1Cu^1Cl^1$) and 86.89(10)° ($O^1Cu^1Cl^{1a}$). The distortion of the plane geometry of the complex can result from steric difficulties caused by the presence of methyl groups in positions 2 of quinolinic rings, as is the case with similar complex of 2,6-lutidine *N*-oxide with $CuCl_2$ (Table 3, no. **36**) where chlorine and oxygen atoms are in vertexes of a strongly distorted tetrahedron.

The dihedral angle between the aromatic ring plane and the plane passing through NOCu atoms is 74.19°. It excludes a possibility of the conjugation of the oxygen atom of with the aromatic ring. In this case the most probable type of the oxygen atom hybridization is sp^3.

The main distinction of the complex formation involving a zinc atom is the fact that its *d* orbitals are energy degenerated and filled. In this case their

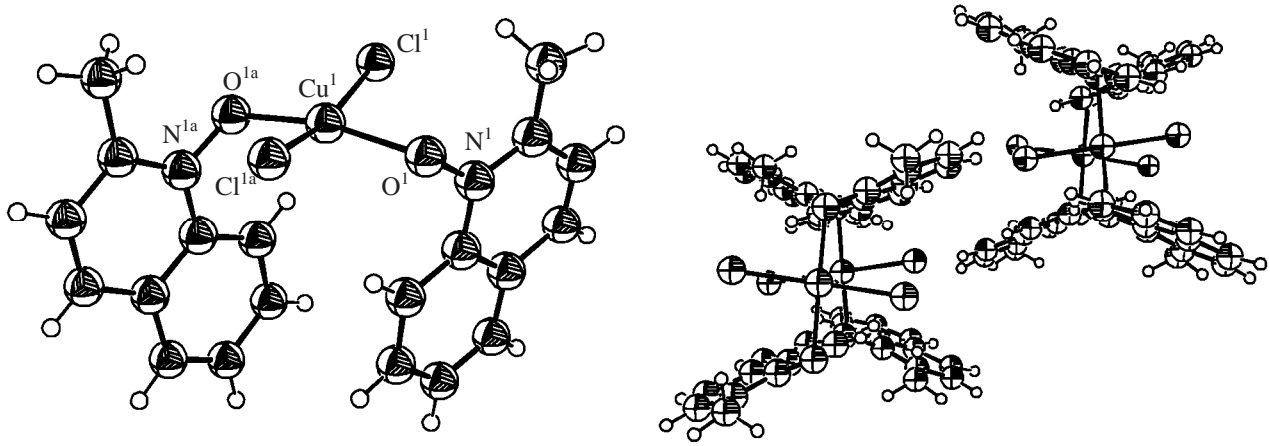


Fig. 2. Structure of the complex of 2-methylquinoline *N*-oxide with $CuCl_2$ (2:1) and package of its molecules in a crystal [10].

Table 3. X-ray crystal analysis for *N*-oxides of pyridine derivatives and their complexes

Comp. no.	Compound	CSD refcode	N–O bond length, Å	NOA angle, deg	Dihedral angle Py–(NOA), deg
1	Pyridine *N*-oxide	–	1.2806 [9]	–	–
		PYRDNO10	1.370	–	–
			1.326	–	–
		PYRDNO11	1.330		–
2	4-Methylpyridine *N*-oxide	PYOHCL	1.379	103.32	53.67
3	Pyridine *N*-oxide·CF_3COOH	PYOTCA01	1.355	107.41	78.04
4	Pyridine *N*-oxide·CCl_3COOH	PYOTCA10	1.379	107.77	81.49
5	(Pyridine *N*-oxide)$_2$·$HClO_4$	LOKFEW	1.352	112.48	29.16
6	(Pyridine *N*-oxide)$_2$·$HAuCl_4$	BALGUQ10	1.362	108.24	70.64
7	(Pyridine *N*-oxide)$_2$·$DAuCl_4$	XUNBAJ	1.314	110.20	19.00
8	Pyridine *N*-oxide OSiF(*t*-Bu)$_2$	CEYSUU	1.316	118.55	77.39
9	(Pyridine *N*-oxide)$_2$·$ZnBr_2$	FIPVUV	1.348	116.04	69.00
			1.324	121.21	35.84
10	(Pyridine *N*-oxide)$_2$·ZnI_2	IPNOZN01	1.350	116.81	64.70
			1.341	117.32	81.41
11	Pyridine *N*-oxide·$SnPh_3NCO$	FOGTIE	1.330	118.44	86.57
12	(Pyridine *N*-oxide)$_6$·$Cu(NO_3)_2$·$2H_2O$	CEKMUA	1.314	114.57	73.76
			1.336	120.62	64.91
			1.347	118.55	86.32
13	(Pyridine *N*-oxide)$_2$·$TlBr_3$	DEPHAH	1.348	115.65	81.56
14	Pyridine *N*-oxide·$Mo(O_2)_2O·H_2O$	ICIVUL	1.354	122.96	90.84
15	4-Methylpyridine *N*-oxide	NUSCAF	1.309	–	–
16	(4-Methylpyridine *N*-oxide)$_2$·2 $CO(NH_2)_2$	BAQZOI[a]	1.315	118.79	33.32
				129.78	40.98
17	(4-Methylpyridine *N*-oxide)$_2$·HI_3	MIWYEW[b]	1.344	114.34	3.95
			1.284	120.74	0.40
			1.329	110.49	92.62
					95.18
18	4-Methylpyridine *N*-oxide · 3,5-dinitrobenzoic acid	IDILAI	1.333	118.14	2.53
19	4-Methylpyridine *N*-oxide · 4-hydroxy-4'-nitrobiphenyl	RIDJOD	1.333	113.28	60.12
20	4-Methylpyridine *N*-oxide · 4-hydroxy-4'-nitrostilbene	RIDKUK	1.326	114.31	58.81
21	(4-Methylpyridine *N*-oxide)$_2$·$HAuCl_4$	JIFREV	1.341	106.92	60.22
22	(4-Methylpyridine *N*-oxide)$_2$·$CuCl_2$	CMPOCU	1.343	122.12	77.54
23	4-Methylpyridine *N*-oxide·$TlBrI_2$	GEHREQ	1.319	116.27	66.16
24	(4-Methylpyridine *N*-oxide)$_6$·$Cu(ClO_4)_2$	BACHIW	1.312	119.47	74.24
			1.325	116.11	91.09
			1.326	120.21	85.66

Table 3. (Contd.)

Comp. no.	Compound	CSD refcode	N–O bond length, Å	NOA angle, deg	Dihedral angle Py–(NOA), deg
25	(4-Methylpyridine *N*-oxide)$_6$·Zn(ClO$_4$)$_2$	BACHOC	1.309	119.44	75.82
			1.338	116.30	89.01
			1.352	118.98	89.26
26	(4-Methylpyridine *N*-oxide)$_6$·Co(ClO$_4$)$_2$	BEHRAH	1.328	120.45	86.99
			1.335	118.39	75.06
			1.340	117.35	88.18
27	(4-Methylpyridine *N*-oxide)$_2$·UO$_2$(NO$_3$)$_2$	EDANAY	1.346	132.33	38.79
28	(4-Methylpyridine *N*-oxide)$_2$·Yb(CF$_3$SO$_3$)$_3$	FUWFAE	1.288	133.59	89.62
			1.344	132.45	50.74
			1.344	128.60	83.89
			1.347	127.68	81.06
			1.348	127.40	81.57
			1.349	130.49	87.31
			1.377	135.64	53.16
29	(4-Methylpyridine *N*-oxide)$_2$·MoO$_2$Cl$_2$·CH$_3$CN	WOTPUQ	1.341	123.13	68.43
			1.349	124.73	87.42
30	2,6-Dimethylpyridine *N*-oxide · succinic acid	QEVMEJ	1.332	141.19	45.99
				112.89	86.95
31	2,6-Dimethylpyridine *N*-oxide · (pentachlorophenol)$_2$	LEQXAG	1.347	113.53	84.87
				103.06	75.04
32	(2,6-Dimethylpyridine *N*-oxide)$_2$·HClO$_4$	DMPOXP	1.341	114.71	90.74
33	(2,6-Dimethylpyridine *N*-oxide)$_2$·H$_2$SO$_4$	SAQKAW	1.361	106.43	72.07
			1.355	99.27	90.09
34	(2,6-Dimethylpyridine *N*-oxide)$_2$·HAuCl$_4$	ZUBDEF	1.354	116.77	74.12
35	(2,6-Dimethylpyridine *N*-oxide)$_2$·ZnCl$_2$	LUTOZN	1.348	118.57	84.86
36	(2,6-Dimethylpyridine *N*-oxide)$_2$·CuCl$_2$	LUTOCU10	1.361	121.73	88.32
			1.316	118.67	81.67
37	(2,6-Dimethylpyridine *N*-oxide)$_2$.Mn(III)ClOd$_4$TPP · *n*-heptane	DIBBAR	1.333	126.43	86.56
			1.326	128.94	87.68
38	2,6-Dimethylpyridine *N*-oxide·Sn(CH$_3$)$_3$Cl	CENCUT	1.326	130.60	86.28
39	2,6-Dimethylpyridine *N*-oxide·Sn(CH$_3$)$_2$Cl$_2$	BENFUV	1.352	123.02	88.42
40	2,6-Dimethylpyridine *N*-oxide·SnPh$_2$Cl$_2$	CENCON	1.346	125.77	87.30
41	*N*-Methoxy-2,6-dimethylpyridinium perchlorate	CANTIU	1.392	110.17	91.02
42	4-Methoxypyridine *N*-oxide · 2,4-dinitrophenol	NELTIH	1.348	112.80	74.88
43	(4-Methoxypyridine *N*-oxide)$_2$·CuCl$_2$	PIJDUH	1.354	121.50	81.72
44	(4-Methoxypyridine *N*-oxide)$_2$·SbF$_2$·H$_2$O	FMXPSB	1.356	120.13	89.25
45	*N*-Benzyloxy-4-methoxypyridinium perchlorate	SIRWUL	1.402	110.79	82.29
46	4-Cyanopyridine *N*-oxide	CYPYRO	1.304	–	–
47	4-Cyanopyridine *N*-oxide · 4-hydroxy-4'-nitrobiphenyl	RIDLEV	1.323	119.37	62.77
48	4-Cyanopyridine *N*-oxide · 4-hydroxy-4'-nitrostilbene	RIDPAV	1.318	114.64	59.42
49	(4-Cyanopyridine *N*-oxide)$_2$·TlCl$_3$	CYPOTL10	1.315,	111.74,	74.93
			1.334	120.13	49.73
50	4-Nitropyridine *N*-oxide	NTPYRO	1.260	–	–
		NTPYRO03	1.297	–	–
		NTPYRO11	1.298	–	–
		NTPYRO12	1.291	–	–

Table 3. (Contd.)

Comp. no.	Compound	CSD refcode	N–O bond length, Å	NOA angle, deg	Dihedral angle Py–(NOA), deg
51	4-Nitropyridine *N*-oxide · 4-aminobenzoic acid	COFCEF10	1.304	126.96	47.89
52	4-Nitropyridine *N*-oxide · 2-aminobenzoic acid	SOJPEM	1.306	124.22	15.73
53	4-Nitropyridine *N*-oxide · 3-hydroxybenzoic acid	SUVZEO	1.309	114.56	88.53
54	4-Nitropyridine *N*-oxide · 4-nitrobenzoic acid	CUZDAC	1.314	126.18	0.61
55	4-Nitropyridine *N*-oxide · 4-nitrophenol	JUDNAX	1.303	122.26	11.16
56	4-Nitropyridine *N*-oxide · 3-aminophenol	NPOAPL	1.283	132.70	10.32
57	4-Nitropyridine *N*-oxide · 4-hydroxy-4'-nitrobiphenyl	RIDPEZ	1.311	118.31	45.80
58	4-Nitropyridine *N*-oxide · 4-hydroxy-4'-nitrostilbene	RIDQIE	1.339	124.72	72.13
			1.318	126.59	76.15
59	(4-Nitropyridine *N*-oxide)$_2$·Cu(NO$_3$)$_2$	KEKXAZ	1.335	124.81	86.69
				119.81	69.20
60	(4-Nitropyridine *N*-oxide)$_2$·Co(NO$_3$)$_2$·4H$_2$O	LESWIP	1.324	124.46	64.14
61	4-Nitropyridine *N*-oxide)$_2$·CdCl$_2$	YARNIO	1.294	127.90	45.81
62	(4-Nitropyridine *N*-oxide)$_2$·CdI$_2$	YARNOU	1.334	114.47	80.47
63	3-Methyl-4-nitropyridine *N*-oxide	MNPYDO	1.292	–	–
		MNPYDO01	1.288		
		MNPYDO02	1.298		
64	3-Methyl-4-nitropyridine *N*-oxide · 2-aminobenzoic acid	NIMBAM	1.310	121.11	19.97
65	3-Methyl-4-nitropyridine *N*-oxide · 3,5-dinitrobenzoic acid	FAFTAH	1.315	128.65	15.23
66	3-Methyl-4-nitropyridine *N*-oxide · 2,4,6-trinitrophenol	FAFTEL	1.505	114.05	6.57
67	3-Methyl-4-nitropyridine *N*-oxide · hydroquinone	PUYTAE	1.316	123.75	0.11
				122.99	46.50
68	(3-Methyl-4-nitropyridine *N*-oxide)$_2$·ZnCl$_2$	LEQVIM	1.333	118.59	51.77
				123.83	55.82
69	(3-Methyl-4-nitropyridine *N*-oxide)$_2$·ZnBr$_2$	PEDKAK	1.326	122.73	48.15
			1.327	124.60	44.94
70	(3-Methyl-4-nitropyridine *N*-oxide)$_2$ ·ZnI$_2$	TETTUH	1.332	122.17	52.86
			1.313	124.35	48.00
71	(3-Methyl-4-nitropyridine *N*-oxide)$_2$·Cd(SCN)$_2$	IWENIH	1.308	123.06	84.17
72	(3-Methyl-4-nitropyridine *N*-oxide)$_2$·CdCl$_2$	TETVIX01	1.308	126.96	42.46
73	(3-Methyl-4-nitropyridine *N*-oxide)$_2$ ·CdBr$_2$	WERMEL	1.311	125.76	45.64
74	(3-Methyl-4-nitropyridine *N*-oxide)$_2$·Sn(CH$_3$)$_2$Cl$_2$	NUMZUQ	1.325	129.31	88.37
75	2,2'-Bipyridine 1-oxide · HReO$_4$	PEPDAP	1.328	106.92	6.92
76	2,2'-Bipyridine *N,N*'-dioxide · (4-aminobenzoic acid)	HUZCUA	1.324	125.66	13.76
77	1,1'-Biisoquinoline *N,N*'-dioxide · binaphthol · CH$_2$Cl$_2$	HIMGUF	1.327	109.56	26.27
			1.314	121.19	16.46
78	2-(Nitramino)pyridine *N*-oxide · methylamine	IJIVOM	1.320	119.02	1.93
				128.19	14.38
79	Picolinic acid *N*-oxide	PICANO	1.340	96.17	0.00
		PICANO03	1.342	98.71	0.00
80	2,6-Dicarboxypyridine *N*-oxide	DCXPYO	1.340	106.61	2.30
			1.337	105.60	0.58
				104.14	4.77
				103.86	3.87
81	2-Carboxy-6-methylpyridine *N*-oxide	CXMPYO	1.341	98.72	0.00

Table 3. (Contd.)

Comp. no.	Compound	CSD refcode	N–O bond length, Å	NOA angle, deg	Dihedral angle Py–(NOA), deg
82	2-Acetylpyridine-*N*-oxide N-dimethylthiosemicarbazone	HOCLUG	1.316	102.84	1.21
83	Quinaldinic acid *N*-oxide	KONNEG	1.333	97.52	3.32
84	8-Hydroxyquinoline *N*-oxide	HQUINO10	1.334	98.96	5.45
85	Bis(2-thio-6-picoline *N*-oxide) · copper(II)	CAQCAY	1.345	117.47	3.15
86	Bis(2-thio-6-picoline *N*-oxide) · zinc(II)	CAQCAY	1.340	115.85	6.51
			1.342	114.75	6.48
87	Bis[bis(2-thiopyridine-*N*-oxide) · zinc(II)]	OXPZND	1.373	115.41	8.53
				115.16	71.59

[a] Two carbamide molecules form hydrogen bridges with the sp^2-hybrid oxygen atom of *N*-oxide: the dihedral angle Py–($NOC_{carbamide}$) is equal to zero. [b] Two conformation varieties of salt in one sample.

participation in hybridization would not be expected and, therefore, the sp^3 hybridization is most probable for this complexing agent, that makes impossible overlapping of its orbitals with the non-hybrid oxygen orbital in the 2-methylquinoline *N*-oxide complex with $ZnCl_2$, which we have studied [11] (Fig. 3). The values of valence angles of all bonds with zinc atoms point to it. The value of the ClZnCl angle as high as 120.43° is connected with the electrostatic repulsion between chlorine anions. The dihedral angle between the heteroaromatic ring plane and the plane passing through NOZn atoms (89.68°) and general geometry of the complex point to the withdrawal of the oxygen atom from the conjugation with the aromatic system and correspond to its sp^3-hybrid state. The same pattern is also observed for similar complexes of zinc chloride with pyridine *N*-oxide (Table 3, nos. **9, 10, 35**).

At the same time, in some cases the dihedral angle Py–(NOA) is very small that can point to the sp^2-hybrid state of the oxygen atom of the *N*-oxide group. It follows from Table 3 that it refers to the complexes formed by low-basic *N*-oxides and/or weak acids (Table 3, nos. **16, 18, 52, 54–57, 64–67**, and **75–78**). In spite of the fact that an adduct is formed by a proton donor, the NOA angle is about 120°, that is typical for

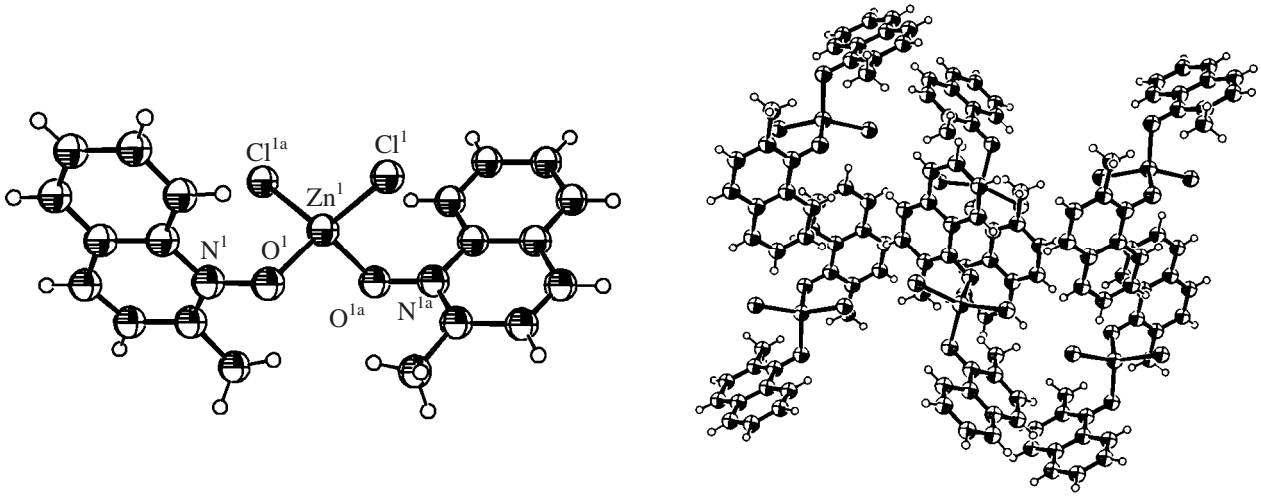


Fig. 3. Structure of the complex of 2-methylquinoline *N*-oxide with $ZnCl_2$ (2:1) and package of its molecules in a crystal [11].

the sp^2-hybrid trigonal state. Deviations from this angle (Table 3, nos. **54, 56, 65, 66**, and **75–78**) can result from special features of the complex structure a steric stress (**75–78**) or features of the crystal lattice formation.

The dihedral angle Py–(NOA) in *N*-oxides containing a proton-donor centre (Table 3, nos. **79–84**) is practically equal to zero. The similar pattern is observed in the complexes of bidentate *N*-oxides with a functional group in the second position of the pyridine ring capable to a complex formation. In these cases we also can assume that the oxygen atom is in the sp^2-hybridization state. However, it is necessary to note that theoretically, owing to the free rotation around the single N→O bond in the case of the sp^3-hybride oxygen atom, this dihedral angle can accept any values including those close to zero. In particular, in the dinuclear complex of 2-thiopyridine *N*-oxide with Zn(II) (Table 3, no. **87**) the oxygen atom of the *N*-oxide group is linked with two zinc atoms to form the dihedral Py–(NOZn) angles of 8.53° and 71.59°, that obviously point to the sp^3-hybridization of the oxygen atom. Therefore, most likely, a small dihedral angle cannot be the absolute criterion for the sp^2-hybridization of the oxygen atom of the *N*-oxide group. However, taking into account steric restrictions imposed by substituents in the *ortho* position, we can assume that it is so in most cases.

It is most probable that the oxygen atom in binuclear complexes can be in the sp^2-hybride state. However in this case the oxygen atom is not conjugated with an aromatic heterocycle. The X-ray powder data for the binuclear complex of $CuCl_2$ with quinoline *N*-oxide of (1:1, 2:2) composition (Fig. 4) point to the exit of oxygen from the conjugation with a heterocycle upon the complex formation [12]. In this case a four-membered cycle involving two copper atoms and two oxygen atoms of *N*-oxide groups is formed. The planes of the quinolinic rings are oriented at right angels 90(2)° to the plane of the four-membered cycle $Cu^1O^1Cu^{1a}O^{1a}$. Such mutual arrangement of cycles makes the conjugation of oxygen to aromatic system impossible. It is necessary to note that copper and oxygen atoms are in the same plane that excludes the sp^3-hybrid state of the oxygen atom. Therefore, we can assume that the oxygen atom in similar complexes is in the sp^2-hybrid state, and the hybrid orbitals participate in bonding with copper atoms. The non-hybrid *p* orbital with an electron pair (Scheme 3) in complex **C** should be arranged perpendicularly to the four-membered cycle $Cu^1O^1 \cdot Cu^{1a}O^{1a}$. It is necessary to emphasize that Cu–O bonds are unequal: the Cu^1–O^1 and Cu^{1a}–O^{1a} bonds have the length of 2.11(2) Å, and Cu^1–O^{1a} and Cu^{1a}–O^1 2.00(2) Å. The shortening of one of Cu–O bonds points to the additional overlapping of oxygen non-hybrid *p* orbital and a metal orbital.

The valence angle CuOCu [102(1)°] is less than that for the sp^2-hybrid state, which is caused the rigidity of the four-membered Cu^1–O^1–Cu^{1a}–O^{1a} cycle; if this angle is increased up to 120°, the OCuO angle, which is 78(1)° in this adduct, would be decreased, whereas for the copper(II) atom in the sp^2d-hybridization state it should be 90°. The small CuOCu valence angle gives rise to causes the increase in NOCu angles up to 126.3(15) and 129.7(15)°, which is also observed for binuclear complexes of *N*-oxides of pyridine derivatives (Table 4). As is the case with binuclear complexes of pyridine derivatives, the length of the N→O bond in complex **C** [1.30(2) Å] is essentially longer that this bond of 1.269(7) Å in the

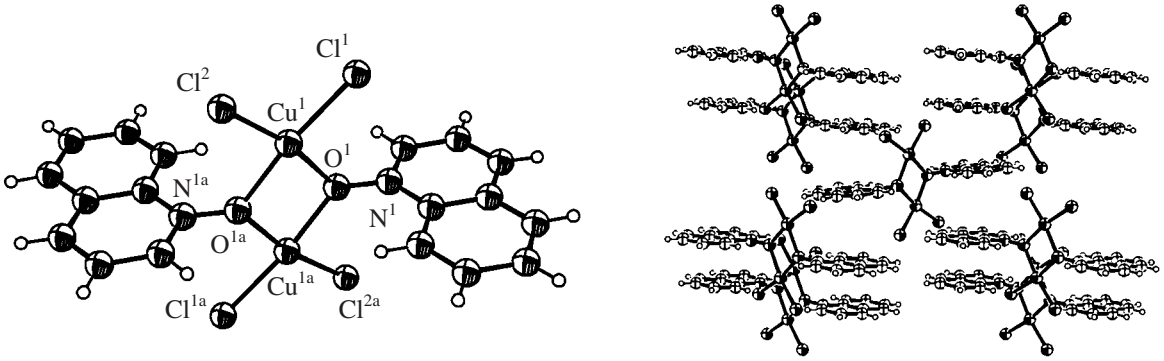
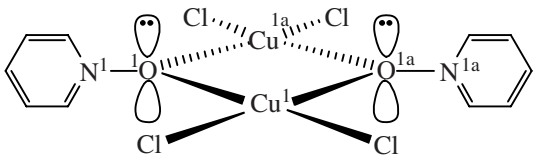


Fig. 4. Structure of the binuclear complex of quinoline *N*-oxide with $CuCl_2$ (1:1) and package of its molecules in a crystal [12].

Scheme 3.



C

initial *N*-oxide [13]. Most likely, the elongation of the N→O bond, as is the case with complexes of trimethylamine *N*-oxide (Table 2), is caused by the repulsion of donor and acceptor molecules.

Thus, the oxygen atom in the complexes of *N*-oxides with $CuCl_2$ (1:1) may be considered as being in the sp^2-hybridization state, in which the orbital with an unshared electron pair ruled out from the conjugation with the aromatic ring, is overlapped with a vacant copper orbital.

EXPERIMENTAL

The molecular complexes of heteroaromatic *N*-oxides were synthesized according to the published procedures [14-16]. The ^{1}H NMR spectra were taken on a Bruker WM 400 instrument at room temperature in DMSO-d_6 using TMS as an interior standard.

Conditions of the powder single-crystal X-ray experiments and the determination of atomic-molecular structure of compounds are described in [10–13].

Bond lengths and angles were calculated using the Mercury 1.4 program [17]. For the molecular graphics the program ORTEP-3 for Windows was used [18].

Table 4. X-ray crystal analysis data for binuclear complexes of *N*-oxides with metals (M)

Comp. no.	Compound	CSD refcode	N–O bond length, Å	NOM angle, deg	Dihedral angle Py–(NOM), deg	Dihedral angle Py–(NOM'O'), deg
1	(Pyridine *N*-oxide)$_2$·(CuCl$_2$)$_2$	CUCPYO11	1.345	127.82, 123.49	63.44, 75.64	70.01
2	Pyridine *N*-oxide)$_4$·(CuCl$_2$)$_2$[a]	CPYOCU	1.343 1.323	125.15, 124.70 126.31	69.54, 64.99 32.48	67.24 –
3	(Pyridine *N*-oxide)$_2$·(CuCl$_2$)$_2$·2H$_2$O[b]	CAPYOC CAPYOC01 CAPYOC02	1.353 1.386 1.346	124.67, 125.72 123.89, 125.61 124.13, 125.23	89.54, 84.39 89.44, 84.13 80.76, 86.36	87.59 86.95 87.42
	(Pyridine *N*-oxide)$_2$·(CuCl$_2$)$_2$·2DMSO[b]	POCSCU10	1.368	124.18, 124.46	60.48, 78.21	69.37
4	(Pyridine *N*-oxide)$_2$·(CuBr$_2$)$_2$	PYOCDB	1.371	124.45, 125.16	76.77, 89.39	83.30
5	(Pyridine *N*-oxide)$_2$·[Cu(NO$_3$)$_2$]$_2$	CUNPYO10	1.362 1.361	118.66, 124.11 119.43	88.51, 41.01 64.45	70.56 –
6	(4-Methylpyridine *N*-oxide)$_2$·(CuBr$_2$)$_2$	DURYIY	1.358	123.07,127.43	76.86, 69.56	73.81
7	(4-Methylpyridine *N*-oxide)$_4$·(CuCl$_2$)$_2$[a]	CMPYUC	1.350 1.350	123.57, 124.89 123.88	66.67, 46.72 27.50	57.64 –
8	(4-Phenylpyridine *N*-oxide)$_2$·(CuCl$_2$)$_2$·H$_2$O[b]	PHPYOC	1.371 1.348	123.08, 126.59 124.07, 124.57	84.86, 72.82 71.06, 87.97	79.67 79.22
9	(4-Methoxypyridine *N*-oxide)$_4$·[Cu(NO$_3$)$_2$]$_2$[a]	MXPOCU	1.311 1.337	114.71, 124.96 118.46	86.65 76.08	77.38 –
10	(4-Nitropyridine *N*-oxide)$_2$·(HgCl$_2$)$_2$	JEXMOO	1.316	121.03, 117.57	61.77, 73.06	86.23

[a] Binuclear complexes, in which two *N*-oxide molecules participate in the formation of an (MOM'O') cycle, and two other molecules are extraligands, forming bonds with metal atoms. [b] Water and DMSO are extraligands.

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