Chemistry of Heterocyclic Compounds, Vol. 39, No. 9, 2003

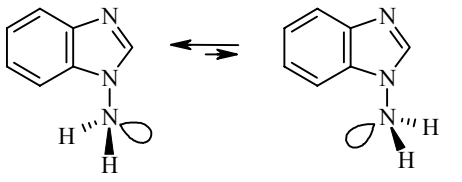
N-AMINO DERIVATIVES OF CONDENSED IMIDAZOLE SYSTEMS

M. G. Koroleva[1], O. V. Dyablo[1], A. F. Pozharskii[1], and Z. A. Starikova[2]

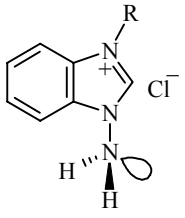
The previously unknown 1-amino- and 3-aminonaphtho[1,2-d]imidazoles, 1-aminonaphtho[2,3-d]-imidazole, 1-aminophenanthro[9,10-d]imidazole and the N-amino-N'-methylimidazolium picrates corresponding to them have been obtained by direct amination of a series of condensed imidazoles with O-picrylhydroxylamine. An X-ray structural investigation of 1-amino-3-methylnaphtho[1,2-d]-imidazolium picrate showed that, in difference to 1-aminobenzimidazolium salts, a conformation exists in it in which the hydrogen atoms of the N–NH_2 group are directed to the side of the meso carbon atom.

Keywords: N-aminoazoles, O-picrylhydroxylamine, conformations of the N-amino group, X-ray structural analysis, electrophilic amination.

It is known that the amino group in N-amino azoles is in a pyramidal configuration (sp^3-hybridization of the nitrogen atom) and several types of conformation are shown for it differing in the deflection angle relative to the N–(NH_2) bond [1,2]. For example, in 1-aminobenzimidazole derivatives the amino group is usually folded in such a way that the unshared electron pair of the nitrogen atom lies exactly in the plane of the cyclic system and may be turned either towards the μ-carbon atom (conformation **1A**) or in the direction of the benzene ring (**1B**). It was shown by X-ray structural analysis that in the solid form both for 1-aminobenzimidazole itself [2] and for its quaternary salts **2a,b** [3] conformation **1A** exists which is presumably stabilized by electrostatic attraction between the unshared pair of electrons of the amino group and the strongly positive hydrogen atom at position 2 of the imidazole ring. It is interesting that a similar conformation was also discovered in the crystals of 9-amino-1-methylxanthine (**3**) [4] and 1-aminoperimidine (**4**) [5].



1A **1B**



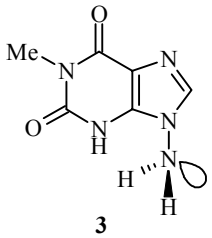
2a,**b**

2 a R = Me, **b** R = NH_2

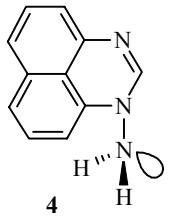
[1] Rostov State University, Rostov-on-Don 344090, Russia; e-mail: ODyablo@chimfak.rsu.ru. [2] A. N. Nesmeyanov Institute of Organoelement Compounds, Moscow 117813, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1324-1335, September, 2003. Original article submitted December 13, 2001.

0009-3122/03/3909-1161$25.00

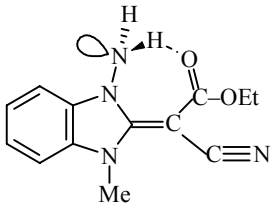
There is little reliable information on the **1A** ↔ **1B** equilibrium in solution. However it was established with the aid of dipole moments that in solution form **1A** is predominant [6]. As far as we know, only in crystals of 1-amino-2-(1-cyano-1-ethoxycarbonylmethylene)-3-methylbenzimidazoline (**5**) was the opposite orientation of the NH protons established, due to the formation of an intramolecular hydrogen bond [7].



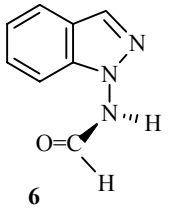
3



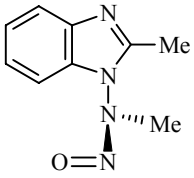
4



5

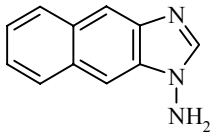


6

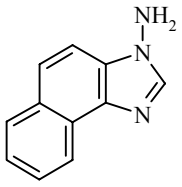


7

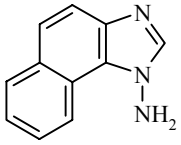
The configuration of the amino group is clearly changed in N-amino azoles containing electron-withdrawing substituents, such as CHO and NO, at the exocyclic nitrogen atom. In 1-formylaminoindazole (**6**) [8] and 2-methyl-1-(nitrosomethylamino)benzimidazole (**7**) [9] the nitrogen atom of the substituted amino group is completely flattened (sp^2-hybridization) while the formamido- and nitrosomethylamino groups are disposed almost perpendicular to the plane of the aromatic system.



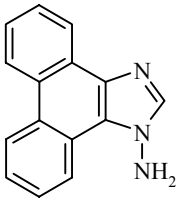
8



9



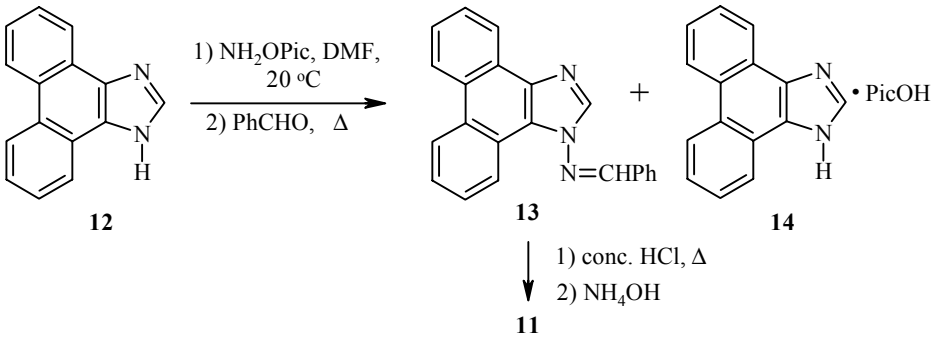
10



11

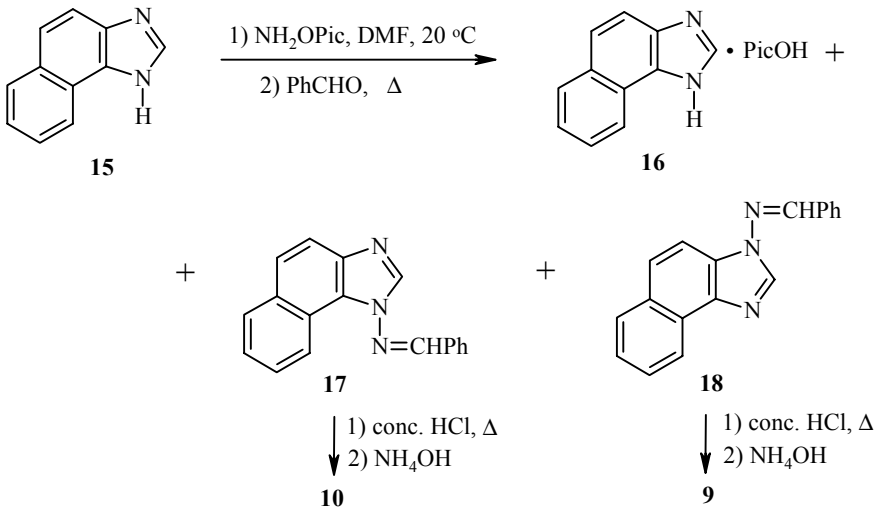
The aim of the present work was to investigate the conformations of the amino group in N-aminoimidazoles condensed with naphthalene **8-10** and phenanthrene **11** systems. It may be assumed that in some of these compounds, particularly **10** and **11**, the conformation of the NH_2 group for steric reasons will be closer to type **1B**, i.e. different from 1-aminobenzimidazole.

Regretably, due to the poor solubility of the initial imidazoles in aqueous and aqueous alcoholic solutions of alkali their amination with hydroxylamine O-sulfate was unsuccessful. Consequently as aminating agent we used O-picrylhydroxylamine which is less available but capable of working in nonaqueous media [10]. The amination of phenanthro[9,10-*d*]imidazole (**12**) was carried out in DMF solution at room temperature. A twofold excess of the initial imidazole was put into the reaction since half of it is consumed to form picrate **14**. The amine was not isolated, the reaction mixture was treated with benzaldehyde and the resulting Schiff's base **13** was purified by column chromatography. The yield was 37%. Hydrolytic decomposition of **13** on boiling in conc. HCl gave 1-aminophenanthro[9,10-*d*]imidazole (**11**) in 94% yield.



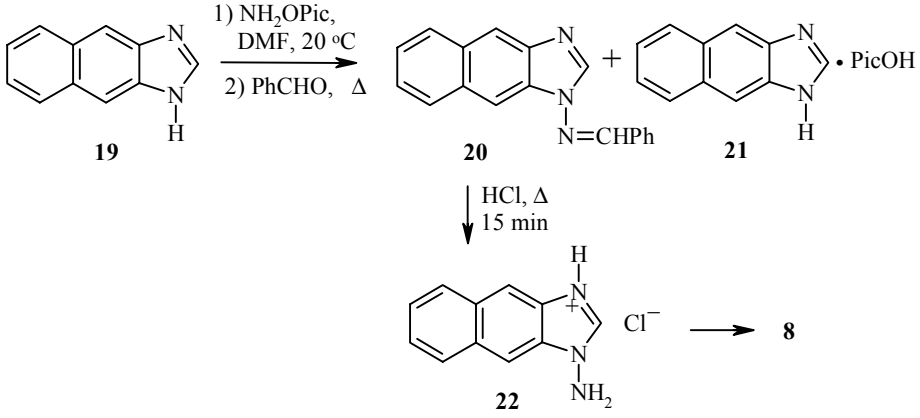
12 **13** **14** **11**

The amination of naphtho[1,2-*d*]imidazole (**15**) with subsequent boiling of the reaction mixture with benzaldehyde leads to the formation of the isomeric 1-benzylideneamino- (**17**) and 3-benzylidene-aminonaphtho[1,2-*d*]imidazoles (**18**). Their yields were 8 and 49% respectively, which is very close to the ratio of the similar isomers on methylation of naphtho[1,2-*d*]imidazole [11]. The hydrolysis of azomethines **17** and **18** proceeds smoothly and gives amines **10** and **9** in good yield.



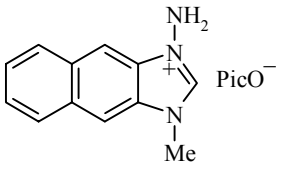
15 **16** **17** **18** **10** **9**

Naphtho[2,3-*d*]imidazole (**19**) is aminated by O-picrylhydroxylamine somewhat worse. The yield of azomethine **20** did not exceed 31%. Subsequent boiling in conc. HCl gives 1-aminonaphtho[2,3-*d*]imidazole (**8**).

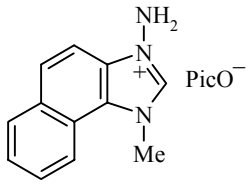


19 **20** **21** **22** **8**

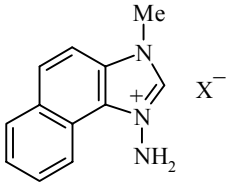
N-Methyl derivatives of imidazoles are aminated by O-picrylhydroxylamine at room temperature in a mixture of chloroform and acetonitrile with the formation of N-aminoimidazolium salts **23-26**. Yields were 84-99%.



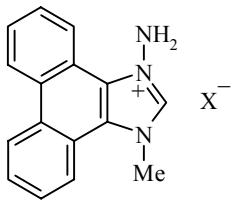
23



24



25a,b



26a,b

25, **26 a** X = PicO, **b** X = Cl

Analysis of the ^{1}H NMR spectra of the amines obtained enabled some opinions to be expressed on their predominant conformation in solution. As is seen from Table 1 the chemical shifts of the 2-H proton in bases **1**, **8-11** (8.12-8.35 ppm) and imidazolium salts **23-26** (9.61-9.87 ppm) were little changed. On the other hand the position of the signal of the NH_2 group protons varied within very wide limits, from 6.13 for 1-aminobenzimidazole to 6.69 and 6.73 ppm respectively for 1-aminonaphtho[1,2-*d*]imidazole and 1-aminophenanthro[9,10-*d*]imidazole. The particularly significant displacement towards low field of the δNH_2 signal in the case of the latter two substances is logically explained in our opinion by the fact that in them the NH_2 protons undergo the effect of the diamagnetic field from the side of two benzene rings, while for all the remaining amines only one benzene ring exerts such an effect. This indirectly points in favor of the existence of conformation **1A**, since in conformations of type **1B** the NH_2 group protons if covered by the magnetic force lines of the ring current are unimportant. It is also impossible to exclude however the mobile equilibrium between both forms with a predominance of form **1A**. Regretably, there is no information up to the present on the size of the barrier to amino group rotation about the N–N bond in N-amino azoles, without which it is difficult to make an unequivocal choice in favor of one or the other possibility. The data of ^{1}H NMR spectroscopy for the N-aminoimidazolium salts obtained may also be interpreted in favor of the predominance of conformation **1A** in solution.

Regretably we did not succeed in growing crystals of amines **8-11** suitable for X-ray structural analysis. However such crystals were obtained for 1-amino-3-methylnaphtho[1,2-*d*]imidazolium picrate (**25a**). On the basis of the investigations carried out (see Fig. 1 and Tables 2-5) it is possible to draw the following conclusions.

1. The naphthoimidazole fragment in salt **25a** is practically planar.

2. The nitrogen atom of the N-amino group is in the sp^3-hybridized state (sum of the valence angles at the amine nitrogen is 324.4°).

3. A conformation of type **1B** stabilized by hydrogen bonds with the picrate anion (Fig. 1) has been detected for the first time for N-aminoimidazolium salts in the crystals of compound **25a**. One of the NH protons forms a bifurcated bond with the *ortho*-nitro group and the phenolic oxygen (this is the most stable

TABLE 1. Data of ^{1}H NMR Spectroscopy of the Compounds Synthesized

Compound	Chemical shifts, δ, ppm (*J*, Hz)*				
	N–CH_3	N–NH_2	H(2)	CH=N	Other protons
1*[2]	—	6.13	8.07	—	—
2*[2]	4.04	6.92	9.71	—	—
8	—	6.22	8.35	—	7.40 (2H, m, 6-, 7-H); 7.99 (1H, s, 9-H); 8.03 (2H, m, 5-, 8-H); 8.18 (1H, s, 4-H)
9	—	6.34	8.15	—	7.48 (1H, m, 8-H); 7.61 (1H, m, 7-H); 7.74 (2H, m, 6-, 9-H); 8.00 (1H, d, J_{54} = 8.0, 5-H); 8.45 (1H, d, J_{45} = 8.1, 4-H)
10	—	6.69	8.12	—	7.60 (4H, m, 6-, 7-, 8-, 9-H); 8.00 (1H, d, J_{54} = 8.0, 5-H); 9.08 (1H, d, J_{45} = 8.1, 4-H)
11	—	6.75	8.12	—	7.65 (4H, m, 5-, 6-, 9-, 10-H); 8.51 (1H, m, 11-H); 8.83 (2H, m, 7-, 8-H); 9.22 (1H, d, J_{45} = 7.5, 4-H)
13	—	—	8.97	9.30	7.70 (7H, m, 3'-, 4'-, 5'-, 5-, 6-, 9-, 10-H); 8.09 (2H, m, 2'-, 6'-H); 8.59 (1H, m., 11-H); 8.88 (2H, m, 7-, 8-H); 9.09 (1H, m, 4-H)
17	—	—	8.53	8.87	7.52 (4H, m, 2'-, 3'-, 5'-, 6'-H); 7.67 (1H, m, 4'-H); 7.84 (2H, m, 7-, 8-H); 7.96 (3H, m, 5-, 6-, 9-H); 8.66 (1H, d, J_{45} = 8.1, 4-H)
18	–	–	9.07	9.30	7.58 (4H, m, 2'-, 3'-, 5'-, 6'-H); 7.68 (1H, m, 4'-H); 7.95 (4H, m, 6-, 7-, 8-, 9-H); 8.21 (1H, d, J_{54} = 8.2, 5-H); 8.51 (1H, d, J_{45} = 8.1, 4-H)
20	–	–	8.56	8.89	7.46 (2H, m, 3'-, 5'-H); 7.52 (3H, m, 2'-, 4'-, 6'-H); 7.98 (4H, m, 5-, 6-, 7-, 8-H); 8.19 (1H, s, 9-H), 8.30 (1H, s, 4-H)
23	4.11	6.98	9.87	—	7.66 (2H, m, 6-, 7-H); 8.23 (2H, m, 5-, 8-H); 8.44 (1H, s, 4-H); 8.56 (1H, s, 3-H); 8.57 (2H, s, 3'-, 5'-H)
24	4.47	7.06	9.70	—	7.83 (2H, m, 7-, 8-H); 7.96 (1H, d, J_{67} = 9.0, 6-H); 8.21 (1H, d, J_{45} = 9.0, 5-H); 8.26 (1H, d, J_{98} = 8.0, 9-H); 8.59 (2H, s, 3'-, 5'-H); 8.64 (1H, d, J_{45} = 9.0, 4-H)
25a	4.14	7.38	9.61	—	7.79 (2H, m, 7-, 8-H); 8.10 (3H, m, 5-, 6-, 9-H); 8.56 (2H, s, 3'-, 5'-H); 9.12 (1H, d, J_{45} = 8.1, 4-H)
25b	4.17	7.50	9.75	—	7.81 (2H, m, 6-, 7-H); 8.12 (2H, m, 8-, 9-H); 8.24 (1H, d, J_{54} = 8.4, 5-H); 9.16 (1H, d, J_{45} = 8.4, 4-H)
26b	4.50	7.48	9.67	—	7.87 (4H, m, 5-, 6-, 9-, 10-H); 8.63 (1H, m, 4-H); 9.02 (2H, m, 7-, 8-H), 9.35 (1H, m, 11-H)

* The ^{1}H NMR spectra were taken in $CDCl_3$ (compounds **17** and **20**) and in DMSO-d_6 (remaining compounds).

*[2] Data were taken from [3] and are given for comparison.

hydrogen bond with a distance of 2.13 Å), while the second NH proton forms a second hydrogen bond with the *para*-nitro group of another picrate anion. It is interesting that forked hydrogen bonds also exist between the 2-H of the imidazolium ring and the phenolate oxygen and the second *ortho*-nitro group. It remains unclear whether the existence of conformation **1B** for salt **25a** is a consequence of the impossibility of the existence of form **1A** due to steric obstacles from the side of the 10-H atom or is the result of the energetically more beneficial formation of a cation–anion pair. The existence of 1-amino-3-methylbenzimidazolium picrate in the solid state as form **1A** [12] points indirectly in favor of the first hypothesis.

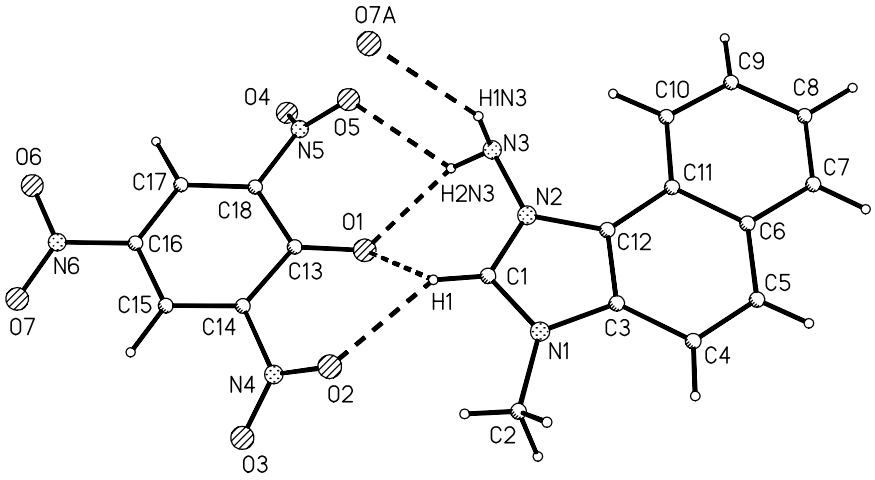


Fig. 1. Crystallographic numbering of atoms and molecular structure of compound **25a**.

TABLE 2. Crystallographic Data for Compound **25a**.

Empirical formula	$C_{18}H_{14}N_6O_7$
Molecular weight	426.35
Unit cell type	Triclinic
Unit cell parameters	a = 8.366(13) Å; α = 78.04(9) deg. b = 9.869(12) Å; β = 84.34(12) deg. c = 11.355(12) Å; 74.39(12) deg.
Unit cell volume, Å^3	882.4(19)
Z, calculated density, mg/m^3	2, 1.605
Absorption coefficient, mm^{-1}	0.127
Crystal dimensions	0.45 × 0.30 × 0.25
Type and color	Rhombohedron, bright yellow
Range of θ, deg	1.84-30.21
Completeness of data obtained, %	98.8
Method of refinement	Full matrix least squares for F_{hkl}^2
Number of independent reflections	5016 (R_{int} = 0.0262)
Number of parameters refined	336
Final R factors [for 3241 reflections with $I > 2\sigma(I)$]	R_1 = 0.0593, wR_2 = 0.1467
Final R factors for all independent reflections	R_1 = 0.0819, wR_2 = 0.1613

TABLE 3. Coordinates of Atoms and Equivalent Isotropic Factors (U_{eq}) and Isotropic Factors (U_{iso}) for Hydrogen Atoms in the **25a** Molecule

Atom	x	y	z	U_{eq}/U_{iso}
1	2	3	4	5
O(1)	0.2537(2)	0.7274(1)	-0.1365(1)	29(1)
O(2)	0.4819(2)	0.8881(2)	-0.1429(1)	39(1)
O(3)	0.5676(2)	0.8464(1)	0.0382(1)	32(1)
O(4)	-0.1328(2)	0.6256(1)	0.0300(1)	31(1)
O(5)	-0.0851(2)	0.7452(2)	-0.1472(1)	34(1)
O(6)	-0.1191(2)	0.9350(1)	0.3218(1)	31(1)
O(7)	0.1248(2)	0.9692(1)	0.3390(1)	29(1)

TABLE 3 (continued)

1	2	3	4	5
N(1)	0.5448(2)	0.7973(2)	-0.4373(1)	23(1)
N(2)	0.2999(2)	0.7520(2)	-0.4218(1)	22(1)
N(3)	0.1372(2)	0.7434(2)	-0.3765(2)	27(1)
N(4)	0.4593(2)	0.8596(2)	-0.0330(1)	27(1)
N(5)	-0.0667(2)	0.7119(2)	-0.0380(1)	24(1)
N(6)	0.0270(2)	0.9330(2)	0.2836(1)	23(1)
C(1)	0.4006(2)	0.8082(2)	-0.3732(2)	24(1)
C(2)	0.6862(2)	0.8448(2)	-0.4096(2)	29(1)
C(3)	0.5368(2)	0.7299(2)	-0.5319(2)	22(1)
C(4)	0.6584(2)	0.6920(2)	-0.6230(2)	25(1)
C(5)	0.6167(2)	0.6244(2)	-0.7031(2)	26(1)
C(6)	0.4573(2)	0.5919(2)	-0.6968(2)	24(1)
C(7)	0.4181(2)	0.5222(2)	-0.7833(2)	28(1)
C(8)	0.2673(2)	0.4915(2)	-0.7792(2)	30(1)
C(9)	0.1457(2)	0.5281(2)	-0.6867(2)	28(1)
C(10)	0.1783(2)	0.5943(2)	-0.6000(2)	25(1)
C(11)	0.3335(2)	0.6285(2)	-0.6041(1)	21(1)
C(12)	0.3818(2)	0.6997(2)	-0.5218(1)	20(1)
C(13)	0.2003(2)	0.7815(2)	-0.0460(2)	22(1)
C(14)	0.2946(2)	0.8465(2)	0.0162(1)	21(1)
C(15)	0.2421(2)	0.8930(2)	0.1224(2)	21(1)
C(16)	0.0835(2)	0.8850(2)	0.1728(1)	21(1)
C(17)	-0.0188(2)	0.8266(2)	0.1184(2)	21(1)
C(18)	0.0382(2)	0.97784(2)	0.0144(1)	21(1)
H(1)	0.3740(20)	0.8480(20)	-0.3048(17)	23(5)
H(2A)	0.7880(30)	0.7550(30)	-0.3890(20)	63(8)
H(2B)	0.7210(30)	0.9070(30)	-0.4780(20)	51(7)
H(2C)	0.6590(30)	0.8790(30)	-0.3430(20)	56(7)
H(1N3)	0.0690(30)	0.8280(30)	-0.3999(19)	37(6)
H(2N3)	0.1420(30)	0.7210(30)	-0.2950(20)	47(7)
H(4)	0.7650(30)	0.7170(20)	-0.6226(17)	32(5)
H(5)	0.6960(30)	0.5930(20)	-0.7627(19)	36(6)
H(7)	0.5030(30)	0.4980(20)	-0.8470(20)	40(6)
H(8)	0.2380(30)	0.4450(20)	-0.8461(18)	33(5)
H(9)	0.0410(30)	0.5060(20)	-0.6813(18)	30(5)
H(10)	0.0920(30)	0.6190(20)	-0.5309(19)	32(5)
H(15)	0.3190(20)	0.9360(19)	0.1635(16)	20(4)
H(17)	-0.1380(30)	0.8220(20)	0.1601(18)	32(5)

TABLE 4. Some Bond Lengths (*l*) and Valence Angles (ω) in the **25a** Molecule

Bond	*l*, Å	Angle	ω, deg
1	2	3	4
O(1)–C(13)	1.244(2)	O(4)–N(5)–C(18)	118.16(16)
O(2)–N(4)	1.229(2)	O(7)–N(6)–O(6)	122.64(17)
O(3)–N(4)	1.236(3)	O(7)–N(6)–C(16)	118.96(17)
O(4)–N(5)	1.234(2)	O(6)–N(6)–C(16)	118.40(17)
O(5)–N(5)	1.230(2)	N(1)–C(1)–N(2)	110.25(18)
O(6)–N(6)	1.252(3)	N(1)–C(1)–H(1)	124.9(12)
O(7)–N(6)	1.243(2)	N(2)–C(1)–H(1)	124.9(12)
N(1)–C(1)	1.336(3)	N(1)–C(3)–C(12)	107.55(18)

TABLE 4 (continued)

1	2	3	4
N(1)–C(3)	1.391(3)	N(1)–C(3)–C(4)	129.24(17)
N(1)–C(2)	1.467(3)	N(2)–C(12)–C(3)	105.86(17)
N(2)–C(1)	1.338(3)	N(2)–C(12)–C(11)	131.96(16)
N(2)–C(12)	1.387(3)	O(1)–C(13)–C(14)	124.25(17)
N(2)–N(3)	1.425(3)	O(1)–C(13)–C(18)	123.52(18)
N(3)–H(1N3)	0.88(2)	C(14)–C(13)–C(18)	112.12(17)
N(3)–H(2N3)	0.91(3)	C(15)–C(14)–C(13)	124.09(17)
N(4)–C(14)	1.463(3)	C(15)–C(14)–N(4)	116.58(17)
N(5)–C(18)	1.459(3)	C(13)–C(14)–N(4)	119.29(17)
N(6)–C(16)	1.428(3)	C(14)–C(15)–C(16)	118.97(18)
C(1)–H(1)	0.92(2)	C(17)–C(16)–N(6)	118.96(17)
C(3)–C(12)	1.396(3)	C(15)–C(16)–N(6)	119.67(17)
C(3)–C(4)	1.412(3)	C(17)–C(18)–N(5)	117.54(17)
C(4)–C(5)	1.354(3)	C(17)–C(18)–C(13)	125.10(17)
C(5)–C(6)	1.445(3)	N(5)–C(18)–C(13)	117.29(17)
C(6)–C(7)	1.419(3)	C(1)–N(1)–C(3)	107.55(17)
C(6)–C(11)	1.432(3)	C(1)–N(1)–C(2)	125.59(18)
C(7)–C(8)	1.369(3)	C(3)–N(1)–C(2)	126.83(17)
C(8)–C(9)	1.420(3)	C(1)–N(2)–C(12)	108.78(17)
C(9)–C(10)	1.373(3)	C(1)–N(2)–N(3)	125.69(17)
C(10)–C(11)	1.421(3)	C(12)–N(2)–N(3)	125.51(16)
C(11)–C(12)	1.425(3)	N(2)–N(3)–H(1N3)	107.5(14)
C(13)–C(14)	1.450(3)	N(2)–N(3)–H(2N3)	105.9(15)
C(13)–C(18)	1.463(3)	H(1N3)–N(3)–H(2N3)	111(2)
C(14)–C(15)	1.369(3)	O(2)–N(4)–O(3)	123.03(18)
C(15)–C(16)	1.408(3)	O(2)–N(4)–C(14)	118.54(18)
C(15)–H(15)	1.049(19)	O(3)–N(4)–C(14)	118.38(17)
C(16)–C(17)	1.401(3)	O(5)–N(5)–O(4)	123.49(17)
C(17)–C(18)	1.360(3)	O(5)–N(5)–C(18)	118.35(16)

TABLE 5. Hydrogen Bonds for Compound **25a**

D–H···A	D–H, Å	H···A, Å	∠ DHA, deg.	D···A, Å
N(3)–H(1)N(3)···O(7) [*-x*, *-y* + 2, *-z*]	0.88(2)	2.39(3)	146(2)	3.162(4)
N(3)–H(2)N(3)···O(1)	0.91(3)	2.13(3)	149(2)	2.943(4)
N(3)–H(2)N(3)···O(5)	0.91(3)	2.41(3)	128(2)	3.047(5)
C(1)–H(1)···O(1)	0.92(2)	2.33(2)	119(1)	2.891(4)
C(1)–H(1)···O(2)	0.92(2)	2.27(2)	144(2)	3.068(4)
O(5)···H(2)N(3)···O(1)	76.3(8)			2.805(3)
O(1)···H(1)···O(2)	74.3(6)			2.778(3)
H(2)N(3)···O(1)···H(1)	70.0(8)			

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker 250 (250 MHz) spectrometer, and the IR spectra on a Specord IR 75 spectrometer in nujol. A check on the course of reactions was effected by TLC on Al_2O_3 (Brockmann activity grade IV-V), eluent was chloroform, and visualization with iodine vapor. Melting points were measured in sealed glass capillaries on a PTP instrument and are uncorrected.

TABLE 6. Data of Elemental Analysis of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %		
		C	H	N
8	$C_{11}H_9N_3$	72.00 / 72.11	4.90 / 4.95	22.70 / 22.93
9	$C_{11}H_9N_3$	72.22 / 72.11	4.98 / 4.95	22.85 / 22.93
10	$C_{19}H_{11}N_3$	72.25 / 72.11	4.87 / 4.95	22.99 / 22.93
11	$C_{15}H_{11}N_3$	77.02 / 77.23	4.77 / 4.75	18.24 / 18.01
13	$C_{22}H_{15}N_3$	82.07 / 82.22	4.81 / 4.70	13.25 / 13.07
17	$C_{18}H_{13}N_3$	79.51 / 79.68	4.79 / 4.82	15.40 / 15.49
18	$C_{18}H_{13}N_3$	79.51 / 79.68	4.79 / 4.82	15.40 / 15.49
20	$C_{18}H_{13}N_3$	79.63 / 79.68	4.72 / 4.82	15.30 / 15.49
23	$C_{18}H_{14}N_6O_7$	50.78 / 50.71	3.20 / 3.31	26.42 / 26.26
24	$C_{18}H_{14}N_6O_7$	50.58 / 50.71	3.42 / 3.31	26.39 / 26.26
25a	$C_{18}H_{14}N_6O_7$	50.63 / 50.71	3.40 / 3.31	26.14 / 26.26
26a	$C_{22}H_{16}N_6O_7$	55.41 / 55.47	3.13 / 3.39	17.84 / 17.64
25b*	$C_{12}H_{12}ClN_3$	61.42 / 61.67	5.03 / 5.18	17.77 / 17.98
26b*[2]	$C_{16}H_{14}ClN_3$	67.65 / 67.72	4.87 / 4.97	14.69 / 14.81

*Found, %: Cl 15.30. Calculated, %: Cl 15.17.

*[2] Found, %: Cl 12.28. Calculated, %: Cl 12.49.

The starting materials were synthesized by the following methods: O-picrylhydroxylamine [10], phenanthro[9,10-*d*]imidazole (**12**) [13], naphtho[1,2-*d*]imidazole (**15**) [14], naphtho[2,3-*d*]imidazole (**19**) [15], 1-methylnaphtho- and 3-methylnaphtho[1,2-*d*]imidazoles [11], 1-methylnaphtho[2,3-*d*]imidazole [16], and 1-methylphenanthro[9,10-*d*]imidazole [17].

X-ray Structural Investigation of 1-Amino-3-methylnaphtho[1,2-*d*]imidazolium Picrate (25a). Bright yellow crystals of **25a** were obtained by recrystallization from methanol. The experimental set (10319 reflections) was obtained on a Bruker SMART 1000 CCD area detector diffractometer at 110 K. Processing of the data was carried out with SAINT [18] and SADABS [19] programs.

The structure was solved by the direct method, all the nonhydrogen atoms were localized in difference syntheses of electron density and were refined in an anisotropic approach. All the hydrogen atoms were localized and refined in an isotropic approach. All calculations were carried out with the SHELXTL PLUS 5 set of programs [20].

The structure has been deposited in the Cambridge Bank of Structural Data (Cambridge Crystallographic Data Centre), registration number CCDC 174548.

N-Benzylideneaminoimidazoles (General Procedure). O-Picrylhydroxylamine (0.363 g, 1.5 mmol) in DMF (20 ml) was added during 5 min to a solution of the appropriate imidazole (3 mmol) in DMF (16 ml) at 20°C. The mixture was stirred for 1 h, then benzaldehyde (0.3 ml, 3 mmol) was added, and the mixture boiled for 1 h. The solvent was distilled off under reduced pressure to dryness, $CHCl_3$ (7 ml) was added to the residue, and yellow crystals of the picrate of the corresponding heterocycle were filtered off.

Phenanthro[9,10-*d*]imidazole Picrate (14). Yellow needles; mp 305-308°C (DMF–butanol, 3:1). Yield 0.55 g (82%).

Naphtho[1,2-d]imidazole Picrate (16). Yellow needles; mp 210°C (ethanol). Yield 0.298 g (50%).

Naphtho[2,3-d]imidazole Picrate (21). Yellow needles; mp 145-148°C (ethanol). Yield 0.297 g (50%).

The chloroform solution was chromatographed on a column of Al_2O_3, eluent was chloroform (in the case of compound **13** a mixture of $CHCl_3$–EtOH, 3:1).

1-Benzylideneaminophenanthro[9,10-*d*]imidazole (13). The fraction with R_f 0.7 was taken. Light brown crystals; mp 300-302°C (DMF–butanol, 3:1). Yield 0.178 g (37%).

1-and 3-Benzylideneaminonaphtho[1,2-*d*]imidazoles (17, 18). The chloroform solution was passed through a column of Al_2O_3, two fractions were collected. The first (R_f 0.74) was compound **17**. Colorless crystals; mp 189-191°C (butanol). Yield 0.2 g (49%). The second fraction (R_f 0.7) was compound **18**. Colorless crystals; mp 198-200°C (butanol). Yield 0.033 g (8%).

1-Benzylideneaminonaphtho[2,3-*d*]imidazole (20). The fraction with R_f 0.6 was collected. Light brown crystals; mp 140°C (water–ethanol, 1:1). Yield 0.126 g (31%).

N-Aminoimidazoles (General Method). A suspension of the appropriate azomethine (0.5 mmol) in conc. HCl (10 ml) was boiled for 1 h 30 min. Activated carbon was added and the mixture boiled a further 5 min. After separating the carbon the filtrate was neutralized with concentrated ammonia solution to pH 8-9. The solid base was filtered off, and washed with water (1-2 ml).

1-Aminonaphtho[2,3-*d*]imidazole (8). Yield 0.046 g (50%). Colorless crystals; mp 167-170°C (ethanol). IR spectrum, ν, cm^{-1}: 3100, 3150 (NH_2).

3-Aminonaphtho[1,2-*d*]imidazole (9). Yield 0.055 g (60%). Colorless crystals; mp 185-187°C (benzene–ethanol, 2:1). IR spectrum, ν, cm^{-1}: 3359, 3106 (NH_2). Mass spectrum, *m/z* (I_{rel}, %): 183 (100) $[M]^+$, 168 (23) $[M\text{-}NH]^+$, 155 (37) $[M\text{-}N_2]^+$, 140 (26) $[M\text{-}HCN\text{-}NH_2]^+$, 128 (16), 113 (12), 101 (7), 77 (6), 59 (6), 44 (23).

1-Aminonaphtho[1,2-*d*]imidazole (10). Yield 0.07 g (77%). Colorless crystals; mp 225-227°C (butanol). IR spectrum, ν, cm^{-1}: 3332, 3146 (NH_2).

1-Aminophenanthro[9,10-*d*]imidazole (11). Yield 0.11 g (94%). Colorless crystals; mp 280-283°C (DMF–butanol, 3:1). IR spectrum, ν, cm^{-1}: 3293, 3106 (NH_2).

1-Aminonaphtho[2,3-*d*]imidazolium Chloride (22). A suspension of compound **20** (0.054 g, 0.2 mmol) in conc. HCl (3 ml) was boiled for 15 min. The mixture was evaporated to dryness on a boiling water bath. Dark green crystals of chloride **22** were obtained. Yield 0.033 g (75%); mp 120-122°C (ethanol–benzene, 3:1). IR spectrum, ν, cm^{-1}: 3386, 3186 (NH_2), 2700 (NH^+). Mass spectrum, *m/z* (I_{rel}, %): 183 (100) $[M\text{-}HCl]^+$, 168 (40) $[M\text{-}HCl\text{-}NH]^+$, 155 (50) $[M\text{-}HCl\text{-}N_2]^+$, 140 (63), 127 (39), 113 (22), 101 (11), 77 (16), 44 (15).

N-Amino-N'-methylimidazolium Picrates (General Method). A solution of O-picrylhydroxylamine (0.268 g, 1.1 mmol) in CH_3CN (3 ml) was added with stirring to a solution of the appropriate N-methylimidazole (1 mmol) in $CHCl_3$ (10 ml). The mixture was stirred for 2 h. The yellow solid of compound **27-30** was filtered off, washed with $CHCl_3$ (5 ml), and crystallized from DMF–butanol, 3:1.

1-Amino-3-methylnaphtho[2,3-*d*]imidazolium Picrate (23). Yield 0.422 g (99%). Yellow crystals; mp 228-229°C. IR spectrum, ν, cm^{-1}: 3359, 3239 (NH_2).

3-Amino-1-methylnaphtho[1,2-*d*]imidazolium Picrate (24). Yield 0.383 g (90%). Yellow crystals; mp 225-226°C. IR spectrum, ν, cm^{-1}: 3333, 3173 (NH_2).

1-Amino-3-methylnaphtho[1,2-*d*]imidazolium Picrate (25a). Yield 0.388 g (91%). Yellow crystals; mp 210-213°C. IR spectrum, ν, cm^{-1}: 3332, 3186 (NH_2).

1-Amino-3-methylphenanthro[9,19-*d*]imidazolium Picrate (26a). Yield 0.4 g (84%). Yellow crystals; mp 225-227°C. IR spectrum, ν, cm^{-1}: 3352, 3186 (NH_2).

N-Amino-N'-methylimidazolium Chlorides (General Method). A suspension of compound **25a** or **26a** (0.3 mmol) in conc. HCl (2 ml) was evaporated on a boiling water bath. The residue was treated with ether (3 × 10 ml), each time filtering off the undissolved solid chloride of **25b** or **26b**. **1-Amino-3-methylnaphtho[1,2-*d*]imidazolium chloride (25b)** (0.035 g, 50%) was obtained as colorless crystals; mp 244-245°C (DMF–butanol, 3:1) or **1-amino-3-methylphenanthro[9,10-*d*]imidazolium chloride (26b)** (0.043 g, 50%) as colorless crystals; mp 254-255°C (DMF–butanol, 3:1).

REFERENCES

1. V. V. Kuzmenko and A. F. Pozharskii, *Adv. Heterocycl. Chem.*, **53**, 85 (1992).
2. C. Foces-Foces, F. N. Cano, R. M. Claramunt, D. Sanz, J. Catalan, F. Fabero, A. Fruchier, and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 237 (1990).
3. A. F. Pozarskii, V. V. Kuz'menko, C. Foces-Foces, A. L. Llamas-Saiz, R. M. Claramunt, D. Sanz, and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 841 (1994).
4. V. V. Kuz'menko, T. A. Kuz'menko, G. G. Aleksandrov, A. F. Pozharskii, and A. V. Gulevskaya, *Khim. Geterotsikl. Soedin.*, 836 (1987).
5. A. F. Pozharskii, O. V. Kryshtalyuk, G. G. Aleksandrov, and V. V. Kuz'menko, *Khim. Geterotsikl. Soedin.*, 103 (1995).
6. S. B. Bulgarevich, N. A. Ivanova, V. V. Kuz'menko, D. Ya. Movshovich, and A. F. Pozharskii, *Zh. Obshch. Khim.*, **65**, 1168 (1995).
7. T. A. Kuz'menko, V. V. Kuz'menko, A. F. Pozharskii, O. V. Kryshtalyuk, and G. G. Aleksandrov, *Khim. Geterotsikl. Soedin.*, 205 (1992).
8. L. Salazar, M. Espada, D. Sanz, R. M. Claramunt, J. Elguero, S. Garcia-Granga, M. R. Diaz, and F. Gomez-Beltran, *J. Chem. Soc., Perkin Trans. 2*, 377 (1993).
9. A. F. Pozharskii, O. V. Dyablo, A. V. Belyaev, Z. A. Starikova, and A. I. Yanovskii, *Tetrahedron*, **54**, 9677 (1998).
10. J. Tamura, J. Minamikawa, K. Sumoto, S. Fujii, and M. Ikeda, *J. Org. Chem.*, **38**, 1239 (1973).
11. A. I. Belyashova, N. N. Zatsepina, E. N. Malysheva, A. F. Pozharskii, L. P. Smirnova, and I. F. Tupitsin, *Khim. Geterotsikl. Soedin.*, 1544 (1977).
12. R. M. Claramunt, D. Sanz, J. Catalan, F. Fabero, N. A. Garcia, C. Foces-Foces, A. L. Llamas-Saiz, and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1687 (1993).
13. E. A. Steck and A. R. Day, *J. Am. Chem. Soc.*, **36**, 2567 (1942).
14. A. F. Pozharskii, V. N. Anisimova, and E. B. Tsupak, *Practical Studies on the Chemistry of Heterocycles* [in Russian], Izd. Rostov Gos. Univ., Rostov-on-Don (1988), p. 86.
15. A. F. Pozharskii and E. N. Malysheva, *Khim. Geterotsikl. Soedin.*, 103 (1970).
16. N. J. Leonard and A. M. Hyson, *J. Am. Chem. Soc.*, **43**, 1961 (1949).
17. E. A. Steck and A. R. Day, *J. Am. Chem. Soc.*, **40**, 771 (1946).
18. Bruker (1998a) SAINTPlus Data Reduction and Correction Program v. 6.01, Bruker AXS, Madison, Wisconsin, USA.
19. G. M. Sheldrick (1998a), *SADABS* v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA.
20. G. M. Sheldrick (1998b), *SHELXTL* v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA.