Russian Journal of Organic Chemistry, Vol. 40, No. 4, 2004, pp. 567–574. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 4, 2004, pp. 595–602.

Structure and Reactivity of the 1,10-Phenanthroline Complex with Nitrenium Cation

R. V. Andreev, G. I. Borodkin, Yu. V. Gatilov, M. M. Shakirov, and V. G. Shubin

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: gibor@nioch.nsc.ru

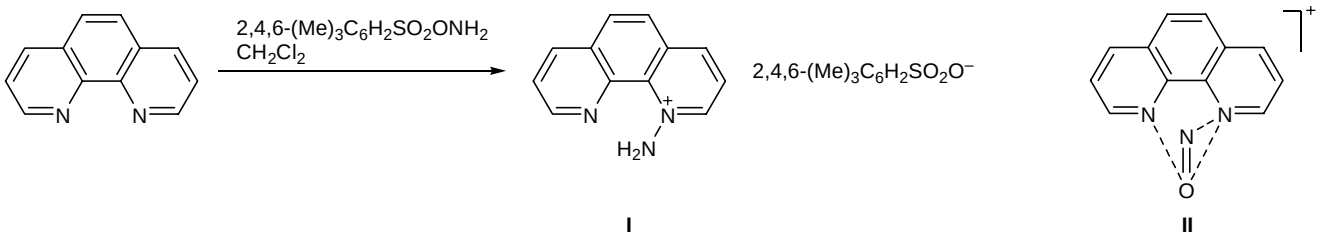
Received June 30, 2003

Abstract—According to the X-ray diffraction data, the cationic fragment in 1-amino-1,10-phenanthrolinium mesitylenesulfonate is a unidentate *n*-complex whose asymmetric structure is retained in solution. Quantum-chemical calculations by the AM1 method and *ab initio* (6-31G, 6-31G*, MP2/6-31G) give geometric parameters of the cation, which are similar to those determined experimentally. No dynamic processes involving intra- or intermolecular transfer of the NH_2 group was observed up to 100°C by NMR spectroscopy. 1-Amino-1,10-phenanthrolinium cation does not react with 4-methylpyridine and 4-methyl-1,10-phenanthroline with transfer of the amino group, and it fails to react with mesitylene and anthracene at elevated temperature.

Azine complexes with nitrenium ions have been studied relatively poorly, as compared with other cationic complexes derived from other nitrogen-containing heterocycles [1–23]. However, studies of their structure and reactivity are important from the viewpoint of understanding mechanisms of a wide series of organic reactions, such as photochemical and thermal amination of arenes [2, 6–10, 18], synthesis of imines [1, 4, 5, 17], and other processes [1, 4, 5, 13, 20, 21]. The goal of the present work was to examine the molecular and crystaline structure of 1-amino-1,10-phenanthrolinium mesitylenesulfonate (**I**) and the ability of the corresponding cation to react with intra- or intermolecular transfer of the amino group.

1-Amino-1,10-phenanthrolinium mesitylenesulfonate (**I**) was synthesized by reaction of 1,10-phenanthroline with *O*-mesitylsulfonylhydroxylamine in methylene chloride [8] (Scheme 1). According to the X-ray diffraction data, the cations and anions of salt **I** in crystal give rise to centrosymmetrical stacks. Their planes are almost parallel to each other, presumably due to π-stacking interactions (Figs. 1, 2). The interplanar distance and the angle between the cation and anion planes are 3.55 Å and 7.2°, respectively, and for the anion–anion couple, 3.39 Å and 0.0°. Unlike nitrosonium complex of 1,10-phenanthroline (**II**) [24], the cation of **I** in crystal is unidentate. The N^1–NH_2 bond length [1.403(3) Å] approach those found for *N*-amino-3,5-dimethylpyridinium chloride [1.399(4) Å] [22], *N*-amino-2,4,6-triphenylpyridinium perchlorate [1.418(4) Å] [16], and 1-amino-2-(*p*-methoxyphenylamino)-4-(*p*-tolyl)pyrimidinium iodide [1.413(4) Å] [15]; it occupies an intermediate place between the standard N(sp^2)–N(sp^3) (1.420 Å) and N(sp^2)–N(sp^2) bonds (1.401 Å) [25]. The distance between the amino group nitrogen atom and N^{10} is 2.689(4) Å, i.e., it is considerably shorter than the average value for intermolecular N···N contacts (3.00 Å) [26]. The N–NH_2

Scheme 1.



I **II**

1070-4280/04/4004-0567 © 2004 MAIK "Nauka/Interperiodica"

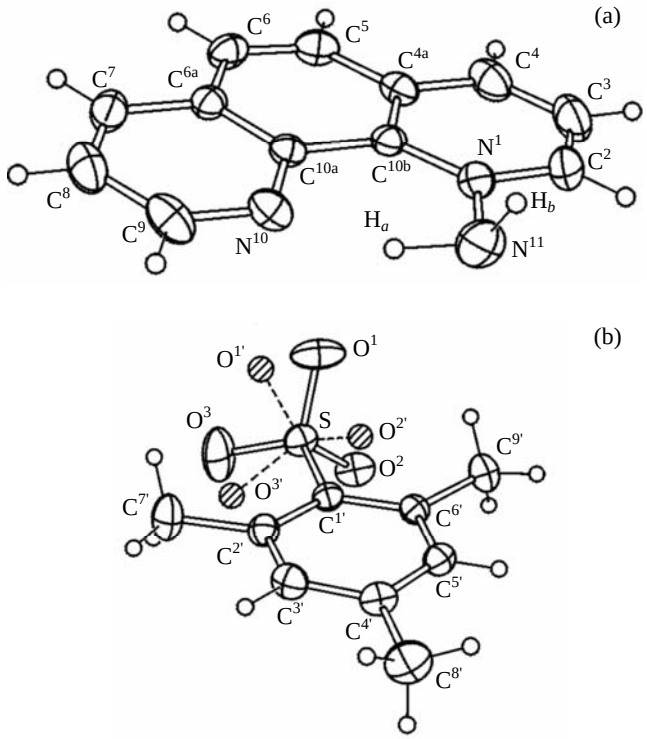


Fig. 1. Molecular structure of 1-amino-1,10-phenanthrolinium mesitylenesulfonate (**I**): (a) cation and (b) anion. The SO_3^- group in the anion is disordered by two positions.

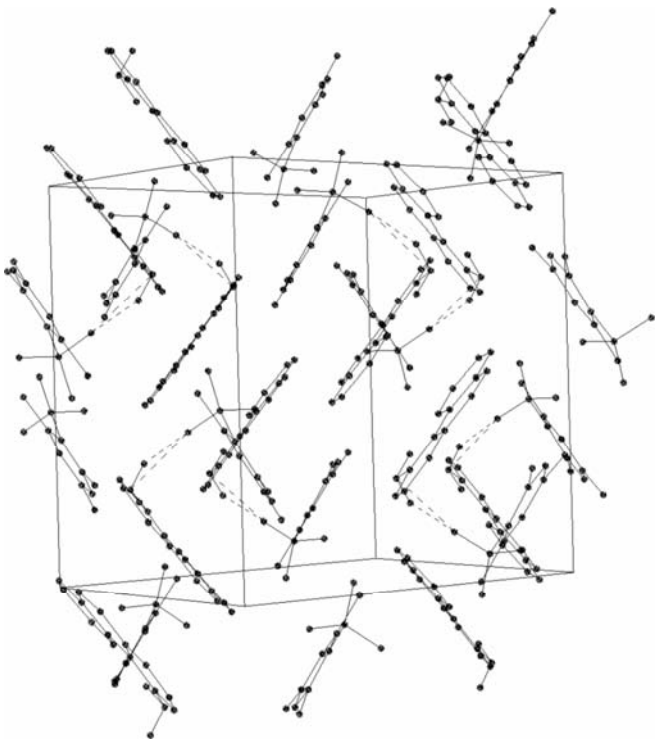


Fig. 2. Arrangement of cations and anions in the crystalline structure of 1-amino-1,10-phenanthrolinium mesitylenesulfonate (**I**).

fragment has a pyramidal structure, and the amino group nitrogen atom lies in the plane of the phenanthroline skeleton which is planar within ±0.057 Å. Both hydrogen atoms of the amino group are involved in formation of hydrogen bonds, one of which is intracationic N^{11}–H···N^{10} [1.67(5) Å], and the other is interionic $N^{11}H$···O, [1.84(5) Å]. It should be noted that the bond angle $C^2N^1N^{10b}$ [121.9(2)°] is larger than $C^9N^{10}C^{10a}$ [117.9(2)°] and the CNC angle in 1,10-phenanthroline; the average value for the two kinds of structures in crystal is 117.7(3)° [27], which is consistent with Bent's rules [22, 28].

The asymmetric structure of the cation in salt **I** is retained in going to solution. This follows from the NMR data: ^{1}H NMR spectrum in DMSO-d_6, δ, ppm: 11.3 br.s (2H, NH_2), 9.25 d.d (1H, 9-H, J = 4.5, J = 1.7 Hz), 9.20 d.d (1H, 2-H, J = 6.3, J = 1.3 Hz), 8.92 d.d (1H, 4-H, J = 8.2, J = 1.3 Hz), 8.83 d.d (1H, 7-H, J = 8.2, J = 1.7 Hz), 8.35 (1H, 5-H, J = 8.9 Hz, *AB* system), 8.30 (1H, 6-H, J = 8.9 Hz, *AB* system), 8.25 d.d (1H, 3-H, J = 8.2, J = 6.3 Hz), 8.11 d.d (1H, 8-H, J = 8.2, J = 4.5 Hz); ^{13}C NMR spectrum in DMSO-d_6, δ_C, ppm: 148.5 (C^9), 139.9 (C^{10a}), 139.0 (C^2), 138.4 (C^4), 138.3 (C^7), 132.3 (C^{4a}), 130.6 (C^{6a}), 130.0 (C^5), 129.6 (C^{10b}), 127.1 (C^6), 125.5 (C^8), 124.4 (C^3). NMR spectra of the anion 2,4,6-$Me_3C_6H_2SO_3^-$: ^{1}H, δ, ppm: 6.67 (2H, 3'-H, 5'-H), 2.47 (6H, 2'-Me, 6'-Me), 2.11 (3H, 4'-Me); ^{13}C, δ_C, ppm: 142.7 ($C^{1'}$), 135.8 ($C^{2'}$, $C^{6'}$), 136.2 ($C^{4'}$), 129.8 ($C^{3'}$, $C^{5'}$) (cf. [8]). The NMR signals were assigned using different proton–proton and carbon–proton shift correlation techniques: ^{1}H-2D NOESY spectroscopy and two-dimensional proton–carbon spin correlation spectroscopy (COLOC, HXCO) [29]. The spin–spin coupling constant $J_{8,9}$ is smaller than $J_{2,3}$, and both these are considerably smaller than $J_{7,8}$ and $J_{3,4}$. This pattern is typical of pyridinium-like cations and those derived from six-membered azines [30]. The NH_2 proton signal is displaced downfield, presumably due to formation of intamolecular hydrogen bond between these protons and spatially close N^{10} atom (see above; cf. [8]).

According to the results of AM1 quantum-chemical calculations, the most stable is asymmetric complex **IA** (Fig. 3) where hydrogen atoms of the amino group are forced out from the phenanthroline ring plane and are located at almost equal distances to that plane. In addition, these atoms approach the N^{10} atom, so that lone electron pairs on the amino nitrogen atom and N^{10} appear maximally distant from each other. *Ab initio* calculations of structures **IA** and **IB** using 6-31G and

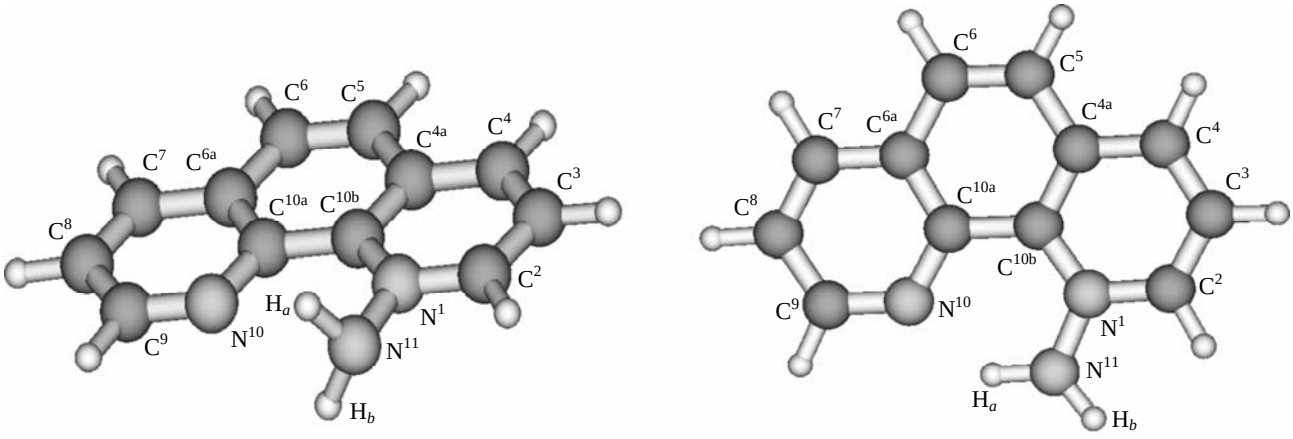


Fig. 3. Structure of 1-amino-1,10-phenanthrolinium cation according to the RHF/6-31G calculations (symmetry group C_s).

6-31G* basis sets with symmetry limitations corresponding to the C_S point symmetry group also give preference to asymmetric structure **IA** (Fig. 3; Tables 1, 2). Analysis of the Hesse matrix [31] in the framework of the MP2/6-31G procedure showed that structure **IB** is characterized by two imaginary frequencies and that this structure is transformed into **IA** via IRC routine. The geometric parameters of complex **IA** calculated by both AM1 method and *ab initio* were similar to those determined experimentally by X-ray analysis (Table 1). With account taken of electronic correlation, the energy of the cation decreases, while the bonds therein become slightly longer than those calculated by the RHF/6-31G and RHF/6-31G* methods and experimental values (Table 1).

Unlike phenanthroline complex with nitrosonium cation, which also has asymmetric structure in solution and gives rise to fast (on the NMR time scale) degenerate rearrangement involving transfer of the NO group from one endocyclic nitrogen atom to the other [32], the cation of salt **I** is "static." This follows from the fact that we observed no broadening of the corresponding signals in the ^{1}H NMR spectrum on heating a solution of salt **I** in DMSO to 100°C. This means that neither intramolecular (path *a* in Scheme 2) nor intermolecular (path *b* in Scheme 2) transfer of the amino group takes place.

All calculation methods showed a considerable difference in the energies of asymmetric (**I**) and symmetric (**III**) cations (Table. 2; Figs. 4, 5), and structure **III** turned out to be appreciably less favorable than the asymmetric structure. These data are likely to explain the high energy barrier to migration of the amino group in the cation under study.

Analysis of the Hesse matrix showed [31] (with limitations intrinsic to the C_S point symmetry group; 6-31G and 6-31G* basis sets) that symmetric structure **IIIA** (Fig. 4) has two imaginary frequencies which correspond to composite out-of-plane skeletal vibrations involving nitrogen-containing fragments. Further

Scheme 2.

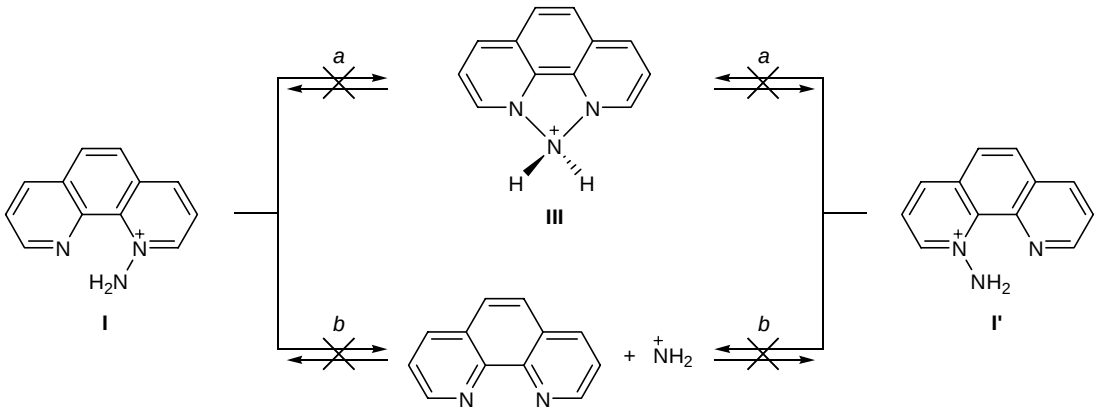


Table 1. Selected bond lengths (Å) and bond angles (deg) in the 1,10-phenanthroline complex with nitrenium cation, determined from the X-ray diffraction data and calculated *ab initio*

Bond or angle	X-Ray diffraction data	*Ab initio*[a]			
		IA (6-31G)	**IA** (6-31G*)	**IA** (MP2/6-31G)	**IIIB** (6-31G)
N^1–C^2	1.341(4)	1.332	1.324	1.369	1.425
N^1–C^{10b}	1.377(3)	1.378	1.378	1.403	1.417
N^1–C^{11}	1.403(3)	1.420	1.411	1.435	1.490
C^2–C^3	1.352(5)	1.382	1.383	1.404	1.340
C^3–C^4	1.362(5)	1.372	1.367	1.397	1.460
C^4–C^{4a}	1.400(4)	1.407	1.407	1.422	1.349
C^{4a}–C^{10b}	1.410(3)	1.405	1.402	1.442	1.431
C^{4a}–C^5	1.426(4)	1.434	1.435	1.450	1.469
C^5–C^6	1.329(4)	1.344	1.339	1.375	1.347
C^6–^{6a}	1.421(3)	1.432	1.432	1.448	1.469
C^{6a}–C^7	1.410(3)	1.412	1.412	1.427	1.349
C^{6a}–C^{10a}	1.405(3)	1.404	1.401	1.437	1.431
C^7–C^8	1.355(4)	1.365	1.359	1.398	1.460
C^8–C^9	1.381(4)	1.406	1.408	1.420	1.340
C^9–N^{10}	1.327(3)	1.311	1.299	1.357	1.425
N^{10}–C^{10a}	1.362(3)	1.352	1.345	1.385	1.417
C^{10a}–C^{10b}	1.449(3)	1.447	1.454	1.462	1.316
$C^2N^1C^{11}$	114.0(2)	112.8	112.5	114.4	120.4
$C^2N^1C^{10b}$	121.9(2)	122.5	122.4	122.5	117.0
$C^9N^{10}C^{10a}$	117.9(2)	120.4	119.4	119.1	117.0
$C^2N^1C^{11}H_a$	–179(1)	118.8	123.0	–169.6	84.5

[a] *Ab initio* calculations of asymmetric complex **IA** were performed with symmetry limitations corresponding to the C_s (6-31G, 6-31G*) and C_1 (MP2/6-31G) point symmetry groups.

optimization of cation **IIIA** with respect to imaginary frequencies by the IRC procedure leads to a bent structure like **IIIB** (Fig. 5), which occupies the true minimum on the potential energy surface, but its energy exceeds that of asymmetric structure **IA** by ~500 kJ/mol. It should be noted that structure **III** has 16 π electrons, and it may be regarded as antiaromatic (cf. [33]), which is responsible for its unfavorableness from the viewpoint of energy.

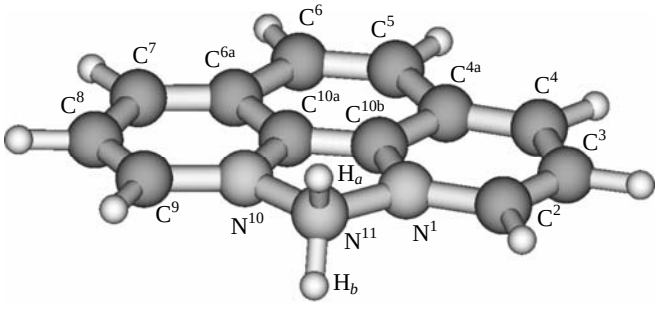


Fig. 4. Structure of symmetric 1,10-phenanthroline complex with nitrenium cation (**IIIA**) according to the RHF/6-31G calculations (symmetry group C_{2v}).

In order to estimate the degree of aromaticity of structures **IA** and **III**, let us consider the parameter $HOMA_d$ which takes into account leveling of bond lengths in a polycyclic system and their conformity to an optimal length [33–35]:

$$HOMA_d = 1 - (98.89 : n) \times [\Sigma(1.397 - l_{CC})^2 + \Sigma(1.338 - l_{CN})^2]. \quad (1)$$

Here, n is the number of CC and CN bonds, and l_{CC} and l_{CN} are the lengths of the corresponding bonds. Calculation of $HOMA_d$ for structure **IA** from the experimental bond lengths and those calculated by the RHF/6-31G method gives values of 0.90 and 0.92, respectively, which indicate aromatic character of this structure. The corresponding value determined for

Table 2. Total energies (E, a.u.) of complexes **IA**, **IB**, **IIIA**, and **IIIB** and affinity of 1,10-phenanthroline for NH_2^+ cation [$A(NH_2^+)$, kJ/mol]

Structure	6-31G		6-31G*		MP2/6-31G	
	E	$A(NH_2^+)$	E	$A(NH_2^+)$	E	$A(NH_2^+)$
IA	–623.12978	685.7	–623.37681	667.8	–624.49048[a]	777.7
IB[b]	–623.12305		–623.36126		–624.48776	
IIIA[c]	–622.91687	–	–623.16307	–	–624.27946	–
IIIB	–622.93254	–	–623.19216	–	[d]	–

[a] The calculation was performed by the IRC procedure with symmetry limitations corresponding to the C_1 point group.
[b] Structures **IB** do not occupy local minima, and they are characterized by one (6-31G, 6-31G*) and two (MP2/6-31G) imaginary frequencies.
[c] Structures **IIIA** are characterized by two (6-31G, 6-31G*) and four (MP2/6-31G) imaginary frequencies.
[d] IRC procedure transforms structure **IIIA** into asymmetric structure like **IA**.

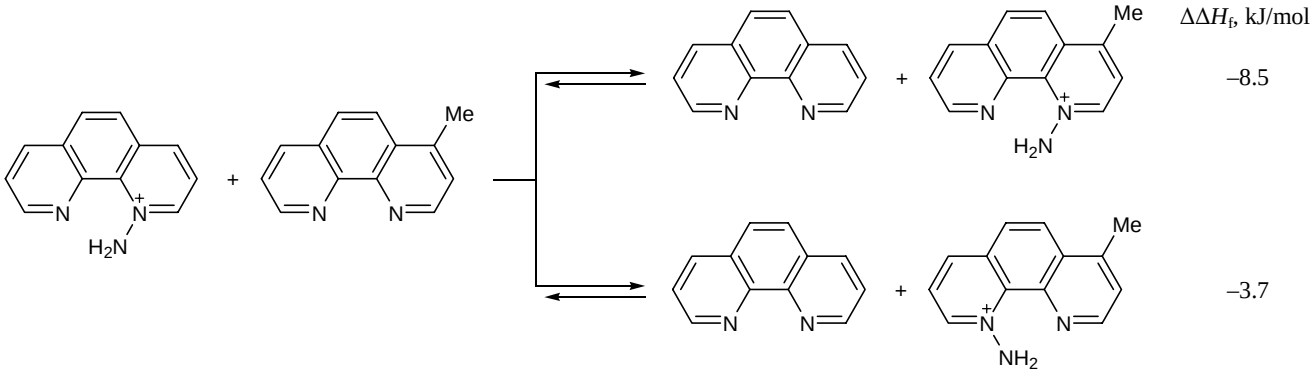
structure **IIIA** is much lower (0.58); therefore, it may be regarded as antiaromatic (cf. [33–35]).

Calculation of the charge distribution in asymmetric structure **IA** showed localization of a considerable negative charge on the nitrogen atoms of the phenanthroline skeleton and the amino group (Table 3). Therefore, migration of the amino group from one endocyclic nitrogen atom to another is unfavorable from the electrostatic viewpoint. It should be noted that the nitrogen atom of the NO group in analogous 1,10-phenanthroline complex with nitrosonium cation possesses an appreciable positive charge [24].

Takeuchi *et al*. [8] used cation **I** as a reagent in photochemical amination of arenes. It seems important to elucidate whether analogous thermal reaction is feasible or not. Such activation mode was utilized in the amination of benzene with 2-methyl-1-phenylamino-4,6-diphenylpyridinium tetrafluoroborate [7]. Taking into account the high affinity of NH_2^+ ion for 1,10-phenanthroline [$A(NH_2^+)$, Table 2], we presumed that electrophilic amination would require very severe conditions. In fact, no amination products were obtained by heating a solution of salt **I** in DMSO in the presence of mesitylene or anthracene for 1 h even at 150°C. Further raising the temperature leads to decomposition of the initial salt which, according to the ^{1}H NMR data, is converted (at least partially) into 1,10-phenanthroline and ammonium mesitylenesulfonate. Likewise, we failed to effect under the same conditions transfer of the NH_2 group from cation **I** to 4-methyl-1,10-phenanthroline which is likely to be a stronger nucleophile than 1,10-phenanthroline. The latter statement is supported by the data of AM1 quantum-chemical calculations. The calculated enthalpies of formation of the corresponding cations and nitrogenous bases for the isodesmic equilibria shown in Scheme 3 indicate greater affinity of nitrenium ion for 4-methyl-1,10-phenanthroline than for 1,10-phenanthroline. Also, nitrenium cation is not transferred from **I** to another strong base, 4-methylpyridine.

Thus our results demonstrate static nature of 1-amino-1,10-phenanthrolinium cation which does not tend to intra- or intermolecular transfer of the amino group.

Scheme 3.



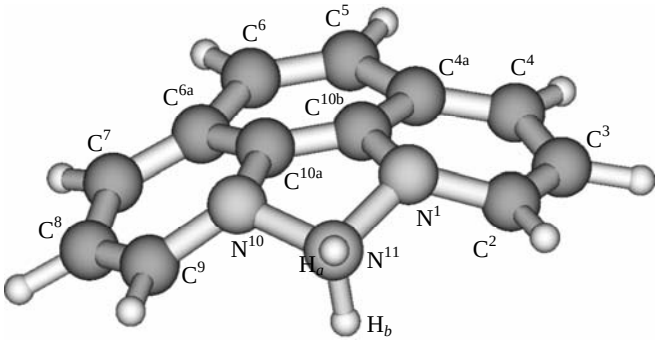


Fig. 5. Structure of symmetric 1,10-phenanthroline complex with nitrenium cation (**IIIB**) according to the RHF/6-31G calculations (refined by the IRC procedure).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer at 500.13 and 125.76 MHz, respectively, using residual proton and carbon signals of the solvent (DMSO-d_6) as internal reference (δ 2.50 ppm, δ_C 39.5 ppm). The IR spectra were measured on a Bruker Vector 22 instrument. The X-ray diffraction data were obtained on a Bruker P4 diffractometer (MoK_α radiation, graphite monochromator, θ/2θ-scanning to 2θ < 50°).

Table 3. Mulliken charge distribution in complexes **IA** and **IIIB**, calculated *ab initio* using 6-31G, 6-31G*, and MP2/6-31G basis sets

Atom no.	**IA** (6-31G)	**IA** (6-31G*)	**IA** (MP2/6-31G)	**IIIB** (6-31G)
1	–0.934	–0.637	–0.583	–0.598
2	0.316	0.209	0.162	0.066
3	–0.288	–0.300	–0.161	–0.198
4	–0.052	–0.068	–0.110	–0.210
4a	–0.149	–0.072	–0.013	0.090
5	–0.151	–0.196	–0.142	–0.126
6	–0.129	–0.170	–0.111	–0.126
6a	–0.024	–0.010	0.031	0.090
7	–0.125	–0.130	–0.128	–0.210
8	–0.235	–0.256	–0.149	–0.198
9	0.105	0.099	0.063	0.066
10	–0.633	–0.649	–0.530	–0.598
10a	0.214	0.298	0.208	0.210
10b	0.561	0.430	0.386	0.210
11	–0.465	–0.553	–0.499	–0.450

The following reagents were used: 1,10-phenanthroline of analytical grade was additionally purified by recrystallization from anhydrous benzene and dried over P_2O_5 under reduced pessure; 4-methyl-1,10-phenanthroline (98%) from Aldrich; 4-methylpyridine (95%) from Fluka; mesitylene of pure grade was distilled and dried over molecular sieves; anthracene of analytical grade; *O*-mesitylsulfonylhydroxylamine was synthesized by the procedure described in [3]; CH_2Cl_2 was purified by distillation over P_2O_5.

1-Amino-1,10-phenanthrolinium mesitylenesulfonate was synthesized by the procedure reported in [8] and was purified by recrystallization from EtOAc–MeOH (~1:1), mp 189.5–191°C; published data [8]: mp 174–176°C. IR spectrum (KBr), ν, cm^{-1}: 678, 708, 849, 1012, 1086, 1214 br, 1403, 1542, 1597, 3060 br (cf. [8]). Crystals suitable for X-ray analysis were obtained by slow crystallization of the salt from a solution in EtOAc–MeOH (1:1, by volume) at ~5°C.

Monoclinic crystals, $C_{21}H_{21}N_3O_3S$; M 395.47; unit cell parameters: a = 10.0837(8), b = 13.717(1), c = 13.706(1) Å; β = 95.615(7)°; V = 1886.8(3) Å^3; Z = 4; ρ_4^{20} = 1.392 g/cm^3; μ = 0.200 mm^{-1}; space group $P2_1/n$; crystal habit 0.72×0.4×0.2 mm. Intensities of 3311 independent reflections were measured, for which corrections for absorption were introduced empirically using Ψ-curves (transmission 0.915, 0.995). The structure was solved by the direct method using SHELXS-97 program and was refined by the least-squares procedure in anisotropic–isotropic approximation using SHELXL-97 program to wR_2 = 0.1374 and S = 1.030 for all reflections (R = 0.0470 for 2555 reflections with $F_0 > 4\sigma$). The positions of hydrogen atoms in the amino group were determined by the difference synthesis and were refined in isotropic approximation; the parameters of the other hydrogen atoms were calculated from geometry considerations. The SO_3 group in the anion is disordered by two positions at a ratio of 0.868(9):0.132(9). The complete set of crystallographic data was deposited to the Cambridge Structural Database.

Reaction of 1-amino-1,10-phenanthrolinium mesitylenesulfonate with 4-methyl-1,10-phenanthroline, 4-methylpyridine, mesitylene, and anthracene. A solution of 1-amino-1,10-phenanthrolinium mesitylenesulfonate in DMSO-d_6 ($c \approx 0.1$ M) containing an equimolar amount of 4-methyl-1,10-phenanthroline or 4-methylpyridine, 2 equiv of mesitylene, or 1.5 equiv of anthracene was heated for about 1 h at

150°C, and the ^{1}H NMR spectrum of the resulting solution was recorded.

Quantum-chemical calculations were performed with the aid of GAMESS software package [36]. Standard 6-31G and 6-31G* basis sets were used in the geometry optimization by the restricted Hartree–Fock (RHF) procedure. Electronic correlation was taken into account in terms of the MP/2 method. Critical points on the potential energy surface were identified by calculating Hesse's matrix [31]. The IRC procedure (GS2 method) was performed for all imaginary frequencies in Hesse's matrix.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 02-03-32431). The authors are also grateful to the Russian Foundation for Basic Research for providing the possibility of accessing the Cambridge Structural Database (project no. 02-07-90322).

REFERENCES

1. *Comprehensive Heterocyclic Chemistry*, Katritzky, A.R., Ed., Oxford: Pergamon, 1984, vols. 1–8; Katritzky, A.R. and Savage, G.P., *Rev. Heteroatom Chem.*, 1990, vol. 3, p. 160; Gromov, S.P., *Heterocycles*, 2000, vol. 53, p. 1607; Mishra, A., Behera, R.K., Behera, P.K., Mishra, B.K., and Behera, G.B., *Chem. Rev.*, 2000, vol. 100, p. 1973; Ke, W., Xu, H., Liu, X., and Luo, X., *Heterocycles*, 2000, vol. 53, p. 1821.
2. Simonova, T.P., Nefedov, V.D., Toropova, M.A., and Kirilllov, N.F., *Usp. Khim.*, 1992, vol. 61, p. 1061.
3. Tamura, Y., Minamikawa, J., and Ikeda, M., *Synthesis*, 1977, p. 1.
4. Katritzky, A.R., Lewis, J., and Nie, P.-L., *J. Chem. Soc., Perkin Trans. 1*, 1979, p. 446.
5. Katritzky, A.R., Ballesteros, P., and Tomas, A.T., *J. Chem. Soc., Perkin Trans. 1*, 1981, p. 1495.
6. Takeuchi, H., *J. Chem. Soc., Chem. Commun.*, 1987, p. 961.
7. Takeuchi, H. and Koyama, K., *J. Chem. Soc., Perkin Trans. 1*, 1988, p. 2277.
8. Takeuchi, H., Hayakawa, S., Tanahashi, T., Kobayashi, A., Adachi, T., and Higuchi, D., *J. Chem. Soc., Perkin Trans. 2*, 1991, p. 847.
9. Takeuchi, H., Higuchi, D., and Adachi, T., *J. Chem. Soc., Perkin Trans. 1*, 1991, p. 1525.
10. Takeuchi, H., Hayakawa, S., and Murai, H., *J. Chem. Soc., Chem. Commun.*, 1988, p. 1287.
11. Klötzer, W., Baldinger, H., Karpitschka, E.M., and Knoflach, J., *Synthesis*, 1982, p. 592.
12. Sosnovsky, G. and Purgstaller, K., *Z. Naturforsch., Teil B*, 1989, vol. 44, p. 582.
13. Billert, T., Beckert, R., Doring, M., Wuckelt, J., Fehling, P., and Gorls, H., *J. Heterocycl. Chem.*, 2001, vol. 38, p. 205.
14. Lund, H. and Skov, K., *Acta Chem. Scand.*, 1999, vol. 53, p. 639.
15. Liebscher, J., Hassoun, A., van der Plas, H., and Stam, C., *J. Heterocycl. Chem.*, 1990, vol. 27, p. 1441.
16. Filipenko, O.S., Aldoshin, S.M., Shilov, G.V., Makarova, N.I., Kharlanov, V.A., and Knyazhanskii, M.I., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1995, p. 296.
17. Andreev, R.V. and Borodkin, G.I., *Materialy konferentsii "Organicheskii sintez v novom stoletii"* (Proc. Conf. "Organic Synthesis in the New Century), St. Petersburg, 2002, p. 64.
18. Srivastava, S., Kercher, M., and Falvey, D.E., *J. Org. Chem.*, 1999, vol. 64, p. 5853.
19. Messmer, A., Kover, P., Riedl, Z., Gomory, A., and Hajos, G., *Tetrahedron*, 2002, vol. 58, p. 3613.
20. Vinogradova, O.V., Kryshtalyuk, O.V., Rudnev, M.I., Pozharskii, A.F., and Kuz'menko, V.V., *Khim. Geterotsikl. Soedin.*, 1994, p. 1364.
21. Abe, N., Odagiri, K., Otani, M., Fujinaga, E., Fujii, H., and Kakehi, A., *J. Chem. Soc., Perkin Trans. 1*, 1999, p. 1339.
22. Palenik, G.J., Qian, K., Koziol, A.E., and Sisler, H.H., *Inorg. Chem.*, 1990, vol. 29, p. 4016.
23. Riviere, F., Romanenko, V., Mazieres, M.-R., Sanchez, M., and Wolf, J.-G., *Tetrahedron Lett.*, 1998, vol. 39, p. 4809.
24. Andreev, R.V., Borodkin, G.I., Gatilov, Yu.V., and Shubin, V.G., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 845.
25. Allen, F.H., Kennard, D., and Watson, D.G., *J. Chem. Soc., Perkin Trans. 2* (Suppl.), 1987, p. 1.
26. Zefirov, Yu.V. and Zorkii, P.M., *Zh. Strukt. Khim.*, 1976, vol. 17, p. 994.
27. Nishigaki, S., Yoshioka, H., and Nakatsu, K., *Acta Crystallogr., Sect. B*, 1978, vol. 34, p. 875.
28. Bent, H.A., *Chem. Rev.*, 1961, vol. 61, p. 275.
29. Derome, A.E., *Modern NMR Techniques for Chemistry Research*, New York: Pergamon, 1987.
30. Emsley, J.W., Feeney, J., and Sutcliffe, L.H., *High-Resolution Nuclear Magnetic Resonance Spectroscopy*, Oxford: Pergamon, 1966, vol. 2. Translated under the title *Spektroskopiya YaMR vysokogo razresheniya*, Moscow: Mir, 1969, vol. 2, p. 122; Chernyuk, I.N., Pridan, V.E., Bazhutin, V.A., and Kornilov, M.Yu., *Zh. Obshch. Khim.*, 1974, vol. 44, p. 1584; Ditch-

field, R. and Gil, V.M.S., *J. Chem. Soc. A*, 1969, p. 533; Zarin', P.P., Lavrinovich, E.S., and Aren, A.K., *Khim. Geterotsikl. Soedin*., 1974, p. 112; Carman, R.M. and Hall, J.R., *Aust. J. Chem.*, 1964, vol. 17, p. 1354; von Rosenberger, H. and Pettig, M., *Chem. Ber*., 1969, vol. 73, p. 662.

31. Minkin, V.I., Simkin, B.Ya., and Minyaev, R.M., *Kvantovaya khimiya organicheskikh soedinenii. Mekhanizmy reaktsii* (Quantum Chemistry of Organic Compounds. Reaction Mechanisms), Moscow: Khimiya, 1986, p. 10.
32. Andreev, R.V., Borodkin, G.I., and Shubin, V.G., *Russ. J. Org. Chem*., 2001, vol. 37, p. 144.
33. Krygowski, T.M., Cyraňski, M.K., Czarnocki, Z., Hafelinger, G., and Katritzky, A.R., *Tetrahedron*, 2000, vol. 56, p. 1783; Glukhovtsev, M.N., Simkin, B.Ya., and Minkin, V.I., *Usp. Khim.*, 1985, vol. 54, p. 86.
34. Kruszewski, J., *Pure Appl. Chem.*, 1980, vol. 52, p. 1525.
35. Kruszewski, J. and Krygowski, T.M., *Tetrahedron Lett*., 1972, p. 3839.
36. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Ngugen, K.A., Su, S.J., Widus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem*., 1993, vol. 14, p. 1347.