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SHORT COMMUNICATIONS

Structure and Dynamics of the 1,10-Phenanthroline Complex with Nitrosonium Cation[*]

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Cationic complexes formed by nitrogen-containing heterocyclic compounds attract close attention for a long time [1]. However, available information on such complexes with nitrosonium cation is very limited [2–4], although studies of the structure and reactivity of complexes formed by N-heterocycles and nitrosonium ion have become very urgent since the unique role of NO molecule in processes occurring *in vivo* has been discovered [5]. It is assumed that NO molecule is involved in these processes in the form of nitrosonium cation [6]. The goal of the present study was to examine the structure and dynamics of the complex formed by 1,10-phenanthroline and nitrosonium ion.

According to the ^{1}H and ^{13}C NMR spectra, the reaction of 1,10-phenanthroline (**I**) with $NO^{+}BF_{4}^{-}$ in acetonitrile or DMSO-d_6 gives *n*-complex **II** with tetrafluoroborate as counterion (cf. [2–4]), which undergoes fast (on the NMR time scale) degenerate rearrangement (Scheme 1; Tables 1, 2). The formation of complex **II** follows from the downfield shift of the averaged signals from aromatic protons and upfield shift of the C^{2}, C^{9}, C^{10a}, and C^{10b} signals (cf. [7]). Characteristically, the ^{13}C chemical shifts of dynamic complex **II** (**A** $\rightleftarrows$ **B**) are similar to the corresponding values found for 1-methyl-1,10-phenanthrolinium iodide (**VI**) (Table 2).

The transformation **A** $\rightleftarrows$ **B** could be simulated by formation of structure **III**. However, the IR data contravert this assumption: the NO frequency of complex **II** (tetrafluoroborate) in CH_3CN is very close to that observed for *N*-nitrosopyridinium tetrafluoroborate [2] (1857 and 1858 cm^{-1}, respectively; cf. [2, 4]). Raising the ratio **I**–$NO^{+}BF_{4}^{-}$ to 1 : 2 and then to 1 : 3 produces variation of the carbon chemical shifts; the change observed in going from the 1 : 2 ratio to 1 : 3 is considerably smaller than that occurring in going from the 1 : 1 ratio to 1 : 2 (Table 2). These data may be

Scheme 1.

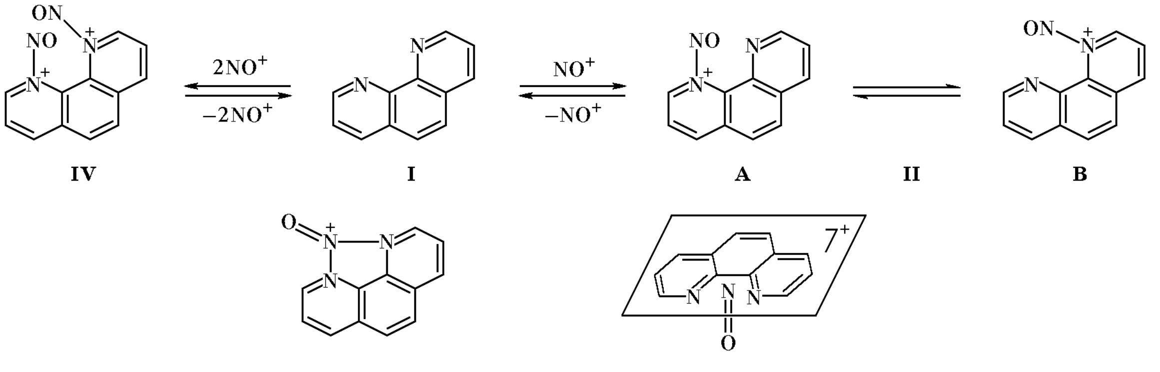

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Table 1. ^{1}H NMR spectra of 1,10-phenanthroline (**I**) and *n*-complexes **II** and **IV** at 25°C

Compound no.	Solvent	Ratio **I**:$NO^+BF_4^-$	Chemical shifts δ,[a] ppm ($J_{H,H}$, Hz)			
			2-H, 9-H	3-H, 8-H	4-H, 7-H	5-H, 6-H
I	CH_3CN	–	9.05 d.d (1.7, 4.3)	7.63 d.d (4.3, 8.1)	8.30 d.d (1.7, 8.1)	7.82 s
I	$(CD_3)_2SO$	–	9.09 d.d (1.8, 4.4)	7.73 d.d (4.4, 8.2)	8.45 d.d (1.8, 8.2)	7.93 s
II	CH_3CN	1:1	9.07 d.d (1.2, 4.8)	7.79 d.d (4.8, 8.2)	8.47 d.d (1.2, 8.2)	7.89 s
II	$(CD_3)_2SO$	1:1	9.16 d.d (1.4, 4.8)	8.09 d.d (4.8, 8.2)	8.87 d.d (1.4, 8.2)	8.13 s
II $\rightleftarrows$ **IV**	$(CD_3)_2SO$	1:2	9.06 d.d (1.6, 4.9)	8.05 d.d (4.9, 8.2)	8.82 d.d (1.6, 8.2)	8.05 s
II $\rightleftarrows$ **IV**	$(CD_3)_2SO$	1:3	9.00 d.d (1.4, 4.9)	7.98 d.d (4.9, 8.3)	8.75 d.d (1.4, 8.3)	8.00 s

[a] The chemical shifts were measured relative to the solvent signals (CH_3CN, δ 1.93 ppm, or DMSO-d_6, δ 2.50 ppm) and were recalculated to TMS. For complexes **II** and **IV**, averaged chemical shifts are given for the pairs 2-H/9-H, 3-H/8-H, 4-H/7-H, and 5-H/6-H.

Table 2. ^{13}C NMR spectra of 1,10-phenanthroline (**I**) and *n*-complexes **II**, **IV**, and **VI** at 25°C

Compound no.	Solvent	Ratio **I**:$NO^+BF_4^-$	Chemical shifts δ,[a] ppm ($J_{H,H}$, Hz)					
			C^2, C^9	C^3, C^8	C^4, C^7	C^5, C^6	C^{4a}, C^{6a}	C^{10a}, C^{10b}
I	CH_3CN	–	150.8	124.0	137.0	127.6	129.7	146.9
I	$(CD_3)_2SO$	–	149.8	123.2	136.1	126.5	128.4	145.4
II	CH_3CN	1:1	147.2	125.4	139.6	128.0	131.1	136.9
II	$(CD_3)_2SO$	1:1	147.3	125.4	141.4	127.1	129.0	136.8
II $\rightleftarrows$ **IV**	$(CD_3)_2SO$	1:2	147.7	126.0	142.1	127.6	129.6	137.0
II $\rightleftarrows$ **IV**	$(CD_3)_2SO$	1:3	147.8	126.1	142.2	127.7	129.7	137.1
VI[b]	$(CD_3)_2SO$	–	148.7	124.5	143.3	128.2	131.5	138.5

[a] The chemical shifts were measured relative to the solvent signals [CH_3CN, δ_C 118.2 ppm (CN), or DMSO-d_6, δ_C 39.5 ppm] and were recalculated to TMS. For complexes **II** and **IV**, averaged chemical shifts are given for the pairs C^2/C^9, C^3/C^8, C^4/C^7, C^{4a}/C^{6a}, and C^{10a}/C^{10b}.

[b] Averaged (in pairs) chemical shifts are given.

explained by shift of the equilibrium toward formation of dication **IV**.

The results of AM1 quantum-chemical calculations are consistent with the experimental data. Addition of one or two NO^+ cations to molecule **I** with formation of *n*-complexes **II** and **IV** is an exothermic process accompanied by liberation of 214.2 and 49.8 kJ/mol, respectively. The formation of symmetric structure **III** is less exothermic ($\Delta\Delta H_f$ = –45.6 kJ/mol). The energy of structure **V** in which the N–O bond is oriented orthogonally to the phenanthroline system is by 51.5 kJ/mol greater than the energy of initial complex **II**.

Solution of 1-nitroso-1,10-phenanthrolinium tetrafluoroborate in $(CD_3)_2SO$. A solution of 59 mg of 1,10-phenanthroline in 0.6 ml of $(CD_3)_2SO$ was added with stirring under argon to 41 mg of $NO^+BF_4^-$. An additional amount of $NO^+BF_4^-$ was then added to attain the **I**–$NO^+BF_4^-$ ratio 1:2 and 1:3.

Solution of 1-nitroso-1,10-phenanthrolinium tetrafluoroborate in CH_3CN. A solution of 109 mg of 1,10-phenanthroline in 2 ml of CH_3CN was added under argon to a suspension of 73 mg of $NO^+BF_4^-$ in 2 ml of CH_3CN.

1-Methyl-1,10-phenanthrolinium iodide (VI) was synthesized by the procedure reported in [8], mp 210–211°C (published data [8]: mp 200–203°C).

The NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.13 MHz for ^1H and 50.3 MHz for ^{13}C. The IR spectra were obtained on Bruker Vector 22 and Specord M-80 instruments from solutions in CH_3CN.

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