from cold $CHCl_3$–CH_3OH it melted at 83.5–84° dec. It was further characterized by its nmr and ir spectra (1770 and 1800 cm^{-1}).

Anal. Calcd: C, 65.44; H, 5.49. Found: C, 65.51; H, 5.47.

The reaction with NBS in $CDCl_3$ decomposed the peroxide extensively to a complex mixture. This was not further investigated after it became clear from the nmr spectrum that extensive degradation of the CH_3O part structure had occurred.[26]

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(26) See ref 25 for cleavage of methyl benzyl ether by the same reagent.

Steric Effects of *N*-Alkyl Groups on the First Acid Ionization Constant of 1,10-Phenanthroline

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Abstract: Acid ionization constants of protonated *N*-methyl- and *N*-ethyl-1,10-phenanthrolinium cations were determined spectrophotometrically in sulfuric acid solutions and compared with ionization constants of diprotonated 1,10-phenanthroline and of analogous bipyridyl cations. Ionization constant ratios $K_{BH_2^{2+}}/K_{BHR^{2+}}$ of 0.28 and 0.039 for R = CH_3 and R = C_2H_5 in the phenanthroline series indicate a steric effect for which a minimum quantitative value is estimated.

A procedure for the quantitative evaluation of the effect of hydrogen bonding on the strengths of dibasic acids was advanced by Westheimer and Benfey[1] and applied to the ionization constants of diprotonated 2,2′-bipyridyl and of its protonated *N*-alkyl cation. In the absence of hydrogen bonding, the ratio $K_{BH_2^{2+}}/K_{BHR^{2+}}$ of the ionization constants of the diprotonated amine and of the corresponding protonated *N*-alkyl cation was assumed to be equal to the statistical factor 2. Hydrogen bonding would stabilize the monoprotonated species BH^+, leading to an increased $K_{BH_2^{2+}}$ value and hence to a larger value for the ratio $K_{BH_2^{2+}}/K_{BHR^{2+}}$. No value less than 2 for this ratio was expected. In the bipyridyl case, $K_{BH_2^{2+}}/K_{BHR^{2+}}$ was found to be 6.7.

It was of interest to consider the corresponding hydrogen-bonding and possible steric effects in 1,10-phenanthroline in which the two pyridine rings are rigidly maintained in the coplanar cis position ideally suited for internal hydrogen bonding of the monoprotonated species.

Experimental Section

All melting points were determined on a Kofler micro hot stage. Spectra were recorded on a Beckman DB spectrophotometer and precise measurements in the 278-mμ region were obtained on a Beckman DU spectrophotometer at 23 ± 2°.

1,10-Phenanthroline. Eastman Organic Chemical's 1,10-phenanthroline monohydrate, dehydrates 97–98°, mp 117 5–119°, was dried *in vacuo* over silica gel for 5 hr.

***N*-Methyl-1,10-phenanthrolinium Iodide.** 1,10-Phenanthroline monohydrate (2.0 g) and methyl iodide (6.8 g) were warmed in nitrobenzene (50 ml) at 37° for 24 hr.[2] Crystals were separated and more methyl iodide (4.6 g) was added to the reaction mixture, which was heated at 37° for a further 24 hr. After washing with benzene, recrystallization to constant melting point from ethanol containing a few drops of water and drying at 107° over P_2O_5 *in vacuo* gave fine yellow plates: mp 200–203°; total yield 1.8 g or 53%. Its ultraviolet spectrum in H_2O shows peaks at 221 (partly due to iodide ion) and 271 mμ (ϵ 3.2 × 10^4). *Anal.* Calcd for $C_{13}H_{11}N_2I$: C, 48.5; H, 3.44; I, 39.4; N, 8.70. Found: C, 48.3; H, 3.41; I, 39.4; N, 8.76.

***N*-Ethyl-1,10-phenanthrolinium Iodide.** A mixture of 1,10-phenanthroline monohydrate (5.0 g) and ethyl iodide (42 g, bp 71.0–71.3°, uncorrected) in nitrobenzene (100 ml) was heated at 80–95° for 48 hr. After chilling the mixture, yellow needles were separated, washed with benzene, and recrystallized to constant melting point (fine yellow plates) from absolute ethanol: yield 4.4 g or 52%; mp: after drying over silica gel, 184.0–184.5°; after drying at 107° over P_2O_5 *in vacuo*, 180.0–181.5°. Its ultraviolet spectrum in H_2O shows a peak at 221 mμ partly due to iodide ion and a flat peak at 270–273 mμ (ϵ 3.2 × 10^4). *Anal.* Calcd for $C_{14}H_{13}N_2I$: C, 50.0; H, 3.90; I, 37.8; N, 8.33. Found: C, 49.8; H, 3.99; I, 37.6; N, 8.14.

Preparation of Test Solutions of *N*-Alkyl-1,10-phenanthrolinium Chlorides. The *N*-methyl- and *N*-ethyl-1,10-phenanthrolinium iodides were converted to the corresponding chlorides by shaking with freshly prepared silver chloride according to the method of Westheimer and Benfey.[1] The *N*-methyl cation has peaks at 218 (ϵ 3.3 × 10^4) and 271 mμ (ϵ 3.2 × 10^4). The *N*-ethyl cation has a peak at 215 mμ (ϵ 3.2 × 10^4) and a flat peak at 270–273 mμ (ϵ 3.2 × 10^4).

Determination of Ionization Constants of 1,10-Phenanthroline and of Its *N*-Methyl and *N*-Ethyl Cations. The spectrophotometric procedure has been described earlier.[1] H_0 values are those of Paul and Long.[3] No significant lateral shifts due to solvent were detected. Spectral data and ionization constant calculations are shown in Table I.

1,10-Phenanthroline. Our value $pK_{BH_2^{2+}} = -1.55 \pm 0.05$ (K = 35.5) obtained at 278 mμ compares with $pK_{BH_2^{2+}} = -1.6$ of Linnell and Kaczmarczyk,[4] determined from the variation of molar extinction coefficients at the maximum for each band as H_0 changes.

***N*-Methyl-1,10-phenanthrolinium Cation.** The protonated *N*-methyl cation has maxima at 225 (ϵ 2.9 × 10^4) and 278 mμ (ϵ 4.1 × 10^4). Extinction coefficients at 278 mμ at varying values of H_0 yielded $pK_{BHR^{2+}} = -2.11 \pm 0.09$ (K = 129).

***N*-Ethyl-1,10-phenanthrolinium Cation.** The protonated *N*-ethyl cation has maxima at 226 (ϵ 2.4 × 10^4) and 279 mμ (ϵ 3.8 × 10^4).

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Table I. Spectral Data and Calculated Acid Ionization Constants

Concn H_2SO_4, %	H_0	$\epsilon_{278} \times 10^{-4}$ l. mol^{-1} cm^{-1}	p*K*
	1,10-Phenanthroline-H_2^{2+}		
	pH 1.45	2.47 } (mean ϵ_{base}	
	pH 2.45	2.48 } 2.48)	
19.7	−0.99	2.83	−1.52
24.5	−1.33	3.08	−1.52
29.9	−1.71	3.35	−1.59
34.6	−2.04	3.67	−1.50
39.2	−2.35	3.78	−1.60
59.2	−4.39	3.98 } (mean ϵ_{acid}	
63.6	−4.88	4.04 } 4.01)	
	$pK_{BH_2^{2+}} =$ −1.55 ± 0.05		
	N-Methyl-1,10-phenanthroline-H^{2+}		
	pH 0.45	2.46 } (mean ϵ_{base}	
13.6	−0.57	2.46 } 2.46)	
29.9	−1.71	2.83	−2.23
32.7	−1.91	3.15	−2.05
34.6	−2.04	3.24	−2.09
39.2	−2.35	3.59	−2.02
44.2	−2.77	3.80	−2.16
59.2	−4.39	4.10 } (mean ϵ_{acid}	
69.0	−5.53	4.16 } 4.13)	
	$pK_{BMeH^{2+}} =$ −2.11 ± 0.09		
	N-Ethyl-1,10-phenanthroline-H^{2+}		
9.8	−0.23	2.50 } (mean ϵ_{base}	
15.0	−0.66	2.50 } 2.50)	
34.6	−2.04	2.68	−2.79
39.6	−2.38	2.84	−2.78
44.2	−2.77	3.08	−2.80
49.7	−3.35	3.43	−2.81
69.0	−5.52	3.64 (ϵ_{acid} (estimated) 3.70)	
	$pK_{BEtH^{2+}} =$ −2.80 ± 0.01		

Table II. Ionization Constants of Some Mono- and Diprotonated Diamines and Their *N*-Alkyl Derivatives

	$pK_{BH_2^{2+}}$	$K_{BH_2^{2+}}$	pK_{BH^+}[a]	$K_{BH_2^{2+}}/K_{BH^+}$	$pK_{BHR^{2+}}$	$K_{BHR^{2+}}$	$K_{BH_2^{2+}}/K_{BHR^{2+}}$
2,2′-Bipy	−0.52	3.3	4.4	8.3×10^4	0.31 (R = CH_3)	0.49	6.7
1,10-Pha	−1.55	35.5	5.0	3.6×10^6	−2.11 (R = CH_3)	129	0.28
					−2.80 (R = C_2H_5)	903	0.039

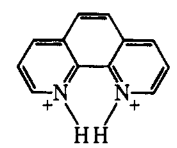
[a] L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. **17**, 616, 664 (1964).

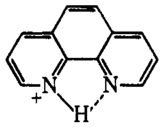
Extinction coefficients at 278 mμ at varying values of H_0 gave $pK_{BHR^{2+}} = -2.80 \pm 0.01$ (K = 903).

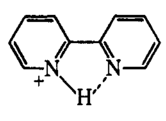
Discussion

Table II summarizes ionization constant data for 2,2′-bipyridyl,[1] 1,10-phenanthroline, and their *N*-alkyl derivatives.

The ratio $K_{BH_2^{2+}}/K_{BH^+}$ of first to second acid ionization constant is 3.6×10^6 for 1,10-phenanthroline as compared with 8.3×10^4 for 2,2′-bipyridyl. Whereas $BipyH^+$ is a slightly stronger acid than 1,10-$PhaH^+$ ($K_{BH^+} = 4.0 \times 10^{-5}$ and 1.0×10^{-5}, respectively) the $K_{BH_2^{2+}}$ values are in the reverse order (1,10-$PhaH_2^{2+}$ = 35.5, $BipyH_2^{2+}$ = 3.3). The 11-fold higher K_1 value for 1,10-$PhaH_2^{2+}$ is probably caused by three factors: (a) steric strain between the N hydrogens of the diprotonated 1,10-phenanthroline (in bipyridyl, the rings can twist out of the coplanar positions to avoid steric strain); (b) greater electrostatic repulsion between positive charges on nitrogen atoms due to their closer proximity; (c) greater hydrogen bonding in the monoprotonated 1,10-phenanthroline compared with the bipyridyl analog, because the rigidity of the molecular framework would favor the hydrogen-bonded form.


1,10-$PhaH_2^{2+}$


1,10-$PhaH^+$


2,2′-$BipyH^+$

The calculations of the effect of hydrogen bonding on the $K_{BH_2^{2+}}/K_{BH^+}$ ratio[1] had led to the conclusion that the ratio $K_{BH_2^{2+}}/K_{BHR^{2+}}$ should have a minimum value of 2 (statistical factor, no hydrogen bonding). Any excess above 2 was ascribed to hydrogen bonding, since the electrostatic environment of the acid and base forms should be little affected by replacement of N–H by *N*-alkyl.

The ratio $K_{BH_2^{2+}}/K_{BHR^{2+}}$ of 0.28 and 0.039 for the *N*-methyl- and *N*-ethylphenanthrolinium ions can only be ascribed to a sizable steric effect of the alkyl group decreasing the stability of the protonated doubly charged form. The smaller ratio for the ethyl group strengthens this conclusion. The ionization constant for 1,10-$PhaH_2^{2+}$ of 35.5 is increased to 129 when one proton is replaced by CH_3 and to 903 when replaced by C_2H_5. Assuming no contribution from electrostatic effects when N–H is replaced by N–R, and no hydrogen bonding, the steric effect reduces the ratio from 2 to 0.28 in the case of *N*-methyl and to 0.039 in the case of *N*-ethyl. If we assume that hydrogen bonding is of the same magnitude as for 2,2′-bipyridyl, then the ratio without steric effects would be 6.7 and the steric effect reduces this ratio from 6.7 to 0.28 and 0.039, respectively. Since the hydrogen bonding factor is almost certain to be larger in phenanthroline than in bipyridyl, these ratios of 24 for methyl and 170 for ethyl give a quantitative minimum measure of the steric effect of these alkyl groups.

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