Tetrahedron. Vol. 30, pp. 401 to 403. Pergamon Press 1974. Printed in Great Britain

ACID DISSOCIATION CONSTANTS OF MONO- AND DIPROTONATED SPECIES OF SOME POLYALKYL SUBSTITUTED 1,10-PHENANTHROLINES AND THE PECULIAR EFFECTS OF 2,9-DIALKYL SUBSTITUENTS

A. A. SCHILT* and W. E. DUNBAR
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

(*Received in the USA* 9 *July* 1973; *Received in the UK for publication* 9 *October* 1973)

Abstract—Acid dissociation constants of protonated species of some selected polyalkyl substituted 1,10-phenanthrolines were determined spectrophotometrically. The results confirm the existence of diprotonated species and indicate that polyalkyl substituents enhance both protonation steps, but not necessarily to the same degree. A peculiar effect, presumably steric in nature, was discovered for the 2,9-dialkyl substituted derivatives which suggests that a different mode of protonation is involved for these than for other substituted 1,10-phenanthrolines.

Early studies of 1,10-phenanthroline indicated that it behaved as a monoacidic base,[1] even though it has two potentially basic nitrogen atoms. The close proximity (2·5 Å) of the two N atoms in the inflexibly fused ring system is believed to favor addition of one proton but to exclude or discourage by steric or electrostatic factors the addition of a second proton.

There is now considerable evidence that diprotonated species of 1,10-phenanthroline and of some of its derivatives do exist in strongly acidic media. Several different investigators have reported isolating salts containing the diprotonated phenanthrolium cation, with anions such as iodide,[2] hexachlorouranate(4),[3] pentachloromanganate(3),[4] and hexachloroplatinate(4).[5] Other observations consistent with diprotonation include UV spectral shifts caused by concentrated acids[6] and the pH dependence of the distribution ratio for 5-methyl-1,10-phenanthroline between chloroform and aqueous solutions.[7] The acid dissociation constant of the diprotonated phenanthroline species has been estimated spectrophotometrically by various workers.[8-11] Values for some substituted derivatives have also been determined.[10,12]

The present work was undertaken to gain further evidence of diprotonated phenanthroline species and to study the influences of alkyl substituents on their acidities. It was also of interest to examine the results for clues as to possible steric effects and as to how the two protons are accommodated, either individually or mutually by the two N atoms.

EXPERIMENTAL

Spectra were recorded with a Cary Model 14 spectrophotometer, and pH was measured at 25 ± 2° with a Beckman Model G pH meter.

Materials. The 1,10-phenanthroline monohydrate and the 2, 9-dimethyl-4, 7-dimethyl-, and 3, 4, 7, 8-tetramethyl-substituted derivatives, obtained from the G. Frederick Smith Chemical Co., were used without further purification. The other four phenanthroline derivatives were pure samples provided by F. H. Case from his original, analyzed preparations described elsewhere.[13,14] All other reagents were Analytical Reagent grade.

Determination of pK values. A spectrophotometric procedure, described previously by various workers,[9,10,15] was used. Buffered solns of pH between 1 and 9, prepared for measurement of the pK values, had ionic strengths of 0·10 molar and were prepared from HCl or AcOH, KCl or NH_4OAc, and NH_3. For solns of pH less than one, appropriate standardized solns of HCl were employed, and the ionic strength was not controlled or adjusted. Some solns, those of pH > 6 that contained the tetra- or hexa-alkyl substituted phenanthrolines, also contained 10% by volume EtOH to provide the necessary solubility. Acidity functions of the type H_0, as determined for HCl by Paul and Long,[16] were applied to convert analytical concentration of HCl to pH ($H_0 = pH$).

RESULTS

The 8 compounds, selected for investigation on the basis of their special structural features, are listed in Table 1 together with the most pertinent spectral data obtained and used in the spectrophotometric measurement of their protonation equilibria. Table 2 presents the results of the pK measurements as well as some comparisons between pK_{BH_2} (the negative log of the acid dissociation constant of the diprotonated species) and pK_{BH} (that of the monoprotonated species) for each compound. The results are also plotted in Fig 1, which includes literature data for two other related compounds, to compare relative values and the effects of alkyl substituents.

Table 1. Spectral data

B Compound	λ max, nm H_2B^{2+}	HB^+	B	Isobestic points, nm, for equilibria $H_2B^{2+} = HB^+ + H^+$	$HB^+ = B + H^+$
Phen (1,10-phenanthroline)	278	270	265	212, 224, 239, 274, 335	239, 267, 284, 294
2,9-Dimethylphen	283	282	270	210, 225, 235, 270, 336	233, 274, 290, 296
4,7-Dimethylphen	279	274	265	214, 229, 244, 274, 325	234, 268, 287, 296
2,3,4-Trimethylphen	283	276	270	225, 278, 350	240, 273, 285, 299
2,3,4,6-Tetramethylphen	290	280	275	226, 250, 285, 350	241, 275, 303, 310
3,4,7,8-Tetramethylphen	284	277	272	220, 279, 335	237, 274, 292, 307
2,9-Diethyl-4,7-dimethylphen	283	282	272	229, 242, 276, 325	230, 275, 295, 305
2,3,4,7,8,9-Hexamethylphen	285	275	270	216, 238, 246, 279, 338	235, 276, 294, 303

Table 2. Acid dissociation constants

Compound	pK_{BH_2}	pK_{BH}	$(K_{BH_2}/K_{BH})10^{-6}$	ΔpK_{BH_2}[a]	ΔpK_{BH}[b]	$\Delta pK_{BH_2} - \Delta pK_{BH}$
Phen (1,10-phenanthroline)	−1·8	4·84	4·4	0	0	0
4,7-Dimethylphen	−1·1	5·95	11	0·7	1·11	−0·4
3,4,7,8-Tetramethylphen	−0·7	6·48	15	1·1	1·64	−0·5
2,3,4-Trimethylphen	−0·9	6·18	12	0·9	1·34	−0·4
2,3,4,6-Tetramethylphen	−0·9	6·42	21	0·9	1·58	−0·7
2,9-Dimethylphen	−0·4	5·77	1·5	1·4	0·93	0·5
2,9-Diethyl-4,7-dimethylphen	0·5	6·81	2·0	2·3	1·97	0·3
2,3,4,7,8,9-Hexamethylphen	1·36	7·37	1·0	3·16	2·53	0·63

[a] $\Delta pK_{BH_2} = (pK_{BH_2})_{compound} - (pK_{BH_2})_{phen}$.
[b] $\Delta pK_{BH} = (pK_{BH})_{compound} - (pK_{BH})_{phen}$.

DISCUSSION

The results clearly demonstrate the validity of diprotonation, proposed earlier to explain the spectral shifts produced by strong acids. For each compound studied here, a separate set of well-defined isobestic points was found to be associated with each protonation step. The possibility that the spectral shifts arise mainly from solvent or solution effects other than pH is very remote, particularly since two of the compounds (listed last in Table 2) gave spectral changes under conditions of constant ionic strength due only to changes in pH. These same two compounds are sufficiently strong as bases, weak as acids when protonated, to permit accurate measurement of their pK_{BH_2} values without the necessity of applying acidity functions of the type H_0, which admittedly are not appropriate to the charge type involved here (but used here and by previous workers because of the unavailability of H_+ acidity functions).

An interesting observation, which may be significant as to how the protons are bonded, is that the ratio K_{BH_2}/K_{BH} is nearly the same for the symmetrically substituted alkyl derivatives (4,7-dimethylphen and 3,4,7,8-tetramethylphen) as for the unsymmetrically substituted derivatives 2,3,4-trimethylphen and 2,3,4,6-tetramethylphen. One could reasonably assume that the substituent effects of the former would enhance the basicities of the two nitrogen atoms to the same degree but that the substituent effects of the latter two would

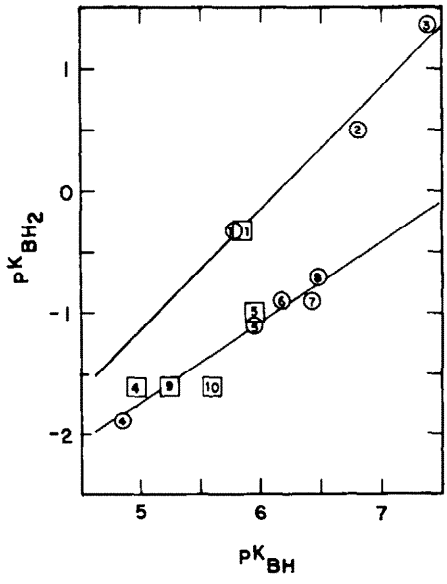

Fig 1. Plot of pK_{BH_2} for diprotonated *vs* pK_{BH} for monoprotonated species of various alkyl substituted 1,10-phenanthrolines. Circles represent data from Table 2, and squares represent data of McBryde.[10] Numbers identify compounds as follows: (1) 2,9-dimethylphen; (2) 2,9-diethyl-4,7-dimethylphen; (3) 2,3,4,7,8,9-hexamethylphen; (4) phen; (5) 4,7-dimethylphen; (6) 2,3,4-trimethylphen; (7) 2,3,4,6-tetramethylphen; (8) 3,4,7,8-tetramethylphen; (9) 5-methylphen; and (10) 5,6-dimethylphen.

enhance the basicity of the nitrogen in position 1 more than in position 10. If true, the ratio of the K values for the symmetrically substituted derivatives would be expected to be considerably less than that for the unsymmetrically substituted derivatives. This, however, was not found to be the case. A reasonable conclusion is that the protons do not bond individually to separate nitrogens but rather that each proton bonds in such a manner that it interacts strongly with both basic N atoms. Such a conclusion is consistent with previously proposed structures for monoprotonated 1,10-phenanthroline. Beattie and Webster[17] proposed a structure consisting of a hydronium ion bonded to phenanthroline by two N···H···O H-bonds. Fahsel and Banks[18] proposed similar structures involving the trihydrated hydronium ion $H_9O_4^+$ rather than the hydronium ion for protonated phenanthroline species of the type $H(phen)_n^+$, where n = 1, 2, or 3.

An especially remarkable observation, and one which may also be meaningful as to how and where the protons are bound, is the unique relationships found for the pK values of the 2,9-dialkyl substituted derivatives (the last three compounds in Table 2) as compared to those found for the other compounds. It is seen from Table 2 that not only are the K_{BH_2}/K_{BH} ratios less for the former but, more significantly, the differences $\Delta pK_{BH_2} - \Delta pK_{BH}$ are positive for the 2,9-dialkyl derivatives and negative for the others. These differences are also apparent on examination of Fig 1 which includes other data taken from the literature. The slope of the plot for the 2,9-dialkyl derivatives is unity and that for the others is 0·66. Simply stated, these results indicate that the combined substituent effects enhance the basicities of both nitrogen atoms (diminish the acidities of both protonated species) but with one important distinction: the 2,9-dialkyl substituents enhance the second protonation step as much as they do the first, whereas other alkyl substituents enhance the first more than the second protonation step. This peculiar effect appears to be uniquely associated with 2,9-disubstituted derivatives and not with 2- or 9-monosubstituted derivatives.

In order to explain these observations we suggest that the two alkyl substituents in the 2- and 9-positions give rise to a combined steric effect that inhibits the addition of both solvated protons to essentially the same degree. If the solvation energies for both protons are similarly affected, and if both solvated protons interact mutually with both nitrogen atoms, the above observations are qualitatively predictable. In the absence of bulky substituents in both positions 2 and 9, there should be less steric inhibition towards the first protonation step than the second. The relatively tight solvation shell around the first protonated species could seriously interfere with the second protonation process. Thus the second solvated proton would not experience the inductive effects of the alkyl substituents as fully as the solvated proton added first. The results obtained can thus be explained. Other effects could conceivable account for the results found, so further studies are desirable. In this regard, it is unfortunate that NMR studies to date have not provided structural evidence other than to indicate the probable existence of three protonated forms of phenanthroline: phen H^+, phen H_2^{+2}, and phen $_2H^+$.[19]

REFERENCES

[1]T. S. Lee, I. M. Kolthoff and D. L. Leussing, *J. Am. Chem. Soc.* **70**, 2348 (1948)
[2]L. H. Berka and S. W. Press, *Inorg. Nucl. Chem. Lett.* **6**, 439 (1970)
[3]H. K. Saha, *Indian Chem. Soc.* **47**, 88 (1970)
[4]H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.* **18**, 1743 (1965)
[5]R. N. Sylva and H. A. Goodwin, *Ibid.* **19**, 1735 (1966)
[6]R. Nasanen and E. Uusitalo, *Suomen Kemistilehti* **B, 29**, 11 (1950)
[7]G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.* 4953 (1964)
[8]D. W. Margerum, R. Bystroff, and C. V. Banks, *J. Am. Chem. Soc.* **78**, 4211 (1956)
[9]R. H. Linnell and A. Kaczmarczyk, *J. Phys. Chem.* **65**, 1196 (1961)
[10]W. A. E. McBryde, *Canad. J. Chem.* **43**, 3472 (1965)
[11]O. T. Benfey and J. W. Mills, *J. Am. Chem. Soc.* **93**, 922 (1971)
[12]P. Levillain and R. Bourdon, *Bull. Soc. Chim. Fr.* 377 (1971)
[13]F. H. Case and H. H. Wisneski, *J. Heterocyclic Chem.* **5**, 789 (1968)
[14]K. C. John and F. H. Case, *J. Chem. Eng. Data* **13**, 568 (1968)
[15]F. H. Westheimer and O. T. Benfey, *J. Am. Chem. Soc.* **78**, 5309 (1956)
[16]M. A. Paul and F. A. Long, *Chem. Rev.* **57**, 1 (1957)
[17]I. R. Beattie and M. Webster, *J. Phys. Chem.* **66**, 115 (1962)
[18]M. J. Fahsel and C. V. Banks, *J. Am. Chem. Soc.* **88**, 878 (1966)
[19]J. V. Rund and P. C. Keller, *J. Chem. Soc.* (A), 2821 (1970)