817. *Studies in the Phenanthridine Series. Part II*[1]

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The ionisation constants of some alkyl- and benzo-phenanthridines and their α-amino-derivatives have been determined; it is concluded that nonplanarity due to molecular overcrowding has no significant effect on basic strength in either series. The N–H stretching frequencies of the amino-derivatives have been determined, together with the corresponding band intensities. All the bases exist in the amino-form.

In Part I[1] we described the preparation of 1- and 10-methyl- and 1,10-dimethyl-phenanthridine, their 6-amino-derivatives, and 5-aminobenzo[*a*]- and 6-aminobenzo[*k*]-phenanthridine. In 6-amino-1,10-dimethylphenanthridine the degree of overcrowding was shown to be sufficient to permit resolution. Analogy with 4,5-dimethylphenanthrene[2] suggests that strain is relieved primarily by twisting of the 1a,1b-bond, with concomitant distortion of the heterocyclic ring. The marked effect of this distortion on the polarographic behaviour of the phenanthridine system has been described elsewhere,[3] and to examine further the possible influence of nonplanarity on chemical behaviour, we have now determined the ionisation constants of a number of suitable substituted phenanthridine derivatives. The examination of an *N*-heterocyclic system in this context appeared worthwhile, since the reactive centre here forms an intrinsic part of the ring system; effects due to nonplanarity might therefore be correspondingly larger than in the case of substituents on overcrowded aromatic systems. Newman and his co-workers[4-6] have recently described related work in the benzo[*c*]phenanthrene series. In particular, by comparing the strengths of the benzo[*c*]phenanthroic acids with those of other aromatic acids, Newman and Boden[4] attempted to correlate acid strength with the degree of ring-warping at the adjacent ring-carbon atom; unfortunately, the small differences between the measured ionisation constants rendered definite conclusions difficult to draw.

The geometry of the phenanthridine ring system suggests that nonplanarity might affect basic strength by (*a*) slightly changing the state of hybridisation of the nitrogen atom so as to increase the amount of *p* character, (*b*) reducing any steric hindrance to protonation produced by the *peri* hydrogen atom, or (*c*) decreasing steric hindrance to solvation of the phenanthridinium cation. All three influences should, in principle, be base-strengthening but since major effects do not normally result, in this connection at least, from the steric requirements of a single proton,[7] it seemed probable that changes in the extent of steric hindrance to protonation would be unimportant. Since either, or both, of the remaining factors might exert some influence on basic strength we first determined the ionisation

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[1] Part I, *J.*, 1965, 3032.
[2] R. I. T. Cromartie and J. N. Murrell, *J.*, 1961, 2063.
[3] B. R. T. Keene and P. Tissington, *Rec. Trav. chim.*, 1965, **84**, 488.
[4] M. S. Newman and H. Boden, *J. Amer. Chem. Soc.*, 1961, **83**, 115.
[5] M. S. Newman and J. Blum, *J. Amer. Chem. Soc.*, 1964, **86**, 503.
[6] M. S. Newman and J. Blum, *J. Amer. Chem. Soc.*, 1964, **86**, 1835.
[7] G. S. Hammond, " Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley, New York, 1956, ch. IX.

constants of the phenanthridines listed in Table 1. pK_a values were determined spectrophotometrically[8] in aqueous solution (total concentration 0·01M), and, since our interest lay in differences, the values obtained (pK_a^M) have not been corrected to the corresponding " thermodynamic " values (pK_a^T).[9] 3- and 8-Methylphenanthridine were included since the methyl groups in these reference compounds should exert essentially the same electronic influence as in 1- and 10-methylphenanthridine, respectively. Spectral data for the bases and their cations are also given in Table 1.

All the monomethylphenanthridines were found to be slightly more basic than phenanthridine itself, although no simple relationship appears to exist between substituent position and the corresponding pK_a value. The increase in basic strength is in every case only that expected on the basis of methyl-group substitution,[10] bearing in mind the rapid attenuation of substituent effects across aromatic rings.[11] The increased basic strength of 1,10-dimethylphenanthridine compared with the monomethyl derivatives is insufficient to suggest a significant steric influence. The values obtained for the two benzophenanthridines support this conclusion, since these differ only very slightly from that of the parent base; annellation at sites remote from the basic centre normally produces only small changes in basic strength.[11]

TABLE 1

The ultraviolet absorption spectra and ionisation of the phenanthridines

Substituent	pH	$\lambda_{max.}$ (log ε)	pK_a (in water at 22°)
None	1·00	248(4·54), 316(3·83), 355(3·53)	4·47 ± 0·03[a]
	9·17	248(4·61), 290(3·75), 330(3·22), 346(3·18)	
1-Me	1·00	242(4·62), 328(3·89)	4·70 ± 0·02
	9·17	246(4·69), 294(3·83), 332(3·16), 348(3·11)	
3-Me	1·00	252(4·61), 316(3·85), 370(3·56)	4·76 ± 0·01[b]
	9·17	250(4·68), 292(3·71), 320(3·06), 336(3·26), 350(3·25)	
8-Me	1·00	252(4·64), 318(3·86), 372(3·57)	4·93 ± 0·02[b]
	9·17	250(4·70), 290(3·73), 320(3·06), 336(3·27), 350(3·27)	
10-Me	1·00	244(4·64), 324(3·86)	4·60 ± 0·02
	9·12	246(4·72), 294(3·82), 334(3·24), 348(3·24)	
1,10-Me$_2$	1·00	250(4·56), 346(3·90)	4·96 ± 0·04
	9·17	250(4·58), 310(3·87)	
Benzo[*a*]	1·00	238(4·32), 248(4·33), 282(4·49), 400(3·66)	4·48 ± 0·02
	9·20	276(4·50), 312(3·88), 340(3·13), 358(3·30), 376(3·36)	
Benzo[*k*]	1·00	254(4·30), 282(4·61), 330(3·79), 344(3·87), 380(3·46), 410(3·57)	4·44 ± 0·01
	9·22	272(4·66), 310(3·89), 340 * (3·12), 358(3·34), 376(3·38)	

* Inflexion.

[a] Osborn, Schofield, and Short (ref. 13) report 4·52 ± 0·01 at 20°. [b] Measured at 24°.

The pK_a values of the aminophenanthridines are recorded in Table 2, together with details of their ultraviolet absorption spectra. The determinations were carried out at 25° to avoid solubility difficulties, particularly in the case of the aminobenzophenanthridines.

The enhanced basic strength of α-amino-N-heterocyclic compounds has been ascribed to the presence of an amidine-like system,[10] involving considerable localisation of the ring π-electrons. The ring nitrogen atom is normally the basic centre.[10,12,13] The ionisation constants of nonplanar systems of this type are therefore of some interest, since warping of the hetero-ring might produce some additional localisation, with a consequent increase in basic strength. The results obtained from the parent phenanthridines suggested that the

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[8] A. Albert and E. P. Serjeant, " Ionization Constants of Acids and Bases," Methuen, London, 1962, ch. 4.

[9] A. Albert, " Physical Methods in Heterocyclic Chemistry," Academic Press, London, 1963, Vol. I, ch. 1.

[10] A. Albert, R. Goldacre, and J. Phillips, *J.*, 1948, 2240.

[11] J. Clark and D. D. Perrin, *Quart. Rev.*, 1964, 295.

[12] D. P. Craig and L. N. Short, *J.*, 1945, 419.

[13] A. R. Osborn, K. Schofield, and L. N. Short, *J.*, 1956, 4191; K. Schofield, *J.*, 1958, 1312.

influence of the *peri* hydrogen atom can only be slight, whilst any steric effect due to the neighbouring amino-group should remain essentially constant throughout the series. In fact, the pK_a values of 6-amino-1- and 6-amino-10-methylphenanthridine showed the slight increase expected on the basis of methyl substitution, and while the increment observed in passing from either value to that of 6-amino-1,10-dimethylphenanthridine is somewhat larger than might be expected, the overall increase is still not sufficient to be attributed unambiguously to nonplanarity of the ring system.

TABLE 2

Substituent	pH	$\lambda_{max.}$ ($\log_{10} \varepsilon$)	pK_a (in water at 25°)
None	2·00	240(4·62), 294(3·68), 332(3·94), 348(3·93)	7·23 ± 0·03 [a]
	10·00	238(4·66), 302(3·76), 316(3·77), 332(3·80), 348(3·79)	
1-Me	2·00	240(4·58), 290 * (3·82), 334(3·89), 350(3·88)	7·49 ± 0·02
	10·00	238(4·59), 250 * (4·40), 334(3·71), 350(3·68)	
10-Me	2·00	242(4·64), 290 * (3·75), 336(3·90), 350(3·90)	7·51 ± 0·01
	10·00	240(4·65), 284 * (3·80), 304(3·80), 334(3·75), 352(3·74)	
1,10-Me_2	2·00	228(4·28), 250(4·52), 346(3·84)	7·91 ± 0·02
	10·00	246(4·55), 316(3·83), 360(3·67)	
Benzo[*a*]	2·00	272(4·68), 310(4·00), 364(3·93), 382(3·94)	6·67 ± 0·03
	10·00	258(4·53), 272(4·50), 344(3·62), 360(3·74), 378(3·75)	
Benzo[*k*]	2·00	272(4·70), 310(3·86), 320(3·93), 348(3·64), 364(3·89), 382(3·93)	6·64 ± 0·04
	10·00	258(4·54), 318(4·02), 362(3·67), 380(3·72)	

* Inflexion.

[a] Albert, Goldacre, and Phillips (ref. 10) report 7·31 at 20°.

The possibility of amine–imine tautomerism in 6-aminophenanthridine has been examined spectrophotometrically by Reese,[14] who concluded that the base existed predominantly in the amino-form. Mason [15] reached a similar conclusion from a study of the infrared spectrum of the compound in the 3300—3600-cm.$^{-1}$ region. Since, however, in a nonplanar system the increased flexibility of the imino-form might compensate for the decrease in resonance energy involved, it seemed possible that a suitably substituted aminophenanthridine might contain detectable amounts of the imino-form at equilibrium. Accordingly, we examined the infrared spectrum of the aminophenanthridines listed in Table 3.

While this work was in progress Newman and Blum [5] reported that none of the six possible hydroxybenzo[*c*]phenanthrenes showed carbonyl absorption, indicating that in this series strain is not relieved by tautomerism. More recently, the same authors [6] have reported that 3-aminobenzo[c]phenanthrene does not appear to contain appreciable amounts of the imino-form, since the compound can be recovered unchanged after boiling with aqueous sodium hydroxide. Also listed in Table 3 are the approximate force constants calculated from Linnett's equations.[16] Imines absorb relatively weakly near 3300 cm.$^{-1}$, whereas the corresponding primary amines show two bands [15] of greater intensity at approximately 3400 and 3500 cm.$^{-1}$. None of the compounds examined showed significant absorption in the 3300-cm.$^{-1}$ region but the symmetric and antisymmetric N–H stretching transitions (ν_s and ν_a, respectively) appeared as sharp bands close to 3400 and 3500 cm.$^{-1}$.

TABLE 3

The infrared spectra of α-aminophenanthridines in chloroform

Substituent	ν_a (cm.$^{-1}$)	ν_s (cm.$^{-1}$)	$k \times 10^{-5}$ (dyne cm.$^{-1}$)	Substituent	ν_a (cm.$^{-1}$)	ν_s (cm.$^{-1}$)	$k \times 10^{-5}$ (dyne cm.$^{-1}$)
None	3511	3404	6·62	1,10-Me_2	3511	3405	6·62
None [a]	3513	3409		Benzo[*a*]	3508	3403	6·62
1-Me	3509	3404	6·62	Benzo[*k*]	3510	3407	6·63
10-Me	3500	3399	6·58				

[a] Values obtained by Mason in carbon tetrachloride.

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[14] C. B. Reese, *J.*, 1958, 895.

[15] S. F. Mason, *J.*, 1959, 1281.

[16] J. W. Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223.

The frequencies of these bands varied little throughout the series, and this is reflected in the closely similar N–H force constants, with the surprising exception of 6-amino-10-methylphenanthridine.

The intensity of the symmetric N–H vibrational transition in aromatic amines depends on the extent of delocalisation of the lone pair on the nitrogen atom. Elliott and Mason [17] have shown that, whilst annellation of the aromatic system has little effect on the intensity of the antisymmetric band, that of the corresponding symmetric band shows a marked increase. Since the extent of delocalisation of the lone pair should be decreased by forcing the ring system into a nonplanar configuration, we also examined the intensities of the N–H bands of the aminophenanthridines (Table 4). The intensities were calculated from the band half-widths and maximum extinction coefficients [18] and while the errors inherent in this method render their absolute values unreliable, differences are probably significant.

TABLE 4

Band intensities of the symmetric and antisymmetric N–H transitions of the α-aminophenanthridines

	Antisymmetric			Symmetric		
Substituent	ε (cm.^{2} mole^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm.$^{-1}$)	I (cm. mole^{-1})	ε (cm.^{2} mole^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm.$^{-1}$)	I (cm. mole^{-1})
None	44·6	45	3226	82·0	37	4677
1-Me	40·2	43	2711	80·5	35	4424
10-Me	49·0	35	2693	92·3	30	4349
1,10-Me$_2$	28·9	41	1861	56·3	33	2920
Benzo[*a*]	43·5	36	2669	122·3	29	5571
Benzo[*k*]	42·6	41	2739	91·1	35	5010

In the case of the aminobenzophenanthridines the expected increase in intensity of the symmetric band was observed, but in 6-amino-1,10-dimethylphenanthridine both bands showed a marked decrease in intensity. Since, however, the symmetric to antisymmetric intensity ratio differs only slightly from that of 6-aminophenanthridine it seems doubtful whether the change may be simply interpreted in terms of decreased delocalisation, particularly since no decrease in the corresponding force constant is apparent (Table 3). It is noteworthy, however, that in related work Essery and Schofield [19] have shown that methyl substitution at the 3- and 5-positions of 4-aminopyridine produced a decrease in intensity of both symmetric and antisymmetric N–H stretching bands, again without a decrease in the force constant.

EXPERIMENTAL

3- and 8-Methylphenanthridine were obtained by the method of Arcus and Coombs.[20] We also gratefully acknowledge the gift of samples of these compounds by Dr. M. M. Coombs. Phenanthridine was a commercial specimen obtained from B. Newton Maine and Co. The preparation of the remaining compounds in Tables 1 and 2 has been described previously.[1] All materials were crystallised to constant melting point immediately before use.

Ultraviolet absorption curves were determined using a Unicam S.P. 500 spectrophotometer fitted with a thermostatically controlled cell compartment.

The infrared data were obtained with a Grubb–Parsons DB3/DM3 grating spectrophotometer. 2×10^{-2}M-solutions were prepared in chloroform which had previously been distilled from phosphorus pentoxide. The solutions were examined in cells of 5·0-cm. path-length with potassium bromide endplates.

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[17] J. Elliott and S. F. Mason, *J.*, 1959, 1275.

[18] D. A. Ramsey, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

[19] J. M. Essery and K. Schofield, *J.*, 1961, 3939.

[20] C. Arcus and M. M. Coombs, *J.*, 1954, 4319.