

Studies on the 1,8-Diazanaphthalene (napht) - Hydrogen Ion System and Isolation of the  $[H(napht)_2]^+$  Complex Cation

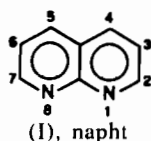
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By reaction of 1,8-diazanaphthalene (napht) and aqueous perchloric acid two compounds of formulae  $napht.HClO_4$  and  $(napht)_2.HClO_4$  were isolated. P.m.r. and i.r. studies suggest that the latter compound contains the hydrogen ion complex  $[H(napht)_2]^+$ . The bonding of the hydrogen ion in this complex is discussed. The potentiometric formation constants of the mono- and bis-ligand adducts in aqueous solution at 25.0°C in 0.5 M  $KNO_3$  were found to be 3.60 and 4.57 respectively.

Recent studies, including p.m.r.<sup>1</sup> and calorimetric<sup>2</sup> measurements, on the reaction between the hydrogen ion and 1,10-phenanthroline (phen) in aqueous solution, showed the existence of equilibria involving species with stoichiometric ratios  $H^+/phen$  of 1:1, 1:2 and perhaps 1:3.<sup>3</sup> In the solid state the mono-hydrogen salt  $[H(phen)]ClO_4$  and a solid compound of analytical formula  $(phen)_2.HClO_4$  were isolated:<sup>1,4</sup> the latter was shown to contain the mono-hydrogen-bis-(1,10-phenanthroline) cation  $[H(phen)_2]^+$ .<sup>4</sup> I.r. analysis and preliminary X-ray data suggested the non-equivalence of the two basic molecules in this ion.<sup>4</sup>

We were thus interested in studying whether a similar ligand behaviour could be exhibited by the bidentate base 1,8-diazanaphthalene (1,8-naphthyridine (I), abbreviated as napht), which has recently arisen special interest for forming transition metal complexes with unusual stereochemistry.<sup>5</sup>



From aqueous solutions of 1,8-diazanaphthalene and perchloric acid, two different anhydrous compounds with analytical formula  $napht.HClO_4$  and  $(napht)_2.HClO_4$ , respectively, have been isolated, depending on the  $napht/HClO_4$  molar ratio.

Conductometric measurements in nitroethane solution have shown that both compounds behave as univalent electrolytes. Molecular weights about one-half of those calculated for the above formulae have

been found for the two compounds. These data agree with ionic structures of the type  $[H(napht)]ClO_4$  and  $[H(napht)_2]ClO_4$ , respectively. Moreover the i.r. spectrum of  $[H(napht)_2]ClO_4$  significantly differs both from that of the free ligand and that of the mono-adduct  $[H(napht)]ClO_4$ , indicating that the former compound is a definite chemical species and not a mixture of the latter two.

The solid-phase i.r. spectrum of  $[H(napht)]ClO_4$  shows a broad band centered at *ca.* 2650  $cm^{-1}$  which shifts to *ca.* 2000  $cm^{-1}$  upon deuteration. This band is thus attributable to the  $\nu(N-H)$  vibration in a quadrivalent nitrogen atom.<sup>6</sup> The low frequency value and broadness of this band are indicative of intra- or intermolecular hydrogen bonding. On the contrary, we were unable to identify any band attributable to  $\nu(N-H)$  vibration for  $[H(napht)_2]ClO_4$ , its i.r. spectrum being practically identical with that of  $[D(napht)_2]ClO_4$ . However, it is known that  $\nu(X-H)$  bands in compounds exhibiting  $X-H \dots Y$  hydrogen bonds shift to lower frequency, at the same time becoming *less prominent*, as the  $X-H \dots Y$  distance decreases, (*i.e.*, with increasing  $H \dots Y$  bond strength).<sup>6,7</sup> This effect is maximum when the hydrogen bond is symmetrical. The absence of any discernible  $\nu(N-H)$  bond in  $[H(napht)_2]ClO_4$  thus suggests the presence of symmetrical hydrogen bonds joining the two molecules of ligand. Possibly the bonds could be equally shared among all four nitrogen atoms. It is not unlikely that  $\nu(N \dots N)$  vibration frequencies for the  $N-H \dots N$  group could be detected at frequency values lower than *ca.* 200  $cm^{-1}$ ,<sup>8</sup> that is, outside our range of investigation.

P.m.r. data for napht and the two proton adducts in  $d_3$ -nitromethane solution are reported in Figure 1 and Table I. As for the free ligand,<sup>9</sup> three distinct aromatic proton signals are observed for both  $[H(napht)]ClO_4$  and  $[H(napht)_2]ClO_4$ ; this indicates either a symmetrical or a tautomeric time-averaged position of the hydrogen ion with respect to the nitrogen donors. As expected, downfield shifts with respect to the free ligand are observed for these signals in the protonated species, but while the shifts

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**Table I.** Proton magnetic resonance spectra.

| Compound  | Chemical shifts ( $\tau$ ) |                  |                  | Coupling constants (cps)         |                                  |                                  |
|---|----------------------------|------------------|------------------|----------------------------------|----------------------------------|----------------------------------|
|   | H <sub>2,7</sub>           | H <sub>3,6</sub> | H <sub>4,5</sub> | J <sub>23</sub> =J <sub>67</sub> | J <sub>24</sub> =J <sub>57</sub> | J <sub>34</sub> =J <sub>56</sub> |
| napht   | 0.92                       | 2.41             | 1.63             | 4.2                              | 2.0                              | 8.0                              |
| [H(napht) <sub>2</sub> ] <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> | 0.44                       | 1.96             | 1.15             | 4.2                              | 2.0                              | 8.0                              |
| [H(napht)] <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>               | 0.59                       | 1.78             | 0.85             | 5.0                              | 1.8                              | 8.7                              |

of 3,6 and 4,5 protons increase on passing from napht to [H(napht)<sub>2</sub>]<sup>+</sup> and to [H(napht)]<sup>+</sup>, *i.e.*, with increasing acidity, the shift of the 2,7 protons is larger for the bis-adduct than for the mono-adduct (Figure 1). This is probably accounted for by assuming that in the former compound the two molecules of ligand surround the hydrogen ion in a staggered configuration, so that the *ortho* protons are mostly affected by the magnetic anisotropy of the neighbour aromatic ring giving rise to dipolar shift contributions.

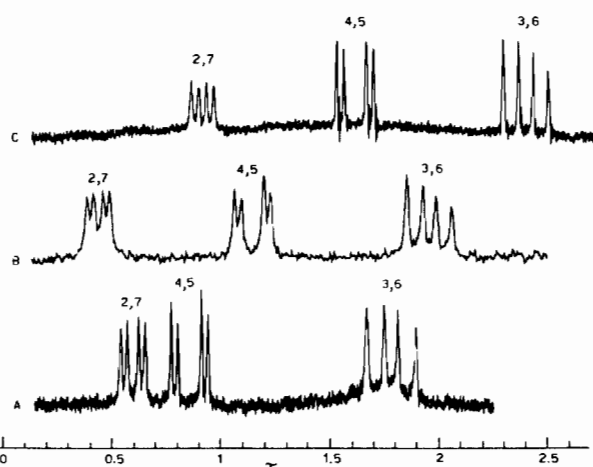


Figure 1. Proton magnetic resonance spectra of d<sub>3</sub>-nitromethane solutions of. A, [H(napht)]ClO<sub>4</sub>; B, [H(napht)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup>; C, napht.

The hydrogen ion signal is not strictly reproducible and is not reported.

Computer analysis of potentiometric titration curves indicates the existence in aqueous solution of two species having the stoichiometries [H(napht)]<sup>+</sup> and [H(napht)<sub>2</sub>]<sup>+</sup>. The stability constants obtained at 25.0°C in 0.5 M KNO<sub>3</sub> are 3.60 ± 0.01 and 4.57 ± 0.07 for the mono- and bis-ligand adduct respectively. The low degree of formation of the latter species, under the experimental conditions employed, precludes any possibility to gain further information on its nature by calorimetric measurements.

## Experimental Section

**Preparation of the compounds.** 1,8-diazanaphthalene was prepared as previously described.<sup>10</sup> [H(napht)]ClO<sub>4</sub> and [H(napht)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> were obtained by concentration of aqueous solution of napht and HClO<sub>4</sub> in 1:10 and 3:1 molar ratios respectively. They were recrystallized from water or acetone, and dried under

vacuum at 70°C. The deuterated compounds were prepared by standard exchange methods.

**Analytical data.** [H(napht)]ClO<sub>4</sub>, white crystals, m.p. 214-215°C (Found: C, 41.3; H, 3.1; N, 11.9; C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>ClO<sub>4</sub> requires C, 41.65; H, 3.05; N, 12.15).

$\nu_{\max}$ : 3090 w, 3030 sh, 2650 br,m, 1650 m, 1605 m, 1590 sh, 1565 m, 1540 sh, 1480 m, 1415 m, 1380 sh, 1285 m, 1240 m, 1215 m, 1155 m, 1140 m, 1080 br,s, 1015 m, 1005 sh, 980 w, 960 s, 935 m, 855 s, 838 m, 792 s, 780 vw, 770 w, 725 m, 635 s, 625 s, 545 w, 540 m, 482 m, 475 m, 405 m.

Molar conductivity in nitroethane: 89 cm<sup>2</sup>/ohm mole (Reference value: [NBu<sub>4</sub>]<sup>+</sup>Br<sup>-</sup>, 80 cm<sup>2</sup>/ohm mole).

[H(napht)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, pale yellow crystals, m.p. 172-173°C (Found: C, 53.0; H, 3.8; N, 15.8; C<sub>16</sub>H<sub>13</sub>N<sub>4</sub>ClO<sub>4</sub> requires C, 53.25; H, 3.65; N, 15.55).

$\nu_{\max}$ : 3065 w, 1660 w, 1605 m, 1590 sh, 1570 sh, 1488 m, 1415 w, 1300 m, 1265 sh, 1235 m, 1205 w, 1140 m, 1095 s, 980 m, 910 sh, 840 m, 805 m, 775 m, 700 br, 660 br,m, 625 m, 550 br,m, 485 m, 470 m, 410 br,m, 350 br,m.

Molar conductivity: 90 cm<sup>2</sup>/ohm mole.

**Physical measurements.** P.m.r. spectra were recorded on a Varian DA 60 spectrometer operating at 60 MHz and at 26°C. All the spectra were obtained in d<sub>3</sub>-nitromethane solution and referenced directly to internal tetramethylsilane.

Conductivity measurements were performed at 20°C on 10<sup>-3</sup>M solutions with a WTW model LBR/B conductance bridge.

Molecular weights were determined in nitroethane at 37°C with a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzil.

I.r. spectra were recorded in the range 4000-250 cm<sup>-1</sup> on Nujol mulls supported on CsI disks, using a Perkin Elmer Model 457 spectrophotometer.

The apparatus and the experimental procedure for the e.m.f. measurements were described.<sup>11</sup> Calculation of the formation constants was carried out on an IBM 1130 computer using the already described LEAST programme.<sup>12</sup> The calculations were performed on 65 data points deriving from two different titration curves.

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