Communications to the Editor

The Bisphenanthrolinium Ion. An X-ray Crystal Structure

Luciana Maresca, Giovanni Natile,* and
Francesco P. Fanizzi

Dipartimento Farmaco-Chimico
via G. Amendola 173, 70126 Bari, Italy

Francesca Stasi

Dipartimento Geomineralogico
via Salvemini, 70126 Bari, Italy

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The bisphenanthrolinium ion, $Hphen_2^+$, was first reported some 40 years ago;[1] the following studies established the high thermodynamic stability of this species.[2] However, all attempts to determine its X-ray crystal structure were unsuccessful so that the intimate nature of this complex remained controversial ranging from that of a discrete molecular species with a naked proton encapsulated by the four nitrogens of two phenanthrolines[2,3] to that of self-stacking association of various phenanthroline molecules.[4]

We have finally succeeded in determining the X-ray crystal structure of $(Hphen_2)(ClO_4)$.[5] The two phenanthrolines are linked together by three hydrogen bonds which involve the two nitrogens and one ortho hydrogen of each phenanthroline. This particular arrangement is essential for the stability of the molecular edifice.

Phenanthroline is sparingly soluble in water; in the presence of acid twice as many moles of base dissolve giving a clear solution (HCl, 0.5×10^{-3}; phen, 10^{-3} mol; H_2O, 3-4 cm^3). By addition of ClO_4^- white small crystals of $(Hphen_2)(ClO_4)$ precipitate immediately.

Crystals are triclinic, space group $P\bar{1}$, with eight phenanthrolines and four ClO_4^- per unit cell. Each couple of phenanthrolines shares an acidic proton forming a total of four complex cations (Figure 1); there are two crystallographically independent cations in the asymmetric unit (a and b in Figure 2).[5,6]

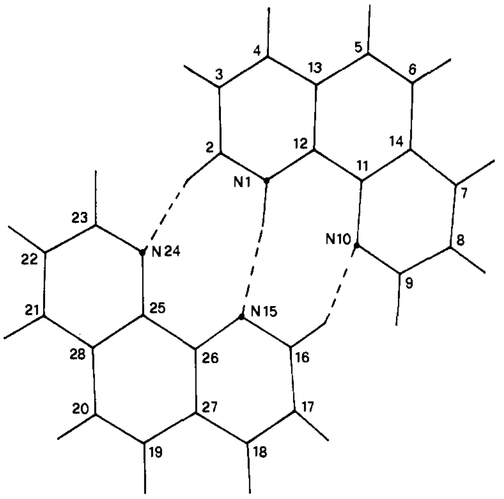

Figure 1. Numbering scheme of $Hphen_2^+$ cations.

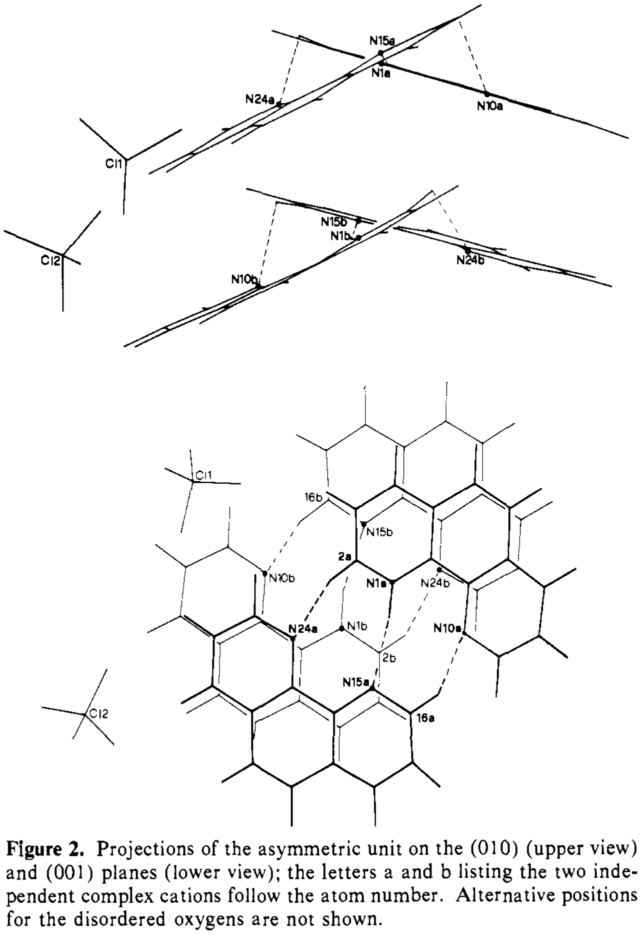

Figure 2. Projections of the asymmetric unit on the (010) (upper view) and (001) planes (lower view); the letters a and b listing the two independent complex cations follow the atom number. Alternative positions for the disordered oxygens are not shown.

The acidic proton is clearly distinguishable on the Fourier difference map, and it is accurately located at a N(1)-H distance

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[5] Crystal data: $C_{24}H_{17}N_4ClO_4$, $F_w = 460.89$. Triclinic, $P\bar{1}$, $a = 13.211$ (6) Å, $b = 22.386$ (12) Å, $c = 7.352$ (5) Å, $\alpha = 95.37$ (5)°, $\beta = 97.36$ (4)°, $\gamma = 77.41$ (4)°, $V = 2099.68$ Å^3, $Z = 4$, $D_x = 1.463$ Mg m^{-3}. Mo Kα, $\lambda = 0.71069$ Å, $F(000) = 952$. Colorless transparent crystal with dimensions $0.3 \times 0.2 \times 0.05$ mm was used to measure the cell parameters and record 7960 reflections (4903 unique) by a Nonius CAD-4 diffractometer by ω-2θ scan mode and $\theta \leq 25°$. LP correction, no absorption, and secondary extinction correction. Data affected by the bad quality of crystal caused some difficulties in the crystal structure solution. The structure was solved by direct methods (SIR88 package, ref 6) by application of so called P10 formula (usual tangent formula was unsuccessful). Refinement by SHELX76 using 2362 independent reflections with $I \geq 3\sigma(I)$. After anisotropic least-squares refinement for C, N, and Cl atoms, all 34 H atoms were located in the difference Fourier map. The H atoms, 28 fixed in calculated positions and six (four C-H and two N-H involved in hydrogen bonding) with no constraints, were included in the final circles of refinement. Anisotropic thermal parameters for C, N, and Cl atoms and isotropic for H and O atoms belonging to the disordered perchlorate anions. Final $R = 0.072$.

[6] Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.*, in press.

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of 0.96 (3) and 1.05 (3) Å in a and b, respectively. These values are in agreement with those found for covalent N–H bonds in similar compounds.[7] An efficient hydrogen bond is set up with one nitrogen atom of the opposite ligand [N(1)···N(15) distance of 3.00 (3) and 3.01 (3) Å, N(1)–H···N(15) angle of 166 (1) and 158 (1)° in a and b, respectively].[8] Two more interactions take place between the two phenanthrolines of each complex. One ortho hydrogen of each phenanthroline (that adjacent to the nitrogen atom interacting with the acidic proton) comes close to the free nitrogen atom of the counter ligand giving rise to the formation of a hydrogen bond [C(2)···N(24), 3.07 (2) and 3.07 (3) Å; C(2)–H···N(24), 122 (1) and 118 (1)°; C(16)···N(10), 3.13 (3) and 3.19 (2) Å; C(16)–H···N(10) 118 (1) and 119 (1)° in a and b, respectively].[9,10] The resulting dihedral angle between the two phenanthrolines is 41°, and one phenanthroline is translated with respect to the other of ca. 2.4 Å.

The key role of the additional C–H···N hydrogen bonds in stabilizing the Hphen$_2^+$ complex is supported by the observation that analogous species are not formed in the case of phenanthrolines in which both ortho hydrogens have been substituted by alkyl or aryl groups. If a self-stacking association was operating in the Hphen$_2^+$ species,[4] one would expect this to be favored by the presence of hydrophobic substituents.[11] However, 2,9-dimethyl-1,10-phenanthroline dissolves in water only in the presence of at least 1 equiv of acid, and partial neutralization of this solution causes the immediate precipitation of the free base. Moreover in a recent study it has been shown that the catenand, formed by two interlocked 2,9-diphenyl-1,10-phenanthroline moieties, gives the monoprotonated species in which the two phenyl substituents of one link are located one on either side of the phenanthroline plane of the other link and the resulting internal stacking was estimated to increase the basicity by several orders of magnitude.[8] The 2,9-bis(*p*-methoxyphenyl)-1,10-phenanthroline would be able to give the same molecular arrangement found in the proton catenate, but it does not appear to form the two to one adduct.[8] Finally, since the formation of Hphen$_2^+$ species appears to occur only in the case of phenanthrolines bearing ortho hydrogens, the pK_A evaluation of protonated phenanthrolines, which does not take into account the presence of dimeric cations, leads to correct values only in the case of 2,9-disubstituted phenanthrolines.[12]

The NMR spectra of phen, (Hphen$_2$)I, and (Hphen)I were recorded.[13] All C–H protons experience a downfield shift going from left to right in the above series; however, only for the ortho protons is this shift smaller going from phen to Hphen$_2^+$ (0.20 ppm) than going from Hphen$_2^+$ to Hphen$^+$ (0.35 ppm). The acidic protons exchange very rapidly even with moisture present in the solvent. In our experimental conditions they fell at 16.0 and 14.7 ppm downfield from TMS, for Hphen$_2^+$ and Hphen$^+$, respectively, and are in very good agreement with those found for the mono- and bis-protonated catenand.[8]

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Registry No. (Hphen$_2$)(ClO$_4$), 21532-75-2.

Supplementary Material Available: Final atomic coordinates and thermal parameters (Tables I and II) and bond distances (Tables III and IV) and angles (Table V) (6 pages). Ordering information is given on any current masthead page.

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[9] Taylor, R.; Kenhard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070.

[10] The distance between the acidic proton and the second nitrogen atom of the same phen is rather short [N(1)–H···N(10) distance of 2.43 (2) and 2.35 (2) Å in a and b, respectively], but it appears to be geometrically determined.

[11] Barbet, J.; Roques, B. P.; Combrisson, S.; Le Pecq, J. B. *Biochemistry* **1976**, *15*, 2642–2650. Delbarre, A.; Roques, B. P.; Le Pecq, J. B.; Lallemand, J. Y.; Nguyen-Dat-Xuong *Biophys. Chem.* **1976**, *4*, 275–279. Schimmack, W.; Sapper, H.; Lohmann, W. *Biophys. Struct. Mechanism* **1975**, *1*, 113–120.

[12] Schilt, A. A.; Dunbar, W. E. *Tetrahedron* **1974**, *30*, 401–403.

[13] NMR spectra (20 °C, Varian XL200 instrument) were recorded for equimolar solutions (10^{-2} M) of phen, (Hphen$_2$)I, and (Hphen)I in anhydrous CD$_2$Cl$_2$. Chemical shifts (δ, ppm, downfield TMS) of H(2), H(3), H(4), and H(5) were as follows: phen, 9.13, 7.64, 8.28, and 7.82; Hphen$_2^+$, 9.34, 7.89, 8.57, and 8.02, Hphen$^+$, 9.69, 8.11, 8.78, and 8.16.

A Note on Some Reported C and N Isotope Effects

Dominik Marx, Dirk Kleinhesselink, and Max Wolfsberg*

Department of Chemistry, University of California
Irvine, California 92717

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Stevenson and co-workers[1] recently measured values of isotopic exchange equilibrium constants K_1 involving a neutral organic molecule A and its anion radical A^-

$$A^* + A^- \rightleftharpoons A^{*-} + A \qquad (1)$$

Here, * refers to substitution by heavier isotope (D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$). Some of the systems studied are indicated in Table I. The focus of the study was the large C and N isotope effects (ie's) in the condensed phase (large deviations of K_1 from unity). Stevenson and co-workers suggested that these K_1's be used as the basis of isotope separation processes economically more feasible than those presently employed. We point out here that the reported magnitudes of the carbon and nitrogen ie's are at variance with conclusions based on the statistical mechanical theory of equilibrium ie's.

The theory of equilibrium ie's is well understood.[2] Usually the Born–Oppenheimer approximation is employed, with the additional assumption of the harmonic oscillator-rigid rotor approximation. Quantitative theory requires corrections for these assumptions; however, semiquantitative arguments of the type used here are valid without these corrections.[3] Much work has demonstrated that the heavier isotope in eq 1 will concentrate in that species in which the force constants (fc's) at the position of isotopic substitution are larger and that the magnitude of the ie reflects the difference in the fc's at this position between the species A^- and A. Thus, $K_1 > 1$ if the fc's in A^- are larger.

Table II gives theoretically calculated values of K_1 with nitrobenzene or fluorenone the neutral molecule. The calculations were made by using the well-tested cut-off procedure—only portions of the molecules were included which are no more than two bonds removed from the position of isotopic substitution.[4] The fc's for A were estimated from compilations of fc's.[5] Specific solvation or ion pairing effects were not taken into account for A. The column headings I, II, ... in Table II refer to different

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