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Structural Reinvestigation of Ammonium Hypophosphite: Was Dihydrogen Bonding Observed Long Ago?

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The past decade has seen the explosive emergence of "dihydrogen bonds", interactions between the electrons of M–H σ-bonds, where M is less electronegative than H (M = Al, B, Ga, Ir, Mo, Mn, Os, Re, Ru, W) and traditional proton donors. But 70 years ago, such an interaction was proposed by Zachariasen and Mooney [*J. Chem. Phys.* **1934**, *2*, 34–37] on the basis of their single-crystal X-ray diffraction structure (heavy atoms positions only) of ammonium hypophosphite ($NH_4H_2PO_2$). We redetermined this structure at high resolution with a focus on the hydrogen atoms, using a modern diffractometer equipped with a CCD detector. Molecular orbital calculations were performed to investigate the charge density and the bond polarity of the P–H bonds and to assess their potential for participation in dihydrogen bonds. Neither the theory nor the X-ray structure supports the original claim of H···H interactions in this salt.

Introduction

Hydridic-to-protonic hydrogen bonding has been found to occur between positive hydrogens of A–H (A=O, N, halogen, C) proton donors and hydridic sites on σ M–H (M=Al, B, Ga, Ir, Mo, Mn, Os, Re, Ru, W) bonds. This novel interaction, dubbed "dihydrogen bonding" by Crabtree et al., affects structure, reactivity, and selectivity, so it has implications for catalytic and stoichiometric reactions, crystal engineering, and materials chemistry.[1−12]

Though the study of dihydrogen bonding has only really blossomed in the past decade, the possibility of an interaction between protonic and hydridic hydrogens was suggested in 1934 by Zachariasen and Mooney (Z&M) on the basis of their X-ray diffraction study of ammonium hypophosphite ($NH_4H_2PO_2$).[13] Having only been able to determine the heavy atom positions, these authors assumed a P–H distance of 1.50 Å from which they calculated an ammonium ion–hydrogen distance of 3.08 Å. Using this distance, and treating the hypophosphite hydrogens as H^- with an ionic radius of 1.52 Å, they inferred a "binding", that today would be called a "dihydrogen bond", between the hydrogens of the hypophosphite and of the ammonium fragments. This suggestion was made at the dawn of the structural era in chemistry, a time when few papers had noted the interaction now understood as conventional hydrogen bonding. Recognition of this phenomenon's ubiquity came later with the classic papers of Huggins[14] and with Linus Pauling's monograph, *The Nature of the Chemical Bond*.

Dihydrogen bonding seems plausible in this ammonium hypophosphite; phosphorus is slightly less electronegative than hydrogen, suggesting that the hydrogens of hypophosphite may be hydridic and capable of hydrogen bonding with the H–N bond of the ammonium ion. Furthermore, hypophosphite salts are commonly used as reducing agents. With its ability to act as either a proton or a hydride donor, ammonium hypophosphite can reduce alkenes in a process

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in which protonolysis and H_2 loss compete with hydrogenation.[15] The hypophosphite ion also finds application as a reducing agent in electrochemistry[16] and electroless deposition.[17] In the presence of catalysts such as platinum black, palladium, and copper, hydrated hypophosphite salts give hydrogen gas, where one H in each H_2 molecule comes from water and the other comes from hypophosphite.[18] These applications are not unlike those associated with BH_4^-, an anion whose dihydrogen bonding capabilities have been extensively studied in our group and which, to our knowledge, represents the first recognized dihydrogen bond donor.[19,20]

Given our own interest[12] in hydridic-to-protonic hydrogen bonding, we sought to explore its possible presence in ammonium hypophosphite using X-ray diffraction and structural analysis together with molecular orbital calculations to improve our understanding of the compound's electronic structure.

Results and Discussions

Crystallography. Crystals of ammonium hypophosphite were grown by slow diffusion of ether into a nearly saturated solution of ammonium hypophosphite in methanol. The crystal on which X-ray diffraction was performed measured $0.36 \times 0.26 \times 0.10$ mm^3.

The new structure, Figure 1, is orthorhombic, space group *Cmma*, with unit cell dimensions $a = 11.5192(18)$ Å, $b = 7.4977(12)$ Å, $c = 3.6907(6)$ Å at 173 K. Each NH_4^+ is surrounded by four $H_2PO_2^-$ ions oriented in such a way that every oxygen atom participates in a bifurcated hydrogen bond.

The Z&M structure was also orthorhombic with space group *Acmm*; their unit cell dimensions were $a = 3.98(20)$ Å, $b = 7.57(38)$ Å, $c = 11.47(57)$ Å. Our X-ray diffraction was carried out at 173 K; their temperature was not specified but was presumably higher, which could account for the differences in unit cell dimensions. In general, the new structure's heavy atom positions agree with those found by Z&M. The classical hydrogen bonds, H(N)···O(P) at 2.00 Å, correspond to a N−O distance of 2.84 Å, similar to the 2.81 Å determined by Z&M. In contrast, the found P−H distance was 1.31 Å, quite different from the value Z&M assumed in their estimation of hydrogen atom positions.

Typically, dihydrogen bonds M−H···H−A are characterized by M−H···H angles of 90−135°, H···H−A angles of 160−180°, and H−H distances of 1.7−2.2 Å.[12] The present structure of $NH_4H_2PO_2$ has P−H···H angles in the normal range at 114.8° and 118.7°, but the H···H−N angles, at 105.4° and 108.0°, are too acute for typical dihydrogen bonds. Most importantly, the smallest N−H···H−P distances are 2.79 and 2.82 Å, substantially longer than van der Waals contacts.[21]

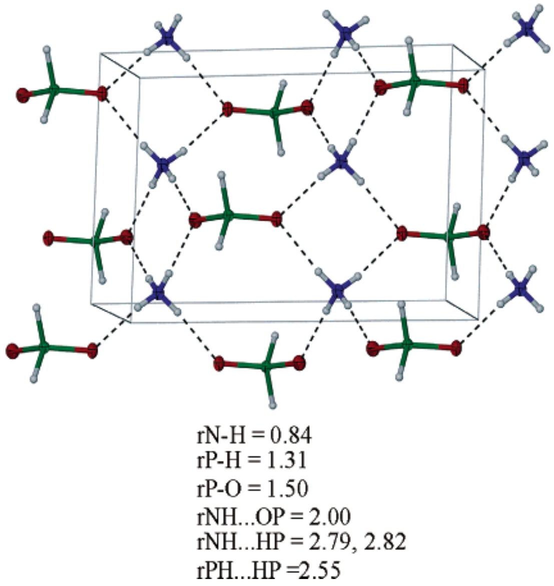

Figure 1. X-ray structure of $NH_4H_2PO_2$ displayed with atom colors as follows: H, white; N, blue; O, red; P, green. Dotted lines denote N−H···O classical hydrogen bonds. The P−H sites show no close contacts. Distances are in Å.

Ab Initio Calculations. In hopes of shedding light on the P−H sites' electronic structure and specifically on their capacity for dihydrogen bonding, we examined the NH_4^+-$H_2PO_2^-$ ion pair via quantum chemical methods. Ab initio calculations were performed on $NH_4H_2PO_2$ at the B3LYP/6-311++G** level using the Gaussian98[22] package. We considered two symmetry arrangements, C_1 and C_s, for the structure of the ammonium hypophosphite depending on the number of interactions (hydrogen or dihydrogen bonds) that take place between the two ions, NH_4^+ and $H_2PO_2^-$. When the calculations were performed in the "gas phase", proton transfer took place from the ammonium to the oxygen of the hypophosphite, due to the overwhelming dominance of electrostatic forces. Water as solvent seemed to us a

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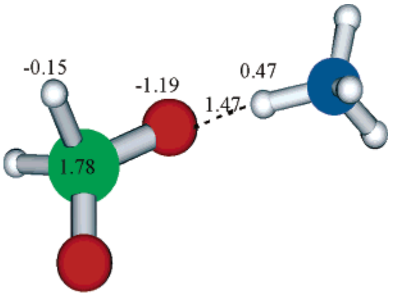
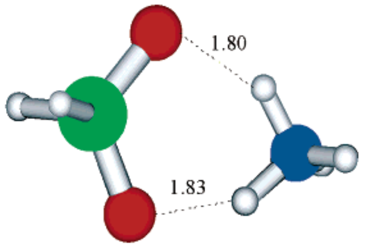


C_1 Structure



C_s Structure

Figure 2. "Aqueous" $NH_4H_2PO_2$ arrangements. Distances are in Å.

reasonable approximation for a polar condensed phase like that in a crystal. Modeling of the "solvated" $NH_4H_2PO_2$ using the CPCM dielectric continuum model[23−31] showed only conventional hydrogen bonds, regardless of symmetry, Figure 2.

The interaction strength of 8.65 kcal/mol in the "aqueous" C_1 structure was calculated as the difference between the complex and the monomers (with zero point vibrational energies included). The calculated P−H bond length was found to be 1.40 Å.[32,33] The difference from the experimentally determined value can be attributed to the X-ray analysis, which typically underestimates X−H bond lengths. In order to explore the P−H bond character, we calculated the atoms' charges on the C_1 structure using the natural bond orbital analysis method incorporated into Gaussian98.[34−41] As expected, the hydrogen atoms belonging to the $H_2PO_2^-$ are slightly negative, −0.15, but the negative charge density is much higher on the oxygen atoms (−1.19). These values are surprisingly insensitive to interaction with the ammonium ion or to the presence or absence of simulated "solvation". Thus, the assumption made by Z&M that the phosphorus hydrogens can be treated as hydrides is not supported by the results of our calculations.

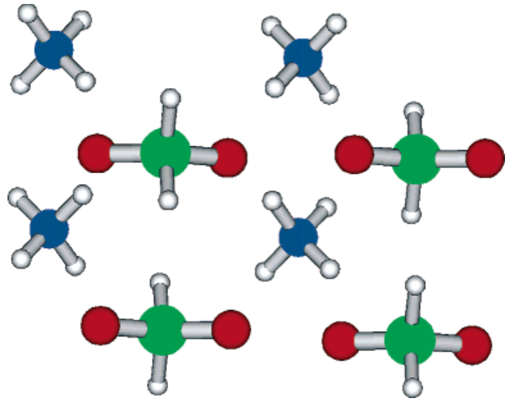


Figure 3. $NH_4H_2PO_2$ periodic calculation structure.

The C_s structure is a transition state (one imaginary frequency), less stable than the C_1 form by 3.63 kcal/mol. This higher energy may reflect strain arising from the accommodation of two interactions in a cyclic arrangement, Figure 2. All attempts to locate structures with hydridic-to-protonic close contacts resulted in optimization to geometries, such as the C_1 form, with classical N−H···O hydrogen bonding.

One of disadvantages of using X-ray structure determination is that it is difficult to determine the exact hydrogen atom positions. In order to augment our understanding of the $NH_4H_2PO_2$ structure, we used the Gaussian03[42] program suite to perform a lattice calculation at the B3LYP/STO-3G level,[43] starting from the X-ray structure's atom coordinates. Though it differs from the experimental structure in details of bond lengths and angles, the lattice geometry was qualitatively unchanged upon optimization as Figure 3 shows. The calculated P−H and N−H distances were 1.41 and 1.12

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Å, which may be compared to 1.31 and 0.84 Å from the crystal structure; as noted above, the typical underestimation of bond lengths to hydrogen is seen in this X-ray structure. Nonetheless, the calculated hydrogen atom positions still place the N−H and P−H sites much too far apart (2.65 and 2.94 Å) for van der Waals contact, allowing only for the traditional N−H···O hydrogen bonds.

Conclusions

In summary, a single crystal X-ray diffraction study of ammonium hypophosphite has revealed only conventional N−H···O hydrogen bonds and no H···H close contacts. In agreement with X-ray results, molecular orbital calculations showed that the hypophosphite's classically hydrogen bonded oxygen sites are strongly negative as expected. These results contrast with the initial interpretation offered by Zachariasen and Mooney. In retrospect, however, the original authors may be forgiven; their work was reported well before what is now viewed as the "classical" hydrogen bond had been widely recognized, and the resources available for estimating hydrogen atom positions or charges in their heavy-atom-only structure were limited. Indeed, the P−H hydrogen atoms do appear to bear negative charge, as Z&M suggested, but only a tiny amount; they are far from being the originally proposed isolated hydride ions. Arguably, it is a tribute to the insight of these early workers that though it was not present in the specific case of $NH_4H_2PO_4$, hydridic-to-protonic hydrogen bonding would, more than half a century later, explosively emerge as a "new" class of molecular interaction.

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Supporting Information Available: X-ray data, together with the ab initio calculated geometries and frequencies of ion pairs. This material is available free of charge via the Internet at http://pubs.acs.org.

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