

# NEUTRON DIFFRACTION: A REVIEW OF STRUCTURAL STUDIES OF SHORT HYDROGEN BONDS

M. Sakhawat Hussain

Department of Chemistry, University of Petroleum and Minerals, Dhahran,  
Saudi Arabia

الخلاصة :

أفسحت تقدمات الصناعة الحديثة في تفاعلات الإنشطار النووي ومصادر النيوترون النابض في المجالات العريضة لما يمكن الحصول عليه من شدة الشعاع النيوتروني إجراء دراسات وإختبارات فنية في دراسة التركيب والحركات الداخلية للذرة والجزيء التي كان متعذر القيام بها بأي وسائل أخرى . وليس كما هو الحال في أشعة أكس فتأثر النيوترونات يعتمد بدرجة قليلة على العدد الذري للذرة المشتركة جاعلاً تعيين أوضاع نواة الأيدروجين بواسطة الحيود النيوتروني معداً وكذلك أيضاً بالنسبة لأنوية العناصر الثقيلة وبالمثل يمكن التحقيق من التغييرات التي تحدث عند تكوين الرابطة الكيميائي في توزيع الإلكترونات داخل الذرات باستخدام أشعة أكس والحيود النيوتروني مجتمعين ويستعمل علم النيوترون البللوري بكثرة في تحديد مواضع ذرات الهيدروجين وكذلك دراسة الأربطة الهيدروجينية التي تم ملاحظتها في المركبات الكيماوية المختلفة والتي أصبحت من الأهمية في الأعوام الحديثة . وتعطي المناظرة الحديثة بعض الفروض الأساسية عن مطاطية النيوترون المتبعثر والنتائج العديدة من الدراسات وتأثير عملية الديوثيرات (تأثير الظواهر العلوية) في التركيب الداخلي للمركبات المترابطة والمسئول عنها الروابط الهيدروجينية القصيرة وفي الكانيونات الثنائية — ودراسات أخرى مسئولة عن توزيع الكثافة الإلكترونية كلها تشير بصفة خاصة عن العمل الذي قام به المؤلف وأتجاه آخر في مجال البحث تم تعيينها وتعميمها من توضيح الدراسات التركيبية والتي أتم دراستها في الأعوام السابقة سيتم أبرزها .

## **ABSTRACT**

Recent advances in the technology of fission-based nuclear reactors and pulsed-neutron sources have vastly increased the intensity that can be obtained in a neutron beam, making available a powerful technique for the investigation of important aspects of atomic and molecular structures and dynamics not easily accessible by other means. Unlike X-rays, the scattering of neutrons is much less dependent on the atomic number of the atom involved, thus making the determination of the positions of hydrogen nuclei as easy as those of heavier nuclei. Similarly, a combination of X-ray and neutron diffraction data can be used to reveal the changes in electron distribution that atoms undergo in the formation of a chemical bond. Neutron crystallography has been extensively used for the location of hydrogen atoms, in general, and hydrogen bonding studies have been of particular interest in recent years in attempting to understand the nature of the short (strong) hydrogen bond observed in various chemical compounds. The present review gives some basic concepts of elastic neutron scattering, and the results of several studies involving short hydrogen bonds in chelated structures and dimeric cations, the effects of deuteration (isotope effects) and studies concerning electron density distribution are summarized with special reference to the work done by the author. Further trends in this area of research are identified and generalizations drawn from the structural studies done in the past few years are presented.

# NEUTRON DIFFRACTION: A REVIEW OF STRUCTURAL STUDIES OF SHORT HYDROGEN BONDS

## 1. INTRODUCTION

When radiation passes through matter it is scattered by the atoms with a certain amplitude without (elastic scattering) or with (inelastic scattering) a change in energy. If the wavelength of the radiation is of the order of magnitude of the interatomic distances in the crystalline solids the scattering waves may have well-defined phase relationship (coherent scattering) or they may have random phases (incoherent scattering). The coherently scattered beam components reinforce each other giving rise to a diffraction pattern. The direction in which diffraction occurs is given by the well-known Bragg relation ( $n\lambda = 2d\sin\theta$ ). Neutron crystallography uses thermal neutrons as radiation and, in general, the apparatus and computational techniques for neutron and X-ray diffraction are essentially the same. However, because of the difference between the scattering processes, the information obtained from the two are different. The X-rays are scattered from the detailed electron density whereas neutron scattering depends on the intrinsic properties and distribution of atomic nuclei in the crystal. Because a nucleus is essentially a point scatterer, a more precise description of the thermal motion of atoms can be derived from a diffused intensity distribution [1] in neutron scattering studies. Thus, the neutron technique allows interpretation of thermal motion in terms of rigid-body models [2,3] and correlation with spectroscopic studies is possible. Neutron diffraction is particularly capable of providing information about light atoms in the presence of heavier ones [4] since unlike X-rays, neutrons are, in general, scattered as well by light as by heavy atoms. This allows a precise location, within a few thousandths of an angstrom, of the hydrogen atom in relation to the atoms with which it is bonded. These advantages of neutron diffraction are often exploited in structural chemistry especially in studies involving hydrogen atoms. Such areas of research include studies on metal hydrides, organometallic catalysts, material with unidirectional solid state properties, biochemical molecules with hydrogen bonding, electron and spin density distributions in crystalline solids and studies involving short (strong) hydrogen bonds. The present paper reviews the structural aspects of several compounds having short hydrogen bonds with special reference to the work done by the author in this area

using neutron diffraction. A very elementary treatment of the coherent neutron scattering experiments is given as an introduction to the technique with emphasis on the results obtained from the studies.

## 2. BASIC CONCEPT OF ELASTIC SCATTERING STUDIES

In the case of single crystal Bragg diffraction the scattering is elastic in nature and we need to measure scattered neutron intensities only as a function of the direction of scattering i.e. as a function of  $2\theta$ . A schematic diagram of a neutron diffraction spectrometer used in elastic scattering experiments is shown in Figure 1. In a nuclear reactor, neutrons are produced by fission and thermalized by a moderating material. The neutron-beam velocity distribution in the reactor is Maxwellian, with a maximum intensity at approximately  $1.0 \text{ \AA}$ , corresponding to a velocity of  $4 \times 10^5 \text{ cm s}^{-1}$ . In the measurement of Bragg scattering, a monochromator crystal, usually of graphite,

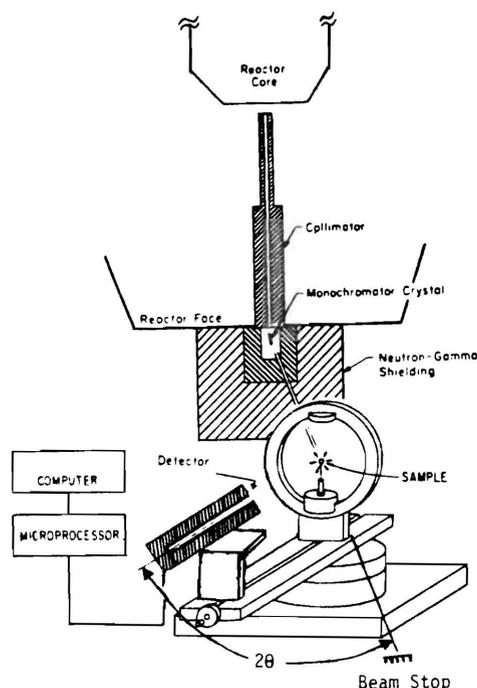


Figure 1. Schematic Diagram of a Neutron Diffraction Spectrometer Used for Single-Crystal Elastic Scattering Studies

Be, Cu, Ge, or Pb, selects a narrow wavelength band from the Maxwellian spectrum of the reactor neutrons and the resulting beam travels down a collimating tube to strike a sample crystal (or powder). Scattered neutrons are detected at angle  $2\theta$  using either  $^{10}\text{BF}_3$  or  $^3\text{He}$  gas-filled proportional counters. For single-crystal studies the sample is mounted on a four-circle diffractometer which allows three-dimensional orientation of any plane ( $hkl$ ) in such a way that the scattered beam can be detected at a given  $2\theta$  where the intensity profile of the diffracted beam is measured. The total intensity is corrected by subtracting background intensity to obtain the integrated intensities which are used in the solution of the crystal structure.

There are some technical difficulties connected with the available neutron fluxes. The shielding requirements for neutron diffraction experiments are also more severe than those for X-ray experiments. The constraints of heat removal and fuel cost of research reactors place a limit on the available core neutron fluxes at about  $10^{14}$ – $10^{15}$   $\text{cm}^{-2} \text{s}^{-1}$ , which is further reduced due to monochromatization such that a flux of only  $10^5$ – $10^7$   $\text{cm}^{-2} \text{s}^{-1}$  is available at the sample position. One way to overcome this difficulty is to use larger sample crystal for neutron diffraction, but the growth of larger crystals sometimes becomes a real problem. A pulsed-neutron source is the other alternative since it can produce a neutron flux which can be much more intense than that obtained in a reactor. Scattering experiments utilizing neutrons from a pulsed source use the time-of-flight technique to measure the wavelength of neutrons; this is given by the flight time between the source and detector. This new generation of neutron sources offers great prospects for future neutron crystallography. The investigations concerning hydrogen bonding is one of the research areas which will continue to be explored extensively using these new techniques. Some of the

work done in the past few years in this area at the University of Missouri Research Reactor (MURR) facility in Columbia, Missouri is discussed below along with the related work in the field.

### 3. STUDIES INVOLVING SHORT HYDROGEN BONDS

The study of hydrogen bonds, A—H---B where A and B are generally small, highly electronegative atoms such as F, O, N, and Cl has been an area of continuing research in neutron crystallography. Short, symmetrical or nearly symmetrical hydrogen bonds are generally restricted to F—H---F and O—H---O systems. Available data to date indicate a very significant difference in the nature of the short (about 2.40 Å) O---O hydrogen bonds compared with the much longer (2.80 Å) ones which are common in many systems such as ice and liquid water. The short hydrogen bonds have been observed (a) in complicated species similar to the classical example [5] of bis(dimethylglyoxime)nickel(II) and (b) in simple diadducts of Lewis bases with structure analogous to the well-known  $\text{H}_5\text{O}_2^+$  ion [6,7]. A large number of examples are known in both of the above categories where structures are determined by X-ray diffraction. Neutron diffraction analyses are not very common but are necessary for the exact information regarding the position of a hydrogen atom for the reasons given earlier. Some of the studies done by neutron diffraction in order to understand the nature of the short hydrogen bond are given below.

#### 3.1. Intramolecular Hydrogen Bond in Chelated Structures

Neutron diffraction structure determinations have been completed [8–14] on several alpha-amine dioxime complexes (Table 1) related to bis(dimethyl-

Table 1. Neutron Diffraction Studies of the Hydrogen Bonds in Amine Oximes Complexes\*

Compound	O—O(Å)	O—H(Å)	H—O(Å)	$\Delta(\text{O—H})$	Ref.	Figure
[Ni(AO) <sub>2</sub> —H]C1·H <sub>2</sub> O	2.420(3)	1.187(5)	1.242(5)	0.055	[8]	2
[Ni(AO) <sub>2</sub> —D]C1·H <sub>2</sub> O	2.439(8)	1.058(9)	1.391(10)	0.333	[9]	3
[Pt(AO) <sub>2</sub> —H]C1·3.5H <sub>2</sub> O	2.472(5)	1.087(7)	1.389(7)	0.302	[14]	—
[Ni(EnAO—H)]C10 <sub>4</sub>	2.478(5)	1.171(8)	1.316(8)	0.145	[10]	4
[Ni(PnAO—H)]C1·H <sub>2</sub> O	2.409(10)	1.158(16)	1.260(20)	0.102	[11]	5
orthorhombic [Ni{(PnAO—7H)NO <sub>2</sub> }]	2.389(9)	1.197(14)	1.199(14)	0.002	[12]	6
[Ni{(PnAO—7H)NO}]	2.407(9)	1.146(14)	1.267(14)	0.121	[13]	7

\*The numbers in parentheses in this table, in Table 2, and in the text are estimated standard deviations in the last digit(s).

glyoxime)nickel(II) [5]. The ligands in these complexes are either bidentate or tetradentate as is evident from the structure of these complexes given in Figures 2 to 7. The metal ions in these complexes are coordinated to oxime- and amine-nitrogen atoms. The short hydrogen bonds in these complexes have no symmetry constraints and the O---O separation can be varied over a significant range to allow systematic investigation of the corresponding changes in symmetry of the bond. These studies reveal that steric constraints of five-membered chelate ring opposite to the hydrogen bond results in lengthening of the O---O distance to 2.478 (5) Å in  $[\text{Ni}(\text{EnAO}-\text{H})]^+$  (Figure 4) compare to the 2.420(3) Å in  $[\text{Ni}(\text{AO})_2-\text{H}]^+$  ion (Figure 2). Increasing the size of the chelate ring to six members (Figure 5) in  $[\text{Ni}(\text{PnAO}-\text{H})]^+$  removes the strain, and the O---O distance drops to 2.409(10) Å. The introduction of aromaticity in the six-membered chelate ring in  $[\text{Ni}(\text{PnAO}-7\text{H})\text{NO}_2]$  (Figure 6) and

in  $[\text{Ni}(\text{PnAO}-7\text{H})\text{NO}]$  (Figure 7) has little effect on the O---O distance which is 2.389(9) Å in the former and 2.407(9) Å in the latter case. An interesting multiple bonding of the nitrogen atoms to the nickel was observed in these complexes which is evident from significant shortening of the Ni-N distances (Figures 6 and 7) in these complexes. The hydrogen bond in these chelate structures are close to the shortest reported [15]. The hydrogen atoms in these chelate structures are symmetric ( $\Delta(\text{O}-\text{H})=0.002$  Å) to nearly symmetric ( $\Delta\text{O}-\text{H}=0.333$  Å). These observations are perhaps indicative of a potential function of the single-minimum type in the symmetric cases with hydrogen bonded to both oxygen atoms, a situation seldom observed for the hydrogen atom except in three-centered bonds. The hydrogen maleate ion  $[\text{HMA1}]^-$  (Figure 8) is another interesting example having symmetry-free short O---O bond [17]. The nature of centricity in this bond can either be a result of

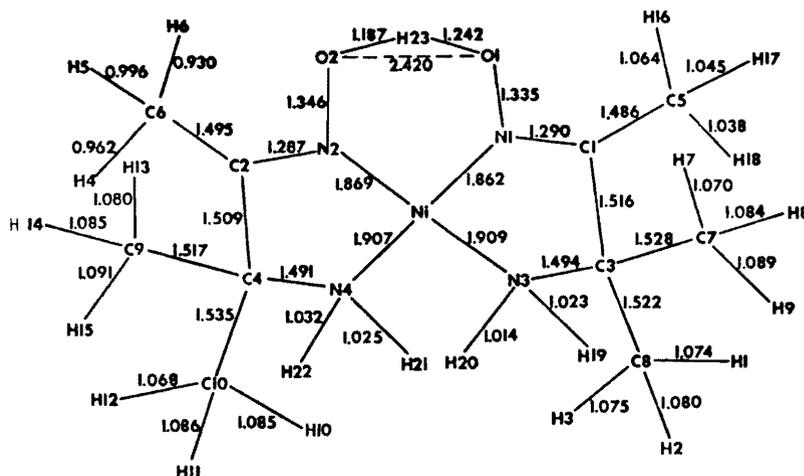


Figure 2. Neutron Study of  $[\text{Ni}(\text{AO})_2-\text{H}]^+$  Cation

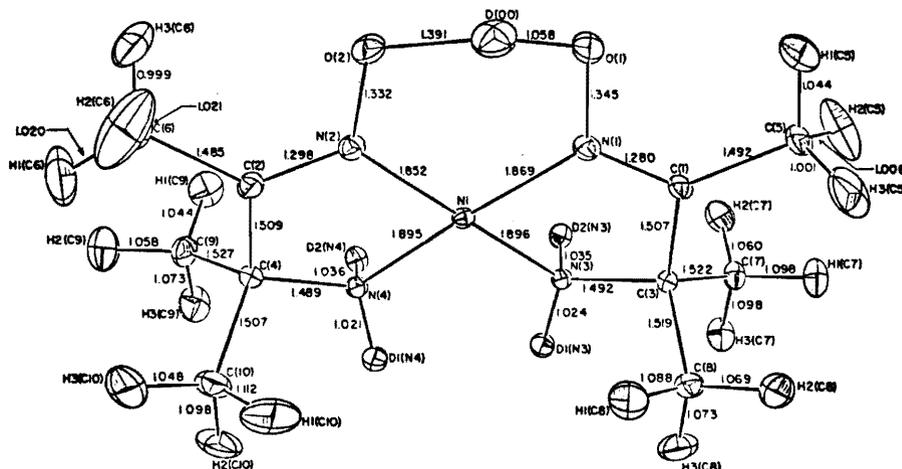


Figure 3. Neutron Study of Deuterated  $[\text{Ni}(\text{AO})_2-\text{H}]^+$  Cation.

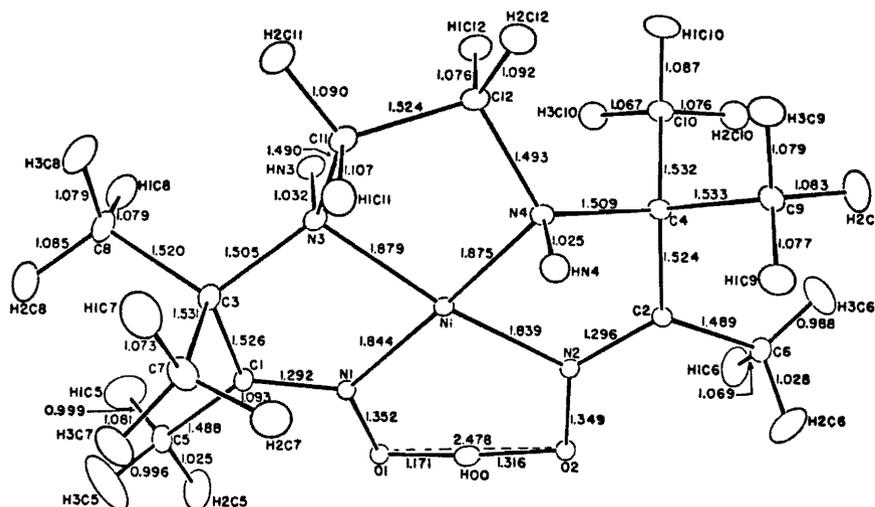


Figure 4. Neutron Study of  $[\text{Ni}(\text{EnAO}-\text{H})]^+$  Cation in Perchlorate Salt

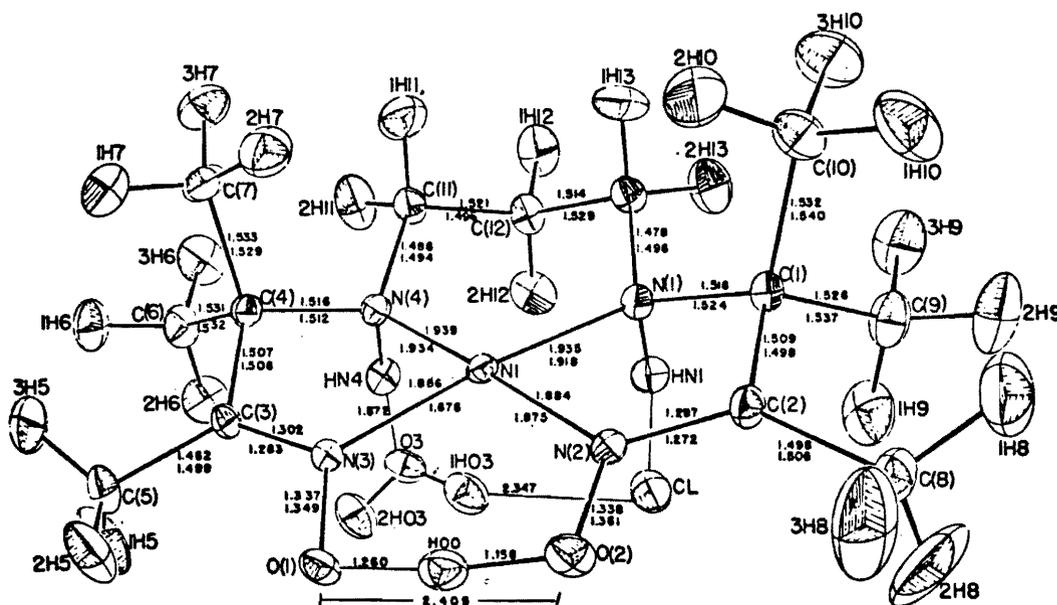


Figure 5. Neutron and X-ray Studies of  $[\text{Ni}(\text{PnAO}-\text{H})]^+$  Cation. (Top Line Gives Neutron Values.)

covalency in the bond or is a consequence of constraints resulting from the preference of the conjugated system to remain planar. The relevant data for the  $[\text{HMa1}]^-$  ion is given in Table 2.

### 3.2. Short Hydrogen Bond in Dimeric Cations of the Type $[\text{BHB}]^+$

The diadducts of neutral Lewis bases with a proton, analogous to  $\text{H}_5\text{O}_2^+$  ion, are quite common but very few have been studied using neutron diffraction. Unlike the closed symmetry-free hydrogen bond in the chelate structures given above, all known examples of

the dimeric cations have 'open-symmetry-fixed' hydrogen bonding. The O---O distance in the cation from  $[\text{H}(\text{dma})_2][\text{AuCl}_4]$  is  $2.430(16)\text{Å}$  (Figure 9) which is within the range commonly observed for the short hydrogen bond [18]. The two halves of the  $[\text{H}(\text{dma})_2]^+$  cation are related by a center of symmetry at the midpoint of the O---O bond. The structural analysis of  $[\text{H}(\text{dma})_2][\text{AuCl}_4]$  contradicted the assumption of Ziegler [19] for six-coordinated gold(III) in this compound based on spectroscopic data. A recent X-ray structural analysis has revealed similar short hydrogen bonds in the dimeric cations of pyridine N-oxide [20] and various

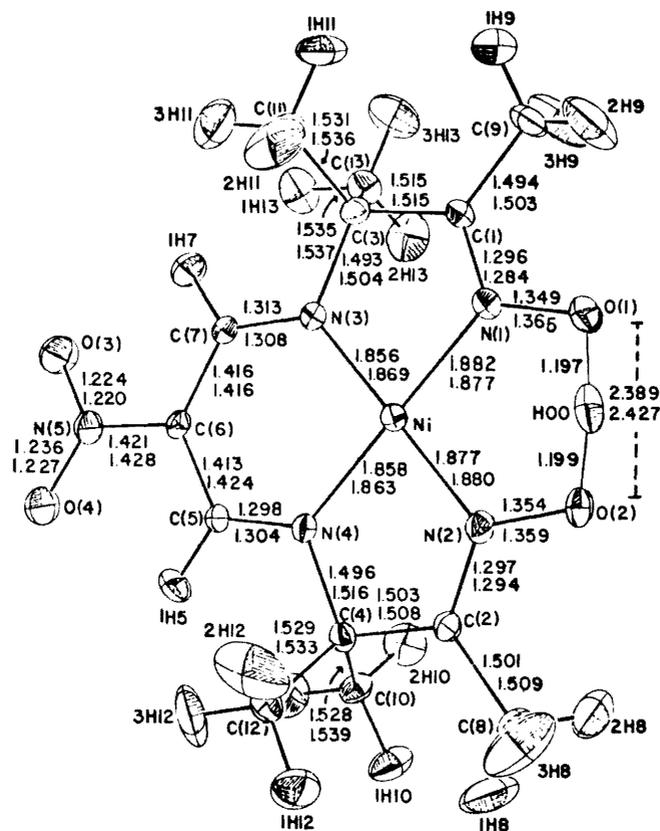


Figure 6. Neutron (Top Line) Results for the Orthorhombic Form and X-ray (Bottom Line) Results for the Monoclinic Form of the  $[Ni\{(PnAO-7H)NO_2\}]^0$  Complex

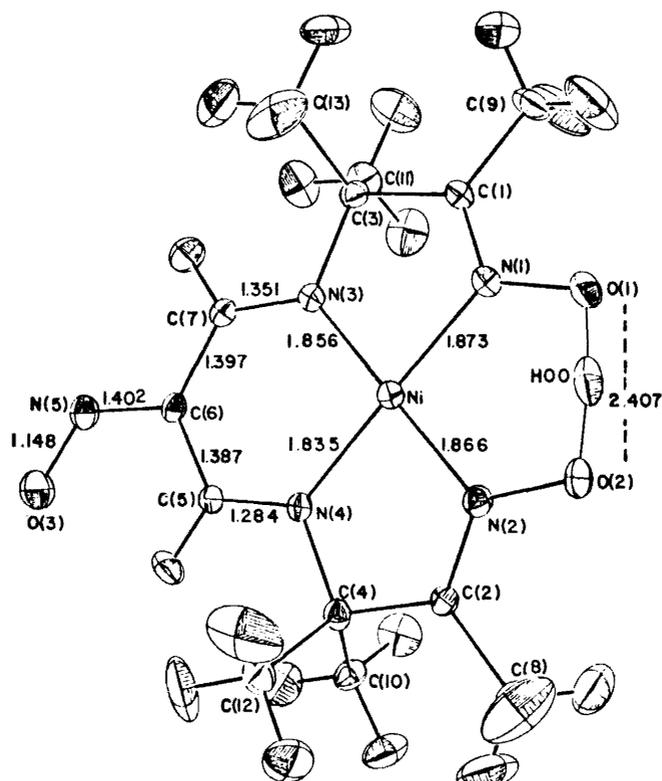


Figure 7. Neutron Diffraction Study of  $[Ni\{(PnAO-7H)NO\}]$

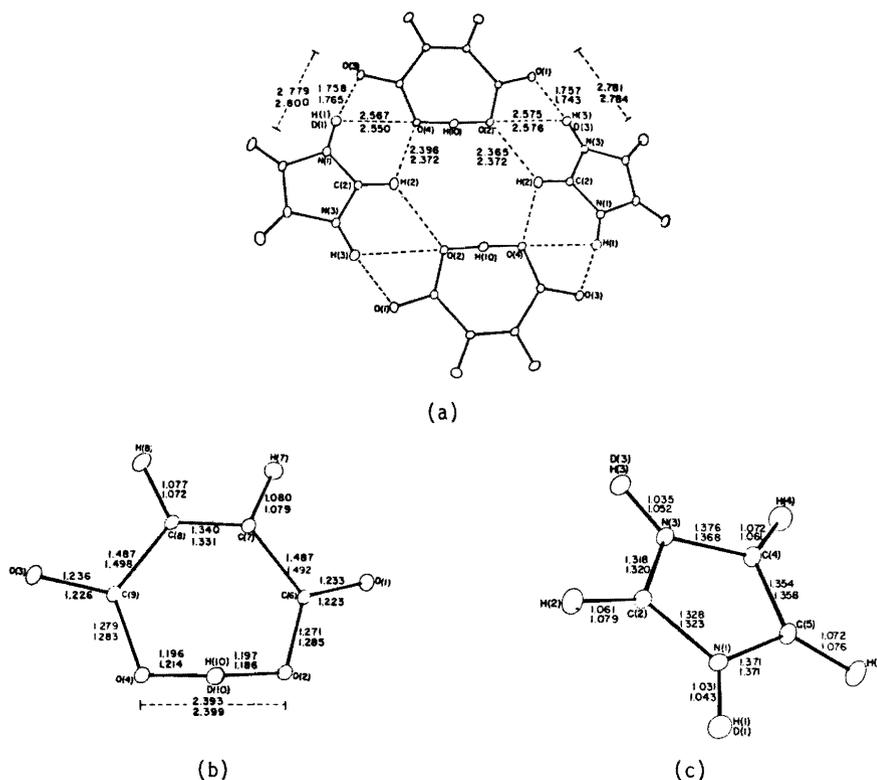


Figure 8. Neutron (Top Line) and X-ray Diffraction (Bottom Line) Analysis Results for  $[\text{ImH}][\text{HMa}]$  and  $[\text{ImD}][\text{DMa}]$  Showing (a) Hydrogen Bond Environment, (b) Bond Distances for the Hydrogen Maleate Ion, and (c) Bond Distances for the Imidazolium Ion

picoline N-oxides [21] when these heterocyclic N-oxides are stabilized by a larger anion such as  $\text{AuCl}_4^-$ . In the case of alpha-picoline N-oxide the cation,  $[(2\text{-picNO})_2\text{H}]^+$ , has a symmetry-free open short O---O hydrogen bond and this compound offers a suitable example of an isolated O---H---O system for deuteration studies mentioned below. The beta- and gamma-picoline N-oxides form symmetry-fixed hydrogen bonded compounds with gold(III). Neutron diffraction studies on all of these diadducts are planned in the near future. These studies using gold(III) are also significant in their own right since

similar gold compounds are being used successfully for gold treatment [22] and for photometric extraction of gold [23]. Although N---N hydrogen bonds are generally not as strong as F---F and O---O hydrogen bonds and a symmetric bond of this type has not been observed, the pyridinium-pyridine cation,  $\text{Py}_2\text{H}^+$ , and  $[(4\text{-NH}_2\text{Py})_2\text{H}]^+$  cation [24,25] exhibit symmetry-free asymmetric N---N bond distances of 2.737(3) and 2.698(8) Å, respectively (Figure 9). Neutron diffraction studies on further N---N systems need to be done to generalize any trends in short N---N hydrogen bonds.

Table 2. Neutron Diffraction Results for Hydrogen Maleate Ion and in Some Dimeric Cations\*

Compound	O---O(Å)	O-H(Å)	H---O(Å)	$\Delta(\text{O-H})$	Ref.	Figure
$[\text{ImH}]^+[\text{HMa}]^-$	2.393(3)	1.196(4)	1.197(4)	0.001	[16]	8
$\text{Ca}(\text{HMa})_2 \cdot 5\text{H}_2\text{O}$	2.424(2)	1.121(3)	1.305(3)	0.184	[17]	11
$[\text{ImD}]^+[\text{DMa}]^-$	2.399(4)	1.186(6)	1.214(6)	0.028	[16]	8
$[\text{DMA}_2\text{H}]^+[\text{AuCl}_4]^-$	2.430(16)	1.215(8)	1.215(8)	0	[18]	9
	<u>N---N(Å)</u>	<u>N-H(Å)</u>	<u>H-N(Å)</u>			
$[\text{Py}_2\text{H}]^+[\text{ZnCl}_{3/2}\text{Br}_{3/2}\text{Py}]$	2.737(3)	1.086(7)	1.658(6)	—	[24]	9

\*Other important distances are shown in the figures.

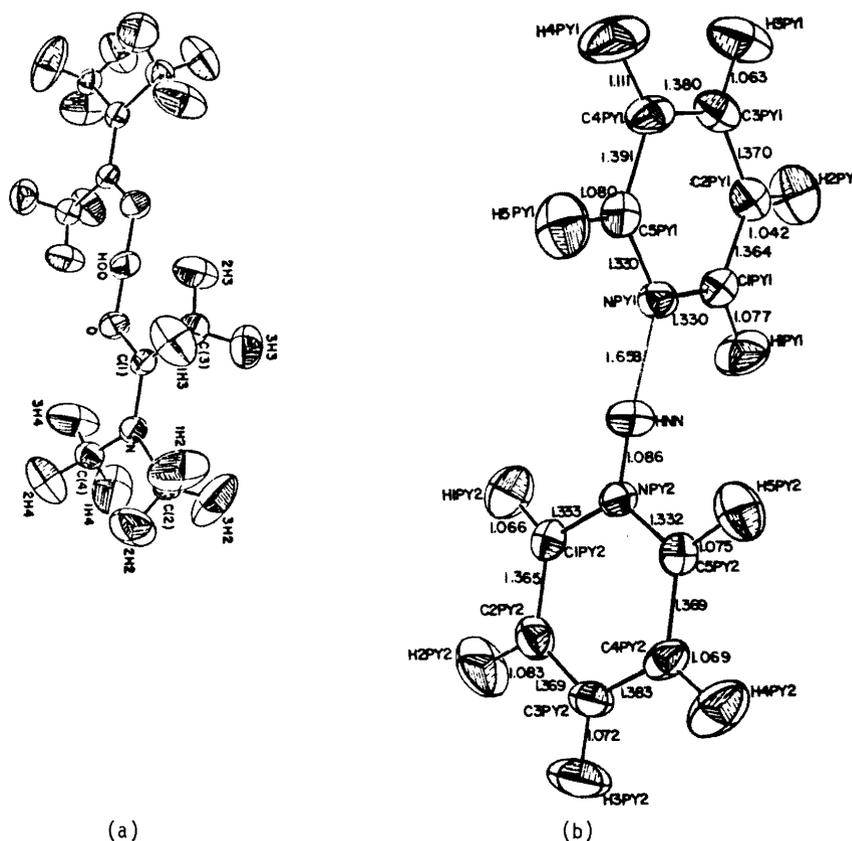


Figure 9. Neutron Analysis Results for Dimeric Cations (a)  $[(dma)_2H]^+$  and (b)  $[(py)_2H]^+$ .

### 3.3. Effect of Deuteration (Isotope Effect)

Replacing the H of the hydrogen bond by D may be expected to cause changes in some or all of the physical properties of the bond. Singh and Wood [26,27] calculated that the internuclear separation  $R(A---B)$  would increase on deuteration if the potential function of the system were a double minimum but decrease if it were a single minimum. Within experimental error strong bonds remain of the same length on deuteration. However, these predictions based upon room-temperature isotope effect studies can only be applicable to structures having isolated hydrogen bonds without any intramolecular constraints [28]. Studies of isotope effects are very useful for providing insight for the potential functions involved in these short hydrogen bonds. Additional studies on isolated short hydrogen bonds appear warranted. The neutron diffraction results for the normal and deuterated forms of imidazolium salt of hydrogen maleate are shown in Figure 8 and Table 2. In the deuterated compound, the H atom moves approximately 0.01 Å towards one of the oxygen atoms as a result of isotopic substitution, but the O---O separation exhibits no significant change, being

2.393(3) Å in the normal form compared with 2.399(4) Å in the deuterated compound. A similar shift of 0.025 Å towards one O atom without any significant change in the O---O distance was observed in the case of quinolinic acid [29]. In agreement with the calculations, the above observations are perhaps indicative of a potential function of single-minimum type, symmetric or slightly asymmetric for the above two compounds. In contrast to the null isotope effect in  $[ImH][HMa1]$ , a positive isotope effect was observed in  $[Ni(AO)_2-H]Cl \cdot H_2O$  as shown in Figures 2 and 3 (Table 1) [8,9]. A lengthening of 0.019 Å in the O---O distance and a shift of about 0.129 Å towards one oxygen atom was observed in  $[Ni(AO)_2-D]Cl \cdot D_2O$ . This observation indicates a double-minimum-type potential function for the short hydrogen bond in the case of  $[Ni(AO)-H]-Cl \cdot H_2O$ . Since intramolecular constraints are operative in both the above structures, the conclusions regarding potential barrier in these structures should be regarded as qualitative, at the most. An ideal situation for a genuine isotope effect which would conform to the theoretical predictions would be a single, structurally independent hydrogen bond [30]. As pointed out earlier, the  $[(2-picNO)_2H][AuCl_4]$  may be a good

candidate for deuteration studies by neutron diffraction, since X-ray results have indicated the existence of a symmetry-free isolated short hydrogen bond in this compound [21].

### 3.4. Electron Density Distribution in Crystalline Solids

Information from X-ray and neutron diffraction experiments could be combined to display the changes in electron distribution that atoms undergo when involved in chemical bonding [31]. This process, called X-ray minus neutron (X-N) mapping assumes that the parameters measured by neutron diffraction are a better description of the system whereas the parameters from the X-ray model are biased by the effects of chemical bonding. Several studies of this type have been done and in most cases the observed bonding electron distributions reinforce simple bonding theories. The cross-sectional views of bonds in several simple compounds have confirmed the shapes expected from simple sigma- and pi-orbital models. Hydrogen-bonded systems are most appropriate for these studies. The X-N map should essentially show no electron density at the hydrogen atom position but should give sharp electron density gradients in the direction of the donor atoms. The

results of these electron distributions may be used for a quantitative correlation with other observable effects such as proton NMR shifts, isotopic substitution effects and acidity. The X-N method has been applied by Schlemper and co-workers to both imidazolium hydrogen maleate and calcium hydrogen maleate at room temperature [32]. The X-N deformation density maps for  $[\text{HMal}]^-$  ion in both cases are shown in Figures 10 and 11. In both cases essentially no electron density appears along the O...O direction near the oxygen atoms. Well-defined maxima are found in all covalent bonds in the molecule, and peaks are observed near both oxygen atoms in the regions normally associated with 'lone-pair' charge density. The room-temperature X-N deformation density mapping has also been completed on 2,4-dihydroxybenzophenone [33] which revealed an intramolecular O...O hydrogen bond of 2.55 Å.

Additional theoretical as well as low-temperature experimental work in the area of deformation density mapping is definitely needed to check the consistency of these experimental observations with the bonding picture obtained from theoretical calculations. Such comparisons, on the one hand, may serve as a calibration on the experimental procedures, but may also focus attention on the deficiencies of some approximate theoretical wavefunctions [34].

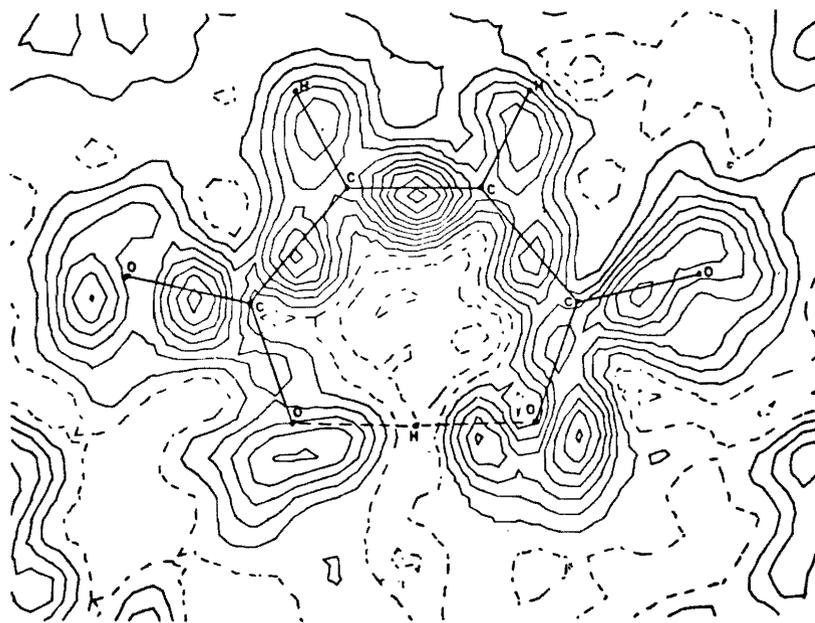


Figure 10. X - N Deformation Density for  $[\text{HMal}]^-$  in  $[\text{ImH}]^+[\text{HMal}]^-$ . (Contours at  $0.05e^-/\text{\AA}^3$ ; Dashed Lines for Negative Contours).



Figure 11. X-N Deformation Density for  $[H\text{ Mal}]^-$  in  $\text{Ca}(\text{H Mal})_2 \cdot 5\text{H}_2\text{O}$ . (Contours at  $0.05e^-/\text{\AA}^3$ ; Dashed Lines for Negative Contours).

#### 4. CONCLUDING REMARKS

The use of neutron scattering as a technique in physics, chemistry, and biology as well as in fundamental physics continues to grow. Low-temperature neutron diffraction experiments have a considerable promise for studies involving phase transitions and the concomitant molecular rearrangements in structures such as that of  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  [35]. Such studies will reinforce our ESR findings related to the changes in point-group symmetry at lower temperatures. The foregoing sampling of recent neutron diffraction studies of hydrogen bonds is indicative of extraordinary promise of research in this field. The obvious areas for further research along these lines are the studies involving isotope effects, X-N mapping at low temperatures, studies on isolated hydrogen bonds with O---O separation less than 2.70 Å. Although a reasonable amount of data is available, precise determinations at low temperatures are very scarce and further work is definitely needed.

New reactors and pulsed sources are being built in many countries at the moment which will no doubt be a great stimulus to the whole technique of neutron scattering. Important advances in neutron instrumentation are now developing from new techniques for manipulating and detecting neutron beams. These can re-establish the competitiveness of medium-flux sources with higher-flux sources in some area of research.

#### ACKNOWLEDGMENT

The author acknowledges all facilities provided by the University of Petroleum and Minerals (Grant CY/ORGOMETL/64) for the preparation of this review. Most of the work described here was done in collaboration with Professor E. O. Schlemper at the Research Reactor Facility and the Department of Chemistry, University of Missouri, Columbia. The author expresses his deepest gratitude to Professor Schlemper for his cooperation throughout the period this work was done.

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Paper Received 30 March 1983; Revised 26 July 1983.