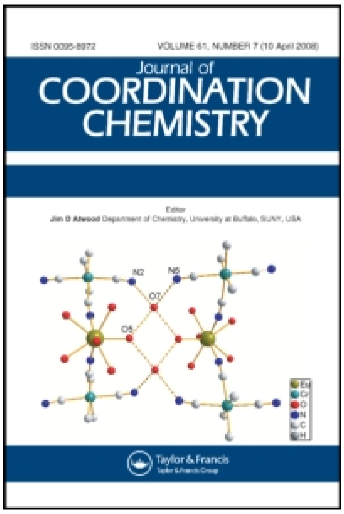

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SHORT INTRAMOLECULAR HYDROGEN BONDS: PROTON-NMR AND IR SPECTRA AS A FUNCTION OF O---O DISTANCE

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Infrared absorption frequencies and ^{1}H NMR chemical shifts have been measured as a function of O---O distances in compounds with short intramolecular hydrogen bonds. Two types of molecules were investigated, those with intramolecular O–H–O bonds within chelate or constrained systems having no degree of rotational freedom along the O–H–O axis, and molecules possessing symmetry-restricted or unrestricted hydrogen bonds with complete rotational freedom along the O--H--O axis. While electronic factors are most important for the nature of the short hydrogen bond in the latter compounds (such as dimeric hydronium ions of pyridine-*N*-oxides), steric constraints play a dominant role for the former (such as metal glyoximates). ^{1}H MMR chemical shifts δ(O–H–O) (ppm) and IR absorption frequencies ν(O–H–O) (cm^{-1}) as a function of the O---O distance are discussed.

Keywords: Hydrogen bonds, NMR, IR, oximes

INTRODUCTION

The term 'hydrogen bond' generally refers to [A---H] or [H---B] interactions in the [A---H–B] or [A–H---B] systems where A and B are strongly electronegative elements and the proton is covalently bonded to either A or B. However, many systems are known where the proton is covalently bonded neither to A nor B, but instead is equally attracted to both. Such systems are written as [A–H–B] and the term 'strong (or very short) hydrogen bond' is used for the [A–H–B] system as a whole. On the basis of criteria mainly stemming from the dichotomy in the A---B distance, strong hydrogen bonding has been recognized as being quantitatively different from the weak (or normal) hydrogen bonding.[1–3] Some of these criteria are: (a) the bond length R(A---B): which is only slightly less than the sum of the van der Waals radii of A and B in the normal H-bond but is significantly less (in the range 230 to 260 pm) for the strong hydrogen bond; (b) the location of proton: which is covalently bonded to the parent atom in the normal H-bond but is centred (or roughly so) without any appreciable covalent interaction in the case of strong H-bond; (c) the broad band for the vibrational mode ν(A–H---B): which is slightly shifted to lower wave numbers (but still in the 2000–3000 cm^{-1} region) for the normal hydrogen bond but appears as very broad and intense bands shifted to around 1700–1800 cm^{-1} for the strong hydrogen bond;[4] and (d) a large downfield shift: which was observed for ^{1}H NMR signals for the short hydrogen bond due to

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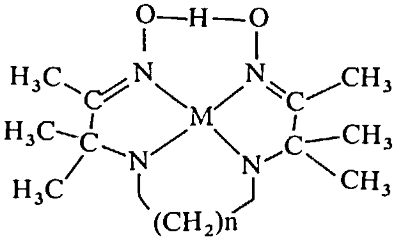
strong deshielding as compared to only a slight downfield shift relative to the non-hydrogen-bonded proton for normal hydrogen bonding. The frequencies of the vibrational modes of O–H–O and the shielding effects of the hydrogen bonded proton are strongly dependent upon A---A or A---B distances. Thus, some correlations are expected to exist between ν(A–H–B) (cm^{-1}) and δ(A–H–B) (ppm) as a function of A---A or A---B (pm) distances for compounds having short hydrogen bonds of the type [A–H–A] where A = N or O and/or [A–H–B] where A = O and B = N.

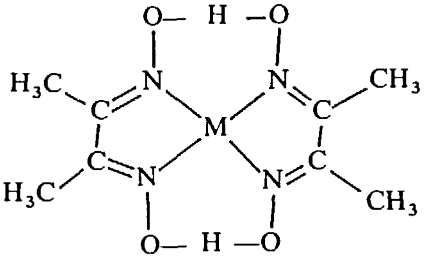
As a part of our continuing research[5–13] dealing with structure determination of compounds having short intramolecular O–H–O hydrogen bonds, we have investigated the ν(O–H–O) and proton δ(O–H–O) values in the following two series of compound as a function of O---O distances in an effort to evaluate any correlation that might exist between crystallographic data and spectroscopic measurements.

Compounds with constrained intramolecular [O–H–O] bonding having no freedom of rotation about the O–H–O axis as for metal chelates of alpha-aminedioximes (I) and vicinal glyoximes extensively have been studied by Hussain and Schlemper.[8–12]



n = 2 Enao, n = 3 Pnao, n = 4 Bnao

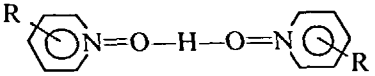
(I)



[M(dmg-H)$_2$]

(II)

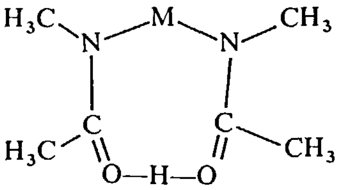
Unconstrained hydrogen bonded compounds possessing rotational degrees of freedom (with or without symmetry restrictions) along the O–H–O axis such as dimeric *N*-oxide hydronium ions (III) or other similar species (IV) were investigated by Hussain and coworkers.[13–16]



R = CH_3, NO_2

[H(diadduct)$_2$]$^+$

(III)



[H(dma)$_2$]$^+$

(IV)

EXPERIMENTAL

Chemicals and Materials

All starting chemicals for preparing the compounds with short hydrogen bonding were of analytical grade (Fluka Chemical) and were used without further purification. High purity spectral grade d_6-DMSO was further dried over molecular sieves before NMR measurements.

Preparation of Compounds

The *vic*-glyoximates, α-aminedioximates and compounds containing $[H(pyNO)_2]^+$, $[H(py)_2]^+$, $[H(Me\text{-}pyNO)_2]^+$, $[H(dea)_2]^+$ and $[H(dma)_2]^+$ hydronium ions (py = pyridine, pyNO = pyridine-*N*-oxide, MepyNO = Me-pyridine-*N*-oxide, dea = diethylacetamide and dma = dimethylacetamide) were prepared by reported procedures.[5-12] The compound $[H(dea)_2][AuCl_4]$, which has not been reported earlier, was prepared by the dropwise addition of dea to a concentrated methanol solution of $HAuCl_4$, until a yellow crystalline precipitate appeared. No more dea was added after this point since any excess dea resulted in the formation of a viscous solution from which crystals of the complex could not be easily recovered.

Spectroscopic Measurements

IR spectra (KBr pellets) in the range 4800–200 cm^{-1} were recorded with a Nicolet 5DXB FT-IR spectrometer. The cell compartment and the optical bench of the instrument was constantly purged with a slow stream of pre-dried nitrogen. The ^{1}H NMR spectra of freshly prepared d_6-DMSO solutions were recorded on a Varian XL-200 or a Brucker AC80 FT-NMR spectrometer using TMS as external standard. Owing to the possibilities of rapid exchange of the short hydrogen bonded proton with moisture in the solvent, maximum care was exercised in using pre-dried, moisture-free solvent for preparing solutions for NMR studies.

RESULTS AND DISCUSSION

Most of the spectral data reported in this study are new and even for previously available data all measurements were repeated using exactly identical experimental conditions to ensure maximum reliability for values of δ(O–H–O) (ppm) and ν(O–H–O) (cm^{-1}). An accurate remeasurement of all spectral data under exactly similar experimental conditions is necessary due to the very nature of the measurements which involve very small changes and also for the validity of any conclusions drawn from this study. The IR frequencies ν(O–H–O)(cm^{-1}) and the chemical shifts δ(O–H–O) (ppm) for the short hydrogen-bonded proton in constrained and unconstrained hydrogen bonded compounds along with the reported values of the O - - - O distance (pm) are given in Tables I and II.

TABLE I

IR frequencies and ^{1}H nmr chemical shifts for the bridged proton as a function of O---O distances in constrained, short hydrogen bonded compounds.[a]

Compound	O---O (pm)	ν(O-H-O) (cm^{-1})	δ(O-H-O) (ppm)	Ref.
[Ni(Ao)$_2$-H]Cl.H$_2$O	242.0(3)	1802	18.7	19
[Ni(Pnao-H)Cl.H$_2$O	240.9(3)	1780	18.6	9
[Ni(Bnao-H)I.H$_2$O	241.7(7)	1798	18.5	21
[Ni(Bnao-H)I.H$_2$O	242.1(5)	1790	18.7	21
[Cu(Bnao-H)H$_2$O]ClO$_4$	242.1(5)	1790	18.8	21
[Rh(Bnao-H)Cl$_2$]$_2$	238.7(5)	1792	19.5	23
[Ni(Pnao-7HNO$_2$)]$^{(b)}$	239.0(8)	1780	19.1	29
[Ni(Pnao-7HNO$_2$)]$^{(c)}$	242.7(5)	1780	18.9	18
[Ni(Pnao-7HNO)]	241.1(3)	1750	18.8	30
[Ni(PreH)]ClO$_4$	242.5(3)	1760	18.7	24
[Pd(Pnao-H)]NO$_3$	247.4(5)	1750	18.2	6
[Cu(Pnao-H)CN].1/2CH$_3$CN	247.5(5)	1780	18.3	26
[Cu(Pnao-H)(ORO$_3$)]	246(2)	1785	18.2	11
[Ni(Hdmg)$_2$]	246.2(3)	1770	18.2	10
[Pd(Hdmg)$_2$]	263(1)	1726	18.1	10
[Pt(Hdmg)$_2$]	262(2)	1680	18.1	10
[Pd(Hafdo)$_2$]	258.3(4)	1730	18.2	8
[Co(Hafdo)$_2$(thio)$_2$]NO$_3$.2H$_2$O	249.7(5)	1750	18.2	7
[Co(Hafdo)$_2$(tppAs)$_2$]ClO$_4$	(d)	1745	18.2	7
[Co(Hafdo)$_2$(tpp)$_2$]NO$_3$	(d)	1720	18.0	7
[Co(Hafdo)$_2$(tppSe)$_2$]NO$_3$	(d)	1745	18.3	7
[Rh(H-Ao)$_2$]Cl	247(1)	1785	18.3	23
[Ni(Enao-H)]ClO$_4$	247.8(5)	1750	18.3	20

[a] H$_2$afdo = α-furilglyoxime ν(O-H-O) = 3200 cm^{-1}, Hafdo = α-furilglyoxime anion, Hdmg = dimethylglyoxime anion, H$_2$pnao = 3,3'(trimethylenediimino)bis(3-methyl-2-butanoneoxime), ν(O-H-O) = 3323 cm^{-1}, Hao = α-amineoxime anion, tppSe = triphenylphosphineselenide, tppAs = triphenylphosphinearsine, thio = thiourea. [b] Orthorhombic form. [c] Monoclinic form. [d] Data not available.

TABLE II

IR frequencies and ^{1}H nmr chemical shifts for the bridged proton as a function of O---O distances in unconstrained short hydrogen bonded compounds.

Compound	O---O (pm)	ν(O-H-O) (cm^{-1})	δ(O-H-O) (ppm)	Ref.
[H(dma)$_2$][AuCl$_4$]	246(5)	1660	14.0	15, 27
[H(dea)$_2$][AuCl$_4$]	(a)	1650	11.3	(b)
[H(2-MepyNO)$_2$][AuCl$_4$]	239.3(6)	700–1050	10.0	13
[H(2-MepyNO)$_2$]Cl$_2$.3H$_2$O	241.4	750–1050	12.0	28
[H(3-MepyNO)$_2$][AuCl$_4$]	240.6(9)	750–1150	9.82	16
[H(4-MepyNO)$_2$][AuCl$_4$]	244.2(9)	750–1100	10.0	14
[H(pyNO)$_2$][AuCl$_4$]	241(1)	790–1100	11.2	15
[H(p-NO$_2$-pyNO)$_2$][AuCl$_4$]	(a)	750–1050	11.9	14
[H((CH$_3$)$_2$-pyNO)$_2$][AuCl$_4$]	234.5(13)	750–1100	10.8	22

[a] Data not available. [b] This work.

Proton NMR spectra and the O - - - O distance

The position of the hydrogen atom within the short intramolecular hydrogen bond in chelated compounds appears to be related with the O - - - O distance. The hydrogen atom is virtually covalently bonded to one of the oxime oxygen and only weakly bonded to the other oxygen in compounds having O - - - O distances in the range 245–265 pm. Complexes with O - - - O distances of 245–265 pm exhibit a value of 18.0 to 18.4 ppm for the δ(O–H–O) signal. In general, the accentric hydrogen bond with an O - - - O distance of 245–265 pm exhibits a chemical shift around 18.2 ppm whereas when the O - - - O distance is below 245 pm the proton chemical shift is above 18.6 ppm. Thus, the shorter the O - - - O distance the higher is the δ(O–H–O) value (*e.g.*, 18.6 ppm for [Ni(Pnao-H)]Cl with O - - - O = 240.9 pm and 19.5 ppm for $[Rh(Bnao\text{-}H)Cl_2]_2$ with O - - - O = 238.7 pm) as depicted in Figure 1.

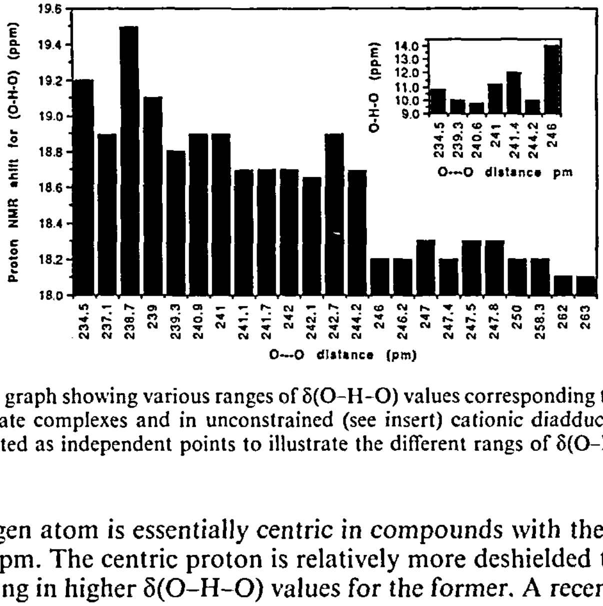


FIGURE 1 Bar graph showing various ranges of δ(O–H–O) values corresponding to O - - - O distances in constrained chelate complexes and in unconstrained (see insert) cationic diadducts. All data in Tables I and II are plotted as independent points to illustrate the different rangs of δ(O–H–O) as a function of O - - - O.

The hydrogen atom is essentially centric in compounds with the O - - - O distance less than 250 pm. The centric proton is relatively more deshielded than the accentric proton resulting in higher δ(O–H–O) values for the former. A recent X–N study[17] of 1,4-dihydroxybenzophenone, a compound having short hydrogen bond, revealed almost zero deformation density around the bridged proton, substantiating the strong deshielding of protons involved in strong hydrogen bonding. Though no linear correlation exists between the O - - - O distance and the δ(O–H–O) values, all available data on hydrogen bonded chelated complexes show two sets of δ(O–H–O) values: one below 18.4 ppm corresponding to O - - - O distances of 245–265 pm and the other above 18.5 ppm for O - - - O distances of 235–245 pm.

In cationic adducts of aromatic *N*-oxides, δ(O–H–O) values of about 10–14 ppm were observed for O - - - O distances less than 250 pm, significantly less than 18.0–19.5 ppm observed for the corresponding chelate complexes. This can only be explained on the basis of inductive effects *alone* playing a dominant role in the cationic diadducts, as compared to the chelate complexes where steric constraints also contribute towards deshielding of the bridged proton (in addition to inductive effects of groups attached to the N=O moiety). The δ(O–H–O) resonance in both types of compounds is mainly related with shielding effects through the N=O groups, which in the case of cationic aromatic diadducts, is not as effective as in chelate complexes, due to the absence of any constraints in the former molecules. Thus the bridged protons are not as highly deshielded in the cationic diadducts as in the chelate complexes, thus resulting in higher δ(O–H–O) values in the latter species.

IR spectra and the O - - - O distance

The existence of short hydrogen bonding was confirmed in the chelate complexes by the disappearance of the O–H–O absorption band upon replacement of O–H–O by O–BF_2–O in macrocyclization reactions of the metal chelates [Ni(Pnao-H)]Cl, forming the corresponding macrocycle [Ni(PnaoBF_2)]Cl. The ν(O–H–O) bands for the short hydrogen bonded compounds are consistently shifted to 1770–1800 cm^{-1} as compared to 2000–2200 cm^{-1} for the normal hydrogen bond. In fact, a strong absorption around 1750 cm^{-1} can be regarded as diagnostic of the existence of a short hydrogen bond. However, no clear trends between the O - - - O distance and the ν(O–H–O) frequency were revealed, partly because the IR bands constitute a set of peaks rather than single absorption and a precise value cannot be assigned to ν(O–H–O) as was the case for δ(O–H–O). Furthermore, ν(O–H–O) has overlapping absorptions from ligands and counter anions which further interfere with the explicit assignment of ν(O–H–O). The observed ν(O–H–O) modes are also independent of changes in the O - - - O distance and no trends similar to those revealed in the NMR spectra were observed except that for short (or strong) hydrogen bonds a very strong absorption band consistently appeared around 1750 cm^{-1}. In contrast to the disappearance of ν(O–H–O) upon BF_2-macrocyclization of the chelate complexes, the replacement of O–H–O by O–BF_2–O in the cationic diadducts was not possible.

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