ARTICLES

Two-Bond Spin−Spin Coupling across a Hydrogen Bond: X−Y Coupling in the Presence and Absence of the Proton

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Received: January 21, 2004

This paper addresses the question of whether spin−spin coupling between X and Y across an X−H−Y hydrogen bond is proof that the hydrogen bond is covalent. The results of ab initio equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations are used to compare coupling constants ($^{2h}J_{X-Y}$) for hydrogen-bonded complexes and related complexes that have the same X−Y distance but no hydrogen bond. The results show that even in the absence of a hydrogen bond, X−Y coupling can occur. The magnitude of this coupling constant may be greater or less than it is in the hydrogen-bonded complex. Thus, these data suggest that X−Y spin−spin coupling is not a proof of covalency. The role of the hydrogen bond is to allow X and Y to approach each other close enough to form a stable complex, for which an X−Y coupling constant can be measured experimentally. The presence of the proton does influence the magnitude of the coupling constant by altering the s-electron densities on X and Y.

Introduction

In their landmark paper, Dingley and Grzesiek reported the first experimental measurements of two-bond spin−spin coupling constants across N−H···N hydrogen bonds in the AU and GC pairs.[1] In this and a subsequent review article,[2] these authors stated that the experimental verification of the existence of such two-bond couplings proves that the hydrogen bond is covalent. Others have addressed this question, and support can be found both pro and con.[3−11] Those who do not support this claim noted that through-space couplings can occur between atoms in a repulsive orientation, an example being $^{19}F-^{19}F$ coupling in *cis*-1,2-difluorothene.[12] Pecul has computed a coupling constant between two ^3He atoms, noting that coupling can occur in such a complex, which is stabilized by a very weak van der Waals interaction.[6] In a recent review, Contreras et. al. have argued that coupling can be transmitted between two atoms as long as there is an overlap of their electron clouds.[11]

It is not the purpose of this paper to debate whether the hydrogen bond is covalent or not.[13−15] Certainly, there is a contribution to the stabilization energy of a hydrogen-bonded complex due to covalency. Perhaps the most convincing evidence of this comes from the structures of hydrogen-bonded complexes. In neutral complexes, for example, the hydrogen bond tends to form in one of the lone pair directions relative to the proton-acceptor atom, that is, in the same direction in which protonation occurs. The hydrogen bond does not form in the direction that coincides with the molecular dipole moment vector of the base, the direction in which a cation such as Li^+ interacts with a simple base. Excellent illustrative examples are the gas-phase structures of the water[16] and hydrogen fluoride[17] dimers.

In this paper two questions will be addressed: (1) Is the existence of a spin−spin coupling constant between a pair of hydrogen-bonded atoms proof that the hydrogen bond is covalent? (2) What role does the proton play in spin−spin coupling across a hydrogen bond?

To answer these questions, a direct comparison will be made of two-bond X−Y coupling constants in hydrogen-bonded complexes computed in the presence and absence of the hydrogen-bonded proton.

Methods

Ab initio equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations in the CI-like approximation[18−21] have been carried out on selected hydrogen-bonded complexes, and on some related non-hydrogen-bonded structures derived from them. The hydrogen-bonded complexes were optimized at second-order Møller−Plesset perturbation theory (MP2)[22−25] with the 6-31+G(d,p) basis set.[26−29] The EOM-CCSD calculations were performed with use of the Ahlrichs qzp basis on non-hydrogen atoms and qz2p on the hydrogen-bonded hydrogen.[30] The Dunning cc-pVDZ basis set[31,32]was used for all other hydrogens. For consistency and comparison purposes, the calculations on the water dimer and related structures employed the qz2p basis set on all hydrogen atoms. This level of theory has been found to give good agreement with experimental two-, three-, and four-bond coupling constants across hydrogen bonds when these are available.[33−37] The EOM-CCSD calculations were carried out with the ACES II program[38] on the Cray SV1 computer or the Itanium cluster at the Ohio Supercomputer Center.

Results and Discussion

Table 1 reports data for five systems that are stabilized by X−H−Y hydrogen bonds. These include two hydrogen-bonded cations, $O_2H_5^+$ and $N_2H_7^+$, that are stabilized by symmetric O···H···O and N···H···N hydrogen bonds, respectively; two

10.1021/jp0400465 CCC: $27.50

TABLE 1: Two-Bond Spin−Spin Coupling Constants ($^{2h}J_{X-Y}$, Hz) and X−Y Distances (Å) for Hydrogen-Bonded Complexes and Related Structures

complex	R_{X-Y}	$^{2h}J_{X-Y}$	related structure	R_{X-Y}	J_{X-Y}
$O_2H_5^+$ (C_2)	2.386	39.9	O_2H_4 (C_2)[a]	2.386	25.6
			O_2H_4 (C_2)[b]	2.386	25.0
$N_2H_7^+$ (D_{3d})	2.598	17.2	N_2H_6 (D_{3d})	2.598	13.5
FH:NH_3	2.637	−45.2	F^-:NH_3	2.637	−51.7
HOH:OH_2 (C_s)	2.914	1.5	H_2O:OH_2 (D_{2h})[c]	2.914	5.8
$C_3H_4O_2$ (C_s)[d]	2.600	3.5	$C_3H_4O_2$ (C_s)[e]	2.600	5.1

[a] The two H_2O molecules have the same orientation as in the equilibrium protonated dimer $O_2H_5^+$ with the hydrogen-bonded proton removed, but with the basis functions on this proton remaining. [b] The two H_2O molecules have the same orientation as in the equilibrium protonated dimer $O_2H_5^+$ with the hydrogen-bonded proton and its basis functions removed. [c] A planar arrangement of two optimized H_2O molecules with D_{2h} symmetry and no hydrogen bond. The two O atoms are adjacent, and the H atoms are on the outside of the two oxygens. [d] The optimized equilibrium structure of malonaldehyde with an asymmetric O−H···O hydrogen bond. [e] A conformer of malonaldehyde derived from the optimized structure by rotating the O−H bond of the C−O−H group by 180° about the C−O bond, thereby destroying the O−H···O hydrogen bond.

neutral complexes, $(H_2O)_2$ and FH:NH_3, which are stabilized by traditional O−H···O and F−H···N hydrogen bonds, respectively; and one molecule, malonaldehyde, which is stabilized by an intramolecular O−H···O hydrogen bond. The equilibrium X−Y distances and the coupling constants ($^{2h}J_{X-Y}$) for the equilibrium structures are reported in Table 1, columns 2 and 3, respectively. Since it has been shown that the Fermi-contact (FC) term is an excellent approximation to the total coupling constant ($^{2h}J_{X-Y}$) for O−H−O, N−H−N, and F−H−N hydrogen bonds,[35,39−41] only values of the FC terms are reported. Column 4 reports complexes that do not have hydrogen bonds, but which will be used for comparison with the corresponding complexes in column 1. Columns 5 and 6 report the X−Y distances and the computed X−Y spin−spin coupling constants for the related complexes.

The first complex in Table 1 is the cationic complex $O_2H_5^+$, which has C_2 symmetry and is stabilized by a symmetric proton-shared O···H···O hydrogen bond. The O−O distance in this complex is 2.386 Å and $^{2h}J_{O-O}$ is 39.9 Hz. For comparison, two related complexes with the formula O_2H_4 are also reported in Table 1.[10] These two contain two H_2O molecules in the same orientation and therefore with the same O−O distance as the two H_2O molecules in $O_2H_5^+$, but with the hydrogen-bonded proton (H^+) removed. In this orientation, the two water molecules are not bound, but are repulsive relative to two isolated molecules. In the first example, the hydrogen-bonded proton has been removed, but its basis functions have been retained. The O−O coupling constant is less than it is in $O_2H_5^+$, but it is still substantial at 25.6 Hz. In the second example, the proton basis functions have also been removed, and the coupling constant drops only slightly to 25.0 Hz. The fact that the coupling constant decreases when the proton is removed suggests that the presence of the proton that forms the hydrogen bond has an effect on the magnitude of the coupling constant. The fact that the coupling constant is appreciable even though there is no hydrogen bond indicates that the measurement of such a coupling constant does not constitute proof that the hydrogen bond is covalent. Moreover, since the coupling constant changes little whether the proton basis functions are present or not indicates that there is no significant basis-set superposition effect on coupling constants.

The second example is similar, this time involving the cation $N_2H_7^+$ in its nonequilibrium D_{3d} orientation in which the hydrogen bond is symmetric, and a related system in which the two NH_3 molecules are in the same orientation as the two NH_3 molecules in the cationic complex, with the same N−N distance of 2.598 Å. Once again, removing the hydrogen-bonded proton reduces the coupling constant from 17.2 to 13.5 Hz. However, the N−N coupling constant is still significant, despite the fact that there is no hydrogen bond and the interaction between the two NH_3 molecules is repulsive.

The next complex, FH:NH_3, is compared to a system in which the hydrogen-bonded proton has been removed to give the anion−molecule, F^-:NH_3, with the F−N distance fixed at 2.637 Å in both. The hydrogen-bonded FH:NH_3 complex has a computed F−N coupling constant of −45.2 Hz. However, when the proton is removed, the F−N coupling constant increases (in an absolute sense) to −51.7 Hz, even though there is no hydrogen bond and the interaction of F^- with NH_3 is repulsive.

The first three examples involve the removal of H^+, so that the charge on the complex changes, either from +1 to 0, or from 0 to −1. In the next two examples, the charge is unchanged. The equilibrium water dimer, which has C_s symmetry, has a very small coupling constant of 1.5 Hz at an O−O distance of 2.914 Å, as reported in Table 1. The species given for comparison is an arrangement of two neutral water molecules that has planar D_{2h} symmetry, and an O−O distance of 2.914 Å. The two water molecules are arranged such that the two oxygen atoms are adjacent, and the four hydrogen atoms lie outside of the two oxygens. In this arrangement there is no hydrogen bond, and the interaction of the pair of H_2O molecules is repulsive. Yet, the O−O coupling constant increases relative to the water dimer, to 5.8 Hz at the same O−O distance. Thus, despite the fact that there is no hydrogen bond, the value of J_{O-O} in this arrangement of two water molecules is even greater than that in the water dimer itself.

The final example listed in Table 1 is malonaldehyde in two different conformations. The first is the equilibrium structure that is stabilized by an asymmetric O−H···O hydrogen bond. It has an O−O coupling constant of 3.5 Hz at an O−O distance of 2.600 Å. For comparison, the same molecule with the O−H bond rotated by 180° about the C−O bond has an O−O coupling constant of 5.1 Hz. In this conformation there is no hydrogen bond.

The examples presented above provide convincing evidence that the existence of a two-bond spin−spin coupling constant across a hydrogen bond does not prove that the hydrogen bond is covalent. What then is the role of the hydrogen bond and the hydrogen-bonded proton in spin−spin coupling? The presence of the proton is not necessary to have X−Y coupling across an X−H−Y hydrogen bond, that is, the mechanism of coupling between X and Y does not directly involve H. However, the formation of the X−H−Y hydrogen bond is necessary to enable the proton donor and proton acceptor molecules to form a stable complex in which X and Y are close enough to couple. In this stable arrangement, spin−spin coupling between X and Y gives rise to a signal that can be measured experimentally. The presence of the proton and the formation of the hydrogen bond do influence the magnitude of X−Y spin−spin coupling constants, since hydrogen-bond formation alters the electron densities on both X and Y in ground and excited triplet states. In the sum-over-states expression for the Fermi-contact term,[42] the FC term arises from a sum of contributions which involve coupling between excited triplet states and the ground state. This coupling involves only states that have s-electron densities on X and Y.

Acknowledgment. This work was supported by the National Science Foundation through grant CHE-9873815 and by the Ohio Supercomputer Center. This support is gratefully acknowledged. It is a pleasure to acknowledge many insightful discussions with Dr. José Elguero.

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