Are Hydrogen Bonds Covalent or Electrostatic? A Molecular Orbital Comparison of Molecules in Electric Fields and H-Bonding Environments

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The extent to which hydrogen-bonding can be considered to be a covalent or resonance effect, rather than an electrostatic or electrostatic plus polarization effect, is modeled by ab initio molecular orbital calculations in graded uniform electric fields of molecules that form chains of H-bonds. The stabilization energy, dipole moments, and relaxed geometrical structural parameters of these molecules are tabulated as a function of applied field. The H-bonding interactions of a molecule are judged to be due to electrostatic and polarization effects if all of the tabulated parameters agree with those calculated for an infinite chain of H-bonding molecules at the same value of the applied electric field. If these parameters individually agree with those of the infinite chain of H-bonding dimers at substantially different values of the applied field, effects other than electrostatic and polarization, such as covalent or resonance effects, must be important. Of the two molecules studied, urea appears to be reasonably well-described by electrostatic plus polarization effects, whereas the other molecule, the enol of 1,3-cyclohexanedione, clearly is not.

Introduction

The precise definition of a hydrogen bond continues to be elusive.[1] The nature of the physical interactions that contribute to hydrogen bonds has been the subject of numerous discussions in the chemical literature.[2] At one extreme, hydrogen bonds are attributed to purely electrostatic interactions, or electrostatic plus polarization interactions; at the other, covalent interactions are held to be extremely important. The comparison between the H_2O/HF[3] and H_2O/HCN[4] hydrogen-bonding dimers is useful. An electrostatic dipole−dipole interaction between the water dipole and that of either H-donor would lead to a planar dimer. However, the first is predicted to be nonplanar, and the second planar. Clearly, there must be a difference in the H-bonding interactions. Fowler and Legon reported evidence for partial H-transfer from HCl to trimethylamine in their H-bonding dimer.[5]

Kollman[6] used a Morokuma analysis[7] of the results of an ab initio calculation to break down the interaction energy of the water dimer into four components: electrostatic, polarization, charge transfer, and dispersion. In this study, they found that the contributions of various components varied with intermolecular distance. Roughly half the interaction is attributed to electrostatic interaction at the equilibrium distance for this calculation (2.98 Å).

Weinhold used a natural bond orbital (NBO) analysis to eliminate the charge-transfer component from the Hamiltonian of H-bonded dimers. They reported that this component constituted the major energetic contribution, whereas electrostatic attraction was largely canceled by exchange repulsion, for many H-bonds. Thus, the electrostatic component can be considered to be a consequence of the charge-transfer interaction.[8]

Gilli suggested that certain hydrogen bonds can be stabilized by resonance.[9] These resonance-assisted hydrogen bonds (RAHB) must clearly have appreciable covalent character. They are characterized by very short X...H...X interactions (where X might be O, for example). His analysis is largely based upon interpretation of crystal structures. Alternatively, short H-bonding interactions in infinite chains of hydrogen bonds in certain crystal structures could simply be explained by an increase in the electric field felt by each molecule due to the polarization of its neighbors. This explanation would not require covalent interaction or RAHB.

Extensive cooperativity has been reported for many different kinds of hydrogen-bonding chains. Theoretical results have been reported for H-bonding chains of HCN,[10] H_2O,[11] acetic acid,[12] and *N*-methylformamide,[13] as well as the systems discussed in this paper. Cooperative interactions have been noted in crystal structures of finite H-bonding chains in studies of carbohydrates[14] and peptides. The longer H-bonding chains have shorter H-bonding interactions.

Most recently, Grzesiek,[15] and Bax[16] reported $^{1}H-^{15}N$, $^{15}N-^{15}N$, and $^{13}C-^{15}N$ couplings in the NMR spectra of several hydrogen-bonded systems that are held rigid sufficiently long that molecular exchange processes do not obscure them. These couplings have been interpreted as experimental evidence for covalent interactions through hydrogen bonds.

In this paper we test the hypothesis that hydrogen bonds can be attributed to classical interactions such as electrostatic plus polarization interactions by comparing the properties of hydrogen-bonding molecules in electric fields with the same molecules in aggregates containing infinite chains of hydrogen bonds. If the electric field that reproduces the interaction energy of the hydrogen bond also reproduces the changes in the molecular geometries induced by the infinite hydrogen-bonding chains, one might conclude that the classical explanation is valid. However, if the interaction energy and the various parameters of the molecular geometry in the infinite hydrogen-bonding chain are reproduced at significantly different values of applied electric field, one might conclude that classical interactions between the molecules are insufficient to explain hydrogen bonding. Unlike the Morokuma analysis, the test we perform

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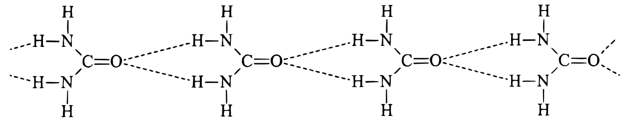

Figure 1. A hydrogen-bonding chain of urea molecules.

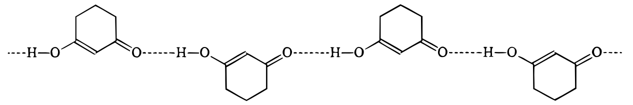

Figure 2. A hydrogen-bonding chain of 1,3-cyclohexanedione in its enol form. The calculations were performed on 1,3-propanedione constrained to mimic the region of 1,3-cyclohexanedione that is involved in hydrogen bonding.

here does not depend on any analysis of the wave function. No approximations or definitions need to be made to partition the wave function or density matrix. All of the quantities discussed are potentially physically observable.

We apply this test to two different kinds of molecules. Both have dipole moments that are expected to align well with the direction of the interaction in a hydrogen-bonding chain. We previously calculated the energies of infinite hydrogen-bonding chains for each of the molecules.[17,18] The first molecule, urea, forms a hydrogen-bonding chain in its crystal structure (Figure 1) in which the oxygen of one urea is simultaneously hydrogen bonded to two different amino Hs.[17] In this structure, the hydrogens are covalently bonded to the N while they formed a hydrogen bond to the O. The second molecule, the enol of 1,3-propanedione, is a smaller analogue of the enol of 1,3-cyclohexanedione, which forms infinite chains of hydrogen bonds (Figure 2) in which the hydrogen bound to an O forms a hydrogen bond with an O on the adjacent molecule. We previously suggested that the hydrogen bonding pattern in the crystal is due to the cooperative interactions of the hydrogen bonds.[18] In this structure, one can imagine the hydrogen-bonded hydrogen moving from one O to the other in each molecule of an infinite chain to form an equivalent structure. Structures of this type are good candidates for resonance-assisted hydrogen bonding, as suggested by Gilli. If his analysis is correct, there should be a substantial contribution of covalent bonding in this kind of hydrogen bond.

Studies of hydrogen bonds in electric fields have been reported in other contexts: Scheiner[19] and Zundel[20] investigated the effect upon proton-transfer, whereas others used electric fields to simulate solvation[21] and other effects[22] upon H-bonded species.

Methods

The two molecules in question were individually optimized in uniform applied electric fields using steps of 0.005 from 0.0 field to 0.050 au. All internal coordinates of urea were individually optimized with the exception that it was constrained to a planar C_{2v} structure. Previous work has shown this to be justified.[23] The 1,3-propanedione was contrained to be planar in the conformation that mimics the corresponding part of the 1,3-cyclohxanedione. We used the GAMESS program[24] to perform ab initio calculations at the HF/D95** level. This is the same Hartree–Fock procedure that was used to calculate the hydrogen-bonding aggregates containing up to 10 monomeric hydrogen-bonding units of urea.[17] The aggregates of the enol of 1,3-cyclohexanedione[18] were recalculated using the HF/D95** level for this paper. The differences with the results of the previous work[18] are minor. The energies and geometric parameters for infinite chains were obtained using the following extrapolations procedure. The lines denoting the values for stabilization energy and geometric parameters for an infinite chain of enols correspond to values that were extrapolated from the H-bonding interaction energies of chains containing from 1 to 8 molecules. The energy (or geometric parameter) of adding an additional momomeric unit to the growing chain, corrected for counterpoise and zero point vibration, was used in the extrapolation. The extrapolation was performed as in ref 18 using eq 1, where ΔE_n is the interaction energy of adding a monomer to a chain of $n-1$ monomers, and the parameters a and b are determined by a least-squares fit.

$$\Delta E_n = E_1 + a(1 - e^{-b(n-1)})$$

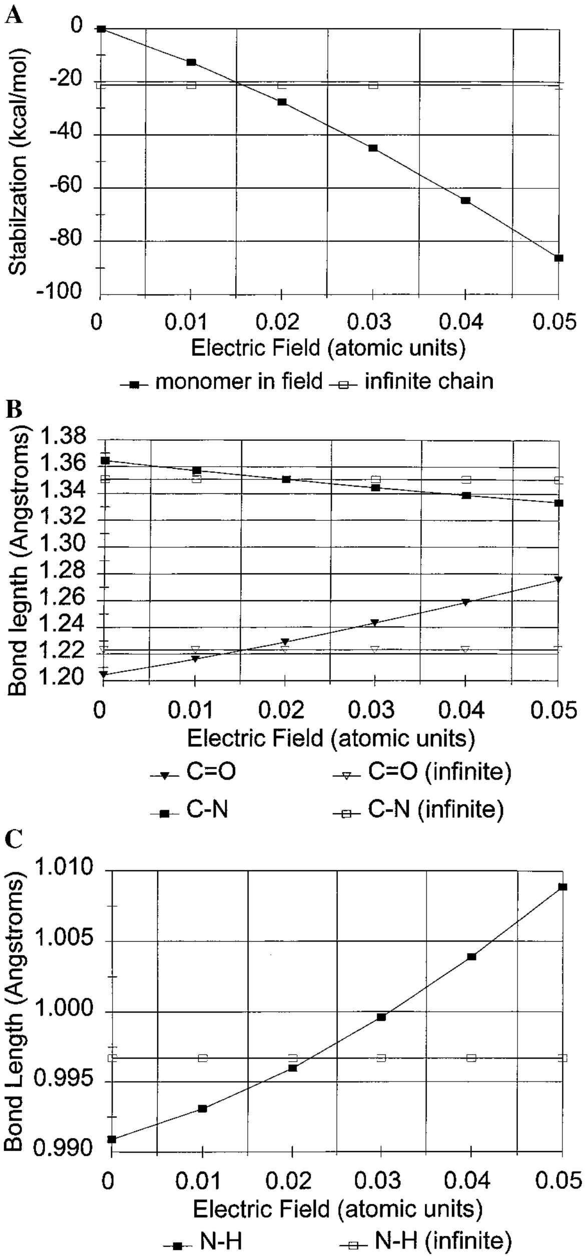

Figure 3. Urea in an electric field. (A) Stabilization energy (equivalent to H-bonds at each end); (B) geometric parameters (C=O and C–N); (C) geometric parameters (N–H). The unfilled markers that form the horizontal lines indicate extrapolated values for infinite H-bonding chains at the HF/D95** level.

Results and Discussion

The results for urea are summarized in Figures 3A–C. One notices that, in these figures, the line denoting the stabilization

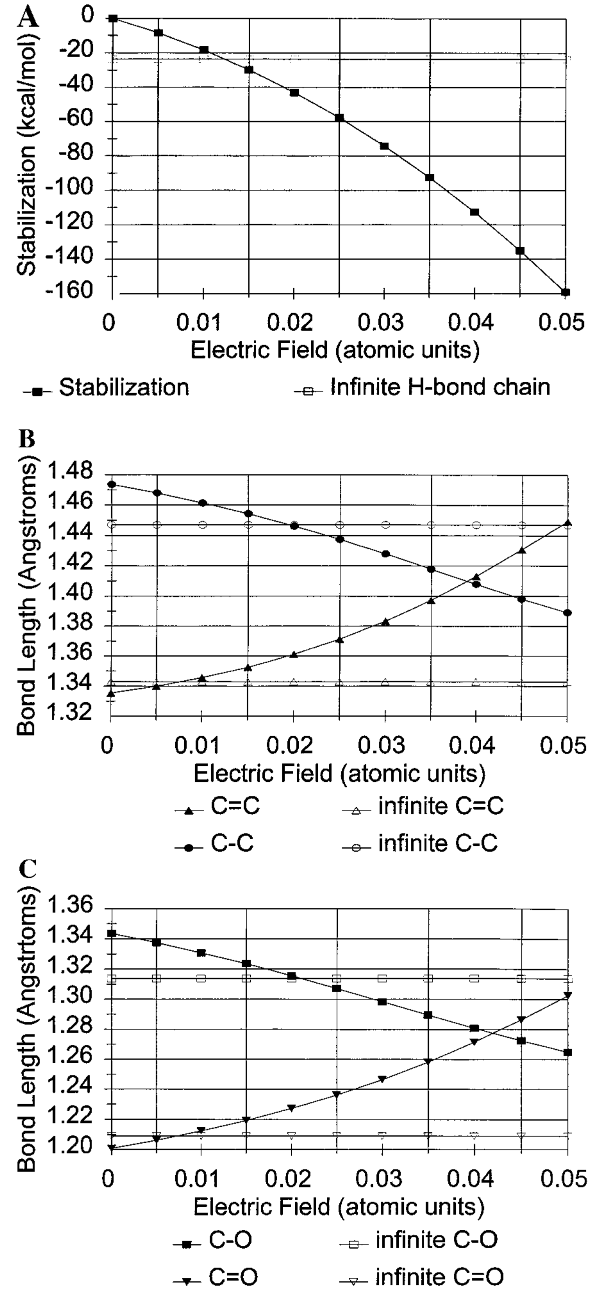

Figure 4. Enol of 1,3-propanedione in an electric field. (A) Stabilization energy (equivalent to H-bonds at each end); (B) geometric parameters (C−C and C=C); (C) geometric parameters (C−O and C=O). The unfilled markers indicate extrapolated values for infinite H-bonding chains at the HF/D95** level.

energy and the relevant geometric parameters (C=O, C−N, and N−H bond lengths) all cross, at approximately the same applied electric field, the horizontal line marks the value for an infinite chain. The stabilization that corresponds to an infinite chain of H-bonding urea molecules occurs at an applied field of 0.016 au (1 au = 27.21 V). The C−N bond attains the value in the infinite chain at an applied field of 0.018 au, whereas the C=O and N−H bonds attain the infinite chain value at applied fields of 0.016 and 0.021 au, respectively. Thus, all of the infinite chain parameters for urea become equivalent to those in an applied field at field strengths that vary from 0.016 to 0.021 au. Thus, urea seems to form hydrogen bonds which can be reasonably described using classical electrostatic and polarization arguments although some covalent interaction might contribute.

The results for the enol of 1,3-propanedione, which are summarized in Figures 4A−C, are in marked contrast to those for urea. An applied field of about 0.012 au corresponds to the stabilization of an infinite chain. The C=C and C−C bond lengths reach the infinite chain values at applied fields of 0.008 and 0.020 au, respectively, whereas the C=O and C−O bonds reach the corresponding values at applied fields of 0.007 and 0.021 au, respectively.

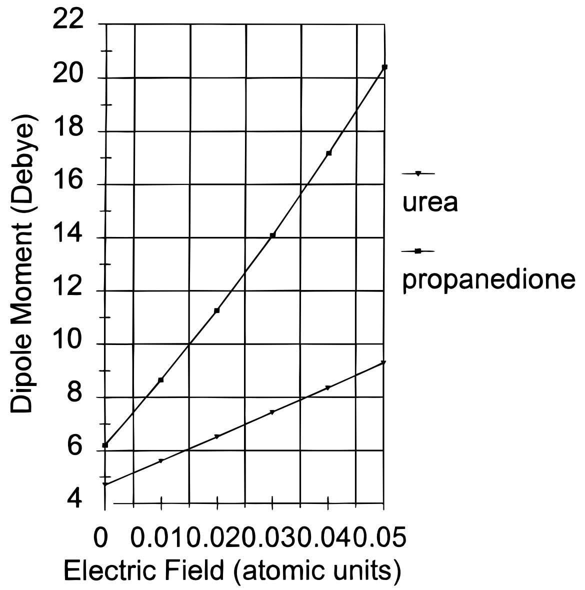

Figure 5. Dipole moments in an electric field.

The value of the applied electric field which reproduces the stabilization of an individual molecule as calculated in an infinite hydrogen-bonding chain is very different from that needed to reproduce the changes of most of the geometric parameters (C−C, C=C, C−O, and C=O bond lengths). Fields of 0.007 to 0.021 au are needed to reproduce all of the infinite chain data for 1,3-propanedione. This range of fields is almost three times that calculated for urea (above). Thus, the hydrogen bonds in infinite chains of urea and 1,3-propanedione seem to fall into distinctly different categories. 1,3-Propanedione seems to have much more covalent character in its H-bonding than does urea. These results support the suggestions made by Gilli that such bonds are RAHBs.[9]

Figure 5 illustrates the behavior of the dipole moments of urea and 1,3-cyclohexanedione in an applied electric field. The dipole moment of urea increases approximately linearly with applied field. The dipole of 1,3-propanedione has a greater initial slope. It also shows a distinct curvature. The figure indicates that 1,3-propanedione must have a significant hyperpolarizability. Clearly, the two molecules participate in hydrogen bonds that are distinctly different in character.

Conclusions

The work described suggests that the term "hydrogen bond" designates intermolecular interactions that can result from very different kinds of physical interactions. Thus, the conclusions drawn from the detailed study of a particular hydrogen bond do not necessarily apply to hydrogen bonds in general. Hydrogen bonds can be mostly due to electrostatic (and polarization) interactions, or they may have very large components of covalent bonding. Proper modeling of hydrogen bonds needs to take the different interactions into account.

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