C−H Bond-Shortening upon Hydrogen Bond Formation: Influence of an Electric Field

Artëm Masunov and J. J. Dannenberg*

Department of Chemistry, City University of New York, Hunter College and the Graduate School,
695 Park Avenue, New York New York 10021

Rubén H. Contreras

Departamento de Fisica, Fac. De Sc. Exactas y Naturales, U. B. A., Cdad. Universitaria,
*Pab. I, 1428, Buenos Aires, Argentina*

Molecular orbital calculations on methane, acetylene, and HCN in electric fields of various strengths have been performed at the HF/D95** level. The molecules were oriented in the field so that one C−H bond was aligned with the field in the direction appropriate for a stabilizing polarization of that bond. Although the C−H bonds of acetylene and HCN lengthen as the field increases, that of methane shortens until the field reaches 0.02 au then lengthens as the field is further increased. Electron density analyses using three different methods (Mulliken populations, Natural Bond Orbitals, and Atoms in Molecules) all show a shift of electron density from the putative H-bonding hydrogen toward the bulk of the molecule (although they disagree with each other in several other ways). We interpret the data to suggest that the hydrogen in methane is electron rich with respect to the carbon (in contrast to those of HCN and acetylene). At small electric fields, electron density from the hydrogen moves into the C−H bond, both strengthening and shortening it. When the electric field increases beyond 0.02 au, net electron density starts to move from the C−H bond toward the carbon causing the bond to begin to weaken and lengthen. The C−H bonds of HCN and acetylene both lengthen as the field is increased. The behavior of all three molecules in the fields is sufficient to explain their H-bonding behavior.

The definition of the hydrogen-bond has been elusive.[1,2] The importance of weak H-bonds involving C−H donors has recently caught the attention of many chemists.[3] Although the covalent bond to the H-bonding donor generally lengthens upon H-bonding, several experimental studies suggest that the C−H covalent bond may shorten upon H-bonding under certain circumstances. These interactions have been classified as H-bonds from the directionality and interaction distances obtained from crystallographic studies. The experimental evidence for C−H bond-shortening is indirect, coming from NMR, $^1J(^{13}C-^1H)$ coupling, and IR, C−H stretching frequencies, evidence rather than direct structural measurements such as X-ray, neutron or electron diffraction, or microwave spectroscopy. However, theoretical calculations have appeared that support C−H bond shortening in several cases including intramolecular hydrogen bonds of the C=O···H−CH$_2$ type,[4] HF/CH$_4$,[5] and CH$_4$/H$_2$O.[6]

The origin of the C−H bond shortening has been the subject of numerous discussions. Several groups have studied the relationships between $^1J(^{13}C-^1H)$ nuclear spin−spin couplings and the geometric parameters within H-bonds. A comprehensive review of the angular dependence of these couplings has recently appeared.[7] Similar studies on intramolecular C−H···N interactions have been reported.[8] In particular, experimental evidence for the shortening of the C−H bond in HF/CH$_4$ and CH$_4$/H$_2$O, as well as several intramolecular examples of C−H···O[9] and C−H···F[10] has been reported. The effect of an electric field upon the C−H bond length was incorrectly reported for methane in ref 6. Hobza et al. have reviewed the experimental infrared

data (characterized by a blue-shift) and compared them with theoretical calculations in a recent review.[11] In certain cases, these interactions have even been referred to as "anti-hydrogen-bonds" (inappropriate as they are neither anti-hydrogen, nor antibonding). In fact, such larger than expected C−H frequencies have long been known in systems that contain internal C−H···O H-bonds such as ortho-nitrobenzaldehyde.[12] One should also note that Hermansson has shown that a blue-shift in the ir vibration of OH$^-$ can be expected in an applied electric field.[13] One of us has reported the effect of the electric field of a nitro group on the coupling of a C−H bond.[14]

I
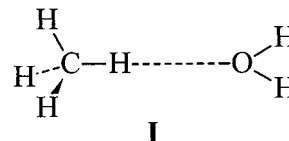
A stabilizing interaction between water and methane, **I**, leads to a structure that can be thought of as a H-bond[15] although this structure is a saddle point not a minimum.[16] In the optimized structure for this complex, the H-bonding C−H bond is shorter than the other three C−H bonds (see below). In contrast, the C−H bonds of C−H···O interactions between water and HCN and ethylene both lengthen.[17] In this paper, we report the results of an investigation of the differences between these three interactions. In particular, the effect of an electric field upon the three different species H-bonding to water will be presented. We have previously compared H-bonding interactions to interactions with electric fields to help distinguish between the
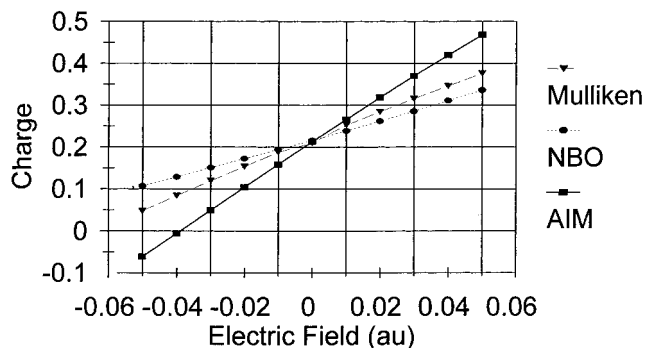
Figure 1. Charge on the hydrogen atom of HCN (calculated using three different conventions) as a function of the applied electric field.

covalent and the electrostatic (plus polarization) interpretations of H-bonding.[18]

Methods

Calculations were performed using the Gaussian 98[19] and GAMESS[20] programs. We used the Gaussian 98 program to calculate the H-bonding complexes of methane, acetylene, and HCN with water. In the case of methane, the C$-$H$\cdots$O interaction was constrained to be linear. This structure in not a minimum on the potential energy surface, PES, (one imaginary force constant). However, the interaction between methane and water in the geometry is attractive. Using GAMESS, we optimized the geometries of methane, acetylene, and HCN in a dipolar electric field applied along the axis of the H-bond each would have with water.

All calculations were performed at the HF/D95** level. To determine the change in atomic charges with variation of the electric field, some index of atomic (or local) charge is necessary. Because atomic charge density is dependent upon the arbitrary manner in which an "atom" is defined within a molecule, we decided to use several different methods for this purpose. In this manner, we can determine if the results are dependent upon the arbitrary nature of the local charge definition. Thus, charge distributions were calculated using three different methods: Mulliken populations, natural bond orbital analyses (NBO),[21] and the atoms in molecules (AIM)[22] procedure.

Results and Discussion

We shall discuss each of the three molecules individually, then compare the three. The effects of the applied field upon the charges on the H-bonding H-atoms for each of the three molecules are depicted in Figures 1$-$3, whereas the corresponding effects upon the dipole moments and the C$-$H bond lengths for all three molecules are compared in Figures 4 and 5.

For purpose of discussion, we shall define the direction of the applied electric field as increasing if it enhances H-bonding to the C$-$H bond aligned with it. The electric field is defined as a vector in the direction of attraction of a positive charge, our definition is consistent with this convention if one considers the H-bonding hydrogen as a proton moving in this field.

HCN. HCN is the only molecule of the three studied that has a nonzero dipole moment. The charge on the H-atom is calculated to be almost the same (0.210$-$0.216) by all three methods at zero applied field. The sensitivity of the charge on the H-atom to the change in applied field follows the order AIM > Mulliken > NBO. One should note that the dipole moment is not a function of the assignment of charge to the H-atom (see below). As the applied electric field is increased (see
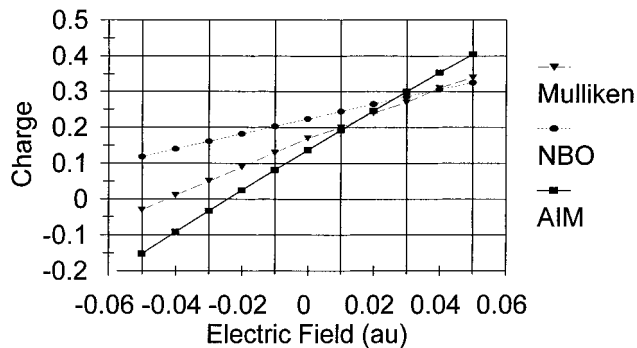

Figure 2. Charge on the hydrogen atom of acetylene that would H-bond (calculated using three different conventions) as a function of the applied electric field.
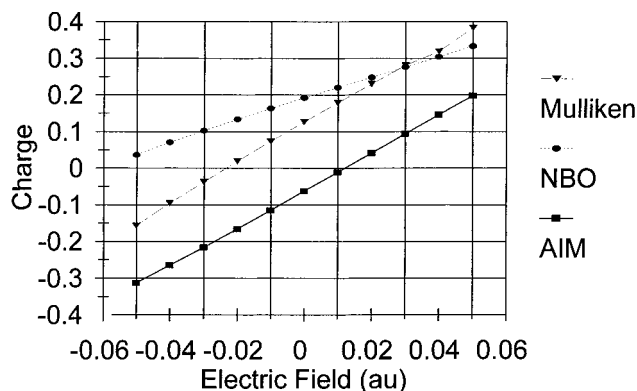

Figure 3. Charge on the hydrogen atom of methane that would H-bond (calculated using three different conventions) as a function of the applied electric field.
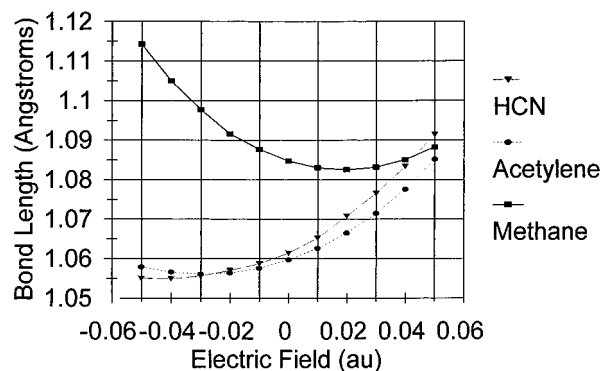

Figure 4. Variation of C$-$H bond lengths (for the H-bonding donor) with the applied electric field.

definition above), the H-atom becomes more positive (Figure 1), the C$-$H bond length increases (Figure 4) and the dipole moment increases (Figure 5). All of these are characteristics that would normally be expected of an H-bonding donor.

Acetylene. Acetylene has no dipole moment due to its symmetry. Unlike the case of HCN, the charge on the H-atoms at zero applied field varies significantly depending upon the method used to evaluate it (Figure 2). It varies from 0.137 (AIM) to 0.224 (NBO). The latter value is higher than the NBO charge on the hydrogen of HCN. As in the case of HCN, the sensitivity of this charge to the applied field follows the order AIM > Mulliken > NBO. The H-bonding C$-$H bond length increases with the applied field, as expected. However, at negative fields greater than about 0.03 au, the C$-$H bond shortens (Figure 4). This behavior is not observed with HCN within the range of negative applied fields used (up to $-$0.05 au).

Influence of an Electric Field

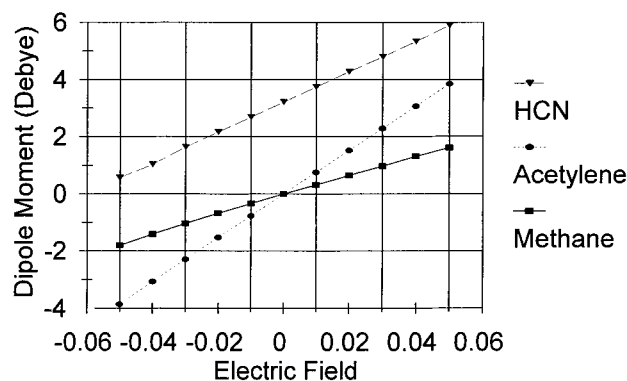*J. Phys. Chem. A, Vol. 105, No. 19, 2001* **4739**

Figure 5. Variation of dipole moments with the applied electric field.

Methane. Like acetylene, methane has no permanent dipole moment due to symmetry. Methane is significantly less acidic than either HCN or acetylene. It is not generally considered to be a strong H-bond donor. The calculated charge on each hydrogen of methane in zero applied field (Figure 3) varies considerably with the method used from a low of -0.063 (AIM) to a high of 0.192 (NBO). Although the NBO value of the charge on H is similar to those calculated for HCN and acetylene, both the AIM and the Mulliken values for this charge vary considerably from molecule to molecule. For methane, the order of sensitivity of the charge on the H aligned with the applied field is Mulliken > AIM > NBO, different from the analogous order for both HCN and acetylene.

The bond length of the C−H bond aligned with the field varies quite differently with the applied field from the two cases discussed above. In particular, the C−H bond length *decreases* with applied field until it reaches a minimum at an applied field of about 0.02 au, after which it increases with the applied field. The electric field generated by a water molecule at the H-bonding hydrogen in the optimized geometry for **I** is calculated to be 0.007 au.[23]

Comparison and General Discussion. H-bonding, particularly weak H-bonding,[24] is often described as an "electrostatic" interaction. Strictly speaking, "electrostatic" applies to interactions between entities that have fixed electron densities, such as point charges. Often, the term is rather loosely used to include polarization (which is emphatically not "static"). Under the strict definition of "electrostatic", there can be no interaction between either acetylene or methane and a uniform bipolar electric field. Both have zero dipole moment, so that $\partial E/\partial F = 0$ (where E is the energy and F is the electric field). Thus, any stabilization in an electric field (and presumably any loosely considered "electrostatic" H-bond) must depend entirely upon the polarizability of these two molecules. On the other hand, HCN has both a permanent dipole and reasonably high polarizability, so both will contribute to its "electrostatic" interactions.

The order of acidities of the three molecules is HCN > acetylene > methane. The order of the charges on the acidic H-atom follows the order of acidity (with the exception of the NBO values where the charge on the H-atom of acetylene is greater than that on the corresponding atom of HCN). From Figures 1−3, one cannot discern any clear correspondence between the three methods used to evaluate the charge. Although they all agree for the charge on the H-atom of HCN, they differ markedly for the charges on the H-atoms of acetylene and methane and in their sensitivities to an applied electric field. These observations reinforce the significance of the arbitrariness of the definitions for atomic charge densities. Nevertheless, they all agree in at least one respect: The charge on the H of the

C−H bond aligned with the applied field increases with the strength of this field.

The dipole moments necessarily increase with the strength of the applied field. Figure 5 illustrates that this effect (polarizability, $\partial^2 E/\partial F^2$) is greatest for HCN and least for methane. All three methods for calculating the atomic charge are consistent with a net migration of charge in the direction of the H-atom of the C−H bond aligned with the field. If the H-atom of this bond was originally electron deficient with respect to the rest of the molecule, increasing the field should increase this deficiency. The effect would be to move electron density away from the C−H bonding region into the bulk of the molecule. Such behavior would be expected to lower the electron density in the region of the C−H bond, causing it to weaken and lengthen. The C−H bonds of both HCN and ethylene lengthen in the presence of a positive applied field. However, the C−H bond of methane initially shortens upon application of a positive applied field, then lengthens when the field exceeds 0.02 au. Clearly, applying a positive electric field cannot cause a net migration of electron density in the direction of the field. The applied field must be drawing electron density away from the H-atom toward the bulk of the molecule. If the H-atom was electron rich (compared to the central carbon), electron density would be (initially) drawn from the region of the H-atom into the region of the C−H bond, both strengthening and shortening it. After the field increases beyond the value of about 0.02 au, the bond begins to weaken and lengthen. These observations suggest that at applied fields > 0.2 au, electron density is moving out of the C−H bond.

The C−H bond shortenings previously have been analyzed with respect to the differences in the position of the bond critical point (BCP) of the C−H bond in isolated molecules and H-bonded complexes.[25] This analysis led to the suggestion that dispersion interactions might be important for the "anti-hydrogen bonds". Although the point of view is somewhat different from ours, there is nothing in this analysis that is inconsistent with the suggestions made here. In fact, dispersion interactions are easily confused with dipole/induced-diople interactions as both vary as r^{-6} (where r is the distance between the dipoles) for oriented systems. Nevertheless, one should note that conclusions based upon the positions of BCPs have been criticized.[26]

Conclusion

The observed changes in C−H bond length upon formation of H-bonds is consistent with the behavior of HCN, acetylene, and methane in varying eclectic fields. In particular, the C−H bond shortening observed for that C−H bond of methane which forms a H-bond follows its behavior in a weak electric field. This behavior strongly suggests that the hydrogen in this bond is electron rich compared to the carbon. Polarization of this bond by the electric field a H-bond acceptor moves electron density from the hydrogen into the bond leading to a strengthening and shortening of the C−H bond. Although some covalent interaction cannot be unambiguously ruled out, the interaction of methane with the electric field is sufficient to explain the phenomenon.

References and Notes

(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 11, 1997.

(2) Aakeroy, C. B.; Sneddon, K. R. *Chem. Soc. Rev.* **1993**, 397.

(3) For reviews see (a) Steiner, T., *Cryst. Rev.* **1996**, *6*, 1. (b) Desiraju, G. R., *Acc. Chem. Res.* **1991**, *24*, 290.

(4) Popelier, P. L. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *189*, 542.

(5) Vizioli, C.; Ruiz de Azúa, M. C.; Giribet, C. G.; Contreras, R. H.; Turi, L.; Dannenberg, J. J.; Rae, I. D.; Weigold, J. A.; Malagoli, M.; Zanasi, R.; Lazzeretti, P. *J. Phys. Chem.* **1994**, *98*, 8858.

(6) Giribet, C. G.; Vizioli, C. V.; Ruiz de Azúa; Contreras, R. H.; Dannenberg, J. J.; Masunov, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3029.

(7) Contreras, R. H.; Peralta, J. E. *Prog. Nucl. Magn. Spectrosc.* **2000**, *34*, 321.

(8) (a) Afonin, A. V.; Vashchenko, A. V.; Fujiwara, H. *Bull. Em. Oc. Jpn.* **1996**, *69*, 933. (b) Afonin, A. V.; Vashchenko, A. V.; Takagi, T.; Kimura, A.; Fujiwara, H. *Can. J. Chem.* **1999**, *77*, 416.

(9) (a) Satonaka, H.; Abe, K.; Hirota, M. *Bull. Chme. Soc. Jpn.* **1987**, *60*, 953; (b) Satonaka, H.; Abe, K.; Hirota, M. *Bull. Chme. Soc. Jpn.* **1988**, *61*, 2031.

(10) (a) Alfonin, A. V.; Andriyankov, M. A. *Zh. Org. Khim.* **1988**, *24*, 1034; (b) Alfonin, A. V.; Sigalov, M. V.; Kurastova, S. E.; Aliev, I. A.; Vaschenko, A. V.; Trofimov, B. A. *Magn. Reson. Chem.* **1990**, *28*, 580.

(11) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.

(12) Pinchas, S. *Anal. Chem.* **1957**, *29*, 234. *J. Phys. Chem.* **1963**, *67*, 1862.

(13) Hermansson, K. *Internat. J. Quantum Chem.* **1993**, *45*, 747.

(14) de Kowalewski, D. G.; Kowalewski, V. J.; Peralta, J. E.;. Eskuche, G.; Contreras. R. H; Esteban, A. L.;. Galache, y E.; Díez, M. P. *Magn. Reson. Chem.* **1999**, *37*, 227.

(15) In fact, this structure is not a minimum on the potential energy surface (PES). A more stable structure has the oxygen between three H's.

(16) Szczesniak, M. M.; Chalasinski, G.; Cybulski, S. M.; Cieplak, P. *J. Chem. Phys.* **1993**, *98*, 3078.

(17) Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1993**, *97*, 7899.

(18) Dannenberg, J. J.; Haskamp, L.; Masunov, A. *J. Phys. Chem. A* **1999**, 7083.

(19) Revisions A3 and A7 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Keth, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Lahan, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslwski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andre, J. L.; Replogle, E. S., Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Deefres, D. J.; Baker, J.; Stewar, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 98: Gaussian, Inc., Pittsburgh, PA, 1998.

(20) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(21) NBO version 3.1, Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F., as programed in Gaussian 98.

(22) Bader, R, F, W, *Atoms in Molecules—A Quantum Theory*; Oxford University Press: Oxford, U. K., 1990.

(23) Masunov, A., Ph.D. Thesis, 1999, City University of New York, 102.

(24) See ref 1, pp 8−16 and Coulson, C. A., *Hydrogen Bonding;* Hadzi, D., Ed.; Perganon Press: New York, 1959, pp 339−60.

(25) Cubero, E.; Orozco, M.; Hobza, P.; Luque, F. J. *J. Phys. Chem. A.* **1999**, *103*, 6394.

(26) Perrin, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 2865.