Electrostatic Potential at Atomic Sites as a Reactivity Descriptor for Hydrogen Bonding. Complexes of Monosubstituted Acetylenes and Ammonia

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The applicability of molecular electrostatic potential values at atomic sites as a reactivity descriptor for the process of hydrogen bonding is assessed for a series of complexes involving acetylene and diacetylene derivatives as proton donors and ammonia as a model proton acceptor. The acetylenic compounds studied were of the type R−C≡C−H, where R represents H, F, Cl, CH_3, CH_2F, CHF_2, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CN, H−C≡C, F−C≡C, Cl−C≡C. Density functional theory computations at the B3LYP/6-31G(d,p) level were employed. An excellent linear relation between the molecular electrostatic potential at the acetylenic hydrogen atom in the isolated acetylenes with the energy of hydrogen-bond formation is found. It is concluded that the value of the electrostatic potential at the acidic hydrogen atomic site can be used as a reactivity descriptor for the hydrogen bonding ability of the molecules studied.

I. Introduction

The aim of the present study is to rationalize the reactivity of a series of monosubstituted acetylene derivatives toward the formation of a hydrogen bond with ammonia as a model proton acceptor. Hydrogen-bonded complexes with participation of a C−H group as proton donor have been long established.[1] The crystallographic evidence of C−H···X hydrogen bonds has been surveyed by Taylor and Kennard.[2] The microwave structure of the acetylene−NH_3 dimer has also been reported.[3] The results show that the complex is a symmetrical top with the acetylene subunit hydrogen bonded to ammonia. The binding energy is established to be less than 2.81 kcal/mol. An early theoretical study of Frisch, Pople, and Del Bene[4] at the MP4SDS/6-31G-(d,p) level determined a binding energy of 3.6 kcal/mol, while larger basis set computations suggest a binding energy of 3 kcal/mol. The C−H···N hydrogen bonds have been subject to numerous experimental and theoretical studies in later years.[5] In a recent work Hartmann and Radom[6] reported state-of-the-art computational results for the acetylene−ammonia dimmer. The authors apply a number of theoretical methods (HF, B3LYP, MP2, QCISD, and CCSD(T)) and basis sets from 6-31G(d) to 6-311+G(3df,2p). At the highest level of theory employed (CCSD(T)/6-311+G(3df, 2p)), the calculated contact distance r(H···N) is 2.280 Å and the equilibrium binding energy ΔE^e is calculated to be 14.1 kJ/mol (3.369 kcal/mol).

In a series of works from this laboratory, we explored various options to quantify the reactivity of molecules with respect to the process of hydrogen bonding.[7−9] The systems studied included the following: a series of aliphatic carbonyl derivatives and their complexes with hydrogen fluoride as proton donor;[7] a series of aliphatic nitrile derivatives and their complexes with hydrogen fluoride;[8] $(HCN)_n$ clusters of different length.[9] A number of properties of the isolated molecules were theoretically estimated and plotted against the binding energy for the complexation process. It was found that, among several different electric charge properties of the isolated molecules studied, the molecular electrostatic potential at the site of the electron donor

atom could be successfully employed as reactivity index for the process of hydrogen bonding.

In the present study the effect of changes in structure of the proton donor molecules on the energy profile of the interaction is studied in the case of monosubstituted acetylene derivatives with general formula R−C≡C−H, where R represents H, F, Cl, CH_3, CH_2F, CHF_2, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CN, H−C≡C, F−C≡C, Cl−C≡C. Ammonia is used as a model proton acceptor in the respective hydrogen-bonded complexes. The selected series of molecules and their complexes offer also an opportunity to analyze the reactivity of C−H acidic systems.

II. Computational Details

Density functional theory at B3LYP/6-31G(d,p)[10] level was applied for calculating the optimized geometries and vibrational frequencies for the isolated acetylenic derivatives and their hydrogen-bonded complexes with ammonia. The Gaussian 98 program package was used.[11] The estimated energies of hydrogen-bond formation were corrected for zero-point vibrational energy, basis-set superposition error,[12] and fragment relaxation energy contributions.[13]

The completely corrected energy represents the sum of uncorrected energy and all corrections:

$$\Delta E^{cor} = \Delta E + \Delta E^{zpe} + \Delta E^{bsse} + \Delta E^{rel} \qquad (1)$$

In eq 1, the different terms are as described below.:

ΔE is the uncorrected energy of hydrogen-bond formation estimated as a difference between the energy of fully optimized structures of the complex and monomers:

$$\Delta E = E_{R-C≡C-H\cdots NH_3} - (E_{R-C≡C-H} + E_{NH_3}) \qquad (2)$$

ΔE^{zpe} is the zero-point vibrational energy correction calculated as

$$\Delta E^{zpe} = k[E^{zpe}_{R-C≡C-H\cdots NH_3} - (E^{zpe}_{R-C≡C-H} + E^{zpe}_{NH_3})] \qquad (3)$$

where k is a scaling factor, depending on the quality of the

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method/basis set used. For B3LYP/6-31G(d,p) calculations the scaling factor for the zero-point vibrational energy is $k = 0.9804$.[14]

ΔE^{bsse} is a correction for basis-set superposition error (BSSE) calculated according to the method of Boys and Bernardi:[12]

$$\Delta E^{bsse} = (E_{R-C\equiv C-H} + E_{NH_3}) - (E^{gc}_{R-C\equiv C-H\{NH_3\}} + E^{gc}_{NH_3\{R-C\equiv C-H\}}) \quad (4)$$

In this expression, $E_{R-C\equiv C-H\{NH_3\}}$ is the energy of the acetylenic monomer in the respective complex geometry using the full basis set of the complex.

ΔE^{rel}, the fragment relaxation energy, is the energy necessary for distorting the equilibrium geometry of the isolated monomer toward the "flexed" geometry in the respective molecular complex.[13]

$$\Delta E^{rel} = E^{rel}_{R-C\equiv C-H} + E^{rel}_{NH_3} \quad (5)$$

$$E^{rel}_{R-C\equiv C-H} = E^{gc}_{R-C\equiv C-H} - E_{R-C\equiv C-H} \quad (6)$$

$$E^{rel}_{NH_3} = E^{gc}_{NH_3} - E_{NH_3} \quad (7)$$

$E^{gc}_{R-C\equiv C-H}$ and $E^{gc}_{NH_3}$ are the energies of $R-C\equiv C-H$ and NH_3 from single point calculations with the geometry of the hydrogen-bonded complex. In effect, the fragment relaxation energy term represent a correction to the BSSE term.

Electric charge properties of the isolated acetylene derivatives were theoretically determined in order to describe the reactivity of the molecules studied with respect to the process of hydrogen bonding with ammonia. Atomic charges, according to the schemes of the Mulliken,[15] Breneman and Wiberg (CHELPG),[16] Kollman and co-workers (MK),[17] and Bader (AIM),[18] were evaluated using the Gaussian 98 program package.[11]

The molecular electrostatic potential at the site of the acetylenic hydrogen was also evaluated. The electrostatic potential at a particular nucleus (A) is defined by eq 8 at $r = R_Y$ (radius vector of the hydrogen nuclei) as the term at $R_Y = R_A$ is dropped out:[19,20]

$$V_Y \equiv V(R_Y) = \sum_{A \neq Y} \frac{Z_a}{|R_Y - R_A|} - \int \frac{\rho(r')}{|R_Y - r'|} dr' \quad (8)$$

In this equation, Z_A is the charge on nucleus A with radius-vector R_A, $\rho(r)$ is the electronic density function of the respective molecule as obtained from ab initio calculations, and r' is a dummy integration variable. Equation 8 is written in atomic units and contains a summation over all atomic nuclei, treated as positive point charges as well as integration over the continuous distribution of the electronic charge. The molecular electrostatic potential at each atom of the isolated molecules from the series studied is obtained as a standard output of the Gaussian 98 program.[11]

III. Results and Discussion

The noncorrected energy of hydrogen bond formation calculated as a difference between the respective total energies (ΔE), the zero-point vibrational energy correction (ΔE^{zpe}), the basis-set superposition error correction (ΔE^{bsse}), the relaxation correction (ΔE^{rel}), and totally corrected energy of hydrogen bond formation (ΔE^{cor}) for the hydrogen-bonded monosubstituted acetylenes and diacetylenes studied are presented in Table 1.

TABLE 1: B3LYP/6-31G(d,p) ab Initio Calculated Non-corrected Energy of Hydrogen-Bond Formation (ΔE), Zero-Point Vibrational Energy Correction (ΔE^{zpe}), BSSE Correction (ΔE^{bsse}), Relaxation Correction (ΔE^{rel}), and Totally Corrected Energy (ΔE^{cor}) for the Substituted Acetylene Derivatives[a]

acetylenic monomer	ΔE	ΔE^{zpe}	ΔE^{bsse}	ΔE^{rel}	ΔE^{cor}
H−C≡C−H	−5.28709	1.40207	0.89602	0.11126	−2.87774
F−C≡C−H	−5.52887	1.39714	0.89069	0.16290	−3.07814
Cl−C≡C−H	−5.88234	1.35223	0.87293	0.14069	−3.51649
H$_3$C−C≡C−H	−4.35423	1.24273	0.83842	0.11051	−2.16257
FH$_2$C−C≡C−H	−5.54851	1.31039	0.82888	0.14734	−3.26190
F$_2$HC−C≡C−H	−6.50094	1.35900	0.80277	0.20858	−4.13059
F$_3$C−C≡C−H	−7.23965	1.41745	0.82518	0.23349	−4.76353
ClH$_2$C−C≡C−H	−5.75414	1.33132	0.80189	0.16924	−3.45169
Cl$_2$HC−C≡C−H	−6.79662	1.37684	0.75734	0.23507	−4.42737
Cl$_3$C−C≡C−H	−7.42457	1.39653	0.71216	0.26964	−5.04624
NC−C≡C−H	−8.19045	1.51649	0.76927	0.24297	−5.66172
H−C≡C−C≡C−H	−6.04851	1.39284	0.81997	0.15656	−3.67914
F−C≡C−C≡C−H	−5.86188	1.33747	0.82047	0.15279	−3.55115
Cl−C≡C−C≡C−H	−6.12720	1.39284	0.82022	0.15487	−3.75927

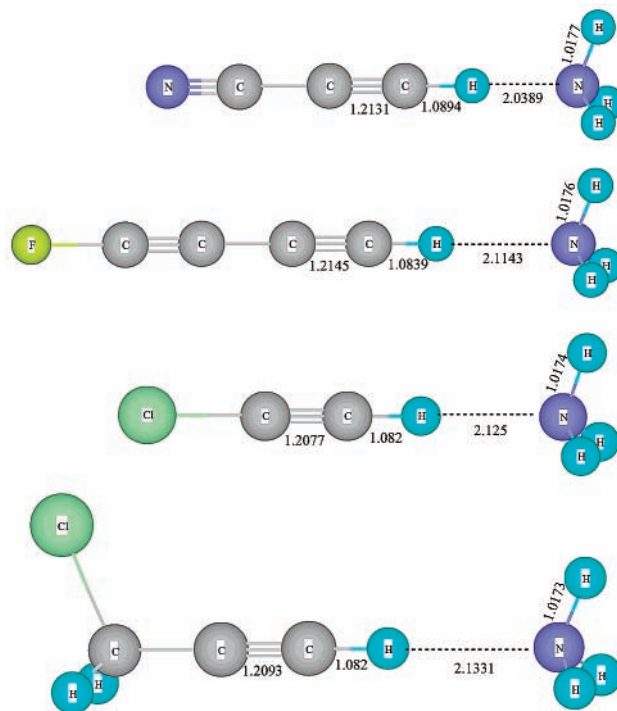*[a]* All values are in kcal/mol.

Figure 1. Optimized structures of hydrogen-bonded complexes for some acetylene derivatives with ammonia from B3LYP/6−31(d,p) computations.

A. Structural and Infrared Spectral Parameters. Theoretically calculated structural parameters of the complexes studied are presented in Table 2. The parameters shown include geometry parameters and frequencies of C−H stretching vibration in isolated molecules (r_{C-H}) and in the respective complexes (r^{compl}_{C-H}), as well as the hydrogen bond length ($r_{H\cdots N}$). Four of the complexes have C_s symmetry (Cl$_2$HC−C≡C−H, ClH$_2$C−C≡C−H, F$_2$HC−C≡C−H, and FH$_2$C−C≡C−H) and all the rest have C_{3v} symmetry. The optimized structures of the hydrogen-bonded complexes for some molecules of the series are shown in Figure 1. The infrared frequency shifts upon complexation for the C−H bond stretch ($\Delta\nu_{C-H}$) are also given in Table 2. As can be expected, the C−H bond length increases in hydrogen-bonded systems as result of the complexation process. The C−H stretching frequency decreases with the

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TABLE 2: B3LYP/6-31G(d,p) ab Initio Calculated Values of Hydrogen Bond Length r_{C-H} (in Å), Changes in the Acetylenic C-H Bond Length Δr_{C-H} (in Å), C-H Stretching Mode Frequencies and Shifts (in cm^{-1}) for Acetylene Derivatives and Their Hydrogen-Bonded Complexes with Ammonia $r_{H\cdots N}$

acetylenic monomer	$r_{C-H}{}^a$	$r_{C-H}^{compl\ b}$	$\nu_{C-H}{}^a$	$\nu_{C-H}^{compl\ b}$	$\Delta r_{C-H}{}^c$	$\Delta \nu_{C-H}{}^c$	$r_{H\cdots N}$
H−C≡C−H	1.0657	1.0804	3486^d	3262	0.0147	−224	2.1565
F−C≡C−H	1.0635	1.0802	3513	3277	0.0167	−236	2.1284
Cl−C≡C−H	1.0653	1.0820	3492	3251	0.0167	−241	2.1205
H₃C−C≡C−H	1.0651	1.0789	3492	3299	0.0138	−193	2.1850
FH₂C−C≡C−H	1.0658	1.0815	3489	3265	0.0157	−224	2.1430
F₂HC−C≡C−H	1.0663	1.0843	3487	3231	0.0180	−256	2.1009
F₃C−C≡C−H	1.0666	1.0856	3485	3204	0.0190	−281	2.0719
ClH₂C−C≡C−H	1.0657	1.0821	3489	3256	0.0164	−233	2.1331
Cl₂HC−C≡C−H	1.0662	1.0853	3486	3215	0.0191	−271	2.0868
Cl₃C−C≡C−H	1.0664	1.0872	3485	3189	0.0208	−296	2.0617
NC−C≡C−H	1.0667	1.0894	3482	3158	0.0227	−324	2.0389
H−C≡C−C≡C−H	1.0654	1.0832	3490^d	3237	0.0178	−253	2.1172
F−C≡C−C≡C−H	1.0653	1.0823	3490	3247	0.0170	−243	2.1276
Cl−C≡C−C≡C−H	1.0656	1.0839	3489	3228	0.0183	−261	2.1143

^{a} For isolated acetylenic compounds. ^{b} For hydrogen-bonded complexes. ^{c} $\Delta r_{C-H} = r_{C-H}^{compl} - r_{C-H}$; $\Delta \nu_{C-H} = \nu_{C-H}^{compl} - \nu_{C-H}$. ^{d} Averaged values between the C-H symmetric and antisymmetric stretching frequencies.
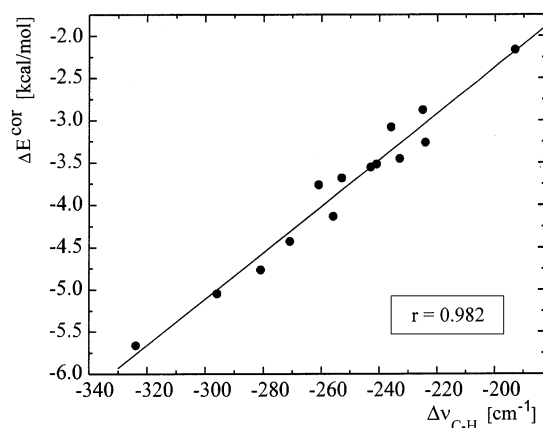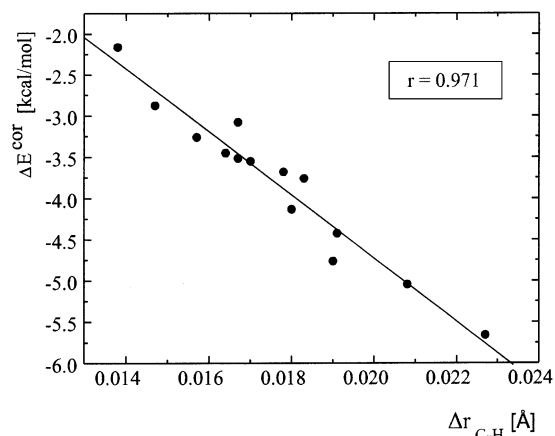

Figure 2. Dependence between energy of hydrogen-bond formation (ΔE^{cor}) and C-H stretching frequency shifts ($\Delta \nu_{C-H}$) for the hydrogen bonded to ammonia complexes of acetylene derivatives studied.

Figure 3. Dependence between the energy of hydrogen-bond formation (ΔE^{cor}) and changes in C-H bond length (Δr_{C-H}) for the hydrogen bonded to ammonia complexes of acetylene derivatives.

formation of hydrogen-bonded complex, due to the weakened C-H bonds in the dimers.

In accord with the rule of Badger and Bauer[1a,21] a linear correlation between binding energy of hydrogen-bond formation and C-H stretching frequency was found. The dependence between the energy of the hydrogen-bond formation ΔE^{cor}, and the change in C-H stretching frequency $\Delta \nu_{C-H}$ in the series of molecules studied is shown in Figure 2. $\Delta \nu_{C-H}$ is calculated as a difference between B3LYP/6-31G(d,p) computed C-H frequencies in isolated molecules and the respective values in their hydrogen-bonded complex. For the monomeric acetylene and diacetylene, the frequencies used are the average values between the C-H symmetric and antisymmetric stretching frequencies. The linear regression coefficient is calculated to be 0.982. The dependence is illustrated in Figure 2.

The relationship between the energy of hydrogen-bond formation and the variations of C-H bond length (Δr_{C-H}) is illustrated in Figure 3. A linear relation is found, with correlation coefficient value of $r = 0.971$.

B. Properties Depending on the Electron Density Distribution. It is well-known that electrostatic forces play an important role in hydrogen bonding.[22−24] In the attempt to seek appropriate molecular parameters that may characterize the reactivity of the acetylene derivatives toward hydrogen bonding, several quantities linked to the electric charge distribution in molecules were theoretically estimated. Four types of charges associated with atomic sites for the acidic hydrogens of the

acetylenic C-H bonds were theoretically determined. These included the following: atomic charges obtained by the Mulliken scheme,[15] the electrostatic-potential-related charges evaluated according to the scheme of Breneman and Wiberg (CHELPG)[16] and Kollman and co-workers (MK),[17] as well as charges obtained by the "atoms-in-molecule" method of Bader (AIM).[18] Finally, the electrostatic potential at the site of the C-H hydrogen were also evaluated. The computed values are presented in Table 3.

All of these quantities were plotted against the calculated binding energies. In general, the partial atomic charges at the binding site of the substituted acetylene derivatives are expected to describe the reactivity of molecules toward formation of hydrogen-bonded complexes with ammonia. The results obtained can be summarized as follows:

(1) The Mulliken charges[15] do not correlate well with the variation of binding energy (linear regression correlation coefficient $r = 0.750$).

(2) The electrostatic-potential-related atomic charges CHELPG[16] and MK[17] also do not provide a quantitative description of the ability of the acetylenic compounds to form a hydrogen bond with ammonia. The respective linear regression coefficients are $r = 0.087$ for CHELPG charges and $r = 0.142$ for MK charges.

(3) A satisfactory description of the hydrogen bonding ability of the acetylenic derivatives is provided by the AIM atomic charges of Bader.[18] The following equation linking binding

TABLE 3: B3LYP/6-31G(d,p) ab Initio Calculated Values of Atomic Charges (in electrons) at the Acetylenic Hydrogen Atom in Isolated Molecules Q_H, Derived via Different Procedures (Mulliken, CHELPG, MK and AIM) and Molecular Electrostatic Potential Φ_H (in atomic units)

acetylenic monomer	$Q_H^{\text{Mulliken }a}$	$Q_H^{\text{CHELPG }b}$	$Q_H^{\text{MK }c}$	$Q_H^{\text{AIM }d}$	$\Phi_H^{\;e}$
H−C≡C−H	0.1487	0.2372	0.2664	0.1257	−1.0444
F−C≡C−H	0.1534	0.2939	0.3202	0.1403	−1.0392
Cl−C≡C−H	0.1604	0.2623	0.2678	0.1387	−1.0349
H₃C−C≡C−H	0.1477	0.2706	0.3154	0.1139	−1.0595
FH₂C−C≡C−H	0.1647	0.2638	0.3037	0.1306	−1.0396
F₂HC−C≡C−H	0.1776	0.2611	0.2959	0.1429	−1.0247
F₃C−C≡C−H	0.1887	0.2602	0.2941	0.1524	−1.0134
ClH₂C−C≡C−H	0.1676	0.2739	0.3131	0.1335	−1.0364
Cl₂HC−C≡C−H	0.1809	0.2816	0.3136	0.1468	−1.0211
Cl₃C−C≡C−H	0.1904	0.2926	0.3087	0.1565	−1.0103
NC−C≡C−H	0.2095	0.2576	0.2789	0.1666	−0.9985
H−C≡C-C≡C−H	0.2004	0.2622	0.2892	0.1417	−1.0325
F−C≡C−C≡C−H	0.1956	0.2788	0.2994	0.1385	−1.0351
Cl−C≡C−C≡C−H	0.2029	0.2646	0.2789	0.1424	−1.0309

[a] Ref 15. [b] Ref 16. [c] Ref 17. [d] Ref 18. [e] Φ_H − electrostatic potential at the site of the hydrogen atom in the acetylenic C−H bond in isolated molecules.
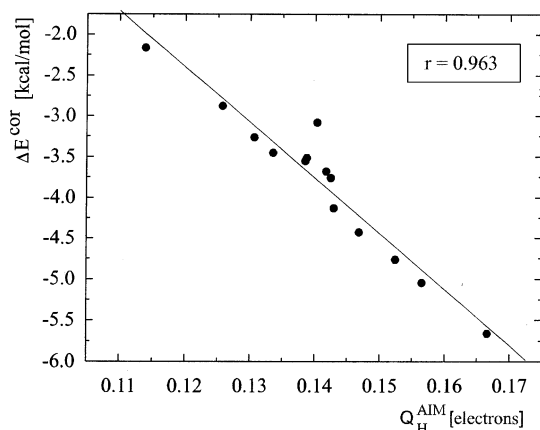

Figure 4. Dependence between energy of hydrogen-bond formation (ΔE^{cor}) and the partial hydrogen atomic charge in the isolated acetylene derivatives, derived via AIM scheme.

energy and AIM atomic charges is obtained:

$$\Delta E^{\text{cor}} = -68.17 Q_H^{\text{AIM}} + 5.78 \qquad (9)$$

where $n = 14$, $r = 0.963$, and SD = 0.260. The dependence is illustrated in Figure 4.

As already mentioned, in earlier studies from this laboratory[7−9] it was shown that the electrostatic potential at atomic sites can be used as an excellent reactivity parameter describing the ability of proton accepting molecules to form hydrogen bonds. It was of interest, therefore, to study the applicability of the atomic electrostatic potential as descriptor of the hydrogen bonding ability of proton donor molecules such as the studied series of acetylene derivatives. The atomic potentials were determined as a standard option in the Gaussian 98 program package. The values are given in Table 3. An excellent linear link, as shown in Figure 5, is found between the electrostatic potential at the acetylenic hydrogen and the binding energy. The relationship is as follows:

$$\Delta E^{\text{cor}} = -59.43 \Phi_H - 65.02 \qquad (10)$$

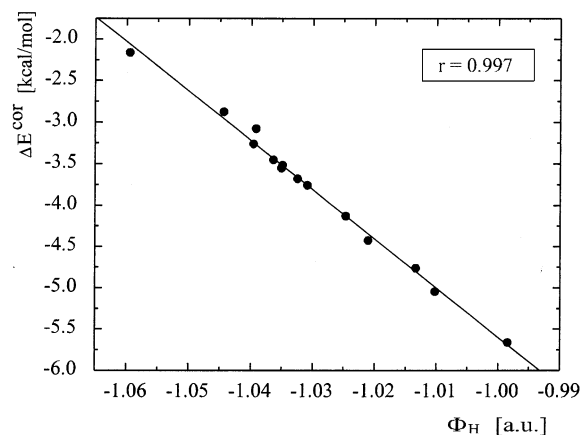where $n = 14$, $r = 0.997$, and SD = 0.075.

Figure 5. Dependence between energy of hydrogen-bond formation (ΔE^{cor}) and the molecular electrostatic potential at the acetylenic hydrogen atoms in isolated molecules (Φ_H).

It should be underlined that, in recent years, the molecular surface electrostatic potential (MSEP) has been mostly employed in describing hydrogen bonding.[25,26] In strict scientific terms, the use of the MSEP appears more plausible. However, the analysis involves considerable additional computations. The present results underline the applicability of the electrostatic potential at nuclei as a reactivity index describing in quantitative terms the ability of proton donor molecules to form hydrogen bonds. As is well-known, several different factors besides electrostatic forces contribute to hydrogen bonding. According to Morocuma,[22−24] the following terms contribute to the binding energy: electrostatic interaction, polarization interaction, exchange repulsion, and charge transfer of electron delocalization interaction. The results obtained in the present and in the earlier studies underline once again that the electrostatic forces play a key role in hydrogen bonding. The electrostatic potential at the sites of the interacting atoms may, therefore, be considered as an appropriate descriptor reflecting accurately the hydrogen bonding ability of specific sites in molecules.

IV. Conclusions

B3LYP/6-31G(d,p) density functional studies of the hydrogen bonding between acetylene and diacetylene derivatives and ammonia confirm the accepted linear relations between the energy of hydrogen-bond formation (ΔE^{cor}) and the variations of C−H bond length (Δr_{C-H}) and the respective vibrational frequency shift ($\Delta \nu_{C-H}$). The variations in the energy of hydrogen-bond formation (ΔE^{cor}) are interpreted in terms of properties of the isolated proton donor molecules. The theoretical data obtained show that there is no clear dependence between ΔE^{cor} and the partial atomic charge at the C−H hydrogen atom evaluated via the Mulliken method, as well as the CHELPG and MK schemes. A satisfactory linear dependence between binding energy and partial atomic charges evaluated theoretically by the AIM method is found. An excellent linear relationship between electrostatic potential (Φ_H) at the site of the acidic hydrogen atom in the systems studied and binding energy confirms the possibility of employing the atomic electrostatic potential as a reactivity descriptor for the process of hydrogen bonding.

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