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# Carbenes and Silylenes as Hydrogen Bond Acceptors

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A theoretical study of the capability of carbenes and silylenes as hydrogen bond (HB) acceptors has been carried out. The complexes formed by singlet $H_2C$**:**, $H_2Si$**:**, and $F_2C$**:**, as electron donors, and HF, HCN, $H_2O$, $NH_3$, and $CH_3^+$, as electron acceptors, have been analyzed. The calculations have been carried out using the 6-31G** and 6-311++G** at the HF, MP2, and MP4 levels of theory. The topology of the electron density of the HB complexes has been characterized using the AIM methodology. The results show that carbenes are good electron donors as indicated by the large interaction energies and electron densities on the HB critical bonds.

## Introduction

Carbenes are in general highly reactive species with short lifetimes; consequently, very few examples of carbenes stable at room temperature are known.[1] Thus, the knowledge of the structure of these intermediates is very limited, most of the experimental and theoretical studies dealing with their reactivity.[2,3]

Recently, Arduengo et al.[4] reported the X-ray structure of a stable carbene which shows an electrostatic bond that suggests the existence of a new type of intermolecular hydrogen bond. It involves a carbonium and a carbene with an almost linear hydrogen bond. The only theoretical precedent, to the best of our knowledge, of this kind of HB corresponds to the studies of the $H_2C$**:**⋯HF complex by Pople et al.[5,6] In these articles, the potential energy surfaces of several polyatomic neutral species are explored; however, for several systems the corresponding carbene hydrogen bond is missing as we will show.

In the present article, a model of the structure reported by Arduengo ($H_2C$**:**⋯H−$CH_2^+$) has been theoretically studied and this new type of hydrogen bond has been generalized in two ways: (i) to HB donors other than $C^+$−H; (ii) to acceptors other than methylene. HB donors include $CH_3^+$, HCN, HF, and $H_2O$, and HB acceptors include $CH_2$**:** (singlet methylene), $SiH_2$**:** (singlet silylene), and $CF_2$**:** (singlet difluorocarbene).

## Methods

The systems studied are shown in Figure 1. In all the cases the molecules have been calculated as singlets. This agrees with the experimental and theoretical ground state of difluorocarbene[7,8] and silylene.[9,10] The ground state of the methylene is the triplet;[11] however, it is usually formed as a singlet.[12]

The geometries of the monomers and complexes have been fully optimized with the Gaussian-94 program[13] using the standard 6-31G**[14] and 6-311++G**[15] bases sets at the Hartree−Fock (HF) and second- and fourth-order Moller−Plesset perturbation theory levels (MP2 and MP4).[16] Whenever possible, symmetry conditions have been used. The minimum nature of the complexes at the RHF/6-31G** level has been confirmed by calculating the corresponding frequencies. The interaction energies have been corrected for the inherent basis set superposition error (BSSE) using the Boys−Bernardi counterpoise technique.[17] The topological properties of the
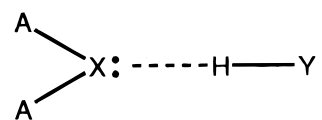
**Figure 1.** Schematic representation of the HB complexes studied.

electronic charge density have been characterized using the atoms in molecules methodology (AIM)[18] with the AIMPAC program package[19] and as implemented in the Gaussian-94 program by Ciolowsky and co-workers.[20]

## Results and Discussion

The HB distances and the interaction energies obtained for the complexes studied with all the methods used are gathered in Table 1. Quantitatively, all the methods indicate the presence of HB's due to the short X**:**⋯H distances and interaction energies between 2 and 22 kcal mol⁻¹, depending on the complex studied. A more detailed analysis of these results shows that, in general, the 6-311++G** basis set provides larger HB distances than the 6-31G** ones at the HF level, except for the silylene complexes where the opposite is observed. The inclusion of correlation (MP2) produces a shortening of these distances as high as 0.25 Å in the $H_2Si$**:**⋯HCN complex and reduces the differences obtained with the two basis sets. Higher order perturbation (MP4) does not produce any significant variation of the HB distances of the complexes.

Regarding the interaction energies, their values are parallel to the HB bond distances at each level of calculation, and thus shorter HB induces larger interaction energies. The differences found in the estimation of these properties are in the worst cases around 20% which indicates that even the values obtained at

**TABLE 1: Hydrogen Bond Distances (Å) and Interaction Energies (kcal/mol) of the Complexes Studied**

| | RHF/6-31G** | | RHF/6-311++G** | | MP2/6-31G** | | MP2/6-311++G** | | MP4/6-31G** | | MP4/6-311++G** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| system | X:···H | energy | X:···H | energy | X:···H | energy | X:···H | energy | X:···H | energy | X:···H | energy |
| $H_2C$:···HF | 1.978 | −10.32 | 1.976 | −9.51 | 1.870 | −10.64 | 1.831 | −10.73 | 1.895 | −9.76 | 1.849 | −9.93 |
| $H_2C$:···HCN | 2.353 | −6.16 | 2.447 | −5.12 | 2.252 | −5.98 | 2.333 | −5.07 | 2.252 | −5.39 | 2.331 | −4.73 |
| $H_2C$:···$H_2O$ | 2.274 | −5.13 | 2.313 | −4.47 | 2.144 | −5.42 | 2.166 | −5.30 | 2.148 | −4.91 | 2.208 | −4.80 |
| $H_2C$:···$H_3N$ | 2.622 | −2.17 | 2.663 | −1.86 | 2.457 | −2.49 | 2.440 | −2.38 | 2.457 | −2.26 | 2.441 | −2.20 |
| $H_2C$:···$H_3C^+$ | 2.064 | −20.66 | 2.139 | −18.02 | 1.943 | −22.40 | 1.988 | −19.66 | 1.943 | −21.47 | 1.986 | −19.04 |
| $H_2Si$:···HF | 2.788 | −3.41 | 2.698 | −3.89 | 2.599 | −3.35 | 2.488 | −4.32 | | | | |
| $H_2Si$:···HCN | 3.231 | −2.17 | 3.226 | −2.06 | 2.988 | −2.09 | 2.961 | −2.07 | | | | |
| $F_2C$:···HF | 2.120 | −4.32 | 2.134 | −4.38 | 1.984 | −4.75 | 1.984 | −5.27 | | | | |
| $F_2C$:···HCN | 2.543 | −2.35 | 2.663 | −2.02 | 2.526 | −2.67 | 2.526 | −2.37 | | | | |

**TABLE 2: Interatomic Distances (Å) and Bond Angles (deg) Obtained at the MP2/6-311++G** Level for the Isolated Monomers and the HB Complexes**

Isolated Monomers

| | electron donors | | electron acceptors | |
|---|---|---|---|---|
| | A−X: | A−X−A | | H−Y |
| $H_2C$: | 1.110 | 101.76 | HF | 0.917 |
| $H_2Si$: | 1.510 | 92.46 | HCN | 1.068 |
| $F_2C$: | 1.302 | 104.87 | $H_2O$ | 0.959 |
| | | | $H_3N$ | 1.013 |
| | | | $H_3C^+$ | 1.091 |

HB Complexes[a]

| | ΔA−X: | ΔA−X−A | X:···H | X:···H−Y | ΔH−Y |
|---|---|---|---|---|---|
| $H_2C$:···HF | −0.007 | 3.18 | 1.831 | 180.00 | 0.028 |
| $H_2C$:···HCN | −0.003 | 1.43 | 2.333 | 180.00 | 0.011 |
| $H_2C$:···$H_2O$ | −0.006[b] | 2.30 | 2.166 | 171.74 | 0.009 |
| $H_2C$:···$H_3N$ | −0.002 | 0.84 | 2.440 | 162.19 | 0.004 |
| $H_2C$:···$H_3C^+$ | −0.008 | 3.17 | 1.988 | 180.00 | 0.041 |
| $H_2Si$:···HF | −0.009 | 2.75 | 2.488 | 180.00 | 0.011 |
| $H_2Si$:···HCN | −0.005 | 1.71 | 2.961 | 180.00 | 0.005 |
| $F_2C$:···HF | −0.011 | 1.47 | 1.984 | 180.00 | 0.012 |
| $F_2C$:···HCN | −0.005 | 0.69 | 2.526 | 180.00 | 0.004 |

[a] Some of the data are relative to the monomers values. [b] Average of the two protons.

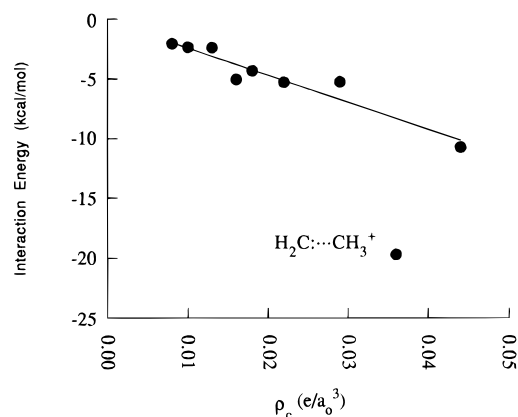**TABLE 3: Atomic Charges (e) of the Monomers and HB Complexes at the MP2/6-311++G** Level Using the AIM Methodology**

Isolated Monomers

| | electron donors | | electron acceptors | |
|---|---|---|---|---|
| | A | X: | H | Y |
| $H_2C$: | 0.008 | −0.016 | HF | 0.712 | −0.712 |
| $H_2Si$: | −0.726 | 1.453 | HCN | 0.204 | 0.817 |
| $F_2C$: | −0.648 | 1.297 | $H_2O$ | 0.567 | −1.133 |
| | | | $H_3N$ | 0.348 | −1.043 |
| | | | $H_3C^+$ | 0.275 | 0.176 |

HB Complexes[a]

| | ΔA | ΔX: | ΔH | ΔY | electron transfer |
|---|---|---|---|---|---|
| $H_2C$:···HF | 0.045 | −0.010 | −0.007 | −0.073 | 0.080 |
| $H_2C$:···HCN | 0.026 | −0.024 | 0.065 | −0.047 | 0.028 |
| $H_2C$:···$H_2O$ | 0.069[b] | −0.100 | −0.010 | −0.018 | 0.038 |
| $H_2C$:···$H_3N$ | 0.012 | −0.006 | 0.040 | −0.037 | 0.018 |
| $H_2C$:···$H_3C^+$ | 0.084 | −0.084 | 0.098 | −0.093 | 0.084 |
| $H_2Si$:···HF | 0.008 | 0.046 | −0.021 | −0.041 | 0.062 |
| $H_2Si$:···HCN | 0.006 | 0.014 | 0.018 | 0.022 | 0.026 |
| $F_2C$:···HF | 0.012 | 0.024 | −0.002 | −0.046 | 0.048 |
| $F_2C$:···HCN | 0.007 | 0.000 | 0.030 | −0.023 | 0.014 |

[a] The atomic charges are relative to the monomers values. [b] Average of the two protons.

the lowest level provide qualitatively similar results to the highest ones.

A detailed description of the geometry of the monomers and the complexes at the MP2/6-311++G** level is included in Table 2. The values described by Arduengo et al.[4] [C:···H = 2.026(45) Å, C:···H−C = 172.5°, and H−C = 1.159(45) Å] for this new kind of hydrogen bond are very similar to the ones obtained for the simplified model $H_2C$:···$CH_3^+$ (C:···H = 1.988 Å, C:···H−C = 180.0°, and C−H = 1.102 Å). This model system shows a very strong HB (approximately 20 kcal mol$^{-1}$) in agreement with another report that indicates similar energetic results for the HB between $CH_3^+$ and $CH_3OH$ or $CH_3OCH_3$.[21]

The comparison of the geometries obtained for the isolated monomers and the HB complexes shows an increase of the H−Y bond length, a shortening of the A−X bond length, and a small increase of the AXA angle. The first effect, H−Y bond lengthening, is similar to what happens in standard HB systems.[22] The second one, A−X shortening, is the opposite of what is commonly observed. However, it can be explained if we consider the HB complexes as an intermediate between the isolated electron donor monomers ($A_2X$:) and the protonated ones ($A_2XH^+$); in this case, the corresponding geometries of the latter at the MP2/6-311++G** are $CH_3^+$, C−H = 1.091 Å; $SiH_3^+$, Si−H = 1.458 Å; and $CF_2H^+$, C−F = 1.244 Å which in all the cases are shorter than the corresponding monomers (the opposite is observed in the protonated species $OH_3^+$ or $H_2C=OH^+$ which correspond to standard electron donors).

The electronic results corresponding to the atomic charges and bond critical points of the isolated monomers and the HB

**TABLE 4: Electron Density $\rho_c$ (e/a$_o^3$) and Laplacian $\nabla^2\rho_c$ (e/a$_o^5$) of the Isolated Monomer and HB Complexes at the Bond Critical Points Calculated at the MP2/6-311++G** Level Using the AIM Methodology**

Isolated Monomers

| | electron donors | | electron acceptors | |
|---|---|---|---|---|
| | A−X: | | H−Y | |
| | $\rho_c$ | $\nabla^2\rho_c$ | | $\rho_c$ | $\nabla^2\rho_c$ |
| $H_2C$ | 0.275 | −0.954 | HF | 0.370 | −2.836 |
| $H_2Si$ | 0.114 | 0.224 | HCN | 0.283 | −0.248 |
| $F_2C$ | 0.279 | 0.248 | $H_2O$ | 0.364 | −2.515 |
| | | | $H_3N$ | 0.334 | −1.532 |
| | | | $H_3C^+$ | 0.293 | −1.166 |

HB Complexes

| | A−X: | | X:···H | | H−Y | |
|---|---|---|---|---|---|---|
| | $\rho_c$ | $\nabla^2\rho_c$ | $\rho_c$ | $\nabla^2\rho_c$ | $\rho_c$ | $\nabla^2\rho_c$ |
| $H_2C$:···HF | 0.280 | −0.988 | 0.044 | 0.081 | 0.329 | −2.407 |
| $H_2C$:···HCN | 0.277 | −0.966 | 0.016 | 0.044 | 0.277 | −1.032 |
| $H_2C$:···$H_2O$ | 0.274 | −0.933 | 0.022 | 0.065 | 0.345 | −0.236 |
| $H_2C$:···$H_3N$ | 0.276 | −0.958 | 0.013 | 0.036 | 0.331 | −1.602 |
| $H_2C$:···$H_3C^+$ | 0.281 | −1.002 | 0.036 | 0.059 | 0.265 | −1.037 |
| $H_2Si$:···HF | 0.116 | 0.232 | 0.018 | 0.032 | 0.354 | −2.672 |
| $H_2Si$:···HCN | 0.115 | 0.228 | 0.008 | 0.017 | 0.280 | −1.038 |
| $F_2C$:···HF | 0.288 | 0.287 | 0.029 | 0.078 | 0.351 | −2.664 |
| $F_2C$:···HCN | 0.283 | 0.267 | 0.010 | 0.030 | 0.281 | −1.043 |

complexes calculated at the MP2/6-311++G** level using the AIM methodology are listed in Tables 3 and 4. In addition,

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**Figure 2.** Electron density at the hydrogen bond critical points $\rho_c$ (e/$a_o^3$) vs the interaction energy (kcal/mol). The linear correlation, excluding the $H_2C:\cdots H_3C^+$ system, corresponds to the following equation: energy $= -0.14 - 227.35\rho_c$, $r = 0.96$, $n = 8$.



**Figure 3.** Electron density at the HB critical points $\rho_c$ (e/$a_o^3$) vs the HB distance (Å). The second-order correlation corresponds to the following equation: HB distance $= 3.25 - 64.62\rho_c + 758.60\rho_c^2$, $r = 0.94$, $n = 9$. If we exclude the three systems that are above the curve: HB distance $= 2.97 - 47.88\rho_c + 499.48\rho_c^2$, $r = 0.9991$, $n = 6$.
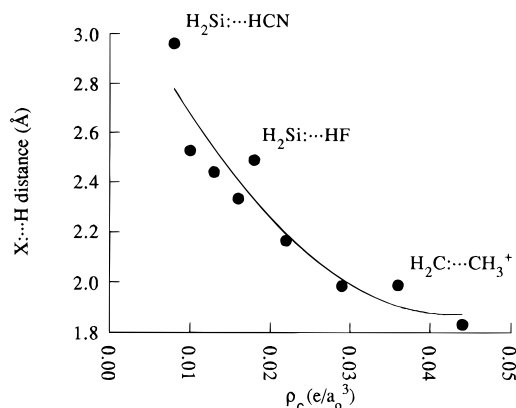
the charge transfer between the electron donor and electron acceptor in the formation of the hydrogen bond is included in Table 3.

The analysis of the charges shows a flow of electrons from the atoms attached to the carbene or silylene (A) that become more positive, to the more electronegative atom of the electron acceptor (Y). The variation of the electron densities on the bond critical points between the isolated monomers and the HB complexes is in agreement with the observed bond length variations: an increment in the bond length implies smaller electron density on the bond critical points (H–Y bond) and shorter bonds, larger electron densities (A–X: bond). Both the values of the electron densities and their corresponding Laplacians at the bond critical points of the HB indicate a strong attractive interaction between the monomers together with electron densities, in some cases higher than the ones observed in strong HBs like the ones observed between FH and different conventional electron donors.[23]
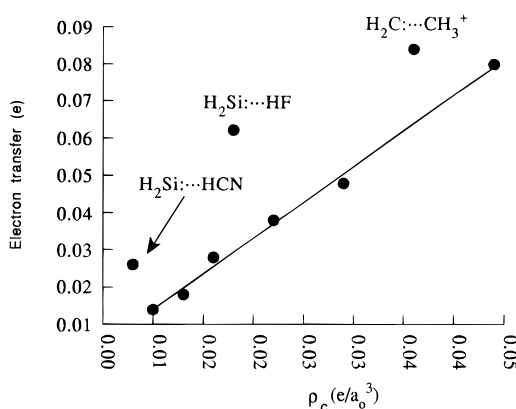
Several relationships have been tried between the different parameters that characterize these HB (HB distance, electron transfer, electron density on the HB critical point, and interaction energy) in the complexes studied. Thus, a good linear correlation has been found between the electron density at the HB critical point and the interaction energy of the complexes (Figure 2), excluding the charged system. Similar relationships have been described in other HB systems.[23-25] An acceptable second-order relationship has been found between the HB distance and the value of the electron density at the HB critical point (Figure 3). The three values above the curve that correspond to the silylene and the charge complexes worsen this relationship. Another case in which these three complexes deviate from a possible relationship is in the case of the electron transfer vs the electron density at the bond critical points (Figure 4). Excluding these points a linear relationship with an $r^2 > 0.99$ is obtained.

## Conclusions

The capability of carbenes and silylenes as electron donors in HB have been studied theoretically. The calculations show that the complex formed by singlet $H_2C:$, $H_2Si:$, and $F_2C:$ with HF, HCN, $H_2O$, $NH_3$, or $CH_3^+$, as electron acceptors are stabilized by HB. The interaction energies of these systems can be as large as 20 kcal mol$^{-1}$ for the $H_2C:\cdots CH_3^+$ system or 10 kcal mol$^{-1}$ for the stronger neutral complex ($H_2C:\cdots$ HF). Another indication of the formation of these HB has been the electron density on the HB critical point calculated using the AIM methodology. In addition, several relationships



**Figure 4.** Electrom density at the HB critical points $\rho_c$ (e/$a_o^3$) vs the electron transfer (e) in the formation of the HB. The linear correlation excluding the three systems shown in the figure is the following: electron transfer $= -0.005 + 1.92\rho_c$, $r = 0.997$, $n = 6$.

between the parameters that define these HB (HB distance, electron transfer, electron density on the HB critical point and interaction energy) have been found.

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