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C—H···N and C—H···S Hydrogen Bonds—Influence of Hybridization on Their Strength

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Simple complexes connected through C—H···S and C—H···N interactions are investigated: $CH_4\cdots NH_3$, $C_2H_4\cdots NH_3$, $C_2H_2\cdots NH_3$, $CH_4\cdots SH_2$, $C_2H_4\cdots SH_2$, and $C_2H_2\cdots SH_2$. Ab initio and DFT calculations are performed (SCF, MP2, B3LYP) using different basis sets up to the MP2/aug-cc-pVQZ//MP2/aug-cc-pVDZ level of approximation. The Bader theory is applied since MP2/6-311++G(d,p) wave functions are used to find and to characterize bond critical points in terms of electron densities and their Laplacians. The influence of hybridization on the properties of C—H···S and C—H···N systems is also studied showing that the strength of such interactions increases in the following order: C(sp^3)—H···Y, C(sp^2)—H···Y, C(sp)-H···Y, where Y = S, N—it is in line with the previous findings on C—H···O hydrogen bonds. The results also show that $CH_4\cdots SH_2$ and $C_2H_4\cdots SH_2$ complexes should be rather classified as van der Waals interactions and not as hydrogen bonds. The frequency associated with the C−H stretch of C(sp^3)—H···S is blue-shifted.

Introduction

The existence of C—H···Y hydrogen bonds in crystal structures has been claimed early on by a number of workers.[1−3] Taylor and Kennard have shown[4] that for C—H···Y systems, H-bonds with the oxygen atom acceptor (Y = O) are of the most frequent occurrence; it is 54% the full sample of C—H···Y contacts taken from the Cambridge Structural Database;[5] the occurrence of the other C—H···Y (X = N, P, Cl, Br, S, C) interactions is much smaller. C—H···N and C—H···S short contacts are not as common as C—H···O ones but might be found in many molecular crystals with interesting properties such as electrical conductivity or superconductivity.[6] Very recently, C(sp^2)—H···S(sp^3) and C(sp^2)—H···N(sp^3) intramolecular contacts were analyzed in the crystal structures of thiazolidine derivatives.[7] The analysis based on X-ray diffraction measurements, and results obtained from the Bader theory[8] have shown that for thiazolidine derivatives, C—H···S intramolecular contacts may be classified as H-bonds and C—H····N may not.[7]

On the other hand, ab initio and DFT calculations on the simple modeled complexes containing C—H···S and C—H···N hydrogen bonds have been performed. The calculations on systems with C(sp^3)—H···S interactions have been carried out showing the low S(sp^3) sulfur ability as proton acceptor and low ability of C(sp^3)−H bond as proton donor. For example, the calculations on $CH_4\cdots OH_2$,[9] $CH_4\cdots NH_3$,[10] and $CH_4\cdots SH_2$[11] complexes performed at the MP2/6-311++G(d,p) level of theory and corrected by BSSE show that the binding energies are −0.34, −0.31, and −0.07 kcal/mol, respectively. It is in line with other studies since it has been pointed out that C—H···S interactions are weaker than C—H···O hydrogen bonds.[3] However, these results are not in agreement with the crystal structure investigations on thiazolidine derivatives,[7] showing that steric effects and intermolecular interactions may influence molecular geometries and the arrangement of molecules in crystals. There are the other examples of theoretical studies on C—H···Y interactions, among them C—H···N and C—H···S hydrogen bonds. One can mention the following studies: ab initio calculations and the topological analysis on N≡C—H···OH_2 and H_3C—H···OH_2 complexes;[12] topological and NBO analysis performed for C—H···O H-bonds within dimers with $CH_{4-n}X_n$ (X = F, *n* = 1, 2, 3) and NO_2CH_3 donors and H_2O as the acceptor;[13] ab initio studies and the analysis of the potential energy surfaces for $CH_4\cdots OH_2$, $C_2H_4\cdots OH_2$, and $C_2H_2\cdots OH_2$ complexes;[14] the study on different configurations of $CH_4\cdots SH_2$ complex;[11] and the ab initio study up to the MP2(full)/6-311++G(3df,2p) level of approximation and NBO analysis of the $CH_4\cdots NH_3$ dimer.[15] There are also investigations concerning intramolecular C—H···N and C—H···S interactions.[16]

One can mention other numerous examples of studies on systems containing C—H···Y interactions. However, it seems that the C—H···O hydrogen bond is the most often explored because of its occurrence and importance. Many interesting findings for the latter interaction were reported. The study on the influence of hybridization and substitution effects on the properties of the C—H···O hydrogen bond is an example.[17] The authors have performed the SCF, MP2, and DFT calculations on complexes with C_2H_4, C_2H_2, HCN, and their chloro and fluoro derivatives as proton donors and H_2O as an acceptor using different basis sets. The results have been compared with the earlier calculations on complexes with CH_4 and its derivatives as proton donors and H_2O as an acceptor.[18] It was found that the binding energy calculated at the MP2/6-311++G(d,p) level of approximation for acetylene with water amounts to −2.5 kcal/mol, for ethylene with water −0.9 kcal/mol, and for methane as a proton donor −0.3 kcal/mol. It should be pointed out that it is in line with the early study where it was found that the acidity of donors decrease as follows: C(sp)−H > C(sp^2)−H > C(sp^3)−H.[19] One can compare these results with those where H_2S acts as a proton acceptor. The latter were mentioned here as systems where the binding energies for corresponding complexes are lower. It supports the well-known statement of the lower basicity of sulfur than oxygen as the proton acceptor within hydrogen bonds.

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It is also worth mentioning that for methane and its fluoro derivatives as proton donors and H_2O, H_2CO, and CH_3OH as proton acceptors, the shortening of the C−H proton donor bond is observed and connected with such effect the shift in frequency of antisymmetric stretch mode to higher values. Such interactions are known as blue-shifting hydrogen bonds, and they have been investigated early on[20] and explored later extensively.[21] The existence of blue-shifting hydrogen bonds was also studied for chloro and fluoro derivatives of the previously mentioned hydrocarbons as donors and lithium hydride as an acceptor, in other words, the C−H···H dihydrogen bonds were considered, and the frequency modes of C−H bonds were analyzed.[22] However, for these dihydrogen bonded systems, it was found that the changes of the proton donating C−H bonds depends on the level of calculations. The blue-shifting H-bonds recalculated at higher levels of approximation may be treated as red-shifted as is usual for typical H-bonded dimers. For example, it was found that for some of species, a slight shortening was observed for often applied in calculations of the unsaturated 6-311++G(d,p) basis set. In other words, the effect of the shortening of the proton donating bonds due to complexation, detected for lower levels of approximation, disappears for higher levels. The calculations on the previously mentioned dihydrogen bonded systems have been performed up to the MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ levels.[22] The dependence of the change of the C−H bond length due to complexation on the level of theory was analyzed recently for the $F_3CH\cdots FH$ dimer.[23] The authors detected a red-shift for the Hartree−Fock method and nonsaturated basis sets and a blue-shift for higher levels of approximation up to MP2(full)/6-311++G(d,p); however, the more extended basis sets were not applied.

The aim of this study is to investigate the complexes of methane, ethane, and acetylene as the proton donors and ammonia or hydrogen sulfide as acceptors to have deeper insight into the nature of C−H···N and C−H···S hydrogen bonds. The Bader theory[8] is also applied to characterize such interactions. The goal of our study is also to check if the same tendencies for C−H···O interactions are fulfilled here (i.e., if the hybridization effect is also observed and if, similar to the $C(sp^3)$-H···O interactions, the blue-shifting H-bonds are observed for $C(sp^3)$−H···Y (Y = N, S) but not for the $C(sp^2)$−H···Y ($Y \simeq$ N, S) and C(sp)−H···Y ($Y \simeq$ N, S) systems).

Computational Details

Calculations were carried out with the Gaussian 98[24] and Gaussian 03[25] sets of codes. The following complexes were analyzed: $CH_4\cdots NH_3$, $C_2H_4\cdots NH_3$, $C_2H_2\cdots NH_3$, $CH_4\cdots SH_2$, $C_2H_4\cdots SH_2$, and $C_2H_2\cdots SH_2$ with C−H···N and C−H···S hydrogen bonds. The SCF as well as the second-order perturbation Møller−Plesset (MP2)[26] calculations were performed. The Pople type basis sets[27−30] were used: 6-31G, 6-31+G, 6-31+G(d), 6-31+G(d,p), 6-31++G(d,p), and 6-311++G(d,p). Also, the following Dunning type basis sets[31,32] were applied: aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ. Full optimizations have been performed with the use of the Pople type basis sets up to the MP2/6-311++G(d,p) level of approximation and for the MP2/aug-cc-pVDZ level; for the latter optimized geometries, the single point MP2/aug-cc-pVTZ and MP2/aug-cc-pVQZ calculations were carried out.

Since the basis sets applied are not saturated, the basis set extension effects were checked using the extrapolation formula

$$E(X) = E(\mathrm{CBS}) + A/X^3 \tag{1}$$

where CBS designates the complete basis set,[33] and X is the cardinal number of the basis set (aug-cc-pVXZ). Since the convergence of the SCF and correlation energies differs, it is usual to separate these energy terms and use a different formula for them.[34] We have applied eq 1 to obtain the CBS energy limit for the correlation term and eq 2 given next to extrapolate the Hartree−Fock energy contribution.

$$E(X)^{\mathrm{HF}} = E(\mathrm{CBS})^{\mathrm{HF}} + A\exp(-\alpha X) \tag{2}$$

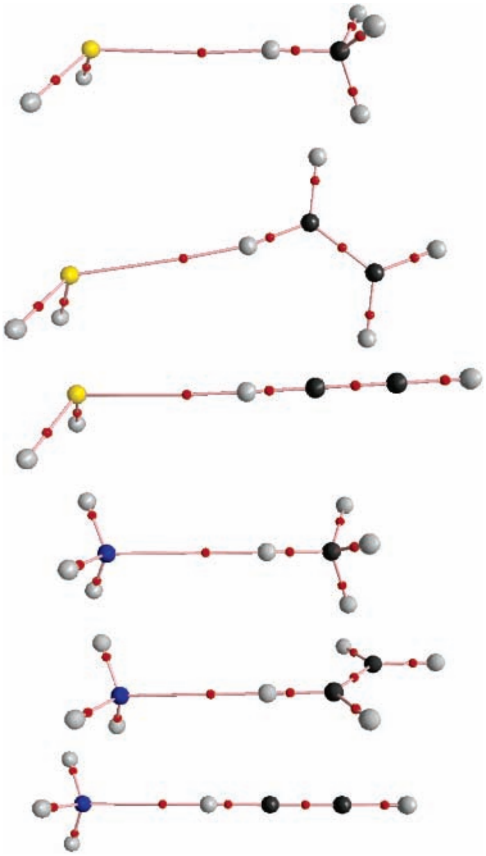
One can see that the calculations for two cardinal numbers are required to obtain the CBS correlation energy (eq 1), while for Hartree−Fock energy terms, three cardinal numbers are needed (eq 2). Hence, MP2/aug-cc-pVXZ ($X = 3, 4$) levels of approximations were used here to obtain the correlation energies, and MP2/aug-cc-pVXZ ($X = 2-4$) was used to assess the Hartree−Fock energy terms. The binding energies for the analyzed complexes have been computed as the difference between the total energy of the complex and the energies of the isolated monomers. The binding energies calculated for different levels of approximation have been corrected for the basis set superposition error (BSSE) via the standard counterpoise method.[35] Such corrections were not performed for CBS energies where BSSE vanishes.

To have the deeper insight into the nature of C−H···S and C−H···N interactions, the Bader theory[8,36] was applied here. The bond critical points (BCPs) of the H···Y ($Y \simeq$ S, N) interactions were found, and the features of them were analyzed since it is well-known that characteristics of BCPs, such as the electron densities, their Laplacians,[37] and the energetic properties of BCPs,[38] allow us to categorize interactions, and these topological parameters are also treated as measures of H-bonding strength.[39]

Results and Discussion

Scheme 1 presents the molecular graphs of the dimers considered in this study (i.e., $CH_4\cdots NH_3$, $C_2H_4\cdots NH_3$, $C_2H_2\cdots NH_3$, $CH_4\cdots SH_2$, $C_2H_4\cdots SH_2$, and $C_2H_2\cdots SH_2$). These graphs present the positions of attractors and of bond critical points (BCPs) as well as bond paths connecting critical points. The MP2/6-311++G(d,p) wave functions were used for further atoms in molecules (AIM) analysis. For different levels of approximation, the full optimizations were performed; hence, the configurations of the systems obtained at other levels than MP2/6-311++G(d,p) were slightly different than those presented at Scheme 1. The greater differences were observed for the SCF optimizations where the correlation of electrons is not taken into account. Table 1 presents the binding energies of the complexes considered. The following conclusions may be pointed out. The proton donor abilities decrease in the following order: C(sp)−H, $C(sp^2)$−H, $C(sp^3)$−H as it was found earlier.[17,19] Additionally, it is evident that nitrogen is the stronger acceptor center than the sulfur atom. For the $CH_4\cdots SH_2$ complex, the binding energy is low; even for some of MP2 results, it is positive showing that the system is unstable. For the strongest H-bond, for the $C_2H_2\cdots NH_3$ dimer the binding energy calculated at the MP2/6-311++G(d,p) level amounts to −3.2 kcal/mol. This is less than the binding energy (comparing the absolute values) of the water dimer, which amounts to −4.5 kcal/mol (calculated at the same level of approximation). It means that only for the $C_2H_2\cdots NH_3$ dimer the H-bond may be hardly accepted as medium in strength. The remaining hydrogen bonds should be classified as weak ones, as the existence of the H-bond for the $CH_4\cdots SH_2$ complex is even

SCHEME 1: Molecular Graphs of Complexes Considered: $CH_4\cdots NH_3$, $C_2H_4\cdots NH_3$, $C_2H_2\cdots NH_3$, $CH_4\cdots SH_2$, $C_2H_4\cdots SH_2$, and $C_2H_2\cdots SH_2$



problematic, and one may state that this is the van der Waals interaction. The binding energies of the MP2 method are systematically greater than those calculated at HF levels, showing the importance of the electron correlations. The ethylene and methane complexes with H_2S are exceptions because for these interactions, the binding energies amount to −1.2 and −0.4 kcal/mol, respectively (MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level; for the other levels, these energies, if comparing the absolute values, are less). The differences between HF and MP2 results are evidently reflected in the geometries of the complexes (Table 2), the H···Y (Y ≃ S, N) distances are systematically smaller for the latter results showing the role of the dispersion energies since the dispersion energy component is the most important attractive term within the correlation energy component. However, the distances for $CH_4\cdots SH_2$ and $C_2H_4\cdots SH_2$ complexes, even calculated at MP2 levels of approximation, are close to the corresponding sum of van der Waals radii (3.0−3.1 Å), indicating that such interactions should be classified as van der Waals interactions.

Table 1 presents the binding energies obtained from the complete basis set (CBSs) energies. Such CBS energies were extrapolated here according to eqs 1 and 2, the correlation energy according to eq 1 and the Hartree−Fock energy term according to eq 2. For the correlation CBS energies, the MP2 results and aug-cc-pVXZ ($X = 3, 4$) basis sets were applied, while for the HF energies, the MP2 results and aug-cc-pVXZ ($X = 2-4$) basis sets were used. Geometries were optimized here within the MP2 method, and the Hartree−Fock energy terms of such MP2 energies were further used for extrapolations. One can see that hydrogen bond energies calculated from complete basis sets are close to those calculated with the use of aug-cc-pVDZ basis sets or to those obtained with the use of aug-cc-pVTZ basis sets. This may mean that the higher level MP2/aug-cc-pVQZ calculations are not needed to consider the approximate H-bond energies. The other reasons for disagreement between MP2/CBS and MP2/aug-cc-pVQZ results may be connected with the inaccurate estimations of BSSEs included within the binding energies of the latter level.

Table 3 presents the topological parameters (electron densities and their Laplacians) of H···Y and C−H bond critical points. One can observe only slight changes of C−H bond parameters due to the complexations. This means that the complexes analyzed are bound by weak hydrogen bonds. The bond paths between H and Y attractors indicate the existence of interacting systems. The other topological criteria of the existence of hydrogen bonding are also fulfilled since the topological parameters at H···Y BCPs are within the proper range of 0.002−0.04 au for the electron density and 0.02−0.15 au for its Laplacian, as was pointed out by Koch and Popelier.[37] $CH_4\cdots SH_2$ is the only exception since the Laplacian of the electron density at H···S BCP is below the range proposed. This finding also supports the statement that for $CH_4\cdots SH_2$ complexes, there is the van der Waals interaction. Figure 1 shows the relief map of the electron density in the plane passing through N···H−C≡C−H atoms, as this is visible, that the electron density between N-acceptor and H-attractors is only slightly above the background. It is worth mentioning that for this complex, the strongest hydrogen bond was detected, and the electron density at H···N BCP is the greatest if it is compared with the other complexes analyzed here.

All the geometrical, energetic, and topological results (Tables 1−3) show that nitrogen within ammonia is the stronger acceptor than sulfur within hydrogen sulfide. Besides the well-known dependence between the hybridization of carbon and the proton donor abilities of the corresponding C−H bond, this is supported here since acetylene is a stronger donor than ethylene, and further, the latter is a stronger donor than methane. Figure 2 shows the relationship between the H···Y distance and the binding energy that supports these statements. However, one can observe two subsets, each of them related to the kind of acceptor, nitrogen or sulfur. The similar subsets are visible for the correlation between the electron density at H····Y BCP and the binding energy (Figure 3). However, in such a case, the linear correlation coefficient for all systems amounts to 0.97, and the linear correlation between Laplacian of the electron density at H···Y BCP and the binding energy is even better amounting to 0.99 (Figure 4).

Table 4 shows the frequency stretching modes for C−H bonds participating in corresponding H-bonds. For three complexes connected through the strongest hydrogen bonds (i.e., $C_2H_4-NH_3$, $C_2H_2-H_2S$, and $C_2H_2-NH_3$), there are the elongations of CH bonds due to complexations, red-shifts of stretching modes, and the increase of their intensities ($I/I_0 > 1$). Hence, they behave in a similar way as the typical hydrogen bonded systems.[40] For the remaining weaker bonded system, there are sometimes shortenings of CH bonds, and sometimes there are blue-shifts, but these changes are rather negligible. The blue-shifts for hydrogen bonds considered here are not as evident as for H-bonds, where methane and its derivatives are donors, and the oxygen of H_2CO, H_2O, or CH_3OH are acceptors.[17,18] For example, for the $F_3CH\cdots O(H)-CH_3$ complex calculated at the MP2/6-311++G(d,p) level of approximation, the blue-shift is equal to 47 cm^{-1},[18] much more than for the CH_4-H_2S complex investigated here, where the blue-shift amounts to 7.9 cm^{-1}. As it was stated earlier, the latter complex is hardly accepted as H-bonded, as it is rather bound by van der Waals interactions.

TABLE 1: Binding Energies (kcal/mol) of Methane, Ethene and Acetylene with Ammonia and Hydrogen Sulfide, Calculated with Counterpoise Correction of Basis Set Superposition Error

level	$CH_4\cdots H_2S$	$C_2H_4\cdots H_2S$	$C_2H_2\cdots H_2S$	$CH_4\cdots NH_3$	$C_2H_4\cdots NH_3$	$C_2H_2\cdots NH_3$
HF/6-31G*	−0.05	−0.19	−0.86	−0.28	−0.76	−3.31
HF/6-31+G*	−0.05	−0.22	−0.89	−0.23	−0.73	−2.88
HF/6-31+G**	−0.05	−0.23	−0.88	−0.22	−0.73	−2.92
HF/6-31++G**	−0.05	−0.22	−0.88	−0.23	−0.73	−2.88
HF/6-311++G**	−0.03	−0.28	−0.82	−0.21	−0.79	−2.82
HF/aug-cc-pVDZ	−0.08	−0.19	−0.84	−0.21	−0.62	−2.69
MP2/6-31G*	−0.08	−0.20	−0.95	−0.47	−1.05	−3.88
MP2/6-31+G*	0.01	−0.26	−0.97	−0.24	−0.81	−3.16
MP2/6-31+G**	0	−0.21	−0.92	−0.28	−0.86	−3.10
MP2/6-31++G**	−0.02	−0.22	−0.91	−0.29	−0.88	−3.09
MP2/6-311++G**	0.04	−0.18	−0.98	−0.36	−0.94	−3.18
MP2/aug-cc-pVDZ	−0.28	−0.77	−1.44	−0.53	−1.14	−3.41
MP2/aug-cc-pVTZ	−0.41	−1.24	−1.60	−0.64	−1.24	−3.53
MP2/aug-cc-pVQZ	−0.39	−1.34	−1.65	−0.68	−1.29	−3.60
CSB	−0.27	−1.19	−1.37	−0.61	−1.21	−3.37

TABLE 2: Optimized Intermolecular H···Y (Y ≃ N, S) Distances (Å)

level	$CH_4\cdots H_2S$	$C_2H_4\cdots H_2S$	$C_2H_2\cdots H_2S$	$CH_4\cdots NH_3$	$C_2H_4\cdots NH_3$	$C_2H_2\cdots NH_3$
HF/6-31G*	4.021	3.705	3.143	3.058	2.875	2.329
HF/6-31+G*	4.105	3.625	3.144	3.222	2.789	2.349
HF/6-31+G**	4.064	3.606	3.140	3.148	2.773	2.373
HF/6-31++G**	4.039	3.619	3.139	3.163	2.798	2.374
HF/6-311++G**	3.814	3.590	3.172	3.101	2.826	2.421
HF/aug-cc-pVDZ	4.115	3.550	3.116	3.122	2.857	2.422
MP2/6-31G*	3.331	3.082	2.794	2.766	2.570	2.208
MP2/6-31+G*	3.157	3.479	2.776	2.689	2.501	2.232
MP2/6-31+G**	3.138	2.994	2.768	2.682	2.523	2.255
MP2/6-31++G**	3.149	3.006	2.754	2.696	2.537	2.255
MP2/6-311++G**	3.095	2.974	2.796	2.707	2.565	2.290
MP2/aug-cc-pVDZ	3.106	3.231	2.761	2.684	2.555	2.255

TABLE 3: Topological Parameters—Electron Densities at X−H and H···Y BCPs (ρ_{XH} and $\rho_{H\cdots Y}$) and Their Laplacians ($\nabla^2\rho_{XH}$ and $\nabla^2\rho_{H\cdots Y}$)[a]

complex	ρ_{CH}	$\nabla^2\rho_{CH}$	$\rho_{H\cdots Y}$	$\nabla^2\rho_{H\cdots Y}$
CH_4-SH_2	0.273 (0.272)	−0.920 (−0.912)	0.005	0.013
$C_2H_4-SH_2$	0.280 (0.279)	−0.973 (−0.963)	0.006	0.018
$C_2H_2-SH_2$	0.284 (0.284)	−1.030 (−1.026)	0.008	0.024
CH_4-NH_3	0.274 (0.272)	−0.929 (−0.912)	0.008	0.020
$C_2H_4-NH_3$	0.281 (0.279)	−0.982 (−0.963)	0.010	0.026
$C_2H_2-NH_3$	0.281 (0.284)	−1.025 (−1.026)	0.015	0.046

[a] All values were obtained at the MP2/6-311++G(d,p) level of approximation (in au). The values given in parentheses (for CH bonds) correspond to donating systems not involved in hydrogen bonds.

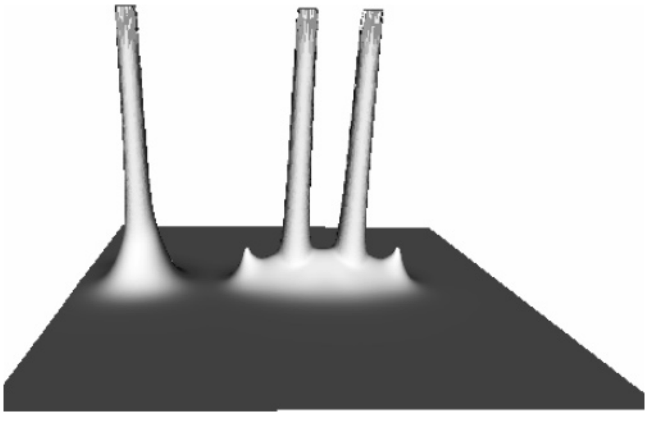


Figure 1. Relief map of the electron density for $H_3N\cdots HCCH$ complex in N···HCCH plane.

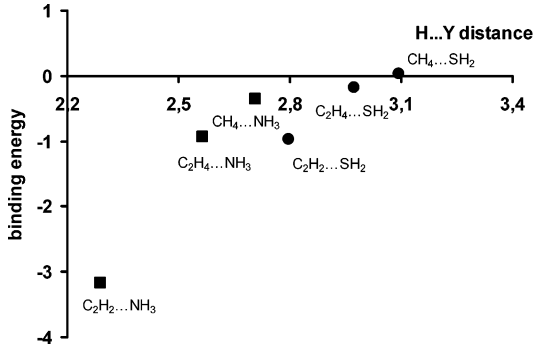


Figure 2. Difference between the proton−acceptor distance (Å) and the binding energy (kcal/mol).

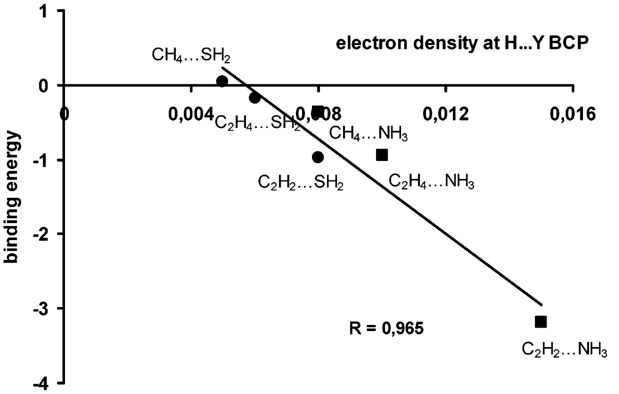


Figure 3. Relationship between the electron density at H···Y (Y = N, S) BCP (in au) and the binding energy (in kcal/mol).

Table 4 shows the transfer of electrons due to the complexation for the dimers analyzed here. There is the transfer of electron charge from donating molecules to acceptors. This is opposite to the well-known situation of the electron density transfer from acceptors to donors for typical hydrogen bonds.[40] For example, such transfer for the dimer of water is equal to 0.019 e (19 me) and concerns the movement of electron density from acceptor to the donating water molecule (based on the MP2/6-311++G-(d,p) calculations). For the systems analyzed here, the amounts

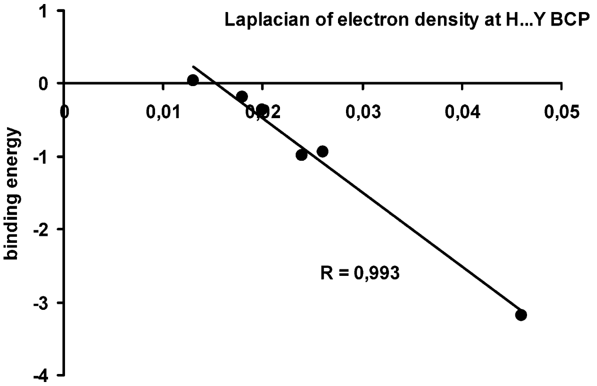


Figure 4. Relationship between Laplacian of electron density at H···Y (Y ≃ N, S) BCP (in au) and the binding energy (in kcal/mol).

TABLE 4: Changes in Properties of Proton Donor Molecules (Proton Donating C—H Bonds) Caused by Complexation with Hydrogen Sulfide and Ammonia[a]

	Δr	$\Delta\mu$, cm^{-1}	I/Io	charge transfer
CH_4—H_2S	0.3	7.9	0.49	21
CH_4—NH_3	0.2	−0.5	0.03	28
C_2H_4—H_2S	−0.6	−1.4	0.79	23
C_2H_4—NH_3	0.7	−11.5	1.35	42
C_2H_2—H_2S	2.2	−18.7	2.22	28
C_2H_2—NH_3	8.8	−94.8	3.57	46

[a] The electron transfer from the donor to the acceptor is also indicated (in me), Δr is in Å × 10^3 (MP2/6-311++G(d,p) level).

of the transferred electron charge are greater than 19 me. The greater values were found for nitrogen accepting centers than for sulfur ones. Additionally such transfers are greater for stronger donors. In other words, the transfer of the electronic charge is greater for stronger hydrogen bonding, and the linear correlation coefficient for the relationship between the transferred electron charge and the H-bond energy is equal to only 0.848; however, there are the stronger dependencies between these values within subsamples (each of the subsamples is characterized by the type of acceptor—H_2S and NH_3).

The results presented here and concerning C—H···Y bonds may be compared with those where the water molecule is an acceptor.[17] For the complexes of methane, ethylene, and acetylene with water, the binding energies calculated at the MP2/6-311++G(d,p) level are equal to −0.3, −0.9, and −2.5 kcal/mol, respectively. It shows that the oxygen atom is a stronger acceptor than sulfur (see binding energies presented in Table 1). The comparison of nitrogen and oxygen proton acceptor abilities in hydrogen bonds is not so evident. If acetylene is a proton donor, nitrogen is stronger acceptor; however, if methane and ethylene are donors, oxygen of the water molecule is a stronger acceptor than nitrogen of ammonia (Table 1 and ref 17). The situation with acetylene as a donor is in line with the MP2/6-311++G(d,p) results for the $(H_2O)_2$ dimer and the HOH···NH_3 complex, where binding energies are equal to −4.5 and −5.8 kcal/mol, respectively.[39b] If one compares sulfur and nitrogen as acceptors of a proton, one may found that sometimes sulfur is stronger acceptor than nitrogen, as for the crystal structures of thiazolidines,[7a] where C—H···S intramolecular H-bonds exist while C—H···N do not. Similarly, ab initio calculations for complexes with thiazolidine show that if sulfur and nitrogen of thiazolidine are acceptor centers, for the latter case, H-bonds are weaker.[7a] It is also difficult to order N, O, and S atoms as related to their proton acceptor abilities for intramolecular hydrogen bonds.[16b]

Summary

The complexes bonded through hydrogen bonds and van der Waals interactions, where hydrocarbons are proton donors and H_2S and NH_3 are proton acceptors, are considered in this study. The results show that the proton donor abilities of C—H bonds increase in the following order: C(sp^3)—H < C(sp^2)—H < C(sp)—H. Additionally, nitrogen is a stronger acceptor than the sulfur center. However, if the results considered here are compared with those where water is an acceptor, then it is difficult to classify the oxygen atom center as a stronger acceptor than the nitrogen atom center.

The results presented here also show that only the complexes with methane as donor may be classified as systems where the blue-shift of the C—H stretch is observed; the remaining complexes are bonded through the typical red-shifted hydrogen bonds.

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