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Quantum Chemical Study of the Hydrogen-bonded $C_4H_2\cdots HCl$ Complex†

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Ab initio molecular orbital calculations at the MP2 full level and density functional calculations using 6-31++G(d,p) basis functions are performed on the $C_4H_2\cdots HCl$ system and it is observed that formation of a weak complex is possible with a $\pi\cdots HCl$ type hydrogen bond between the C_4H_2 and HCl molecules.

The traditional view of H-bonding interactions has been expanded to include many weak interactions.[1–3] Significant among these is the interaction of hydrogen halides with systems having π-electrons (*e.g.* $C_2H_2\cdots HX$). The $XH\cdots\pi$ interaction is also important in the context of crystal engineering and molecular recognition.[4,5] The π-electron rich system behaves as an electron donor in these complexes. Theoretical studies play an important role because it is often not possible to determine precisely the minimum energy structure from the experiment alone, particularly when there are many possible forms of the complexes with comparable energies. The purpose of the present communication is to predict the structure and energetics of the hitherto unknown weak hydrogen-bonded complex between C_4H_2 and HCl molecules. To the best of our knowledge, there is no reported experimental or theoretical study on this system and thus we feel the present calculation will be useful for providing basic information on this complex.

Method

The geometries of the molecules C_4H_2 and HCl and of the complexes were fully optimised at the MP2 = full level and also with density functional theory (DFT) calculations using B3LYP[6,7] and B3PW91[8] exchange-correlation (XC) functionals. 6-31++G(d,p) basis set was used for all the calculations. The DFT calculations with B3LYP and B3PW91 XC functionals are henceforth simply referred to as B3LYP and B3PW91. The Gaussian-94 program package[9] was used for all the calculations involving DFT whereas the HONDO program package was used for the MP2 calculations. Harmonic vibrational frequencies are calculated at the MP2 level and DFT with B3LYMP.

Results and Discussion

We have already mentioned that to the best of our knowledge there is no reported experimental evidence for the complex between C_4H_2 and HCl. Recently, Chandra *et al.*[10] reported a theoretical study on the $C_4H_2\cdots HF$ complex at the MP2 level of theory.[10] It was observed from the theoretical calculations that the most stable complex between diacetylene and HF forms when the H-atom of HF interacts with the π-electron cloud of diacetylene (Lπ complex). A weak sigma complex is another possibility in which the acidic hydrogen atom of the diacetylene forms a hydrogen bond with the fluorine atom of HF. It was not possible, however, to separate these two possible forms from the experimental results.[11] In the case of HCl, we observed that the sigma complex is very weak and the interaction energy is only 0.1 kcal at the MP2 level.

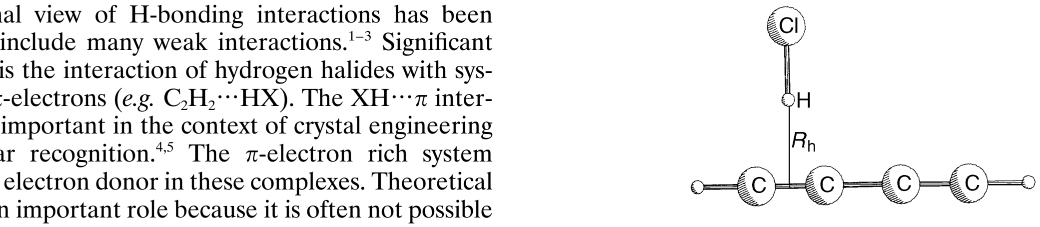

Fig. 1 Schematic diagram of the diacetylene complexes with HCl

The π complex (Fig. 1) was found to be the most stable complex between C_4H_2 and HCl and optimisations were carried out both at the MP2 level and at the B3LYP and B3PW91 levels for this complex. The results obtained are summarised in Tables 1 and 2. It is evident from Table 1 that the monomer geometries do not change significantly upon complex formation. This indicates that the stability and structure of the complex are determined predominantly by long-range electrostatic interactions. The importance of electrostatic interactions for determining the structure of the H-bonded complex was emphasized earlier by Buckingham and Fowler.[12] However, small increments in the C≡C (at which H-bonding takes place) and H—Cl bond lengths have been observed in the complex. Although individual bond lengths are different at MP2 and DFT the increments observed are nearly the same. The hydrogen bond length (R_h, the distance between the centre of the C≡C bond and the hydrogen atom of HCl) increases and the dissociation energy decreases when going from MP2 to B3LYP and B3PW91 levels. The geometrical parameters obtained from B3LYP and B3PW91 are almost identical but the dissociation energy decreases from B3LYP to B3PW91. It should be pointed out that methods using finite basis expansions suffer from the basis set superposition error (BSSE). However, in view of the quality of the basis set used in the present calculations, we did not perform any BSSE corrections. Moreover, the BSSE correction by the counterpoise method has been questioned many times[13,14] and it has been argued that it overcorrects the BSSE. The hydrogen bond length R_h obtained for the $C_4H_2\cdots HCl$ complex is larger when compared to the corresponding HF complex and/or the HCl complex with acetylene.[10,15] For example, the hydrogen bond lengths obtained

Table 1 The optimised geometrical parameters of the C_4H_2–HCl complex. Values in parentheses correspond to isolated molecules.

R/Å	MP2	B3LYP	B3PW91
H—Cl	1.274 (1.269)	1.294 (1.287)	1.292 (1.283)
C—C	1.373 (1.372)	1.369 (1.369)	1.367 (1.367)
C—H	1.064 (1.063)	1.067 (1.066)	1.068 (1.066)
C≡C	1.226 (1.225)	1.214 (1.214)	1.214 (1.214)
C≡C[a]	1.228 (1.225)	1.216 (1.214)	1.216 (1.214)
R_h	2.439	2.468	2.481

[a] C≡C bond involved in the hydrogen bonding.

Table 2 Total energies (a.u.) at the stationary points, binding energies and dipole moments of the C_4H_2–HCl complex. Values in parentheses indicate the binding energies after zero point energy correction

Method	C_4H_2	HCl	C_4H_2–HCl	ΔE/kcal mol^{-1}	μ/D[a]
MP2	−153.03773	−460.21853	−613.25978	2.20 (1.31)	2.02
B3LYP	−153.49587	−460.80328	−614.30212	1.87 (1.05)	2.11
B3PW91	−153.42427	−460.74973	−614.17662	1.65 (0.83)	2.16

[a] Dipole moments of HCl obtained from the MP2, B3LYP and B3PW91 calculations are 1.45, 1.46 and 1.49 D respectively.

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at the MP2 level are 2.22 and 2.43 Å for the HF and HCl complexes of C_4H_2 respectively, which is, of course, expected from the strength of the hydrogen bond. The rotational constants calculated from the B3LYP optimised geometry are 5920.17, 1303.02 and 1067.96 MHz. The dipole moments of the complex obtained from MP2, B3LYP and B3PW91 calculations are 2.02, 2.11 and 2.16 D, respectively. Considering the dipole moments of the isolated HCl molecule, it is clear that complex formation between C_4H_2 and HCl introduces a significant amount of induced dipole moment in the system. The magnitude of the induced dipole moment is nearly the same as that in the $C_2H_2\cdots HCl$ complex.[15]

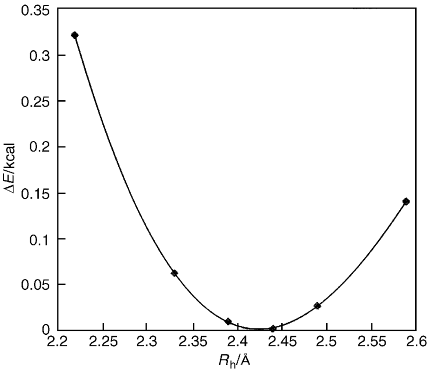

Fig. 2 Intermolecular potential curves for the $C_4H_2\cdots HCl$ complex calculated at MP2 level with 6-31++G(d,p) basis set

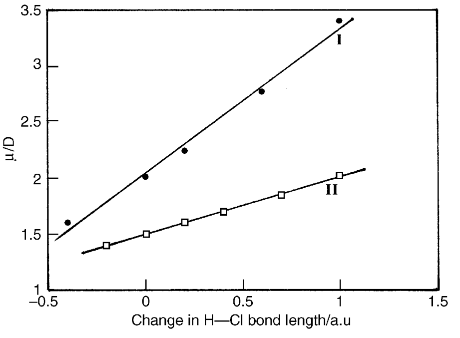

Fig. 3 Variation of dipole moment with the change in H—Cl bond length from the equilibrium value, in (I) the $C_4H_2\cdots HCl$ complex and (II) isolated HCl

A low frequency shift, compared to the isolated molecule values, of the intramolecular hydrogen chloride stretching vibration was observed from the MP2 and DFT calculations (see Table 3). The magnitude of the shifts are 69 and 99 cm^{-1} at the MP2 and B3LYP levels, respectively. The $\pi\cdots HCl$ hydrogen bond is weaker in the diacetylene complex compared to the corresponding acetylene complex and thus a smaller frequency shift of HCl in the diacetylene complex is expected. The same trend was observed from the present theoretical calculations. The HCl frequency shifts observed at the MP2 level for the $C_2H_2\cdots HCl$ and $C_4H_2\cdots HCl$ are 73 and 69 cm^{-1}, respectively and with B3LYP 126 and 99 cm^{-1}, respectively. Bearing in mind the strength of the hydrogen bond, it seems that the B3LYP level estimates vibrational frequencies more accurately than the MP2 level. Recently Geerlings and co-workers also made the same observation.[16] The intermolecular vibrational frequencies for the $C_4H_2\cdots HCl$ complex are given in Table 4. Intermolecular stretching vibrational frequencies obtained from the B3LYP calculations for the C_4H_2 and C_2H_2 complexes with HCl are 80 and 93 cm^{-1}, respectively, which is, of course, expected from the strength of the hydrogen bond of the two complexes. Fig. 2 shows the intermolecular potential curves for the $C_4H_2\cdots HCl$ complex. The variation of the dipole moments of the $C_4H_2\cdots HCl$ complex and isolated HCl with the change in HCl bond length are presented in Fig. 3 which shows that the dipole moment changes more rapidly for the complex. It is, therefore, expected that the intensity of the H—Cl stretching vibration will be increased upon complex formation with diacetylene.

Table 3 Hydrogen halide vibrational frequencies and low frequency complex shifts (ν/cm^{-1})

	MP2	B3LYP	Expt.[a]
Molecule			
HCl	3120	2949	2888
C_4H_2–HCl	3051	2850	
Shift	69	99	

[a] Ref.17.

Table 4 Intermolecular harmonic frequencies for C_4H_2–HCl (cm^{-1})

Method	Stretch	In-plane		Out-of-plane
MP2	101	28	293	234
B3LYP	80	31	298	244

Conclusion

It has been observed from MP2 and DFT calculations with B3LYP and B3PW91 XC functionals that the formation of a weak molecular complex is possible between diacetylene and HCl with a $\pi\cdots HCl$ type hydrogen bond. The hydrogen bond lengths obtained from MP2, B3LYP and B3PW91 are 2.439, 2.468 and 2.481 Å, respectively. The binding energy of the $C_4H_2\cdots HCl$ complex should be around 1 kcal mol^{-1} and the intensity of the H—Cl stretching vibration should increase upon complex formation.

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