

Theoretical studies on hydrogen bonding in π -electron systems: A note on the structural features of diacetylene–hydrogen fluoride complexes

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Abstract. *Ab initio* supermolecular SCF calculations at the STO-3G level are reported for the diacetylene-hydrogen fluoride complexes. The reverse σ -complex is predicted to have somewhat higher stability and H-bond strength than the π -complexes.

Keywords. *Ab initio* supermolecular SCF calculations; intermolecular interactions; diacetylene–hydrogen fluoride complexes; hydrogen bonding in π -systems.

1. Introduction

The possibility of hydrogen-bonding interaction with π -bonded systems has attracted considerable attention in the recent years (Barnes *et al* 1973; McDonald *et al* 1980; Legon *et al* 1981; Andrews *et al* 1982a,b). Of special interest have been systems having π -bonds in conjugation (Baiocchi *et al* 1983; Andrews *et al* 1985; Patten and Andrews 1985). Infrared spectroscopic measurements on conjugated diene–hydrogen fluoride complexes in a solid argon matrix indicate that the HF submolecule oscillates appreciably around its average position in the complex (Patten and Andrews 1985). It points to a model in which the HF submolecule probably oscillates between the two equivalent π -systems in the diene. Diacetylene also has got two equivalent π -systems held in conjugation with the difference that the distance between the two π -sites is much larger, thereby reducing the probability of exchange of an HF submolecule between the two π -bonds. In addition, the electron-withdrawing ability of the C_2H^- group is expected to be large enough to make the acetylinic hydrogen more acidic here than in acetylene itself. This enhanced acidity of the H atoms in diacetylene could lead to the formation of a reverse σ -complex with hydrogen fluoride.

Very recently, IR spectral data on diacetylene–HF complexes in solid argon have been reported (Patten and Andrews 1986). These data conform to the formation of two primary 1:1 products one of which has been identified as the usual π -complex (figure 1a) and the other as the reverse σ -complex (figure 1b). No evidence for the HF oscillation between the two equivalent π -sites could be obtained from the IR spectra. Also, the relative stabilities of the two primary products could not be ascertained from these measurements. It would be of interest therefore to undertake theoretical investigations on these aspects to gain some

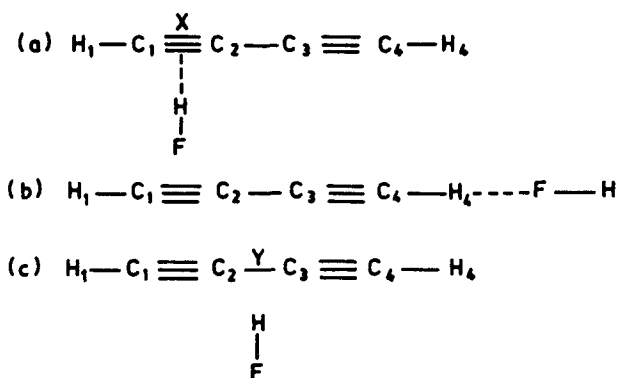


Figure 1. (a) Arrangement of atoms in the non-symmetrical π -complex (b) in reverse σ -complex (c) in symmetrical π -complex.

Table 1. Structures and relative stabilities of different forms of diacetylene-hydrogen fluorides complexes computed by *ab initio* supermolecular SCF method at the STO-3G level.

Structural parameters	σ -Complex (reverse) (figure 1b)	Non-symmetric π -complex (figure 1a)	Symmetric π -complex (figure 1c)
Bond lengths (Å)	C ₁ -H ₁ = 1.065 C ₁ -C ₁ = 1.175 C ₂ -C ₃ = 1.409 C ₃ -C ₄ = 1.175 C ₄ -H ₄ = 1.07 H ₄ ...F = 1.918 F-H = 0.954	C ₁ -H ₁ = 1.065 C ₁ -C ₂ = 1.176 C ₂ -C ₃ = 1.406 C ₃ -C ₄ = 1.174 C ₄ -H ₄ = 1.064 X-H = 2.170 ^a F-H = 0.948	C ₁ -H ₁ = 1.067 C ₁ -C ₁ = 1.175 C ₂ -C ₃ = 1.408 C ₃ -C ₄ = 1.175 C ₄ -H = 1.067 Y-H = 2.426 ^b F-H = 0.948
Bond angles (in degrees)	The Complex is linear H ₄ ...F-H is very close to 180°	H ₁ -C ₁ -C ₂ = 180° C ₁ -X...H = 87.3° X...H-F = 177.8° C ₁ -C ₂ -C ₃ -C ₄ -H ₄ arrangement is linear	H-C ₁ -C-2 = 180° C ₁ -Y...H = 89.9° Y...H-F = 180° C ₁ -C ₂ -C ₃ -C ₄ -H ₄ arrangement is linear
Relative stability (a.u.)	-0.003	0	-0.001
H-bond energy	3.1 k cal/mol	1.6 k cal/mol	0.96 k cal/mol

^a Distance from the middle of the C₁-C₂ bonds (X denotes the mid-point); ^b distance from the middle C₂-C₃ bond (Y denotes the mid-point).

insight into the nature of hydrogen bonding in π systems having π bonds in conjugation.

2. Results and discussion

As a part of our ongoing research programme on theoretical aspects of hydrogen bonding in different types of π -bonded systems we have carried out a series of *ab initio* supermolecular MO-SCF calculations at the STO-3G level on diacetylene-

HF complexes. All structural parameters have been fully optimized. Three probable structures have been identified (figure 1a–c). Of the three, the reverse σ -complex (figure 1b) turns out to be the minimum energy structure. This confirms the speculation of Patten and Andrews (1986). The other two structures represent probable π -complexes of which the symmetrical one (figure 1c) is the more stable one. The optimized structural parameters of the σ and π complexes are reported in table 1. The σ -complex has never been detected experimentally with acetylene or butadiene and theoretically, the reverse σ -complex represents a higher energy structure for the HF...C₂H₂ complex. It is interesting to note further that the symmetrical π -structures of the complex is predicted to be more stable than the usual non-symmetrical π -structure. This shows that the HF exchange, if it has to occur at all, cannot occur in a symmetrical double well potential. However, the energy difference between structures 1a and 1c is very small and further refinements in the calculations are needed to settle this point unambiguously. This has obvious bearing on the speculated exchange of HF between the two π sites for which no experimental evidence was discernible in the IR spectra of the complex. The hydrogen-bond energies in each of the three structures have also been reported in table 1. The hydrogen bond is seen to be strongest in the reverse σ complex. The H–F length slightly increases in the reverse σ -complex (0.004 Å) while a very small decrease is noted in the π -complexes (0.001 Å). Much larger basis set calculations are required to confirm these findings.

A more detailed analysis of these results as well as the corresponding findings for diacetylene–hydrogen chloride complexes will be published in due course of time. The dynamics of the H⁺ exchange between the two equivalent π bonds is also under study.

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