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Strained π -systems as hydrogen bond acceptors: the case of benzyne

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Abstract

The behavior of strained π -systems with regard to their interaction with hydrogen bond (HB) donors was studied. The interaction of a model system, strained acetylene, and *ortho*-benzyne with hydrogen fluoride in their singlet and triplet electronic configuration was explored at the B3LYP/6-311++G** and MP2/6-311++G** levels. The energetic results indicate that there are two preferred approaches, the first with the hydrogen fluoride pointing towards one of the radical carbon atoms and the second that corresponds to the HB perpendicular to the π -bond. The atoms in molecules (AIM) analysis of the electron density shows a conflict catastrophic situation for several of the approaches. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

An increasing number of unusual hydrogen bond (HB) acceptors were reported in the last years [1–3], and in particular, the interaction of HB donors with π -systems attracted considerable attention [4,5]. Since the experimental description of the 1:1 complexes of benzene with water [6] and ammonia [7], several clusters of benzene with a variable number of water and methanol molecules were reported [8]. A blue shift was observed in the complexes of benzene and fluorobenzene with

some C–H HB donors [9]. In addition, the biological importance of the HB between aromatic moieties and proton donors was explored [10].

Ortho-benzyne is one of the simplest molecules with a strained tripled bonded structure. A number of physico-chemical properties of this system have been studied both experimentally and theoretically. The minimum electronic configuration of *ortho*-benzyne is the singlet while the lowest triplet configuration is 37.5 kcal/mol above [11]. The thermochemistry of benzyne was used as a benchmark of different computational methods [12,13]. The biradical character of these compounds make their description difficult and in general, DFT methods are only able to partially describe biradicals as was shown in the description

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of the *ortho*-benzyne [14,15]. In contrast, the two additional members of the benzyne family (*meta* and *para*), which show a larger biradical character, are not properly described by DFT methods. Similar results were recently reported for benzdiynes, where the DFT methods properly calculated the properties of 1,3-benzdiynes using the restricted approximation while the 1,4-benzdiynes and 1,2,3,5-tetradehydrobenzene are well described with the unrestricted wavefunction [16].

In this Letter, the abilities as HB acceptor, of strained models of acetylene were explored. In all cases, hydrogen fluoride was used as HB donor and acetylene was forced to adopt different angular dispositions. Its singlet and triplet electronic configurations were considered. Finally, singlet and triplet *ortho*-benzyne was also studied as HB acceptor.

2. Methods

The geometries of the monomers and the complexes were optimized with the program GAUSSIAN 98 [17] using the standard 6-311++G** [18] basis sets at the hybrid Hartree–Fock density functional method (Becke3LYP) [19] and second order Møller–Plesset (MP2) [20] levels. Frequency calculations were carried out to assess the minimum or transition state nature of the structures obtained at the B3LYP/6-311++G** level.

The stability of the wavefunction for the singlet monomers and complexes was tested in the

B3LYP/6-311++G** calculations. This test indicates the possibility of finding an unrestricted wavefunction with a smaller energy than the restricted one for the given geometry.

The interaction energies, $E_I(AB)$, were calculated as the difference between the energy of the complex and the sum of the energies of the monomers. In addition, a corrected interaction energy (E_{I+BSSE}) excluding the inherent basis set superposition error (BSSE) was evaluated. The BSSE was calculated using the Boys–Bernardi counterpoise technique [21].

The topological properties of the electronic charge density were characterized using the atoms in molecules (AIM) methodology [22] with the AIMPAC program package [23] at the B3LYP/6-311++G** level.

3. Results and discussion

The calculated singlet–triplet gap for the acetylene and *ortho*-benzyne at the B3LYP/6-311++G** level are 87 and 32 kcal/mol, respectively. This last values is in good agreement with previous high level ab initio reports (35.1, 32.6 and 35.3 kcal/mol for CASSCF, CASPT2 and CCSD(T) calculations [14], respectively) and experimental data (37.5 ± 0.3) [11] for the *ortho*-benzyne.

Different approaches of hydrogen fluoride to the strained singlet acetylene were studied for several values of the α angle (Fig. 1). Complexes with the triplet acetylene were studied without

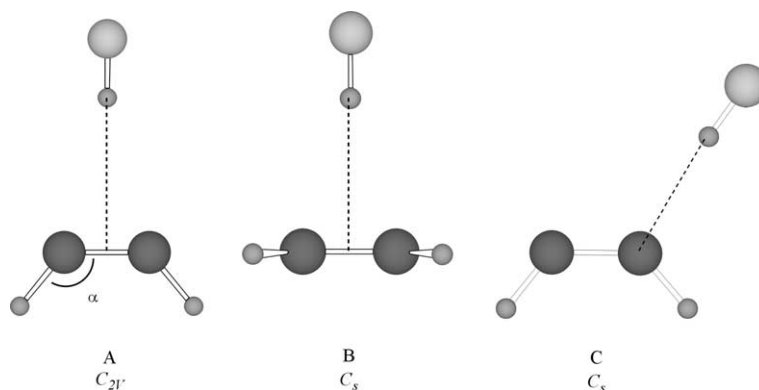


Fig. 1. Representation of the different configurations studied for the HB complexes.

constrains with the exception of those imposed by the symmetry of the systems.

The interaction energies obtained at both, B3LYP/6-311++G** and MP2/6-311++G** levels, are very similar (Table 1). However, the BSSE correction is larger in the MP2 case. Similar behavior of the BSSE correction was already reported [24], because the saturation of the basis set is faster in the DFT methods than in the MP2 ones. To confirm this, a test calculation, MP2/6-311++G(3df,2p)//MP2/6-311++G**, was carried out in the unconstrained complex, obtaining a E_I of -4.81 kcal/mol which is closer to the uncorrected E_I (-4.40 kcal/mol).

Regarding the variation of the interaction energy for different constrained angles of acetylene in its singlet configuration, several aspects are significative. In approach A, a small increment of the interaction energy is observed for an α value of 160° and, as the angle increases, the interaction energy decreases, indicating of smaller electron densities in the interaction space where the HB is formed. In approach B, the interaction energy is very stable showing that the π -bond perpendicular to the molecular plane is almost not altered by the increasing strain. Finally, configuration C is only a stationary structure in the case where acetylene is constrained to 120° , in the remaining cases, it collapses to A.

The small interaction energies obtained in configuration A of the complexes of acetylene in the

triplet configuration (3B_2) indicate the absence of a π -orbital in the molecular plane. The energetic values in configuration B are similar to those of the singlet electronic configuration indicating that the π -orbital in the perpendicular plane is similar. Finally, the values of the interaction energy in configuration C show a very important location of a radical character over the carbon atoms. The frequency analysis of these structures shows that only configuration B is a minimum, while one imaginary frequency is obtained in configuration C and two in A at the B3LYP/6-311++G** level. Interestingly configuration C corresponds to the TS between the two symmetrical dispositions of configuration B, above and below the molecular plane. This process is similar to the proton transfer observed in pyrazole, where the TS shows a C_s symmetry and the structure with the highest symmetry, C_{2v} , corresponds to a second-order saddle point [25].

The geometrical parameters of the complexes between acetylene and hydrogen fluoride are collected in Table 2. In configuration A, the distance between the hydrogen atom of HF and the center of the carbon atoms of acetylene increases from 2.19 to 2.50 Å at the MP2/6-311++G** as the strain of acetylene does, an indication of weaker interactions. In contrast, that distance is almost constant in configuration B (from 2.19 to 2.28 Å). The interaction distances obtained for configuration C are similar to those obtained for other HB between HF and radical species [26].

Table 1

Complexes of acetylene with hydrogen fluoride: total energy (hartree), E_T , interaction energy, E_I , and corrected interaction energy, E_{I+BSSE} (kcal/mol) of the calculated complexes at B3LYP/6-311++G** and MP2/6-311++G** computational levels

	Configuration	α Angle	B3LYP/6-311++G**		MP2/6-311++G**	
			E_I	E_{I+BSSE}	E_I	E_{I+BSSE}
Singlet	A/B	180°	-4.28	-3.97	-4.40	-3.14
Singlet	A	160°	-4.35	-4.01	-4.46	-3.22
Singlet	B	160°	-4.37	-4.04	-4.46	-3.22
Singlet	A	140°	-3.82	-3.45	-3.81	-2.71
Singlet	B	140°	-4.27	-3.88	-4.30	-3.04
Singlet	A	120°	-2.75	-2.42	-2.56	-1.82
Singlet	B	120°	-4.06	-3.59	-3.94	-2.74
Singlet	C	120°	-2.90	-2.43	-2.38	-1.62
Triplet	A	129.3°	-1.57	-1.27	-1.44	-0.67
Triplet	B	128.8°	-3.70	-3.32	-3.12	-2.04
Triplet	C	$131.2^\circ/128.4^\circ$	-3.66	-3.33	-1.55	-0.87

Table 2

Selected geometrical parameters in the acetylene–hydrogen fluoride complexes at the B3LYP/6-311++G** and MP2/6-311++G**

Electronic configuration	α Angle	Configuration A	Configuration B		Configuration C	
Singlet		H... ^a distance	H... ^a distance	H... ^a CH dihedral angle	H...C distance	H...C–C angle
Singlet	180°	2.151 <i>2.194</i>	–	–	–	–
Singlet	160°	2.207 <i>2.255</i>	2.183 <i>2.226</i>	–130.9 <i>–127.7</i>	–	–
Singlet	140°	2.288 <i>2.350</i>	2.176 <i>2.245</i>	–103.8 <i>–108.3</i>	–	–
Singlet	120°	2.410 <i>2.504</i>	2.224 <i>2.282</i>	–99.8 <i>–103.9</i>	2.145 <i>2.339</i>	134.1 <i>134.6</i>
Triplet		2.426 <i>2.513</i>	2.218 <i>2.283</i>	–103.1 <i>–105.5</i>	2.022 <i>2.366</i>	120.1 <i>109.2</i>

Distances in Å, angles and dihedral angles in (deg). The MP2/6-311++G** results are shown in italics.

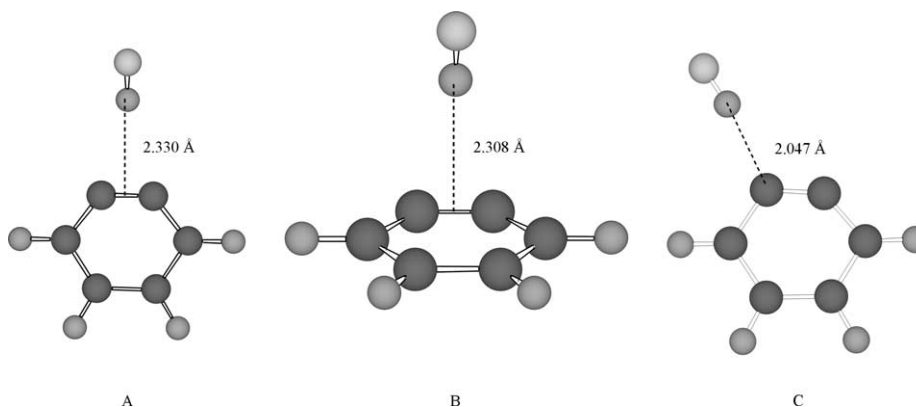
^a Indicates the centroid of the C–C bond.

Fig. 2. Optimized structures for the singlet benzyne–hydrogen fluoride complexes.

The optimized complexes between singlet and triplet *ortho*-benzyne and hydrogen fluoride at the B3LYP/6-311++G** level are shown in Fig. 2, their energetic values are collected in Table 3 and the geometric ones in Table 4. The frequency analysis shows that in the case of the singlet benzyne, configurations B and C are minima, while A corresponds to a transition state connecting the two identical C configurations. In the triplet configuration, as in the case of acetylene triplet, configuration A presents two imaginary frequencies. In contrast, in this case configuration B is a transition state and C is a minimum. The comparison of these energetic results with the corresponding

Table 3

Benzyne–HF complex: total energy (hartree), E_T , interaction energy, E_I , and corrected interaction energy, E_{I+BSSE} (kcal/mol) of the calculated complexes at B3LYP/6-311++G** computational level

Electronic state	Configuration	E_I	E_{I+BSSE}
Singlet	A	–3.71	–3.25
Singlet	B	–3.21	–2.69
Singlet	C	–3.93	–3.42
Triplet	A	–2.09	–1.65
Triplet	B	–3.26	–2.73
Triplet	C	–3.68	–3.18

Table 4

Benzyne–HF complex: interaction parameters in the calculated complexes at the B3LYP/6-311++G** level

Electronic state	Configuration A	Configuration B		Configuration C	
	H... ^a distance	H... ^a distance	H... ^a CH dihedral angle	H...C distance	H...C–C angle
Singlet	2.330	2.308	94.5	2.043	133.0
Triplet	2.372	2.284	105.5	2.003	118.7

Distances in Å, angles and dihedral angles in (deg).

^a Indicates the centroid of the interacting C–C bond.

ones of the benzene–hydrogen fluoride complex ($E_1 = -3.84$ kcal/mol) indicates that in benzyne the π -cloud is weakened over the aromatic ring and reinforced in the localized single unpaired electrons.

The analysis of the electron density shows HB critical points with electron density values in the range of 10^{-2} a.u. (0.007 – 0.025 e/a.u.³) and small and positive laplacians values (0.054 – 0.027 e/a.u.⁵). The topology of the electron density in all A and B configurations studied here indicates that there is a conflict catastrophic configuration with respect to this property. This suggests that a small variation of the system can produce a significant alteration of its topological description. In general, the original bifurcated HB bond is broken maintaining only one of the carbon–hydrogen bonds [27].

4. Conclusion

A theoretical study of the ability of strained π -systems to act as HB acceptors toward hydrogen fluoride was carried out at the B3LYP/6-311++G** and MP2/6-311++G** computational levels. Initially, strained structures of acetylene in its singlet and triplet electronic configurations were considered. As the strain of acetylene increases, the π -bond in the molecular plane weakens due to the formation of a biradical structure, while the π -bond in the perpendicular plane do not change significantly. In the acetylene triplet, the only minimum found corresponds to a structure where the hydrogen fluoride interacts with the π -cloud above the molecular plane. For the benzyne–hydrogen fluoride complexes, the most stable com-

plex, for the singlet and triplet electronic configuration, corresponds to that interacting with one of the biradical carbon atoms (configuration C). The HB with the π -system above the molecular plane (configuration B) is a minimum only for the singlet configuration.

The AIM analysis of these systems in configurations A and B shows that the HB path is bifurcated and overlaps with the C–C interacting bond. The electron density maps of these cases indicates a conflict catastrophic situation.

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