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Chemical Physics 343 (2008) 168–185

Chemical Physics

www.elsevier.com/locate/chemphys

Ab initio and matrix isolation study of the acetylene–furan dimer

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Received 5 April 2007; accepted 15 September 2007
Available online 9 October 2007

Dedicated to Professor Dr. S.D. Peyerimhoff on the occasion of her 70th birthday.

Abstract

Five acetylene–furan dimer structures are identified using ab initio calculations at the second-order Møller–Plesset (MP2) level of theory. The structures are stabilized by two basic types of intermolecular interactions: the CH···O and the CH···π interaction. The CH···π interaction appears in two variants, depending on which molecule provides the hydrogen atom and which molecule the π system. The MP2 results indicate that the CH···π interaction between one of the hydrogen atoms of acetylene and the π system of furan as found in structure **A** is the strongest interaction, followed by the in-plane CH···O interaction in the second most stable acetylene–furan dimer structure **B**. A matrix isolation study shows the acetylene–furan dimer to exist in an argon matrix, but likely rather as structure **B** than as **A**. High level coupled cluster calculations with up to triple excitations (CCSD(T)) yield the interaction energy of structure **A** as about −2.4 kcal/mol in the complete basis set limit and find structure **B** to be nearly isoenergetic with −2.3 kcal/mol. This is confirmed in calculations employing the density functional theory combined with symmetry adapted intermolecular perturbation theory (DFT-SAPT) approach yielding interaction energies of −2.3 and −2.0 kcal/mol for **A** and **B**, respectively. DFT-SAPT also helps to understand the importance of the electrostatic, induction and dispersion interaction energies and their respective exchange counterparts for the stability of the various acetylene–furan dimer structures. The CH···O and CH···π interactions are furthermore analyzed with the help of the atoms in molecules (AIM) theory.

Keywords: Hydrogen bond; Acetylene; Furan; Ab initio calculation; Matrix isolation; Atoms in molecules theory AIM; Intermolecular interactions; Symmetry adapted perturbation theory; Density functional theory

1. Introduction

Furan has many applications in natural product synthesis, material science and other fields of chemistry. It is used as an initial substance for many important syntheses and as a building block for many materials [1]. Therefore, furan and its complexes with small molecules have been subject to many experimental and theoretical studies, and especially the furan–hydrogen halide dimers were studied extensively [2–18].

Recently some of us presented combined theoretical and experimental studies on the interactions of formic acid with acetylene and formic acid with furan [19–21]. Therefore, the investigation of the interactions between acetylene and furan is a logical next step to provide a deeper insight into weakly interacting complexes. Both the π system and the lone electron pairs at the oxygen atom of furan can serve as hydrogen bond acceptors, and to some extent this is also true for the π system of acetylene. On the other

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doi:10.1016/j.chemphys.2007.09.053

hand, the acidic CH groups of acetylene can serve as hydrogen donors. In particular the competition between the two furan acceptor sites makes it interesting and challenging to investigate the acetylene–furan complex.

In this study, computational and experimental results for the acetylene–furan dimer are presented. Experimental results are obtained from matrix isolation infrared spectroscopy, computational results from various levels of ab initio theory such as second-order Møller–Plesset (MP2) theory, its spin-component-scaled variant SCS-MP2 [22], and single and double excitation coupled cluster theory including perturbative triple excitations (CCSD(T)). The latter method generally is believed to be the most accurate supermolecular approach for intermolecular interactions applicable to systems of the size of acetylene–furan.

Symmetry adapted intermolecular perturbation theory (SAPT) [23,24] is an alternative to CCSD(T) which provides a more detailed insight into the physics of intermolecular interactions. In SAPT, the interaction energy is calculated as a sum of terms of distinct physical origin, i.e., first-order electrostatic, $E^{(1)}_{\text{el}}$, second-order induction, $E^{(2)}_{\text{ind}}$, and dispersion, $E^{(2)}_{\text{disp}}$, interaction contributions. Each of these terms is accompanied by a corresponding exchange correction due to the simultaneous exchange of electrons between the monomers, abbreviated as $E^{(1)}_{\text{exch}}$, $E^{(2)}_{\text{exch-ind}}$ and $E^{(2)}_{\text{exch-disp}}$, respectively. Contributions of third- and higher-orders in the intermolecular interaction potential can be estimated by the δ(HF) term which is the difference between the supermolecular Hartree–Fock (HF) energy and the sum of electrostatic, induction and their exchange counterparts obtained at the HF level. Recently, a variant of SAPT called DFT-SAPT [25–28] was introduced having a better scaling behaviour compared to the original many-body version of SAPT [23]. The efficiency of DFT-SAPT and of the similar SAPT(DFT) approach [29–31] was further enhanced by density-fitting implementations [32–34]. DFT-SAPT was shown to yield an accuracy comparable to CCSD(T) for the benzene dimer [32] and the acetylene–benzene [35] dimers, respectively, and was also employed here.

The outline of the paper is as follows. In the next section, all computational methods used in this study are briefly overviewed. This is followed by a short description of the matrix isolation experiments. Afterwards various structures of the acetylene–furan dimer resulting from MP2 geometry optimizations are presented and they are analyzed according to the theory of atoms in molecules (AIM). This subsection is followed by a presentation of the outcome of matrix spectroscopy. The not fully convincing agreement between experiment and theory is further investigated by higher level ab initio computations attempting to reach the complete basis set limit of CCSD(T) and DFT-SAPT in the next subsection. Finally, the interaction energy contributions calculated from DFT-SAPT are presented to show the governing forces in different orientations of acetylene–furan dimer. This study is finished by reporting its most important conclusions.

2. Computational methods

The multiple minima hypersurface (MMH) approach [19,36–40] was used for searching minima of the acetylene–furan dimers. One thousand randomly arranged structures were generated as starting points, and the resulting geometries were optimized and analyzed using the PM3 [41,42] and AM1 [43] semiempirical quantum mechanical Hamiltonians. The relevant configurations were further refined using ab initio methods at various levels of theory.

These ab initio refinements were performed using the Gaussian 98 and Gaussian 03 programs [44,45]. The equilibrium geometries and vibrational frequencies were calculated with tight convergence criteria at the SCF level followed by second-order Møller–Plesset perturbation theory, MP2 [46], correlating valence electrons only. The force constants were calculated when necessary. Pople's 6-31G(d,p) and 6-311++G(d,p) basis sets as well as augmented and non augmented Dunning's correlation consistent double and triple ζ basis sets (cc-pVDZ, aug-cc-pVDZ and cc-pVTZ) were used [47–49]. Here, only the results with the 6-31G(d,p), 6-311++G(d,p) and cc-pVTZ basis sets are discussed. Vibrational frequencies were calculated at all levels of theory. The stabilization energies were calculated by subtracting the energies of the monomers from those of the complexes. Note that the stabilization energy, E_{stab}, may be seen as the sum of two contributions: the relaxation energy, E_{rel}, and the interaction energy, E_{int}. The former is the – necessarily repulsive – energy contribution accompanying changes of the monomer geometry parameters from their *in vacuo* values to the ones they assume in the dimer. The latter is the energy of interaction between the distorted monomers. The interaction (and in consequence also the stabilization) energies were also corrected for the basis set superposition error (BSSE) using the counterpoise (CP) correction scheme of Boys and Bernardi [50]. Vibrational zero point energy (ZPE) corrections to the stabilization energy in the harmonic approximation were also calculated.

To investigate the influence of the BSSE on the geometries of the complexes, the acetylene–furan dimer geometries were also optimized at the MP2/6-31G(d,p) level of theory using CP corrections during the optimization process [50]. In addition, the geometries were optimized without CP correction at the same level of theory to compare the influence of the BSSE on the stabilization energies as well as on the geometries.

Atoms in molecules theory (AIM) has been widely used to study and characterize H-bonds and weak interactions [51]. The localization of critical points and the calculation of electron densities and the Laplacian at these points are useful tools to study molecular interactions. According to this theory, the presence of an atomic interaction line between a pair of atoms is the necessary and sufficient condition to consider that these are bound. The path of maximum charge density between the nuclei is called bond path, and the (3,−1) critical point is called bond critical