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2-Ethynylpyridine dimers: IR spectroscopic and computational study

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ABSTRACT

2-ethynylpyridine (2-EP) presents a multifunctional system capable of participation in hydrogen-bonded complexes utilizing hydrogen bond donating (≡C—H, Aryl—H) and hydrogen bond accepting functions (N-atom, C≡C and pyridine π-systems). In this work, IR spectroscopy and theoretical calculations are used to study possible 2-EP dimer structures as well as their distribution in an inert solvent such as tetrachloroethene. Experimentally, the ≡C—H stretching vibration of the 2-EP monomer absorbs close to 3300 cm^{-1}, whereas a broad band with maximum around 3215 cm^{-1} emerges as the concentration rises, indicating the formation of hydrogen-bonded complexes involving the ≡C—H moiety. The C≡C stretching vibration of monomer 2-EP close to 2120 cm^{-1} is, using derivative spectroscopy, resolved from the signals of the dimer complexes with maximum around 2112 cm^{-1}. Quantum chemical calculations using the B3LYP + D3 model with counterpoise correction predict that the two most stable dimers are of the π-stacked variety, closely followed by dimers with intermolecular ≡C—H···N hydrogen bonding; the predicted red shifts of the ≡C—H stretching wavenumbers due to hydrogen bonding are in the range 54–120 cm^{-1}. No species with obvious hydrogen bonding involving the C≡C or pyridine π-systems as acceptors are predicted. Dimerization constant at 25 °C is estimated to be $K_2 = 0.13 \pm 0.01\ \text{mol}^{-1}\ \text{dm}^3$.

1. Introduction

The simplest multifunctional molecule capable of forming weak hydrogen bonds employing both hydrogen bond donating and accepting sites is ethynylbenzene (EB). With one hydrogen bond donating site (≡C—H) and two hydrogen bond accepting sites (C≡C and phenyl π systems), all of which are classified as rather weak, it can produce versatile interaction patterns. The resulting one is often highly unpredictable and usually considered to be dictated by the distribution and strength of the available hydrogen bonding centers of the another protagonist in a hydrogen-bonded complex [1–4]. In this context, the dimerization of EB attracted considerable interest [4–6]. The combination of IR–UV double resonance spectroscopy and high-level ab initio calculations demonstrated that the most stable EB···EB dimer is the one with an antiparallel π-stacked structure, i.e., the dimerization is primarily driven by π···π dispersion interactions between phenyl rings [5]. Furthermore, it is hypothesized to be the first π-stacked dimer without heteroatoms.

The substitution of a particular C— or H–atom by a heteroatom in EB induces a change in the hydrogen bonding interaction pattern. For instance, the impact of H–atom substituents and their position on the overall disturbance of the hydrogen bonds interplay is demonstrated by the hydrogen-bonded complexes between fluoroethynylbenzenes and alcohols [7], and between ethynylbenzonitrile and water [8]. The impact of the replacement of a C–atom in the phenyl ring by a heteroatom on the dimer formation is not reported so far. In this respect, 2-ethynylpyridine (2-EP) is an appropriate candidate. Unlike 3- and 4-ethynylpyridines, 2-EP is liquid at room temperature [9] implying that, as in EB case, it undergoes self-association but lacks higher ordering at standard conditions. In addition, the N–atom is electronegative and is a stronger acceptor of the hydrogen bond than are the π systems on EB. The ability of 2-EP to make hydrogen-bonded complexes with compounds such as trimethyl phosphate and its analysis by vibrational spectroscopies is already reported [10,11]. We thus expect that the combination of IR spectroscopy and quantum chemical calculations is a promising strategy in the study of the formation of 2-EP dimers.

In this work, the competition between different hydrogen bond donating and hydrogen bond accepting centers and the resulting dimer structures of 2-EP will be examined. IR spectroscopy is proven to be an indispensable tool in the exploration of the hydrogen-bonded systems [12]. Even when weak hydrogen bonds are under study, it can distinguish the signatures that originate due to free and hydrogen-bonded oscillators. As 2-EP can form multimers by employing simultaneously all hydrogen bond donating and hydrogen bond accepting sites, it is of importance to conduct the experiment in a concentration range in which only monomers and dimers can be assumed to exist. This strategy ensures that the signals attributed to hydrogen-bonded oscillators are

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due to dimer formation and are not obscured by the signals of oligomers.

The IR signals of interest in the present investigation are due to the ≡C—H and C≡C stretching vibrations of 2-EP. Free or non-hydrogen-bonded oscillators will be denoted ≡C—H and C≡C, whereas those involved in a hydrogen bond formation are indicated as ≡C—H··· and C≡C···. Apart from the possible assignment of particular signatures to 2-EP···2-EP dimers, the dimerization constant K_2 at room temperature will be determined. The investigation is supported by the results of DFT-D type quantum chemical calculations, i.e., density functional theory (DFT) supplemented with an empirical dispersion correction (D) [13]. Additional information is provided as Supplementary Material (S1 – S12).

2. Calculations

All calculations were carried out with the GAUSSIAN09 software package [14] by using B3LYP density functional theory (DFT) [15,16] together with Grimme's empirical dispersion correction D3 [13]. The B3LYP + D3 combination performed well in the 'blind test' carried out by Taylor et al. [17]. The calculations were carried out with the 6–311++G(d,p) basis set [14], using an ultrafine integration grid and tight convergence criteria (grid = ultrafine, scf = tight, opt = tight) [14]. Calculations on the dimers were corrected for basis set superposition error (BSSE) by applying the counterpoise option [14,18]. The results refer to the gas phase; inclusion of a self-consistent solvent reaction field (SCRF) is not possible with the counterpoise option [14]. The calculated dimer structures are displayed in Fig. 1 with indication of binding energies corrected for BSSE and vibrational zero point energies (ZPE). Pertinent harmonic vibrational wavenumbers scaled by the factor α = 0.96 are collected in Table 1. Nuclear coordinates, energy data, and unscaled wavenumbers are provided as Supplementary Material (S1–S9). Moreover, as a test of the performance of the present theoretical procedure, it was applied to the pyridine-ethyne complex. An outline of the results for this complex is provided as S10: the computed equilibrium geometry with a non-linear hydrogen bond is in good agreement with the results of a high-level ab initio calculation recently published by Mackenzie et al. [19].

3. Experimental

3.1. Chemicals

2-Ethynylpyridine (2-EP; brown liquid at room temperature, b.p. = 85 °C at 12 mmHg, purity 98%) and tetrachloroethene (C_2Cl_4; colorless liquid at room temperature, b.p. = 122 °C, spectroscopic grade) were purchased from Sigma Aldrich and Acros Organics, respectively, and were used as received. Binary mixtures were prepared by dissolving 2-EP in C_2Cl_4 in the concentration range 0.001 mol dm^{-3} ≤ c_0(2-EP) ≤ 9.818 (neat liquid) mol dm^{-3}.

3.2. FT IR Spectra of 2-EP in C_2Cl_4

IR spectra were measured on an ABB Bomem MB102 spectrometer, equipped with CsI optics and a DTGS detector with nominal resolution of 2 cm^{-1} and 10 scans at 25 °C. Spectra of solutions in concentration range 0.00130 mol dm^{-3} ≤ c_0(2-EP) ≤ 9.8175 mol dm^{-3} (neat liquid) were collected by using sealed cells equipped with CaF_2 windows, the path length of which was determined by Bertie's procedure using dichloromethane (CH_2Cl_2) as a secondary standard [20]. Between the measurements of different solutions, the cell was emptied, dried with N_2, washed twice with the studied solution; the cell is then refilled and the data were recollected. The spectra of each sample were collected three times.

3.3. Spectral Analysis

Vibrational signatures that are most strongly affected by the hydrogen bond formation are those originating from the stretching motions of the ≡C—H and C≡C moieties. Therefore, the following spectral ranges were analyzed: 3600–3095 cm^{-1} (ν(≡C—H)) and 2165–2060 cm^{-1} (ν(C≡C)). The parameters of the signal attributed to the ≡C—H stretching are used in determination of the concentration of 2-EP at which dimerization starts and in determination of the dimerization constant (K_2). Spectral analysis was conducted as follows: after the baseline correction, the absorbance of the ≡C—H stretching band of 2-EP was determined from the band maximum (3308 cm^{-1}), divided by the cell pathlength (d), and used in calculation of ε(3308 cm^{-1}) from Lambert–Beer's law. According to the latter, only the spectra of solutions in which ≡C—H stretching band of 2-EP appears at 3308 cm^{-1} (0.00130 mol dm^{-3} ≤ c_0(2-EP) ≤ 0.48898 mol dm^{-3}) are taken in consideration [21]. The parabolic dependence of the absorbance divided by the pathlength on the concentration of 2-EP indicated that the solutions in this concentration range are dominated by monomers and a certain amount of dimers. The dimerization constant (K_2) was estimated simultaneously with ε(3308 cm^{-1}). The relations between K_2 and Lambert–Beer's law are briefly described in Supplementary Materials (S11), whereas more details can be found in [22]. When the analysis of the baseline corrected raw spectra was insufficient in

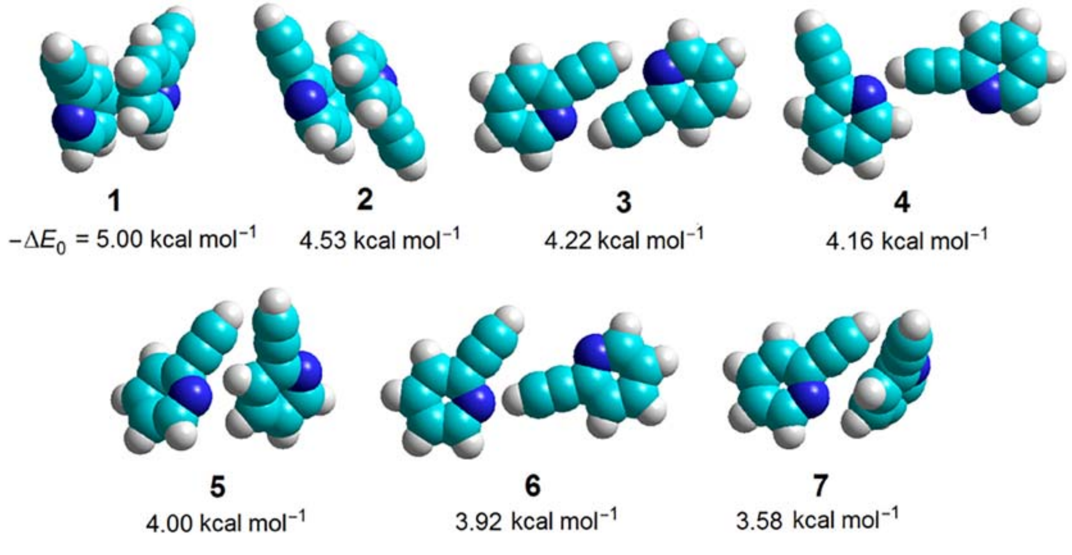

Fig. 1. Calculated structures of dimers **1**–**7** with indication of BSSE and ZPE corrected binding energies.