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Accepted Manuscript

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Please cite this article as: Danijela Bakarić, Josipa Alerić, Tijana Parlić-Risović, Jens Spanget-Larsen , Hydrogen bonding between ethynyl aromates and triethylamine: IR spectroscopic and computational study. Saa (2018), https://doi.org/10.1016/j.saa.2018.10.058

Hydrogen bonding between ethynyl aromates and triethylamine: IR spectroscopic and computational study

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Abstract

Ethynylpyridines (EPs) and ethynylbenzene (EB) are multifunctional systems able to participate in hydrogen-bonded complexes as both donors and acceptors of the H-atom. Their structures and stabilities are mainly a function of the hydrogen-bonding properties of the partner in the complex and the surroundings in which the complexation occurs. In this paper, IR spectroscopy and quantum chemical calculations are employed to characterize hydrogen-bonded complexes of 2- and 3-EP and EB with triethylamine (TEA) in tetrachloroethene (C_2Cl_4) solution. The formation of $\equiv C-H \cdots N$ hydrogen bonds is experimentally confirmed by the appearance of TEA concentration-dependent signals in the IR spectra of the EPs and EB. Along with the signals due to unassociated $\equiv C-H$ and $C \equiv C$ oscillators (2-EP: 3308 cm^{-1} and 2120 cm^{-1}; 3-EP: 3308 cm^{-1} and 2116 cm^{-1}; EB: 3313 cm^{-1} and 2113 cm^{-1}) weak, red-shifted signals arise at ~3215 ± 5 cm^{-1} and ~2105 ± 5 cm^{-1} which are assigned to the stretching vibrations of hydrogen-bonded $\equiv C-H \cdots$ and $C \equiv C \cdots$ oscillators, respectively. This result is at variance with those of previous investigations of EB and TEA in the gas phase. In the 2-EP$\cdots$TEA complex these bands remain at the same position with increasing TEA concentration. However, in the 3-EP$\cdots$TEA and EB$\cdots$TEA complexes the $\equiv C-H \cdots$ stretching band demonstrates a slightly reduced red-shift as the TEA concentration increases, whereas the $C \equiv C \cdots$ stretching band absorbs at the same wavenumber in the investigated TEA concentration range. The results of B3LYP-D3 calculations indicate that complexes with more or less linear $\equiv C-H \cdots N$ intermolecular hydrogen bonds are more stable than other, dispersion-driven complexes. Complexes with the C_s symmetrical TEA conformer are predicted to have larger binding energy than those formed with the C_3 and C_1 symmetrical conformers. The predicted IR spectral shifts are slightly different for complexes with the three different TEA conformers. Association constants of hydrogen-bonded complexes at 26 °C are estimated to be ~0.1 mol^{-1} dm^3.

1. Introduction

Ethynylbenzene (EB) is a relatively simple organic molecule that possesses one weak hydrogen bond donating site (C≡C−H group) and two weak hydrogen bond accepting sites: π system of triple bond (C≡C) and of phenyl ring [1]. In order to examine multi-functionality of EB in terms of hydrogen bond formation, demonstrated to be of outmost importance in crystal engineering [2–4], various hydrogen bond donors and / or hydrogen bond acceptors such as water [5–7], simple alcohols [5,7,8] and amines [5,7–10] were taken as partners in the hydrogen-bonded complex [7]. The utility of IR−UV double resonance spectroscopic techniques supported by the results of MP2 calculations enabled registration of often unexpected interaction patterns. In particular, it was demonstrated that when EB is in interaction with ammonia the primacy is reserved for ≡C−H···N hydrogen bonding interaction [5,8], whereas with methylamine [8,9] hydrogen bonding is overcome by simultaneous interplay of N−H···π and CH_3···C≡C interactions. Moreover, hydrogen-bonded complexes of EB and triethylamine (TEA) in the gas phase are driven by multidentate interactions between −C−H groups of TEA and the π-systems of EB [8,10] and not by anticipated ≡C−H···N interaction, regardless of the high basicity of the N−atom according to the high donor number of TEA (*DN*=1.57) [11]. Overall, a fine balance of electrostatic and dispersion forces between hydrogen bond donor and hydrogen bond acceptor has been assigned as the ultimate factor that determines geometry of the formed hydrogen-bonded complex. One should emphasize that the interaction between EB and TEA was studied in a gas phase and that the presence of a solvent can to a certain extent change the complex structure, especially when the association between weak hydrogen bond donors and acceptors

takes place. For instance, when studying association of EB and ethanol in C_2Cl_4, it was demonstrated that, aside from the complex suggested by Singh and Patwari [12] from IR-UV double resonance measurements, the involvement of C≡C moiety in a hydrogen-bonded complex was experimentally confirmed as well [13]. Thus, it would be of great interest to reveal how the association of TEA with EB is effected by the condensed surroundings. Further, a delicate tuning between electrostatic and dispersive contributions in a hydrogen-bonded complex can be disturbed also by introducing aza-replacements in EB. From this point of view, the interaction of TEA with ethynylpyridines (EPs) would be very informative as well. It has been shown how the position of aza-replacement affects the interaction with trimethylphosphate (TMP) in C_2Cl_4 [14,15] so it is reasonable to expect that the response of 2-EP, when in hydrogen-bonded complex with TEA, would be different from those of 3-EP and EB.

When a hydrogen bonding ability of a certain molecule is to be characterized in terms of thermodynamic parameters, such as association constant (K_c), standard experimental protocol is a high-dilution method. Briefly, a series of ternary solutions constituted from a hydrogen bond donor and a hydrogen bond acceptor in an inert solvent (such as C_2Cl_4 [16,17]) are to be prepared [18]; hydrogen bond donor should be of approximately constant concentration across the series, whereas hydrogen bond acceptor should vary within a certain concentration range. As Allerhand and Schleyer pointed out [16], the signatures of both non-hydrogen-bonded and hydrogen-bonded species generally vary with the solvent change, the latter including also a medium in which the concentration of a hydrogen bond acceptor in the inert solvent is changed. However, if the solvent and the hydrogen bond acceptor have similar G values, the scale of which is derived empirically and presented in their paper [16], the corresponding signals are expected to be independent on the concentration of the hydrogen bond acceptor. Since G values for TEA and C_2Cl_4 are, respectively, 62 and 64, one can expect that in their

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mixtures, regardless of their ratio, the bands originating from the stretching of non-hydrogen-bonded ($\equiv$C$-$H and C$\equiv$C) and hydrogen-bonded ($\equiv$C$-$H$\cdots$ and C$\equiv$C$\cdots$) oscillators should be independent on the concentration of the hydrogen bond acceptor (TEA). Eventual discrepancies from this rule imply higher solvent sensitivity of the hydrogen-bonded oscillators as well as the impact of certain steric and substituent effects [19].

In order to reveal how the medium constituted from the solvents of similar G values impacts the interplay of electrostatic and dispersion forces in multifunctional molecules, hydrogen-bonded complexes between 2-ethynylpyridine (2-EP), 3-ethynylpyridine (3-EP) and EB with TEA will be explored. Since TEA can be found in three different conformations [20], it is anticipated that this may influence behavior of certain vibrational signatures. The investigation is supported by the results of IR spectroscopy and of quantum chemical calculations. Additional information is provided as Supplementary Material, referred to in the ensuing text as S1 – S9.

2. Calculations

Quantum chemical calculations were performed with the GAUSSIAN09 software package [21] by using B3LYP density functional theory (DFT) [22,23] together with Grimme's empirical dispersion correction D3 [24,25]. The B3LYP-D3 calculations were carried out with the 6-311++G(d,p) basis set, using an ultrafine integration grid and tight convergence criteria (grid=ultrafine, opt=tight) [21]. Detailed results for the three conformers of TEA and for monomer 2-EP, 3-EP, and EB are provided as S1 – S4. Calculations on the complexes of 2-EP, 3-EP, and EB with TEA were corrected for basis set superposition error (BSSE) by applying the counterpoise option [21,26]. In a previous study, the present level of theory lead to adequate prediction of the vibrational key frequencies of 2-EP dimers [27]. Computed

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geometries and other data for the most significant complexes are provided as S5 − S7. All calculational results refer to systems in the gas phase.

3. Experimental

3.1 Chemicals

Ethynylbenzene (EB; a dark yellow liquid at room temperature, b.p.=142-144 °C, purity 99 %, ρ(26 °C)= 0.924700 g cm^{-3}) and tetrachloroethene (C$_2$Cl$_4$; a colorless liquid at room temperature, b.p.= 122 °C, spectroscopic grade, ρ(26 °C)= 1.612728 g cm^{-3}) were purchased from Acros Organics. 2-Ethynylpyridine (2-EP; a dark brown liquid at room temperature, b.p.=85 °C at 12 mmHg, purity 99 %, ρ(26 °C)= 1.009796 g cm^{-3}) and 3-ethynylpyridine (3-EP; a solid at room temperature, m.p.=39-40 °C, purity 99 %) were purchased from Sigma Aldrich. All abovementioned chemicals were used as received. Triethylamine (TEA; a colorless liquid at room temperature, b.p.= 88-90 °C, purity p. a. 99 %, ρ(26 °C)= 0.723322 g cm^{-3}) was purchased from Sigma Aldrich and additionally dried under reflux on KOH and distilled over active molecular sieves (4 Å) under Ar. Densities of the studied liquids were determined by a densitometer DMA 5000-Anton Paar.

3.2 Preparation of solutions

The experimental design for characterization of the final outcome of hydrogen bond interplay is based on high dilution method [18]. Briefly, a set of binary mixtures of hydrogen bond acceptor (TEA) is prepared in certain concentration range in an inert solvent (C$_2$Cl$_4$), the lower and upper limits of which are chosen depending on the expected interaction strength (more details on choosing the concentration range is provided in [28]. This binary mixtures set is further used for preparation of ternary mixtures set, in which the third compound is

hydrogen bond donor (ethynyl aromates). The concentration of hydrogen bond donor is held aproximatelly constant across the set and is chosen according to the results presented in [14].

Thus, two sets of the solutions were prepared:

i) a set composed of binary solutions of TEA in C_2Cl_4 in concentration range c_0(TEA)= 0.09794 mol dm^{-3} - 1.00188 mol dm^{-3} was prepared (10 solutions). This set was used for the preparation of ternary solutions set with EPs and EB.

ii) in ternary solution set the concentrations of EPs and EB were held almost constant: c_0(EPs)≈0.05 mol dm^{-3}, c_0(EB)≈0.07 mol dm^{-3}. In ternary solutions with 3-EP dissolved in TEA in C_2Cl_4 the analytical concentrations of TEA were 0.09794 mol dm^{-3} - 1.00188 mol dm^{-3}. For 2-EP and, respectively, EB dissolved in TEA in C_2Cl_4 the final analytical concentrations of TEA was in range 0.09743 mol dm^{-3} - 0.99698 mol dm^{-3} and, respectively, in range 0.09712 mol dm^{-3} - 0.99416 mol dm^{-3}.

This ternary mixtures set was used for determination of the association constants (K_c) of EPs···TEA and EB···TEA hydrogen-bonded complexes.

The concentration of each compound was determined gravimetrically, i. e., by weighing of each compound in particular mixture up to five decimal points.

3.3 Measurements

FTIR spectra were recorded on an ABB Bomem MB102 spectrometer equipped with CsI optics and DTGS detector. IR spectra of solutions at room temperature (t = 26 ± 1 °C) were recorded in sealed cell equipped with CaF_2 windows with effective pathlength determined by employing Bertie's procedure [29] using dichloromethane (CH_2Cl_2) as a secondary standard (*d*= 985.79 μm). Each sample was recorded three times; between sequential measurements, the cell was emptied, dried with N_2, washed twice with the studied solution and the data were recollected.

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All the spectra were obtained with 10 scans and with nominal resolution of 2 cm^{-1}. 10 scans were considered to be sufficient for obtaining very smooth band features in spectral range where ≡C-H and, respectively, C≡C moieties of EPs and EB absorb (3360-3260 cm^{-1} and, respectively, 2145-2080 cm^{-1}).

3.4 Spectral analysis

As the absorbance of the band maximum stands as the most sensitive and the most reliable response of hydrogen bond donors (ethynyl aromates) in the presence of hydrogen bond acceptors (TEA) at given concentration, this spectroscopic parameter was aimed to be determined in all mixtures sets [18].

In order to determine the K_c from ternary (EPs or EB+TEA in C$_2$Cl$_4$) mixtures, spectral range 3360-3260 cm^{-1} was analyzed. After subtracting the spectrum of pure solvent (C$_2$Cl$_4$) from ternary mixtures spectra, the difference spectra were baseline corrected (2 points) and the maximum absorbance of ≡C−H stretching band of ethynyl aromates was determined. Using the molar absorption coefficient of ethynyl aromates at the maximum of absorbance [14] and initial concentrations of hydrogen bond donor and acceptor, K_c was determined [18] (exact numbers are provided in the Section 4.3).

C≡C stretching signals of ethynyl aromates (EPs and EB with TEA in C$_2$Cl$_4$) were analyzed in a qualitiative fashion in the spectral range 2155-2080 cm^{-1}.

Apart from determination of K_c, spectral phenomena related to the displacement of vibrational signatures in the ≡C−H stretching range are discussed.

4. Results and discussion

4. 1 Calculations: structures and vibrational spectra of monomers and complexes

TEA. As analysed in detail by Takeuchi et al. [20] in 1992, TEA is distributed in the gas phase and in solution as three conformers with molecular symmetries C_3, C_s, and C_1; in the following the three conformers are referred to as TEA(C_3), TEA(C_1), and TEA(C_s). According to the gas electron diffraction results by Takeuchi et al. [20], the composition is 56% TEA(C_3) + 33% TEA(C_1) + 11% TEA(C_s). The conformer TEA(C_3) is thus expected to be the most abundant of the three, and also the most stable [20].

More recently, Chandra et al. [30] investigated the structure of TEA with B3LYP calculations, but found only two stable configurations which they labeled as the symmetric and the asymmetric one, TEA-S and TEA-AS. As far as we can judge form the data provided [30], TEA-S corresponds to TEA(C_3) and TEA-AS to TEA(C_s). Our B3LYP-D3 results for TEA are provided as S1. The relative energies (including zero point vibrational energies, ZPVE) predicted for TEA(C_3), TEA(C_1), and TEA(C_s) are 0, +0.60, and +0.69 kcal/mol, respectively. This is consistent with the results of Takeuchi et al. [20] and Chandra et al. [30]. TEA(C_s) is thus probably the least stable of the three conformers, but as we shall see below, TEA(C_s) is predicted to form stronger hydrogen-bonded complexes with 2-EP, 3-EP, and EB than the other two TEA conformers. Chandra et al. [30] have discussed the hydrogen bonding properties of TEA in terms of anomeric effects.

2-EP, 3-EP, and EB and their complexes with TEA. Predicted molecular geometries and energies for monomer 2-EP, 3-EP, and EB are provided as S2 − S4. The calculated harmonic ≡C–H and C≡C stretching transitions are listed in Table 1 (headings ≡C–H and C≡C). A large number of calculations were carried out in order to investigate the possible formation of complexes with TEA. The most stable ones were found to involve direct, more or less linear

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≡C–H···N hydrogen-bonding. A number of less stable, primarily dispersion-driven complexes were predicted, displaying a variety of structures. See for example Fig. 1 which shows five different complex geometries for 2-EP + TEA(C$_3$); the hydrogen-bonded complex is shown as the top-left structure. We cannot be sure that we have located all possible complex structures. However, the predicted ≡C–H and C≡C stretching transitions for the located dispersion-driven structures were in all cases insignificantly shifted from those of the uncomplexed monomers. For this reason, we shall in the following consider only those complexes with ≡C–H···N hydrogen-bonding, for which substantial IR spectral shifts are calculated (Table 1, headings ≡C–H··· and C≡C···).

$-\Delta E_0$ = 4.57 kcal mol^{-1} 3.79 kcal mol^{-1} 3.56 kcal mol^{-1}
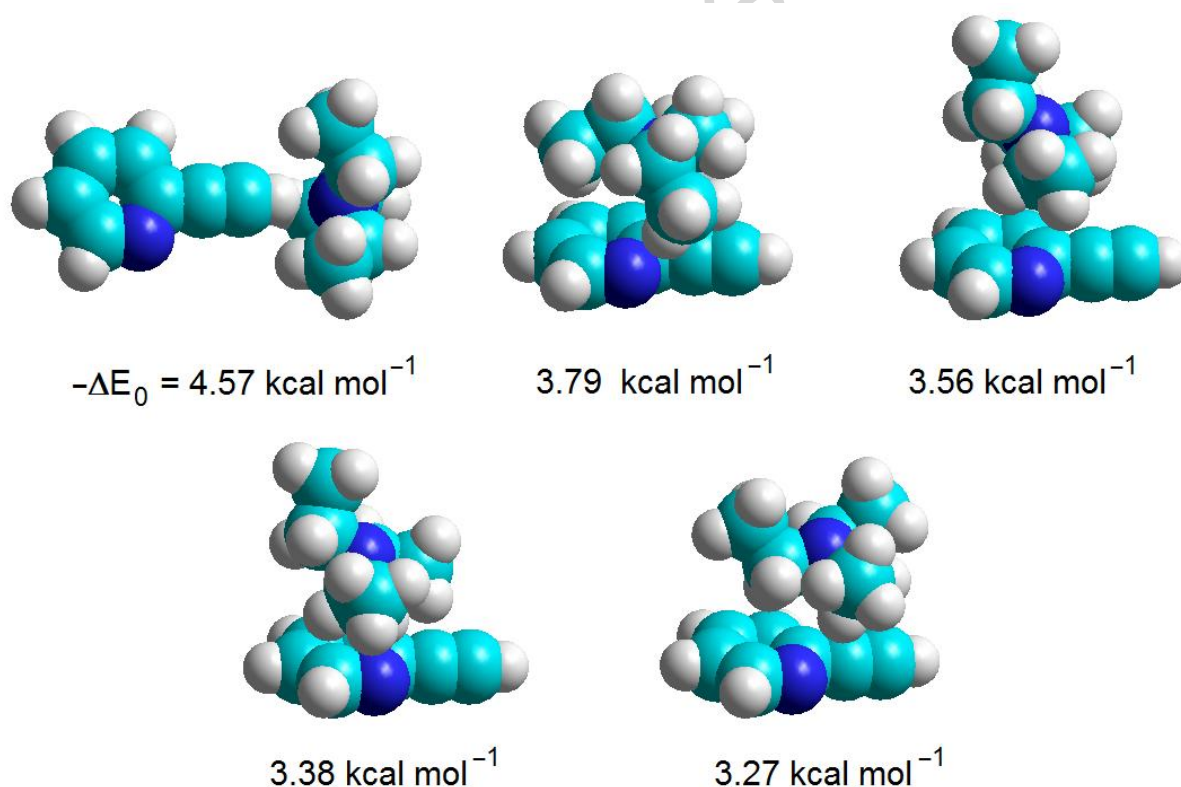
3.38 kcal mol^{-1} 3.27 kcal mol^{-1}

Fig. 1. Calculated complexes between 2-ethynylpyridine (2-EP) and the most stable conformation of triethylamine (TEA(C$_3$)) with indication of calculated BSSE and ZPVE corrected binding energies.

Fig. 2 shows the computed hydrogen-bonded complexes of 2-EP (Fig. 2a), 3-EP (Fig. 2b) and EB (Fig. 2c) with the three TEA conformers TEA(C_3), TEA(C_1), and TEA(C_s). In some cases, the existence of different rotamers of the hydrogen-bonded complexes were predicted, corresponding to rotation around the C–H···N hydrogen bond axis. For example, three individual rotamers of the 2-EP···TEA(C_1) complex were obtained, while only one was found for 2-EP···TEA(C_3) and 2-EP···TEA(C_s). But since binding energies and vibrational transitions for different rotamers were predicted to be nearly indentical, we present here only results for one representative rotamer (Fig. 2, S5 - S7).
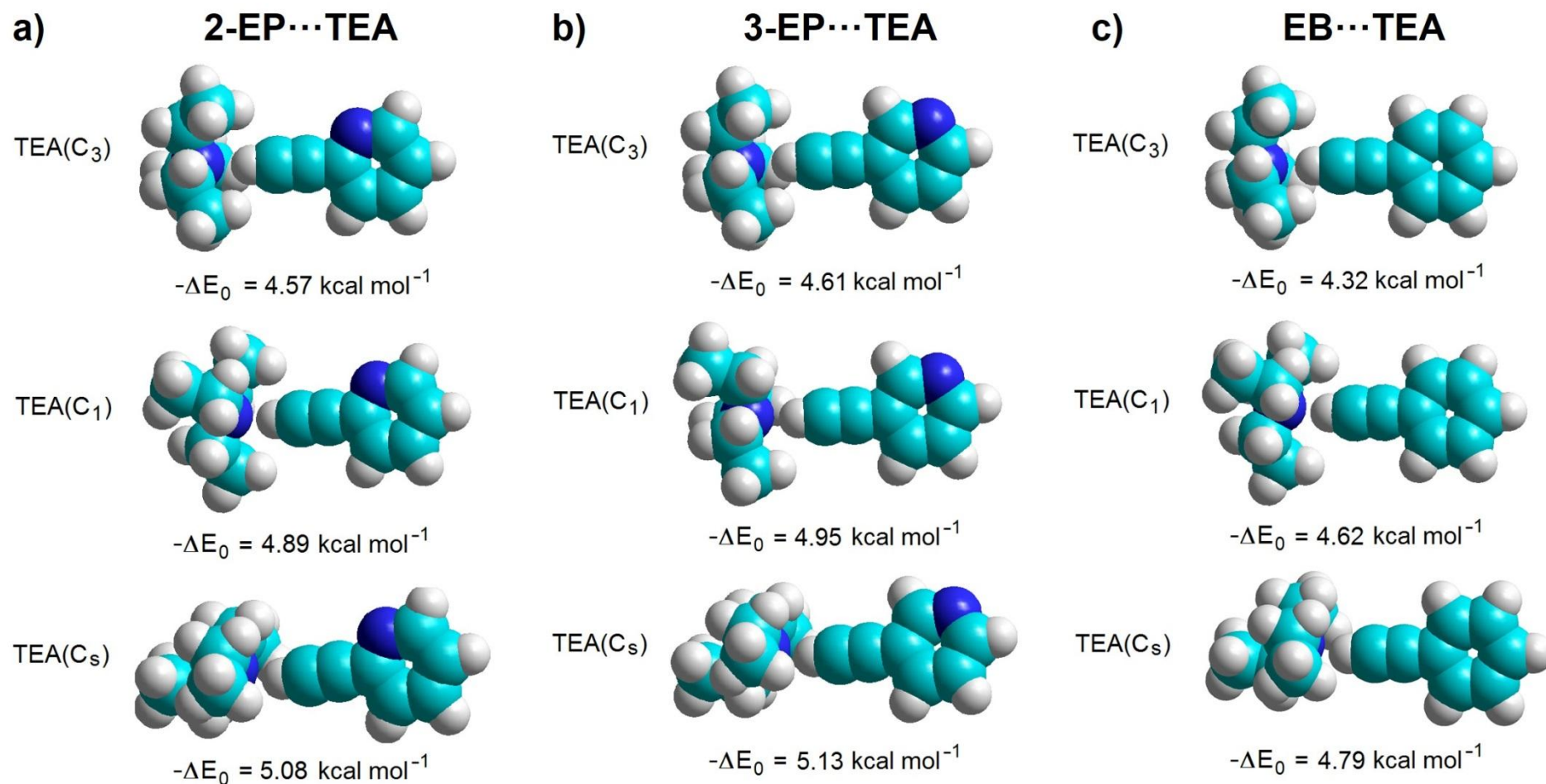
Fig. 2. Examples of calculated hydrogen-bonded complexes between ethynyl aromates and the three stable conformations of triethylamine (TEA(C_3), TEA(C_1), TEA(C_s)) with indication of calculated BSSE and ZPVE corrected binding energies: a) 2-ethynylpyridine (2-EP); b) 3-ethynylpyridine (3-EP), c) ethynylbenzene (EB).

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In all cases, the hydrogen-bonded complex with TEA(C_s) is predicted to have the largest binding energy, and the one with TEA(C_3) the lowest. Hence, the order of the stabilities of the complexes is the inverse of that of the conformers TEA(C_3), TEA(C_1), and TEA(C_s). The hydrogen bond geometries of the complexes with TEA(C_s) are characterized by marked deviations from linearity; for example, the C–H···N bond angles are 178°, 173°, and 163° for the complexes of 2-EP with TEA(C_3), TEA(C_1), and TEA(C_s), respectively (further geometrical details are given in S5 - S7). The peculiar hydrogen-bonding properties of TEA(C_s) can probably be explained by anomeric effects [30].

For the monomers, the ≡C–H and C≡C stretching transitions are computed around 3473 and 2210 cm^{-1} (unscaled). Complex formation with ≡C–H···N intermolecular hydrogen-bonding is predicted to lead to red-shifts of both transitions. In fact, both vibrational modes involve mechanical coupling of the stretching motions of the ≡C–H and C≡C bonds. For example, an analysis of the results for monomer 2-EP in terms of internal coordinates describes the ≡C–H stretching mode (3474 cm^{-1}) as 85% ≡C–H stretch and 11% C≡C stretch, and the C≡C stretching mode (2211 cm^{-1}) as 40% C≡C stretch, 28% C–C≡ stretch, and 15% ≡C–H stretch (S2). Almost identical analyses are obtained for 3-EP and EB (S3, S4). The predicted red-shifts are generally around 200 cm^{-1} and 30 cm^{-1} for the ≡C–H and C≡C stretching transitions, respectively (unscaled values). At the same time, the predicted IR intensities are strongly increased. Individual transitions for characteristical complexes are provided in S5 - S7. The range of predicted values are given in Table 1.

Table 1. Experimental and calculated ≡C−H and C≡C stretching vibrational transitions for 2-EP, 3-EP, EB and their mixtures with TEA: Wavenumbers in cm^{-1}, intensities in parantheses. ≡C–H and C≡C indicate monomer transitions, ≡C–H··· and C≡C··· indicate transitions shifted due to formation of complexes with TEA. The calculated wavenumbers are harmonic gas phase values (unscaled) and the corresponding intensities are in km mol^{-1}.

system	≡C–H		≡C–H···		C≡C		C≡C···	
	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.
2-EP + TEA	3308 (vs)	3473 (83.9)	3217 (vvw)	3260-3230 (750-910)	2120 (w)	2211 (0.84)	2105 (vw)	2183-2180 (94-119)
3-EP + TEA	3308 (vs)	3473 (97.6)	3219-3209 (vw)	3255-3215 (806-1027)	2116 (w)	2205 (17.4)	2102 (w)	2179-2175 (38-61)
EB + TEA	3313 (vs)	3474 (97.3)	3217-3212 (vvw)	3274-3246 (770-931)	2113 (w)	2202 (10.4)	~2098 (vvw)	2178-2175 (20-32)

4.2 IR spectra of ternary mixtures at room temperature

Ethynylpyridines. In the absence of other hydrogen bond donors or acceptors, the $\equiv$C−H stretching of the ethyne group of 2-EP in C_2Cl_4 solution absorbs at 3332 cm^{-1} (w), 3308 cm^{-1} (vs) and 3290 cm^{-1} (w). The corresponding values for 3-EP are 3332 cm^{-1} (w), 3308 cm^{-1} (vs), 3297 cm^{-1} (w) and 3286 cm^{-1} (w) (Fig 3a). In the case of 2-EP, the presence of TEA induces the appearance of an additional weak band (full width at half maximum labeled as Δ) positioned at about 3217 cm^{-1} in C_2Cl_4 solution (vw; $\Delta \approx$ 40-45 cm^{-1}), but only when the concentration of TEA is higher than 0.79023 mol dm^{-3} (Fig. 3a). In 3-EP + TEA in C_2Cl_4 mixtures the novel band appears already at c_0(TEA)= 0.39957 mol dm^{-3} and absorbs at 3209 cm^{-1} (Fig. 3c). As the concentration of TEA gradually increases, the band gains intensity and shifts towards higher wavenumbers so that at c_0(TEA)= 1.00188 mol dm^{-3} it absorbs at 3219 cm^{-1} (vw; $\Delta \approx$ 30-50 cm^{-1}). Since the displacement of the discussed band is not anticipated according to the theory of Allerhand and Schleyer [16], one should first be absolutely sure that the shift is unambigously a real spectral occurence. Thus, the uncertainty in determination of the band maximum will be further discussed (see *Interpretation of the observed spectral behavior* in the continuation of the text and sections S8 and S9 in Supplementary Materials.). In both compounds the intensity of the strong peak at 3308 cm^{-1} decreases as the concentration of TEA increases.

The influence of hydrogen-bonded association on the C$\equiv$C moiety in is manifested by the appearance of a new IR band attributed to the stretching of the C$\equiv$C moiety in the complex (C$\equiv$C$\cdots$). In IR spectra of 2-EP + TEA in C_2Cl_4 mixtures, along with the band assigned as monomer C$\equiv$C stretching at 2120 cm^{-1} (w), a new feature appears at 2105 cm^{-1} (w; $\Delta \approx$ 12-15 cm^{-1}) (Fig. 3b). In IR spectra of 3-EP + TEA in C_2Cl_4 mixtures, apart from the band attributed to the stretching of the unassociated C$\equiv$C moiety (at 2116 cm^{-1} (w)), a band due to the stretching of C$\equiv$C$\cdots$ appears at 2102 cm^{-1} (w; $\Delta \approx$ 12 cm^{-1}) (Fig. 3d). Interestingly, the

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intensity distributions between C≡C··· and C≡C moieties in EPs are different. For 2-EP + TEA in C_2Cl_4 mixtures the intensity of the C≡C··· stretching band increases with TEA concentration, simultaneously with a decrease of the band attributed to the stretching of unassociated C≡C moiety, although it never exceeds the latter one. In 3-EP + TEA in C_2Cl_4 mixtures the intensity distribution is quite different; both C≡C··· and C≡C stretching bands gain intensities, but the former exceeds the latter one whose intensity increase is, however, rather small.

Fig. 3. IR spectra of EPs in EP+TEA in C_2Cl_4 mixtures recorded at room temperature after TEA in C_2Cl_4 mixtures subtraction (d=985.79 μm): a) ≡C−H and ≡C−H··· stretching of 2-EP in spectral range 3360-3170 cm^{-1} (emphasized 3260-3175 cm^{-1} in which ≡C−H··· stretching band appears); b) C≡C and C≡C··· stretching of 2-EP in spectral range 2080-2145 cm^{-1}. The analytical concentration of TEA presented were c_0(TEA)= 0.19208 mol dm^{-3}, 0.39764 mol

dm^{-3}, 0.5957 mol dm^{-3}, 0.79023 mol dm^{-3} and 0.99698 mol dm^{-3} and c_0 (2-EP)≈0.05 mol dm^{-3}. c) ≡C−H and ≡C−H⋯ stretching of 3-EP in spectral range 3360-3170 cm^{-1} (emphasized 3260-3175 cm^{-1} in which ≡C−H⋯ stretching band appears); d) C≡C and C≡C⋯ stretching of 3-EP in spectral range 2080-2145 cm^{-1}. The analytical concentration of TEA presented were c_0 (TEA)= 0.19304 mol dm^{-3}, 0.39957 mol dm^{-3}, 0.59869 mol dm^{-3}, 0.79504 mol dm^{-3} and 1.00188 mol dm^{-3} and c_0 (3-EP)≈0.05 mol dm^{-3}.

Ethynylbenzene. When not involved in a hydrogen bond, spectroscopic signature of ≡C−H stretching of EB reveals complex envelope with three distinguished features positioned 3313 cm^{-1} (vs), at 3302 cm^{-1} (s) and 3287 cm^{-1} (m) (Fig. 4a). The strongest one is assigned as the fundamental transition of ≡C−H group [31] and its position and intensity will be further discussed in the text, as well as utilized for the determination of the association constant (section 4.3).

The presence of TEA at concentration c_0(TEA)=0.29812 mol dm^{-3} induces the appearance of a very weak band at 3212 cm^{-1} assigned to the stretching of the ≡C−H⋯ group. A corresponding transition was not observed in the gas phase experiments conducted by Patwari and associates [8−10]. Further increase in TEA concentration causes a decrease in intensity of the band assigned to the stretching of the unassociated ≡C−H moiety and an intensity increase of the associated one. In addition, for c_0(TEA) = 0.99416 mol dm^{-3} the ≡C−H⋯ stretching band absorbs at 3217 cm^{-1} (vw; $\Delta \approx$ 40-45 cm^{-1}) so the frequency difference between ≡C−H and, respectively, ≡C−H⋯ stretching bands decreases, just as in IR spectra of 3-EP + TEA in C_2Cl_4 mixtures.

As far as the C≡C moiety is concerned, this part of the spectrum is not so information rich as in the EPs case. The weak asymmetric band centered at 2113 cm^{-1} slightly decreases as TEA concentration increases simultaneously with the band broadening at the low-frequency side and, effectively, gretaer band asymmetry (Fig. 4b). It is assumed that the increase in band

assymetry is due to the appearance of at least one new band (vvw) attributed to the stretching of C≡C··· moiety with maximum estimated at 2098 cm^{-1}.
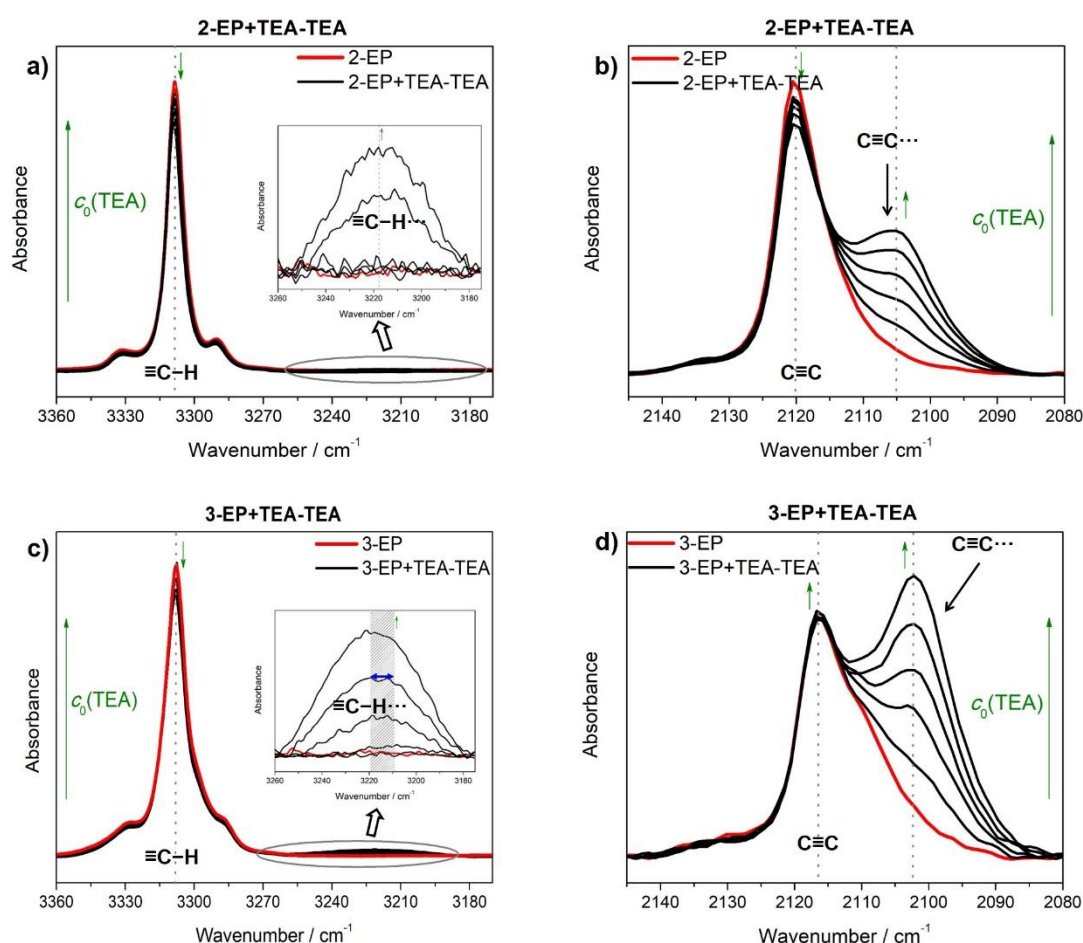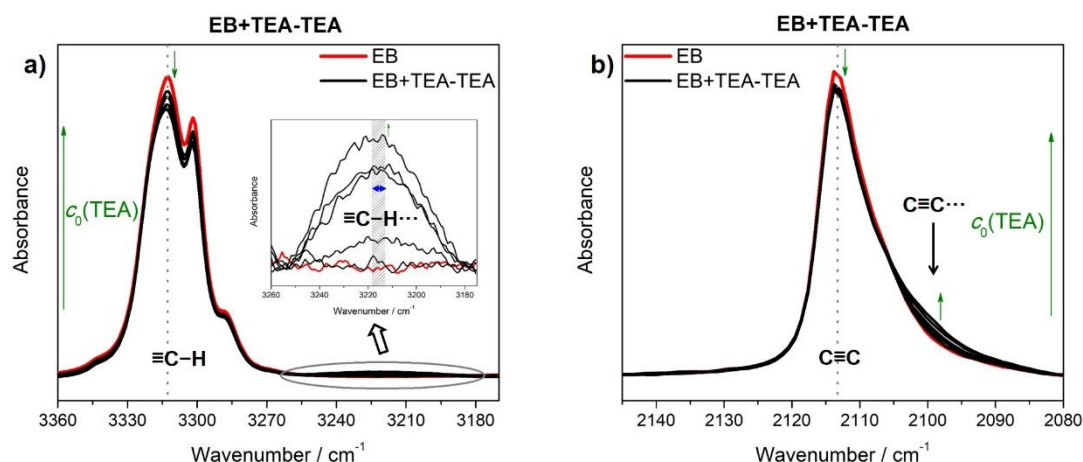

Fig. 4. IR spectra of EB in EB+TEA in C_2Cl_4 mixtures recorded at room temperature after TEA in C_2Cl_4 mixtures subtraction (d=985.79 μm): a) ≡C−H and ≡C−H··· stretching of EB in spectral range 3360-3170 cm^{-1} (emphasized 3260-3175 cm^{-1} in which ≡C−H··· stretching band appears); b) C≡C and C≡C··· stretching of EB in spectral range 2080-2145 cm^{-1};. The analytical concentration of TEA presented in both mixtures sets were c_0 (TEA)= 0.19147 mol dm^{-3}, 0.39633 mol dm^{-3}, 0.59391 mol dm^{-3}, 0.78883 mol dm^{-3} and 0.99416 mol dm^{-3} and c_0 (EB)≈0.07 mol dm^{-3}.

Interpretation of the observed spectral behavior. The central issues that emerge in the analysis and interpretation of the experimental data are as follow: i) to assign the observed spectrosopic signature(s) to the particular dimer(s) (ethynyl compound···TEA) and ii) to discuss the significance of the displayed reduced red shift of the ≡C−H··· stretching band in 3-EP+TEA and EB+TEA mixtures as TEA concentration rises.

As far as i) is concerned, even derivation spectroscopy is powerless when weak and broad signals as those obtained here are to be explored [32]. As suggested by the calculated results, the signal at ~3215 ± 5 cm^{-1} (≡C−H···) is produced by various more or less linear ≡C–H···N

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hydrogen-bonded complexes in all systems (Fig. 2). Moreover, this association is accompanied by the redistribution of the electron density on C≡C moiety as well, according to the signal at ∼ 2105 ± 5 cm^{-1} (C≡C···) in all explored systems.

Regarding issue ii), one should first recall the theory of Allerhand and Schleyer [16] according to which ethynyl aromates in the liquid mixtures used here (TEA as the hydrogen bond acceptor and C_2Cl_4 as the inert solvent) should not produce any TEA concentration-dependent displacement of bands related to the vibrations of associated species. Since the "reduced displacement" is rather small (up to ∼10 cm^{-1} for 3-EP + TEA in C_2Cl_4 mixtures and up to ∼5 cm^{-1} for EB+TEA in C_2Cl_4 mixtures) and demonstrated on generally very weak vibrational features, one should first discuss experimental precision and accuracy in determination of the band maximum. First, it should be highlighted that the bands of interest are visible only when the binary mixture spectrum (TEA in C_2Cl_4) is subtracted from the ternary mixture spectrum (3-EP/EB + TEA in C_2Cl_4); when only solvent spectrum is subtracted, these signatures cannot be observed (more details are provided in Supplementary Materials, section S8, Fig. S1A). Although this operation is not optimal (see Supplementary Materials, section S9), this was the only way for the signatures to be extracted. Further, the parameters of the discussed band(s) might be seriously compromised when the baseline correction is taken, especially since the very weak and broad bands (in both systems) are situated between very strong (≡C–H stretching) and medium intense to strong (=C–H stretching) bands. Finally, when the band maximum is to be estimated, one has to take in consideration the high noise level accompanied with this signal (Fig. S1B, section S8 in Supplementary Materials). Except for the highest concentration of TEA in 3-EP+TEA in C_2Cl_4 mixtures, the band maximum is actually tedious to determine. However, as the bands are rather symmetric, center of gravity and the band maximum coincide so the latter can be obtained with systematical uncertainty.

After the detailed analysis of the impact of the spectral treatment on the spectral parameters, and considering the fact that every solution has been recorded at least three times, one can conclude that the TEA concentration-dependent shift still remains and is a real physico-chemical phenomenon. Regarding its origin, we can provide only a tentative explanation: As TEA can be found in three conformations (C_1, C_s and C_3) it might be that EPs (and EB) make hydrogen-bonded complexes with all three conformers, but of different abundances. In particular, it may be that in solution one conformer is preferred by 2-EP, whereas another by 3-EP (and EB). The signatures of hydrogen-bonded complexes with different TEA conformers presumably appear at slightly different wavenumbers so that the overall position of the band assigned to the stretching of $\equiv C-H\cdots$ oscillator might display the band shift [33,34]. On the other hand, the present gas phase calculations predict that the most stable hydrogen-bonded complexes are with the TEA(C_s) conformer (Fig. 2), but the situation may differ in solution. At room temperature, we most likely have a dynamical situation with rapid formation and breaking of a variety of complexes, including hydrogen-bonded as well as a variety of dispersion-driven complexes. The present experimental conditions disable the discrimination of TEA conformers involved in interaction with the ethynyl aromates.

4. 3 Determination of the association constants at room temperature

In EPs the band maximum (3308 cm^{-1}) is regarded as fundamental transition of $\equiv C-H$ stretching group. Further, molar absorption coefficient (ε) in C_2Cl_4 at 3308 cm^{-1} is determined (at room temperature) and is 253±2 mol^{-1} dm^3 cm^{-1} for 2-EP in C_2Cl_4 [14], 221±2 for 3-EP in C_2Cl_4 [14], and for EB in C_2Cl_4 (at 3313 cm^{-1}) is 123.7±0.3 [14]. The association constants (K_c) are determined by using the high dilution method [18] and are presented in Table 2.

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Table 2. Association constants (K_c) of ethynyl aromates and TEA in C_2Cl_4 at 26 ± 1 °C determined by high dilution method.

system	$K_c{}^{a}$
2-EP⋯TEA	0.07±0.03
3-EP⋯TEA	0.07±0.02
EB⋯TEA	0.10±0.02

^{a} In mol^{-1} dm^3

It should be emphasized that the K_c values determined here are obtained only for solutions with 1 mol $dm^{-3} \geq c_0(TEA) \geq 0.5$ mol dm^{-3}. Even though greater concentrations of TEA were desirable, according to the conditions presented in [28], due to strong background signal of TEA [19] and inherently weak signatures of hydrogen-bonded species, the latter signals would not be possible to detect for $c_0(TEA) > 1$ mol dm^{-3}. Thus, these values should be taken only aproximately.

Conclusions

The hydrogen bond donating capability of 2- and 3-ethynylpyridine (2-EP and 3-EP) and ethynylbenzene (EB) was explored in interaction with triethylamine (TEA) in tetrachloroethene solution. The IR spectra revealed weak signatures of ≡C−H and C≡C groups involved in hydrogen-bonded (⋯) complexes: The ≡C−H⋯ stretching absorbs at ~3215 ± 5 cm^{-1} in all systems, whereas the C≡C⋯ stretching displays a signature at 2105 ± 5 cm^{-1}. Relative to the ethynyl aromate monomers, these signals are red-shifted by 95 ± 5 and 15 cm^{-1}, respectively. A correspondingly red-shifted ≡C−H⋯ stretching band was not observed in the previously published investigations of EB + TEA in the gas phase [8,10]. We assign them to complexes with intramolecular ≡C−H⋯N hydrogen bonding. With increasing TEA concentration, the spectra of the 3-EP⋯TEA and EB⋯TEA complexes display a slight

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displacement of the $\equiv$C−H··· stretching band toward higher wavenumber range, corresponding to a reduced red shift. This issue may possibly be due to the changes in the abundances of the three TEA conformers (C_1, C_s and C_3) involved in the hydrogen-bonded complexes with the ethynyl aromates. Association constants (at 26 °C) between ethynyl aromates and TEA in tetrachloroethene are estimated to be approximately 0.1 mol^{-1} dm^3.

The present calculations within the B3LYP-D3 model predict that complexes with more or less linear $\equiv$C−H···N hydrogen bonding are more stable than other complexes. The results support the suggested assignments of the observed red-shifted IR signals to complexes with $\equiv$C−H···N hydrogen bonding; numerous dispersion-driven complexes were predicted, but the computed IR band shifts for these structures were predicted to be insignificant. The most stable hydrogen-bonded complexes were obtained with the C_s symmetrical TEA conformer. On the other hand, the present calculations refer to the gas phase and do not consider the possible impact of the tetrachloroethene solvent.

Acknowledgements

Supplementary Materials

Supplementary Materials associated with this paper can be found on the online version at http://.

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2-ethynylpyridine (2-EP)
3-ethynylpyridine (3-EP)
ethynylbenzene (EB)
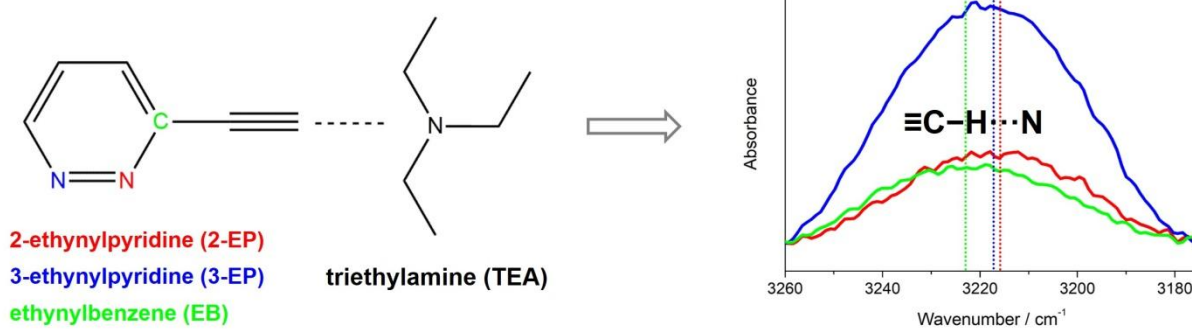
triethylamine (TEA)

Graphical abstract

Highlights:

- Triethylamine makes complexes with 2- and 3-ethynylpyridine and ethynylbenzene

- IR signals from free and hydrogen-bonded $\equiv$C$-$H and C$\equiv$C groups are identified

- Shifts of some hydrogen-bonded signals depend on triethylamine concentration

- Complexes with C_3, C_1, and C_s symmetrical triethylamine conformers are calculated

- Complexes with nearly linear $\equiv$C$-$H$\cdots$N hydrogen bonds are the most stable