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The exploration of hydrogen bonding properties of 2,6- and 3,5-diethynylpyridine by IR spectroscopy

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HIGHLIGHTS

- IR spectra of hydrogen-bonded complexes made by diethynylpyridines were presented.
- Thermodynamic parameters of investigated hydrogen-bonded complexes were determined.
- The participation of C≡C moiety in hydrogen-bonded complex is exhibited.
- The role of cooperativity effects is proposed.

GRAPHICAL ABSTRACT
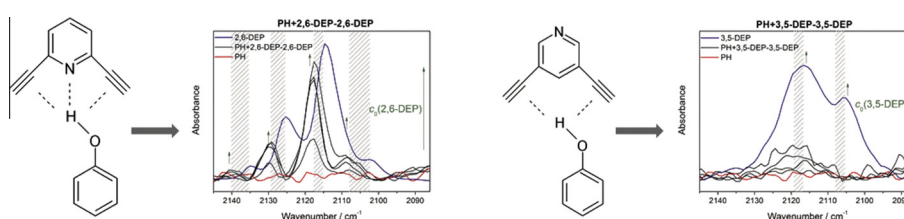
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ABSTRACT

Hydrogen bonding properties of 2,6- and 3,5-diethynylpyridine were analyzed by exploring of their interactions with trimethylphosphate, as hydrogen bond acceptor, or phenol, as hydrogen bond donor, in tetrachloroethene C_2Cl_4. The employment of IR spectroscopy enabled unravelling of their interaction pattern as well as the determination of their association constants (K_c) and standard reaction enthalpies ($\Delta_r H^\ominus$). The association of diethynylpyridines with trimethylphosphate in stoichiometry 1:1 is established through ≡C—H···O hydrogen bond, accompanied by the secondary interaction between C≡C moiety and CH_3 group of trimethylphosphate. In the complexes with phenol, along with the expected OH···N interaction, C≡C···HO interaction is revealed. In contrast to 2,6-diethynylpyridine where the spatial arrangement of hydrogen bond accepting groups enables the simultaneous involvement of phenol OH group in both OH···N and OH···C≡C hydrogen bond, in the complex between phenol and 3,5-diethynylpyridine this is not possible. It is postulated that cooperativity effects, arisen from the certain type of resonance-assisted hydrogen bonds, contribute the stability gain of the latter. Associations of diethynylpyridines with trimethylphosphate are characterized as weak ($K_c \approx 0.8$–0.9 mol^{-1} dm^3; $-\Delta_r H^\ominus \approx 5$–$8$ kJ mol^{-1}), while their complexes with phenol as medium strong ($K_c \approx 5$ mol^{-1} dm^3; $-\Delta_r H^\ominus \approx 15$–$35$ kJ mol^{-1}). Experimental findings on the studied complexes are supported with the calculations conducted at B3LYP/6-311++G(d,p) level of theory in the gas phase. Two conformers of diethynylpyridine···trimethylphosphate dimers are formed via ≡C—H···O interaction, whereas dimers between phenol and diethynylpyridines are established through OH···N interaction.

Introduction

When discussing the bonding capability of multifunctional molecules with interaction centers being weak hydrogen bond (HB) donors and acceptors, ethynylbenzene (EB) can be presented as one of the most comprehensively explored systems [1]. The

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possibility of employing both ethynyl and phenyl moieties, either as HB accepting or HB donating centers, has been found to be dependent on the another protagonist in a HB complex, which in turn have resulted with the uncertainty in the prediction of EB interaction pattern [2–4].

The attempts to clarify the EB bonding hierarchy have been further continued by undertaking the studies on substituted EBs in which one of its H-atoms have been replaced by the HB accepting centers such as fluorine (F) atoms [5,6] or cyano (CN) groups [7]. In contrast to expectations that strong HB acceptors may take a primacy in the bonding pattern, in the former example they are not even directly involved in HB interplay, while in the latter they can be, at best, regarded as equal with the phenyl moiety.

The certain predictability in the bonding hierarchy in multifunctional molecules with weak HB donating and accepting sites has been found in 2 and 3-ethynylpyridine (2- and 3-EP) [8]. By employing IR spectroscopy, coupled with the calculations, Vojta et al. [8] have analyzed and, in thermodynamic terms, characterized HBs formed by 2- and 3-EP and EB with trimethylphosphate (TMP) and phenol (PH) in C_2Cl_4, respectively. Expectedly, the complexes between EPs or EB with TMP have been found to be weak and directed by $C≡C-H\cdots O$ interaction, while when PH is their partner in HB complex, the association is of medium strength and governed by $OH\cdots N$ interaction. In structural terms, however, some exceptional phenomena addressed to the participation of $C≡C$ moiety in HB formation, have appeared – when in interaction with TMP (via CH_3 group), $C≡C$ bond becomes longer (the stretching of associated $C≡C$ oscillator ($C≡C\cdots$) shifts to the lower frequencies when compared with the stretching of unassociated $C≡C$ oscillator ($C≡C$)), while when in interaction with PH (via OH group), it shortens ($C≡C\cdots$ stretching shifts to the higher frequencies, respectively). The latter was observed only in $PH\cdots2$-EP complex since simultaneous $OH\cdots N$ and $OH\cdots C≡C$ interactions have been enabled. In 3-EP the additional interaction was absent and explained due to two reasons: (i) steric limitation does not allow simultaneous arrangements of $OH\cdots N$ and $OH\cdots C≡C$ HB so OH group certainly prefers HB with N-atom over $C≡C$ group, and (ii) the molar absorption coefficient (ε) of $C≡C$ stretching is rather low so even if the bond is formed, it is too weak to be observed in these experimental conditions. However, the participation of $C≡C$ moiety in making of HB complex, presumably as secondary interaction established due to favorable geometrical arrangement in which N-atom takes hierarchical primacy in HB formation, resulted with the following idea: $C≡C$ group, through cooperative actions, may be promoted to the interaction site competitive to the N-atom when exposed to the HB donor such as OH group.

The understanding of the cooperativity [9] in self-organizing structures [10], as well as the quantitative assessment of cooperativity related effects [11], is usually based on well-defined systems mostly capable for the simultaneous formation of several strong or at least medium strong HB like in trialkylbenzene-1,3,5-tricarboxamide [12]. To the best of our knowledge, the most recent attempt to quantify the contributions of weak intermolecular interactions in certain complex requires a development of a platform based on strong HB donors and HB acceptors such as bisurea [13]; then, by combining theoretical and experimental methods, subtle differences as weak as 1 kJ mol^{-1} can be registered. However, in systems able only to form weak or medium strong HBs in solutions such investigations are scarce and, in general, weak HBs in solutions are rather poorly explored and characterized. As the interactions as weak as $C≡C\cdots HCH_2$ and $C≡C\cdots OH$ have been observed in solution at room temperature [8], one may expect that the interactions, formed by 2- and 3-EP, might be amplified if additional substituent on ethynylpyridines is introduced. With this respect, it seems interesting to investigate the influence of additional ethynyl

moiety on 2- and 3-EP, especially when ethynyl groups are placed symmetrically regarding N-atom.

Thus, in this paper, HB capability of 2,6-diethynylpyridine (2,6-DEP) and 3,5-ethynylpyridines (3,5-DEP) was explored (Fig. 1). Their associations with TMP as HB acceptor and PH as HB donor was characterized by using high dilution method [14] and expressed in terms of K_c, $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ both experimentally and computationally. Spectral features associated with engagement of $C≡C$ moieties of DEPs in HB complexes, at least at qualitative level, were used for discussing the hierarchy between HB centers in terms of their cooperative action.

Calculations

Geometries of monomers **1–4** (Fig. 1), were optimized at B3LYP/ 6-311++G(d,p) level of theory. Geometries of dimers $DEPs\cdots TMP$ and $PH\cdots DEPs$ (Fig. 2) were treated at the same level of theory. HB systems require flexible [15] basis set in order to properly describe its thermodynamic properties. Triple-zeta basis set 6-311G++(d,p) with diffuse functions on both heavy and hydrogen atoms were chosen. On all optimized structures, harmonic frequencies were calculated on the same level of theory as the geometry optimizations. NBO charges were also calculated on optimized geometries [16]. Association energies were calculated as a difference between energies of monomers and energies of a dimer. Correction for the basis set superposition error (BSSE) was accounted for with the Boys–Bernardi counterpoise scheme [17]. ΔrH was calculated according to Eq. (1):

$$\Delta_r H = \Delta E^{BSSE}(AB) + ZPE(AB) - ZPE(A) - ZPE(B) + H^{trv}(AB)$$
$$- H^{trv}(A) - H^{trv}(B) \qquad (1)$$

where ΔE^{BSSE} is the association energy, corrected for BSSE, ZPE is zero point energy and H^{trv} is translational, rotational and vibrational contribution to the enthalpy at temperature T. All harmonic ZPE are scaled with scaling factor 0.9877 [18] before using them in the calculation of $\Delta_r H$. All calculations have been performed in Gamess program package [19,20].

Experimental

Chemicals

2,6-Diethynylpyridine (2,6-DEP) and 3,5-diethynylpyridine (3,5-DEP) are white powders prepared by Sonogashira rection [21]. The procedure on the compounds preparation and purification can be found in Supporting Materials.

Tetrachloroethene (C_2Cl_4; b. p. = 122 °C, spectroscopic grade) and trimethylphosphate (TMP; b. p. = 192–194 °C, 99+% purity) are transparent liquids purchased from Acros Organics and Sigma Aldrich, respectively, and were used as received. Phenol (PH) is white crystalline substance obtained from Kemika (m. p. = 40–41 °C, pro analysis) and was additionally purified by recrystallization. Densities of the studied liquids were determined by a densitometer DMA 5000-Anton Paar.
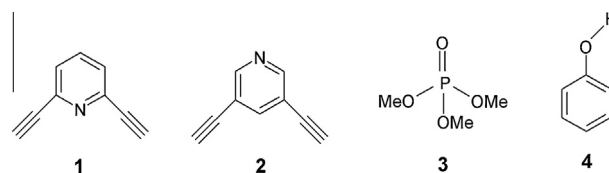

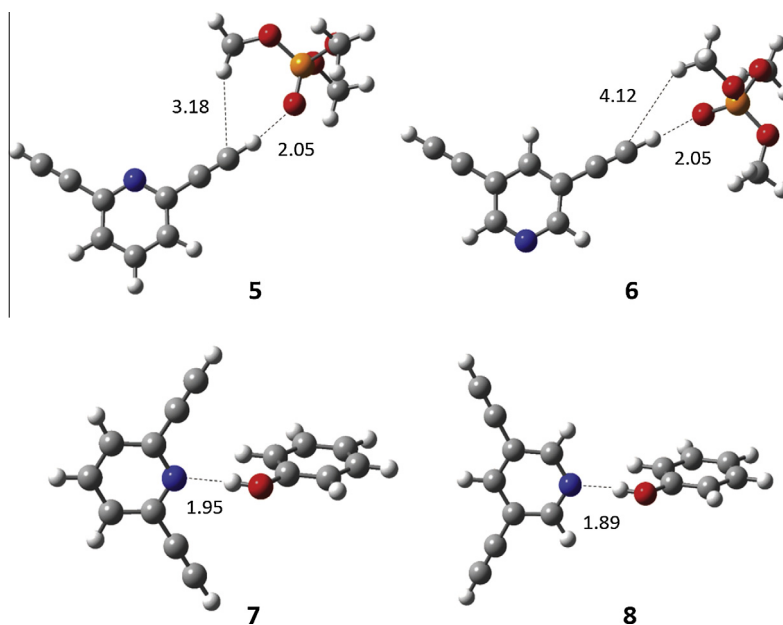**Fig. 1.** (1) 2,6-DEP; (2) 3,5-DEP; (3) TMP; (4) PH.

Fig. 2. Structures **5–8**, optimized at the B3LYP/6-311++G(d,p) level of theory. The most important interactions between monomers are shown as dashed bonds and the distance between atoms in Ångström units are shown next to it.

Preparation of solutions

High dilution method, used for determination of relevant thermodynamic parameters of HB systems, is comprehensive described in the literature (for instance, see Ref. [22]); more details are also given in Supporting Materials. Here, the details on the preparation of particular set of solution are presented.

Acidity of DEPs

Three sets of the solutions were prepared:

(i) Solutions of DEPs in C_2Cl_4 in certain concentration range (c_0(2,6-DEP): 0.00082–0.07763 mol dm^{-3}; c_0(3,5-DEP): 0.00066–0.09708 mol dm^{-3}) in order to determine molar absorption coefficient (ε) of $\equiv$C—H stretching at the band maximum in both cases.
(ii) A set composed of binary solutions of TMP in C_2Cl_4 in concentration range c_0(TMP) = 0.09816–1.02256 mol dm^{-3}, used for the preparation of ternary solutions set, which is DEP(s) dissolved in TMP in C_2Cl_4. In the latter, the concentration of DEPs across ternary solutions set were held almost constant (c_0(DEPs) $\approx$ 0.025 mol dm^{-3}). These two sets were used for determination of association constant K_c of DEPs$\cdots$TMP complex.
(iii) A set composed of one binary solution of DEPs in C_2Cl_4 (c_0(2,6-DEP) = 0.01894 mol dm^{-3}; c_0(3,5-DEP) = 0.02037 mol dm^{-3}), used for determination of temperature dependence of ε of $\equiv$C—H stretching band, and three ternary solutions made from DEPs and TMP in C_2Cl_4. In 2,6-DEP$\cdots$TMP complex, the concentrations were c_0(2,6-DEP) = 0.02369 mol dm^{-3}, 0.02808 mol dm^{-3} and 0.02549 mol dm^{-3} while c_0(TMP) = 0.18211 mol dm^{-3}, 0.60178 mol dm^{-3} and 0.92479 mol dm^{-3}, respectively. In 3,5-DEP$\cdots$TMP complex, the concentrations were c_0(3,5-DEP) = 0.02677 mol dm^{-3}, 0.02248 mol dm^{-3} and 0.024 mol dm^{-3} while c_0(TMP) = 0.1971 mol dm^{-3}, 0.54035 mol dm^{-3} and 0.92479 mol dm^{-3}, respectively. The latter three sets were used for determination of temperature dependence of K_c.

Basicity of DEPs

Two sets of the solutions were prepared:

(i) A set composed of binary solutions of DEPs in C_2Cl_4 in concentration range c_0(2,6-DEP) = 0.0091–0.03984 mol dm^{-3} (4 solutions); c_0(3,5-DEP) = 0.02127–0.05164 mol dm^{-3} (4 solutions), used for the preparation of ternary solutions set, which is PH dissolved in DEPs in C_2Cl_4. In the latter, the concentration of PH across ternary solutions set were held almost constant (c_0(DEPs) $\approx$ 0.005 mol dm^{-3}). These two sets were used for determination of K_c of PH$\cdots$DEPs complexes.
(ii) A set composed of one ternary solution made from PH and DEPs in C_2Cl_4. In PH$\cdots$2,6-DEP complex, the concentrations were c_0(PH) = 0.00713 mol dm^{-3} and c_0(2,6-DEP) = 0.0104 mol dm^{-3}. In PH$\cdots$3,5-DEP complex, the concentrations were c_0(PH) = 0.00471 mol dm^{-3} and c_0(3,5-DEP) = 0.02037. The latter set was used for determination of temperature dependence of K_c.
(iii) The concentration of each compound was determined gravimetrically, i.e. by weighting of each compound in particular mixture up to five decimal points.

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 cells equipped with CaF$_2$ windows with effective pathlengths determined by employing Bertie's procedure using either dichloromethane (CH$_2$Cl$_2$) or benzene (C$_6$H$_6$) as a secondary standard [23] (2,6-DEP in C$_2$Cl$_4$: d = 4812.53 μm, 1000.73 μm, 518.19 μm; 2,6-DEP + TMP in C$_2$Cl$_4$: d = 985.14 μm; PH + 2,6-DEP in C$_2$Cl$_4$: d = 988.83 μm; 3,5-DEP in C$_2$Cl$_4$: d = 4816.47 μm, 999.94 μm, 226.33 μm; 3,5-DEP + TMP in C$_2$Cl$_4$: d = 985.14 μm; PH + 3,5-DEP in C$_2$Cl$_4$: d = 987.06 μm, 985.72 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.

Temperature dependent IR spectra were recorded by using Specac 3000 Series high stability temperature controller with heating jacket for the regulation of the heating rate. IR spectra of solutions were recorded in a sealed cell with CaF_2 windows and $d = 984.18$ μm; the heating rate was $2\ °C\ min^{-1}$ and the sample was held at each temperature for 3 min. IR spectra of solids were recorded in KBr pellets (about 2 mg of DEPs and 120 mg of KBr) with heating rate of $1\ °C\ min^{-1}$ and stabilization time of 5 min. In solution samples the spectra were collected every 10 °C between 25 °C and 115 °C, while in measurements of the pellets the spectra were collected every 5 °C.

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 moieties of DEPs absorb. Regarding OH stretching band of PH, the absorbance of OH stretching band has to be determined with certain accuracy and reliability, while, at the same time, the accumulation of water from the atmosphere which absorbs in the same spectral range and, consequently, brings up the unreliability in the absorbance measurements (Fig. S3 in Supporting Materials) should be minimized. Thus, 10 scans in the systems related with PH is the result of a certain compromise.

Spectral analysis

As the band maximum, i.e. the band absorbance, provides the most sensitive and the most reliable response of HB donors (DEPs or PH) in the presence of HB acceptor (TMP or DEPs) at given concentration, this spectroscopic parameter was aimed to be determined in all mixtures sets. (More details on tuning optimal absorbance value at the band maximum is given in Supporting Materials).

In order to determine the ε of ≡C—H stretching in binary (DEPs in C_2Cl_4) mixtures and, consequently, K_c from ternary (DEPs + TMP in C_2Cl_4) mixtures, spectral range 3360–$3260\ cm^{-1}$ was analyzed. After the baseline correction, the absorbance of ≡C—H stretching band of both DEPs was determined from the band maximum ($3308\ cm^{-1}$) and used in calculation of ε from Lambert–Beer's law and K_c.

In PH + DEPs in C_2Cl_4 mixtures, K_c was determined by analyzing O—H stretching band of PH in spectral range 3680–$3540\ cm^{-1}$ (maximum at $3610\ cm^{-1}$) after the baseline correction.

Additionally, C≡C stretching in IR spectra of both 2,6-DEP in C_2Cl_4 and, respectively, 3,5-DEP in C_2Cl_4 binary mixtures were analyzed (2155–$2080\ cm^{-1}$). Only value ε at the band maximum is estimated; for 2,6-DEP at $2125\ cm^{-1}$ and for 3,5-DEP at $2117\ cm^{-1}$.

Mentioned quantities were measured both at room temperature and in temperature dependence.

Results and discussion

Calculations: structures and vibrational spectra of monomers and dimers

HB complexes of monomers **1** and **2** (Fig. 1) with **3** are formed via hydrogen bonds between DEP ethynyl group and oxygen atoms in TMP (structures **5** and **6**). In the case of dimers **7** and **8**, HBs are formed between hydroxyl group of **4** and DEP nitrogen atom (Fig. 2). Thus, for discussing the structures of HB complexes, the most important spectral parameters are the positions of the stretching of ≡C—H, C≡C and OH moieties, both free and associated ones. The former originate from monomers (**1**, **2** and **4**), while the latter from species involved in HB complexes. Both are presented in Table 1. The main difference in designation of the stretching of free and associated moieties is presented using the mark···that refers to the associated moieties. As far as monomers 2,6-DEP and 3,5-DEP are concerned (structures **1** and **2** in Fig. 1), their complete vibrational analysis (gas phase calculations, IR spectra of their solutions in C_2Cl_4, IR spectra of solid and melt 2,6-DEP and 3,5-DEP) is given in Table S1 in Supporting Materials.

The structural analysis of DEPs···TMP and PH···DEPs dimers is elaborated in more detail. The initial geometry for the search was taken from the already determined conformations of dimers of TMP and 2-EP and 3-EP [8]. The most stable conformers of the dimers **5** and **6** are shown in Fig. 2. We should note that since different conformers of TMP exist depending on the orientation of methyl groups, we used the most stable one for the further analysis (other conformers are located as well and are higher in energy by ca. 2–$3\ kJ\ mol^{-1}$). The most significant interaction between

Table 1
Calculated fundamental vibrational modes (in cm^{-1}) for ≡C—H and C≡C stretching in DEPs monomers and DEPs dimers, as well O—H vibration of free PH and PH in complexes with DEPs. All frequencies are scaled with scaling factor 0.9679 [18]. Intensities are reported in parenthesis. Calculated intensities are in $km\ mol^{-1}$ units.

System	$\tilde{\nu}^a$											
	≡C—H		≡C—H···		C≡C		C≡C···		OH		OH···	
	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc
1	3308 (s)	3363 (125.50)	–	–	2125 (w)	2142 (1.23)	–	–	–	–	–	–
	3289 (w)	3364 (50.12)			2115 (w)	2141 (2.81)						
					2102 (vw)							
2	3308 (s)	3363 (168.40)	–	–	2117 (w)	2138 (1.18)	–	–	–	–	–	–
	3289 (w)	3364 (38.33)			2105 (vw)	2136 (4.52)						
4	–	–	–	–	–	–	–	–	3610	3710 (61.38)	–	–
5	3308 (s)	–	3211–3208	3237 (586.75)^b	2122 (w)	–	2101 (w)	2125 (84.74)^b	–	–	–	–
	3289 (w)			3365 (87.61)^b	2108 (w)			2140 (0.52)^b				
					2101 (vw)							
6	3308 (s)	–	3209–3206	3238 (688.72)^b	2117 (w)	–	2110 (w)	2122 (42.38)^b	–	–	–	–
	3289 (w)			3364 (103.31)^b	2103 (vw)			2135 (7.06)^b				
7	3308 (s)	–	3308 (s)	3362 (131.65)	2122 (w)	–	2129 (w)	2145 (14.71)	3610	–	3306	3402 (1134.73)^c
	3289 (w)		3289 (w)	3362 (21.00)	2108 (w)		2118 (w)	2146 (3.47)				
					2101 (vw)		2108 (vw)					
8	3308 (s)	–	3308 (s)	3360 (166.79)	2117 (w)	–	2120 (vw)	2140 (0.03)	3610	–	3204	3336 (1932.51)^c
	3289 (w)		3289 (w)	3361 (12.72)	2103 (vw)			2141 (0.27)				

^{a} cm^{-1}.

^{b} Structures **5** and **6** (≡C—H···O and C≡C···HCH_2).

^{c} Structures **7** and **8** (N···HO).

monomers in the dimers **5** and **6** is the HB P=O···H—C≡ which makes a significant change in vibrational frequencies of ethynyl groups. The shift in vibrational frequencies makes this conformer detectable in vibrational spectra (Table 1). Aside P=O···H—C≡ HB, a secondary interaction between methyl groups of TMP and one C≡C moiety of particular DEP is predicted. This is manifested by the low-frequency shift of the symmetric stretching of C≡C oscillators for $\varDelta = -17$ cm^{-1} in 2,6-DEP···TMP (dimer **5**) association and, respectively, $\varDelta = -16$ cm^{-1} in 3,5-DEP···TMP (dimer **6**) association. The analogous phenomenon was previously observed in [8], where it was hypothesized that ethynyl group of EPs, when in interaction with HB acceptor, becomes longer. The same conclusion can be drawn in the systems studied here.

The optimized structures of the dimers PH···DEP complexes (**7** and **8**) are expectedly defined by OH···N HB (Fig. 2). Simultaneously with OH···N HB, in PH···2,6-DEP complex (dimer **7**), an additional OH···π interaction can be theoretically formed (π is for C≡C groups). According to the calculations conducted on this level of theory, OH group of PH is not shared between N-atom and C≡C moieties of 2,6-DEP. Since this is in contrast with results obtained for the complex between PH and 2-EP [8], the explanation is proposed as follows: HB donating and HB accepting sites of monomers, although close enough, are not nearly collinear and directional [24] due to unfavorable steric interactions imposed by two ethynyl groups. In PH···3,5-DEP complex formation (dimer **8**), we performed additional conformational analysis in order to examine the theoretical possibility for OH···π interaction as an interaction competitive to OH···N HB. We found that this dimer is less stable than **8** by ca. 21 kJ mol^{-1} and therefore considered as not probable.

The analysis of NBO charges of the structure of dimers **5–8** and their illustration is given in Supporting Materials (Figs. S6–S9).

The existence of trimers DEPs···2TMP, although possible in theory, is suspected to be experimentally improbable. The theoretical predictions of their structures and thermodynamic parameters, along with experimental findings that exclude their existence in studied solutions, are presented in the Supporting Materials.

IR spectra of binary mixtures at room temperature

Acidity

The most useful spectral feature for probing HB acidity of 2,6-DEP and 3,5-DEP in C$_2$Cl$_4$ solution is the symmetric and antisymmetric stretching of ≡C—H groups (Fig. 3a and b). In IR spectra of both 2,6-DEP and 3,5-DEP solutions the corresponding normal modes produce the bands at 3289 cm^{-1} (weak) 3308 cm^{-1} (strong), the former being assigned as symmetric and the latter as antisymmetric stretching. In addition, there is a shoulder at high frequency side of 3308 cm^{-1} band in IR spectrum of 2,6-DEP (3329 cm^{-1}, very weak) which remains unassigned at the moment. Molar absorption coefficient of the band at 3308 cm^{-1} of 2,6-DEP and, respectively, 3,5-DEP dissolved in C$_2$Cl$_4$ is obtained from Lambert–Beer's law and is $\varepsilon = 518 \pm 4$ mol^{-1} dm^3 cm^{-1}, and, respectively, $\varepsilon = 575 \pm 2$ mol^{-1} dm^3 cm^{-1}.

Basicity

When exposed to certain HB donor like phenol (PH), 2,6-DEP and 3,5-DEP can serve as HB acceptors primary via N-atom on pyridine ring. In characterizing their basicity in thermodynamical terms, OH signal of PH (3610 cm^{-1}) is used as a probe. Its molar absorption coefficient in C$_2$Cl$_4$ is determined elsewhere [8] and is $\varepsilon = 235 \pm 1$ mol^{-1} dm^3 cm^{-1}. Aside N-atom, DEPs possess two C≡C groups that can act as weak HB acceptors. The antisymmetric and symmetric stretching of C≡C groups produces, in general, rather weak and complex feature in IR spectrum of dissolved

2,6-DEP: 2102 cm^{-1} (very weak), 2115 cm^{-1} (weak, $\varepsilon = 29.90 \pm 0.01$ mol^{-1} dm^3 cm^{-1}), 2125 cm^{-1} (weak) and 2135 cm^{-1} (very weak) bands (Fig. 3c). In IR spectrum of 3,5-DEP solution the envelope attributed to the stretchings of C≡C groups is somewhat simpler since it is composed from seemingly two bands; the one at 2105 cm^{-1} (very weak) attributed to the antisymmetric stretching, and the other at 2117 cm^{-1} (weak, $\varepsilon = 1.77 \pm 0.04$ mol^{-1} dm^3 cm^{-1}), attributed to the symmetric stretching (Fig. 3d). In both of the compounds there is one very weak band at 2158 cm^{-1} which remains unassigned. Aside to the appearance of multiband structure in 2,6-DEP solution, the C≡C stretching bands are, in both cases, rather weak, as indicated from ε values given in parenthesis. Thus, these signals will be used only as diagnostic tools for assessment whether the C≡C moieties also participate in HB formation and C≡C will be free from any quantitative analysis.

Since thermodynamic parameters are to be determined only from the maximum of the band at 3308 cm^{-1}, we will not discuss eventual mechanical and/or electrical anharmonicites that appear in IR spectra of studied compounds. This implies that thorough interpretation of all the signals observed in the spectral range where only ≡C—H and C≡C stretching, symmetric and antisymmetric is expected, is not the aim of this paper.

### Temperature dependent IR spectra of binary mixtures

Acidity

In the temperature interval 25–115 °C the most intensive band originated due to ≡C—H stretching (Fig. 3a and b), the one at 3308 cm^{-1} (25 °C) in both 2,6-DEP and 3,5-DEP solutions, decrease in intensity and shift to the higher wavenumbers; at 115 °C it absorbs at 3311 cm^{-1} in 2,6-DEP solution, while in 3,5-DEP solution at 3310 cm^{-1}. The band at 3289 cm^{-1} (25 °C) in IR spectra of both of the compounds moves to the higher wavenumbers with the temperature increase (3292 cm^{-1} at 115 °C), although, in contrast to the 3308 cm^{-1} band, it gains intensity in temperature range 25–115 °C. In 2,6-DEP solution the additional band at 3329 cm^{-1} diminishes immediately when heated above 25 °C. Temperature dependence of molar absorption coefficient at 3308 cm^{-1} is given by the equation.

$\varepsilon(t/°C, 3308$ cm$^{-1}) = (532 \pm 1$ mol^{-1} dm^3 cm$^{-1}) - (1.56 \pm 0.02$ mol^{-1} dm^3 cm^{-1} °C$^{-1}) \cdot (t/°C - 25$ °C) for 2,6-DEP, while corresponding expression for 3,5-DEP is $\varepsilon(t/°C, 3308$ cm$^{-1}) = (572 \pm 2$ mol^{-1} dm^3 cm$^{-1}) - (1.63 \pm 0.02$ mol^{-1} dm^3 cm^{-1} °C$^{-1}) \cdot (t/°C - 25$ °C). In the above equations, t stands for the temperature expressed in °C (if it were expressed in Kelvins, then T would stand).

The signals attributed to the C≡C moieties in both compounds (Fig. 3c and d) in general decrease upon heating, although certain changes in band shapes and in relative intensities can be observed. In 2,6-DEP solution spectra the band at 2102 cm^{-1} observed at 25 °C vanishes when heated, while the bands at 2115 cm^{-1}, 2125 cm^{-1} and 2135 cm^{-1} at 25 °C shift to 2112 cm^{-1}, 2123 cm^{-1} and 2134 cm^{-1} at 115 °C. The bands also became broader and, consequently, the splitting between them is not so pronounced at 115 °C as at 25 °C. In 3,5-DEP in C$_2$Cl$_4$ solution at 25 °C, two bands at 2105 cm^{-1} and at 2117 cm^{-1} appear; the former, being weaker than the latter, generates one broad asymmetric band at 115 °C with the asymmetry pronounced on low-frequency side and the center estimated at 2108 cm^{-1}. In both of the compounds the band at 2158 cm^{-1} (25 °C) shifts to 2157 cm^{-1} (115 °C).

Basicity

Temperature dependence of O—H stretching band of PH in C$_2$Cl$_4$, the purpose of which is to exerts HB accepting abilities of 2,6-DEP and 3,5-DEP, is described in our previous paper [8] and can be presented with the equation
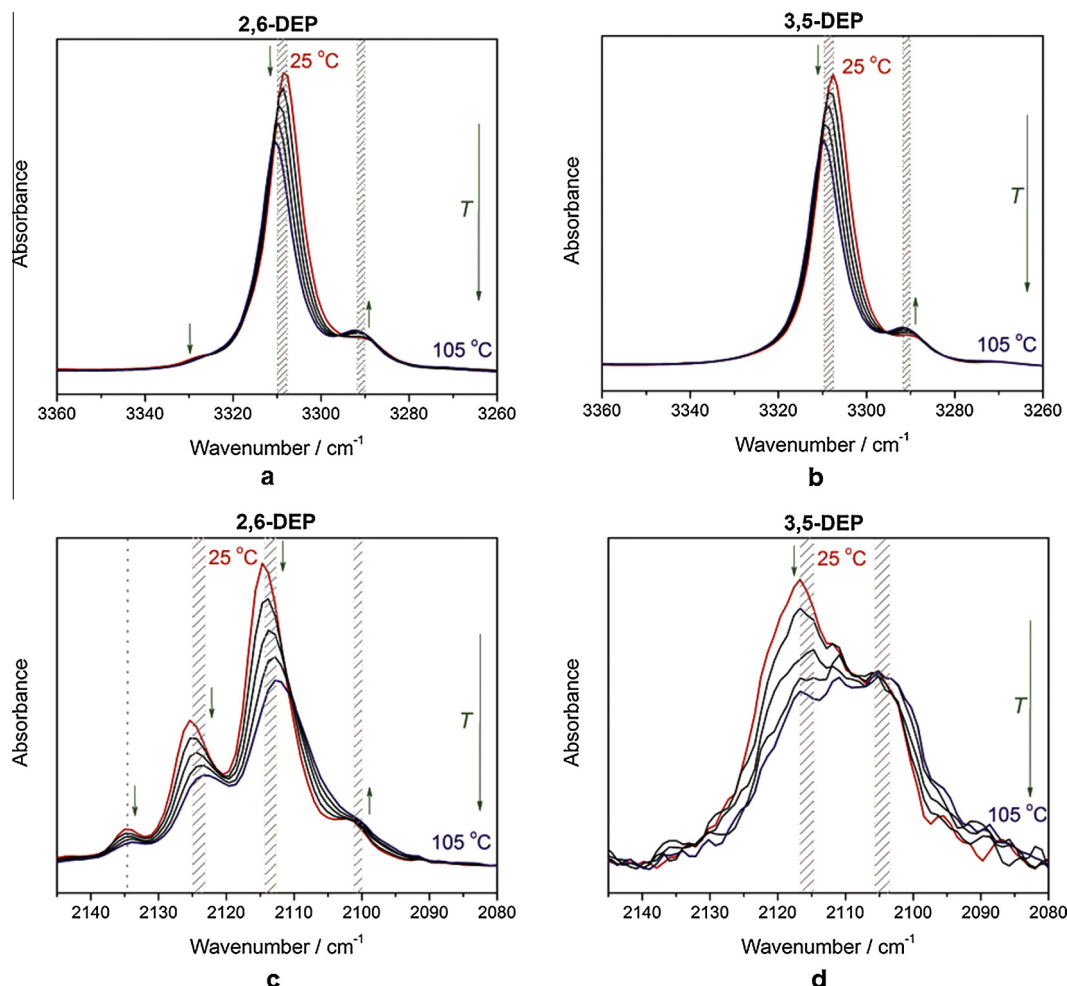
Fig. 3. Temperature study (25–115 °C) of DEPs in C_2Cl_4, after C_2Cl_4 subtraction: (a) $\equiv$C—H stretching (3360–3260 cm^{-1}) of 2,6-DEP (c_0 = 0.01894 mol dm^{-3}); (b) $\equiv$C—H stretching (3360–3260 cm^{-1}) of 3,5-DEP (c_0 = 0.02037 mol dm^{-3}); (c) C$\equiv$C stretching (2145–2080 cm^{-1}) of 2,6-DEP (c_0 = 0.01894 mol dm^{-3}); (d) C$\equiv$C stretching (2145–2080 cm^{-1}) of 3,5-DEP (c_0 = 0.02037 mol dm^{-3}).

$$\varepsilon(t/°C,\ 3610\ \text{cm}^{-1}) = (271 \pm 16\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1})$$
$$- (1.25 \pm 0.32\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}\ °\text{C}^{-1})$$
$$\cdot (t/°\text{C} - 25\ °\text{C})$$

IR spectra of ternary mixtures at room temperature

Acidity

Upon mixing DEPs and TMP, the first and obvious evidence that HB is formed it the appearance of new band at low-frequency side of $\equiv$C—H stretching bands, with intensity and position being dependent on the concentration of TMP (Fig. 4a and b). In concentration range 0.09816 mol dm^{-3} $\leqslant$ c_0(TMP) $\leqslant$ 1.02256 mol dm^{-3} the band attributed to the stretching of $\equiv$C—H$\cdots$O oscillator shifts from 3211 cm^{-1} to 3208 cm^{-1} in 2,6-DEP + TMP in C_2Cl_4 mixture, while from 3209 cm^{-1} to 3206 cm^{-1} in 3,5-DEP + TMP in C_2Cl_4 mixture. The positions of symmetric and antisymmetric $\equiv$C—H stretching bands remain unchanged (3289 cm^{-1}, 3308 cm^{-1} and 3329 cm^{-1} in 2,6-DEP + TMP in C_2Cl_4 mixture and, respectively, 3289 cm^{-1} and 3308 cm^{-1} in 3,5-DEP + TMP in C_2Cl4 mixture), while their intensities are, as expected, reduced with an increase in TMP's concentration. The presence of TMP in both of the compounds induced the changes in C$\equiv$C stretching region as well (Fig. 4c and d), but it has to emphasized that they are more distinguished when TMP in C_2Cl_4 mixture is subtracted from DEPs + TMP in C_2Cl_4 mixtures.

First, we shall discuss 2,6-DEP + TMP in C_2Cl_4 mixtures. Gradual increase in TMP's concentration causes two phenomena: (i) one additional band at about 2101 cm^{-1} appears and gains intensity as TMP is getting more concentrated. Consequently, very weak band at 2102 cm^{-1} merges with the newly formed band; (ii) the band at 2115 cm^{-1} shifts to 2108 cm^{-1}, the band at 2125 cm^{-1} shifts to 2122 cm^{-1}, while the band at 2135 cm^{-1} remains on the same position. In 3,5-DEP + TMP in C_2Cl_4 mixtures new band appears at about 2110 cm^{-1} and, as the concentration of TMP increases, it rapidly gains intensity so that it exceeds by far the bands at 2105 cm^{-1} and 2117 cm^{-1}, where the former exhibits slight shift to the lower wavenumbers (2103 cm^{-1}). Due to the position of the newly formed band and the fact that it is much greater than other two bands, it is hard to estimate whether symmetric stretching of C$\equiv$C moieties (2117 cm^{-1}) shifts or remains at the same position. Overall, the low-frequency shift of C$\equiv$C stretching when involved in HB complex indicates the shortening of C$\equiv$C when DEPs interact with TMP as HB donors [8].

According to the calculations, both free $\equiv$C—H and associated $\equiv$C—H$\cdots$O stretching is shifted to the higher wavenumbers when compared to experimental data (Table 1). Although the magnitude of change ($\Delta \approx -30$ cm^{-1}) is much smaller than the observed change in experiment ($\Delta \approx -100$ cm^{-1}), the observed shift in wavenumbers corresponds to formation of dimers **5** and **6**. The difference in C$\equiv$C and C$\equiv$C$\cdots$stretching bands, although smaller in
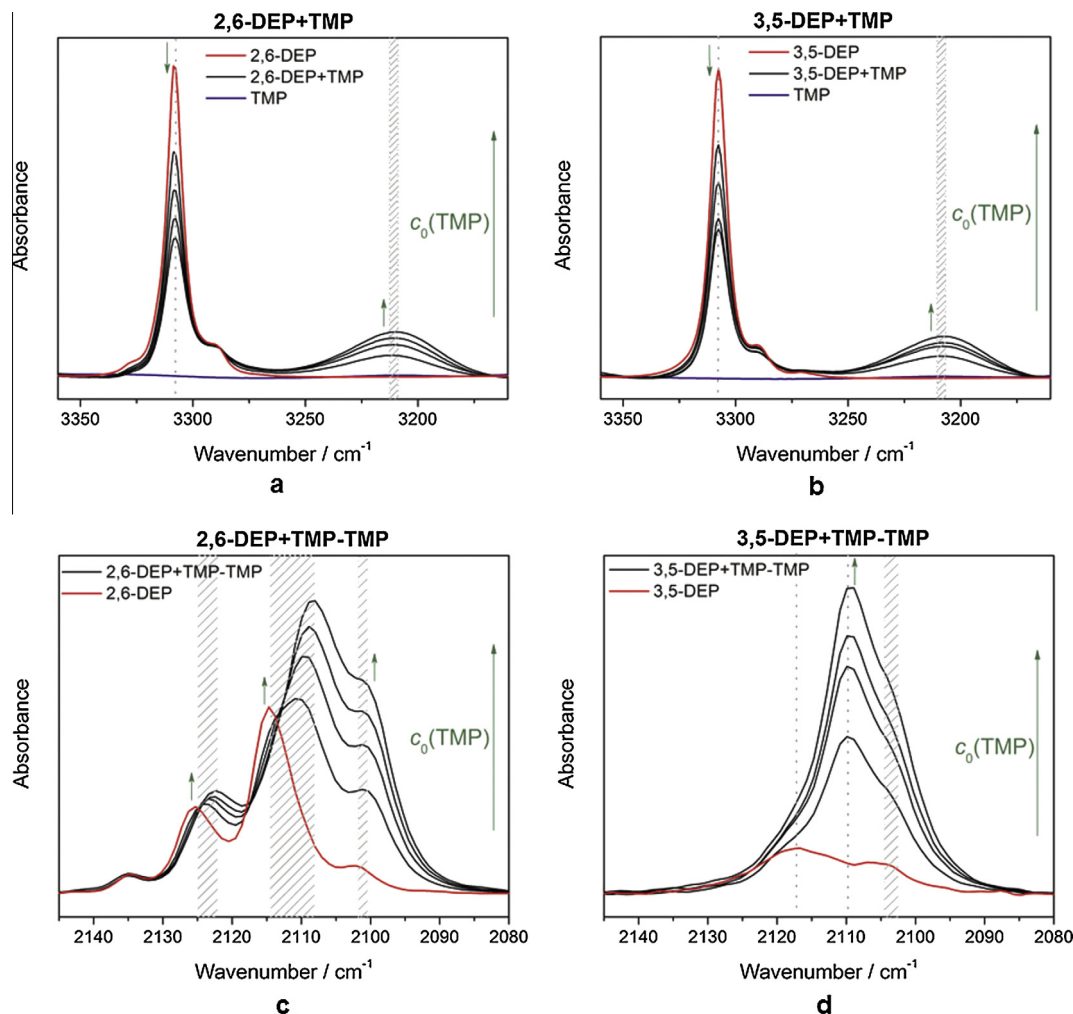
Fig. 4. TMP's concentration dependence (at 26 ± 1 °C) of: (a) ≡C—H and ≡C—H⋯ stretching of 2,6-DEP in a 2,6-DEP + TMP in C_2Cl_4 mixture (3360–3160 cm^{-1}); (b) ≡C—H and ≡C—H⋯ stretching of 3,5-DEP in a 3,5-DEP + TMP in C_2Cl_4 mixture (3360–3160 cm^{-1}); (c) C≡C and C≡C⋯ stretching of 2,6-DEP in a 2,6-DEP + TMP in C_2Cl_4 mixture (2145–2080 cm^{-1}); (d) C≡C and C≡C⋯ stretching of 3,5-DEP in a 3,5-DEP + TMP in C_2Cl_4 mixture (2145–2080 cm^{-1}). IR spectra of (a) and (b) are obtained after C_2Cl_4 subtraction, while (c) and (d) after TMP + C_2Cl_4 subtraction.

predicted ($\Delta \approx -16$ cm^{-1}) than experimentally obtained spectra ($\Delta \approx -25$ cm^{-1}), also corresponds to the formation of dimers **5** and **6**.

Basicity

The differences between PH + 2,6-DEP in C_2Cl_4 mixtures, when compared with the sum of PH in C_2Cl_4 and 2,6-DEP in C_2Cl_4 mixtures, although being rather subtle, are still enough to serve as conclusive evidence on the HB formation between PH and 2,6-DEP (Fig. 5a); there is the rise of one really broad and shallow band with the maximum that almost coincides with the band maximum of ≡C—H stretching bands (~3306 cm^{-1}) and the appearance of the bands attributed to the stretchings of C≡C⋯ oscillators shifted with respect to the bands of monomers 2,6-DEP (from 2102 to 2108 cm^{-1}, from 2115 to 2118 cm^{-1}, from 2125 to 2129 cm^{-1} and from 2135 to 2140 cm^{-1}) (Fig. 5c), while their relative intensities remain the same. In both of the phenomena a concentration dependence of intensities is observed. The shift in frequencies of C≡C⋯ vibrations can be attributed to the charge redistribution caused by the interaction between C≡C and phenyl groups [25]. In PH + 3,5-DEP in C_2Cl_4 mixtures (Fig. 5b), the maximum at the OH⋯N stretching band is estimated to be at about 3204 cm^{-1} so, according to the shift of almost 100 cm^{-1} wavenumbers in lower

spectral range, one can assume that PH and 3,5-DEP form stronger HB that PH and 2,6-DEP.

Optimized structures (Fig. 2) indeed show shorter HB in the dimer **8** than in the dimer **7**. The lack of any other interactions between monomers in **8** enables ideal relative orientation between PH and 3,5-DEP. This may be expected when taking into account the steric hindrance of N-atom in 2,6-DEP. Furthermore, simultaneous engagement of PH's OH group in OH⋯N and OH⋯C≡C HBs is not expected due to spatial limitations, i.e. due to too large distance between N-atom and ≡C⋯H groups in the positions 3 and 5. However, according to the IR spectra in Fig. 5d, with the rise in concentration of 3,5-DEP, one very weak and broad feature emerges at about 2120 cm^{-1}. This phenomenon implies that ≡C⋯H group, regarding its weakness in HB accepting capability in comparison with N-atom of pyridine ring, probably form C≡C⋯OH complexes but not as secondary interaction. The number of such HB complexes is certainly by far below the number of OH⋯N complexes, but they still live long enough to be captured by IR spectroscopy and in certain amount. Unfortunately, due to exceptionally low ε value of even C≡C stretching band profile in the maximum (ε(2117 cm^{-1}) = 1.77 ± 0.04 mol^{-1} dm^3 cm^{-1}), it is not very likely to expect that at given experimental conditions (the room temperature and the medium) the feature assigned as C≡C⋯ stretching band could be better resolved. In both cases,

however, the observed high-frequency shift of C≡C··· oscillator goes along with the assumption that in PH···DEPs complexes the respective moiety lengthens when DEPs play role of HB acceptors [8,25].

Temperature dependent IR spectra of ternary mixtures

Acidity

When mixture of 2,6-DEP + TMP in C_2Cl_4 (c_0(2,6-DEP) = 0.02549 mol dm^{-3}, c_0(TMP) = 0.92479 mol dm^{-3}) is heated from 25 °C to 115 °C, the most important spectral changes are related to the stretching of ≡C—H oscillator, both free and associated (Fig. 6a). At 25 °C, the band at 3208 cm^{-1}, attributed to the stretching of ≡C—H··· oscillator, shifts to 3216 cm^{-1} and continuously decrease intensity when heated up to 115 °C. At the same time, the bands at 3289 cm^{-1} and 3308 cm^{-1} shifts to, respectively, 3292 cm^{-1} and 3310 cm^{-1}. Aside the shift of the band center, another phenomenon that should be discussed is the gain of their intensities when heated up to 85 °C; above that temperature the former keeps increasing, while the latter starts to decrease. The band at 3329 cm^{-1}, as when TMP is absent, vanishes above 25 °C.

In a 3,5-DEP + TMP in C_2Cl_4 mixture (c_0(3,5-DEP) = 0.024 mol dm^{-3}, c_0(TMP) = 0.92479 mol dm^{-3}), ≡C—H··· oscillator shifts from 3206 cm^{-1} (25 °C) to 3214 cm^{-1} (115 °C) simultaneously with an intensity reduction (Fig. 6b). The shift of ≡C—H oscillators, from 3289 cm^{-1} and 3308 cm^{-1} at 25 °C to 3292 cm^{-1} to

3310 cm^{-1} at 115 °C, is accompanied by continuous increase of the former band and the redistribution of intensity of the latter. As in the case of 2,6-DEP + TMP in C_2Cl_4 mixture, up to certain temperature (here 65 °C) there is gain in intensity, while at temperatures above that it decreases.

Regarding C≡C stretching bands in 2,6-DEP + TMP in C_2Cl_4 mixture, the most distinguished change is associated with the decrease of C≡C··· stretching band(s) (Fig. 6c) and their shift from 2101 cm^{-1} (25 °C) to 2099 cm^{-1} (115 °C). The bands at 2108 cm^{-1}, 2122 cm^{-1} and 2135 cm^{-1} absorb at the same wavenumbers in the whole temperature interval and gradually decrease in intensity.

3,5-DEP + TMP in C_2Cl_4 mixture the bands attributed to the stretchings of C≡C and C≡C··· oscillators form rather asymmetric band (Fig. 6d), with asymmetry being changed from 25 °C to 115 °C. One might argue that, at analytical concentrations of 3,5-DEP and TMP, two band could be distinguished at 25 °C, the one at 2105 cm^{-1} and another at 2110 cm^{-1}. When the temperature reaches 115 °C, one rather broad band with slight asymmetry on its low-frequency side appears at 2109 cm^{-1}.

Basicity

Since 2,6-DEP and 3,5-DEP are not very soluble in C_2Cl_4 and, hence, prevent higher analytical concentrations so that temperature dependence of K_c can be more thorough explored, they will be described only qualitatively. In both cases, when PH + DEPs in
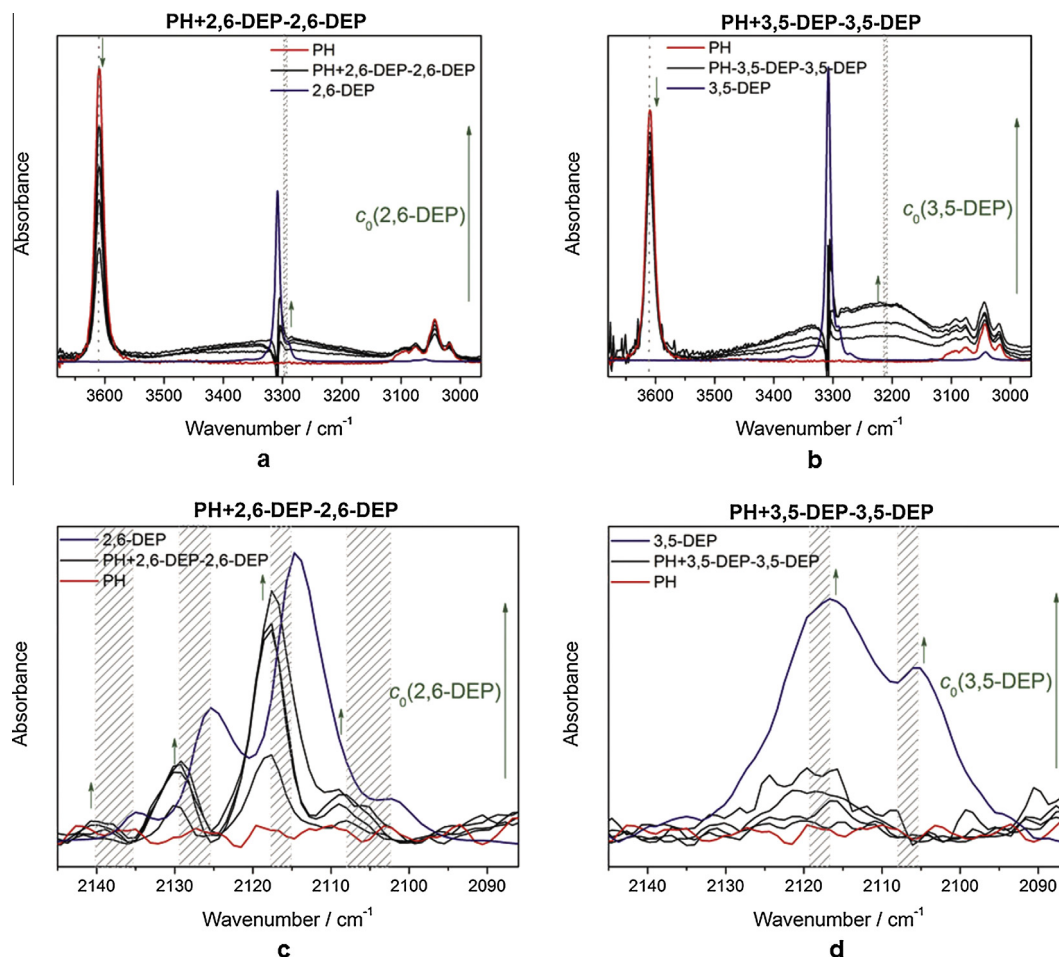
Fig. 5. PH's concentration dependence (at 26 ± 1 °C) of: (a) OH and OH··· stretching of 2,6-DEP in a PH + 2,6-DEP in C_2Cl_4 mixture (3680–2965 cm^{-1}); (b) OH and OH··· stretching of 3,5-DEP in a PH + 3,5-DEP in C_2Cl_4 mixture (3680–2965 cm^{-1}); (c) C≡C and C≡C··· stretching of 2,6-DEP in a PH + 2,6-DEP in C_2Cl_4 mixture (2145–2085 cm^{-1}); (d) C≡C and C≡C··· stretching of 3,5-DEP in a PH + 3,5-DEP in C_2Cl_4 mixture (2145–2085 cm^{-1}). IR spectra of (a) and (b) are obtained after C_2Cl_4 subtraction, while (c) and (d) after DEPs + C_2Cl_4 subtraction.

C_2Cl_4 mixtures are heated in the temperature interval 25–115 °C (Fig. 7a and b), the broad feature centered at about 3308 cm^{-1}, vanishes at the temperatures above 65 °C, as well as the envelope attributed to the stretching of C≡C··· oscillators (Fig. 7c). In 3,5-DEP in C_2Cl_4 mixtures (Fig. 7d) this band is very weak and disappears immediately when heated above 25 °C.

Determination of thermodynamical parameters

When discussing theoretically determined thermodynamic parameters, one has to consider that all calculations were done on isolated molecules, without the influence of solvent molecules. These conditions are more appropriate for isolated molecules in vacuum and some thermodynamic quantities should be different if determined for reactions in vacuum. For example, entropy of reactions in great deal depends on the rotational and translational degrees of freedom of reactants and products and interaction with solvent molecules can limit these degrees of freedom. Nevertheless, it is informative to report calculated thermodynamic parameters, since in this case weak interactions are not influenced by solvent molecules.

As the dimer **5** have two intermolecular interactions, whereas the dimer **6** has only one, respectively, the lower stabilization energy and enthalpy in **5** is observed when compared with **6**. Reaction enthalpy for association of dimer **8** (Table 2) is lower than the

enthalpy of association of structurally similar dimer **8**, due to the stronger hydrogen bond between its constituents (Fig. 2).

Calculated reaction entropy (in vacuum) (Table 2) is much more negative than the experimental result. The large difference can be explained with the interaction of solute molecules with the molecules of solvent. That interaction makes translational and rotational contributions to entropy (that are larger in monomers) lower since the interaction with the solvent restricts these degrees of freedom.

Assuming the 1:1 stoichiometry in both DEPs···TMP and PH···DEPs complexes, association constants K_c were determined from the relationship

$$K_c = \frac{c_0(A) - \frac{A_f}{d \cdot \varepsilon}}{\frac{A_f}{d \cdot \varepsilon} \cdot \left(c_0(B) - c_0(A) + \frac{A_f}{d \cdot \varepsilon}\right)} \tag{2}$$

In expression (2), A_f designates the band absorbance of unassociated HB donor (A) estimated in ternary mixtures (A + B in C_2Cl_4). In particular, when DEPs + TMP in C_2Cl_4 are to be analyzed, the absorbance of ≡C—H stretching at 3308 cm^{-1} (for both DEPs) is to be measured in dependence of the concentration of DEPs (A) and TMP (B). When PH + DEPs in C_2Cl_4 mixtures are concerned, the absorbance of OH stretching (3610 cm^{-1}) is measured as the function of concentration of PH (A) and DEPs (B). ε is molar absorption coefficient of ≡C—H stretching of DEPs (3308 cm^{-1}) and,
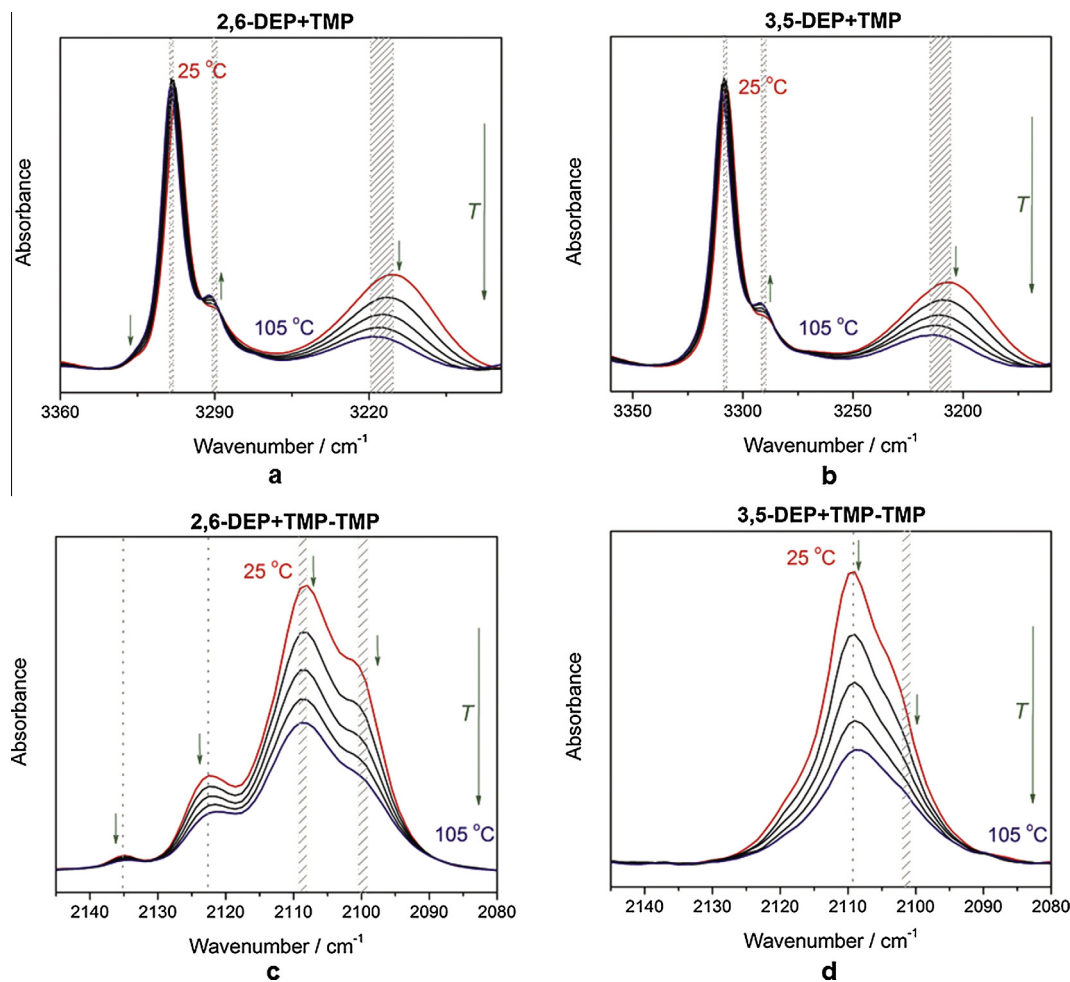
Fig. 6. Temperature study (25–115 °C) of DEPs + TMP in C_2Cl_4 mixture: (a) ≡C—H and ≡C—H··· stretching (3360–3160 cm^{-1}) of 2,6-DEP; (b) ≡C—H stretching and ≡C—H··· stretching (3360–3160 cm^{-1}) of 3,5-DEP; (c) C≡C stretching (2145–2080 cm^{-1}) of 2,6-DEP; (d) C≡C stretching (2145–2080 cm^{-1}) of 3,5-DEP. IR spectra of (a) and (b) are obtained after C_2Cl_4 subtraction, while (c) and (d) after TMP + C_2Cl_4 subtraction. Initial concentrations in (a) and (c) were c_0(2,6-DEP) = 0.02549 mol dm^{-3} and c_0(TMP) = 0.92479 mol dm^{-3}, while in (b) and (d) c_0(3,5-DEP) = 0.024 mol dm^{-3} and c_0(TMP) = 0.92479 mol dm^{-3}.
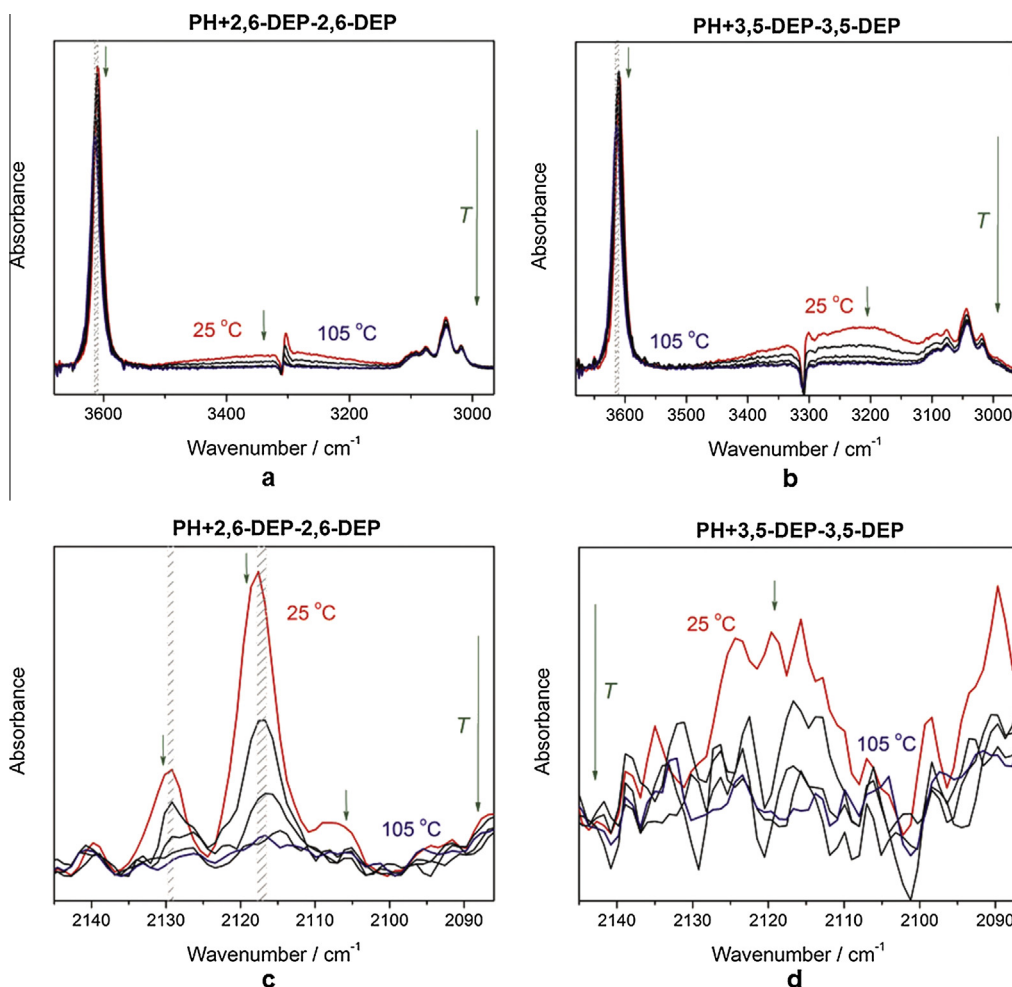
Fig. 7. Temperature study (25–115 °C) of PH + DEPs in C_2Cl_4 mixture: (a) OH and OH$\cdots$ stretching of PH in a PH + 2,6-DEP in C_2Cl_4 mixture (3680–2965 cm^{-1}); (b) OH and OH$\cdots$ stretching of OH in a PH + 3,5-DEP in C_2Cl_4 mixture (3680–2965 cm^{-1}); (c) C≡C and C≡C$\cdots$ stretching of 2,6-DEP in a PH + 2,6-DEP in C_2Cl_4 mixture (2145–2080 cm^{-1}); (d) C≡C and C≡C$\cdots$ stretching of 3,5-DEP in a PH + 3,5-DEP in C_2Cl_4 mixture (2145–2080 cm^{-1}). IR spectra of (a) and (b) are obtained after C_2Cl_4 subtraction, while (c) and (d) after DEPs + C_2Cl_4 subtraction. Initial concentrations in (a) and (c) were c_0(PH) = 0.00713 mol dm^{-3} and c_0(2,6-DEP) = 0.0104 mol dm^{-3}, while in (b) and (d) c_0(PH) = 0.00471 mol dm^{-3} and c_0(3,5-DEP) = 0.02037 mol dm^{-3}.

respectively, OH stretching of PH (3610 cm^{-1}) bands determined from binary mixtures measurements (ε = 518 ± 4 mol^{-1} dm^3 cm^{-1} for 2,6-DEP, ε = 575 ± 2 mol^{-1} dm^3 cm^{-1} for 3,5-DEP and ε = 235 ± 1 mol^{-1} dm^3 cm^{-1} for PH in, respectively, C_2Cl_4). c_0(A) and c_0(B) are analytical concentrations of HB donor (DEPs or PH) and, respectively, HB acceptor (TMP or DEPs). The procedure for determination of the absorbance of the analyzed bands is described in detail in Section 'Spectral analysis', while more details on the relationship between Lambert–Beer's law and K_c are given in Supporting Materials and in Ref. [22].

Experimentally obtained values for K_c, from both room temperature measurements (solution set (ii) in Section 'Preparation of

solutions') and temperature dependent measurement (solution set (iii) in Section 'Preparation of solutions'), employing the relations $\Delta_r G^\ominus = -RT \ln K_c$ and $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$, are presented in Table 3.

Let us begin with the interpretation of thermodynamic parameters for DEPs + TMP in C_2Cl_4 mixtures. According to K_c values obtained from the measurements at room temperature, DEPs$\cdots$TMP complexes are weak (K_c(2,6-DEP$\cdots$TMP) = 0.81 ± 0.09 mol^{-1} dm^3, K_c(3,5-DEP$\cdots$TMP) = 0.89 ± 0.09 mol^{-1} dm^3) and can be considered as equal. Moreover, they are almost equal to the corresponding values of monosubstituted EPs [8] (K_c(2-EP$\cdots$TMP) = 0.82 ± 0.06 mol^{-1} dm^3, K_c(3-EP$\cdots$TMP) = 0.74 ± 0.05 mol^{-1} dm^3), implying that the additional ethynyl moiety on ethynylpyridines does not influence its HB donating properties. The differences between the K_c and, consequently, $\Delta_r G^\ominus$ values measured at room temperature and those obtained from temperature dependent measurements in DEPs$\cdots$TMP complexes are explained as follows: (i) when applying high dilution method in studying HB systems, the uncertainty in the $\Delta_r H^\ominus$ values of HB can be up to ±2.1 kJ mol^{-1} [26]. Although this finding does not present significant obstacle when medium strong or strong HBs are to be characterized ($-\Delta_r H^\ominus \approx 17-170$ kJ mol^{-1}), in the analysis of weak HBs, as are in the systems studied here ($\Delta_r H^\ominus = -8.6 ± 0.8$ kJ mol^{-1} for 2,6-DEP$\cdots$TMP and

Table 2
Energies (BSSE values), enthalpies and entropies at 298.15 K for HB complexes of **5–8** in the gas phase. Values are calculated at the B3LYP6-311++G(d, p) level of theory.

System	ΔE[a]	$\Delta_r H$[a]	$\Delta_r G$[a]	$\Delta_r S$[b]
5	−17.4	−7.9	25.1	−110.5
6	−16.9	−6.5	24.5	−104.2
7	−27.6	−16.4	19.6	−121.0
8	−29.4	−17.6	15.7	−111.8

[a] In kJ mol^{-1}.
[b] In J K^{-1} mol^{-1}.

Table 3
Thermodynamic quantities of DEPs···TMP and PH···TMP complexes obtained from IR spectra at 26 ± 1 °C.

System	K_c [a,d]	$-\Delta_r G^{\ominus}$ [b,d]	$-\Delta_r H^{\ominus}$ [b,e]	$-\Delta_r S^{\ominus}$ [c,e]	$-\Delta_r G^{\ominus}$ [b,e]	K_c [a,e]
5	0.81 ± 0.09	−0.5 ± 0.3	8.6 ± 0.8	28 ± 4	−0.2 ± 0.9	0.9±0.4
6	0.89 ± 0.07	−0.3 ± 0.2	5.7 ± 0.3	17.6 ± 0.9	0.4 ± 0.4	1.2 ± 0.2
7	5 ± 3	4 ± 1	36 ± 5	103 ± 15	5 ± 7	7 ± 20
8	5 ± 2	4 ± 1	15.3 ± 0.8	27 ± 2	7 ± 1	17 ± 9

[a] In mol^{-1} dm^3 at 26 ± 1 °C.
[b] In kJ mol^{-1}.
[c] In J K^{-1} mol^{-1}.
[d] From concentration dependent measurements at room temperature.
[e] From temperature dependent measurements.

$\Delta_r H^{\ominus} = -5.7 \pm 0.3$ kJ mol^{-1} for 3,5-DEP···TMP), this can be rather serious drawback since it counts 20–30% of the magnitude of measured $\Delta_r H^{\ominus}$; (ii) $\Delta_r G^{\ominus}$ values for complex **6**, obtained from room temperature measurements and from single solution in temperature dependent regime, although of opposite signs, in both cases are, expectedly (for $K_c \sim 1$ mol^{-1} dm^3), around zero ($\Delta_r G^{\ominus d} = +0.3$ kJ mol^{-1} and $\Delta_r G^{\ominus e} = -0.4$ kJ mol^{-1}. The superscripts [d] and [e] designate different measurements sets, as given in Table 3). The magnitude of their range ($\Delta\Delta_r G^{\ominus} \equiv \Delta_r G^{\ominus d} - \Delta_r G^{\ominus e} = 0.7$ kJ mol^{-1}) is still smaller than the average thermal energy in solution which counts up to 2 kJ mol^{-1}. In turn, in both cases, K_c determined from temperature dependent measurements is considered as less reliable than K_c obtained from concentration study at room temperature.

As far as PH···DEPs complexes are concerned, certain predictions regarding K_c's orders of magnitude can be made. For HB complexes of PH and pyridines substituted with electron withdrawing groups such as F, Cl or CN in CCl$_4$, K_c values span the range 5–15 mol^{-1} dm^3 [27–30]. As CCl$_4$ is found to be very similar to C$_2$Cl$_4$ [31], in the systems studied here, K_c values are expected to be found in this interval as well. For obtaining as accurate as possible K_c values of these orders of magnitude, it is of utmost importance that HB acceptors (DEPs) are of concentrations 0.01–0.1 mol dm^{-3}, if not even higher [32]. Unfortunately, due to the low solubility of DEPs in C$_2$Cl$_4$, it was impossible to make their solutions with concentrations higher than 0.04 mol dm^{-3} for 2,6-DEP and 0.05 mol dm^{-3} for 3,5-EP. Thus, K_c values, determined only from 4 solutions of PH + 2,6-DEP in C$_2$Cl$_4$ mixtures and, respectively, PH + 3,5-in C$_2$Cl$_4$ mixtures will be reported and they are K_c(PH···2,6-DEP) = 5 ± 3 mol^{-1} dm^3 and K_c(PH···3,5-DEP) = 5 ± 2 mol^{-1} dm^3. Their $\Delta_r H^{\ominus}$ values are, respectively, $\Delta_r H^{\ominus}$ (PH···2,6-DEP) = −36 ± 5 kJ mol^{-1} and $\Delta_r H^{\ominus}$ (PH···3,5-DEP) = −15.3 ± 0.8 kJ mol^{-1}. Additional obstacle in obtaining more precise values of thermodynamic parameters is the analytical concentration of PH in ternary mixtures. As PH undergoes self-association at concentrations higher that 0.1 mol dm^{-3} [33], although some authors reported even as low as 0.003 mol dm^{-3} [34], the most often used analytical concentration of PH in studies concerned HB was about 0.005 mol dm^{-3} [35] and this was also the case in this research. However, when collecting IR spectra of PH, either in binary or ternary mixtures, the OH signal is at the limit of recommended interval of absorbance values (see Supporting Materials, Fig. S2) and, thus, of poor reproducibility. In turn, great uncertainty is generated in these measurements; this is reflected in the values of thermodynamic parameters for complexes **7** (PH···2,6-DEP) and **8** (PH···3,5-DEP) and, respectively, their uncertainties. Additional issue that naturally arises in investigation of HBs produced by OH oscillators is their overlap with OH stretching of water which is always present in measurements, regardless to the fact that background spectrum was collected before collecting the IR spectrum of each sample.

However, one other interesting phenomenon rises related to the involvement of C≡C moieties of DEPs in HBs. C≡C moieties,

according to their IR spectra, certainly participate in PH···2,6-DEP complex. This is not surprised since, sterically, if PH's OH group associates with N-atom, simultaneous interaction with C≡C groups is straightforward. In PH···3,5-DEP complex, on the contrary, simultaneous engagement of OH group of PH with both N-atom and C≡C moieties is disabled due to spatial arrangement. Interestingly, the bands attributed to the C≡C stretching of 3,5-DEP, when PH is added and its concentration is gradually increased, and shifted to higher wavenumbers. This observation indicates that C≡C groups participate in HB and, in contrast to our calculations, likely compete for OH group with N-atom of 3,5-DEP. This is certainly different situation than in PH···3-EP complex, in which this phenomenon has not been observed. Although the absence of this phenomenon in the latter may be explained by small value of $\left(\frac{d\mu}{dQ}\right)^2$ of C≡C stretching, it is also possible that the appearance of this phenomenon in PH···3,5-DEP complex is a result of the cooperativity of two ethynyl moieties. In effect, it can be considered that C≡C groups, together with OH group, form some kind of resonance-assisted HB (RAHB), as proposed by Gilli et al. [36]. Although they based this model on strong and medium strong HBs, due to electron flow through triple bond system, mediated by phenyl (pyridine) ring, it may be that the strength of mutual interaction by far overcomes the solitary C≡C—H···OH interaction (Fig. 8).

Due to the weakness of the observed band it is not possible to quantify the magnitude of the proposed effect and, in turn, characterize the cooperativity in numeric terms. However, it is very likely that this phenomenon may be more thorough investigated and characterized by using other spectroscopic techniques, such as IR UV double resonance spectroscopy or at least matrix isolated IR, that are more efficient in both detection and subsequent characterization of weak HBs. The employment of explicit solvation computational models, along with the more sensitive spectroscopic techniques, is also highly recommended.
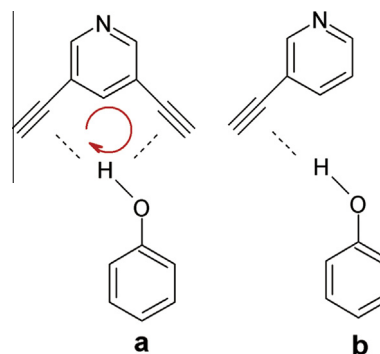
Fig. 8. Possible resonance-assisted HB in (a) PH···3,5-DEP complex in contrast to (b) PH···3-EP complex.

Conclusions

Hydrogen bonding properties of 2,6- and 3,5-DEP were explored by IR spectroscopy and were further supported by computational approach. High dilution method was used for determination of thermodynamic parameters, K_c and $\Delta_r H^{\ominus}$, that characterize the associations of DEPs with TMP and, respectively, DEPs with PH molecules in C_2Cl_4. In the former case it is assumed that the association stoichiometry is 1:1 and the corresponding parameters, K_c and $\Delta_r H^{\ominus}$, for 2,6-DEP$\cdots$TMP and, respectively, 3,5-DEP$\cdots$TMP HB systems are $0.81 \pm 0.09 \, \text{mol}^{-1} \, \text{dm}^3$ and $-8.6 \pm 0.8 \, \text{kJ} \, \text{mol}^{-1}$ and, respectively, $0.89 \pm 0.09 \, \text{mol}^{-1} \, \text{dm}^3$ and $-5.7 \pm 0.3 \, \text{kJ} \, \text{mol}^{-1}$. In PH$\cdots$DEPs HB complexes, with 1:1 stoichiometry, K_c and $\Delta_r H^{\ominus}$ are $5 \pm 3 \, \text{mol}^{-1} \, \text{dm}^3$ and $-36 \pm 5 \, \text{kJ} \, \text{mol}^{-1}$ for PH$\cdots$2,6-DEP, while $5 \pm 2 \, \text{mol}^{-1} \, \text{dm}^3$ and $-15.3 \pm 0.8 \, \text{kJ} \, \text{mol}^{-1}$ for PH$\cdots$3,5-DEP. In all associations, regardless to the HB donating or HB accepting role of DEPs, C≡C moiety was found to participate in the HB complex formation. This was shown to be of exceptional importance in PH$\cdots$3,5-DEP complexes, were simultaneous involvement of OH group in both OH$\cdots$N and OH$\cdots$C≡C association is disabled due to spatial arrangement. Therefore, it is postulated that cooperativity between two ethynyl groups covalently linked to a resonance system, plays an important role in augmentation of HB accepting strength of C≡C moieties of 3,5-DEP.

The calculations were conducted at the B3LYP/6-311++G(d,p) level of theory in the gas phase and are supporting experimental data. The most stable conformers in gas phase are characterized by HB formed via ≡C—H$\cdots$O interactions, whereas dimers between phenol and diethynylpyridines are formed only through OH$\cdots$N HB interaction. Both experimental and calculated values excluded the existence of trimers, i.e. DEPs$\cdots$2TMP hydrogen bonded complexes.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.10.107.

References

[1] S. Maity, M. Guin, C. Singh, G. Naresh Patwari, Phenylacetylene: a hydrogen bonding chameleon, ChemPhysChem 12 (2011) 26–46.

[2] P. Chandra Singh, B. Bandyopadhyay, G. Naresh Patwari, Structure of the phenylacetylene–water complex as revealed by infrared-ultraviolet double resonance spectroscopy, J. Phys. Chem. A 112 (2008) 3360–3363.

[3] R. Sedlak, P. Hobza, G. Naresh Patwari, Hydrogen-bonded complexes of phenylacetylene with water, methanol, ammonia, and methylamine. The origin of methyl group-induced hydrogen bond switching, J. Phys. Chem. A 113 (2009) 6620–6625.

[4] P. Chandra Singh, G. Naresh Patwari, IR-UV double resonance spectroscopic investigation of phenylacetylene–alcohol complexes. Alkyl group induced hydrogen bond switching, J. Phys. Chem. A 112 (2008) 5121–5125.

[5] S. Maity, G. Naresh Patwari, Hydrogen bonding to multifunctional molecules: spectroscopic and ab initio investigation of water complexes with fluorophenylacetylenes, J. Phys. Chem. A 113 (2009) 1760–1769.

[6] S. Maity, D.K. Maity, G. Naresh Patwari, Interaction of alcohols with 2-fluoro- and 4-fluorophenylacetylenes: infrared-optical double resonance spectroscopic and computational investigation, J. Phys. Chem. A 115 (2011) 11229–112237.

[7] S. Maity, G. Naresh Patwari, Hydrogen bonding to multifunctional molecules: spectroscopic and ab initio investigation of 4-ethynylbenzonitrile-(water)1–3 complexes, J. Phys. Chem. A 114 (2010) 8337–8344.

[8] D. Vojta, I. Matanović, G. Kovačević, G. Baranović, The study of secondary effects in vibrational and hydrogen bonding properties of 2- and 3-ethynylpyridine and ethynylbenzene by IR spectroscopy, Spectrochim. Acta A 132 (2014) 215–224.

[9] C.A. Hunter, H.L. Anderson, What is cooperativity?, Angew Chem. Int. Ed. 48 (2009) 7488–7499.

[10] T.F.A. de Greef, M.M.J. Smulders, M. Wolffs, A.P.H.J. Schenning, R.P. Sijebesma, E.W. Meijer, Supramolecular polymerization, Chem. Rev. 109 (2009) 5687–5754.

[11] A. Camara-Campos, D. Musumeci, C.A. Hunter, S. Turega, Chemical double mutant cycles for the quantification of cooperativity in H-bonded complexes, J. Am. Chem. Soc. 131 (2009) 18518–18524.

[12] I.A.W. Filot, A.R.A. Palmans, P.A.J. Hilbers, R.A.V. Santen, E.A. Pidko, T.F.A. de Greef, Understanding cooperativity in hydrogen-bond-induced supramolecular polymerization: a density functional study, J. Phys. Chem. B 114 (2010) 13667–13674.

[13] M. Roman, C. Cannizzo, T. Pinault, B. Isare, B. Andrioletti, P.V.d. Schoot, L. Boutieller, Supramolecular balance: using cooperativity to amplify weak interactions, J. Am. Chem. Soc. 132 (2010) 16818–16824.

[14] E.M. Arnett, L. Joris, E. Mitchell, T.S.S.R. Murty, T.M. Gories, P.V.R. Schlayer, Studies of hydrogen-bonded complex formation III. Thermodynamics of complexing by infrared spectroscopy and calorimetry, J. Am. Chem. Soc. 92 (1970) 2365–2377.

[15] S.-i-. Kawahara, T. Uchimaru, Basis set effect on hydrogen bond stabilization energy estimation of the Watson–Crick type nuclei acid base pairs using medium-size basis sets: single point MP2 evaluations at the HF optimized structures, Phys. Chem. Chem. Phys. 2 (2000) 2869–2872.

[16] A.E. Reed, R.B. Weinstock, F. Weinhold, Natural population analysis, J. Chem. Phys. 83 (1985) 735–746.

[17] S.F. Boys, F. Bernardi, The calculations of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, Mol. Phys. 19 (1970) 553–566.

[18] M.P. Andersson, P. Uvdal, New scale factors for harmonic vibrational frequencies using the B3LYP density functional method with the triple-zeta basis set 6-311+G(d, p), J. Phys. Chem. A 109 (2005) 2937–2941.

[19] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347–1363.

[20] M.S. Gordon, M.W. Schmidt, in: C.E. Dykstra, G. Frenking, K.S. Kim, G.E. Scuseria (Eds.), Theory and Applications of Computational Chemistry, the First Forty Years, Elsevier, Amsterdam, 2005, pp. 1167–1189.

[21] R. Chinchilla, C. Nájero, The Sonogashira reaction: a booming methodology in synthetic organic chemistry, Chem. Rev. 107 (2007) 874–922.

[22] E.M. Arnett, L. Joris, E. Mitchell, T.S.S:R. Murty, T.M. Gories, P.v.R. Schlayer, Studies of hydrogen-bonded complex formation III. Thermodynamics of complexing by infrared spectroscopy and calorimetry, J. Am. Chem. Soc. 92 (1970) 2365–2377.

[23] J.E. Bertie, C.D. Keefe, R.N. Jones, Tables of intensities for the calibration of infrared spectroscopic measurement in the liquid phase, first ed., Blackwell Science Ltd., Oxford, 1995, p. 13.

[24] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, first ed., Oxford University Press, New York, 1999, pp. 40–80.

[25] D. Vojta, M. Vazdar, The study of hydrogen bonding and π$\cdots$π interactions in phenol$\cdots$ethynylbenzene complex by IR spectroscopy, Spectrochim. Acta A 132 (2014) 6–14.

[26] E.M. Arnett, E.J. Mitchell, T.S.S.R. Murty, Basicity. A comparison of hydrogen bonding and proton transfer to some lewis bases, J. Am. Chem. Soc. 96 (1974) 3875–3889.

[27] M.H. Abraham, P.L. Grellier, D.V. Prior, J.J. Morris, P.J. Taylor, Hydrogen bonding. Part 10. A scale of solute hydrogen-bond basicity using log$K$ values for complexation in tetrachloromethane, J. Chem. Soc. Perkin Trans. 2 (1990) 521–529.

[28] L. Joris, P.V.R. Schlayer, π-deficient N-heteroaromatics as proton acceptors in hydrogen-bonding, Tetrahedron 24 (1968) 5991–6005.

[29] H.P. Hopkins Jr., C.J. Alexander, S. Zakir Ali, A quantitative comparison of the relative hydrogen bonding basicities and the gas-phase proton affinities of substituted pyridines, J. Phys. Chem. 82 (1978) 1268–1272.

[30] J. Rubin, G.S. Panson, Hydrogen bonding. II. Phenol interactions with substituted pyridines, J. Phys. Chem. 69 (1965) 3089–3091.

[31] J. Graton, M. Berthelot, C. Laurence, Hydrogen-bond basicity pK_{HB} scale of secondary amines, J. Chem. Soc., Perkin Trans. 2 (2001) 2130–2135.

[32] R. Adámek, Z. Ksandr, Accuracy of the determination of hydrogen bond association constant by IR spectroscopy, Collect. Czech. Chem. Commun. 33 (1968) 3053–3056.

[33] K.B. Whetsel, J.H. Lady, Self-association of phenol in non-polar solvents, Spectrometry of Fuels, Plenum Press, 1970, pp. 259–279.

[34] J.M. Widom, R.J. Philippe, M.E. Hobbs, A study of the association of phenol with several ketones by infrared, J. Am. Chem. Soc. 79 (1957) 1383–1386.

[35] J. Brandmüller, K. Seevogel, Infrarotspektroskopische untersuchungen zur wasserstoffbrükenbindung bei pyridin-alkohol-gemischen, Spectrochim. Acta 20 (1964) 453–465.

[36] P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, Predicting hydrogen-bond strengths from acid–base molecular properties. The pK slide rule: toward the solution of a long-lasting problem, Acc. Chem. Res. 42 (2009) 33–44.