ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/6224597

Proton transfer in hydrogen-bonded pyridine/acid systems: The role of higher aggregation

ARTICLE *in* PHYSICAL CHEMISTRY CHEMICAL PHYSICS · JULY 2007

Impact Factor: 4.49 · DOI: 10.1039/b701775h · Source: PubMed

CITATIONS
20

READS
53

6 AUTHORS, INCLUDING:

Vytautas Balevicius
Vilnius University
57 PUBLICATIONS **244** CITATIONS

SEE PROFILE

Ruta Bariseviciute
Center for Physical Sciences and Technology
8 PUBLICATIONS **41** CITATIONS

SEE PROFILE

Available from: Ruta Bariseviciute
Retrieved on: 26 January 2016

Proton transfer in hydrogen-bonded pyridine/acid systems: the role of higher aggregation

Vytautas Balevicius,*[a] Ruta Bariseviciute,[a] Kestutis Aidas,†[a] Ingrid Svoboda,[b] Helmut Ehrenberg[b] and Hartmut Fuess[b]

Received 5th February 2007, Accepted 27th March 2007
First published as an Advance Article on the web 16th April 2007
DOI: 10.1039/b701775h

In this work the role of higher molecular aggregation in the proton transfer processes within hydrogen bond (H-bond) is investigated. The H-bonded complex consisting of 4-cyanopyridine (CyPy) with trichloroacetic acid (TCA) has been studied in the solutions of acetonitrile, carbon tetrachloride, chloroform and dichloroethane as solvent by FTIR spectroscopy and quantum chemical DFT calculations. In order to illustrate the effect of increasing H-bond strength FTIR investigations have also been performed on solutions of CyPy with H_2O, acetic-, trifluoroacetic- and methanesulfonic acids. Proton states in the H-bond have been monitored using vibrational CyPy ring modes in FTIR spectra. The stabilization of the CyPy/TCA complex in its protonated form upon increasing polarity of the solvent has been evidenced. It was shown that formation of the CyPy/$(TCA)_2$ aggregates in the solutions favors the proton transfer process. An X-ray diffraction study has been performed on a single 1 : 2 co-crystal of pyridine/3,5-dinitrobenzoic acid. The H-bond motif found in this system exhibits the same connectivity by strong hydrogen bonds N–$H^+\cdots O^-$ and O–H···O as that in the CyPy/$(TCA)_2$ complex predicted by DFT calculation. Certain discrepancies are observed in C–H···O connectivity only. The networks of H-bonds in both assemblies differ from those usually pictured for 1 : 2 base/carboxylic acid complexes in the literature.

Introduction

The proton transfer belongs to the class of simplest chemical reactions that are very important in many physical, biochemical and technological processes, and thus selected simple hydrogen-bonded systems are reasonable models to study this phenomenon.[1–3] Derivatives of pyridine (Py) occupy in the field of hydrogen bond research a very particular place.[2–5] Their proton accepting abilities can be varied in a broad range by proper substitution in a definite position of the π-electron 'carcass' of these molecules. Hence, one can manipulate the H-bond strength and thus gain or damp the proton transfer and its dynamics.

The proton transfer in rather concentrated solution can be coupled with aggregation processes *via* formation of complexes with various stoichiometric ratios (1 : 2, 2 : 1, or even higher). These species have been recognized in NMR and FTIR spectra of some Py/acid systems[3,6,7] and found theoretical support by quantum chemical DFT calculations.[8] This concept of higher aggregation would explain the nature of H-bond in solution that sometimes looks 'more ionic' than in the solid. It is well known that a formation of additional O–H···O bonding after the second carboxylic acid molecule joined to a 1 : 1 complex leads to strengthening of the already existing O–H···N one.[7] From the physical point of view it seems to be a more general phenomenon that was already discussed in terms of specific solvation,[8] or in ref. 9 as a short-range order solvent effect. Namely, an 'extra' polar molecule (it may be the one either from solvent or solute or even from impurities, *e.g.* water[10]) placed near the complex in proper position and proper orientation can strengthen the H-bond. Thus it initiates or deepens the proton transfer process. It is obvious that such regrouping of molecules can happen only in solution due to a high degree of motional freedom, whereas it is a rarity for solid phases.

We report in this paper new data concerning the role of higher molecular aggregation in proton transfer in H-bond complex of 4-cyanopyridine (CyPy) and trichloroacetic acid (TCA) in various solutions (acetonitrile (AN), chloroform (CLF), carbon tetrachloride (CCl_4), dichloroethane (DCE) as solvent based on the data from FTIR measurements and quantum chemical DFT calculations. In order to illustrate the effect of increase of H-bond strength some additional FTIR investigations have been performed on solutions of CyPy with H_2O, acetic (AA), trifluoroacetic (TFA) and methanesulfonic (MSA) acids. The X-ray diffraction study has been carried out on a single 1 : 2 co-crystal of Py/3,5-dinitrobenzoic acid (DNBA).

Experimental

Samples

Commercial acetonitrile (AN), chloroform (CLF), carbon tetrachloride (CCl_4), dichloroethane (DCE), 4-cyanopyridine

[a] *Faculty of Physics, Vilnius University, LT-10222 Vilnius, Lithuania. E-mail: vytautas.balevicius@ff.vu.lt; ruta.bariseviciute@ff.vu.lt; kestutis.aidas@ff.vu.lt*
[b] *Institute for Materials Science, University of Technology Darmstadt, D-64287 Darmstadt, Germany. E-mail: svoboda@tu-darmstadt.de; Ehrenberg@tu-darmstadt.de; hfuess@tu-darmstadt.de*
† Present address: Department of Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark.

(CyPy), acetic (AA), trichloroacetic (TCA), trifluoroacetic (TFA) and methanesulfonic (MSA) acids were preliminarily purified by standard methods. The solutions of CyPy/TCA were prepared in a dry box by weighing (±0.1 mg) the components. A single 1 : 2 co-crystal of Py/3,5-dinitrobenzoic acid (DNBA) was obtained from methanol at the National Institute of Chemistry (Ljubljana, Slovenia).

Spectroscopic measurements

FTIR spectra were recorded on a NICOLET-400 FTIR spectrometer on line with a standard computer. Solutions were contained in a cell between NaCl windows with Teflon™ spacer (0.05 and 0.603 mm). The instrument was purged with dry nitrogen to avoid CO_2 absorption. The spectral resolution was 1–2 cm^{-1}, and a total of 64 interferograms were added and averaged for each spectrum. Difference spectra were obtained by interactive subtraction using Opus program package.

X-Ray diffraction study

Diffraction data have been collected in ω and φ-scans on the Xcalibur system from Oxford Diffraction (TU Darmstadt) equipped with a CCD area-detector. No absorption corrections were applied. The structure was solved from X-ray data using SHELXS.[11] The refinement was performed with SHELXL.[12] All H atoms were located in a difference Fourier map, and their atomic coordinates were refined with U_{iso}(H) set to $1.2U_{eq}$ of the parent atom. Details of data acquisition, lattice constants and hydrogen bonding scheme are collected in Tables in the Results and discussion section.

CCDC reference number 635846. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701775h

Density functional theory (DFT) calculation

In order to obtain supplementary insight into the experimental findings, we have conducted the DFT electronic structure calculations using the GAUSSIAN 03 program package.[13] The DFT has been proven to yield rather reliable results for molecular geometries and vibrational frequencies for most H-bond systems (see ref. 14–16 and references therein). A B3LYP exchange–correlation functional[17] was chosen for the calculation of the equilibrium geometries, energies and harmonic vibrational frequencies of the considered molecular systems. The polarizable continuum model (PCM)[18,19] was employed to model the liquid phase. We have used default settings of the PCM as implemented in GAUSSIAN 03, but United Force Field (UFF) model was applied for the construction of the molecular cavities. According to the UFF model, individual spheres are built for both the heavy atoms and hydrogens. Such procedure leads to more realistic molecular cavities for small hydrogen-bonded complexes and, to some extent, accounts for the directionality of the hydrogen bonds. We refer to the next section for the discussion on the choice of the basis set used in these calculations.

Results and discussion

The CyPy/TCA has been chosen in the present work for several reasons. First, high-quality neutron and X-ray diffraction,[20] as well as some basic FTIR data of solid samples[21] are available for this system. Moreover, there are plenty of X-ray data that describe the hydrogen bond between carboxylic acids and pyridines in relation to very special topics of crystal engineering (co-crystallization, supramolecular synthons, *etc.*), *e.g.*, ref. 22–24, or contribute to more or less traditional problems of H-bonding.[25–27] All these data are useful for comparative purposes. We selected several closely related systems, such as H-bond complexes of derivatives of pyridine with dinitrobenzoic acid,[26,27] where proton transfer and related properties were also studied by FTIR spectroscopy.

A comparison of diffraction data with FTIR observations allows to assign rigorously some sensitive vibrational bands that may be used to study proton transfer processes. The complex shaped νOH band (due to this complexity it is not always possible to determine reliably its spectral parameters (center of gravity, integrated intensity, *etc.*)) and that of carbonyl stretching vibrations (νC=O), located at 1650–1750 cm^{-1}, are exploited to study the H-bond features in these systems most frequently.[6,7,26–28] However, the information obtained by the analysis of these bands seems sometimes so overfilled that it does not even allow unambiguous interpretation.

Another, rather unusual, feature is observed in the spectral range of 1550–1650 cm^{-1} where the pyridine ring modes are located. For one of these modes FTIR investigations of series of Py/acid solutions in CLF[28] give the values covering 1630 (Py/cyanoacetic acid, *i.e.* the 'weakest' acid, where this band was observed)—1635 cm^{-1} (Py/TFA). This band was assigned to a pyridinium (PyH^+) vibration,[28] but not used for more detailed studies. Due to the small influence of substitution of Py on its frequency this vibration is rather characteristic. On the other hand, because of such large sensitivity on protonation ('blue' shift of $\sim$40 cm^{-1} with respect to the 'non-bonded' Py), its frequency can be accepted as a universal criterion of proton transfer for the whole family of pyridines. Note that it was already successfully used to monitor proton transfer processes in some polymers and supramolecular nanostructures.[29,30]

The behavior of two pyridine ring modes (designed as ν1 and ν2, Fig. 1) with changing dielectric properties of the media and H-bond strength has been studied by FTIR and DFT methods. We have measured FTIR spectra of non-H-bonded CyPy (further referred to as 'free' CyPy) and CyPy/TCA aggregates in various solvents (AN, CLF, CCl_4, and DCE). In order to illustrate the effect of increasing H-bond strength,

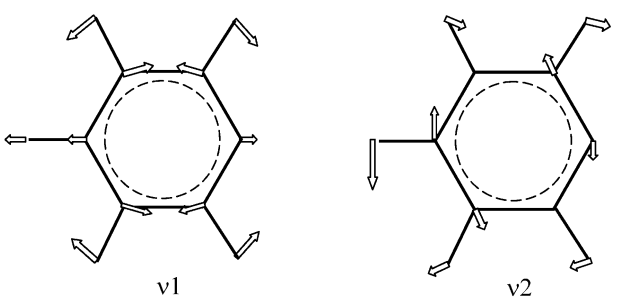

Fig. 1 The pyridine ring modes.

This journal is © the Owner Societies 2007

Table 1 The B3LYP basis set analysis on CyPy vibrational frequencies (all in cm^{-1})

Mode	6-311++G	6-311++G(d,p)	6-311++G(2df,2pd)	6-311++G(3df,3pd)	Experiment[a]
	{152}[b]	{204}	{332}	{384}	
	1014.1	1008.9	1016.8	1014.3	990.0
	1099.8	1092.2	1095.0	1095.6	1068.5
	1252.8	1246.1	1246.3	1246.5	1209.2
	1255.8	1265.5	1262.0	1262.9	1219.4
	1442.7	1439.5	1444.2	1443.5	1407.6
	1518.4	1519.4	1524.7	1523.2	1487.9
$\nu 2$	1567.9	1585.9	1586.1	1586.1	1552.7
$\nu 1$	1619.3	1628.7	1629.1	1629.5	1592.5
ν(CN)	2272.7	2341.2	2339.8	2341.2	2240.1

[a] 1 M solution in CCl_4. [b] Corresponding numbers of basis functions are given in parenthesis {···}.

FTIR investigations have also been performed on solutions of CyPy with H_2O, AA, TFA and MSA.

In combination with the B3LYP functional, we have tested a series of Pople style basis sets[31–35] including 6-311++G, 6-311++G(d,p), 6-311++G(2d,2p) and 6-311++G(3df,3pd) by calculating the vibrational spectrum of the CyPy in the solution of CCl_4. The reaction field of the solvent was taken into account by the PCM-UFF method. The calculated vibrational frequencies for different basis sets in the spectral range of 1000–2400 cm^{-1} are collected in Table 1. Corresponding experimental data are also included in Table 1 for comparison. The obtained results indicate that 6-311++G(d,p) vibrational frequencies are fairly converged with respect to the basis set size and flexibility. They differ from the corresponding 6-311++G(3df,3pd) values by less than 7 cm^{-1}. Thereby, we use the B3LYP functional together with the 6-311++G(d,p) basis set for all electronic structure calculations in the present work. We note that the computed vibrational frequencies using any basis set are overestimated as compared to the experimental data (see Table 1). However, the qualitative agreement of the theoretical B3LYP/6-311++G(d,p) and experimental vibrational spectra is rather satisfactory (Fig. 2).

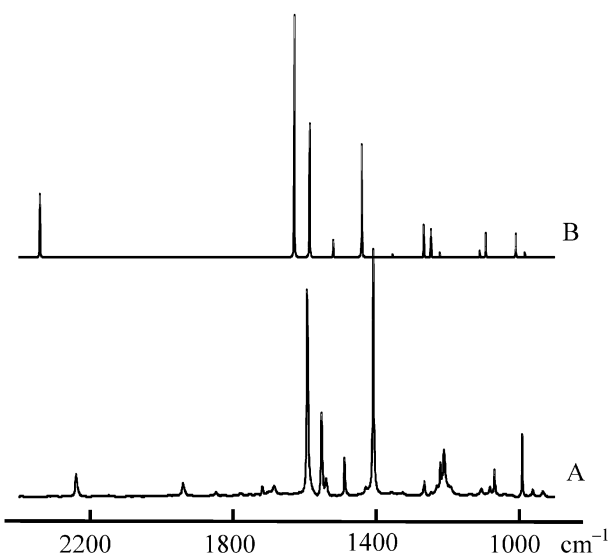

Fig. 2 Experimental (A, 0.066 M CyPy solution in CCl_4, 0.6 mm spacer) and calculated (B, DFT B3LYP functional combined with 6-311++G(d,p) basis set) FTIR spectra of CyPy.

The CyPy/TCA complexes were investigated in various solvents. The main attention was focused on the pyridine ring modes $\nu 1$ and $\nu 2$, located at *ca.* 1593 and 1553 cm^{-1}, respectively. The FTIR spectra in this region are shown in Fig. 3. The behavior of these modes is very different: the position of the $\nu 2$ mode is rather stable, while $\nu 1$ is very sensitive to the H-bonding and dielectric properties of the solvent. The shift of $\nu 1$ frequency from 1593 cm^{-1} ('free' CyPy) to 1607 (CyPy/TCA complex in CCl_4) and 1615 cm^{-1} (complex in AN) is caused by H-bonding and solvation effects. The survival of the band at 1593 cm^{-1} (*i.e.* 'free' CyPy) in experimental spectra indicates that some part of non-bonded CyPy molecules is always present in the solution due to chemical equilibrium.

In order to explain the observed changes in the FTIR spectra, full geometry optimization of CyPy/TCA complex was performed, and vibrational frequencies were calculated in each solvent using the PCM-UFF method. There exists an opinion that static calculations, even at high level and applying PCM with high values of dielectric constants (ε) fail to simulate proton transfer processes. However, the DFT calculation at the level of theory of the present work, *viz.* B3LYP/6-311++G(d,p) with PCM, allowed to reveal the proton transfer in pyridine-N-oxide(PyO)/TCA and in PyO/TFA complexes in AN solutions, *i.e.* in very closely related systems.[36]

In the present case, *i.e.* the CyPy/TCA complex, the H-bond exhibits rather dynamical features upon solvent polarity effects. This is seen on its structural parameters and binding

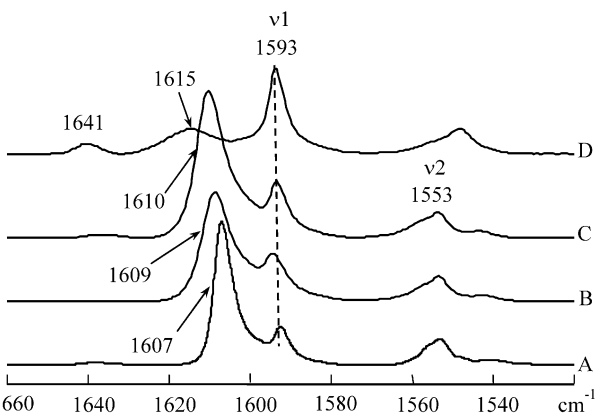

Fig. 3 FTIR spectra of CyPy/TCA in pyridine ring modes region in solutions of CCl_4 (A), CLF (B), DCE (C) and AN (D).

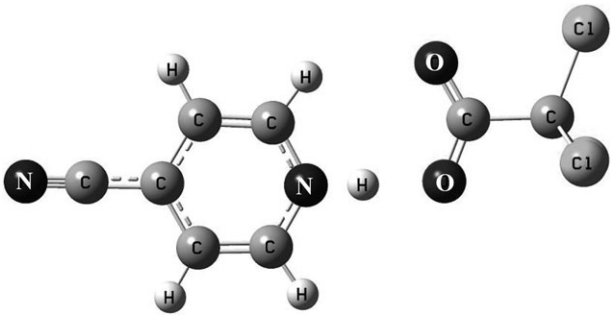

Fig. 4 Optimized structure of CyPy/TCA complex. Structural parameters of H-bond are given in Table 2.

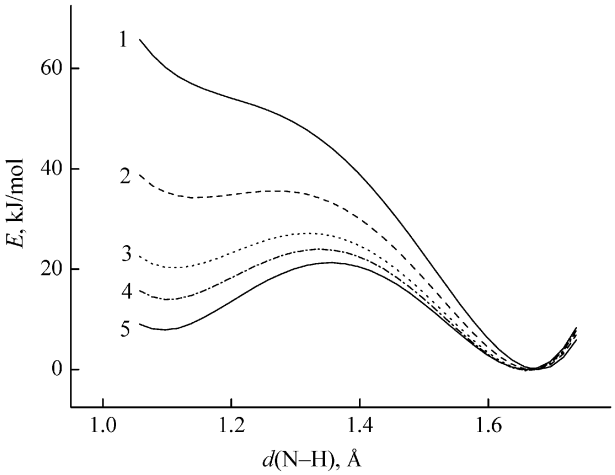

Fig. 5 Solvent effect on the proton potential function of CyPy/TCA complex at $d(N\cdots O) = 2.6941$ Å (*i.e.* as *in vacuo*): 1 – *in vacuo*; 2 – in CCl_4; 3 – in CLF; 4 – in DCE and 5 – in AN. The potentials are shifted to coincidence of energy minimums at $d(N–H) \approx 1.68$ Å.

energies (Fig. 4 and Table 2), and it is also clearly illustrated on the shape of proton potential energy function in Fig. 5.

The calculations using fixed value $d(N\cdots O) = 2.6941$ Å (*i.e.* as *in vacuo*) show that the inflection on the energy surface close to TCA oxygen (distanced by $\sim$1.02 Å) evolves into a second minimum close to CyPy nitrogen (at $d(N\cdots H) \approx 1.1$ Å) and gradually deepens with increasing polarity of the solvent. Note the second minimum is always above the first one close to TCA oxygen. This situation is very similar to that found for picolinic acid N-oxide in various solvents.[37] However, the situation changes when the N···O distance becomes 'unfrozen'. In this case the second inflection on the potential energy surface (PES) can become deeper than the first one (located nearby TCA oxygen), if the dielectric permittivity of the solvent is high enough. The complete scanning of multidimensional PES was out of the scope of the present work. The main attention in these studies was concentrated on the properties (geometry, binding energies and vibrational frequencies) of CyPy/TCA complex at both energy minima. A protonated form of CyPy/TCA was found to be not stable *in vacuo* and CCl_4 solution—in a run of a full optimization the proton returns to the site at TCA oxygen. It was succeeded to stabilize the proton at $d(N–H) = 1.1201$ Å in CLF solution, although the binding energy of this structure is lower than in the case of neutral complex (Table 2). In DCE ($\varepsilon = 8.93$) the protonated geometry-optimized CyPy/TCA structure is already by $\sim$1.2 kJ mol^{-1} more stable than the neutral form. In AN solution this energy gain due to protonation reaches even $\sim$6.9 kJ mol^{-1}. A similar polar medium effect was found in trimethylamine/formic acid complex,[38] where its ionic form becomes more favorable with respect to the neutral one, if $\varepsilon > 10$. Summarizing these features, it seems that the most exact definition of H-bond in CyPy/TCA and in some other related complexes was proposed by Hadži,[21] identifying such class of H-bond systems as 'proton-shared hydrogen bond with incipient proton transfer'.

The calculated binding energies vary from 53.53 (*in vacuo*) to 43.16 kJ mol^{-1} (neutral complex in DCE, Table 2). Strictly speaking, some problems arise when 'binding energy in solution' is to be defined in the frame of PCM. The ΔE values, given in Table 2, have been evaluated in the most natural way as the difference of free energies $\Delta E = E$(CyPy/TCA complex) $-$ (E(TCA) $+$ E(CyPy)), where each structure was fully optimized in solvent reaction field. Note that no clear correlation between binding energies and dielectric constant was observed for the neutral complex, whereas the stabilization of protonated form upon increasing polarity of solvent can be deduced. It supports a widely accepted concept that in highly polar media, beside the factor of strength of H-bond, the solvation process plays a crucial role gaining PT. Its contribution becomes more significant if 'partners', involved in H-bonding, become more 'charged'. It has been properly discussed by Limbach *et al.* in terms of PT coupling with an

Table 2 Structural parameters of H-bond of CyPy/TCA (Fig. 4) and complex binding energies (ΔE) in various solvents

	In vacuo	CCl_4	CLF	DCE	AN
ε	1	2.228	4.9	8.93	36.64
Neutral complex (N···H–O)					
d(N···H)/Å	1.6779	1.6204	1.5721	1.5518	1.5241
d(H–O)/Å	1.0162	1.0300	1.0441	1.0512	1.0619
d(N···O)/Å	2.6941	2.6501	2.6155	2.6021	2.5852
∠(N···H–O)/°	179.95	178.42	177.21	177.14	176.95
$-\Delta E$/kJ mol^{-1}	53.53	48.37	44.89	43.16	44.92
Complex with PT ($N^+H\cdots O^-$)					
d(N–H)/Å	—	—	1.1201	1.0989	1.0830
d(H···O)/Å	—	—	1.4359	1.4903	1.5407
d(N···O)/Å	—	—	2.5559	2.5890	2.6233
∠(N–H···O)/°	—	—	178.78	178.67	177.98
$-\Delta E$/kJ mol^{-1}	—	—	41.77	44.41	51.80

 This journal is © the Owner Societies 2007

ordering of the electric dipoles of individual solvent molecules at the solute site.[2]

An increase in the dielectric constant (from 2.228 to 36.64, going from CCl_4 to AN) acts on the H-bond in the neutral complex compressing the N···O distance and shifting the bridge proton towards the nitrogen atom of CyPy (Fig. 4 and Table 2). These changes in the H-bond at the increasing dielectric constant are reflected experimentally in the FTIR spectra as a monotonic 'blue shifting' of the ring mode $\nu 1$ in CyPy/TCA from 1607 (solution in CCl_4) to 1615 cm^{-1} (in AN, Fig. 3). However, the PCM method does not reproduce the observed evolution of FTIR spectra upon the changing polarity of the solvent (Table 3). Even an opposite tendency is identified in the calculated spectra, *viz*. the rather stable position of $\nu 1$ and significant 'blue shift' in a frequency of $\nu 2$. The unsatisfactory results of PCM may be caused by its pure electrostatic origin. This means that the short-range repulsion and solute–solvent dispersion interactions are important in the studied system.

The origin of the FTIR band at 1641 cm^{-1}, experimentally observed in AN solution (Fig. 3D), has to be discussed in more detail. As has been mentioned above, the bands in some Py/acid solutions at 1630–1635 cm^{-1} are assigned to a protonated pyridine (PyH^+) vibration.[28] An additional support for this statement comes from the solid-state studies of co-crystals of derivatives of pyridine with carboxylic acids. Neutron and X-ray diffraction studies on CyPy/TCA evidence the unique form of H-bond in the crystalline phase.[20] Namely, the hydrogen-bonding scheme is characterized by a relatively short N···O distance of 2.577 Å with N–H equal to 1.128 and O···H equal to 1.443 Å. This scheme indicates the almost complete proton transfer from TCA to CyPy. On the other hand, one band is indeed always present at 1632 cm^{-1} in FTIR spectra of solid samples of CyPy/TCA.[21] Very similar observations are reported for the co-crystal of Py/2,4-DNBA.[27] The proton transfer is also observed in this system (N···O, N–H and O···H distances are 2.561, 1.05 and 1.51 Å, respectively), and the vibrational band at 1626 cm^{-1} in the FTIR spectrum can be surely assigned to a pyridinium ring mode $\nu 1$. A more intriguing situation has to be noted in the co-crystal of 3,5-Py/3,5-DNBA.[26] Very strong H-bonding N···H···O with fully disordered bridge hydrogen atoms between nitrogen and oxygen was found there. The occupancy factors for H at the N- and O-side were approximately 0.5. It is most remarkable that this occupancy is reflected in the shape of the $\nu 1$ band—two bands at 1625 and at *ca*. 1615 cm^{-1} are seen in the FTIR spectrum of 3,5-Py/3,5-DNBA.[39] Hence, the working hypothesis to attribute the band at 1641 cm^{-1} (Fig. 3) to the protonated CyPy seems to be well motivated. In this context the calculated very large 'blue shift' upon protonation (45 and 18 cm^{-1} with respect to the 'free' CyPy and to the neutral CyPy/TCA complex, respectively, AN solution, Table 3) should be considered as a support for this hypothesis as well.

The competence of the DFT at the chosen level (B3LYP/6-311++G(d,p)) in predictions of H-bond properties was checked more thoroughly applying this method on some other CyPy/acid systems gradually increasing the H-bond strength.

Experimental FTIR investigations have been performed on the solutions of CyPy with H_2O, acetic (AA), trifluoroacetic (TFA) and methanesulfonic (MSA) acids. Experimental spectra are shown in Fig. 6. Two marginal cases can be differentiated here. (i) The peak at 1639 cm^{-1} is absent in the spectra of CyPy interacting with the weakest partners—with H_2O (not shown in Fig. 6 in order not to overload the figure) and with AA (Fig. 6B). This means that these H-bond complexes are too weak to allow proton transfer to take place. In these cases only the bands at 1594 ('free' CyPy) and at 1599 (CyPy/H_2O) or 1603 cm^{-1} (CyPy/AA) are observed. We can assign them as CyPy ring modes of relatively weak H-bond complexes O–H···N with the proton on the oxygen side, *i.e*. the neutral complex. (ii) In the 'strongest' interacting couple, *i.e*. CyPy/MSA, the bands of ionic $O^-\cdots H^+N$ bonding at 1637 cm^{-1} and 'free' CyPy are seen, but no peak in-between was found (Fig. 3E). This result can be compared with that of the X-ray study on Py/MSA in the crystalline state,[10] where the proton transfer structure with the refined N–H distance of 0.916 Å was estimated. However DFT and RHF calculations do not reveal the proton transfer in the isolated Py/MSA complex.[10] The role of added water was studied by optimizing the geometry of this complex in the presence of 1 or 2 water

Table 3 Calculated frequencies of CyPy ring modes in non-H-bonded CyPy and CyPy/TCA complex in various solvents using B3LYP/6-311++G(d,p) and PCM (all in cm^{-1})

	CyPy	CyPy/TCA (neutral complex)	CyPy/TCA (complex with PT)
Mode $\nu 1$			
In vacuo	1628.7	1644.9	—
CCl_4	1629.4	1645.8	—
CLF	1629.1	1647.2	1673.9
DCE	1629.3	1647.7	1674.7
AN	1629.7	1647.5	1675.2
Mode $\nu 2$			
In vacuo	1585.9	1589.4	—
CCl_4	1584.2	1593.3	—
CLF	1582.9	1599.0	1562.7
DCE	1582.4	1602.9	1562.4
AN	1581.8	1609.0	1560.9

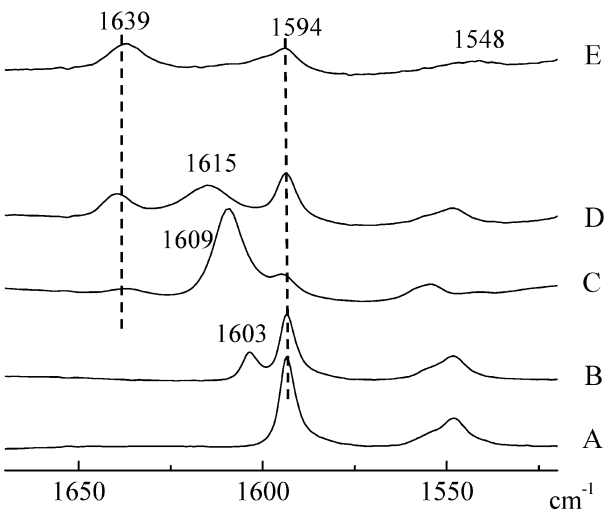

Fig. 6 FTIR spectra of 'free' CyPy (A), CyPy complexes with AA (B), with TCA (C, D) and with MSA (E) in solutions, respectively (all 1 M in AN (A, B, D) and in CLF(C), E – 0.125 M, due to weak solubility of CyPy/MSA in AN).

molecules. In such cases the proton is observed to transfer. Some amount of moisture can be present in our samples, but it is certainly much less than a 1 : 1 water/acid ratio. In-between those two marginal bands an intermediate one is observed in FTIR spectra of CyPy interacting with TCA and TFA (the last one not shown). It is located at 1616 (CyPy/TCA) and at 1617 cm^{-1} (CyP/TFA), respectively. Its frequency is sufficiently higher than for CyPy bonded to H_2O or AA, *i.e.* the cases of relatively weak H-bond.

DFT calculations were carried out choosing one intermediate system, and namely—the CyPy/AA complex. Furthermore, in order to evaluate the role of higher aggregation, a calculation was also carried out on the CyPy/$(TCA)_2$ structure. It is extremely important to elucidate the coupling between the proton transfer in solution and processes of higher aggregation *via* formation of complexes with various stoichiometric ratios (1 : 2, 2 : 1, or even higher).[3,6–8] As it will be shown later, the proton transfer in CyPy/$(TCA)_2$ structure is found already *in vacuo* calculations. It is also observable at certain conditions in FTIR spectra of CyPy/TCA in non-polar solvents, *i.e.* in the media were electrostatic intermolecular interactions play a minor role. Therefore, further calculations (full geometry optimization and vibrational spectra) on these structures were performed *in vacuo*. The results are presented in Fig. 4 and 7 and in Table 4. Note that the main features of the CyPy/AA structure are the same as for CyPy/TCA (Fig. 4, with slightly different geometry only), which is therefore not shown.

The tendency of changes in FTIR spectra with increasing strength of H-bond (going from non-bonded CyPy to CyPy/AA and to CyPy/TCA) is correctly reproduced at the present level of DFT calculations. Namely, a perfect agreement between the calculated and experimental 'blue' shifts of the mode $\nu 1$ in CyPy/AA and CyPy/TCA complexes (Table 4) is obtained. Moreover, the position of $\nu 2$ mode is rather stable, as observed in the experimental spectra (Fig. 6).

In return to the problem of higher aggregation the most important finding is that the attachment of the second TCA molecule to CyPy/TCA complex indeed induces the proton transfer to CyPy nitrogen (Fig. 7, H-bond scheme in Table 5). It causes the increase of $\nu 1$ frequency up to 1668 cm^{-1}, *i.e.* towards much higher values than commonly observed for non-protonated species (*i.e.* the 'middle' bands at 1603–1615 cm^{-1} in Fig. 6). Its 'blue' shift of 39 cm^{-1} (Table 4) is also in fairly good agreement with experimentally observed 45 cm^{-1}.

However, comparing the data collected in Tables 3 and 4, it is not clear whether PT takes place already in the 'simplest' 1 : 1 complex or a formation of higher structures is necessary to stimulate this process. In both cases a large 'blue shift' of mode $\nu 1$ ($\sim$45 cm^{-1} for 1 : 1 complex in AN (Table 3) and 39 cm^{-1} for 1 : 2 one (Table 4)) is produced. The answer comes from experiment. Indeed, the band that is observed in AN solution at 1641 cm^{-1}, but not seen in CCl_4 and DCE (Fig. 3) and that is assigned to a protonated CyPy (mode $\nu 1$), can also appear in less polar media if the fraction of the acid is present in solution in excess. The band at 1639 cm^{-1} is observed in this case even in those solvents (Fig. 8) where the protonated form of 1 : 1 CyPy/TCA complex was stated to be unstable. This finding supports the concept of stimulation of proton transfer processes in 1 : 2 complexes, and on the other hand, it indicates that a higher aggregation of CyPy and TCA molecules is pivotal for PT in this system.

Table 4 Calculated frequencies and 'blue' shifts (Δ, respect to non-bonded CyPy) of CyPy ring modes in various H-bond structures (*in vacuo*, all in cm^{-1})

	CyPy	CyPy/AA	CyPy/$(TCA)_1$	CyPy/$(TCA)_2$
$\nu 1$	1628.7	1640.4	1644.9	1667.7
Δ(theory)	0	11.7	16.1	39.0
Δ(experiment)	0	10	14–15	45
$\nu 2$	1585.9	1585.5	1589.4	1557.1

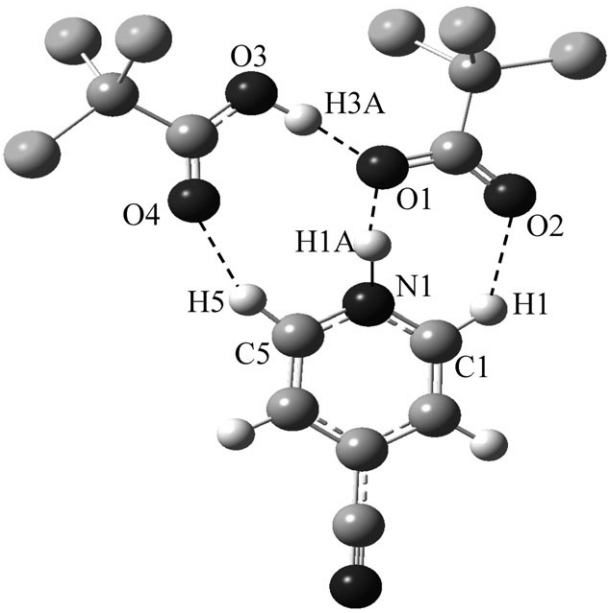

Fig. 7 Optimized structure of CyPy/$(TCA)_2$ H-bond complex *in vacuo*. H-bond scheme is given in Table 5.

A rather peculiar H-bond motif in the CyPy/$(TCA)_2$ aggregate (Fig. 7) has to be discussed in more details. Usually in the literature 1 : 2 base/acid complexes are pictured arbitrarily as chain- or zigzag-like structures.[3,7,40–42] The CyPy/$(TCA)_2$ structure, obtained by a full geometry optimization, shows a certain 'packing' around the central N–$H^+\cdots O^-$ bond. This structure cannot be considered as a straw offspring of the theoretical treatment. Experimental support for such arrangement has been found in the 1 : 2 co-crystal of Py/3,5-DNBA. Details of X-ray experiment, lattice constants and hydrogen bonding scheme are collected in Tables 5 and 6. The H-bond network is shown in Fig. 9.

In both cases (Fig. 7 and 9) the second carboxylic acid molecule joins the 1 : 1 complex bonding not *via* the carbonyl group of the first acid molecule, but directly to the existing N···H–O bridge. Both assemblies show similar connectivity by strong hydrogen bonds N5–H5A···O1, O8–H8···O1 (Fig. 9) and N–H1···O1, O2–H2···O1 (Fig. 7). Discrepancies are, however, observed in the C–H···O connectivity. Whereas the H15···O7 contact is almost identical in both cases, formation of the additional C7–H7···O8 interaction in the 1 : 2 Py/3,5-

This journal is © the Owner Societies 2007

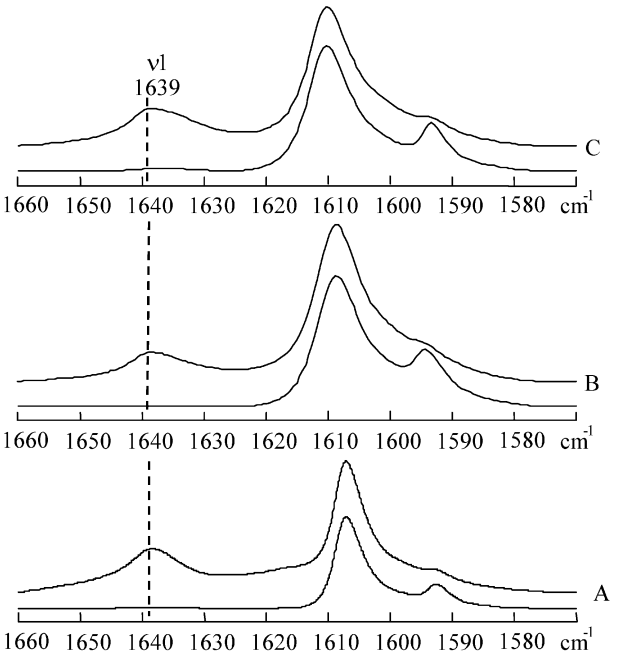

Fig. 8 Appearance of the protonated CyPy mode ($\nu 1$) in less polar solvents as CCl_4 (A), CLF (B), DCE (C). The upper spectra correspond to the composition of CyPy/TCA solution when the acid is present in excess (the concentration of TCA is 0.132 M, the concentration of CyPy 0.066 M) and the lower spectra—to the cases of equal concentrations of components in solution (both 0.066 M). The cell of 0.603 mm thickness was used during these measurements.

DNBA complex results in (i) significant bending of the N5–H5A···O1 hydrogen bond (∠N5–H5A···O1 = 151°); (ii) elongation of the H19···O2 contact. All these factors may contribute to the compression and strengthening of the central N···H–O bond, and consequently $N–H^{+}\cdots O^{-}$ is formed. Whether the interaction N5–H5A···O7 in 1 : 2 Py/3,5-DNBA and thus a bifurcated H-bond exists, seems questionable. Given the geometry d(N5···O7) = 3.141 Å, d(H5A···O7) = 2.56 Å and an angle ∠N5–H5A···O7 = 113° this bonding should be classified as extremely weak. We therefore conclude that both the calculated (Fig. 7) and the experimentally determined structure (Fig. 9) possess networks of H-bonds of very similar topology.

Table 5 Hydrogen bonding schemes of CyPy/$(TCA)_2$ and Py/3,5-DNBA 1 : 2 complexes (Å, deg)

D–H···A	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°
CyPy/$(TCA)_2$				
N1 H1A O1	1.109	1.480	2.587	176.8
O3 H3A O1	1.009	1.619	2.626	176.0
C1 H1 O2	1.085	2.176	3.028	133.6
C5 H5 O4	1.084	2.076	3.086	153.9
Py/$(3,5\text{-DNBA})_2$				
N5 H5A O1	1.08(6)	1.79(6)	2.789(5)	151(4)
N5 H5A O7	1.08(6)	2.56(5)	3.141(6)	113(3)
O8 H8A O1	0.83(5)	1.68(5)	2.510(4)	173(6)
C7 H7 O8	0.91(4)	2.31(4)	3.127(4)	149(3)
C15 H15 O7	1.00(4)	2.20(4)	2.998(5)	136(3)
C19 H19 O2	0.99(4)	2.41(4)	3.279(3)	145(5)

Table 6 X-ray diffraction results and structure refinement on Py/3,5-DNBA 1 : 2 co-crystal

Empirical formula	C19 H13 N5 O12
Formula weight	503.34
Temperature/K	299(2)
Wavelength	0.71073
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	
a/Å	6.860(2)
b/Å	13.404(5)
c/Å	22.474(9)
α, β, γ/°	90.00
Volume/Å^3	2066.5(13)
Z	4
Calculated density/Mg m^{-3}	1.618
Absorption coefficient/mm^{-1}	0.138
F(000)	1032
Crystal description and size/mm	Rod-shaped, colorless, 0.72 × 0.20 × 0.20
Θ range for data collection/°	4.25 to 26.37
Limiting indices	$-8 \leftarrow h \leftarrow 4$, $-16 \leftarrow k \leftarrow 16$, $-27 \leftarrow l \leftarrow 27$
Reflections collected	12 628
Independent reflections	2153, [R(int) = 0.0444]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2153/1/364
Goodness-of-fit on F^2	0.952
Final R indices ($I > 2\sigma(I)$)	$R1$ = 0.0420, $wR2$ = 0.0913
R indices (all data)	$R1$ = 0.0729, $wR2$ = 0.1078
Largest diff. peak and hole/e^{-3}	0.182 and −0.162

Very recently, an X-ray diffraction study has been performed on the 1 : 2 co-crystal Py/3,5-DNBA at lower temperatures (T = 203 ± 2 K).[43] According to this work the 'frozen' 1 : 2 complex is neutral (d(N5···O1) = 2.80 Å, d(N5···H5A) = 1.98 Å, *i.e.* with H5A proton nearby O1). However, it was *ibidem* found the proton transfer occurs in the 1 : 1 : 1 Py/3,5-DNBA/water complex at T = 298 ± 2 K, *i.e.* at the same temperature as in the present work. These findings indicate that both aggregates of Py/3,5-DNBA and CyPy/TCA, belong

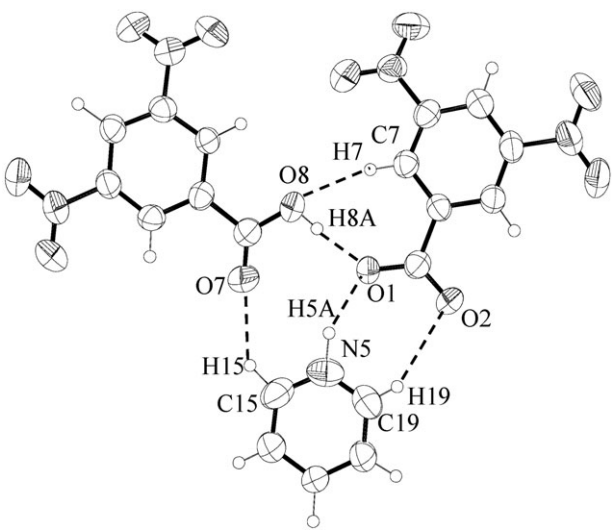

Fig. 9 H-Bonding network and labelling of atoms in the 1 : 2 co-crystal of Py/3,5-DNBA. Displacement ellipsoids are plotted at the 50% probability level. Crystallographic data and geometrical values of hydrogen bonding are given in Tables 5 and 6.

most probably to the same class of complexes which involve 'proton-shared hydrogen bonds with incipient proton transfer' as discussed above in the light of DFT calculations of the proton potential energy function. These H-bond systems are easy to perturb and to disorder by medium polarity and temperature effects. Some features of the bridge proton disorder are noticeable also in FTIR spectra. Namely, strongly overlapped bands are present at 1614–1635 cm^{-1} in spectra of solid Py/3,5-DNBA in the KBr pellet.[44] These bands could be attributed to the $\nu 1$ modes of neutral and protonated complexes.

Finally, note that the 1 : 2 co-crystal of Py/3,5-DNBA is not the unique case that provides an experimental support to the calculated structure of $CyPy/(TCA)_2$ aggregate found in this work by the full geometry optimization using DFT. Another very similar H-bond motif is formed in pyridinium 3,5-dinitrosalicylate 3,5-dinitrosalicylic acid crystal.[45]

Conclusions

The pyridine ring modes $\nu 1$ and $\nu 2$ (Fig. 1) are certainly very suitable information sources monitoring the H-bond properties in various complexes of different pyridine derivatives with acids in a crystalline phase as well as in solutions. Due to the high sensitivity of the $\nu 1$ mode on protonation ('blue' shift of $\sim$40–45 cm^{-1} with respect to 'non-bonded' Py), its frequency can be accepted as a universal criterion of proton transfer for the whole family of pyridines.

The DFT at the B3LYP/6-311 + + G(d,p) level is a competent method for predictions of the changes in FTIR spectra at increasing strength of H-bond in Py/acid systems. Namely, a perfect agreement between the calculated and experimental 'blue' shifts of the mode $\nu 1$ in CyPy/AA and CyPy/TCA complexes is obtained, and the position of the $\nu 2$ mode in the spectrum is rather stable, as observed experimentally. The theoretical very large 'blue' shift of mode $\nu 1$ in the protonated CyPy (39–45 cm^{-1}) is also in fairly good agreement with experiment (45 cm^{-1}).

The PCM method does not reproduce the observed evolution of FTIR spectra upon changing the polarity of the solvent. Even an opposite tendency is observed in the calculated spectra, *viz.* rather stable position of $\nu 1$ and significant 'blue shift' of $\nu 2$ frequency. Most probably, the unsatisfactory results of PCM can be due to its pure electrostatic origin. The short-range repulsion and solute–solvent dispersion interactions that are important in the studied systems were not taken into consideration.

The crucial role of higher aggregation in the proton transfer processes in H-bond systems has been newly elucidated by finding a peculiar H-bond motif in the $CyPy/(TCA)_2$ aggregate. The structure found by a full geometry optimization using DFT is formed by a second carboxylic acid molecule which joins a 1 : 1 complex by bond formation directly to the existing N···H–O bond. Experimental support for this structure has been found in the 1 : 2 co-crystal of Py/3,5-DNBA by single crystal X-ray diffraction.

Acknowledgements

Support of the Alexander von Humboldt Foundation is kindly acknowledged. One of us (R.B.) thanks Marie Curie Foundation for fellowship and the Group of Section for Physical Chemistry of Wroclaw University and Prof. Alexander Koll for hospitality. Special thanks are due to Prof. Dušan Hadži for single-crystal, FTIR data for solids and many guiding ideas. We are grateful to Mrs Silva Zagorc for crystal growing and to Prof. Maria Gdaniec for discussions. We thank the Danish Center for Scientific Computing (Copenhagen, Denmark) for the possibility to use computational facilities and GAUSSIAN 03 program package.

References

1 *Theoretical Treatments of Hydrogen Bonding*, ed. D. Hadži, John Wiley & Sons Ltd., Chichester, 1997.
2 N. S. Golubev, I. G. Shenderovich, S. N. Smirnov, G. S. Denisov and H. H. Limbach, *Chem.–Eur. J.*, 1999, **5**, 492.
3 S. S. Smirnov, N. S. Golubev, G. S. Denisov, H. Benedict, P. Schah-Mohammedi and H. H. Limbach, *J. Am. Chem. Soc.*, 1996, **118**, 4094.
4 Z. Dega-Szafran and M. Szafran, *Heterocycles*, 1994, **37**, 627.
5 *Pyridine and Its Derivatives*, ed. R. A. Abramovich, Wiley-Interscience, New York, 1974, vol. 2.
6 Z. Dega-Szafran, M. Gdaniec, M. Grunwald-Wyspianska, Z. Kosturkiewicz, J. Koput, P. Krzyzanowski and M. Szafran, *J. Mol. Struct.*, 1992, **270**, 99.
7 N. V. Drichko, G. Yu. Kerenskaia and V. M. Schreiber, *J. Mol. Struct.*, 1999, **477**, 127.
8 M. J. Fernandez-Berridi, J. J. Iruin, L. Irusta, J. M. Mercero and J. M. Ugalde, *J. Phys. Chem. A*, 2002, **106**, 4187.
9 K. Aidas and V. Balevicius, *J. Mol. Liq.*, 2006, **127**, 134.
10 O. Lehtonen, J. Hartikainen, K. Rissanen, O. Ikkala and L. O. Pietilä, *J. Chem. Phys.*, 2002, **116**, 2417.
11 G. M. Sheldrick, *A Program for Automatic Solution of Crystal Structures*, University of Goettingen, 1997.
12 G. M. Sheldrick, *A Program for Crystal Structure Refinement*, University of Goettingen, 1997.
13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03, (Revision B.05)*, Gaussian, Inc., Pittsburgh PA, 2003.
14 K. Pei, Y. Li and H. Li, *J. Mol. Struct.*, 2003, **660**, 113.
15 K. Schoone, J. Smets, R. Ramaekers, L. Houben, L. Adamowicz and G. Maes, *J. Mol. Struct.*, 2003, **649**, 61.
16 G. Liu, H. Wang and W. Li, *J. Mol. Struct. (Theochem)*, 2006, **772**, 103.
17 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
18 M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43.
19 S. Miertus, E. Scorocco and J. Tomasi, *Chem. Phys.*, 1982, **55**, 117.
20 V. Balevicius, H. Ehrenberg, H. Fuess, S. Mason, D. Hadzi, deposited in Cambridge Crystallographic Data Centre (CCDC No. 288490-92).

This journal is © the Owner Societies 2007

21 D. Hadži, private communication.
22 T. L. Nguyen, F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 2001, **123**, 11057.
23 G. S. Papaefstathiou, A. J. Kipp and L. R. MacGillivray, *Chem. Commun.*, 2001, 2462.
24 R. D. Bayley Walsh, M. W. Bradner, S. Fleischman, L. A. Morales, B. Moulton, N. Rodriguez-Hornedo and M. J. Zaworotko, *Chem. Commun.*, 2003, 186.
25 J. R. Bowers, G. W. Hopkins, G. P. A. Yap and K. A. Wheeler, *Cryst. Growth Des.*, 2005, **5**, 727.
26 L. B. Jerzykiewicz, Z. Malarski, L. Sobczyk, T. Lis and E. Grech, *J. Mol. Struct.*, 1998, **440**, 175.
27 L. Sobczyk, T. Lis, Z. Olejnik and I. Majerz, *J. Mol. Struct.*, 2000, **552**, 233.
28 R. Langner and G. Zundel, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3831.
29 J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke and O. Ikkala, *Science*, 1998, **280**, 557.
30 J. Ruokolainen, M. Torkkeli, R. Serimaa, S. Vahvaaselkä, M. Saariaho, G. ten Brinke and O. Ikkala, *Macromolecules*, 1996, **29**, 6621.
31 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294.
32 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
33 P. M. W. Gill, B. G. Johnson, J. A. Pople and M. J. Frisch, *Chem. Phys. Lett.*, 1992, **197**, 499.
34 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.
35 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.
36 K. Aidas *et al.*, in preparation.
37 J. Stare, J. Mavri, G. Ambroič and D. Hadži, *J. Mol. Struct. (Theochem)*, 2000, **500**, 429.
38 T. Liljefors and P. O. Norrby, *J. Am. Chem. Soc.*, 1997, **119**, 1052.
39 We thank Professors L. Sobczyk and E. Grech for sending us the FTIR spectrum of 3,5-Py/3,5-DNBA crystal in digital form.
40 Z. Dega-Szafran, M. Grunwald-Wyspianska and M. Szafran, *Spectrochim. Acta, Part A*, 1991, **47**, 543.
41 G. Zundel, *Hydration and Intermolecular Interaction*, Academic Press, New York, 1969.
42 I. P. Gragerov, V. K. Pogorelij and I. F. Franchuk, *Hydrogen Bond and Fast Proton Exchange*, Naukova Dumka, Kiyv, 1978, in Russian.
43 K. K. Arora, J. PrakashaReddy and V. R. Pedireddi, *Tetrahedron*, 2005, **61**, 10793.
44 I. Svoboda, H. Fuess, V. Balevicius and D. Hadži, in *Abstracts of International Conference on Structure and Spectroscopy*, Vilnius, Lithuania, September 23–26, 2004, p. 22.
45 G. Smith, U. D. Wermuth, P. C. Healy and J. M. White, *Aust. J. Chem.*, 2003, **56**, 707.