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Journal of Molecular Structure 660 (2003) 25–40

Journal of MOLECULAR STRUCTURE

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Infrared and ab initio studies of hydrogen bonding and proton transfer in the complexes formed by pyrazoles

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Received 18 June 2003; revised 11 July 2003; accepted 11 July 2003

Abstract

The results of experimental studies and quantum mechanical calculations of vibrational spectra and structure of hydrogen bonded complexes formed by pyrazole (P) and 3,5-dimethylpyrazole (DMP) are presented. IR spectra of pyrazoles in solutions, gas phase, and solid state have been investigated in wide range of concentrations and temperatures. It has been found that in the gas phase both P and DMP reveal the equilibrium between monomers, dimers, and trimers. In solutions the equilibrium between monomers and trimers dominates, no bands, which can be attributed to dimers were detected. DMP retains the trimer structure in solid state, while in the case of pyrazole P, formation of the crystal provides another type of association. Geometrical and spectral characteristics of dimers and trimers, obtained by ab initio calculations, are presented and compared with experimental data.

IR spectra of solutions containing P and DMP with a number of acids (acetic and trifluoroacetic acids, pentachlorophenol, HBr) have been studied in parallel with ab initio calculations. It has been found that pentachlorophenol forms with pyrazoles complexes with one strong hydrogen bond O–H···N, while NH pyrazole group remains unbonded. With carboxylic acids DMP forms 1:1 cyclic complexes with two hydrogen bonds. In the case of acetic acid, the complex in CH_2Cl_2 solution reveals molecular structure with OH···N and C=O···HN bonds, in accordance with results of the calculations. For trifluoroacetic acid, the calculations predict the molecular structure to be energetically more stable in the case of the isolated binary complex (in gas phase), while the experimental spectrum of CH_2Cl_2 solution gives an evidence of the proton transfer with formation of the cyclic ionic pair with two $NH^+\cdots O^-$ bonds. The agreement with experimental results can be improved by taking into account the influence of environment in the framework of Onsager or Tomasi models. The shape of proton potential function of the complexes and medium effect on its parameters, resulted from experimental data and calculations, are discussed. It has been found that the number of potential minima and their relative depth depend strongly on the method of calculations and the basic set. Under excess of trifluoroacetic acid, the formation of 2:1 acid–DMP complex has been detected. Spectral characteristics and results of calculations point to the cyclic structure of this complex, which includes homoconjugated bis-trifluoroacetate anion and $DMPH^+$ cation. With HBr both studied pyrazoles were found to form ionic complexes including one or two pyrazole molecules per one acid molecule and correspondingly monocation or homoconjugated cation BHB^+.

Keywords: Pyrazoles; IR spectra; Hydrogen bonding; Proton transfer

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doi:10.1016/j.molstruc.2003.07.010

1. Introduction

In recent years there have been a growing interest in studies of the intermolecular interactions with participation of pyrazole and its derivatives [1–16]. The structure of pyrazole molecules, containing the fragment =N–N(H)–, is favourable to the formation of various hydrogen bonded complexes and associates in solids-cyclic dimers, trimers and tetramers, linear chains and helices, depending on the substituent [6,7, 16–18]. The variety of association forms, structural and spectroscopic properties allows to study the substitution effects on geometry and thermodynamic characteristics of complexes and associates, effects of mutual influence of several conjugated hydrogen bonds, splitting and appearance of complicated structure of νNH bands in the IR spectra, chemical shifts and spin–spin interaction in NMR spectra, effects of H/D substitution. The existence of cyclic associates gives the unique possibility to measure kinetic characteristics of degenerated proton transfer in the cycles of different dimensions and separate the contribution of proton tunnelling effect [9,12]. It was marked that pyrazoles can be suitable objects for studies of molecular selforganization [2,5,9].

The objective of the present work was to study specific features of hydrogen bonding and proton transfer in systems containing pyrazole (P) and 3,5-dimethylpyrazole (DMP). In the framework of this study two main problems were treated.

The first one is the problem of selfassociation of these pyrazoles in solutions and gas phase. According to X-ray studies, DMP crystals consist of cyclic hydrogen bonded trimers with effective D_{3h} symmetry, while crystalline P reveals the catemers (chain) structure [19,20]. Recently, J.M. Orza et al. [5] studied the vibrational spectra of DMP and its deuterated derivatives and concluded that the trimers are present also in DMP solutions and in the melt. The assignment of IR and Raman bands, symmetry and structural parameters of the trimers were analysed in Ref. [5] by RHF/6-31G* treatment. As for the vapour phase, the spectrum presented in Ref. [5] exhibits only the monomer bands. No manifestations of equilibrium between monomers and trimers or other associates are described. The results of the gas phase electron diffraction measurements [21] do not concern the problem of selfassociation; the subject of this work is the study of geometrical parameters of free DMP molecules.

Thus, the data about the selfassociation of considered pyrazoles are based mainly on results of studies of solids, melts and solutions, the cyclic trimers being the only type of DMP associates, which was detected and discussed in the mentioned works.

However, it has been reported much earlier [22,23], that studies of concentration dependence of the intensity of νNH band of monomers lead to the conclusion that some amount of dimers coexists with monomers and trimers in CCl_4 solutions of several pyrazoles, including P and DMP.

Therefore it is important to investigate more carefully, which kinds of stable oligomers of P and DMP can be observed in vapours or solutions in equilibrium with monomers, to examine their structural and spectral characteristics. With this purpose, in the present work the IR spectra of both considered pyrazoles have been obtained in solutions, vapour phase and solid state in the wide range of concentrations and temperatures. Ab initio calculations of geometry, harmonic frequencies and infrared intensities of P and DMP dimers, trimers and tetramers have been performed.

The second problem concerns the complexes formed by pyrazoles with strong proton donors. It seems important to find possible composition and geometry of the complexes and to study the effects of hydrogen bonding on vibrational spectra of pyrazoles and acid molecules, involved in these complexes. Particular attention was paid on those systems where complex formation is accompanied by proton transfer. The structure and spectral peculiarities of the ionic complexes with participation of pyrazoles and their cations is one of the main points of interest in this investigation.

To our knowledge only few works devoted to the studies of this problem have been reported. S.F. Bureiko et al. [24,25] studied the IR spectra of solutions containing complexes of DMP with several carboxylic acids and have concluded that these complexes reveal the cyclic structure with two hydrogen bonds. According to Refs. [24,25], no proton transfer takes place in the complex formed by DMP with formic acid in CCl_4 solution. C. Foces-Foces et al. [42] investigated solid complexes of DMP with 2,4,6-tri-methyl-benzoic acid and also have found that the complexes have molecular structure. It has been marked in Refs. [24,25] that the formation of the ionic complexes with transferred proton was detected for DMP complexes with stronger acids, such as di- and trichloroacetic acids. However, recently K. Inuzuka [11], based on results of the IR studies, has deduced that molecular hydrogen bonded complexes and ionic pairs are presented simultaneously in solutions of 3-methyl-pyrazole (or 5-methyl-pyrazole) and acetic acid in CCl_4. As an additional argument in favour of this suggestion the results of DFT/6-31G* treatment of 3- and 5- methyl-pyrazole + formic acid systems are used. The results indicate the possibility of formation of stable complexes of both types—molecular and ionic with stabilization energies ~80 and ~50 kJ/mol, correspondingly [11]. Thus, there is a discrepancy between conclusions made in Refs. [24,25] and Ref. [11], since DMP seems to be a stronger proton acceptor than 3- or 5-methyl-pyrazoles.

In the present work IR spectra of the complexes formed by P and DMP with pentachlorophenol, acetic and trifluoroacetic acids and hydrogen bromide have been studied experimentally in parallel with ab initio treatment at different levels.

2. Experimental and computational

IR spectra in the range 4000–400 cm^{-1} were obtained with FTIR Bruker IFS-28 spectrometer. The vapour phase measurements were performed using 6 cm length glass cells with welded sapphire or MgF_2 windows. The cell with some amount of solid pyrazole, after evacuation was disconnected from the vacuum unit and placed in the container equipped with KBr windows and electrical heater. Then spectra of the vapours being in equilibrium with the solid sample were recorded under increase of the temperature within the range 330–570 K with different initial amount of solid sample and, correspondingly, at different pressure of the vapour. The temperature of the cell was measured with accuracy ± 1°. Spectra of solutions at the room and higher temperatures were measured using conventional cells equipped with electric heaters.

Commercial samples of pyrazole (Merck–Schuchardt) and 3,5-dimethylpyrazole (Aldrich Chemical Co., Ltd) were used without additional purification; the acids used and the solvents were purified and dried by conventional methods.

In order to determine the number of absorbing components corresponding to different complexes and oligomers, formed by pyrazoles and proton donor molecules, in the most important cases the experimentally observed spectra of solutions were analysed and the separation of the spectra of individual components were made by the method and computer program based on the factor analysis and described earlier in Refs. [26,27].

Quantum mechanical calculations were carried out using RHF, MP2 and DFT (B3LYP) methods with different basis sets by GAUSSIAN 94 and 98 programs [28,29]. Mostly the sufficient agreement with experimental data concerning geometry and vibrational spectrum of pyrazoles was obtained with MP2/6-31G and DFT/B3LYP/6-31G** methods. In some cases MP2/6-31G** and DFT/B3LYP/6-31++G** levels were used.

The accuracy of the calculations was tested by comparison with known experimental and theoretical data. For example, the optimised geometry of pyrazole molecule, obtained in the present work, is very close to that calculated in Ref. [30] at MP2/6-31G** level. Table 1 illustrates rather good agreement of geometrical parameters of DMP resulted from our calculations with electron diffraction data [21]. Calculated harmonic frequencies and intensities of normal vibrations of P and DMP monomers are in the reasonable accordance with those measured in spectra of dilute solutions. The assignment of DMP bands is similar to that performed in Ref. [5]. As usual, majority of calculated frequencies are higher than

Table 1
Comparison of calculated (DFT/B3LYP/6-31G**) geometrical parameters of 3,5-dimethylpyrazole with electron diffraction data [21]

Parameter	Calcd, this work	Exp. [21]
R(NH)	1.008 Å	1.004 Å
R(NN)	1.350 Å	1.361 Å
$R(C_3C_4)$	1.410 Å	1.436 Å
$R(C_4C_5)$	1.380 Å	1.372 Å
$R(C_4H)$	1.080 Å	1.101 Å
∠NNH	118.8°	122°

the experimental ones. The differences are rather small for skeletal and bending modes and more significant for νC=O and especially for NH stretching modes. No force field scaling was used to correct these differences caused mainly by anharmonicity and in some cases by possible solvent effects.

3. Results and discussion

3.1. Selfassociation

Spectra of the vapours over solid pyrazoles, both P and DMP, in the temperature range 330–570 K reveal the presence of three main bands in the νNH region, corresponding to three components which are in equilibrium with each other and with solid phase (Fig. 1(a) and (b)). The band near 3520 cm^{-1} having clear rotational structure, belongs obviously to monomers. This band is observed in the whole temperature range, it increases with temperature and dominates completely at the highest temperatures. Two other bands with intensity firstly increasing and then decreasing with temperature belong to oligomers. One of these bands with centre of gravity in the region 3100–3150 cm^{-1} is broad and has complicated structure. In spectra of both pyrazoles it appears at rather low temperatures (330–350 K) almost simultaneously with monomer band and can be observed in a wide temperature interval. Another smooth broadened band with maximum near 3300 cm^{-1} appears at higher temperatures and can be detected in much narrower interval, especially in the case of DMP vapours where its intensity is much lower compared with other bands (Fig. 1(a)); in the case of P this band reaches rather high intensity at the temperatures about 460 K.

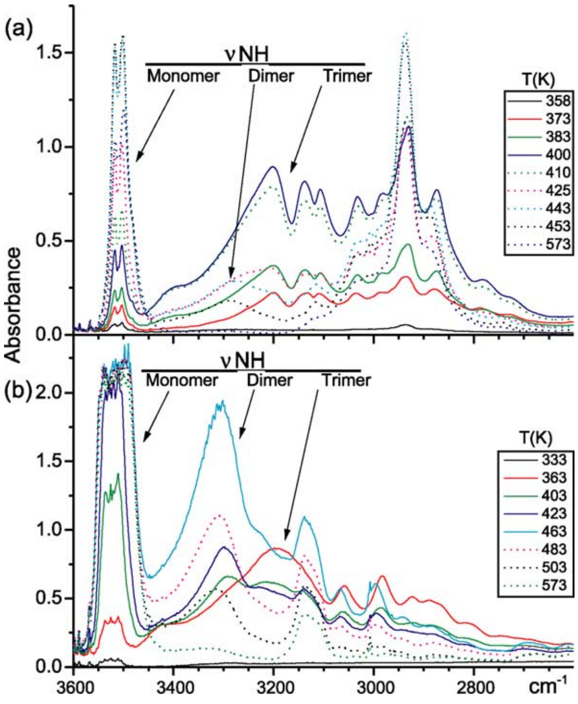


Fig. 1. IR spectra of DMP (a) and P (b) vapours at different temperatures.

Ab initio calculations predict the possibility of formation of stable cyclic dimer and trimer (with C_{2h} and C_{3h} symmetry, respectively) both for P and DMP molecules. For example, the optimised geometry of DMP dimer and trimer is shown in Fig. 2. The most important structural parameters, frequencies and IR intensities of normal vibrations are given in Tables 2 and 3. One can see that MP2/6-31G and DFT (B3LYP/6-31G**) methods give rather close values of the main geometrical parameters of NH···N hydrogen bonds in dimers and trimers (Table 2). Agreement with X-ray data [1] is not so good. It seems that some discrepancy can be caused by that the calculations refer to isolated trimer, while the X-ray data-to the trimer in crystalline lattice. At the same time one can notice that the length of NH bond in the trimer, given in Ref. [1], is implausibly short. It is essentially shorter not only than calculated length for trimer, but even than the experimental value for monomer, obtained by electron diffraction method [21] (Tables 1 and 2) and for trimers in crystals of relative molecules, such as 4-Br- and 3,5-Me$_2$-4-Br-pyrazoles [9].

Hydrogen bonds are practically linear in the case of trimer. The NH bonds are some longer, while N···H distances are shorter in the trimer compared with the dimer. Also νNH frequencies of the trimer are much lower and corresponding intensities are greater. Similar relations between dimer and trimer characteristics were found also in the case of pyrazole P (R(NH) = 1.028 and 1.043 Å, R(H···N) = 1.92 and 1.78 Å, ∠NHN = 143.6° and 179.3° for the dimer and trimer, respectively, at B3LYP/6-31G** level). All these data indicate H-bonds to be essentially stronger

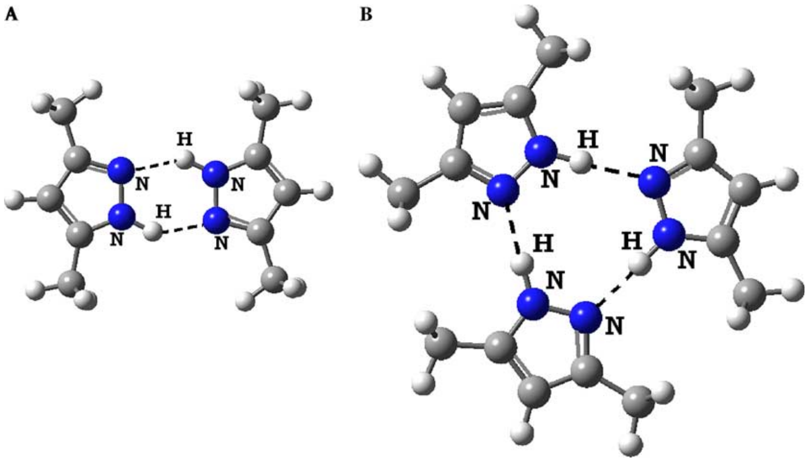


Fig. 2. Calculated structure of DMP dimer and trimer.

in the trimer than in the dimer. One can suggest that there are two reasons of hydrogen bond strengthening in the cyclic trimer compared with the dimer: the linearity of hydrogen bridge and the effect of cooperative interaction, similar to that described in Ref. [31]. Taking into account the character of the temperature changes, it is natural to assign the band near 3300 cm^{-1} in the experimental spectrum (Fig. 1) to the dimer and the broad structural band in the region 3100 cm^{-1}—to the trimer.

Spectrum of DMP solution in CCl_4 reveals the monomer band near 3475 cm^{-1} and the broad structural band in the region 3000–3100 cm^{-1}, very similar to that observed in the gas phase. Thus, in DMP solution there exists the equilibrium only between monomers and trimers. This conclusion is confirmed by factor analysis treatment (the method is described in Refs. [26,27]) of the family of spectra obtained at different concentrations (Fig. 3). The analysis proves the presence of two independent spectral components; the best fit of the experimental spectra is achieved with suggestion that the equilibrium $3A \leftrightarrow A_3$ takes place. Separated spectra of these components are also shown in Fig. 3. Similar situation was found also for solutions of pyrazole P.

In Fig. 4 the spectra obtained in the gas phase, CCl_4 solution and solid state in νNH region are compared. In the case of DMP, parameters and structure of the band assigned as νNH of the trimer in the gas phase and solutions are quite similar to those observed in the solid state, while in the case of P one can see the essential difference between νNH bands in solution

Table 2
Calculated geometrical parameters of NH···N hydrogen bonds in dimer and trimer of 3,5-dimethylpyrazole

Level	Parameter							
	R(NH), Å		R(N···H), Å		∠NH···N		R(N···N)	
	DFT[a]	MP2[b]	DFT[a]	MP2[b]	DFT[a]	MP2[b]	DFT[a]	MP2[b]
Monomer	1.01	1.01						
Dimer	1.02	1.03	1.99	1.96	143.6	144.3	2.88	2.86
Trimer	1.04	1.04	1.89	1.86	179.3	179.5	2.93	2.90
Trimer, exp.[c]	0.88		2.1		172		2.98	

[a] B3LYP/6-31G** level.

[b] 6-31G.

[c] Solid state, X-ray data [1].

Table 3
Frequencies and IR intensities of νNH bands in monomer, dimer and trimer of 3,5-dimethylpyrazole

	Frequency (cm^{-1})		Intensity (km/mol)	
	Calcd, MP2/6-31G	Observed	Calcd, MP2/6-31G	Observed
Monomer	3677	3520 (vapour) 3475 (solution)	75	48 (solution)
Dimer	3365 (B_u) 3331 (A_g)	≈3300 (vapour)	1820 0	–
Trimer	3175 (E′) 3118 (A′)	≈3100 (vapour) ≈3025 (solution)	2640 0	 4230 (solution)

and in solid state. Hence, the structure of considered oligomers in solid state should be different.

Thus, the results obtained give the evidence in favour of cyclic trimer as a dominating form of selfassociation of both considered pyrazoles in the gas phase and inert solutions. At the same time, the possibility of formation of the dimers also has been demonstrated. This possibility is negligible in solutions and turned out to be significantly larger in the vapours. The results are in accordance with the trimer structure of crystalline DMP and with another type (infinite chains) of P crystal structure [1,19,20].

The calculations show the theoretical possibility of formation also of stable tetramer form for both considered molecules, but no indications of its presence were observed experimentally.

On the second stage of this work the complexes formed by P and DMP with strong proton donors—pentachlorophenol, acetic and trifluoroacetic acids and HBr were studied.

3.2. Complexes with strong proton donors

The investigation of the IR spectra of solutions containing DMP and pentachlorophenol or acetic acid shows that 1:1 complexes formed by these molecules have molecular structure with strong hydrogen bond.

In the case of acetic acid factor analysis of spectra recorded in CH_2Cl_2 solutions under excess of DMP shows the presence of five components: DMP monomers and trimers, acid monomers and dimers and acid–DMP complex. The frequency of νC=O band of the acid molecule involved in this complex is lower and its intensity is less than in the acetic acid dimer (Fig. 5(b), Table 5). Similar features were found in spectrum of acetic acid–pyridine complex [32]. The picture observed in the νOH region (Fig. 5(a)) also resembles the spectrum of pyridine–acetic acid complex and other known systems with strong O–H···N hydrogen bonds. There are three broad maxima: near 2900–3000 cm^{-1} (overlapped partly by νCH bands and by the solvent absorption), near 2500 and 1900 cm^{-1}, which are interpreted usually as resulted from Fermi resonance of OH proton stretching and overtones of bending modes (A, B, C bands in terminology of Ref. [33]).

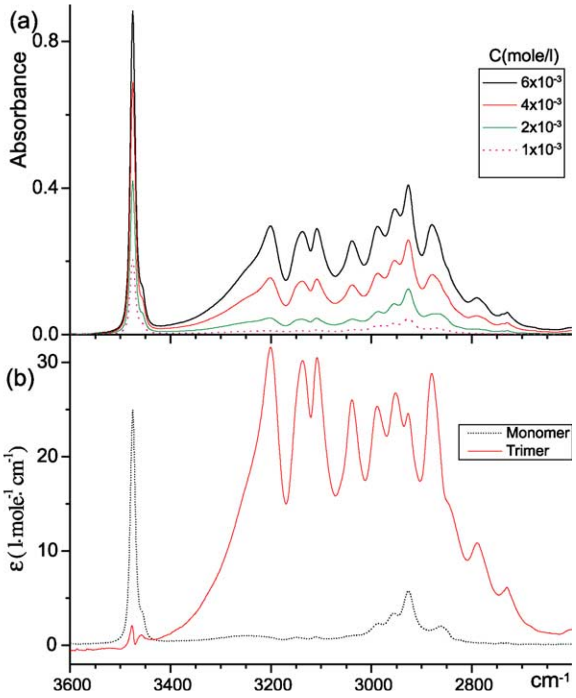


Fig. 3. IR spectra of DMP solutions in CCl_4. (a) Concentration dependence; (b) spectra of individual components obtained by separation.

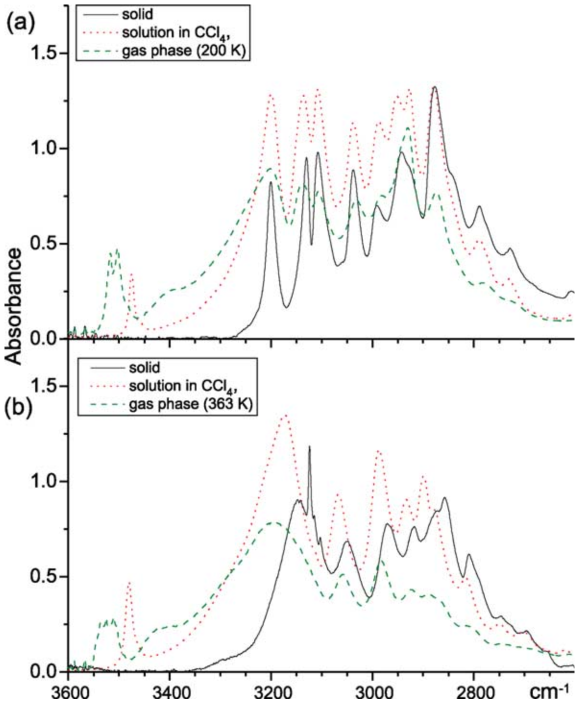


Fig. 4. IR spectra of DMP (a) and P (b) vapours (dashed line), CCl_4 solution, 0.1 mol/l, $d = 1$ mm (dotted line), solid film (solid line).

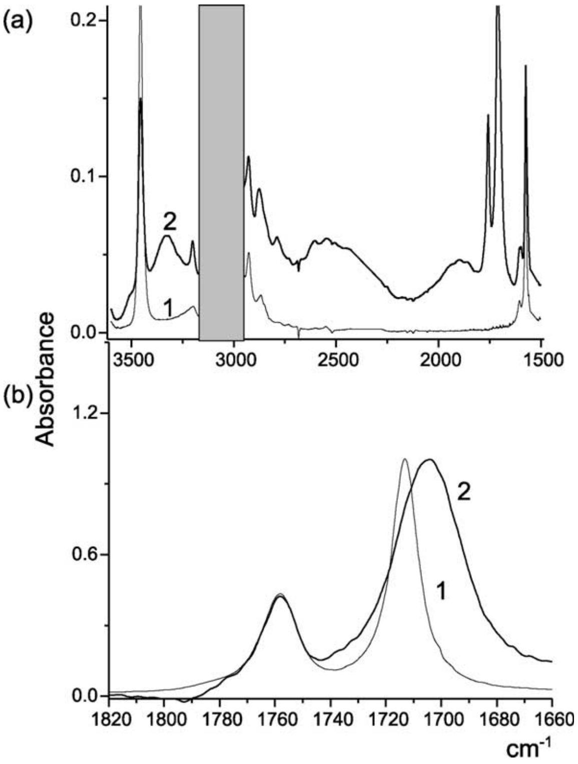


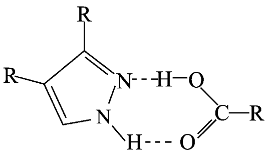
Fig. 5. IR spectra of acetic acid + DMP solutions in CH_2Cl_2. (a) 1—DMP (0.02 mol/l); 2—DMP (0.02 mol/l) + acetic acid (0.015 mol/l), $d = 0.5$ mm. (b) 1—acetic acid (0.002 mol/l); 2—acetic acid (0.005 mol/l) + DMP (0.02 mol/l, the spectra are normalized to make the absorbance equal at maximum of monomer band).

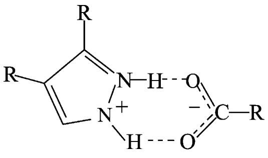
However, in contrast to pyridine, there is one more band near 3320 cm^{-1}, which can be assigned as νNH band of DMP molecule in the complex. Significant shift and broadening of this band relative to νNH of free DMP show that NH group is bonded and, hence, the complex has a cyclic structure with two hydrogen bonds: OH···N and C=O···HN. All these spectral features are rather similar to those described in Refs. [24,25] for DMP complex with formic acid. Therefore, it seems that conclusion about existence of the ionic complexes with transferred proton in the case of 3- and 5-methyl-pyrazoles + acetic acid system, made in Ref. [11], is based on the wrong interpretation of the obtained spectra. Particularly, the above mentioned band in the region 1900 cm^{-1} is attributed in Ref. [11] to the ionic pair, while in fact it is one of the components of Fermi-triad typical for complexes with strong intermolecular OH···N bond with participation of carboxylic acids.

When pentachlorophenol is used as a proton donor, the spectrum reveals very broad νOH band with maximum near 2600 cm^{-1} and narrow νNH band shifted to lower frequencies by ~10 cm^{-1} compared with free DMP. Thus, in this case the complex has an open structure with one strong hydrogen bond OH···N and with NH group of DMP only affected slightly by complex formation, but not involved directly in hydrogen bonding.

The results of calculations performed for 1:1 DMP–acetic acid complex confirm the conclusions drawn from the experimental data. At the same time, it has been found that the structure of the complex and features of its potential energy surface, resulted from calculations, depend essentially on the method and basis set used.

On preliminary stage, the calculations were performed by RHF/6-31G method. It was found that optimised geometry of the cyclic complex CH_3-COOH + $NNHC_3H(CH_3)_2$, obtained at this level, depends on the initial configuration of the complex, taken for computation, particularly on position of OH proton. When the optimisation was started with configuration corresponding to molecular form of the complex, with proton located closer to the oxygen atom, the resulting structure also corresponded to hydrogen bonded molecular complex. When the proton position in the initial configuration was shifted closer to the nitrogen atom, the resulting structure corresponded to hydrogen bonded ionic pair with OH proton transferred to DMP. Hence, the potential energy surface of the complex in this case has two minima corresponding to these two forms:


(1)


(2)

It has been found that molecular complex (1) is energetically more stable, its minimum is deeper by ~6 kcal/mol.

However, it turned out that the potential well of the ionic complex disappears at higher levels of calculations, particularly, when MP2/6-31G, MP2/6-31G** or DFT (B3LYP/6-31G**) methods were used. In these cases the optimisation process leads to the same minimum and the same resulting structure, corresponding to molecular complex (1), independently of proton position in the initial configuration.

Thus, the shape and parameters of potential surface are very sensitive to the level of calculations. This conclusion is in agreement with the results obtained earlier for other strongly hydrogen bonded complexes, for example, such as $NH_3 + HCl$ complex studied by G. Corongui et al. [34].

Since the proton transfer and formation of ionic structures can be induced by the influence of a polar environment, the computations were repeated with inclusion of Onsager reaction field model with dielectric permittivity value close to that of methylene chloride ($\varepsilon \approx 10$). However, the second minimum corresponding to ionic complex did not appear.

Further investigation of the potential surface by DFT (B3LYP/6-31G**) method showed that besides the main deep minimum corresponding to the cyclic molecular complex with two hydrogen bonds there is another minimum corresponding to the open complex with only one $O{-}H\cdots N$ bond. The binding energy of such a complex is less by ~6 kcal/mol. The structure of both complexes is shown in Fig. 6. Geometrical parameters of the cyclic complex are listed in Table 4. One can see that results obtained by B3LYP/6-31G** and MP2/6-31G** methods are rather close. The results show that $O{-}H\cdots N$ hydrogen bond is almost linear, while $N{-}H\cdots O$ bond is far from linear; N–H distance is shorter than in DMP trimer.

Harmonic vibrational frequencies and intensities for the cyclic complex have been obtained by DFT/B3LYP/6-31G^{**++} method, which was used with satisfactory results for analysis of vibrational properties of the acetic acid monomer and cyclic dimer [35]. Parameters of νOH and νC=O vibrations of the complex are presented in Table 5 and compared with those of similar vibrations of acid monomer and dimer. In accordance with the experimental findings, νOH and νC=O frequencies of the acetic acid decrease in the row monomer–dimer–complex with DMP; νC=O intensity changes from 350 km/mol in the monomer to 425 km/mol in the dimer and 260 km/

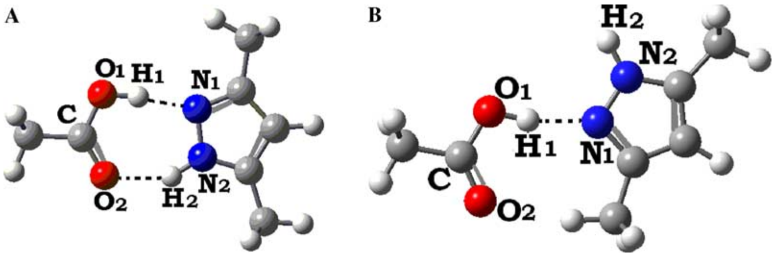


Fig. 6. Calculated structure of the cyclic (1) and open (2) acetic acid–DMP complexes.

Table 4
Calculated geometrical parameters of the acetic acid–DMP cyclic complex

Parameter	DFT/B3LYP/6-31G**	MP2/6-31G**
R(OH)	1.02 Å	1.01 Å
R(H···N)	1.68 Å	1.72 Å
∠OH···N	172°	172°
R(NH)	1.02 Å	1.02 Å
R(H···O)	1.87 Å	1.89 Å
∠NH···O	147°	146°

mol in the complex; νNH frequency (both calculated and observed value) is much higher than in DMP trimer (Table 3). The band of DMP in the region 1600 cm^{-1} is shown to belong to the mixed skeletal vibration including δNH, δCH_3 and νCC movements. Its calculated frequency is less in the complex than in free DMP in accordance with experiment. Taking into account the geometrical parameters (Table 4), one can conclude that O–H···N bond of the complex is stronger than O–H···O bonds in the acetic acid dimer, while N–H···O bond is rather weak and weaker than NH···N bond in DMP trimer.

Thus, the results obtained show that DMP forms with acetic acid the cyclic molecular complex with two hydrogen bonds. No proton transfer takes place in this complex in methylene chloride, as well as in other aprotic solvents of low or medium polarity. Similar results were obtained for P.

In the present work the proton transfer and formation of the ionic complexes have been found spectroscopically for DMP complexes with stronger proton donor–trifluoroacetic acid (TFAA). Preliminary, the ab initio treatment of this system has been performed.

As in the case of acetic acid, calculations for DMP + TFAA system have been carried out at different levels. In all the cases the cyclic complex was found to be energetically more stable than the open complex. The results of the treatment of the cyclic complex by different methods are presented in Tables 6 and 7. One can see in Table 6, that in a number of cases two potential minima corresponding to molecular and ionic structures similar to (1) and (2) has been found. The table shows how the shape of potential surface and relative depth of found minima depend on the method and basis set used for calculations. Strong sensitivity of results to the level of calculations does not allow to make unambiguous conclusions about parameters of the complex and its potential surface. However, some remarkable features can be noted.

(1) For isolated bimolecular cyclic complex, all the methods used (RHF, MP2, DFT) with basis set 6-31G** (or better) give either only one stable configuration corresponding to molecular form of the complex or two configurations corresponding to molecular and ionic forms, the molecular form being more stable. Geometrical parameters of the molecular form, obtained at different levels, are rather close: the length of OH bond varies from 1.03 to 1.06 Å, NH bond from 1.01 to 1.02 Å, H···N distance from 1.53 to 1.60 Å, H···O distance from 1.95 to 2.02 Å; ∠OHN in all the cases is 172°, ∠NHO = 140 ÷ 143°. For example, parameters obtained at B3LYP/6-31G** + level are presented in Table 7. The structure is similar to that shown in Fig. 6(a) for the complex with acetic acid. Parameters of the ionic form, corresponding to higher lying second minimum obtained at this level, also are presented in the table. The energy difference

Table 5
Calculated (DFT/B3LYP/6-31G**++) and observed frequencies (cm^{-1}) and IR intensities (in parentheses, km/mol) of νOH and νC=O vibrations of acetic acid–DMP cyclic complex. Comparison with acetic acid monomer and dimer

	νOH		νC=O	
	Calcd	Observed	Calcd	Observed
Monomer	3754 (60)	3580 (60)[a]	1822 (357)	1785[a]
Dimer (B_u)	3148 (3420)	~2955 (2130)[b]	1764 (850)	1715 (630)[b]
Complex	2847 (2550)	~2950, 2500, 1900[b]	1749 (260)	1704 (~150)[b]

[a] Vapour.

[b] CH_2Cl_2 solution.

Table 6
Potential minima and corresponding structures of DMP + TFAA cyclic complex, found by different methods

Method/basis set	The type of potential surface	More stable structure	ΔE^{a} (kcal/mol)
RHF/6-31G	Double well	Ionic pair	−3
MP2/6-31G	Double well	Ionic pair	−0.8
RHF/6-31G**	Double well	Mol. comp.	6.9
MP2/6-31G**	Single well	Mol. comp.	
DFT/B3LYP/6-31G**	Single well	Mol. comp.	
DFT/B3LYP/6-31G**$^{+}$	Double well	Mol. comp.	1.3
DFT/B3LYP/6-31G**$^{+}$, Onsager model, $\varepsilon = 10$	Double well	Ionic pair	1.4

[a] ΔE—energy difference between molecular complex and ionic pair configurations.

between two minima is 1.3 kcal/mol (Table 6). Comparison of two sets of parameters, particularly the positions of the bridging protons, convinces that the structures described by these sets are essentially different and can be treated just as molecular and ionic ones. In the case of the ionic structure both bridging protons are located near the nitrogen atoms. Thus, this ionic pair contains DMPH^{+} cation and trifluoroacetate anion with two interionic hydrogen bonds (Fig. 7(a)).

(2) Inclusion of polarized environment in the framework of Onsager or Thomasi models either changes the relative depth of two minima in favour of the ionic form minima or leads to appearance of the ionic minimum in the cases when only molecular form minimum has been found for isolated complex. For example, at B3LYP/6-31G** + level, after inclusion of Onsager's reaction field with dielectric permittivity $\varepsilon \approx 10$ the second minimum corresponding to the ionic form becomes deeper than molecular form minimum by 1.4 kcal/mol (Table 6). The set of parameters of the ionic form, obtained for this case, is given in Table 7. The difference between these parameters and those of the ionic form of isolated complex is not very large. One can mark an increase of O···H and O···N distances (increase of the charge separation) within the ionic pair and some symmetrization of the structure of both ions due to the influence of polarized environment.

(3) Independently of the method used, optimisation does not lead to a structure intermediate between molecular and ionic ones. In other words, no minimum corresponding to the complex with quasisymmetrical hydrogen bonds and shared protons was found. However, if in reality the potential surface has two minima with the barrier height less than the energy of the first or even zero vibrational level (low barrier hydrogen bond), then spectral characteristics of the system may be similar to those of the intermediate complex with shared proton. In any case the influence of anharmonic effects on vibrational spectrum of this system should be significant.

Thus, one can expect, basing on results of these calculations, that experimental measurements in

Table 7
Calculated (DFT/B3LYP/6-31G** +) bond lengths (Å) and bond angles (°) in molecular and ionic forms of DMP + TFAA 1:1 cyclic complex

Parameter	Molecular complex	Ionic pair, isolated complex	Ionic pair, Onsager model ($\varepsilon = 10$)
$R(O_1H_1)$	1.06	1.51	1.71
$R(H_1N_1)$	1.52	1.09	1.04
$R(O_2H_2)$	2.02	1.60	1.69
$R(H_2N_2)$	1.01	1.06	1.05
$R(O_1N_1)$	2.57	2.55	2.68
$R(O_2N_2)$	2.86	2.59	2.67
$R(CO_1)$	1.30	1.26	1.25
$R(CO_2)$	1.22	1.25	1.25
$\angle O_1H_1N$	172.5	160	155.4
$\angle O_2H_2N_2$	139.9	155.6	155.4
$\angle H_1N_1N_2$	112.9	113.5	115.1
$\angle H_2N_2N_1$	116.8	113.5	115.1
$\angle O_1CO_2$	127.9	128.8	130.2

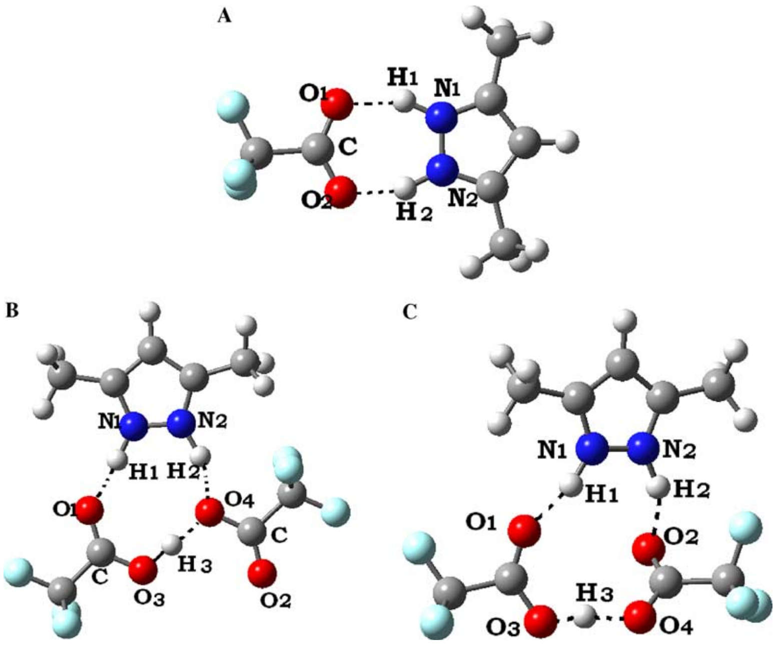


Fig. 7. Calculated structures of the DMP–TFAA ionic complexes. (a) 1:1 cyclic complex; (b and c) 1:2 complexes.

the gas phase most probably should give the structure close to the molecular complex, while in the condensed phase with $\varepsilon \approx 10$—close to the ionic pair. The appearance of spectral features typical for quasisymmetrical hydrogen bonds with shared proton also is not excluded.

Consider now the available experimental data. There is no information about the experimental studies of TFAA complexes with pyrazoles in the gas phase. However, spectroscopical measurements have been performed for the complexes of TFAA with trimethylamine and isoquinoline [36,37]. It has been found that in the gas phase these complexes reveal the molecular structure. This can be considered as an argument in favour of suggestion about molecular structure of DMP–TFAA complex in the gas phase[1].

On the other hand, the investigation of the IR spectra of TFAA + DMP complexes in CH_2Cl_2 solutions in the present work gives the evidences of the proton transfer and formation of the ionic structures. Particularly, in the region of NH, OH stretching vibrations there is no band similar to the band near 3320 cm^{-1} in spectrum of DMP–acetic acid complex, which can be identified as νNH of DMP molecule involved in hydrogen bond NH···O. The interpretation of the intensive broad band in the region ~3300–2100 cm^{-1} and several weaker broadened bands in the lower frequency region, which belong obviously to vibrations with essential contribution of proton movement, is not quite clear, since in general such features can be caused by strong hydrogen bonds of OH···N type, as well as $O^{-}\cdots HN^{+}$ type. However, the picture in the region 1900–1300 cm^{-1} (Fig. 8) confirms the ionic structure of the complex. Thus, spectra of TFAA solutions in presence of equimolar amount of DMP or in excess of DMP, reveal no bands, which can be assigned as νC=O of the acid molecule (for comparison, the bands of TFAA monomer and dimer are shown). Instead, a strong band near 1680 cm^{-1}, which

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[1] According to pK_a values (4.23, 5.14 and 9.8 for DMP, isoquinoline and trimethylamine, respectively), DMP is weaker N-base than isoquinoline and especially trimethylamine. However, it seems that possibility of formation of the cyclic complex with two hydrogen bonds with carboxylic acids increases to some extent the proton accepting ability of DMP and makes it comparable with that of isoquinoline and even trimethylamine.

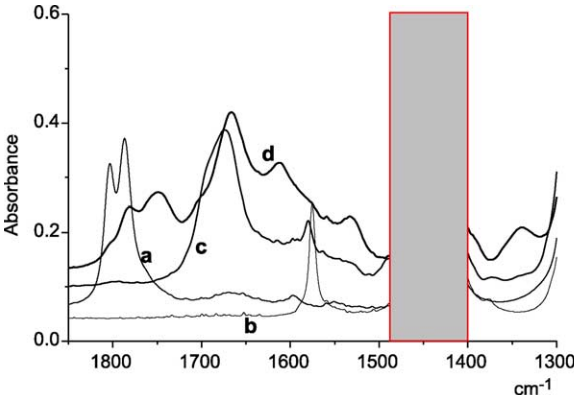
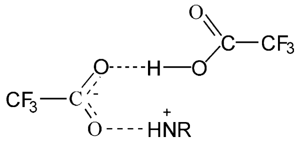


Fig. 8. IR spectra of TFAA + DMP solutions in CH_2Cl_2. (a) TFAA (0.02 mol/l); (b) DMP (0.02 mol/l); (c) DMP + TFAA (0.02 + 0.02 mol/l); (d) DMP + TFAA (0.02 + 0.04 mol/l), $d =$ 0.5 mm.

is known to be typical for $\nu_aCO_2^-$ vibration of trifluoroacetate anion[2] [38–40], is observed. The band of DMP near 1570 cm^{-1}, belonging to mixed $\delta NH/\delta CH_3/\nu CC$ vibration, becomes much weaker and shifts slightly to higher frequencies. Hence, the proton transfer from TFAA to DMP with ionic pair formation takes place, the presence of the broad bands being an indication of the existence of the strong hydrogen bond between the anion and cation.

Fig. 8 shows also that the spectrum of DMP + TFAA solution reveals drastic changes upon addition of an excess of TFAA. These changes are (1) significant increase of background absorption in the region 2000–500 cm^{-1}; (2) complete disappearance of the DMP band near 1570 cm^{-1}; (3) the appearance of several broadened maxima (at ~1750, 1620, 1540, 1350 cm^{-1}). One can mark also that the band near 1680 cm^{-1} undergoes some shift to lower frequencies, while the broad maximum in the region near 2700 cm^{-1} shifts to higher frequencies. All these changes witness that new complex containing two acid molecules and one DMP molecule is formed.

Usually 2:1 complexes formed by TFAA with N-bases, such as aliphatic amines or pyridine, have an open structure and contain TFFA anion, coupled by two hydrogen bonds with a cation RNH^+ and with second acid molecule:



Characteristic feature of such complexes is the simultaneous presence of $\nu C{=}O$ band of bonded TFAA molecule and νCO_2^- bands of the anion in the vibrational spectrum. This is quite different from the picture described above. Hence, the suggestion arises that in the case of DMP its complex with two TFAA molecules has another structure.

In order to find out the main parameters of this structure, DFT/B3LYP/6-31G** calculations have been performed. The calculations gave the possibility of formation of two complexes with rather close energies ($\Delta E \sim 0.3$ kcal/mol) and configurations shown in Fig. 7(b)and (c). Both complexes contain $DMPH^+$ cation and homoconjugated bis-trifluoroacetate anion with very short ($R(O_3\cdots O_4) = 2.43 \div 2.47$ Å) and strong hydrogen bond $O_3{-}H_3\cdots O_4$. Complex ‘c’ energetically is more stable. It has more symmetrical structure and contains homoconjugated anion in *cis* form; $O_3\cdots O_4$ and $O_3\cdots H_3$ distances in this complex are shorter, $O_3{-}H_3$ distance is longer and, hence, hydrogen bond is some stronger, than in complex ‘b’, which contains homoconjugated anion in *trans* form. Geometrical parameters of the anion in the ‘c’ complex are given in Table 8. For comparison,

Table 8
Calculated parameters of the cyclic 1:2 complex DMP–TFAA (structure ‘c’, Fig. 7). Comparison with complex of $(CF_3COO)_2H^-$ anion with K^+

Parameter	DMP + 2TFAA	$(CF_3COO)_2H^- + K^+$
$R(O_3H_3)$	1.09 Å	1.04 Å
$R(O_4H_3)$	1.37 Å	1.47 Å
$R(O_3O_4)$	2.45 Å	2.50 Å
$R(O_1O_2)$	3.41 Å	4.29 Å
$R(O_1H_1)\backslash R(O_1K)$	1.65 Å	2.62 Å
$R(O_2H_2)\backslash R(O_2K)$	1.55 Å	2.65 Å
$\angle O_3H_3O_4$	171.2°	169.5°
$\angle O_1O_3O_4O_2$	−49.1°	−64.7°

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[2] The region of the band of $\nu_sCO_2^-$ vibration is overlapped by solvent absorption.

parameters of such anion in the complex with K^+ cation are presented. In both cases O···H···O hydrogen bond is almost linear and not quite symmetrical, the bridging proton is located closer to one of the oxygen atoms. It is seen that this hydrogen bond is stronger in complex with DMP than with K^+.

It seems obvious that specific features of the IR spectrum of solutions containing DMP and an excess of TFAA are caused by presence of homoconjugated TFAA anion with OH···O hydrogen bond of this type. The calculations show that the important peculiarity of vibrational spectra of all such complexes is a number of intensive bands in the region 1700–1200 cm^{-1}. Their high intensity is determined by contribution of displacements of CO_2^- groups with significant participation of displacements of the O···H···O bridge proton. However, the experimental data obtained which refer to methylene chloride solution do not allow choosing between “c” and “b” structures resulted from treatment of the isolated system.

It should be mentioned that under excess of DMP spectra of DMP + TFAA solutions reveal some changes which give indications of formation of the complexes containing one TFAA and two DMP molecules (2:1 complexes). Similar, but more clear changes are observed in spectra of DMP + HBr system.

Spectrum of solution of solid 1:1 adduct DMP + HBr in CH_2Cl_2 reveals strong broad band with maximum and centre of gravity in the region 2700 cm^{-1} (Fig. 9). Since this frequency is higher than position of the νHBr band of free HBr molecule, this band cannot be attributed to νHBr vibration of molecular hydrogen bonded complex. Hence, the complex formed has an ionic structure, the band 2700 cm^{-1} being due to the νNH vibrations of DMP cation. A shoulder in the region 3000 cm^{-1} reflects probably that there are two overlapped bands corresponding to symmetrical and asymmetrical νNH vibrations. The essential high-frequency shift (from 1573 to 1604 cm^{-1}) of the band belonging to mixed δNH/δCH_3/νCC vibration of pyrazole moiety can be marked. The addition of the excess of DMP leads to noticeable changes: an increase of absorption intensity in the region 3000 cm^{-1} and appearance of a weak broad band

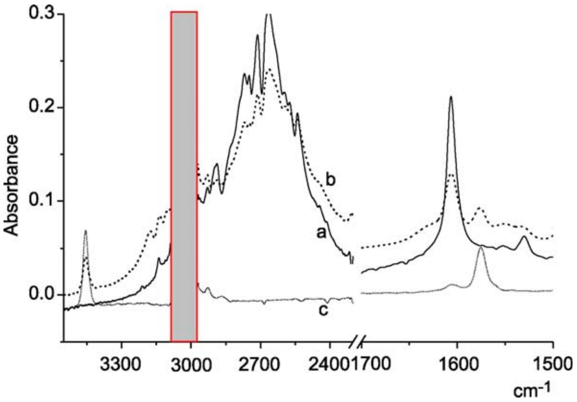

Fig. 9. IR spectra of solutions of DMP + HBr 1:1 adduct in CH_2Cl_2. (a) 0.01 mol/l; (b) 0.01 mol/l + 0.01 mol/l DMP; (c) 0.01 mol/l DMP solution.

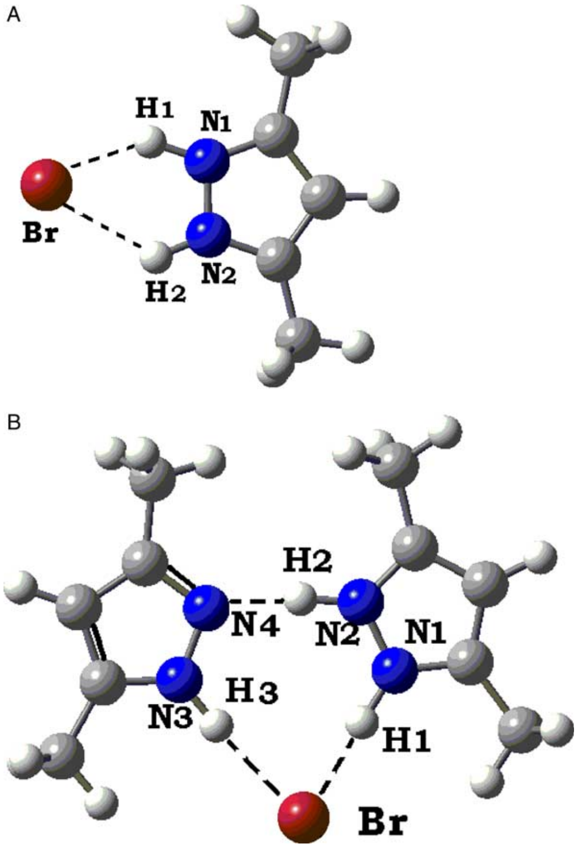

Fig. 10. DFT/B3LYP/6-31** structure of 1:1 and 2:1 DMP + HBr complexes.

near 1800 cm^{-1}. Hence, one can conclude that formation of the ionic 2:1 DMP–HBr complexes takes place.

Possibility of formation of 2:1 complexes in DMP + trichloroacetic acid system has been proved earlier by low temperature NMR studies [41]. It has been shown in Ref. [41] that such complexes contain homoconjugated cation $(DMP)_2H^+$. It is natural to suggest that ionic complexes of 2:1 composition, found in the case of DMP + TFAA and DMP + HBr systems, also contain $(DMP)_2H^+$ cation. The results of DFT/B3LYP/6-31** treatment of DMP + HBr system, performed in the present work, confirm this suggestion. The calculations show the possibility of formation of energetically stable ionic DMP + HBr 1:1 and 2:1 complexes with structures presented in Fig. 10. It is seen that 2:1 complex includes $(DMP)_2H^+$ cation with proton of N···H···N bridge located closer to one of the nitrogen atoms and two NH groups directed towards bromide anion.

More detailed investigation of the structure and vibrational properties of homoconjugated ions included in the complexes formed by pyrazoles will be the subject of the next work.

4. Conclusions

(1) Among the oligomers, which can be formed by studied pyrazoles, the cyclic trimer is the most preferable from the point of view of free energy. This conclusion follows both from results of experimental studies and ab initio treatment. The gain of energy, obtained due to the optimal geometry of the trimer, compensates the entropy loss, as compared with the dimer. In the gas phase both P and DMP reveal the equilibrium between monomers, dimers and trimers. In solutions the equilibrium between monomers and trimers dominates completely: no traces of the dimers are observed. DMP retains the cyclic trimer structure in solid state, while in the case of pyrazole P formation of crystalline lattice provides another type of association.

(2) With pentachlorophenol and acetic acid both studied pyrazoles form molecular complexes without proton transfer in the gas phase, as well as in the aprotic solvents. In the case of pentachlorophenol, the complexes formed have an open structure and contain only one strong hydrogen bond OH···N, while the NH group of pyrazole molecule remains unbonded. In the case of acetic acid, the calculations predict the closed cyclic complex with two hydrogen bonds OH···N and NH···O to be energetically much more stable, than the open complex, that agrees with the spectral data. The OH···N bond in the cyclic complex is strong, stronger than OH···O bond in the acetic acid dimer, while NH···O bond is weak, weaker than NH···N bond in DMP trimer.

(3) The pyrazoles reveal the tendency to form stable cyclic complexes also when interacting with trifluoroacetic acid. According to results of calculations, the cyclic complex of 1:1 composition, formed by DMP with TFAA in the gas phase, has molecular structure with OH···N and NH···O hydrogen bonds, similar to that with acetic acid. Polarizable environment induces the proton transfer and formation of the ionic pair containing $DMPH^+$ cation and trifluoroacetate anion coupled by two $NH^+\cdots O^-$ hydrogen bonds in accordance with results of investigations of the IR spectra of solutions. The attempts to study the shape and parameters of potential energy surface of considered system show that the number of potential wells, particularly the wells corresponding to molecular and ionic configuration of the complex, the relative depth of these wells, the existence of the barrier separating the wells and parameters of this barrier, depend strongly on the method and level of calculations.

(4) The geometry of pyrazoles and carboxylic acids molecules is favorable to formation of trimolecular cyclic complexes containing one molecule of one sort and two molecules of the other sort. Formation of such complexes in DMP + TFAA system in CH_2Cl_2 solutions have been detected experimentally. It has been found in accordance with results of ab initio calculations that these complexes have ionic structure and contain homoconjugated ions with strong almost symmetrical hydrogen bonds. In the case of DMP–TFAA 1:2 complex it is bis-trifluoroacetate anion $(CF_3COO)_2H^-$ with short and strong O···H···O bond, while 2:1 complex contains dimethylpyrazole–dimethylpyrazolium cation $(DMP)_2H^+$ with strong N···H···N bond. Structural and vibrational characteristics of these ions are very sensitive to properties of counterions and environment. Their further investigation is of essential interest.

(5) It has been established that DMP forms with HBr ionic complexes both of 1:1 and 2:1 composition, containing $DMPH^+$ and $(DMP)_2H^+$ cations correspondingly.

Acknowledgements

We thank Prof. J. Elguero for bringing our attention to studies of pyrazoles and Prof. H.-H. Limbach for providing of pyrazoles samples, stimulating discussions and kind permission to perform the part of calculations in his lab using GAUSSIAN 98 program. The work was supported by RFBR, project 02-03-32668.

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