Ab Initio Study of the $(DMF)_m \cdot (HCl)_n$ $(m, n = 0$–$2)$ Complexes

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Abstract—Based on the results of *ab initio* calculations (B3LYP, 6-31++G(d,p)), the structures and stability of the complexes DMFA · HCl, $(DMF)_2$ · HCl, DFF · $(HCl)_2$, and $(DMF \cdot HCl)_2$ are compared. In the complex with a 1 : 1 composition, DMF and HCl form a hydrogen bond of the molecular type. In the heterotrimers with compositions 1 : 2 and 2 : 1, the hydrogen bond noticeably strengthens. In the tetramer $(DMF \cdot HCl)_2$, the most pronounced proton transfer takes place and two quasi-symmetric hydrogen bridges O···H···Cl are formed and stabilize this complex. The results of calculations are compared with data on the structure of complexes between HCl and DMF obtained by crystal-structure XRD and vibrational spectroscopy in solutions.

INTRODUCTION

In solutions of acids, radically different structures may be formed depending on the concentrations of components and their proton-donor and proton-acceptor properties: from molecular AH···B complexes of an acid (HA) and a solvent (B) to protonated forms of a base (solvent) HB^+ and doubly solvated protons with a strong symmetric hydrogen bond $(A\cdots H\cdots A)^-$. The degree of proton transfer in the complexes formed largely determines the physicochemical and catalytic properties of acid solutions [1]. Data on the structure, energetic characteristics and distribution of charges on the atoms of such complexes provide additional information on the detailed mechanism of molecular interactions in solutions.

Direct measurements of geometric parameters of particles in solutions (unlike in the crystal phase) are impossible. Their theoretical determination meets several difficulties and has several limitations. Thus, a calculation of the isolated acid–base complexes may agree well with the experiment in the gas phase, where proton transfer between AH and B molecules has never been observed [2, 3], but this does not take into account a considerable portion of interactions between species in a solution, which stimulate proton transfer from HA to B and stabilize the complexes formed. The calculations of larger molecular systems where the average electrostatic field is additionally taken into account are a more correct approximation for describing the structure and mutual arrangement of species in a liquid but require more time.

The goal of this work was to carry out such calculations and compare the results with the known experimental data for the condensed phase. *N,N*-dimethylformamide (DMF) and hydrogen chloride were chosen for

this study since the isolated DMF · HCl and DMF · $(HCl)_2$ complexes have previously been calculated [4] at the RHF/6-31G level. It was shown that, in contrast to the 1 : 1 complex, the heterotrimer shows a considerable proton shift from one of the HCl molecules to an oxygen atom in DMF.

Complex formation of DMF and HCl has been studied by IR [5] and Raman [6] spectroscopy in solutions and by solid-phase XRD [7]. It has been concluded that in excess base, HCl is entirely bound with DMF in the 1 : 1 complexes due to the formation of a strong quasi-symmetric hydrogen bond O···H···Cl with incomplete proton transfer onto the oxygen atom of the DMF molecule. In an equimolar solution, the components are almost entirely bound in such complexes. Data on the structures of the 1 : 1 HCl complex with DMF obtained from vibrational spectra agree with the result of geometry measurements by XRD [7]. In the crystalline phase, quasi-ionic pairs are dimerized; that is, the formation of symmetric cyclic complexes is energetically favorable.

Geometry optimization and the calculation of the full energies of the complexes DMF · HCl, $(DMF)_2 \cdot$ HCl, DMF · $(HCl)_2$, and $(DMF \cdot HCl)_2$ were carried out using density functional theory with three-parameter functional B3LYP in the 6-31G(d,p) basis set. Zero-point energy correction was not taken into account. Stationary points were identified by analyzing the Hessian matrix. The electrostatic charges on the atoms were calculated by the Chirlian–Frankle method. The parameters of optimal structures of isolated DMF and HCl molecules and dimers $(HCl)_2$ and $(DMF)_2$ were calculated in an analogous manner. When modeling the structural fragment of the solution, the electrostatic interaction of the heterocomplex $(DMF \cdot HCl)_2$ with the

medium was taken into account using the PCM model. Calculations were carried out using the Gaussian-94 program package [8].

The ΔH values were calculated for the formation of complexes from monomeric molecules. The strengths of all hydrogen bonds (E_H) in the systems studied (Fig. 1) were calculated assuming that the full energy of the complex could be described as a sum of the energies of separate fragments and the energies of the bonds between them.

The optimal configurations of the heterocomplexes DMF · HCl, (DMF)$_2$ · HCl, and DMF · (HCl)$_2$, as well as the strengths of their intermolecular interactions are shown in Fig. 1. The full energies of these complexes, the enthalpies of their formation, and geometric parameters are shown in Table 1. Data on atomic charges are summarized in Table 2. In contrast to the complexes DMF · HCl and (DMF)$_2$ · HCl (Figs. 1a, 1b), two stationary points were found on the potential energy surface of the heterotrimer DMF · (HCl)$_2$ corresponding to the global (Fig. 1c) and local (Fig. 1d) minimums. Before considering the specific features of heterocomplexes DMF · HCl, (DMF)$_2$ · HCl, and DMF · (HCl)$_2$, two additional estimates were made.

1. Calculated geometric parameters of the isolated DMF molecule were compared with the results of electron diffraction measurements (Table 1) [9]. It was seen that the calculation describes well the results of experiments (the maximal difference is 0.03 Å for the bond lengths and 5° for the angles). This suggests that intramolecular parameters in the complexes were calculated with acceptable accuracy.

2. Based on the calculated data the effect of self-association of HCl and DMF molecules was analyzed. The strength of the intermolecular bond in the dimer (HCl)$_2$ is 3.0 kcal/mol, and the covalent bond in the Cl–H···Cl bridge is longer than in a free hydrogen chloride molecule by 0.005 Å. The overall charge of the proton-donating molecule H15–Cl16 is –0.035 at. units. The (DMF)$_2$ dimer with a cyclic structure has two equivalent hydrogen bonds between the O1 and H3 atoms. The length of each of these bonds is 2.402 Å, and the strength is 2.3 kcal/mol. In the dimerization of DMF molecules, the charges on these atoms change substantially (Table 2). It follows from the results obtained that the self-association of HCl and DMF molecules does not lead to changes in their geometric parameters, and the strength of the hydrogen bonds in the dimers are small and practically the same.

Calculation showed that, when the DMF and HCl molecules enter the composition of a heterodimer, their geometric characteristics change only slightly. These molecules are in the same plane and form a typical hydrogen bond: (R(O1···H13) = 1.669 Å, ($\angle$O1···H13–Cl14 = 172.9°, the bond strength is 10.2 kcal/mol and the charge at the HCl molecule is –0.148 at. units). As this bond is formed, the strength and the lengths of all covalent bonds in the DMF molecule change according

to the "parity" rule [10]. The O1–C2 bond (the nearest to the hydrogen bond) and all subsequent bonds with odd numbers become weaker (the distances between atoms in these bonds increase). Bonds with even numbers become stronger (Table 1). When a dimer is formed, charges at the carbonyl-group atoms in the DMF molecule noticeably change (Table 2).

When considering the heterotrimer DMF · (HCl)$_2$ it is notable that the structures are cyclic and rather stable. The enthalpy of formation of a planar complex corresponding to the global minimum on the potential energy surface (Fig. 1c) is 16.2 kcal/mol, and that of the nonplanar complex corresponding to the local minimum (Fig. 1d) is 14.0 kcal/mol. In the planar structure, the Cl16 atom forms a slightly stronger hydrogen bond (3.6 kcal/mol) with the carbonyl hydrogen atom H3 than in the (HCl)$_2$ dimer. In the nonplanar structure the bond (2.8 kcal/mol) with the hydrogen atom H8 from the methyl group is weaker. The strengths of the strongest hydrogen bonds (O1···H13) in the cited complexes are 15.2 and 10.4 kcal/mol, respectively. The charge of acid molecules that form these bonds is approximately equal to the charge of the HCl molecule in the DMF · HCl dimer in the first case and approximately an order of magnitude lower in the absolute value and has the opposite sign in the second case. In both cases, the charges of the molecules H15–Cl16 are considerably lower than the charge of the acid molecule in the heterodimer with a 1 : 1 composition. Comparison of strengths and lengths of bonds in a hydrogen bridge O1···H13–Cl14 with the corresponding values calculated for the complex DMF · HCl points to the further approaching of proton H13 to oxygen atom O1. This effect reveals itself most strongly in the case of the planar conformer, in which the O1···H13 distance is shortened by 0.225 Å.

The (DMF)$_2$ · HCl complex, which also has a cyclic structure (Fig. 1b), is the most stable of all heterotrimers. The distances Cl14–H3' and O1'–H3 are 2.791 and 2.200 Å, respectively. The O1···H13 bond in this structure has about the same strength (15.0 kcal/mol) as in the planar complex with a 1 : 2 composition, and the enthalpy of formation (17.1 kcal/mol) and the overall strength of other hydrogen bonds (8.5 kcal/mol) are higher than the corresponding values in both conformers DMF · (HCl)$_2$. The geometric parameters of two DMF molecules are generally close (Table 1). Proton H13 is shifted toward oxygen O1 like in the planar trimer DMF · (HCl)$_2$ (0.012 Å less). The charges on the atoms in the proton-acceptor (with respect to HCl) DMF molecule are close in the sign and the absolute value to the analogous charges in the DMF · HCl complex, and those on the proton-acceptor molecules are close to the charges in the dimer (DMF)$_2$; the charge on the HCl molecule is –0.235 at. units (Table 2).

Calculation showed that the tetramer (DMF · HCl)$_2$, of which the enthalpy of formation is 30.1 kcal/mol, is almost symmetrical with respect to the inversion center
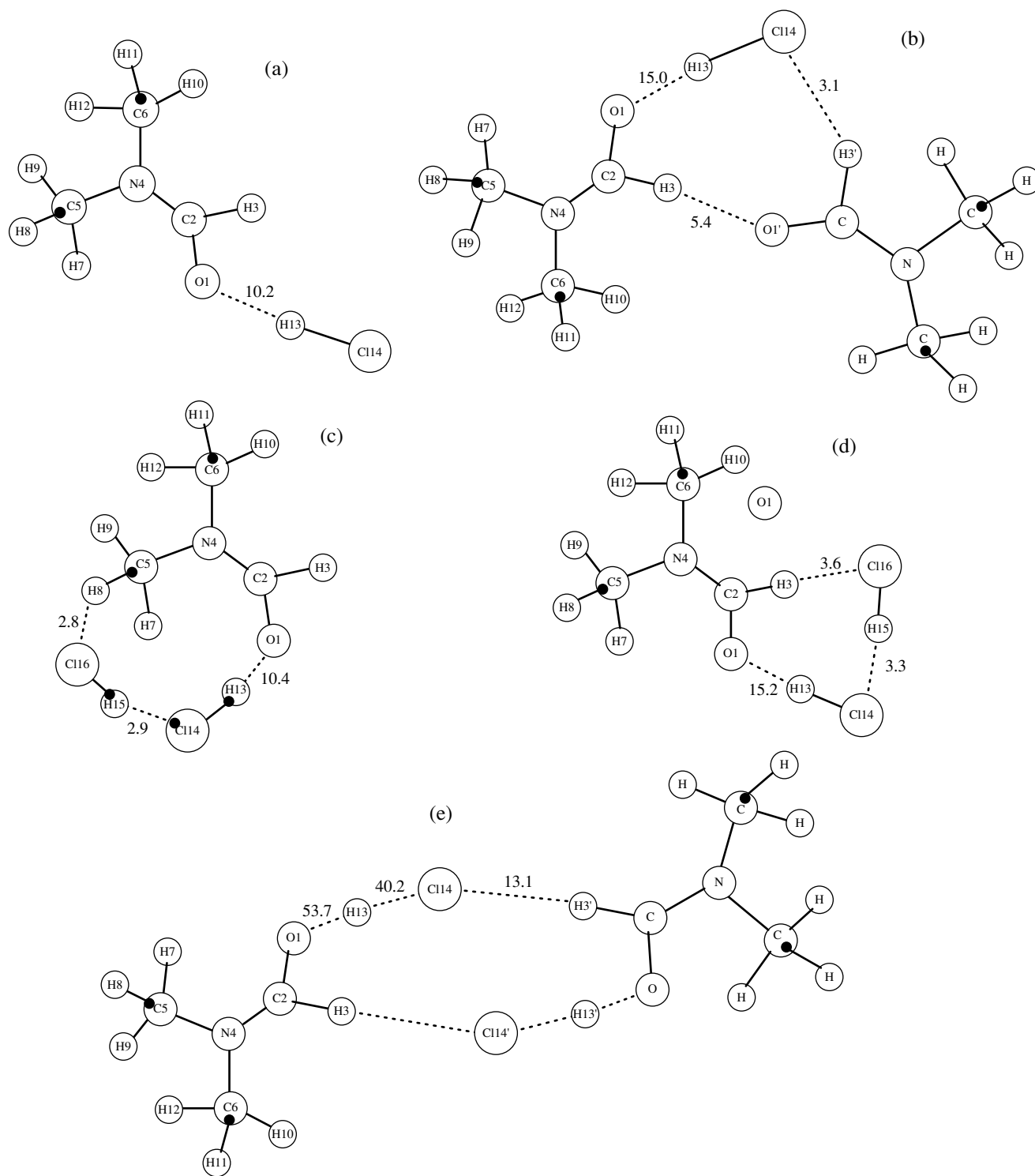
Fig. 1. The structure of complexes (a) DMF · HCl, (b) $(DMF)_2$ · HCl, (c, d) DMF · $(HCl)_2$, (c) global minimum, (d) local minimum, (e) (DMF · HCl)$_2$. The strengths of intermolecular interactions are shown E_H, kcal/mol.

(Fig. 1e). Compared to the complexes considered earlier, in this complex we observe considerable proton transfer from an acid molecule to oxygen atoms in DMF. This is evident from the fact that the distance between atoms O1 and H13 decreases (compared to the distance in the dimer DMF · HCl) by 0.582 Å (Table 3). As a result, two quasi-symmetric hydrogen bridges are formed in the complex and they are equivalent in all parameters. The strengths of the bonds O1···H13 and H13···Cl14 in these bridges are 53.7 and 40.2 kcal/mol.

Table 1. Full energies (E), enthalpies of formation of complexes (ΔH), equilibrium bond distances (R), and angles (α) in the DMF molecule and DMF complexes with HCl

Parameter*	DMF (data from [9])	DMF	$(DMF)_2$	$(HCl)_2$	$DMF \cdot HCl$	$(DMF)_2 \cdot HCl$		$DMF \cdot (HCl)_2$	$DMF \cdot (HCl)_2$**
E, at. units		−248.533596	−497.074087	−921.609192	−709.351378	−957.896728		−1170.163822	−1170.160352
ΔH, kcal/mol			4.2	3.0	9.8	17.1		16.2	14.0
R, Å O1C2	1.224(3)	1.224	1.232	–	1.238	1.251	1.236	1.249	1.241
C2H3	1.112(3)	1.106	1.103	–	1.101	1.098	1.102	1.098	1.101
C2N4	1.391(7)	1.363	1.361	–	1.347	1.339	1.355	1.337	1.344
N4C5	1.453(4)	1.456	1.454	–	1.459	1.458	1.455	1.461	1.462
N4C6	1.453(4)	1.452	1.453	–	1.456	1.461	1.455	1.460	1.458
C5H7	1.112(3)	1.090	1.090	–	1.089	1.089	1.090	1.089	1.089
C5H8	1.112(3)	1.097	1.097	–	1.096	1.096	1.097	1.095	1.095
C5H9	1.112(3)	1.097	1.097	–	1.096	1.096	1.097	1.095	1.094
C6H10	1.112(3)	1.093	1.093	–	1.092	1.091	1.092	1.092	1.092
C6H11	1.112(3)	1.097	1.098	–	1.096	1.096	1.097	1.095	1.096
C6H12	1.112(3)	1.097	1.098	–	1.096	1.096	1.097	1.095	1.095
O1H13	–	–	–	–	1.669	1.456		1.444	1.607
H13Cl14	–	–	–	1.288	1.336	1.399		1.403	1.345
Cl14H15	–	–	–	2.583	–	–		2.226	2.315
H15Cl16	–	–	–	1.292	–	–		1.314	1.305
α, deg O1C2H3	–	122.1	121.7	–	121.4	121.9	121.7	121.2	120.1
O1C2N4	123.5(0.6)	125.7	125.0	–	124.9	123.9	125.1	124.2	126.4
H3C2N4	117.0(2.8)	112.2	113.3	–	113.7	114.2	113.2	114.7	113.5
C2N4C5	120.8(0.3)	120.5	120.9	–	120.8	121.5	121.1	121.2	121.7
C2N4C6	122.3(0.4)	121.8	121.3	–	121.6	120.7	121.2	121.2	121.2
C5N4C6	113.9(0.5)	117.7	117.8	–	117.6	117.9	117.7	117.6	117.0
N4C5H7	–	108.4	108.4	–	108.7	108.9	108.6	108.9	109.4
N4C5H8	–	110.5	110.5	–	110.1	110.0	110.4	109.9	110.6
N4C5H9	–	110.5	110.5	–	110.1	110.0	110.4	109.9	110.1
N4C6H10	–	109.7	109.6	–	109.8	109.6	109.7	109.9	109.9
N4C6H11	–	110.9	110.9	–	110.5	110.1	110.7	110.2	110.4
N4C6H12	–	110.9	110.9	–	110.5	110.1	110.7	110.2	110.3
H7C5H8	–	109.5	109.4	–	109.6	109.6	109.5	109.6	109.3
H7C5H9	–	109.5	109.4	–	109.6	109.6	109.5	109.6	109.3
H8C5H9	–	108.6	108.5	–	108.8	108.7	108.5	108.9	109.2
H10C6H11	–	108.5	108.6	–	108.7	109.2	108.7	108.9	108.7
H10C6H12	–	108.5	108.6	–	108.7	109.2	108.7	108.9	108.8
H11C6H12	–	108.3	108.3	–	108.6	108.5	108.5	108.8	108.8
C2O1H13	–	–	–	–	112.9	112.2		113.6	132.1
O1H13Cl14	–	–	–	–	172.9	176.3		176.2	176.5
H13Cl14H15	–	–	–	100.6	–	–		93.5	93.0
Cl14H15Cl16	–	–	–	171.7	–	–		167.9	170.9
H3Cl16H15	–	–	–	–	–	–		69.5	66.8

* Numbers denote atoms in Fig. 1.
** Less stable conformer.

Table 2. Charges at atoms (at. units) in the DMF molecules complexes

Atom*	DMF	$(DMF)_2$	$(HCl)_2$	DMF · HCl	$(DMF)_2 \cdot$ HCl		DMF · $(HCl)_2$	DMF · $(HCl)_2$**
O1	−0.576	−0.480	−	−0.377	−0.364	−0.502	−0.425	−0.652
C2	0.515	0.312	−	0.323	0.329	0.275	0.337	0.585
H3	−0.041	0.056	−	0.053	0.098	0.099	0.069	−0.017
N4	−0.173	−0.192	−	−0.143	−0.178	−0.113	−0.234	−0.193
C5	0.479	0.249	−	0.338	0.526	0.373	0.337	0.295
C6	−0.341	0.207	−	−0.025	0.034	0.291	0.177	−0.142
H7	−0.045	−0.017	−	−0.058	−0.103	−0.027	−0.017	−0.015
H8	−0.103	−0.036	−	−0.046	−0.104	−0.072	−0.042	−0.031
H9	−0.103	−0.036	−	−0.046	−0.102	−0.068	−0.043	−0.051
H10	0.142	−0.017	−	0.048	0.065	0.115	0.013	0.060
H11	0.124	−0.024	−	0.041	0.010	0.016	0.006	0.094
H12	0.124	−0.024	−	0.041	0.009	0.113	0.006	0.093
H13	−	−	0.244	0.158	0.137	−	0.266	0.362
Cl14	−	−	−0.209	−0.306	−0.372	−	−0.426	−0.346
H15	−	−	0.172	−	−	−	0.357	0.228
Cl16	−	−	−0.207	−	−	−	−0.382	−0.269

*Numbers are for the atoms in Fig. 1.
**Less stable structural conformer.

Note also that the tetramer $(DMF \cdot HCl)_2$ is contrasting to all other complexes in the distribution of charges on the atoms. In this complex, changes in the charges on each atom of the carbonyl group are maximal (compared to a free DMF molecule) and on the dimethylamine group (Tables 2, 4). The dipole momentums of the CH bonds in both methyl groups are directed toward hydrogen atoms only in this complex.

The calculated geometric parameters of the complex $(DMF \cdot HCl)_2$ were compared with the results of measurements [7]. For simplicity of the whole picture in the framework of the PCM model, we calculated this complex taking into account the electrostatic interaction with the medium, which has the same dielectric constant as *N,N*-dimethyl formamide, 36.7. It was found that calculation generally provided a correct description for the specific features of the structure of the 2 : 2 complex. The average deviation of the calculated bond lengths in the isolated complex $(DMF \cdot HCl)_2$ from that measured using the X-ray analysis [7] was smaller than 7% (0.07 Å). In the electrostatic field of the method, this deviation is smaller than 9% (0.086 Å). The average deviation of the angles in the above cases were at most 3.5° and 3.6°, respectively. The results obtained (Table 3) suggest that, for good agreement with the experiment, it is only sufficient to take into account interactions between molecules inside the heterotetramer. The consideration of the external electrostatic field did not result in pronounced changes in the geometry of the complex. It is also notable that calculation allowed rather precise determination of the intramolecular

parameters in the complex $(DMF \cdot HCl)_2$ and the lengths of intermolecular bonds and relevant angles (Table 3).

Analysis of the effect of the electrostatic field of the medium on the distribution of charges on the atoms of the tetramer $(DMF \cdot HCl)_2$ showed that this effect mostly reveals itself in the strong polarization of bonds in the dimethylamine groups. Considerable changes occur in the cyclic substructure of the complex: negative charges on atoms O1 and Cl14 noticeably increase, and the positive charge on atom—2 decreases (Table 4).

Table 5 summarizes the results of calculation of the complexes $DMF_m \cdot HCl_n$ (m, n = 1, 2), which demonstrate that the hydrogen bond O1···H13 is strengthened in the following series: heterodimer, trimers 2 : 1 and 1 : 2, and tetramer 2 : 2. These data help to understand which factors affect the strength of bonds in various complexes. First, it is notable that the addition of the third molecule to the heterodimer is accompanied by the formation of a cyclic structure, strengthens the bond O1···H13 1.5 times (by 5 kcal/mol). The strength of this effect is independent of the basic and acid properties of the added molecule. Therefore, it is quite possible that not only HCl or DMF but rather any other third molecule in the isolated complex would affect the strength of the hydrogen bond. In the case of the tetramer, there is a change both in the size and the structure of the complex. The overall effect of these changes is the strengthening of the hydrogen bond by more then 3 times (by 30 kcal/mol). Such a drastic increase in the strength of the bond is probably due to the optimal composition

Table 3. Full energies (E), equilibrium bond distances (R), and angles (α) in the complex $(DMF \cdot HCl)_2$ calculated without taking into account the electrostatic field of the medium

Parameter*		$(DMF \cdot HCl)_2$ (data from [7])	$(DMF \cdot HCl)_2$	$(DMF \cdot HCl)_2$ (PCM)
E, at. units		–	–1418.719609	–1418.754508
R, Å	O1C2	1.292(3)	1.279	1.295
	C2H3	0.979(26)	1.097	1.095
	C2N4	1.289(3)	1.317	1.303
	N4C5	1.470(3)	1.464	1.468
	N4C6	1.464(4)	1.468	1.469
	C5H7	–	1.088	1.090
	C5H8	0.844(36)	1.094	1.095
	C5H9	0.939(37)	1.094	1.096
	C6H10	0.867(38)	1.091	1.090
	C6H11	1.086(35)	1.094	1.095
	C6H12	1.023(39)	1.094	1.095
	O1H13	1.097(32)	1.087	1.037
	H13Cl14	1.723(15)	1.718	1.843
	H3Cl14'	2.677	2.447	2.409
α, deg	O1C2H3	112.7(14)	121.1	120.0
	O1C2N4	121.5(2)	121.3	121.5
	H3C2N4	116.9(14)	117.6	118.5
	C2N4C5	121.9(2)	122.0	123.1
	C2N4C6	120.8(2)	120.9	120.3
	C5N4C6	117.3(2)	117.2	116.6
	N4C5H7	–	109.7	110.2
	N4C5H8	109.2(23)	109.3	109.0
	N4C5H9	106.0(21)	109.3	108.4
	N4C6H10	109.7(24)	109.9	109.5
	N4C6H11	104.1(17)	109.3	108.8
	N4C6H12	104.9(20)	109.3	109.0
	H7C5H8	–	109.8	109.9
	H7C5H9	–	109.8	110.1
	H8C5H9	106.6(30)	109.0	109.2
	H10C6H11	113.6(31)	109.7	110.1
	H10C6H12	114.6(33)	109.7	110.1
	H11C6H12	109.0(26)	109.1	109.3
	C2O1H13	–	111.3	110.9
	O1H13Cl14	178.8	176.9	178.3
	H13Cl14H3'	–	111.0	116.9
	C2H3Cl14'	–	160.3	166.1

* Numbers are for the atoms in Fig. 1.

Table 4. Charges at atoms (at. units) in the $(DMF \cdot HCl)_2$ complex

Atom*	$(DMF \cdot HCl)_2$	$(DMF \cdot HCl)_2^{**}$
O1	−0.289	−0.348
C2	0.240	0.206
H3	0.185	0.248
N4	−0.054	0.066
C5	0.142	0.041
C6	−0.049	−0.266
H7	0.034	0.051
H8	0.003	0.052
H9	0.002	0.069
H10	0.095	0.134
H11	0.058	0.134
H12	0.058	0.114
H13	0.211	0.206
Cl14	−0.636	−0.708

 * Numbers are for the atoms in Fig. 1.

** Taking into account the electrostatic field of the medium.

and mutual arrangement of the molecules in its structure rather than its size.

Data on the factors affecting the strength of hydrogen bonds in various complexes of DMF with HCl agree with the known experimental data. Thus, dimeric acid–base complexes in the gas phase are formed via a hydrogen bond of the molecular type [3], whereas in solutions of HCl in DMF [5] and in the triple system 1,1,2,2-tetrachloroethane–HCl–DMF (HCl : DMF = 1 : 1) [11], the complexes of HCl with DMF are formed via the strong quasi-symmetric hydrogen bond. The stabilization of the quasi-ionic hydrogen bond O···H···Cl in the considered complexes in the liquid phase can be due to the formation of the cyclic structure (see Fig. 1e) and due to the interaction with other species in the solution. The molecular environment may affect both the hydrogen transfer step and the stabilization of complexes formed in the liquid phase.

Calculation of the four-molecular ensemble $(DMF \cdot HCl)_2$ showed that in the complex with the 2 : 2 composition, proton transfer is most pronounced. Estimated bond strengths O···H and H···Cl in the bridge O···H···Cl are approximately the same and comprise several tens of kilocalories per mole. These facts point to the formation of two strong quasi-symmetric hydrogen bonds in the HCl complex with a 2 : 2 composition and explain the continuous absorption in the vibrational spectra of HCl solutions in DMF. In the HCl–DMF system in the liquid phase, the complexes with such hydrogen bonds are formed in the whole range of acid concentrations. Their IR spectra were interpreted based on one quasi-symmetric hydrogen bond. The results of quantum chemical calculations suggest that complexes of HCl with DMF with the composition 2 : 2 may be formed in the liquid phase. This agrees with earlier conclusions on the structure and on the degree of proton transfer in equimolecular complexes of HCl with DMF [5, 6].

Our calculations open new avenues for further theoretical studies of the effect of self-association of complexes and their molecular environment on the process of proton transfer in acid solutions, which are directly related to their catalytic activity.

Table 5. Parameters of the hydrogen bond O···H···Cl in complexes of HCl with DMF

Complexes	R(O1–H13), Å	R(H13–Cl14), Å	Q(Cl14), at. units	E_H(O···H), kcal/mol
$DMF \cdot HCl$	1.669	1.336	−0.303	10.2
$(DMF)_2 \cdot HCl$	1.444	1.403	−0.426	15.2
$DMF \cdot (HCl)_2$	1.456	1.399	−0.372	15.0
$DMF \cdot (HCl)_2^*$	1.607	1.345	−0.346	10.4
$(DMF \cdot HCl)_2$	1.087	1.718	−0.633	53.7**

 * Less stable structural conformer.

** E_H(H···Cl) = 40.2 kcal/mol.

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