

Hydrogen bonding in ionic systems of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) with 4-cyanophenol: *ab initio* and DFT studies of their structures

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Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

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The structures of the hydrogen-bonded systems of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) with one and two 4-cyanophenol molecules have been investigated employing *ab initio* and DFT calculations at different basis sets. The calculations show that the optimised structures of the studied systems are cyclic. The calculated values of the dissociation energy and the changes of the atomic charges upon hydrogen bonding for the studied hydrogen-bonded systems confirm their ionic structures. The hydrogen bonding of TBD with one and two 4-cyanophenol molecules leads to changes in the structural (bond lengths and angles) and vibrational (vibrational frequencies and infrared intensities) characteristics of the monomers. It was established that the TBD molecule is considerably deformed upon hydrogen bonding, while the deformation of the 4-cyanophenol molecules is smaller. The *ab initio* and DFT predicted vibrational spectra for the complexes TBD: 4-cyanophenol (1:1 and 1:2) demonstrate the ionic character of the forming hydrogen-bonded systems.

Key words: hydrogen-bonded complexes; TBD; 4-cyanophenol; structures; *ab initio*; DFT.

INTRODUCTION

It is known that the organic ions are very important in organic synthesis as powerful synthons and the knowledge of their structure can be used for the understanding of their reactivity [1, 2]. The variations in the IR spectra caused by the changes in the structures of the neutral molecules into ions (carbanions, anion-radicals, dianions, *etc.*) are useful information for studying the mechanism and kinetics of the chemical reaction in which the ions play role as intermediates. The contribution in these studies of Juchnovski *et al.* [3–11] is indisputable.

The ionic systems are very interesting also in the context of the hydrogen bonding. Hydrogen bonds in which either the donor or the acceptor is an ion play an important role in aqueous chemistry and in biological systems. It is, therefore, not surprising that these systems have often been studied by theoretical and experimental methods in the last few years [12–18]. The primary interest is in the structural data as the number of molecules that will fit around an ion, the structure of clusters containing several molecules and the equilibrium distances and angles of these systems. Empirical modeling of ionic systems is not trivial since nonadditivity is expected to be important and so the modern

quantum-chemical methods have an important role in calibrating such models.

Since phenol is a prototype among many hydrogen-donating aromatics, the studies of clusters of phenol with hydrogen-accepting molecules are contributed to the investigation of structures, vibrational spectra and dynamics of various hydrogen-bonded systems [19–22]. In previous studies [23, 24] the complexes between phenols and a range of strong N-bases have been studied extensively by FTIR spectroscopy in order to understand the nature of the intermolecular hydrogen bonds and the structures of the hydrogen-bonded chains. The hydrogen-bonded complexes between 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 4-CNPhOH are studied by FTIR spectroscopy [23]. The formation of cyclic hydrogen-bonded structures between TBD and 4-CNPhOH molecules was observed in chloroform. In this connection the objects of this study are the ionic hydrogen-bonded systems of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) with one and two 4-CNPhOH molecules. The aim of the study is, firstly, to establish the most stable structures of the studied hydrogen-bonded systems, secondly, to study the nature of the hydrogen bonding and charge rearrangement in the monomers forming a complex, and finally to estimate the changes in the structural and vibrational characteristics upon hydrogen bonding.

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CALCULATIONS

The *ab initio* and DFT calculations with various basis sets using the GAUSSIAN 03 series of programs [25] have been performed in order to study the structural and vibrational features of the ionic hydrogen-bonded systems formed between 4-CNPhOH and TBD. It is important to note that the density functional methods for electronic structure calculations [26–28] contain semiempirical elements based on properties of atoms and simple molecules. Prior to routine application in a given field such as hydrogen bonding [29–31], they have to be checked against experimental measurements and more established quantum chemical approaches at least for some prototype systems [32]. The density functional calculations in this work were carried out in the framework of Kohn-Sham density-functional theory [26] (DFT) with the nonlocal gradient-corrected exchange-correlation functional of Becke and Lee, Yang and Parr including partially exact HF-exchange (BLYP) [33]. The combination of *ab initio* and DFT calculations in the studies of hydrogen-bonded systems is very useful in order to obtain better knowledge of hydrogen-bonded structures, their stability and vibrational features.

The dissociation energy calculated by *ab initio* and DFT calculations can be used for the estimation of the stability of the hydrogen-bonded systems between two and more partners. The supermolecular variation method determines dissociation energy (ΔE) as a difference between the energy of the complex and the energies of the isolated molecules. For complexes **1** and **2**, shown in Figures 1 and 2 the dissociation energy is calculated by Eqns (1) and (2):

$$\Delta E_{\text{com.1}} = E_{\text{com.1}} - (E_{\text{TBD}} + E_{4\text{-CNPhOH}}) \quad (1)$$

$$\Delta E_{\text{com.2}} = E_{\text{com.2}} - (E_{\text{TBD}} + 2E_{4\text{-CNPhOH}}) \quad (2)$$

where E_{TBD} and $E_{4\text{-CNPhOH}}$ are the energies of the isolated monomers in their own basis set and $E_{\text{com.1}}$, $E_{\text{com.2}}$ are the energies of the complexes.

Further, to compare the calculated results of the dissociation energy with the respective experimental ones the effect of the zero-point energy (ZPE) should be taken into account. *Ab initio* calculations yield the total molecular electronic energy of the hypothetical vibrationless state at 0K. To convert this energy (U_0^0) to an enthalpy at 298.15K it is necessary to make correction for the zero-point energy ($E_{\text{zp vib}}$) by using the enthalpy function, ($H_{298}^0 - H_0^0$):

$$\Delta H_{298}^0 = (U_0^0) + \Delta(E_{\text{zp vib}}) + \Delta(H_{298}^0 - H_0^0) \quad (3)$$

$$E_{\text{zp vib}} = 0.5h \sum \nu_i \quad (4)$$

The zero-point energy is calculated from Eqn. (4) and the enthalpy function is obtained by standard statistical thermodynamic procedures, using the optimised geometries to provide structural constants.

The zero-point vibrational energy correction for the studied complex can be defined as a difference between the calculated zero-point vibrational energy of the complex and the zero-point energies of the monomers:

$$\Delta E_{\text{zp vib}} = E_{\text{zp vib}}(\text{com.}) - (E_{\text{zp vib}}(\text{TBD}) + E_{\text{zp vib}}(4\text{-CNPhOH})) \quad (5)$$

RESULTS AND DISCUSSION

Hydrogen-bonded structures and their stabilities

Full geometry optimization was made with GAUSSIAN 03 series of programs [25] for the studied hydrogen-bonded systems between TBD and 4-CNPhOH: complex **1** (1:1) and complex **2** (1:2). The optimized structures of complexes **1** and **2** with BLYP/6-31+G(d,p) calculations are shown in Figures 1 and 2. As can be seen the optimized structures are cyclic. In Table 1 are shown the optimum values of the total energy and the selected optimized geometric parameters for free and complexed TBD and 4-CNPhOH, obtained from BLYP/6-31+G(d,p) calculations.

The complex **1** (1:1) has optimum geometry for H...O distance between TBD and 4-CNPhOH molecules 1.665 Å ($H_8 \dots O_1$ and $H_{25} \dots O_1$). The hydrogen bonds $H_8 \dots O_1$ and $H_{25} \dots O_1$ for complex **2** (1:2) are weaker and longer than the hydrogen bonds for complex **1**, moreover these hydrogen bonds are with different lengths namely R ($H_8 \dots O_1$) is shorter and stronger than R ($H_{25} \dots O_1$) (see Table 1). The hydrogen bond for complex **2** formed between 4-CNPhOH molecules: $O_1 \dots H_{45}$ is the strongest.

The changes of the geometrical parameters from monomers to a complex are defined in order to investigate the influence of the hydrogen bonding on the structural parameters of the monomers TBD and 4-CNPhOH. It is seen that the bond lengths and angles for complexes **1** and **2**, shown in Figs. 1 and 2 are perturbed from their values in the monomers. The most sensitive to the complexation are the bonds taking part in the hydrogen bonding. The calculations show that the changes in the geometrical parameters of the TBD molecule are larger than the changes of 4-CNPhOH molecules. The most sensitive to the formation of hydrogen bonds for complexes **1** and **2** are the following bonds: C_2-O_1 , C_2-C_3 , $N_{15}-C_{24}$, $N_{23}-C_{24}$ and $N_{23}-H_{25}$. The bonds C_2-C_3 , $N_{15}-C_{24}$ and $N_{23}-H_{25}$ are lengthened in

the complexes, while the bonds C₂–O₁ and N₂₃–C₂₄ are shortened upon formation of the hydrogen bonds. The bond O₃₈–H₄₅, taking part in the strongest hydrogen bond O₁...H₄₅ for complex **2**, is very sensitive to the hydrogen bonding. In the complex it becomes longer in comparison with its value in the monomer (4-CNPhOH).

Table 1. Selected optimized geometric parameters for free and complexed TBD and 4-CNPhOH, obtained from BLYP/6-31+G(d,p) calculations.

Parameter ^a	Monomers	Complex 1	Complex 2
Bond length, Å			
C ₂ –O ₁	1.379	1.322 (–0.057)	1.343 (–0.036)
C ₂ –C ₃	1.412	1.436 (0.022)	1.428 (0.016)
C ₃ –C ₄	1.401	1.396 (–0.005)	1.398 (–0.003)
C ₄ –C ₅	1.418	1.424 (0.006)	1.421 (0.003)
C ₅ –C ₁₃	1.437	1.432 (–0.005)	1.434 (–0.003)
C ₁₃ –N ₁₄	1.178	1.181 (0.003)	1.179 (0.001)
H ₈ –N ₁₅	-	1.065	1.051
N ₁₅ –C ₁₆	1.457	1.469 (0.012)	1.473 (0.016)
N ₁₅ –C ₂₄	1.304	1.352 (0.048)	1.355 (0.051)
N ₂₃ –C ₂₄	1.393	1.352 (–0.041)	1.357 (–0.036)
C ₂₂ –N ₂₃	1.457	1.469 (0.012)	1.473 (0.016)
N ₁₉ –C ₂₄	1.389	1.376 (–0.013)	1.369 (–0.020)
N ₂₃ –H ₂₅	1.017	1.065 (0.048)	1.043 (0.026)
O ₃₈ –H ₄₅	0.978	-	1.033 (0.055)
O ₃₈ –C ₃₉	1.379	-	1.356 (–0.023)
C ₃₉ –C ₄₀	1.412	-	1.420 (0.008)
C ₄₀ –C ₄₁	1.401	-	1.397 (–0.004)
C ₄₁ –C ₄₂	1.418	-	1.422 (0.004)
C ₄₂ –C ₅₀	1.437	-	1.435 (–0.002)
C ₅₀ –N ₅₁	1.178	-	1.179 (0.001)
O ₁ ...H ₈	-	1.665	1.755
O ₁ ...H ₂₅	-	1.665	1.833
O ₁ ...H ₄₅	-	-	1.573
Angle (°)			
H ₈ ...O ₁ ...H ₂₅	-	75.1	69.6
H ₈ ...O ₁ ...H ₄₅	-	-	103.0
H ₈ –N ₁₅ –C ₂₄	-	113.5	113.4
N ₁₅ –C ₂₄ –N ₂₃	116.5	117.5 (1.0)	117.3 (0.8)
C ₂₄ –N ₂₃ –H ₂₅	111.7	113.5 (1.8)	113.0 (1.3)
E ^{tot} (a.u.)	–399.610848 ^b	–838.282014	–1237.914464
	–438.619198 ^c		

^a See Figs. 1 and 2 for numbering of atoms; ^b E^{tot} for 4-CNPhOH; ^c E^{tot} for TBD; In the parenthesis are given the changes of the parameters from monomer to a complex.

The changes in the angles N₁₅–C₂₄–N₂₃ and C₂₄–N₂₃–H₂₅, taking part in the hydrogen bonding for complexes **1** and **2**, are also estimated. The calculations show that these angles become larger in the complexes in comparison with their monomer values. Bearing in mind the changes in the geometrical parameters for complexes **1** and **2** it can be concluded that the TBD molecule is considerably deformed upon hydrogen bonding, while the deformation of the 4-CNPhOH molecules is smaller.

The next step in the study is to estimate the stability of the hydrogen-bonded systems between

TBD and 4-CNPhOH: complex **1** (1:1) and complex **2** (1:2), shown in Figs. 1 and 2. The dissociation energies, uncorrected and corrected with zero-point energy differences are calculated by *ab initio* and DFT calculations with different basis sets. The results from the calculations are presented in Table 2. The corrected dissociation energy (–24.55 kcal·mol^{–1}) calculated with BLYP/6-31G(d,p) calculations for complex **2** (per one 4-CNPhOH molecule) are in a very good agreement with the experimentally measured heat of formation [6]: –23.42 kcal·mol^{–1}. This agreement confirms the reliability of the determined ionic structure of complex **2**: TBD: 4-CNPhOH (1:2). In agreement with the classification of the hydrogen-bonded systems, given in [37], the calculated values of the dissociation energy for the studied hydrogen-bonded systems confirm their ionic structures.

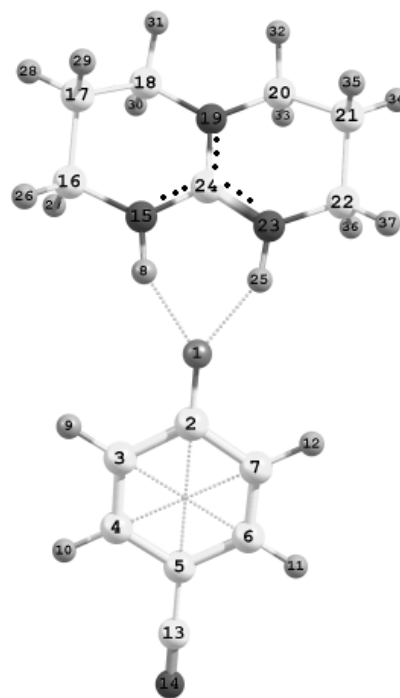


Fig. 1. Optimized structure with BLYP/6-31+G(d,p) calculations and atomic numbering for the hydrogen-bonded systems TBD:4-CNPhOH (1:1).

Charge distribution upon hydrogen bonding

The next aim in this study is to determine the influence of hydrogen bonding on the charge distribution in the studied hydrogen-bonded ionic systems. In this connection the atomic charges (q_i) for the free and complexed TBD and 4-CNPhOH are calculated by BLYP/6-31+G(d,p) calculations, using Mulliken population analysis. In Table 3 are included the atomic charges (q_i) and the changes of the atomic charges (Δq_i) upon hydrogen bonding:

$$\Delta q_i = q_i^{\text{complex}} - q_i^{\text{monomer}} \quad (6)$$

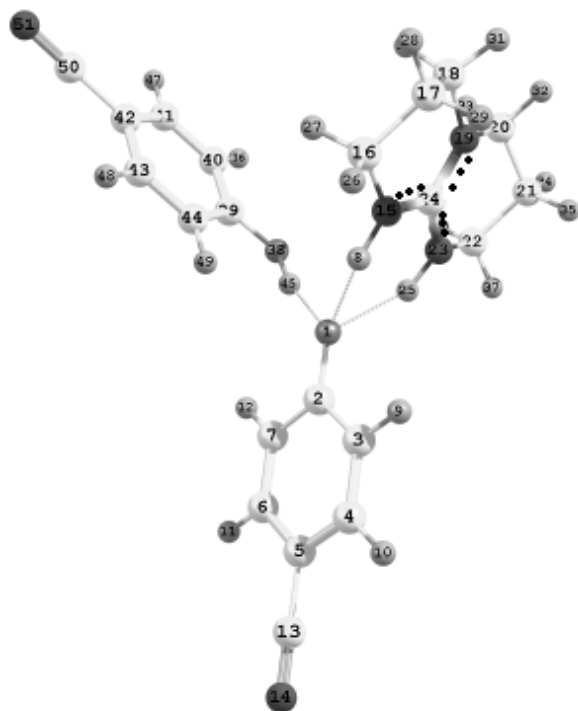


Fig. 2. Optimized structure with BLYP/6-31+G(d,p) calculations and atomic numbering for the hydrogen-bonded systems TBD:4-CNPhOH (1:2).

The calculations show that the most sensitive to the complexation are the atoms, taking part in the hydrogen bonding. The hydrogen bond formations between TBD and 4-CNPhOH lead to more considerable charge rearrangement for the TBD molecule than for the 4-CNPhOH molecules. In complexes **1** and **2** the oxygen atom O(1) (from 4-CNPhOH) acts as acceptor of electric charge. Its negativity increases significantly in the complexes in comparison with the corresponding negativity in the monomer. At the same time, the hydrogen atom H(8) (from OH group of 4-CNPhOH), the carbon atom C(39) and the hydrogen atom H(25) (from TBD) become more positive in the complex.

The changes of the atomic charges (Δq_i) upon hydrogen bonding for complex **1** (1:1) and complex **2** (1:2) show large proton polarizability of the hydrogen bonds within these complexes, i.e. hydrogen-bonded systems with ionic character are formed. It is important to note that in complex **2**, the 4-CNPhOH molecule with retained O–H group is subjected to a very strong charge rearrangement. The negativity of carbon atoms C(40), C(42) and C(44) is larger than the corresponding negativity of carbon atoms C(3), C(4) and C(5) in the 4-CNPhOH molecule which O–H group is strongly polar due to the formation of the O⁻...H⁺N hydrogen bonds with proton transfer, i.e. of the polar structure.

Changes in the vibrational frequencies and infrared intensities arising from the hydrogen bonding

The infrared (IR) spectroscopic signature of the hydrogen bond formation is the shift to the lower frequency and the increase in intensity of the stretching vibrations of the monomer bonds involving in hydrogen bonding. It is known that the *ab initio* and DFT predicted values of the vibrational frequencies depend on the method and the basis set used for the calculations. The frequencies from the calculations with larger basis sets give reasonable prediction of the experimental values, if the vibrations have small anharmonicity.

The prediction of the vibrational characteristics (vibrational frequencies and infrared intensities) of the hydrogen-bonded systems by *ab initio* and DFT calculations at different levels [34–43] has become widely employed in order to elucidate the influence of hydrogen bonding on the vibrational spectra of the monomers forming a complex. In the hydrogen-bonded system, the geometrical symmetry of the monomers often changes under perturbation [11]. The vibrational mixing, derived by a perturbation approach, is the counterpart of the orbital mixing.

Table 2. Dissociation energies ΔE (uncorrected and corrected), zero-point energy differences ΔE_{zpv} in kcal/mol and hydrogen bond distances R in Å for the hydrogen-bonded complexes **1** (1:1) and **2** (1:2), shown in Figures 1 and 2.

Complex	Basis set	ΔE_{uncor}	ΔE_{zpv}	ΔE_{cor}	R , Å		
1:1	SCF/6-31G(d,p)	-29.284	2.017	-27.267	1.748 (O ₁ ...H ₈) 1.723 (O ₁ ...H ₂₅)		
	BLYP/6-31G(d,p)	-35.109	1.522	-33.587	1.632 (O ₁ ...H ₈) 1.632 (O ₁ ...H ₂₅)		
	BLYP/6-31+G(d,p)	-32.610	1.796	-30.814	1.665(O ₁ ...H ₈)		
					1.665 (O ₁ ...H ₂₅)		
1:2	SCF/6-31G(d,p)	-45.647	3.603	-42.044	1.831 (O ₁ ...H ₈) 1.860 (O ₁ ...H ₂₅)		
		(-22.823) ^a		(-21.022) ^a	1.693 (O ₁ ...H ₄₅)		
	BLYP/6-31G(d,p)	-52.493	3.397	-49.096	1.772 (O ₁ ...H ₈)		
					(-26.246) ^a	(-24.548) ^a	1.799 (O ₁ ...H ₂₅)
					1.561(O ₁ ...H ₄₅)		

^a In the parenthesis is given the dissociation energy per one 4-CNPhOH molecule.

Table 3. Mulliken charges (q_i) for free and complexed TBD and 4-CNPhOH, obtained from BLYP/6-31+G(d,p) calculations.

^a No.	^a Atom	q_i			Δq_i	
		Monomers	Comp. 1:1	Comp. 1:2	Comp. 1:1	Comp. 1:2
1	O	-0.1367	-0.7213	-0.7846	-0.5845	-0.6479
2	C	-0.2160	-0.2788	-0.3331	-0.0628	-0.1172
3	C	0.4984	0.4812	0.2064	-0.0173	-0.2920
4	C	-0.3986	-0.5182	-0.3918	-0.1196	0.0068
5	C	0.8384	0.7890	0.6290	-0.0494	-0.2094
6	C	-0.3414	-0.5182	-0.3050	-0.1768	0.0365
7	C	0.5687	0.4812	0.5489	-0.0876	-0.0199
8	H	0.0000	0.3855	0.3771	0.3855	0.3771
9	H	0.0000	0.0830	0.0888	0.0830	0.0888
10	H	0.0000	0.1095	0.1157	0.1095	0.1157
11	H	0.0000	0.1095	0.1183	0.1095	0.1183
12	H	0.0000	0.0830	0.1098	0.0830	0.1098
13	C	-0.2671	-0.2679	-0.2664	-0.0008	0.0007
14	N	-0.5457	-0.5970	-0.5834	-0.0512	-0.0376
15	N	-0.3761	-0.3388	-0.1309	0.0373	0.2452
16	C	-0.2059	-0.0575	-0.0586	0.1484	0.1473
17	C	-0.4477	-0.3986	-0.4842	0.0491	-0.0365
18	C	0.0402	-0.0769	0.0158	-0.1171	-0.0244
19	N	-0.2306	-0.1769	-0.0978	0.0537	0.1327
20	C	0.0909	-0.0769	-0.0015	-0.1678	-0.0924
21	C	-0.4256	-0.3987	-0.4590	0.0270	-0.0333
22	C	-0.1970	-0.0575	-0.0202	0.1395	0.1769
23	N	-0.3591	-0.3388	-0.1529	0.0204	0.2063
24	C	0.1685	0.0768	-0.4070	-0.0917	-0.5755
25	H	0.2962	0.3855	0.3677	0.0893	0.0715

Table 3. Continued.

^a No.	^a Atom	q_i			Δq_i	
		Monomers	Comp. 1:1	Comp. 1:2	Comp. 1:1	Comp. 1:2
26	H	0.1282	0.1536	0.1526	0.0254	0.0244
27	H	0.1282	0.1490	0.1663	0.0208	0.0381
28	H	0.1431	0.1523	0.1592	0.0092	0.0161
29	H	0.1431	0.1679	0.1716	0.0248	0.0286
30	H	0.1321	0.1533	0.1659	0.0212	0.0338
31	H	0.1321	0.1428	0.1470	0.0107	0.0150
32	H	0.1337	0.1428	0.1471	0.0091	0.0134
33	H	0.1337	0.1533	0.1629	0.0196	0.0292
34	H	0.1524	0.1523	0.1565	0.0000	0.0041
35	H	0.1524	0.1679	0.1716	0.0156	0.0192
36	H	0.1337	0.1490	0.1737	0.0153	0.0400
37	H	0.1337	0.1536	0.1528	0.0199	0.0190
38	O	-0.1367	-	-0.4773	-	-0.3406
39	C	-0.2160	-	0.3977	-	0.6136
40	C	0.4984	-	-0.2473	-	-0.7457
41	C	-0.3986	-	-0.1438	-	0.2548
42	C	0.8384	-	0.2714	-	-0.5670
43	C	-0.3414	-	0.0097	-	0.3511
44	C	0.5687	-	-0.1035	-	-0.6722
45	H	0.0000	-	0.4553	-	0.4553
46	H	0.0000	-	0.1101	-	0.1101
47	H	0.0000	-	0.1232	-	0.1232
48	H	0.0000	-	0.1191	-	0.1191
49	H	0.0000	-	0.1210	-	0.1210
50	C	-0.2671	-	-0.0885	-	0.1786
51	N	-0.5457	-	-0.5755	-	-0.0298

^aSee Figs. 1 and 2 for numbering of atoms.**Table 4.** Calculated and experimental vibrational characteristics (ν in cm^{-1} , A in $\text{km}\cdot\text{mol}^{-1}$) for the hydrogen-bonded complexes 1 and 2.

Mode	Exp. [23]		SCF/6-31G(d,p)				BLYP/6-31G(d,p)			
			Complex 1		Complex 2		Complex 1		Complex 2	
	$\nu/\Delta\nu$	$A/\Delta A$	$\nu/\Delta\nu$	$A/\Delta A$	$\nu/\Delta\nu$	$A/\Delta A$	$\nu/\Delta\nu$	$A/\Delta A$	$\nu/\Delta\nu$	$A/\Delta A$
$\nu(\text{H}_8\text{--N}_{15})$	-	-	3388/ -543	3597.0/ 3547.3	3611/ -320	2955.7/ 2906.0	2726/ -815	5491.1/ 5469.9	3101/ -440	3031.9/ 3010.7
$\nu(\text{N}_{23}\text{--H}_{25})$	-	-	3299/ -632	81.1/ 31.4	3513/ -418	381.8/ 332.1	2552/ -989	86.3/ 65.1	2975/ -566	513.1/ 491.9
$\nu(\text{O}_{38}\text{--H}_{45})$	3318/ -270	vs	-	-	3546/ -621	1128.7/ 1011.6	-	-	3010/ -432	1186.1/ 1138.8
$\nu(\text{C}_{13}\equiv\text{N}_{14})$	2204/ -36	s	2569/ -32	244.3/ 168.8	2581/ -20	201.2/ 126.1	2217/ -19	181.9/ 138.2	2225/ -11	158.3/ 114.5
$\nu(\text{C}_{50}\equiv\text{N}_{51})$	2204/ -36	s	-	-	2591/ -10	113.0/ 37.5	-	-	2228/ -8	87.2/ 43.5
$\nu(\text{O}_1\text{...H}_8)$			174	0.7	182	3.3	136	11.6	149	17.7
$\nu(\text{O}_1\text{...H}_{25})$			169	0.9	183	8.2	128	0.2	137	8.3
$\nu(\text{O}_1\text{...H}_{45})$			-	-	118	6.7	-	-	116	6.7

The shifts in the vibrational frequencies ($\Delta\nu_i$) upon formation of the hydrogen-bonded complexes **1** (TBD:4-CNPhOH (1:1)) and **2** (TBD:4-CNPhOH (1:2)) have been calculated by *ab initio* and DFT calculations with 6-31G(d,p) basis set. The predicted frequency shift for each vibration is:

$$\Delta\nu_i = (\nu_i^{\text{complex}} - \nu_i^{\text{monomer}}),$$

The changes in the infrared intensities (ΔA_i) upon hydrogen bond formation are also estimated using *ab initio* and DFT calculations.

$$\Delta A_i = A_i^{\text{complex}} - A_i^{\text{monomer}}$$

The predicted changes in the vibrational frequencies and infrared intensities for the modes more sensitive to the complexation are shown in Table 4 together with the experimentally observed [23] shifts.

The predicted vibrational spectra for the complexes of TBD with one and two 4-CNPhOH molecules by *ab initio* and DFT calculations demonstrate the ionic character of the forming hydrogen-bonded systems. In the vibrational spectra of the complexes two N–H stretching vibrations appear: $\nu(\text{N}_{23}\text{--H}_{25})$ and $\nu(\text{N}_{15}\text{--H}_8)$. The calculations show that these two vibrations are very sensitive to complexation: their vibrational frequencies are shifted to lower wavenumbers and their IR intensities dramatically increase in comparison with the corresponding values for the N–H stretching vibration in the non-hydrogen-bonded TBD molecule. This fact confirms the participation of the $\text{N}_{23}\text{--H}_{25}$ and $\text{N}_{15}\text{--H}_8$ bonds in the hydrogen bonding.

The predicted vibrational spectra for the hydrogen-bonded systems of TBD with two 4-CNPhOH molecules show that one 4-CNPhOH molecule takes part in the hydrogen bonding as non-ionic. The stretching $\nu(\text{O}_{38}\text{--H}_{45})$ vibration of the hydrogen-bonded O–H group is shifted to lower frequencies and its IR intensity increases considerably upon hydrogen bonding. This result is in agreement with the assumption of P. Przybylski *et al.* [23] for the formation of the $\text{O}^-\dots\text{H}^+$ hydrogen bonds with proton transfer, i.e. of the polar structure. The changes in the vibrational characteristics of the stretching $\nu(\text{C}\equiv\text{N})$ vibrations confirm also the polar structures of the studied hydrogen-bonded systems. The vibrational frequencies of $\nu(\text{C}\equiv\text{N})$ in the complexes are shifted to lower wavenumbers indicating that the electron density at the $\text{C}\equiv\text{N}$ group is decreased due to the formation of $\text{O}^-\dots\text{H}^+$ hydrogen bonds. As can be seen from the results in Table 4, the predicted changes in the vibrational characteristics for the stretching $\nu(\text{C}\equiv\text{N})$ vibrations are in a good agreement with the experimentally measured [23].

The hydrogen bonding between TBD and one 4-CNPhOH molecule (complex **1**) leads to arising of two stretching intermolecular vibrations: $\nu(\text{O}_1^-\dots\text{H}_8^+)$ and $\nu(\text{O}_1^-\dots\text{H}_{25}^+)$. The predicted frequencies for these vibrations are very near: 169–174 cm^{-1} (SCF/6-31G(d,p) calculations) and 136–128 cm^{-1} (BLYP/6-31G(d,p) calculations). The calculated IR intensities for these vibrations are low.

For the hydrogen-bonded system between TBD and two 4-CNPhOH molecules (complex **2**) three stretching intermolecular vibrations are predicted: $\nu(\text{O}_1^-\dots\text{H}_8^+)$, $\nu(\text{O}_1^-\dots\text{H}_{25}^+)$ and $\nu(\text{O}_1^-\dots\text{H}_{45})$. As well as for complex **1**, the predicted vibrational frequencies for the vibrations $\nu(\text{O}_1^-\dots\text{H}_8^+)$ and $\nu(\text{O}_1^-\dots\text{H}_{25}^+)$ are very near and their IR intensities are low. The $\nu(\text{O}_1^-\dots\text{H}_{45})$ vibration is calculated with lower frequency in comparison with the vibrations $\nu(\text{O}_1^-\dots\text{H}_8^+)$ and $\nu(\text{O}_1^-\dots\text{H}_{25}^+)$. This phenomenon could be explained with the charge rearrangement upon hydrogen bonding, namely that the hydrogen bond formations between TBD and 4-CNPhOH lead to more considerable charge rearrangement for the TBD molecule than for the 4-CNPhOH molecules.

CONCLUSIONS

The main results in this study are:

- The calculated values of the dissociation energy for the hydrogen-bonded systems TBD: 4-CNPhOH (1:1 and 1:2) confirm their ionic structures.
- The changes of the atomic charges (Δq_i) upon hydrogen bonding show large proton polarizability of the hydrogen bonds within these complexes, i.e. hydrogen-bonded systems with ionic character are formed.
- *Ab initio* and DFT predicted vibrational spectra for the complexes of TBD with one and two 4-CNPhOH molecules demonstrate the ionic character of the formed hydrogen-bonded systems.

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ВОДОРОДНО СВЪРЗВАНЕ В ЙОННИ СИСТЕМИ НА 1,5,7-ТРИАЗАБИЦИКЛО[4.4.0]ДЕЦ-5-ЕН С 4-ЦИАНОФЕНОЛ. ИЗСЛЕДВАНИЯ НА СТРУКТУРИТЕ ИМ С МЕТОДИТЕ *AB INITIO* И ТФП

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(Резюме)

Изследвани са структурите на водородно-свързаните системи на 1,5,7-триазабицикло[4.4.0]дец-5-ен (ТБД) с една и две молекули 4-цианофенол посредством *ab initio* и ТФП пресмятания с различни базисни набори. Пресмятанията показват, че оптимизираните структури на изследваните системи са циклични. Изчислените стойности на енергията на свързване и промените в атомните заряди под действие на водородното свързване за изследваните водородно-свързани системи потвърждават техните йонни структури. Водородното свързване на ТБД с една и две молекули 4-цианофенол води до промени в структурните (дължини на връзки и ъгли) и вибрационните (вибрационни честоти и интензивности на инфрачервените ивици) характеристики на мономерите. Установено е, че молекулата на ТБД е значително деформирана под действие на водородното свързване, докато деформацията на молекулите на 4-цианофенола е по-малка. Предсказаните с *ab initio* и ТФП вибрационни спектри за комплексите ТБД: 4-цианофенол (1:1 и 1:2) доказват йонния характер на образуваните водородно-свързани системи.