

## Theoretical study on the structure, stability and vibrational spectra of the hydrogen-bonded phenoxides, containing strong short hydrogen bonds

Y. Dimitrova\*

Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bl. 9, 1113, Sofia, Bulgaria

Received November 18, 2009; Revised May 18, 2010

The structure, stability, and the vibrational spectra of the 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen-bonded system, containing a strong, short hydrogen bond (SSHB), have been studied by means of *ab initio* and DFT calculations at different basis sets. Full geometry optimization of the hydrogen-bonded system has been performed through HF/6-31G(d,p) *ab initio* and BLYP/6-31+G(d,p) calculations. The calculations show that a strong, almost symmetrical O-H...O<sup>-</sup> bond is observed. The calculated O-H...O<sup>-</sup> distance (1.235 Å) and the OH...O<sup>-</sup> = 179.60° angle are in agreement with the SSHB classification. The corrected values of the dissociation energy (-29.31 - 35.95 kcal.mol<sup>-1</sup>), calculated through HF/6-31G(d,p) and BLYP calculations, confirm the ionic structure of the hydrogen-bonded system. The calculations show that formation of a hydrogen bond of 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> leads to a considerable charge rearrangement in the monomers. The changes of the atomic charges, (Δq<sub>i</sub>), in the complex, resulted from the hydrogen bonding, show large proton polarizability of the SSHB within this complex, i.e. a hydrogen-bonded system of ionic nature is formed. The formation of SSHB leads to significant changes in the vibrational characteristics for most of the vibrational modes. This phenomenon could be explained with the considerable charge rearrangement, occurring under the action of the hydrogen bonding.

**Keywords:** SSHB; structure; stability; vibrational spectra; *ab initio*; DFT.

### INTRODUCTION

Hydrogen bonding is of fundamental importance in the chemistry, physics and biology. The hydrogen bonding, for example, is the key to understand how molecules align themselves, both in crystals and in the gas phase. The hydrogen bonds, in which either the donor or the acceptor is ion, play an important role in the aqueous chemistry and in the biological systems. It is therefore not surprising that these systems have often been studied through theoretical and experimental methods [1-7].

Recently, there has been much interest in a special class of hydrogen bonds called "strong, short hydrogen bonds" (SSHBs) or "low-barrier hydrogen bonds" (LBHBs). The SSHBs are an important factor in enzyme catalysis [8-14]. Notable features of such hydrogen bonds are the short distances between hydrogen donor and acceptor atoms, the strong hydrogen bond energy, the low isotopic fractional factor, the Hadzi type II IR spectra [15]. SSHBs in D...H...A systems are characterized by short D...A distances of 2.2 - 2.5 Å [16]. These bonds are important in biological

catalysis [17,18] and are quantitatively different, in most of their properties, from the molecule or weak bonds. When D is an exceedingly electronegative atom, and A has an exceptionally large excess of electronic charge, strong hydrogen bonds are formed. Strong, almost symmetrical, hydrogen bonds are also observed when the donor group is a cation or the acceptor group is an anion, as O<sup>+</sup> - H...O or O-H...O<sup>-</sup>. Most often these hydrogen bonds are formed from carboxylates and carboxylic acid [19,20].

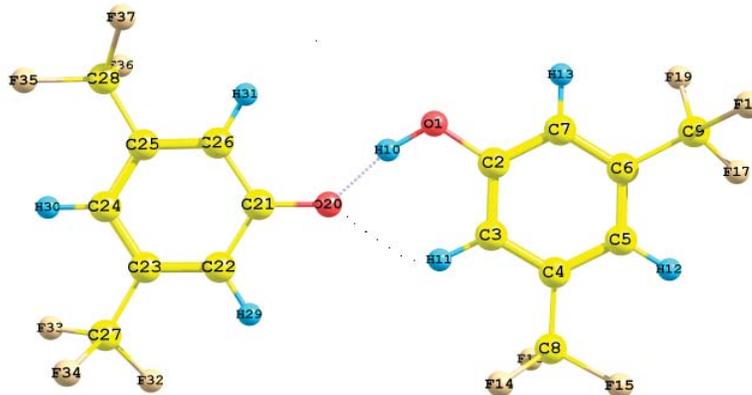
The SSHBs between phenoxides are less observed and are less studied than other systems [21]. They have important relevance in the enzyme active sites that use tyrosine [22-26].

The aim of this study is to investigate, through *ab initio* and DFT calculations at different basis sets, the structure, stability, and the vibrational spectra of the 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen-bonded system which contains SSHB.

### METHODOLOGY

The structure, stability, and vibrational characteristics of the 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and

\*To whom all correspondence should be sent:  
E-mail: E-mail: dimj@orgchem.bas.bg



**Fig. 1.** Optimized structure with BLYP/6-31+G(d,p) calculations for the hydrogen-bonded system:  $[(Ar'O)_2H]^-$ , where  $Ar' = 3,5-(CF_3)_2C_6H_3$ :

$R_{O_{20}\dots H_{10}}=1.235\text{\AA}$ ;  $R_{O_{20}\dots H_{11}}=2.571\text{\AA}$ ;  $R_{O_1-H_{10}}=1.208\text{\AA}$ ;  $R_{O_1-C_2}=1.322\text{\AA}$ ;  $R_{O_{20}-C_{21}}=1.321$ ;

Angles ( $^\circ$ ):  $H_{10}\dots O_{20}\dots H_{11}=64.8$ ;  $O_{20}\dots H_{11}C_3=119.9$ ;  $C_{21}O_{20}\dots H_{11}=114.0$ ;  $C_3H_{11}\dots O_{20}=119.9$ ;  $H_{10}O_1C_2=113.7$ ;

$O_1H_{10}\dots O_{20}=179.5$ .

3.5-  $(CF_3)_2C_6H_3O^-$  hydrogen-bonded system which contain SSHB, have been calculated through *ab initio* and DFT calculations at different basis sets, using the GAUSSIAN 03 series of programs [27]. All calculations were performed on a Pentium IV PC.

The density functional calculations in this work have been carried out in the framework of Kohn-Sham density-functional theory [28] (DFT) with the non-local gradient-corrected exchange-correlation functional of Becke and Lee, Yang and Parr, including partially exact HF-exchange (BLYP) [29]. The density functional methods for electronic structure calculations [28,30,31] contain semi-empirical elements based on the properties of atoms and simple molecules. Prior to routine application in a given field such as the hydrogen bonding [32-34], they have to be checked through experiments and established quantum chemical approaches, applied for some prototype systems [35]. In combination with *ab initio* calculations and experimental data, the semi-empirical character of the density functional methods might be turned into advantage.

The dissociation energy, calculated using the *ab initio* and DFT calculations, can be used for estimation of the stability of the hydrogen-bonded systems of two and more partners. The supermolecular variation method determines dissociation energy ( $\Delta E$ ) as a difference between the energy of the complex and the energies of the isolated molecules. For the complex, studied here and shown in Figure 1, the dissociation energy is calculated by the equation (1):

$$\Delta E = E_{\text{com.}} - [E(3.5-(CF_3)_2C_6H_4O) + E(3.5(CF_3)_2C_6H_3O^-)] \quad (1)$$

where  $E(3.5-(CF_3)_2C_6H_4O)$  and  $E(3.5-(CF_3)_2C_6H_3O^-)$  are the energies of the isolated monomers in their own basis set, and  $E_{\text{com.}}$  is the energy of the complex.

To compare the calculated results of the dissociation energy with the respective experimental energy, 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 0 K. The conversion of this energy ( $U_0^0$ ) into enthalpy at 298.15 K requires correction of the zero-point energy ( $E_{\text{zp vib}}$ ) using the enthalpy function, ( $H_{298}^0 - H_0^0$ ):

$$\Delta H_{298}^0 = (U_0^0) + \Delta(E_{\text{zpvib}}) + \Delta(H_{298}^0 - H_0^0) \quad (2)$$

$$E_{\text{zpvib}} = 0.5h \sum \nu_i \quad (3)$$

The zero-point energy is calculated through Eq. (3), and the enthalpy function is obtained through 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:

$$\Delta E_{\text{zpvib}} = E_{\text{zp vib}}(\text{com.}) - (E_{\text{zp vib}}(3.5-(CF_3)_2C_6H_4O) + E_{\text{zp vib}}(3.5-(CF_3)_2C_6H_3O^-)) \quad (4)$$

**Table 1.** Calculated selected geometrical parameters for free and complexed 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> and changes in the parameters from monomers to a complex obtained from HF/6-31G(d,p) and BLYP/6-31+G(d,p) calculations.

Parameters <sup>a</sup>	Monomers		Complex		Change of the parameters	
	HF	BLYP	HF	BLYP	HF	BLYP
Bond length <sup>b</sup>						
C <sub>2</sub> -O <sub>1</sub>	1.3454	1.3750	1.3174	1.3225	-0.028	-0.0525
C <sub>3</sub> -C <sub>2</sub>	1.3894	1.4079	1.3983	1.4329	0.0089	0.0250
C <sub>4</sub> -C <sub>3</sub>	1.3803	1.4064	1.3815	1.4026	0.0012	-0.0038
C <sub>5</sub> -C <sub>4</sub>	1.3866	1.4042	1.3865	1.4096	-0.0001	0.0054
C <sub>6</sub> -C <sub>5</sub>	1.3806	1.4075	1.3834	1.4084	0.0028	0.0009
C <sub>7</sub> -C <sub>6</sub>	1.3854	1.4028	1.3825	1.4028	-0.0029	0
C <sub>8</sub> -C <sub>4</sub>	1.5056	1.5158	1.5033	1.5096	-0.0023	-0.0062
C <sub>9</sub> -C <sub>6</sub>	1.5059	1.5167	1.5017	1.5084	-0.0042	-0.0083
H <sub>10</sub> -O <sub>1</sub>	0.9429	0.9776	0.9896	1.2060	0.0467	0.2284
H <sub>11</sub> -C <sub>3</sub>	1.0744	1.0927	1.0739	1.0909	-0.0005	-0.0018
H <sub>12</sub> -C <sub>5</sub>	1.0722	1.0889	1.0714	1.0884	-0.0008	-0.0005
H <sub>13</sub> -C <sub>7</sub>	1.0738	1.0900	1.0736	1.0912	-0.0002	0.0012
F <sub>14</sub> -C <sub>8</sub>	1.3223	1.3711	1.3217	1.3709	-0.0006	-0.0002
F <sub>15</sub> -C <sub>8</sub>	1.3228	1.3672	1.3290	1.3788	0.0062	0.0116
F <sub>16</sub> -C <sub>8</sub>	1.3228	1.3712	1.3280	1.3790	0.0052	0.0078
F <sub>17</sub> -C <sub>9</sub>	1.3207	1.3686	1.3268	1.3762	0.0061	0.0076
F <sub>18</sub> -C <sub>9</sub>	1.3232	1.3688	1.3286	1.3799	0.0054	0.0111
F <sub>19</sub> -C <sub>9</sub>	1.3233	1.3711	1.3257	1.3746	0.0024	0.0035
O <sub>20</sub> ...H <sub>10</sub>	-	-	1.5651	1.2353	-	-
O <sub>20</sub> ...H <sub>11</sub>	-	-	2.3474	2.5710	-	-
C <sub>21</sub> -O <sub>20</sub>	1.2386	1.2708	1.2666	1.3201	0.028	0.0493
C <sub>22</sub> -C <sub>21</sub>	1.4440	1.4635	1.4208	1.4319	-0.0232	-0.0316
C <sub>23</sub> -C <sub>22</sub>	1.3689	1.4003	1.3757	1.4012	0.0068	0.0009
C <sub>24</sub> -C <sub>23</sub>	1.3980	1.4152	1.3901	1.4104	-0.0079	-0.0048
C <sub>25</sub> -C <sub>24</sub>	1.3864	1.4152	1.3862	1.4081	-0.0002	-0.0071
C <sub>26</sub> -C <sub>25</sub>	1.3780	1.4003	1.3795	1.4038	0.0015	0.0035
C <sub>27</sub> -C <sub>23</sub>	1.5005	1.5043	1.5018	1.5083	0.0013	0.004
C <sub>28</sub> -C <sub>25</sub>	1.5019	1.5043	1.5021	1.5097	0.0002	0.0054
H <sub>29</sub> -C <sub>22</sub>	1.0739	1.0929	1.0741	1.0908	0.0002	-0.0021
H <sub>30</sub> -C <sub>24</sub>	1.0714	1.0884	1.0709	1.0885	-0.0005	0.0001
H <sub>31</sub> -C <sub>26</sub>	1.0760	1.0929	1.0750	1.0912	-0.001	-0.0017
F <sub>32</sub> -C <sub>27</sub>	1.3269	1.3782	1.3297	1.3729	0.0028	-0.0053
F <sub>33</sub> -C <sub>27</sub>	1.3336	1.3829	1.3311	1.3778	-0.0025	-0.0051
F <sub>34</sub> -C <sub>27</sub>	1.3337	1.3863	1.3293	1.3805	-0.0044	-0.0058
F <sub>35</sub> -C <sub>28</sub>	1.3307	1.3829	1.3306	1.3775	-0.0001	-0.0054
F <sub>36</sub> -C <sub>28</sub>	1.3316	1.3782	1.3270	1.3721	-0.0046	-0.0061
F <sub>37</sub> -C <sub>28</sub>	1.3317	1.3863	1.3270	1.3796	-0.0047	-0.0067
Angle <sup>c</sup>						
C <sub>3</sub> C <sub>2</sub> O <sub>1</sub>	122.45	122.91	122.85	123.30	0.4	0.39
H <sub>10</sub> O <sub>1</sub> C <sub>2</sub>	111.70	108.86	112.27	113.68	0.57	4.82
H <sub>11</sub> C <sub>3</sub> C <sub>2</sub>	120.24	120.57	118.52	118.51	-1.72	-2.06
C <sub>4</sub> C <sub>3</sub> H <sub>11</sub>	120.21	119.80	121.75	120.79	1.54	0.99
C <sub>4</sub> C <sub>3</sub> C <sub>2</sub>	120.21	119.63	121.75	120.70	1.54	1.07
C <sub>7</sub> C <sub>2</sub> O <sub>1</sub>	117.52	117.00	118.38	119.61	0.86	2.61
C <sub>7</sub> C <sub>2</sub> C <sub>3</sub>	120.03	120.10	117.77	117.10	-2.26	-3.00
C <sub>5</sub> C <sub>4</sub> C <sub>3</sub>	121.08	120.85	121.83	121.68	0.75	0.83
C <sub>26</sub> C <sub>21</sub> C <sub>22</sub>	113.79	113.44	115.43	116.91	1.64	3.47
C <sub>25</sub> C <sub>26</sub> C <sub>21</sub>	122.19	122.66	121.56	120.82	-0.63	-1.84
C <sub>23</sub> C <sub>22</sub> C <sub>21</sub>	122.24	122.66	121.69	121.23	-0.55	-1.43
C <sub>24</sub> C <sub>23</sub> C <sub>22</sub>	122.57	122.00	122.07	121.35	-0.5	-0.65
C <sub>22</sub> C <sub>21</sub> O <sub>20</sub>	122.54	123.28	121.41	119.66	-1.13	-3.62
C <sub>26</sub> C <sub>21</sub> O <sub>20</sub>	123.67	123.28	123.16	123.42	-0.51	0.14
C <sub>21</sub> O <sub>20</sub> ...H <sub>10</sub>	-	-	129.40	114.02	-	-
H <sub>10</sub> ...O <sub>20</sub> ...H <sub>11</sub>	-	-	67.89	64.86	-	-
C <sub>21</sub> O <sub>20</sub> ...H <sub>11</sub>	-	-	162.71	127.09	-	-

C <sub>3</sub> H <sub>11</sub> ...O <sub>20</sub>	-	-	126.32	119.97	-	-
O <sub>1</sub> H <sub>10</sub> ...O <sub>20</sub>	-	-	172.14	179.60	-	-
O <sub>20</sub> ...H <sub>11</sub> C <sub>3</sub>	-	-	126.32	119.97	-	-
E <sup>tot</sup> (a.u.)	-976.81128	-981.36639	-1953.10876	-1962.24081		
	-976.24838	-980.81541				

The dissociation energies, uncorrected and corrected with zero-point energy differences, are calculated through *ab initio* and DFT calculations with different basis sets.

The shifts in the vibrational frequencies ( $\Delta v_i$ ), occurring upon formation of the 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen-bonded complex, have been calculated through *ab initio* and DFT (BLYP) calculations. The predicted frequency shift for each vibration is defined as follows:

$$\Delta v_i = v_i^{\text{complex}} - v_i^{\text{monomer}} \quad (5)$$

The changes in the infrared intensities ( $\Delta A_i$ ) upon hydrogen bond formation are also estimated using *ab initio* and DFT calculations:

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

## RESULTS AND DISCUSSION

### Structure and stability

The first objective of this work is to establish the most stable structure of the complex, studied here. Full geometry optimization of the hydrogen-bonded system, formed by 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>, was made with GAUSSIAN 03 series of programs [27]. Fig. 1 shows the optimized structure, calculated through BLYP/6-31+G(d,p) calculations. It can be seen that the optimized structure for the studied ionic hydrogen-bonded system is cyclic. Table 1 shows the optimum values of the total energy and the equilibrium geometries for the monomers (3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>), and for the complex. These optimum values were obtained through BLYP/6-31+G(d,p) and HF/6-31G(d,p) calculations.

The complex has an optimum geometry when H<sub>10</sub>...O<sub>20</sub> distance is 1.235 Å, and the H<sub>11</sub>...O<sub>20</sub> distance is 2.571 Å between 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> molecules. It was noted that SSHBs in the D...H...A systems are characterized by short D...A distances of 2.2 – 2.5 Å [16]. The O<sub>1</sub>...O<sub>20</sub> distance at optimum geometry, calculated through BLYP/6-31+G(d,p) calculations, is 2.441 Å. It is in agreement with the results from the X-ray diffraction studies (2.436 Å) of this hydrogen-bonded system [36]. The calculations

show that a strong, almost symmetrical O-H...O<sup>-</sup> bond is observed. The structure of the bond is of III type according to the Valence Bond analysis [37]. The calculated H<sub>10</sub>...O<sub>20</sub> distance (1.235 Å) and the angle O<sub>1</sub>H<sub>10</sub>...O<sub>20</sub> = 179.60° are in agreement with the SSHB classification, given from Suksangpanya [38] (H...A is within 1.2 to 1.5 Å, and the D-H...A ≅ 180°). The second hydrogen bond distance, H<sub>11</sub>...O<sub>20</sub>, is estimated to be in the range between 2.35-2.57 Å. This hydrogen bond is longer and weaker than the H<sub>10</sub>...O<sub>20</sub> bond.

The changes of the geometrical parameters of the complex are defined to investigate the influence of the hydrogen bonding over the structural parameters of the (3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>) monomers. Table 1 presents the selected optimized geometrical parameters for free and complexed 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>. These parameters were obtained through BLYP/6-31+G(d,p) and HF/6-31G(d,p) calculations. It is seen that the bond lengths and angles for the complex studied, shown on Fig. 1, are perturbed from their values in the monomers. The most sensitive to the complexation are the bonds, taking part in the C<sub>2</sub>-O<sub>1</sub>, O<sub>1</sub>-H<sub>10</sub>, C<sub>21</sub>-O<sub>20</sub>, C<sub>22</sub>-C<sub>21</sub> and C<sub>3</sub>-C<sub>2</sub> hydrogen bonding. The O<sub>1</sub>-H<sub>10</sub>, C<sub>21</sub>-O<sub>20</sub> and C<sub>3</sub>-C<sub>2</sub> bonds are lengthened in the complex, while the C<sub>2</sub>-O<sub>1</sub> and C<sub>22</sub>-C<sub>21</sub> bonds are shortened in the formation of the hydrogen bonds.

The changes in the angles of the monomers in the hydrogen bond formation are also estimated. The data in Table 1 evidence that the most sensitive to complexation are the H<sub>10</sub>-O<sub>1</sub>-C<sub>2</sub> and O<sub>20</sub>-C<sub>21</sub>-C<sub>22</sub> angles which take part in the hydrogen bonding. Their values change significantly in the complex. The calculations show that the changes in the remaining geometrical parameters in the hydrogen bonding are smaller, and in some cases are negligible.

The next step in the study is to establish the stability of the ionic 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3.5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen-bonded system. The dissociation energies, uncorrected and corrected with zero-point energy differences, are calculated through *ab initio* and DFT calculations at different basis sets. The calculation results are presented in Table 2. The corrected values of the dissociation energy (-29.31 - 35.95 kcal.mol<sup>-1</sup>), calculated through HF/6-31G(d,p) and BLYP calculations, are in agreement with the SSHB classification, given in

the ‘Theoretical Treatment of Hydrogen Bonding’ [1], and confirm the ionic structure of the studied hydrogen-bonded system.

**Table 2.** Dissociation energies  $\Delta E$  (uncorrected and corrected), zero-point energy differences  $\Delta E_{\text{zpv}}$  in kcal/mol and interatomic distances in Å for the hydrogen-bonded complex between 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>.

Basis set	$\Delta E^{\text{uncorr}}$	$\Delta E^{\text{zpv}}$	$\Delta E^{\text{corr}}$	$R_{\text{O}\dots\text{H}}$
HF/6-31G(d,p)	-30.8149	1.0103	-29.8046	H <sup>10</sup> ...O <sup>20</sup> = 1.5651
				H <sup>11</sup> ...O <sup>20</sup> = 2.3474
BLYP/6-31+G(d,p)	-37.0222	1.0753	-35.9469	H <sup>10</sup> ...O <sup>20</sup> = 1.2353
				H <sup>11</sup> ...O <sup>20</sup> = 2.5691
BLYP/6-311++G(d,p)	-30.5486	1.2345	-29.3141	H <sup>10</sup> ...O <sup>20</sup> = 1.4022
				H <sup>11</sup> ...O <sup>20</sup> = 2.4820

#### Charge distribution in the hydrogen bonding

It is known from the previous studies [39,40] that the hydrogen bonding leads to charge rearrangement of the monomers forming a complex. The aim of this study is to determine the influence of the hydrogen bonding on the charge distribution in the studied hydrogen-bonded complex. In this connection, the atomic charges ( $q_i$ ) for the monomers (3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>) and for the complex, have been calculated through BLYP/6-31+G(d,p) calculations using the Mulliken population analysis and the Natural Bond Orbital analysis [41-48]. The data are shown in Table 3. Table 3 also contains the changes of the atomic charges ( $\Delta q_i$ ) in hydrogen bonding:

$$\Delta q_i = q_i^{\text{complex}} - q_i^{\text{monomer}} \quad (5)$$

The data in Table 3 show that the atomic charges ( $q_i$ ) in the monomers and in the complex, calculated through the Mulliken population and the Natural Bond Orbital analyses, are different by value in all cases, even by sign sometimes. However, the atomic charges ( $\Delta q_i$ ) in the hydrogen bonding in most cases are similar, both by value and by sign. In view of this result, the conclusion could be that both population analyses are suitable for the estimation of the changes of the atomic charges in the hydrogen bonding.

The calculations show that the most sensitive to complexation are the atoms, taking part in the hydrogen bonding. The oxygen O(1) atom acts as acceptor of electric charge in the studied complex. The negativity of this atom increases significantly in the complex compared to the corresponding negativity in the monomer. In the same time the H(10) and H(11) hydrogen atoms (from OH group), the C(2), C(27), C(28) carbon atoms, and the H(29)- H(31) hydrogen atoms become more positive in the complex. The calculated changes of the atomic charges, ( $\Delta q_i$ ), of the remaining atoms are smaller.

The calculation results show that the 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen bond

formation leads considerable charge rearrangement in the monomers. The changes of the atomic

charges, ( $\Delta q_i$ ), in the complex, resulted from the hydrogen bonding, show large proton polarizability of the SSHB within this complex, i.e. a hydrogen-bonded system of ionic nature is formed.

#### Changes in the vibrational characteristics in SSHB formation

The prediction of vibrational characteristics (vibrational frequencies and infrared intensities) of the hydrogen-bonded systems through *ab initio* and DFT calculations at different levels [39,40, 49-55] has become widely employed in order to elucidate the influence of the hydrogen bonding on the vibrational spectra of the monomers, forming a complex. The geometrical symmetry of the monomers often changes under perturbation [56] in the hydrogen-bonded system. The vibrational mixing, derived by a perturbation approach, is the counterpart of the orbital mixing.

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 calculated frequencies with a larger basis set give reasonable agreement with the experimental values if the vibrations have small anharmonicity.

In order to estimate the influence of the SSHB on the vibrational characteristics of the 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O; 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> monomers, forming a complex, the monomer and complex vibrational spectrum were predicted through (HF/6-31G(d,p)) *ab initio* and DFT (BLYP/6-31+G(d,p)) calculations. Table 4 shows the calculation results.. Table 4 also contains a detailed description of the normal modes based on the potential energy distribution (PED), obtained through HF/6-31G(d,p) calculations. The changes in the vibrational frequencies and the

infrared intensities ( $\Delta v_i$ ;  $\Delta A_i$ ) in the hydrogen bond formation are calculated through Equations 5 and 6 using *ab initio* and DFT calculations.

**Table 3.** NBO and Mulliken charges ( $q_i$ ) for free and complexed 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>, obtained from BLYP/6-31+G(d,p) calculations.

No.	Atom	$q_i$ (NBO)		$\Delta q_i$ (NBO)	$q_i$		$\Delta q_i$
		Monomers	Complex		Monomers	Complex	
1	O	-0.6593	-0.7068	-0.0475	-0.5157	-0.6327	-0.1170
2	C	0.3242	0.3543	0.0301	0.3171	0.3470	0.0299
3	C	-0.2802	0.2780	-0.0022	-0.1197	-0.1569	-0.0372
4	C	-0.1443	-0.1729	-0.0286	0.0000	0.0099	0.0099
5	C	-0.2177	-0.2571	-0.0394	-0.1140	-0.1445	-0.0305
6	C	-0.1449	-0.1772	-0.0323	-0.0016	0.0101	0.0117
7	C	-0.2465	-0.2654	-0.0189	-0.0901	-0.1217	-0.0316
8	C	1.0798	1.0763	-0.0035	0.6889	0.6683	-0.0206
9	C	1.0803	1.0757	-0.0046	0.6905	0.6650	-0.0255
10	H	0.4924	0.4930	0.0006	0.3110	0.4050	0.0940
11	H	0.2487	0.2586	0.0099	0.0748	0.0836	0.0088
12	H	0.2658	0.2450	-0.0208	0.0943	0.0526	-0.0417
13	H	0.2660	0.2430	-0.0230	0.0943	0.0512	-0.0431
14	F	-0.3479	-0.3509	-0.0030	-0.2450	-0.2500	-0.0050
15	F	-0.3430	-0.3601	-0.0171	-0.2390	-0.2621	-0.0231
16	F	-0.3418	-0.3550	-0.0132	-0.2315	-0.2487	-0.0172
17	F	-0.3447	-0.3578	-0.0131	-0.2410	-0.2593	-0.0183
18	F	-0.3452	-0.3564	-0.0111	-0.2416	-0.2505	-0.0089
19	F	-0.3418	-0.3547	-0.0129	-0.2317	-0.2552	-0.0235
20	O	-0.6890	-0.7089	-0.0200	-0.6390	-0.6394	-0.0004
21	C	0.3619	0.3555	-0.0064	0.3742	0.3505	-0.0237
22	C	-0.3014	-0.2671	0.0343	-0.1764	-0.1258	0.0506
23	C	-0.1992	-0.1783	0.0209	0.0250	0.0119	-0.0131
24	C	-0.3020	-0.2591	0.0	-0.1779	-0.1459	0.0320
25	C	-0.1992	-0.1731	0.0261	0.0250	0.0101	-0.0149
26	C	-0.3014	-0.2812	0.0202	-0.1764	-0.1577	0.0187
27	C	1.0719	1.0752	0.0033	0.6481	0.6650	0.0169
28	C	1.0719	1.0758	0.0039	0.6481	0.6678	0.0197
29	H	0.2225	0.2437	0.0212	0.0131	0.0503	0.0372
30	H	0.2306	0.2443	0.0137	0.0232	0.0516	0.0284
31	H	0.2225	0.2560	0.0335	0.0131	0.0798	0.0667
32	F	-0.3622	-0.3542	0.008	-0.2656	-0.2548	0.0108
33	F	-0.3664	-0.3582	0.0082	-0.2714	-0.2601	0.0113
34	F	-0.3658	-0.3570	0.0088	-0.2631	-0.2522	0.0109
35	F	-0.3664	-0.3593	0.0071	-0.2714	-0.2613	0.0101
36	F	-0.3622	-0.3515	0.0107	-0.2656	-0.2505	0.0151
37	F	-0.3658	-0.3558	0.0100	-0.2631	-0.2504	0.0127

Table 4 shows that the C-H stretching vibrations are predicted to be in the range between 3100 and 3400 cm<sup>-1</sup>. Their vibrational characteristics are changed negligibly in the hydrogen bonding.

The  $\nu(\text{O}_1\text{-H}_{10})$  stretching vibration of the hydrogen-bonded O-H group is shifted to lower frequencies and its IR intensity increases considerably in the hydrogen bonding. This result confirms the optimized stable structure of the studied complex (see Figure 1) and shows the formation of the O<sup>-</sup> ...H<sup>+</sup> ...O<sup>-</sup> SSHB with proton transfer, i.e. of the polar structure. The changes in the vibrational characteristics of the stretching

$\nu(\text{C}_{21} - \text{O}_{20}^-)$  vibration confirm also the polar structures of the studied hydrogen-bonded system. The vibrational frequencies of  $\nu(\text{C}_{21} - \text{O}_{20}^-)$  in the complex are shifted to lower wavenumbers indicating that the electron density at the C<sub>21</sub> - O<sub>20</sub><sup>-</sup> group is decreased due to the formation of the O<sup>-</sup> ...H<sup>+</sup> hydrogen bonds.

The calculations show that the  $\delta(\text{HOC})$  deformation is also very sensitive to the hydrogen bonding. Its vibrational frequency is shifted to higher frequencies, and its infrared intensity decreases in the hydrogen bonding. The stretching C-C(F) vibrations are also shifted to higher

frequencies and their IR intensities increase significantly in the complex.

The data in Table 4 show that the formation of the SSHB leads to significant changes in the

**Table 4.** Calculated vibrational characteristics ( $\nu$  in  $\text{cm}^{-1}$  and  $A$  in  $\text{km mol}^{-1}$ ) for the hydrogen-bonded systems between 3,5-( $\text{CF}_3$ ) $_2\text{C}_6\text{H}_4\text{O}$  and 3,5-( $\text{CF}_3$ ) $_2\text{C}_6\text{H}_3\text{O}^-$ .

Approximate description (PED) <sup>a</sup>	HF/6-31G(d,p)		BLYP/6-31+G(d,p)	
	$\nu_i/\Delta\nu_i$	$A_i/\Delta A_i$	$\nu_i/\Delta\nu_i$	$A_i/\Delta A_i$
100 $\nu(\text{C}_{24}\text{-H}_{30})$	3431/11	0.67/-1.03	3161/7	1.09/-2.13
100 $\nu(\text{C}_7\text{-H}_{13})$	3408/9	2.79/2.59	3159/4	1.26/0.84
100 $\nu(\text{C}_3\text{-H}_{11})$	3402/41	45.17/41.85	3141/23	0.36/-5.01
100 $\nu(\text{C}_5\text{-H}_{12})$	3394/-33	1.01/0.47	3138/-26	6.04/5.81
100 $\nu(\text{C}_{26}\text{-H}_{31})$	3374/13	8.20/-12.58	3136/27	0.08/-17.17
100 $\nu(\text{C}_{22}\text{-H}_{29})$	3361/-2	8.81/-3.40	3133/25	6.38/-18.53
100 $\nu(\text{O}_1\text{-H}_{10})$	3164/-1005	3989.86/3880.84	2832/-831	3042.51/3001.26
51 $\nu(\text{C-C}) + 34\delta(\text{CCC})$	1830/16	4.06/0.11	1563/38	0.23/-2.05
45 $\delta(\text{CCC}) + 32\nu(\text{C-C})$	1804/-15	32.42/-23.24	1555/-35	15.98/-54.70
48 $\nu(\text{C-C}) + 30\delta(\text{CCC})$	1785/120	7.84/-13.91	1746/138	24.07/11.14
45 $\nu(\text{C-C}) + 18\delta(\text{CCC})$	1768/136	603.80/-98.42	1631/103	127.92/-82.85
31 $\delta(\text{HOC}) + 15\nu(\text{C-C})$	1739/695	88.69/-54.08	1645/188	75.34/-20.11
40 $\nu(\text{O}_{20}\text{-C}_{21}) + 18\nu(\text{C-C})$	1664/-127	579.70/167.09	1605/-98	275.75/86.06
38 $\nu(\text{C-C}) + 21\delta(\text{HCC})$	1637/267	399.15/194.73	1648/303	195.31/104.25
51 $\nu(\text{C-C}) + 15\delta(\text{HCC})$	1604/3	50.17/-98.08	1595/-5	29.61/-37.97
43 $\nu(\text{C-C}) + 22\nu(\text{C-C(F)})$	1584/5	266.22/162.19	1540/18	138.43/95.14
45 $\nu(\text{C-C}) + 11\nu(\text{C-C(F)})$	1574/217	30.69/-20.04	1512/139	34.82/-17.52
32 $\nu(\text{C-C(F)}) + 20\nu(\text{C}_2\text{-O}_1)$	1559/198	1121.92/549.82	1486/173	1006.42/468.63
71 $\delta(\text{HCC})$	1438/201	170.82/159.01	1423/168	161.91/132.20
48 $\nu(\text{C-C(F)})$	1434/115	527.27/76.51	1399/108	201.50/64.31
32 $\nu(\text{C-C(F)}) + 18\delta(\text{HCC})$	1433/123	421.55/228.01	1384/119	360.28/144.15
62 $\nu(\text{C-F})$	1342/10	510.60/192.05	1285/18	660.09/101.77
68 $\nu(\text{C-F})$	1334/15	223.88/-226.88	1263/18	210.83/52.38
65 $\nu(\text{C-F})$	1331/21	371.87/178.35	1258/42	106.00/48.76
89 $\nu(\text{C-C})$	1260/119	57.20/32.10	1176/95	44.75/26.60
42 $\delta(\text{CCC}) + 18\nu(\text{C-C})$	1218/132	62.24/58.10	1116/108	131.40/29.48
58 $\nu(\text{C-C})$	1199/19	49.05/-7.86	1061/35	28.30/18.95
41 $\nu(\text{C-C}) + 22\delta(\text{CCC})$	1192/-15	82.15/68.27	1059/-28	72.40/56.12
81 $\delta(\text{CCC})$	1082/1	5.90/-28.64	1058/-7	3.54/2.83
66 $\tau(\text{HCCO})$	1076/46	301.94/163.90	926/11	200.90/93.08
78 $\delta(\text{CCC})$	1047/9	83.17/-15.62	886/6	73.14/-32.11
48 $\tau(\text{HCCO}) + 15\tau(\text{CO...HO})$	1037/62	53.41/28.03	878/50	37.40/18.26
48 $\delta(\text{CCC})$	1032/33	11.64/7.88	850/42	3.20/2.45
66 $\tau(\text{HCCC})$	1001/60	20.92/-33.59	846/21	22.57/-5.50
71 $\tau(\text{HCCO})$	989/14	9.04/-16.34	828/0	11.21/-17.28
51 $\tau(\text{CCCC})$	966/82	41.82/21.49	818/62	46.51/15.37
60 $\tau(\text{CCCC})$	792/40	14.36/13.18	796/78	20.88/11.85
85 $\tau(\text{CCCC})$	791/95	12.14/12.13	791/78	16.70/15.12
53 $\tau(\text{HCCC})$	750/-38	3.55/-12.08	691/-29	2.61/-1.82
33 $\tau(\text{CCCO}) + 32\tau(\text{CCCC})$	730/0	2.89/-0.03	689/16	1.16/-5.39
31 $\delta(\text{CCC}) + 30\tau(\text{FCCC})$	627/49	6.83/2.68	578/32	7.78/3.87
42 $\tau(\text{FCCC}) + 18\delta(\text{CCC})$	624/44	1.40/-0.85	542/35	9.77/-4.55
21 $\delta(\text{CCO}) + 20\delta(\text{CCC})$	560/32	10.90/4.95	459/24	10.83/5.88
75 $\tau(\text{FCCC})$	557/-66	0.12/-0.07	423/-50	0.21/-0.22
68 $\tau(\text{FCCC})$	556/-26	0.05/-4.36	422/-31	0.85/-2.78
58 $\delta(\text{FCC})$	410/16	0.23/0.19	358/22	0.07/-1.23
51 $\delta(\text{FCC})$	377/164	0.54/0.1	306/122	0.26/-0.02
54 $\delta(\text{FCC})$	388/62	1.11/-0.22	305/55	4.39/3.29

56τ(CCCO) + 43τ(CCCC)	255/1	1.19/-1.46	271/18	5.45/4.43
54τ(CCCO) + 40τ(CCCC)	236/19	2.46/-1.37	193/14	2.94/-1.97
50ν(O...H)	89	9.18	102	29.63
62δ(O...HO)	52	1.41	63	0.87

<sup>a</sup>PEDs elements lower than 10% are not included. PEDs elements obtained with HF/6-31G(d,p) are given.

vibrational characteristics of most of the vibrational modes. This phenomenon could be explained with the charge rearrangement in the hydrogen bonding, namely the 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen bond formations lead more considerable charge rearrangement in the monomers.

The 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen bonding leads to arising of two intermolecular vibrations the ν(O<sub>1</sub><sup>-</sup>...H<sub>10</sub><sup>+</sup>) and the ν(O<sub>20</sub><sup>-</sup>...H<sub>11</sub>). The predicted frequency of the ν(O<sub>1</sub><sup>-</sup>...H<sub>10</sub><sup>+</sup>) vibration is at 89 – 102 cm<sup>-1</sup>. The calculated IR intensity of this vibration is low. The δ(O...HO) vibration is predicted at lower frequency (52 – 63 cm<sup>-1</sup>), and its IR intensity is lower.

#### CONCLUSION

The structure, stability and vibrational spectra of the 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O and 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> hydrogen-bonded system, containing SSHB, have been investigated using *ab initio* and DFT calculations at different basis sets. The main results of the study are:

- The calculations show that a strong, almost symmetrical, O-H...O<sup>-</sup> bond is formed. The calculated H<sub>10</sub>...O<sub>20</sub> distance (1.235Å) and O<sub>1</sub>H<sub>10</sub>...O<sub>20</sub> = 179.60° angle are in agreement with the SSHB classification (H...A is within 1.2 to 1.5Å and D-H...A ≅ 180°).
- The corrected values of the dissociation energy (-29.31 - 35.95 kcal.mol<sup>-1</sup>), calculated through HF/6-31G(d,p) and BLYP calculations, confirm the SSHB formation as well as the ionic structure of the studied hydrogen-bonded system.
- The changes of the atomic charges (Δq<sub>i</sub>) in the hydrogen bonding show large proton polarizability of the SSHB within this complex, i.e. hydrogen-bonded system of ionic nature is formed.
- The stretching ν(O<sub>1</sub>-H<sub>10</sub>) vibration of the hydrogen-bonded O-H group is shifted to lower frequencies and its IR intensity increases considerably in the hydrogen bonding. This result confirms the optimized stable structure of the complex, and shows the formation of the O<sup>-</sup> ...H<sup>+</sup> ...O<sup>-</sup> SSHBs with proton transfer, i.e. the polar structure.

**Acknowledgements:** The research is supported by the Bulgarian National Science Fund, contract X-1510. This financial support is gratefully acknowledged.

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ТЕОРЕТИЧНО ИЗСЛЕДВАНЕ НА СТРУКТУРИ, СТАБИЛНОСТ И ВИБРАЦИОННИ СПЕКТРИ  
НА ВОДОРОДНО-СВЪРЗАНИ ФЕНОКСИДИ СЪДЪРЖАЩИ СИЛНИ, КЪСИ ВОДОРОДНИ  
ВРЪЗКИ  
Й. Димитрова

Институт по органична химия с Център по фитохимия, Българска академия на науките, ул. "Акад. Г. Бончев"  
бл. 9, 1113 София

Постъпила на 18 ноември 2009 г.; Преработена на 18 май 2010 г.

(Резюме)

Структурата, стабилността и вибрационните спектри на водородно-свързаната система между 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O и 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup>, съдържаща силна, къса водородна връзка са изследвани посредством *ab initio* и ТФП пресмятания с различни базисни набори. Проведена е пълна геометрична оптимизация на водородно-свързаната система с *ab initio* HF/6-31G(d,p) и VLYP/6-31+G(d,p) пресмятания. Пресмятанията показват, че се наблюдава силна, почти симетрична O-H...O<sup>-</sup> връзка. Изчисленото O-H...O<sup>-</sup> разстояние (1.235 Å) и ъгълът OH...O<sup>-</sup> = 179.60° са в съгласие с класификацията за силни, къси водородни връзки. Коригираните стойности на дисоциационната енергия (-29.31 - 35.95 kcal.mol<sup>-1</sup>) изчислени с HF/6-31G(d,p) и VLYP пресмятанията потвърждават йонната структура на водородно-свързаната система. Пресмятанията показват, че образуването на водородна връзка между 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O и 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O<sup>-</sup> води до значително преразпределение на зарядите при мономерите. Промените на атомните заряди (Δq<sub>i</sub>) за комплекса в резултат на водородното свързване показват значителна протонна поляризуемост за силната, къса водородна връзка, т.е. образува се водородно-свързана система с йонен характер. Образуването на силна, къса водородна връзка води до значителни промени на вибрационните характеристики на повечето трептения. Това явление би могло да се обясни със значителното преразпределение на зарядите под действие на водородното свързване.