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Hydrogen Bonded Complexes of Acetylacetone and Methanol: HF and DFT level Study

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Summary. Several possible hydrogen-bonded complexes between the tautomeric forms of acetylacetone and methanol were studied by *ab initio* methods using 6-311G** and D95** basis functions at the HF and DFT (B3LYP) levels of theory. The calculations were carried out for isolated molecules and solvent assisted complexes by means of the isodensity polarized model (IPCM). The theoretical frequencies were compared with the experimental IR spectrum of an equimolar mixture of acetylacetone and methanol. It was proved that the most stable H-bonded complex acetylacetone–methanol is formed between O-bonded methanol- and the enol molecule.

Keywords. *Ab initio* calculations; Complexes; Density functional calculations.

Introduction

Acetylacetone and its two tautomeric forms have been widely studied mainly because of the interest in the mechanism of keto-enol tautomerism in the gas phase (for isolated molecules) as well as in different solvents [1–4]. The solvent polarity influences on the strength of the intramolecular hydrogen bond and on the composition of the acetylacetone tautomers. *Funck et al.* [5, 6] have found by means of IR and NMR spectroscopy that at 100°C in the liquid phase the enol amount is 67% and at the same temperature in the gas phase it is about 90%. This is due to the lower solvation ability and the higher stability of the enol form than the diketo-form. The extraordinary stability of the enol form is related to the formation of an intramolecular H-bond and a cyclic pseudoaromatic structure [7, 8].

The intramolecular H-bond strength in the enol form determines most of the acetylacetone properties as *e.g.* the hydrogen exchange rate between the two oxygen atoms [9–13] and proton potentials [14] in the enol molecule. Therefore, the

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energy of this non-covalent bond is a rather important value. It has been calculated by means of semiempirical methods as 33 kJ mol^{-1} [9] and at the B3LYP/D95** [15] level as 73 kJ mol^{-1}.

Several experimental techniques and theoretical methods have been used for determination of the acetylacetone structure [16–18]. Up to now there is not a clear idea about the possible interactions of acetylacetone with other organic molecules (*e.g.* methanol) by intermolecular hydrogen bonds. Therefore, complexes of the acetylacetone tautomers with methanol are reasonable models for this.

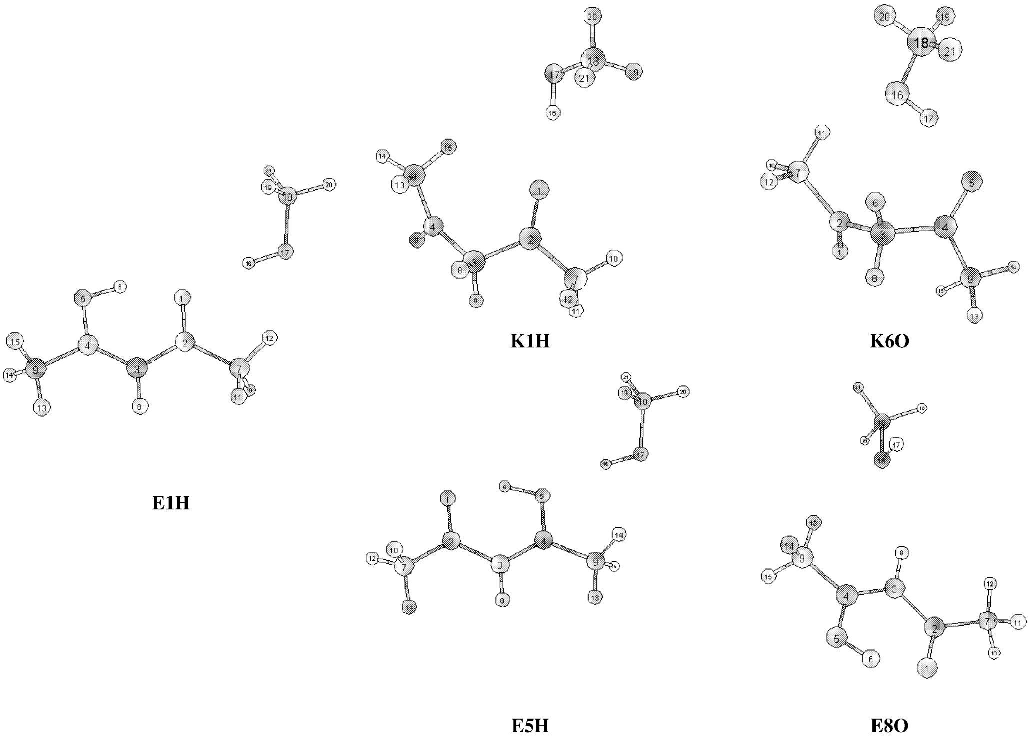
Thus, the aim of this paper is: 1) to study comparatively at four theoretical levels the possible bonding between one acetylacetone molecule and one methanol molecule by intermolecular H-bonds, and 2) to clarify the details of the intermolecular interactions. This theoretical study was performed by means of *ab initio* calculations including density functional (DFT) and *Hartree–Fock* (R*HF*) theory.

Results and Discussions

The theoretical research started with five possible H-bonded complexes (Scheme 1) between acetylacetone and methanol.

The results of the two methods and their combinations with 6-311G** and D95** basis sets will be compared and the results obtained by the B3LYP/(D95**; 6-311G**) method will be discussed in detail below.

Our attempts for full optimization of the K1H complex failed because during the optimization this complex was transformed into the complex K6O, which


K1H **K6O**
E1H
E5H **E8O**

Scheme 1

Table 1. Relative energies and relative zero-point correction energies of the H-bonded complexes

	ΔE/kJ mol^{-1} (E hartree)			
	1	**2**	**3**	**4**
K6O	20	19	0	–
	(−461.629467)	(−461.666723)	(−458.8929754)	–
E1H	0	0	5	0
	(−461.636946)	(−461.673834)	(−458.891091)	(−458.903066)
E5H	6	8	12	8
	(−461.634745)	(−461.670686)	(−458.888440)	(−458.900077)
E8O	16	19	19	14
	(−461.631036)	(−461.666567)	(−458.885812)	(−458.897548)
	$\Delta E^\circ = \Delta E_{\mathrm{el}} + \Delta\mathrm{ZPE}$/kJ mol^{-1} ($E^\circ = E_{\mathrm{el}} + \mathrm{ZPE}$ hartree)			
	1	**2**	**3**	**4**
K6O	18	16	0	–
	(−461.454038)	(−461.491720)	(−458.705031)	–
E1H	0	0	8	0
	(−461.460835)	(−461.497694)	(−458.701793)	(−458.714510)
E5H	4	7	15	7
	(−461.459415)	(−461.495213)	(−458.699506)	(−458.711959)
E8O	13	16	20	12
	(−461.455961)	(−461.491760)	(−458.697460)	(−458.710094)

1: B3LYP/D95**; **2**: B3LYP/6-311G**; **3**: *HF*/D95**; **4**: *HF*/6-311G**

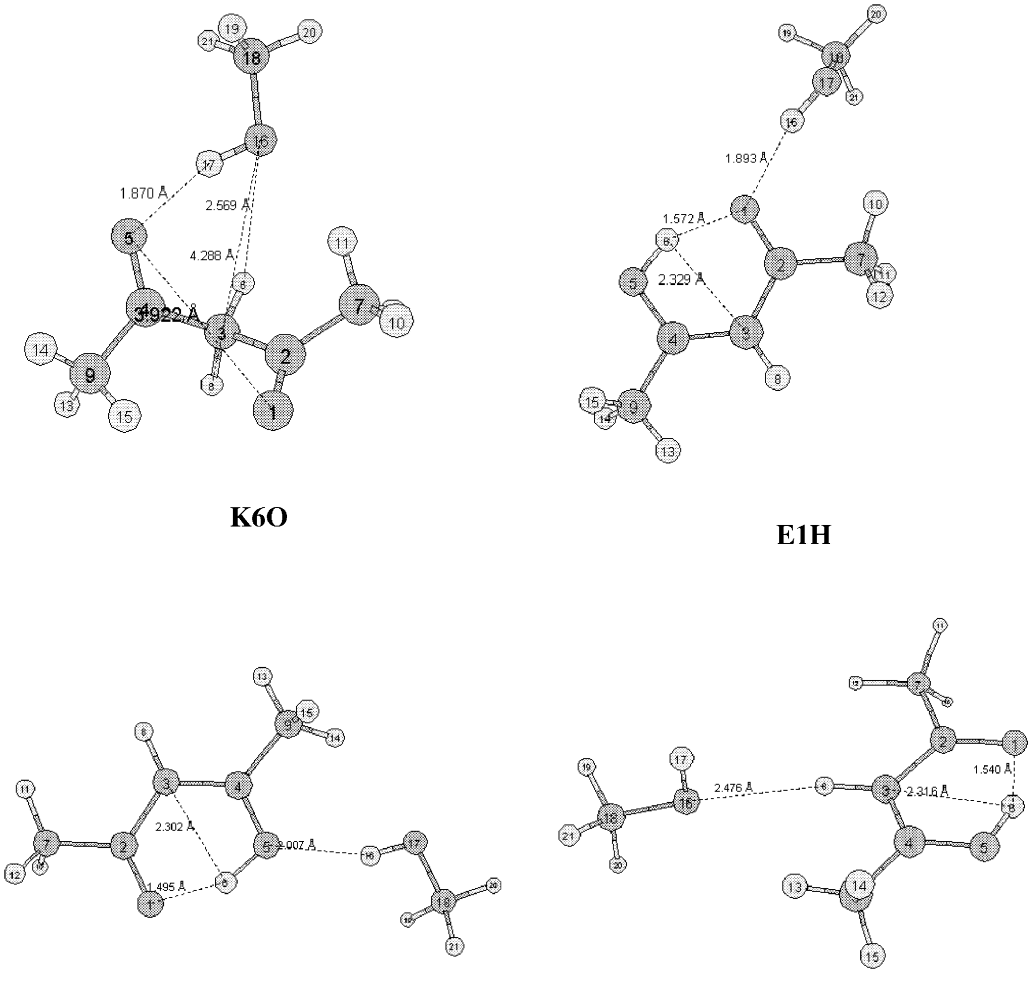
seems to be more stable. Therefore, in our further discussion the K1H complex will be ignored.

The calculated energies (ΔE) related to the energy of the most stable complex for each combination of method and basis set are summarized in Table 1 (as the difference between the energy of a certain complex and the energy of the most stable one).

The values from Table 1 (from DFT calculations) clearly show that the enol-methanol complexes have lower energies than the K6O complex. However, the *Hartree–Fock* calculations predicted that the diketone-methanol complex (K6O) has the lowest energy. That is why in the further discussion we accepted to comment the DFT results. It has been proved that the *Becke*'s three parameter functional B3LYP [19] in a combination with different basis sets produces results in reasonable agreement with experiment for H-bonded complexes between appropriate pairs of organic molecules [20, 21]. The B3LYP functional has given the smallest average absolute error for 91 molecular systems when compared to a number of other functionals [20, 22].

The difference between the energies found using two basis sets and only one method was designated in this work as relative basis set contribution energy (RBSCE). For the B3LYP method RBSCE is $E_{\mathrm{B3LYP/RBSCE}} = E_{\mathrm{B3LYP/D95^{**}}} - E_{\mathrm{B3LYP/6\text{-}311G^{**}}} = 96\,\mathrm{kJ\,mol^{-1}}$ as an average value from all examined H-bonded complexes. For the *HF* calculations RBSCE ($E_{HF/\mathrm{RBSCE}} = E_{HF/\mathrm{D95}^{**}} - E_{HF/6\text{-}311\mathrm{G}^{**}}$) has an average value of 30 kJ mol^{-1}. These values clearly show that the neglect of the configuration interaction in the *HF* procedure leads to lower RBSCEs. The accuracy of the predicted results is enhanced several times when DFT is used as *e.g.* the average difference between the complex energies found by *HF*/6-311G** and B3LYP/6-311G** is 7270 kJ mol^{-1}. Attempts to fully optimize the K6O structure with the *HF*/6-311G** combination failed because the program did not meet the convergence criteria even when the number of the optimization cycles was enhanced drastically.

The optimized geometries (with B3LYP/D95**) of the four stable H-bonded complexes are illustrated in Fig. 1. The energy values from Table 1 revealed that



K6O **E1H**

E5H **E8O**

Fig. 1. Optimized structures of the H-bonded complexes

the E1H system with an intermolecular H-bond between the methanol H atom and O(1) of the enol form has the lowest energy. The structure of the enol form in this system is almost planar (see Fig. 1, second structure) on account of a pseudoaromatic O(1)C(2)C(3)C(4)O(5)H(6) ring in the molecule.

A space angle of 16.9° (C_2–$O_1\cdots H_{16}$–C_{17}) is defined between the interacting atoms from the considerably short intermolecular hydrogen bond. The formation of this bond in the E1H system causes a slight elongation of the intramolecular hydrogen bond by 0.028 Å versus the pure acetylacetone enol form [15, 1]. In other words, the intramolecular hydrogen bond becomes weaker. The same effect is observed in the E5H complex, in which the methanol hydrogen atom is not-covalently bound to the enol O(5) atom. The formation of an intermolecular H-bond between H(8) and the methanol oxygen in the complex E8O causes an insignificant elongation of the intramolecular H-bond (see Fig. 1).

The structures from Fig. 1 show that the longest and accordingly the weakest intermolecular H-bonds are formed when the methanol molecule is H-bonded to the methylene H-atom (from the diketoform of acetylacetone) or to the methyne hydrogen (from the enol form of acetylacetone) (see Fig. 1). Perhaps it is due to the steric hindrance between the methyl groups of the two molecules forming the complex and the lower acceptor ability of the hydrogen atom in the cases of O–$H\cdots O$ complexation.

It was of interest to derive the structures, rendering on account of the field created by the solvents acetonitrile, methanol, and chloroform. The computations were implemented by means of the IPCM performing only single-point calculations [23, 24] and the results are listed in Table 2. The relative energy of each hydrogen complex in a corresponding solvent was calculated as the difference between its isolated state energy and its predicted energy in the solvent environment. The relative energy values give the stabilization of the systems resulting by the solvent field because the energies of the complexes in the isolated state are higher than in solvents. It was found that in polar solvents like acetonitrile and methanol the energy decrease is larger than in less polar ones like chloroform ($\varepsilon = 4.9$). However, the energy decrease of the keto-complex K6O in acetonitrile is larger than of all other enol-complexes. This was found for pure acetylacetone [15] in our recent investigation (in agreement with the experimental fact, that in polar solvents the diketoform of acetylacetone is more stable than the enol form [25–30]).

In the case of solvent assisted systems the average RBSCEs are: $E_{\mathrm{B3LYP/RBSCE}} = E_{\mathrm{B3LYP/D95^{**}}} - E_{\mathrm{B3LYP/6\text{-}311G^{**}}} = 92$ (acetonitrile), 91 (methanol), and 92 kJ mol^{-1} (chloroform); $E_{HF/\mathrm{RBSCE}} = E_{HF/\mathrm{D95^{**}}} - E_{HF/\mathrm{6\text{-}311G^{**}}} = 30$ (acetonitrile, methanol) and 29 kJ mol^{-1} (chloroform). The values are close to these found for the isolated molecules, from where it could be concluded that the basis sets do not contribute significantly to the calculated energies of the complexes in solvents. From Table 2 one can see also that the energies of the hydrogen complexes in acetonitrile and methanol are nearly equal. This is explained by the similar dielectric constants of acetonitrile ($\varepsilon = 36.64$) and methanol ($\varepsilon = 32.63$) [24].

Vibration Spectra

Calculations of the harmonic frequencies of all complexes were carried out in order to study the nature and the behavior of the stationary points (complexes) on the

Table 2. Relative energies of the solvent assisted H-bonded complexes

Solvent	Method	*Relative energy of the H-Bonded complexes/kJ mol^{-1} (hartree)			
		K6O	E1H	E5H	E8O
Acetonitrile	B3LYP/D95**	40	46	37	45
		(−461.644527)	(−461.654546)	(−461.648973)	(−461.648254)
	B3LYP/6-311G**	37	42	35	40
		(−461.680802)	(−461.689725)	(−461.683845)	(−461.681962)
	HF/D95**	53	44	39	53
		(−458.913157)	(−458.907830)	(−458.903332)	(−458.905853)
	HF/6-311G**	–	46	47	51
		–	(−458.920487)	(−458.917978)	(−458.916810)
Methanol	B3LYP/D95**	39	46	37	45
		(−461.644429)	(−461.654447)	(−461.648895)	(−461.648162)
	B3LYP/6-311G**	34	41	34	40
		(−461.679542)	(−461.689633)	(−461.683765)	(−461.681866)
	HF/D95**	53	44	39	52
		(−458.913027)	(−458.907740)	(−458.903240)	(−458.905721)
	HF/6-311G**	–	46	47	50
		–	(−458.920403)	(−458.917870)	(−458.916695)
Chloroform	B3LYP/D95**	30	34	27	32
		(−461.640103)	(−461.649747)	(−461.645076)	(−461.643107)
	B3LYP/6-311G**	22	30	25	29
		(−461.675061)	(−461.685424)	(−461.680216)	(−461.677555)
	HF/D95**	38	32	29	38
		(−458.907427)	(−458.903259)	(−458.899411)	(−458.900199)
	HF/6-311G**	–	–	34	36
		–	–	(−458.912969)	(−458.911269)

* $E_{\text{isolated}} - E_{\text{solvent assisted}}$

energy hypersurface. The calculated frequencies were compared with the measured spectrum of an equimolar mixture of acetylcetone and methanol.

Besides our experimental and theoretical spectra we employed also those given in the works of *Mavri et al.* [31] and *Tayyari et al.* [32, 33] for acetylacetone and several of its derivatives. The established excellent correlation between the theoretical and experimental spectra of acetylacetone in Ref. [32] stimulated us to use the same basic theory for our work. In Ref. [34] it has been shown that the methods based on the density functional theory are accurate enough to reproduce geometry parameters; spectroscopic and energetic values with an error close to the uncertainty in the experimental measure (about 8–12 kJ mol^{-1}). In Table 3 theoretical and experimental frequencies of the complexes are listed. The normal modes of the most characteristic symmetric and asymmetric C=O vibrations of the studied complexes are designated in Fig. 2 by their *Eigen*vectors.

All C=O vibrations are mixed with other motions in the molecules, some of them out of plane. For example, in the enol complexes the C=O vibration is mixed with deformations of the methyl hydrogen atoms. For the system K6O one torsion vibration of the methyl hydrogen atoms was detected at $\bar{\nu} = 1798\,\text{cm}^{-1}$ together

Table 3. Theoretical and experimental vibration wavenumbers (cm^{-1}) of the H-bonded complexes and their theoretical intensity ($kM\,mol^{-1}$)

K6O	Exp.	Assignment
3648/548	3415/0.45	$\nu(OH_{meth})$
3176/6	–	$\nu_{as}(CH_3)$
3172/8	–	$\nu_{as}(CH_3)$
3163/7	–	$\nu_{as}(CH_2)$
3119/5	–	$\nu_{as}(CH_3)$
3118/44	–	$\nu_{as}(CH_{3,meth})$
3106/10	–	$\nu_{as}(CH_3)$
3082/5	–	$\nu_s(CH_2)$
3055/71	–	$\nu_{as}(CH_{3,meth})$
3048/4	–	$\nu_s(CH_3)$
3038/10	–	$\nu_s(CH_3)$
2998/102	2945/0.40	$\nu_s(CH_{3,meth})$
1798/74	1728/0.59	$\nu_s(C{=}O)$
1762/364	1708/0.59	$\nu_{as}(C{=}O)$
1509/2	–	$\delta(CH_{3,meth})$
1488/18	–	$\delta(CH_3 + CH_{3,meth})$
1486/3	–	$\delta(CH_{3,meth})$
1479/4	–	$\delta(CH_2 + CH_3)$
1470/34	–	$\delta(CH_2 + CH_3)$
1464/36	–	$\delta(CH_3)$
1460/6	–	$\delta(CH_2 + CH_3)$
1431/117	–	$\delta(CH_2 + CH_3 + CH_{3,meth})$
1398/38	–	$\delta(CH_3) + \nu(C–CH_3)$
1391/82	–	$\delta(CH_3) + \nu(C–CH_3)$
1301/66	–	$\nu(C–C) + \gamma(H_8)$
1258/123	1172/0.31	$\nu(C–C) + \omega(CH_2)$
1194/110	1158/0.33	$\nu(C–CH_3)$
1166/0	–	$\rho(CH_{3,meth})$
1153/15	–	$\tau(CH_2)$
1125/36	1106/0.21	$\rho(CH_{3,meth})$
1080/80	1029/0.61	$\nu(CO_{meth})$
1077/59	–	$\nu(CO_{meth})$
1055/3	–	$\nu(CH_2) + \delta(C–CH_3)$

E1H	E5H	E8O	Exp.	Assignment
3680/616	3771/325	3853/25	3415/0.45	$\nu(OH_{meth})$
3245/2	3246/1	3246/6	–	$\nu(CH)$
3169/10	3267/7	3169/0	–	$\nu_{as}(CH_3)$
3164/3	3163/12	3156/18	–	$\nu_{as}(CH_3)$
3127/11	3133/9	3131/8	–	$\nu_{as}(CH_3)$
3126/7	3122/6	3117/9	–	$\nu_{as}(CH_3)$
3113/54	3121/46	3140/28	–	$\nu_{as}(CH_{3,meth})$
3058/7	3056/2	3056/180	–	$\nu_s(CH_3)$
3051/5	3053/5	3051/12	–	$\nu_s(CH_3)$

(*continued*)

Table 3 (*continued*)

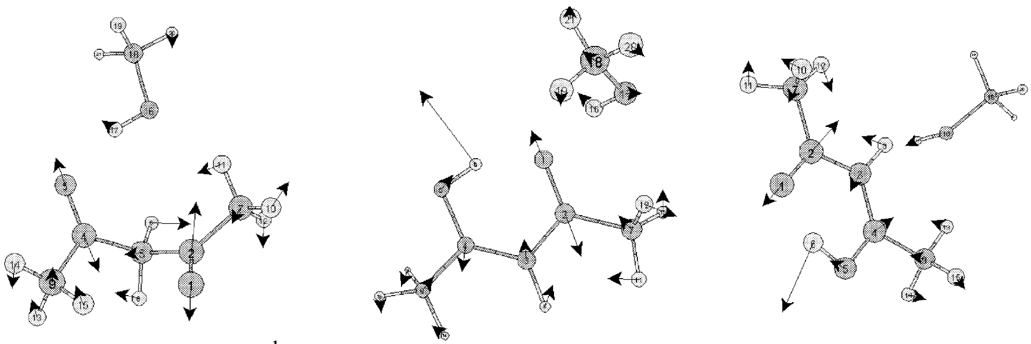
E1H	E5H	E8O	Exp.	Assignment
3041/82	3051/75	3074/58	–	$\nu_{as}(CH_{3,meth})$
2989/87	2996/80	3012/76	2945/0.40	$\nu_s(CH_{3,meth})$
2913/476	2598/583	2784/425	–	$\nu(OH)$
1672/525	1687/577	1677/538	–	$\nu(C{=}C)$
1636/214	1658/121	1654/122	1621/0.81	$\nu(C{=}O)$
1509/82	1508/123	1514/126	–	$\delta(C{-}C) + \delta(CH_3 + CH_{3,meth})$
1489/12	1489/9	1488/4	–	$\delta(CH_3 + CH_{3,meth})$
1486/1	1507/20	1504/17	–	$\delta(CH_{3,meth})$
1481/14	1487/0	1486/8	–	$\delta(CH_3 + CH_{3,meth})$
1473/35	1479/46	1481/14	–	$\delta(CH_3)$
1467/12	1475/40	1478/6	–	$\delta(CH_3)$
1462/89	1467/14	1471/14	–	$\delta(CH_3)$
1433/72	1461/71	1467/110	–	$\delta(CH_3) + \rho(H_{16})$
1410/34	1415/6	1411/6	–	$\delta(CH_3) + \nu(C{-}C)$
1399/35	1393/35	1391/41	–	$\delta(CH_3) + \nu(C{-}CH_3)$
1378/204	1341/121	1370/154	1362/0.62	$\nu_{as}(C{=}C + C{-}O) + \nu(C{=}O)$
1290/99	1295/108	1287/101	1172/0.31	$\nu_s(C{-}CH_3)$
1195/10	1191/15	1203/16	1158/0.33	$\rho(H_8) + \nu(C{-}CH_3)$
1165/0	1165/0	1360/27	–	$\rho(CH_{3,meth})$
1121/20	1112/32	1164/0	1106/0.21	$\rho(CH_{3,meth})$
1081/114	1075/103	1078/1	1029/0.61	$\nu(CO_{meth})$
1057/2	1040/16	1063/9	–	$\delta(CH_3)$
1043/34	1060/8	1040/4	–	$\rho(CH_3)$
1019/62	1088/95	1056/120	–	$\gamma(H_6)$

Vibration frequencies in cm^{-1}/theoretical IR intensity in $kM\,mol^{-1}$

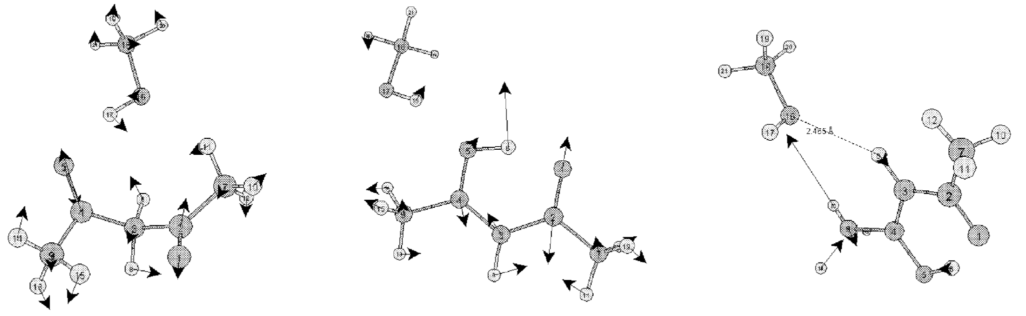
with the characteristic C=O band. In accord with *Tayyari*'s investigations [32] the data from Table 3 show that the methyl stretching vibrations in the interval $\bar{\nu} = 3000$–$3850\,cm^{-1}$ have very low IR intensities. They should be active mainly in *Raman* spectra of the systems. OH stretching vibrations of the enol complexes restricted in the interval $\bar{\nu} = 2784$–$2913\,cm^{-1}$ have quite high intensities. The same vibration in the pure acetylacetone enol form is at $\bar{\nu} = 2800\,cm^{-1}$ in the gas phase and at $\bar{\nu} = 2875\,cm^{-1}$ in the liquid phase [32]. In chloroform this vibration is at $\bar{\nu} = 2750\,cm^{-1}$ as a broad asymmetric stretching band [31] and the carbonyl stretchings are at about $\bar{\nu} = 1550\,cm^{-1}$ [31].

In spite of the fact that the experimental spectrum was measured in the liquid phase and all theoretical spectra from Table 3 refer to isolated systems we obtained very good correlations between experimental and theoretical frequencies with high correlation coefficients (given in brackets): 1) K6O: $\bar{\nu}_{th} = 0.947 \cdot \bar{\nu}_{exp} + 23.48$ (0.998), 2) E1H: $\bar{\nu}_{th} = 0.939 \cdot \bar{\nu}_{exp} + 39.61$ (0.996), 3) E5H: $\bar{\nu}_{th} = 0.910 \cdot \bar{\nu}_{exp} + 83.29$ (0.993), and 4) E8O: $\bar{\nu}_{th} = 0.894 \cdot \bar{\nu}_{exp} + 93.11$ (0.991).

The scaling factor for B3LYP calculations is about 0.980 [23]. Comparing cases 2) – 4) it is seen that the best correlation exists between the frequencies of the E1H hydrogen complex because the linear coefficient in case 2) is closer to the scaling



K6O - $\bar{\nu}_s$(C=O) at 1798 cm^{-1} **E1H - $\bar{\nu}$ (C=O) at 1636 cm^{-1}** **E8O - $\bar{\nu}$ (C=O) at 1654 cm^{-1}**



K6O - $\bar{\nu}_{as}$(C=O) at 1762 cm^{-1} **E5H - $\bar{\nu}$ (C=O) at 1658 cm^{-1}** **E8O - $\bar{\nu}_{as}$(CH$_3$) at 3169 cm^{-1}**

Fig. 2. C=O stretching vibrations in the isolated complexes and the zero-intensive $\bar{\nu}_{as}(CH_3)$ of the E8O complex

factor cited in [23]. That was one of the reasons for us to assign the enol bands in the measured experimental spectrum of the acetylacetone–methanol mixture (1:1) to the E1H complex. Perhaps, the keto-enol tautomerism occurs between the E1H enol complex and the diketocomplex K6O in the liquid phase and in the gas phase. On the other hand, this equilibrium should have the lowest energy barrier because the intramolecular hydrogen bond in the E1H complex is the weakest (the longest). The keto-enol tautomerism between these two forms is responsible for the complicated experimental spectrum of the acetylacetone–methanol mixture.

Bonding Energies

The lower energies of the enol complexes versus the keto-complex found at the DFT level does not come from a large stability of the hydrogen bonds and from the lower energy of the enol structure itself. In order to solve this problem we calculated the bonding energies of the complexes related to the enol and diketone monomers. The energies of the enol form and the diketoform in the gas phase are quite distinguished. For example, the B3LYP calculations with D95** basis functions predicted the energy difference $\Delta E_{\text{diketone/enol}} = E_{\text{diketone}} - E_{\text{enol}}$ about 27 kJ mol^{-1}, and with 6-311G** basis functions it is about 24 kJ mol^{-1}. In solvents the energy difference $\Delta E_{\text{diketone/enol}}$ is lowered: with 10 and 9 kJ mol^{-1} in acetonitrile and methanol found with basis functions D95** and 6-311G**, and with 7 and 6 kJ mol^{-1} in chloroform found with the same basis functions.

Table 4. Bonding energies (kJ mol^{-1}) of the H-bonded complexes in isolated state

Method/ basis set	K6O				E1H				E5H				E8O			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
B3LYP/D95**	−35	−20	−20	−24	−27	−29	−30	−29	−22	−15	−15	−17	−12	−13	−13	−12
B3LYP/6-311G**	−40	−27	−24	−26	−35	−36	−36	−36	−27	−20	−20	−22	−16	−15	−15	−15
HF/D95**	−26	−14	−14	−18	−22	−16	−16	−18	−15	−4	−4	−8	−8	−11	−11	−10
HF/6-311G**	–	–	–	–	−26	−23	−23	–	−18	−17	−17	−17	−12	−14	−14	−12

1: isolated state; **2**: acetonitrile; **3**: methanol; **4**: chloroform

The bonding energies of the complexes in the gas phase and in solvents were calculated by the equation $\Delta E = E_{\text{complex}} - E_{\text{enol(diketon)}} - E_{\text{methanol}}$ (Table 4) in order to estimate the bonding strength of the monomers.

Surprisingly, we established that in the gas phase the diketocomplex formed the strongest intermolecular H-bonds, followed by the enol E1H complex. But in solvents the picture is different: the strongest intermolecular hydrogen bond is formed in the E1H complex while the diketocomplex K6O has a bit lower absolute value of the bonding energy. As a whole, the bonding energies of all complexes in solvents are lower than in the gas phase (isolated state). In other words, the complexes are less stable in solution than in the gas phase.

Conclusion

One of the five possible acetylacetone H-bonded complexes was found to be rather unstable because during the optimization it was transformed into another complex of the acetylacetone diketoform.

It may be concluded that the complex formation of the K6O and E1H systems is much more favorable than the complex formation of the E5H and E8H systems in the gas phase and in solvents. Further, these complexes (K6O and E1H) were found to have the lowest energies and the strongest (shortest) intermolecular hydrogen bonds. Moreover, the measured IR spectrum gave bands similar to the calculated frequencies of the two complexes. The energy differences between the E1H complex and K6O, E5H, and E8O are 20, 6 and 16 kJ mol^{-1}. The first value gives the heat effect of the transformation K6O → E1H (keto-enol tautomerism) in the gas phase. It is seen that the keto-enol conversion between these two forms is enthalpically unfavored.

It was found that the intermolecular H-bonds between the acetylacetone enol form and methanol causes a lengthening of the intramolecular H-bond, *i.e.* a decrease in the intramolecular H-bond energy. This influence is larger in the complexes whose intermolecular hydrogen bonds are from the O(acac)$\cdots$H(meth) type (*e.g.* the E1H complex, in which this effect is the highest) and smaller in the E8O complex in which the intermolecular H-bond is formed between H(8) and the methanol O-atom. It was shown also that the chosen basis sets cause a slight change between the energies of the compounds in isolated states and solvents.

Materials and Methods

The geometries of the complexes were fully optimized by *ab initio* methods [35] at the *HF* and DFT (B3LYP) levels using D95** and 6-311G** basis sets. The calculated geometries were used in subsequent frequency calculations to prove that the complexes correspond to energy minima in the full ($21 \times 3 = 63$ *Cartesian* coordinates, $63 - 6 = 57$ internal coordinates) coordinate hyperspace. The absence of negative frequencies proved that the stationary points found correspond to such minima. The frequency calculations also provided the zero-point energy corrections. The optimized geometries of the complexes were used also for single-point calculations in order to find their energies in solvents with different polarity: acetonitrile, methanol, and chloroform. The calculations were implemented by means of IPCM included in the GAUSSIAN 98 program package [35].

The IR measurement was done on a Perkin-Elmer 1750 Infrared FT-Spectrometer using capillary layer – KBr. Equimolar amounts of acetylacetone and methanol were mixed and measured.

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