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H-bonded complexes between acetylacetone and two molecules of methanol: HF and DFT level study

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Abstract Five stable H-bonded complexes (supersystems) between acetylacetone and two methanol molecules were investigated at the B3LYP and HF levels of theory using the 6-311G** and 6-11++G** basis sets. The most stable complex was found as the one with the highest relative bonding and interaction energies. All vibrational frequencies resulting from calculations with the 6-311++G** basis set were compared with the recorded IR spectrum of acetylacetone/methanol mixture in a molar ratio 1:2.

Keywords Ab initio calculations · Complexes · Density functional calculations · H-bonding

Introduction

Acetylacetone (acac) is one of the simplest β -diketones showing keto-enol tautomerism both in the gas and liquid phases. Acac can exist in two stable tautomeric forms: keto and enol. Many previously published investigations have revealed that the enol tautomer generally predominates, since it is stabilized by formation of a strong intramolecular hydrogen bond [1–7]. The keto-enol equilibrium depends on many factors, e.g. temperature, solvent, etc. There is a large number of experimental data reported, which are related to the temperature dependence of the tautomeric concentration. For example, Lowrey et al. [8] have demonstrated that the concentration of the enol tautomer at 105°C is $66 \pm 5\%$ (found by electron diffraction). It has been found that an increase in temperature causes lowering of

the enol tautomer concentration since creating the enol form is enthalpically favored [7]. As concerns the solvent influence, it is known that the percentage composition of the enol tautomer depends on the dielectric constant of the solvent: it is 13% in aqueous solution –98% in cyclohexane [9, 10]. Moreover, the solvent polarity considerably influences the enol tautomer configuration in β -diketones. For the simplest β -diketone (malonaldehyde) a *trans*-enol configuration is the most stable [11] in aqueous solution, ethanol, and diethyl ether. Unfortunately, no investigation concerning the discrete interactions between acac tautomeric forms and the solvent molecules has been reported. Recently, we have published results investigating the discrete interactions between acac and methanol [12], however no attempt has been made to estimate BSSE and other important interaction parameters between monomers. The discrete interactions between acac and methanol have been described [12]; the stability and effectiveness of the proton transfer in the tautomeric forms is known to depend on the number of the H-bonded molecules to these forms [13].

The aim of the present paper is to find theoretical models of supersystems composed between acac and two molecules of methanol and to compare their structural parameters and stability to the supersystems composed between acac and one methanol molecule.

Materials and methods

The calculations were performed by means of the GAUSSIAN 98 [14] program package at the B3LYP and HF levels of theory together with the 6-311G** and 6-311++G** basis sets. Geometry optimizations were carried out in order to investigate the structure and stability of the systems. Subsequent frequency calculations were run to prove that the complexes correspond to energy minima in the full coordinate hyperspace. SCRF = IPCM single point calculations of the optimized supersystems were performed to find how solvents like

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methanol and chloroform influence the stability of the molecular structures.

The free energies and enthalpies of the complex formations were estimated by the equations:

$$\Delta G_{298}^o = \Delta G_{298}^o(\text{supersystem}) - \Delta G_{298}^o(\text{acac}) - \Delta G_{298}^o(\text{meth 1}) - \Delta G_{298}^o(\text{meth 2}),$$

$$\Delta H_{298}^o = \Delta H_{298}^o(\text{supersystem}) - \Delta H_{298}^o(\text{acac}) - \Delta H_{298}^o(\text{meth1}) - \Delta H_{298}^o(\text{meth2}),$$

whereas the entropy factor and the equilibrium constant by the equations [15, 16]:

$$T\Delta S_{298}^o = \Delta H_{298}^o - \Delta G_{298}^o,$$

$$K_p = e^{-\frac{\Delta G_{298}^o}{RT}}.$$

The bonding energies ΔE_b of the supersystems were estimated as [17]:

$$\Delta E_b = E_{SS} - (E'_A + E'_{M1} + E'_{M2}),$$

where E_{SS} is the energy of the supersystem; E'_A (E'_{M1} and E'_{M2}) is the energy of the acac monomer (methanol 1 and methanol 2) calculated with “ghost” orbitals of the remain aggregate monomers. The BSSE was evaluated using the counterpoise method [17]:

$$\Delta(\text{BSSE}) = \sum_i^3 (E_i - E'_i),$$

where E_i are the energies of the individual monomers frozen in their aggregate geometries, found by single-point calculations.

The interaction energy (ΔE_{int}) was calculated as the difference between the energies of the complex and isolated molecules of acac monomer, methanol 1, and methanol 2.

The experimental IR spectrum of the mixture acac/methanol (1:2) was recorded on a Perkin-Elmer 1750 Infrared FT-Spectrometer in a capillary layer (KBr). The mixture was prepared as follows: 0.5 mol (5.04 cm³) methanol and 0.25 mol (6.39 cm³) liquid acac were mixed at room temperature.

Results and discussion

The hydrogen-bonded systems under investigation are reasonable models for studying the discrete interactions solvent—dissolved substance. In this aspect, five stable hydrogen bonded complexes (supersystems) between acac (acac) and two molecules of methanol were fully optimized and studied at different levels of theory (B3LYP and HF with the basis sets 6-311G** and 6-311++G**). Two of them show the interactions of the diketo form of acac and methanol molecules and three of the enol form of acac and methanol. The structures of the supersystems found with the combination B3LYP/6-

-311++G** (predicting lowest energies) are depicted in Fig. 1.

One exception is the structure of the super system K1, which is shown as obtained by the HF/6-311++G** calculations because during the optimization the aforementioned combination transforms this structure into K2.

One of the methanol molecules in the super systems K1 forms two intermolecular hydrogen bonds with the diketoform of acac. Recently published calculations [12] performed at the B3LYP/6-311G** level considering supersystems between acac and one molecule methanol, also revealed that two bonds are available between the two monomers: O₅...H₁₇ = 1.892 and O₁₆...H₆ = 2.547 Å [12]. In our case the first H-bond is 0.026 Å longer, whereas the second one is 0.067 Å longer (found at the same theoretical level). Obviously, the second molecule of methanol causes such effects on the intermolecular H-bonds. The intermolecular H-bond that is formed between acac diketoform and the second methanol molecule in the frames of the super system K1 is 0.036 Å longer than the O₅...H₁₇ one. If the bond O₁₆...H₆ did not exist, the bonds O₅...H₁₇ and O₁...H₂₂ would probably show equal lengths. In other words, the presence of the H-bond O₁₆...H₆ leads to shortening of the H-bond O₅...H₁₇. Anyway, all the above-mentioned H-bonds are weak (Y...H > 1.9 Å) according to a classification of the H-bonds given in the work of Shishkin et al. [18] and Cleland et al. [19].

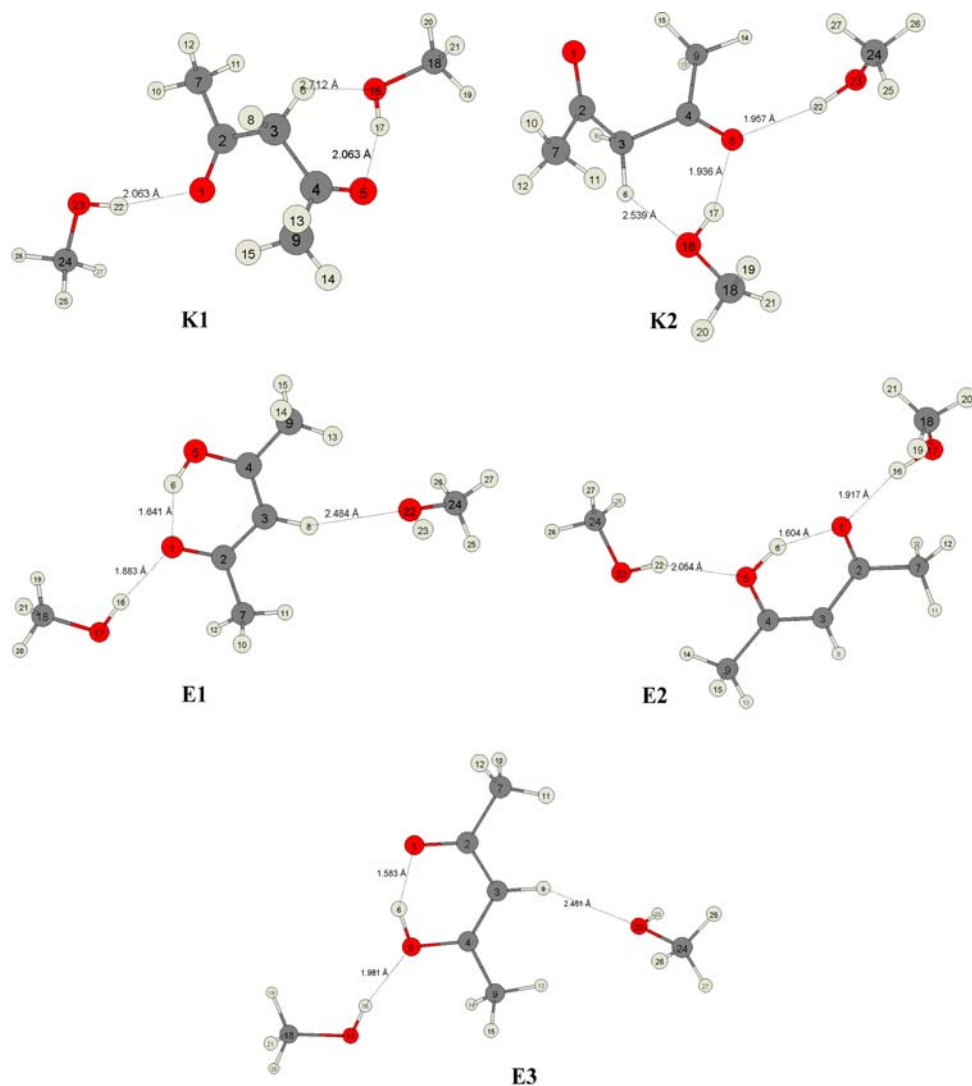
Figure 1 shows that the supersystem K1 has non-planar structure. The distance between the two oxygen atoms was found to be 3.853 Å. This value is 1.086 Å larger than that one predicted by electron diffraction [8] for free acac molecules. The large difference between theory and experiment can be explained with the strong influence of the methanol molecules, which additionally stabilize the diketo-tautomer of acac by forming H-bridges.

The structural parameters of the supersystems K2, E1, E2, and E3 obtained by the B3LYP/6-311++G** combination will be discussed below in detail.

In the supersystem K2 two H-bonds between one of the molecules of methanol and the diketo-form of acac are available. The bonds O₅...H₁₇ and O₁₆...H₆ are 0.044 longer and 0.007 Å shorter, respectively (see Fig. 1), than those given in Ref. [12]. The next methanol molecule is H-bonded to the same oxygen atom of the acac with a bond length of 1.957 Å. In this H-bonded complex the spatial hindrance between the two methanol molecules is larger than in the supersystem K1. This reflects the stability of the diketo-supersystems, which will be discussed in the next section. The O₁...O₅ distance for K2 is larger (3.848 Å) compared to the same distance given in Ref. [8]. The super system K2 has a nonplanar structure due to the strong interactions between the monomers.

The supersystem E1 is formed between O₁-bonded and H₈-bonded methanol molecules to the enol form of acac. One of the H-bonds (O₁...H₁₆ = 1.883 Å) is medium

Fig. 1 Optimized structures of the supersystems at the B3LYP/6-311++G** level. *The structure found at the HF/6-311++G** level



(Y...H 1.6–1.9 [12]), whereas the other is rather long and weak ($O_{22}\dots H_6 = 2.485 \text{ \AA}$). The calculations predict that the complexation between the acac enol form and methanol causes an insignificant elongation of the intramolecular H-bond $O_1\dots H_5$ of 0.008 \AA . The same results have been reported in Ref. [12]. The partially planar structure of the enol form within the E1 supersystem is retained due to the formation of the six-membered ring $O_1C_2C_3C_4O_5H_6$ including the intramolecular H-bond. This bond is 0.018 \AA shorter than the electron diffraction of acac in the vapor phase suggests [8].

The supersystem E2 is bound by two intermolecular H-bonds: $O_1\dots H_{16} = 1.918$ and $O_5\dots H_{22} = 2.054 \text{ \AA}$. Undoubtedly, the attachment of the second methanol molecule to the O_5 atom of the enol form of acac results in an elongation of the intermolecular H-bond $O_1\dots H_{16}$ by 0.029 \AA as compared to the complex E1. Furthermore, this kind of complexation shortens the intramolecular H-bonds by 0.03 \AA compared to the acac enol monomer (1.634 \AA). In other words, this complexation favors the stabilization of the enol monomer itself.

The effect of shortening of the intramolecular H-bond is emphasized much more in the supersystem E3. The intramolecular H-bond is 0.051 \AA shorter than in the acac monomer. However, in this supersystem the intermolecular H-bonds are the weakest: $O_5\dots H_{16} = 2.511$ and $O_{22}\dots H_8 = 2.461 \text{ \AA}$.

Obviously, there is a clear trend for the H-bonds of the type $H(8)_{\text{enol}}\dots O_{\text{meth}}$ to be longer and weaker than those formed between the methanol and the oxygen atoms of the enol form.

Thermodynamic parameters of the complexes and complex formations

The data from Table 1 clearly show that the stability of the complexes is sensitive to the method used. For example, the *Hartree–Fock* method predicted the K1 supersystem to be the most stable.

However, calculations at the B3LYP level gave the lowest energy for the E2 supersystem. Nevertheless, at

Table 1 Relative energies and zero-point energies of the super systems, and thermodynamic parameters of the complex formations (kJ mol⁻¹)

	ΔE				$\Delta E^\circ = \Delta E_{el} + \Delta ZPE$				ΔG_{298}°				ΔH_{298}°				$T\Delta S_{298}^\circ$			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
	11	–	0 _c	0 _d	10	–	0 _g	0 _h	19	–	30	32	–58	–	–41	–31	–77	–	–71	–63
K2	14	17	1	<1	12	15	1	<1	21	37	30	34	–56	–35	–40	–31	–77	–72	–70	–65
E1	6	6	14	13	5	4	17	15	28	31	34	33	–40	–24	–26	–18	–68	–55	–60	–51
E2	0 _a	0 _b	10	9	0 _e	0 _f	13	12	29	36	35	36	–46	–30	–30	–22	–75	–66	–65	–58
E3	17	14	23	20	14	12	24	21	37	40	39	38	–31	–17	–18	–12	68	–57	–57	–50

1 B3LYP/6-311G**; 2 B3LYP/6-311++G**; 3 HF/6-311G**; 4 HF/6-311++G**
 The energies of the most stable super systems
 a–577.440579
 b–577.457360
 c–573.989188

d–574.001118_c–577.211650

f–577.229374

g–573.745596

h–573.758311 hartree were taken as conventional zeroes

the two levels, the supersystem E3 seems to be the least stable, which is in agreement with the strength of the intermolecular H-bonds.

The relative basis set contribution error (RBSCE) was found as the difference between the energies predicted from two basis sets and only one method [12]. The B3LYP methods predicted RBSCE of 44 kJ mol⁻¹ ($E_{B3LYP/6-311G^{**}} - E_{B3LYP/6-311++G^{**}}$) as an average value from all H-bonded systems examined except K1, whereas the HF method gave RBSCE of 33 kJ mol⁻¹ ($E_{HF/6-311G^{**}} - E_{HF/6-311++G^{**}}$) by all supersystems. Here RBSCEs give the contribution of the diffuse functions to the energy of the supersystems examined. Therefore, it is clear why these RBSCEs are about two times lower than those between the basis functions D95** and 6-311G** reported in Ref. [12]. In addition the aforementioned values show that the diffuse functions give more accurate results at the B3LYP level. The use of diffuse functions allows orbitals to occupy a larger region of space. Therefore, basis sets with diffuse functions are important

for systems where electrons are relatively far from the atomic nucleus [20] as in our H-bonded systems, which have many electron lone-pairs.

In order to clarify the nature of the complex formations we also calculated their thermodynamic parameters—free energy, enthalpy and entropy (see Table 1) at standard conditions.

The data from Table 1 show that the complex formations are exothermic. The Gibbs free energies of the complex formations are positive. Therefore, the complexation processes can occur at high temperatures, when the inequality $|\Delta H| < |T\Delta S|$ is satisfied.

Bonding energies and parameters

The relative single-point energies (Table 2) of the monomers (ΔE_i) frozen in their geometries as in the complexes unequivocally show that the enol tautomer in the E1 complex is the most stable. Furthermore, the enol

Table 2 Interaction energies of the supersystems and their components (kJ mol⁻¹)

	$\Delta E' \times 10^2$				$\Delta E \times 10^2$						ΔE_b		ΔE_{int}		ΔE^{SP}		$\Delta BSSE \times 10^1$			
	Acetylacetone		Methanol 1		Methanol 2		Acetylacetone		Methanol 1		Methanol 2		1	2	1	2	1	2		
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2		
K1	–	122	–	0 _d	–	22	–	186	–	11	–	7	–	–42	–	–45	–	–46	–	39
K2	2543	167	92	12	22	3	2548	233	82	6	20	8	–49	–42	–48	–44	–53	–46	40	42
E1	53	5	26	35	0	17	0 _g	0 _h	28	12	0	0	–34	–28	36	–31	–37	–31	35	31
E2	0 _a	0 _b	6	17	99	26	12	14	18	8	5	1	–40	–32	–42	–35	–44	–35	33	33
E3	52	24	0 _c	24	0 _e	0 _f	4	4	0 _i	0 _j	0 _k	0 _l	–26	–21	–28	–23	–29	–24	36	31

1 B3LYP/6-311++G**; 2 HF/6-311++G**

The total energy

a–345.911451

b–343.823862

c–115.765344

d–115.080948

e–115.765588

f–115.080913

g–345.910917

h–343.823405

i–115.764941

j–115.080481

k–115.764982

l–115.080495

hartree of the most stable monomers was taken as a conventional zero, ΔE^{SP} —the energy difference between the energy of the supersystem and the single-point energies of the monomers in the complex

Table 3 Relative energies of the solvent assisted super systems (kJ mol⁻¹)

	K1	K2	E1	E2	E3
Chloroform	20	33	17	7	17
Methanol	28	46	24	9	24

monomer in the supersystem E3 has lower energy than that from the supersystem E2.

Therefore, the lower relative energies of the enol complexes shown in Table 1 do not mean that the stability of the complexes comes from the lower energy of the fully optimized isolated enol form. That is why a better way to discuss the stability of the complexes is by their bonding and interaction energies.

Among all enol complexes, E2 is the most stable because it has the highest relative bonding and interaction

energies as compared to the remaining supersystems. We found recently [12] that the supersystem composed of the diketoform of acac and one methanol molecule is the most stable. Unfortunately, in that paper information on the Δ BSSE was not provided.

Performing IPCM computations, we studied the influence of solvents like methanol ($\epsilon=32.63$) and chloroform ($\epsilon=4.9$) on the stability of the supersystems. The relative energy of each H-bonded complex in a corresponding solvent was calculated as the difference between its isolated state energy and its predicted energy in the solvent environment (see Table 3) all calculated at the HF/6-311++G** level.

According to the data, in polar solvents (methanol here) the energy decrease is larger compared to less polar solvents, e.g. chloroform. Moreover, the energy decrease of the diketo-complexes is larger than for the enol ones. This finding is in agreement with the data in Ref. [12].

Table 4 Calculated and experimental vibration spectra of the super systems (wavenumbers cm⁻¹, theoretical IR intensities km mol⁻¹)

K1	K2		Experiment	Assignment
	1	2		
4120/392	4124/328	3714/417	3392/0.68	$\nu(OH_{\text{meth}})$
4102/313	4108/335	3683/509	–	$\nu(OH_{\text{meth}})$
3289/11	3292/6	3143/8	–	$\nu_{\text{as}}(\text{CH}_3)$
3270/2	3269/1	3132/0	–	$\nu_{\text{as}}(\text{CH}_2)$
3250/54	3251/49	3099/77	–	$\nu_{\text{as}}(\text{CH}_3_{\text{meth}})$
3242/7	3284/13	3083/3	–	$\nu_{\text{as}}(\text{CH}_3)$
3233/8	3241/6	3077/7	–	$\nu_{\text{as}}(\text{CH}_3)$
3184/13	3188/12	3057/3	–	$\nu_{\text{s}}(\text{CH}_2)$
3245/61	3245/67	3042/53	–	$\nu_{\text{as}}(\text{CH}_3_{\text{meth}})$
3172/3	3172/2	3062/2	–	$\nu_{\text{s}}(\text{CH}_3)$
3171/5	3171/5	3021/8	–	$\nu_{\text{s}}(\text{CH}_3)$
3191/78	3195/73	3020/68	–	$\nu_{\text{as}}(\text{CH}_3_{\text{meth}})$
3144/84	3148/83	2991/89	–	$\nu_{\text{s}}(\text{CH}_3_{\text{meth}})$
3140/83	3139/73	2978/71	2945/0.57	$\nu_{\text{s}}(\text{CH}_3_{\text{meth}})$
1976/222	1982/226	1785/121	1728/0.59	$\nu_{\text{s}}(\text{C}=\text{O})$
1950/402	1944/383	1727/384	1708/0.60	$\nu_{\text{as}}(\text{C}=\text{O})$
1632/4	1632/4	1510/8	–	$\delta(\text{CH}_3_{\text{meth}})$
1631/3	1620/2	1496/4	–	$\delta(\text{CH}_3_{\text{meth}})$
1619/3	1631/4	1494/2	–	$\delta(\text{CH}_3_{\text{meth}})$
1599/7	1600/15	1485/13	–	$\delta(\text{CH}_2, \text{CH}_3, \text{CH}_3_{\text{meth}})$
1608/25	1609/27	1481/19	–	$\delta(\text{CH}_3, \text{CH}_3_{\text{meth}})$
1609/14	1597/9	1478/4	–	$\delta(\text{CH}_3_{\text{meth}}, \text{CH}_2)$
1598/16	1585/8	1473/9	–	$\delta(\text{CH}_3)$
1587/13	1581/13	1469/15	–	$\delta(\text{CH}_3, \text{CH}_2)$
1578/12	1529/76	1467/34	–	$\delta(\text{CH}_3)$
1589/17	1593/11	1465/9	–	$\delta(\text{CH}_2, \text{CH}_3)$
1533/54	1523/98	1421/35	–	$\rho(\text{HOH})_{\text{rm meth}}$
1530/82	1519/28	1415/89	–	$\rho(\text{HOH})_{\text{rm meth}}$
1524/60	1527/39	1396/35	–	$\delta(\text{CH}_3)$
1520/46	–	1394/63	–	$\delta(\text{CH}_3)$
1477/75	1473/71	1308/48	–	$\omega(\text{CH}_2)$
1380/36	1385/36	1264/123	1251/0.57	$\nu(\text{C}-\text{C}), \tau(\text{CH}_2)$
1282/42	1282/79	1193/106	1158/0.34	$\nu(\text{C}-\text{C})$
1279/3	1288/10	1171/0	–	$\tau(\text{CH}_3_{\text{meth}})$
1294/46	1278/4	1160/43	–	$\tau(\text{CH}_2)$
1199/44	1200/69	1121/41	1111/0.26	$\rho(\text{CH}_3_{\text{meth}}, \text{HOH})_{\text{rm meth}}$
1194/54	1192/40	1110/10	–	$\rho(\text{CH}_3_{\text{meth}}, \text{HOH})_{\text{rm meth}}$
1181/5	1180/18	1084/5	–	$\rho(\text{CH}_3)$
1158/0	1161/1	1063/10	–	$\rho(\text{CH}_3, \text{CH}_2)$
1183/97	1182/91	1059/115	1030/0.77	$\nu(\text{C}-\text{O}_{\text{meth}})$
1177/150	1177/118	1055/121	–	$\nu(\text{C}-\text{O}_{\text{meth}})$

Table 4 (Contd.)

E1		E2		E3		Experiment	Assignment
1	2	1	2	1			
4185/63	3842/37	<i>4156/217</i>	<i>3770/295</i>	4185/63	3844/37	3392/0.68	$\nu(\text{OH}_{\text{meth}})$
<i>4085/542</i>	<i>3640/815</i>	<i>4101/459</i>	<i>3672/660</i>	<i>4146/333</i>	<i>3745/479</i>	3392/0.68	$\nu(\text{OH}_{\text{meth}})$
3370/3	3210/8	3365/3	3215/2	3369/4	3208/10	–	$\nu(\text{CH}_8)$
3291/5	3141/10	3293/5	3139/6	3290/7	3140/1	–	$\nu_{\text{as}}(\text{CH}_3)$
3289/9	3134/23	3284/13	3135/3	3284/19	3135/12	–	$\nu_{\text{as}}(\text{CH}_3)$
3264/38	3119/22	3253/53	3104/35	3264/39	3118/23	–	$\nu_{\text{as}}(\text{CH}_{3\text{meth}})$
3904/247	3115/352	3859/285	2998/497	3839/259	2903/465	–	$\nu_{\text{as}}(\text{OH})$
3232/13	3097/9	3248/6	3096/9	3237/9	3095/12	–	$\nu_{\text{as}}(\text{CH}_3)$
3239/70	3088/66	3243/66	3094/46	3247/61	3097/42	–	$\nu_{\text{as}}(\text{CH}_{3\text{meth}})$
3234/13	3084/6	3233/12	3088/5	3231/15	3084/4	–	$\nu_{\text{as}}(\text{CH}_3)$
3207/65	3055/45	3189/83	3031/65	3206/65	3055/45	–	$\nu_{\text{as}}(\text{CH}_{3\text{meth}})$
3178/16	3033/2	3185/6	3035/5	3180/11	3033/6	–	$\nu_{\text{s}}(\text{CH}_3)$
3175/5	3032/8	3175/5	3031/3	3174/5	3031/1	–	$\nu_{\text{s}}(\text{CH}_3)$
3177/91	3013/75	3179/89	3019/72	3184/85	3022/69	–	$\nu_{\text{as}}(\text{CH}_{3\text{meth}})$
3156/73	3002/71	3144/71	2985/70	3155/73	3001/67	2945/0.57	$\nu_{\text{s}}(\text{CH}_{3\text{meth}})$
3136/85	2973/97	3137/80	2977/94	3140/79	2979/90	–	$\nu_{\text{s}}(\text{CH}_{3\text{meth}})$
1758/644	1663/437	1766/642	1669/506	1780/575	1677/507	1708/0.60	$\nu(\text{C}=\text{C}, \text{C}=\text{O})$
1863/413	1613/305	1867/394	1620/221	1884/366	1638/163	1625/0.77	$\nu(\text{C}=\text{O}, \text{C}=\text{C})$
1632/2	1511/1	1631/3	1509/1	1631/5	1509/10	–	$\delta(\text{CH}_{3\text{meth}})$
1630/5	1508/10	1630/5	1508/6	1630/5	1508/7	–	$\delta(\text{CH}_{3\text{meth}})$
1613/19	1501/57	1611/17	1496/59	1606/12	1495/73	–	$\delta(\text{CH}_3), \rho(\text{H}_8)$
1621/2	1497/4	1620/3	1496/4	1621/3	1497/2	–	$\delta(\text{CH}_{3\text{meth}})$
1618/2	1493/3	1619/2	1494/3	1619/3	1494/4	–	$\delta(\text{CH}_{3\text{meth}})$
1608/17	1485/11	1608/21	1487/22	1610/17	1485/11	–	$\delta(\text{CH}_{3\text{meth}}, \text{CH}_3)$
1608/21	1477/10	1606/23	1481/5	1609/18	1480/6	–	$\delta(\text{CH}_{3\text{meth}}, \text{CH}_3)$
1601/4	1473/3	1599/9	1477/6	1601/5	1474/26	–	$\delta(\text{CH}_3)$
1597/11	1457/114	1592/9	1476/37	1594/10	1458/169	–	$\delta(\text{CH}_3)$
1539/23	1439/94	1528/21	1426/78	1522/80	1421/44	–	$\rho(\text{H}_{16})$
1586/59	1412/12	1586/9	1471/9	1583/3	1412/23	–	$\delta(\text{CH}_3)$
1565/124	1396/41	1566/131	1456/151	1564/166	1390/46	–	$\delta(\text{CH}_3)$
1482/217	1371/235	1478/159	1354/199	1483/119	1354/118	1363/0.63	$\nu(\text{C}-\text{C}, \text{C}=\text{C}) \rho(\text{H}_6)$
1476/32	1361/20	1507/73	1400/57	1476/34	1360/18	1158/0.34	$\rho(\text{H}_{22,23}), \delta(\text{CH}_{3\text{meth}})$
1343/196	1272/129	1346/227	1277/157	1341/247	1275/178	–	$\nu(\text{C}-\text{CH}_3)$
1302/27	1208/9	1294/23	1196/10	1299/25	1204/11	–	$\nu(\text{C}-\text{CH}_3), \rho(\text{H}_8)$
1277/3	1168/1	1278/3	1169/0	–	–	–	$\tau(\text{CH}_{3\text{meth}})$
1204/40	1124/21	1197/51	1120/29	1189/40	1113/21	–	$\rho(\text{CH}_{3\text{meth}}), \rho(\text{H}_{16})$
1278/3	1072/9	1180/114	1169/0	1152/27	1072/8	1111/0.26	$\rho(\text{CH}_{3\text{meth}})$
1187/106	1065/89	1185/100	1062/115	1181/109	1060/123	1030/0.77	$\nu(\text{C}-\text{O}_{\text{meth}})$
1147/9	1044/15	1162/2	1063/8	1145/9	1066/1	–	$\rho(\text{CH}_3)$
1163/70	1036/137	1177/50	1055/126	1165/101	1037/129	–	$\nu(\text{C}-\text{O}_{\text{meth}})$
1130/29	1029/20	1147/13	1045/14	1132/24	1046/3	–	$\rho(\text{CH}_3)$

The frequencies in *Italic* involve intermolecular vibrations

Vibration spectra

In order to fit the theoretical values to the experimental ones we recorded the IR spectrum of the mixture acac/methanol (mixture 1) in a molar ratio of 1:2. The measured spectrum is compared with that of the acac/methanol mixture (mixture 2) in molar ratio 1:1, discussed in Ref. [12].

Using experimental intensities of the most characteristic C=O vibration (see Table 4) of the enol-forms and diketone-forms in the supersystems it was possible to estimate the ratio diketone:enol. It is 78% in mixture 1 and 73% in mixture 2. Obviously, the amount of the enol form decreases on increasing the amount of methanol (polar solvent) in the liquid mixture. This is in accordance with previously published investigations of

the keto-enol equilibrium of β -diketones in the liquid phase [21, 22].

The experimental IR spectra of mixtures 1 and 2 differ only by the intensities of the bands at 1029–1030 cm^{-1} and those at 2945 and 2832 cm^{-1} . For mixture 1, these bands are much more intense than those for mixture 2. The reason is the higher methanol concentration in mixture 1 since these bands correspond to CH_3 and C–O stretchings in methanol.

From Table 4 it is seen that the B3LYP method predicts frequencies closer to the experimental ones. Although the experimental spectra are recorded in the liquid phase, they are rather similar to the ones calculated for isolated supersystems. The OH stretchings of the methanol molecules in the enol super systems also involve intermolecular vibrations (marked in italics in Table 4) along the intermolecular H-bonds.

Good linear correlations were found between experimental and calculated frequencies at the B3LYP and HF levels. The angular coefficients of the dependencies $\text{freq}_{\text{theor}} = f(\text{freq}_{\text{exp}})$ vary within the interval 1.0187/1.2086 (the correlation coefficients are restricted within the interval 0.9814/0.9949). The correlation factor for this kind of frequency calculations (e.g. for B3LYP/6-311++G**) is 0.9804 [23].

Conclusions

Five stable H-bonded complexes between acac tautomeric forms and two methanol molecules are found at the B3LYP and HF level with 6-311++G** and 6-311G** basis sets. The results at the two theoretical levels predict rather contradictory energies of the complexes. The B3LYP method predicted the E2 and K2 super systems to be the most stable ones, whereas the HF method gives K1. However, the thermodynamic study of the complex formations explicitly demonstrated that the formation of the enol super systems results in a larger positive Gibbs free energy. All formations are enthalpically favored and show a large negative entropy factor.

The bonding-energy analysis of the super systems revealed that the complexes E2 and K2 must be most stable originating from their high relative bonding and interaction energies.

It should be mentioned that the H-bonding in the enol complexes from the type $\text{O}_1(\text{acac})\dots\text{H}(\text{meth})/\text{O}(\text{meth})\dots\text{H}_8(\text{acac})$ causes an elongation of the intramolecular H-bond in the enol tautomer of acac compared to the isolated enol monomer. In all the other cases (supersystems E2 and E3) the H-bonding leads to a slight shortening of this H-bond. This may be one of the reasons for the high stability of the E2 supersystem.

Finally, our results are in agreement with the experimental fact that in polar solvents the amount of the diketoform of acac is higher versus non-polar ones. That is why the diketoform forms more stable complexes with the molecules of the polar solvent than the enol form.

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