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Tautomeric and conformational properties of β-diketones

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ABSTRACT

Available literature data about keto–enol equilibrium in β-diketones with different substituents in β-positions (R1C(O)–CH_2–C(O)R2) has been analyzed. It was concluded that substituents from group I (R = H, CH_3, CF_3, $C(CH3)_3$) strongly favour the enol tautomer, whereas substituents from group II (R = F, Cl, OCH_3, NH_2) favour the keto form. To understand the influence of the nature of the substituents on the keto–enol tautomerism, quantum chemical calculations (B3LYP/aug-cc-pVTZ) were performed for the series of β-diketones with substituents from both groups, with R1 = R2 or R1 ≠ R2. Equilibrium structures of enol and keto forms and vibrational spectra were analyzed for all investigated molecules. The electron density distribution was studied by NBO-analysis. Experiments and quantum chemical calculations demonstrate, that the keto form is preferred only in β-diketones with R1 and R2 from group II. This result can be explained by hyperconjugation between lone pairs of these substituents and the C=O double bond in both R–C=O fragments. Thus, lone pairs at the atom, connected with the C(O)–C–C(O) skeleton, which are present in the substituents from group II, are the reason for favouring to the keto form rather than electronegativity or other properties. In β-diketones with at least one substituent from group I the enol tautomer is preferred. Obviously, the strong hydrogen bond and π-conjugation in the ring are the reasons for stabilizing the enol form. Optimized geometrical parameters of the molecules are in a good agreement with the experimental gas-phase structures. The calculations predict reasonably well the energetically most preferred tautomer. However, exact prediction of the keto/enol equilibrium composition apparently requires methods, more sophisticated than B3LYP or MP2.

1. Introduction

Over many years, β-diketones (β-dicarbonyl compounds) have been of considerable interest to organic, inorganic and physical chemistry. A large group of applications of β-diketones concerns their role as an important organic reagent. Some of these compounds, for instance, are currently used in the perfume and cosmetic industries [1,2]. On the other hand, β-diketones were found to be useful chelating ligands. This feature opens new possibilities for using substances of our interest. Special attention has been paid to the keto–enol tautomerism of β-diketones, the structural properties of both keto- and enol forms, and the nature of the strong intramolecular O–H···O hydrogen bond in the enol form. These properties were subject of intensive studies by different methods, including IR, Raman, microwave and NMR spectroscopy, electron, X-ray and neutron diffraction, as well as quantum chemical calculations and some other techniques. A comprehensive review of the physical properties of β-diketones, mainly in liquid phase, is given by Emsley [3].

It is known that the keto–enol equilibrium is influenced by a variety of different factors, such as solvent, temperature, presence of other species, which are capable of hydrogen bonding. Most of all, the preference of the enol or keto tautomeric form of R1C(O)–CHR3–C(O)R2 depends strongly on the substituents R1, R2, R3. The main focus of our interest are the tautomeric and structural properties of β-diketones in the gas phase and the dependence of the keto:enol ratio on the substituents in β-position (R1 and R2).

2. Keto–enol equilibrium. What does it depend on?

Malonaldehyde (MA) or propandial (R1 = R2 = R3 = H) is the most simple β-diketone and was of a great interest to both, experimentalists and theoreticians. The predominance of the enol form of MA in chloroform solution is confirmed by NMR [4] and in the gas phase at low pressure by FT-IR [5]. Microwave spectroscopy, as well, results in an enol structure with C_S symmetry [6–8]. The authors of [6] note that a large amplitude tunneling motion complicates a complete structure determination, therefore a modified r_s structure of symmetrically and asymmetrically substituted deuterated species has been obtained. A relative energy of

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$\Delta E = (E_{keto} - E_{enol}) = 3.53$ kcal/mol was obtained by CBS-4 calculations [9]. According to the free energy difference $\Delta G^0_{298} = (G^0_{keto} - G^0_{enol}) = 1.48$ kcal/mol, derived from the CBS-4 calculations [9] the equilibrium composition of MA at 298 K is 7.6% of diketo and 92.4% of enol form. On the other hand, DFT/B3LYP calculations [10] predict $\Delta E = 7.6$ kcal/mol, corresponding to the exclusive enol form of MA at 298 K.

The dimethyl derivative of MA, acetylacetone (AcAc), (R1 = R2 = CH_3) is known to exist in two forms – keto and enol, but rather different relative concentrations of the two tautomers were reported in the literature. According to numerous NMR studies [11–14] the enol tautomer prevails from 81% in pure liquid [14] to 91% in CCl_4 solution [11]. Temprado et al. [15] point out that the enol tautomer is more volatile and therefore its concentration in the gas phase should be even higher than that in the liquid. Using the experimental enthalpy of vaporization (10.0 ± 0.1 kcal/mol) for the process of evaporation at 25 °C, Irving and Wadso [16] derived the tautomeric composition of AcAc in the gas phase:

AcAc (liquid, 81.4% enol) → AcAc (gas, 93.3% enol)

^{1}H NMR studies [17] show that the enol form of AcAc predominates in the liquid, in solution, and in the gas phase at all temperatures under investigation. A value of $\Delta G^0_{298} = 2.20(45)$ kcal/mol was derived for the gas phase [17] which corresponds to a percentage of the diketo form of only 2.5(13)% at 298 K. On the other hand, about 10% of diketo tautomer was obtained from matrix FT-IR spectra of AcAc [5]. The equilibrium constant for the keto ↔ enol reaction in the gas phase and its temperature dependence has been obtained from photoelectron spectra at different temperatures [18]. From the values of the equilibrium constant published in [18] we derived enol concentrations of 73% at 25 °C, 60% at 100 °C and about 50% at 175 °C.

Four different gas electron diffraction (GED) studies of AcAc have been reported to date, also with slightly conflicting results [19–22]. Experimental intensities recorded at room temperature [20,21] have been interpreted in terms of the presence of the enol form only. A study performed at 105 °C resulted in an enol contribution of 66 ± 5% [19]. This value is in a good agreement with one derived from the photoelectron spectra at 100 °C [18] (see above). In a recent GED investigation [22] an enol contribution of 78 ± 4% at 155 °C was reported. This value is in agreement with the concentration obtained from the gas phase NMR values (79% enol at 155 °C) [17]. It should be noted that the GED geometries of the enol tautomers reported in [19–22], as well as those of the diketo structures reported in [19,22] are rather different. Thus, experimental data in [19,20] were interpreted for a C_{2v} model of the enol tautomer with a symmetrical O···H···O hydrogen bond, whereas the authors of [21,22] considered a C_S model with an asymmetric O–H···O bond.

According to quantum chemical calculations the keto ↔ enol equilibrium in the case of acetylacetone should be shifted strongly towards enol. CBS-4 calculations [9] performed for AcAc lead to a value of $\Delta G^0_{298} = (G^0_{keto} - G^0_{enol}) = 2.65$ kcal/mol and only 1.1% of diketo form at 298 K. DFT/B3LYP calculations [10] predict $\Delta G^0_{298} = 3.95$ kcal/mol and even stronger predominance of the enol tautomer (only 0.1% of diketo).

It is known, that the substitution of methyl groups in acetylacetone by bulky thrifluoro- or *tert*-butyl groups leads to an increase of the enol content in the liquid phase. ^{1}H NMR studies show 100% of enol form in neat liquid [23] of hexafluoroacetylacetone, HFA (R1 = R2 = CF_3) and >99.5% of its enol form in CCl_4 solution [24]. The amount of enol tautomer for dipivaloylmethane, DPM (R1 = R2 = $C(CH_3)_3$) is 92% in CCl_4 [24]. In comparison, the same study [24] results in only 84% of enol for AcAc in CCl_4 solution. Two independent gas electron diffraction investigations of HFA [25,26] resulted in the presence of only the enol tautomer in the gas phase with symmetric C_{2v} structure and very similar geometric parameters. The main difference between the two obtained structures concerns the orientation of the CF_3 groups. Gas electron diffraction data for DPM [27] were analyzed in terms of only enol tautomer as well. Two different models (symmetric, C_{2v} and asymmetric C_S) were examined. It was revealed that a C_{2v} model with enol hydrogen lying symmetrically relative to the oxygen atoms agrees slightly better with the experiment.

The majority of the investigations of substitution effects on keto–enol equilibrium in β-diketones deals with alkyl-substituted malonaldehyde compounds and in some cases with R = CF_3 [3]. Analysis of the tautomeric properties of this class of compounds leads some authors to the conclusion, that the enol tautomer is the major constituent in all β-diketones [28,29]. However, numerous β-diketones are known to exist predominantly in the keto form.

^{13}C NMR spectroscopic investigation [30] showed that the liquid malonyl difluoride FC(O)–CH_2–C(O)F (R1 = R2 = F) and malonyl dichloride ClC(O)–CH_2–C(O)Cl ((R1 = R2 = Cl)) exist exclusively in diketo form. Gas-phase structures of both mentioned compounds were studied by means of GED and quantum chemical calculations [31,32]. In both cases quantum chemical calculations (HF/3-21G and HF/6-31G(d)) predict the existence of three diketo conformers with close energies. The energy of the enol form is predicted to be a much higher. However, the GED data in both cases could be reproduced reasonably well by only one (ac, sp) diketo conformer with a small contribution of (ac, ac) conformer (see Fig. 1). The main conformer (90(10)%) of FC(O)–CH_2–C(O)F, (ac, sp), possesses C_1 symmetry with one C=O bond anticlinal to the opposite C–C bond (τ_1(C2CC1O1) = 112(2)°) and the other C=O bond synperiplanar (τ_2(C1CC2O2) = 0°). The high energy form (10(10)%), (ac, ac), possesses C_2 symmetry with both C=O double bonds nearly eclipsing C–H bonds of the methylene group [31]. Similar results were obtained for ClC(O)–CH_2–C(O)Cl: 70(15)% of the main conformer, (ac, sp) with τ_1(C2CC1O1) = 95(6)° and τ_2(C1CC2O2) = 12(5)° and 30(15)% of (ac, ac) [32].

According to NMR data [33] dimethylmalonate (R1 = R2 = OCH_3) exists in the liquid state as diketo tautomer. This result is confirmed by ab initio calculations for the free molecule [34], which predict different diketo conformers to be lower in energy by 6–8 kcal/mol than the enol tautomer. Matrix infrared spectra were interpreted in terms of the diketo tautomer, possessing two conformers [35]. Based on quantum chemical calculations, these two conformers were assigned to (ac, ac) and (sp, ac) structures with very similar energies [35]. The geometry of dimethylmalonate was studied also by gas electron diffraction [34]. According to the GED refinement, a mixture of two diketo conformers is present: 69(10)% (ac, ac) conformer with C_2 symmetry (both C=O bonds anticlinal relative to the opposite C–C bond) and 31(10)% (sp, ac) conformer with C_1 symmetry (one C=O bond with synperiplanar, the other C=O bond with anticlinal orientation). Ab initio calculations (at B3LYP and MP2 levels with different basis sets up to cc-pVTZ), however, predict a preference of the (sp, ac) conformer rather than (ac, ac) form [34].

The tautomeric and conformational properties of malonamide (R1 = R2 = NH_2) were studied by different methods. Solid-state Fourier transform infrared and Raman spectra reveal the existence of a diketo tautomer [36]. No enol form is observed for solid malonamide. ^{13}C NMR studies of a solution of malonamide as well show only signals of a diketo tautomer [36]. Several quantum chemical investigations of malonamide have been reported [36–39]. Two stable diketo conformations of malonamide, (sc, ac) and (ac, ap), have been predicted by different computational methods (HF, DFT and MP2) with different basis sets [37]. These authors pointed out that the energy of the (ac, ap) conformer is higher than that of the (sc, ac) form by 4–6 kcal/mol. According

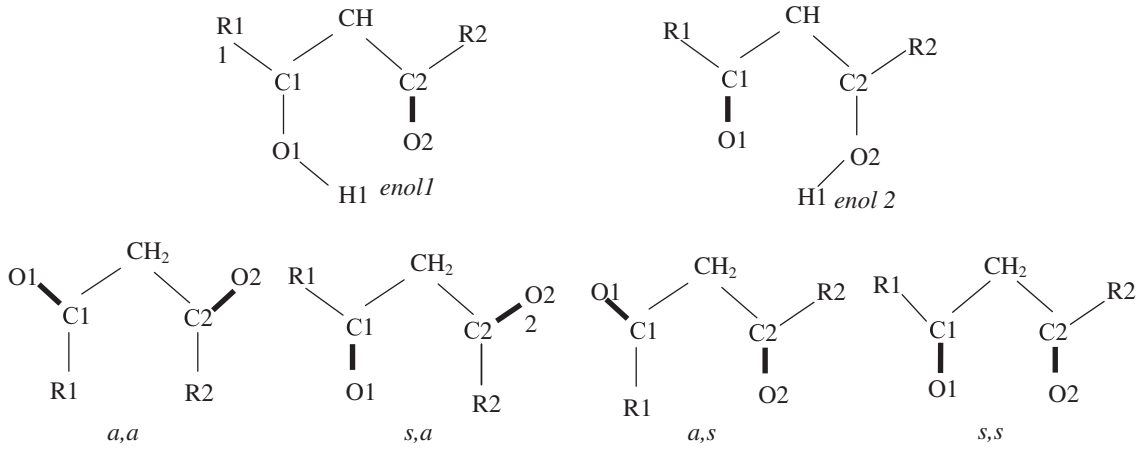

Fig. 1. Enol tautomers (above) and possible conformers of diketo tautomer of R1C(O)–CH_2–C(O)R2 compounds (below). "s" stands for synperiplanar, sp, (which corresponds to dihedral angles τ(O=C–C–C) of 0 ± 30°) or synclinal, sc, (τ(O=C–C–C) = 60 ± 30°) and "a" for anticlinal, ac, (τ(O=C–C–C) = 120 ± 30°) or antiperiplanar, ap, (τ(O=C–C–C) = 180 ± 30°).

to theoretical calculations [36] (HF/6-31G(d) and B3PW91/6-31G(d)) only one stable diketo structure with C_1 symmetry exists. The same result is obtained by B3LYP/6-31G(d,p) calculations [39]. Two stable enol forms, one with O–H···O intramolecular hydrogen bond and the other, so-called "open trans" conformer (with O–H bond located outside the enol ring, but with an N–H···O intramolecular hydrogen bond) are predicted to have much higher energies than the diketo form [36]. Gas electron diffraction data [39] confirm the existence of a single diketo conformer in the vapor of malonamide. According to the GED refinement this conformer possesses (sc, ac) conformation with one C=O bond in synclinal orientation (dihedral angle τ_1(C2CC1O1) = 49.0(3.0)°) and the other C=O bond in anticlinal orientation (dihedral angle τ_2(C1CC2O2) = 139.5(3.3)°).

The analysis of data concerning the tautomeric properties of symmetrically substituted (R1 = R2) β-diketones allows us to subdivide the substituents into two groups. For compounds with R1 = R2 belonging to group I (H, CH_3, $C(CH_3)_3$, CF_3) the enol tautomer is preferred. On the other hand, for compounds with R1 = R2 belonging to group II (F, Cl, NH_2 and OCH_3) only the diketo tautomer is observed. Whereas a single conformer with planar skeleton is expected for the enol form, different conformations are feasible for the diketo tautomer, depending on the relative orientation of C=O bonds (see Fig. 1). The above observation for symmetrically substituted β-diketones arouses great interest in the tautomeric properties of non-symmetrically substituted β-diketones with substituents belonging to different groups.

In methyl acetoacetate (MAA) with R1 = CH_3 and R2 = OCH_3, R1 favours the enol form, whereas R2 favours the keto tautomer. According to ^{1}H NMR and ^{13}C NMR spectra liquid MAA exists exclusively in the keto form [40]. On the other hand vibrational spectra of the liquid obtained in the same study were interpreted in terms of some enol contribution. A further ^{1}H NMR study of MAA [17] shows that exclusively keto form exist in the liquid at room temperature. But at 423 K a mixture of both tautomers with the keto form prevailing is observed in the liquid. Similarly, ^{1}H NMR spectra of gaseous MAA at temperatures between 377 and 417 K are assigned to a mixture of both tautomers, resulting in $\Delta G^0 = G^0$(keto) − G^0(enol) = 0.08 ± 1.45 kcal/mol [17]. Unfortunately, the experimental uncertainty in this NMR study is large, and the result covers a wide range of tautomeric mixtures of enol/keto from 1:13 to 10:1. The tautomeric and conformational properties of gaseous MAA have also been investigated by GED, IR (matrix) spectroscopy and quantum chemical calculations [41]. The IR (matrix) spectrum confirms qualitatively the presence of a mixture of enol and diketo tautomers with the enol form strongly prevailing. The relative energies (ΔE), relative free energies (ΔG^0) and tautomeric composition obtained with different computational methods as well as the GED results are summarized in Table 1. It should be noted, that according to quantum chemical calculations [34,41] only one stable enol form with the O–H bond adjacent to the methyl group exists (CH_3–C(OH)–CH–C(O)–OCH_3). If a starting geometry with the O–H bond adjacent to the methoxy group is used (CH_3–C(O)–CH–C(OH)–OCH_3), the enolic hydrogen atom migrates from the ester group to the acetyl group, and the geometry optimization converges toward the enol form assigned above. For the diketo tautomer the existence of three stable conformers (ac, ac), (ac, sp) and (sc, ac) is predicted by the MP2 method with both basis sets and by the B3LYP method with the small basis set. The B3LYP method with the large basis set results in only two stable conformers for the diketo tautomer. Each method predicts rather similar energies for all diketo conformers, higher than that for the enol tautomer. The predictions of quantum chemical calculations concerning the tautomeric equilibrium depend strongly on the computational method (see Table 1). The analysis of gas electron diffraction data [34] shows that the radial distribution function cannot be reproduced reasonably well with any diketo conformer, and the enol form corresponds much better to the experimental data. However, if the presence of a mixture of enol and diketo tautomer in the vapor is assumed, the agreement between experimental and calculated radial distribution functions is improved. The best agreement factors resulted for a composition of the mixture of 80(7)% enol and 20(7)% keto forms. The GED analysis cannot distinguish between the three diketo conformers predicted by quantum chemical calculations.

Acetoacetamide, CH_3–C(O)–CH_2–C(O)–NH_2, (AAM) as well as methyl acetoacetate has two non-equivalent substituents, R1 = CH_3 which belongs to group I and favours the enol form, and R2 = NH_2 which favours the keto tautomer. Spectroscopic measurements of AAM water solution resulted in an equilibrium constant K_E = [enol]/[keto] = 0.11 which implies a strong preference of the diketo form (90%) [42]. The tautomeric and structural properties of AAM were studied by GED, which was supplemented by quantum chemical calculations [43]. According to quantum chemical calculations, only one stable enol form with the O–H bond adjacent to the methyl group exists, such as in the case of MAA. Furthermore, only a single diketo conformer is present for AAM. The relative energies ($\Delta E = E_{keto} - E_{enol}$) and relative free energies

Table 1
Calculated relative energies and Gibbs free energies and abundance of the enol tautomers of acetoacetamide and methyl acetoacetamide.

Method	$\Delta E = E_{keto} - E_{enol}$ (kcal/mol)			$\Delta G^0 = G^0_{keto} - G^0_{enol}$ (kcal/mol)			Abundance of enol form (%)	Reference
Acetoacetamide (R1 = CH_3, R2 = NH_2)								
MP2/6-31G(d,p)	−2.02			−3.64[a]			0[a]	[43]
MP2/6-311++G(3df,pd)	1.64			−0.44[a]			35[a]	[43]
MP2/aug-cc-pVTZ	2.62			0.87[a]			78[a]	This work
B3LYP/6-31G(d,p)	1.83			0.35[a]			62[a]	[43]
B3LYP/6-311++G(3df,pd)	2.62			1.28[a]			86[a]	[43]
B3LYP/ aug-cc-pVTZ	3.14			1.83[a]			93[a]	This work
GED				0.37(15)[a]			63(7)[a]	[43]
	(ac, ac)	(ac, sp)	(sc, ac)	(ac, ac)	(ac, sp)	(sc, ac)		
Methyl acetoacetate (R1 = CH_3, R2 = OCH_3)								
MP2/6-31G(d,p)	0.79	0.52	0.50	−2.09	−2.19	−2.11	1	[41]
MP2/6-311G(2df)	2.04	2.00	1.86	−0.84	−0.71	−0.75	8	[41]
B3LYP/6-31G(d,p)	5.63	5.42	4.73	2.08	2.25	2.00	92	[41]
B3LYP/6-31++G(3df,pd)	–[b]	5.16	4.76	–[b]	1.34	2.00	87	[41]
B3LYP/aug-cc-pVTZ	–[b]	5.38	5.72	–[b]	2.99	2.87	99	This work
GED				0.85(22)			80(7)	[41]

[a] At 347 K (74 °C).
[b] Not a stable conformer according to this method.

$\Delta G^0 = G^0_{keto} - G^0_{enol}$ obtained with different computational methods are summarized in Table 1. Again, as in the case of MAA, the predictions of quantum chemical calculations concerning the tautomeric equilibrium for AAM depend strongly on the computational method. In the least squares analysis of gas electron diffraction data [43] a mixture of both, diketo and enol forms, was derived. The best agreement between experimental and theoretical radial distribution curves $f(r)$ was obtained for a 37(7)% diketo and 63(7)% enol tautomeric mixture.

Thus, according to the experimental and theoretical data we can conclude exactly that the prevalence of enol or diketo tautomer depends on the nature of the substituents. Symmetrically substituted β-diketones with R1 = R2 belonging to group I (H, CH_3, $C(CH_3)_3$, CF_3) exist in the gas phase mainly in enol form, for β-diketones with R1 = R2 from group II (F, Cl, NH_2 or OCH_3) only diketo tautomer is observed. In the case of non-symmetrically substituted compounds, with R1 and R2 belonging to different groups of substituents, a mixture of both tautomers is expected. Now, the question is, which property of a substituent determines whether it belongs to group I or group II. An intuitive characterization of the substituents would be their electronegativity. Different authors attempted to explain the tautomeric properties of β-diketones by the size or electron-withdrawing and donating character of the substituents [24,44–46]. However, the size of CH_3, belonging to group I, e.g., is very similar to that of NH_2 from group II. Furthermore, the CF_3 group which is well-known as electron-withdrawing favours the enol tautomer as well as the electron-donating methyl group. Although the CF_3 group and Cl possess very similar electronegativities, they belong to different groups. Thus, the rule of thumb to predict tautomeric properties of β-diketones, based on the electronegativities of the substituents, formulated in [43], should be considered as rather crude. Furthermore, group electronegativities depend on the method of their determination and may differ appreciably. An alternative characterization of the substituents is the presence or absence of electron lone pairs. Substituents of group I, which favour the enol tautomer, do not possess any lone pair, whereas substituents of group II, which favour the diketo form, possess one, two or three lone pairs.

To support the understanding of the keto–enol tautomerism in β-diketones and the dependence of keto:enol ratio on the substituents in β-position (R1 and R2), we performed quantum chemical calculations supplemented by NBO-analyses. The substances under investigation possess different kinds of substituents R1 and R2, electron-withdrawing or electron-donating, with or without lone pairs which may be equivalent (R1 = R2) or non-equivalent (R1 ≠ R2).

3. Quantum chemical calculations

3.1. Computational details

All quantum chemical calculations in the present study were performed using the PC GAMESS program [47]. Hybrid density functional B3LYP [48–50] and Dunning et al. augmented correlation consistent basis sets (aug-cc-pVTZ) with one diffuse function of each angular momentum type (s, p, d, f) [51,52] were used. The properties of acetoacetamide were calculated also at the MP2/aug-cc-pVTZ level. All electrons were taken into account in the MP2 calculation.

Geometric parameters of the enol form and all possible keto conformers obtained by rotation of the –C(R1,R2)═O fragments around the C–C bond were optimized. Harmonic vibrational frequencies were calculated for all optimized geometries in order to confirm that they correspond to a stationary point and to calculate zero point energy (ZPE) corrections and mole fractions of the conformers in the gas phase at different temperatures. The thermodynamic functions required to calculate the mole fractions were estimated with the harmonic oscillator–rigid rotator approximation to the partition function.

The NBO 5G program [53], implemented for natural orbital analysis in PC GAMESS, was used to obtain net atomic charges, Wiberg bond orders and to study the effect of hyperconjugation on the structure of the considered molecules. A visualization of the natural bond orbitals was performed using ChemCraft program [54].

3.2. Results and discussion

3.2.1. Tautomeric composition

The relative energies $\Delta E = E_{keto} - E_{enol}$ obtained in this study are presented in the Tables 2 and 3 along with optimized geometries and abundances of stable conformers derived from calculated free energy differences ΔG^0. The comparison of data from Tables 2 and 3 with experimental observations shows, that in all cases the calculations at B3LYP/aug-cc-pVTZ level predict the main tautomer correctly. The values of relative energies and abundances of tautomeric forms confirm our conclusion that the enol form is preferred

Table 2
Optimized geometries of enol end keto form for symmetrically substituted β-diketones. (Å, °).

	R1 = H R2 = H		R1 = CH_3 R2 = CH_3	R1 = CF_3 R2 = CF_3		R1 = Cl R2 = Cl			R1 = F R2 = F			R1 = OCH_3 R2 = OCH_3		R1 = NH_2 R2 = NH_2
Enol 1														
r(C1–C)	1.361		1.367	1.358		1.363			1.358			1.371		1.378
r(C2–C)	1.434		1.440	1.438		1.432			1.428			1.427		1.433
r(O1–C1)	1.318		1.324	1.314		1.309			1.300			1.317		1.320
r(O2–C2)	1.238		1.245	1.228		1.213			1.212			1.244		1.256
r(O1–H1)	1.000		1.006	0.995		0.997			0.998			1.015		1.022
r(O2···H1)	1.675		1.615	1.700		1.707			1.722			1.590		1.547
r(O1···O2)	2.571		2.533	2.579		2.590			2.602			2.522		2.418
∠O1C1R1	113.6		114.0	112.2		113.5			112.3			116.4		113.7
∠O2C2R2	119.0		119.8	118.8		119.4			119.1			121.2		118.8
∠C1CC2	119.6		120.8	118.5		117.5			116.6			117.9		118.7
∠H1O1C1	106.2		105.9	107.0		106.5			106.2			104.8		104.6
Abundance, %	100		100	100		0			0			0		0
	sc, ac	ac, sp	sc,sc	ac, ac	ac, sp	ac, ac	ac, sp	sp, sp	ac,ac	ac, sp	sp, sp	ac, ac	ac, sp	sc, ac
Ketone														
r(C1–C)	1.516	1.512	1.533	1.526	1.517	1.516	1.515	1.514	1.509	1.507	1.507	1.517	1.513	1.520
r(C2–C)	1.523	1.512	1.533	1.526	1.522	1.516	1.513	1.513	1.509	1.508	1.507	1.517	1.518	1.536
r(O1–C1)	1.204	1.204	1.209	1.195	1.195	1.180	1.180	1.176	1.179	1.180	1.177	1.203	1.204	1.223
r(O2–C2)	1.201	1.203	1.209	1.195	1.195	1.180	1.179	1.176	1.179	1.179	1.177	1.203	1.203	1.218
∠O1C1R1	120.9	121.2	123.1	120.0	120.3	121.4	121.5	121.2	121.3	121.4	121.2	124.1	124.4	121.9
∠O2C2R2	121.7	120.8	123.1	120.0	120.3	121.4	121.4	121.2	121.3	121.4	121.2	124.1	124.2	124.3
∠C1CC2	110.5	114.5	108.4	116.3	111.8	114.7	112.1	114.4	113.9	112.5	114.3	114.3	111.8	116.1
∠O1C1C	123.1	123.2	120.6	124.1	124.0	126.3	125.9	128.3	128.2	127.9	129.5	124.9	124.5	122.6
∠O2C2C	123.7	124.7	120.6	124.1	125.4	126.3	127.7	128.3	128.3	129.3	129.5	125.0	125.8	120.1
O1C1CC2	68.4	132.2	89.1	115.8	89.9	125.7	100.7	23.5	132.6	109.6	27.0	130.1	96.7	49.5
O2C2CC1	128.7	2.2	89.1	115.8	5.5	125.7	4.0	22.5	132.4	3.5	27.2	129.2	2.0	143.6
r(O1···H)														2.030
$\Delta E = E_{keto} - E_{enol}$ (kcal/mol)	8.71	8.91	6.43	9.94	8.72	−2.18	−2.75	−1.94	−3.58	−3.97	−2.82	−5.94	−6.15	−6.06
Abundance (%)	0	0	0	0	0	13.9	42.5	43.6	25.3	36.4	38.3	62.0	38.0	100

Table 3
Optimized geometries of enol end keto form for non-symmetrically substituted β-diketones. (Å, °).

	R1 = CH_3 R2 = F			R1 = CH_3 R2 = Cl			R1 = CH_3 R2 = OCH_3		R1 = CH_3 R2 = NH_2	R1 = CF_3 R2 = NH_2	R1 = $C(CH_3)_3$ R2 = NH_2
Enol 1											
r(C1–C)	1.364			1.367			1.360		1.360	1.349	1.362
r(C2–C)	1.430			1.430			1.443		1.451	1.461	1.452
r(O1–C1)	1.328			1.327			1.332		1.329	1.321	1.331
r(O2–C2)	1.209			1.211			1.233		1.247	1.244	1.247
r(O1–H1)	0.987			0.987			0.992		1.002	1.005	1.004
r(O2···H1)	1.764			1.760			1.706		1.638	1.639	1.616
r(O1···O2)	2.634			2.626			2.595		2.550	2.545	2.536
∠O1C1R1	113.5			113.5			113.4		113.7	112.3	113.2
∠O2C2R2	118.8			119.0			121.9		119.9	120.8	119.7
∠C1CC2	119.6			119.7			120.3		120.3	118.7	120.4
∠H1O1C1	108.1			108.2			106.9		106.0	105.2	106.2
Abundance, %	99.7			99.8			98.6		96.6	99.9	95.3
	ac, ac	ac, sp	sp, ac	ac, ac	ac, sp	sp, ac	ac, sc	sp, ac	sc, ac	sc, ap	sc, ac
Ketone											
r(C1–C)	1.546	1.533	1.536	1.548	1.535	1.538	1.538	1.532	1.522	1.507	1.526
r(C2–C)	1.498	1.502	1.501	1.502	1.507	1.505	1.517	1.510	1.534	1.538	1.536
r(O1–C1)	1.204	1.207	1.205	1.204	1.207	1.204	1.208	1.206	1.215	1.203	1.215
r(O2–C2)	1.182	1.182	1.181	1.182	1.181	1.179	1.207	1.204	1.218	1.215	1.218
∠O1C1R1	123.2	123.1	123.1	123.3	123.1	123.2	123.1	122.5	121.5	118.9	121.6
∠O2C2R2	120.1	120.3	120.8	120.3	120.3	120.8	123.9	124.3	123.9	124.1	123.8
∠C1CC2	114.7	114.5	112.4	114.7	114.0	112.5	111.4	112.3	118.7	118.7	116.1
∠O1C1C	119.2	119.3	121.5	119.0	119.3	121.6	120.0	122.1	122.4	126.2	119.9
∠O2C2C	129.4	129.9	128.5	127.7	128.4	127.2	124.8	124.4	119.9	119.1	120.4
O1C1CC2	146.9	116.0	6.6	145.9	114.1	14.3	105.4	8.0	35.9	31.5	49.8
O2C2CC1	105.9	5.3	103.8	100.4	3.4	99.9	62.3	92.5	146.3	150.7	136.5
r(O1···H)									2.023	2.074	2.071
$\Delta E = E_{keto} - E_{enol}$ (kcal/mol)	7.04	6.72	7.00	7.01	6.77	7.20	5.38	5.72	3.14	5.57	2.76
Abundance (%)	0.1	0.1	0.1	0.05	0.1	0.05	0.6	0.8	3.4	0.1	4.7

for symmetrically substituted β-diketones with R1 = R2 belonging to group I (H, CH_3, CF_3), whereas for β-diketones with R1 = R2 from group II (F, Cl, NH_2 or OCH_3) the diketo tautomer possesses lower energy. The calculated abundances for non-symmetrically substi-

tuted molecules with R1 belonging to group I and R2 belonging to group II show a strong preference of the enol tautomer. However, as was mentioned in [43], B3LYP method with large basis sets rather overestimates the enol contribution.

It should be noted, that the prediction of exact tautomeric composition, especially for the β-diketones with R1 and R2 belonging to different groups is the most difficult problem. Table 1 summarizes the data of quantum chemical calculations at different theoretical levels for methyl acetoacetate (MAA) with R1 = CH_3 and R2 = OCH_3 and acetoacetamide (AAM) with R1 = CH_3 and R2 = NH_2. Data in Table 1 demonstrate that the experimental (GED) tautomeric composition is reproduced perfectly by the B3LYP method with large basis sets in the case of MAA and with small basis sets for AAM. Thus, a priori, it is impossible to predict which method has to be used for the calculations of the tautomeric composition of such compounds. It should be pointed out that differences between ΔE and ΔG^0 values are unusually large for these tautomeric systems. Although ΔE values from the B3LYP method and the MP2 approximation with large basis sets possess the correct sign, the corresponding ΔG^0 values in most cases do not predict the correct tautomeric composition. However, we should note that the MP2/6-31G(d,p) method strongly underestimates the enol contribution compared to results derived from GED experiments [41,55,56]. It was also pointed out by G. Fogarasi [57] that theoretical predictions of the enol–keto tautomeric equilibrium for different systems including malonaldehyde depend strongly on computational methods and basis sets. At the same time it was mentioned [39,41] that calculations at different levels predict the structural parameters quite well in most cases.

3.2.2. Molecular parameters

The optimized geometries of keto- and enol forms under investigation are summarized in Tables 2 and 3. The enol form in all cases possesses a planar O2═C2–C–C1–O1–H skeleton with similar structure. Some differences in parameters cannot be related to the type of substituents. In all calculated enol forms the enolic hydrogen is bonded to one of the oxygen atoms. In the case of non-symmetrical substituted molecules, the O1–H bond is adjacent to the substituent from group I (H, CH_3, CF_3, $C(CH_3)_3$). The distances r(O2···H) vary from 1.547 to 1.764 Å, confirming the existence of a strong intramolecular hydrogen bond. The stable diketo conformers are characterized by common features. In each case one or both C═O bonds nearly eclipse C–H bonds of the methylene group. Hence, in the case of R1 = R2 usually two different keto conformers exist, whereas there are three keto conformers for R1 ≠ R2. But in the cases of R1 = R2 = Cl or F also a so-called U-*cis* (sp, sp) conformer is stable. It should be noted that in the case of acetylacetone (R1 = R2 = CH_3) only one stable keto conformer exists instead of two expected forms and only two keto conformers of methyl acetoacetate (R1 = CH_3, R2 = OCH_3) exist instead of three expected forms. This has already been mentioned in [41]. For β-diketones with R2 = NH_2 only one stable keto form exists. Obviously, these keto forms are stabilized by a weak intramolecular N–H···O1 hydrogen bond.

The calculated geometries of β-diketones can be compared with the structural parameters obtained from available GED studies (and microwave in the case of malonaldehyde). The important experimental values for preferred conformers are summarized in the Table 4. We note good agreement between calculated and experimental parameters in most cases. However, some discrepancies should be mentioned. As noted above, four independent GED studies of acetylacetone resulted in rather different vapor compositions as well as geometries of the predominant enol form. Differences in some bond distances and bond angles are larger than their experimental uncertainties. This is not surprising, since two GED studies resulted in C_{2v} structures of the enol form,

Table 4
The experimental and calculated geometrical parameters of the main tautomers of β-diketones (Å, °).

R_1, R_2	$r(C_1–C)$	$r(C_2–C)$	$r(O_1–C_1)$	$r(O_2–C_2)$	r(O...O)	$\angle C_1CC_2$	$\angle O_1C_1R_1$	$\angle O_2C_2R_2$	% of enol	Reference
Main tautomer is enol										
–H, –H	1.348	1.454	1.320	1.234	2.553	119.4	113.2	119.4	100	(MW)[a] [6]
	1.361	1.434	1.318	1.238	2.571	119.6	113.6	119.0	100	Calc., this work
–CH_3, –CH_3	1.416(10)		1.315(7)		2.381	118.0(2.5)	120.0(1.3)		66(5)	(r_g), [19]
	1.405(5)		1.287(5)		2.519(24)	118.3(1.8)	114.8		100	(r_g), [20]
	1.382(7)	1.430(8)	1.319(3)	1.243(2)	2.512(8)	119.7(5)	114.9	118.9	100	(r_g), [21]
	1.359(34)	1.443(19)	1.321(21)	1.262(5)	2.592	120.4(1.0)	112.9(2.7)	118.7(3.1)	78(4)	(r_e), [22]
	1.367	1.440	1.324	1.245	2.533	120.8	114.0	119.8	100	Calc., this work
–CF_3, –CF_3	1.4065(0.0102)		1.2591(0.0061)			115.2(0.8)	113.9		100	(r_g), [26]
	1.422(6)		1.261(4)		2.606(13)	114.9(0.5)	113.9		100	(r_g), [25]
	1.358	1.438	1.314	1.228	2.579	118.5	112.2	118.8	100	Calc., this work
–CH_3, –OCH_3	1.362(4)	1.449(4)	1.339(4)	1.248(4)	2.627(15)	120.0(1.4)	110.9	123.3	80(7)	(r_{h1}) [41]
	1.360	1.443	1.332	1.233	2.595	120.3	113.4	121.9	98.6	Calc., this work
–CH_3, –NH_2	1.375(5)	1.466(5)	1.326(3)	1.245(3)	2.530(44)	119.9(2.1)	114.6	122.2	63(7)	(r_{h1}) [43]
	1.360	1.451	1.329	1.247	2.550	120.3	113.7	119.9	96.6	Calc., this work

R_1, R_2	r(C–C)	r(O–C)	∠OCR	∠OCC	$\angle C_1CC_2$	$\angle O_1C_1CC_2$	$\angle O_2C_2CC_1$	% of main conformer	Reference
Main tautomer is ketone[b]									
–F, –F	1.502(5)	1.177(3)	121.2(1.1)	129.1(0.8)	110.2(1.0)	112.0(2.0)	0.0	90(10)	(r_a) [31]
	1.507 ÷ 1.509	1.177 ÷ 1.180	121.2 ÷ 121.4	127.9 ÷ 129.5	112.5 ÷ 114.3	27.0	27.0	38	Calc., this work
–Cl, –Cl	1.498(5)	1.197(2)	120.0(0.6)	125.8(0.4)	107.2(1.6)	95(6)	12(5)	70(15)	(r_a), [32]
	1.513 ÷ 1.516	1.176 ÷ 1.180	121.2 ÷ 121.5	126.3 ÷ 128.3	112.1 ÷ 114.7	23.5	22.5	44	Calc., this work
–OCH_3, –OCH_3	1.518(4)	1.218(3)	124.3	125.9(1.0)	112.1(1.5)	122.8(2.4)	122.8(2.4)	69(10)	(r_{h1}) [34]
	1.513 ÷ 1.518	1.203 ÷ 1.204	124.1 ÷ 124.4	124.5 ÷ 125.8	111.8 ÷ 114.3	130.1	129.2	62	Calc., this work
–NH_2, –NH_2	1.523(3)	1.224(3)	122.6	122.0(0.5)	114.7(1.0)	49.0(3.3)	139.5(3.3)	100	(r_{h1}) [39]
	1.539(3)	1.218(3)	125.0	119.5(0.5)					
	1.520; 1.536	1.223; 1.218	121.9; 124.3	122.6; 120.1	116.1	49.5	143.6	100	Calc., this work

[a] The structure of trideuterio species of MDA.
[b] The range of bond distances and bond angles in all keto conformers is given. The torsional angles are only for the main conformer.

whereas our calculations result in C_S symmetry. The same situation occurs in the case of hexafluoroacetylacetone. Although the experimental geometries (C_{2v} symmetry) of the two independent GED studies are close to each other, they differ from the calculated geometry (C_S symmetry). The difference between experimental and calculated r(C–C) distances in malonaldehyde is probably due to an experimental inaccuracy. As noted by the authors of [6], the central C atom is located very close to a rotational axis, preventing an accurate determination of its position from rotational constants. For β-diketones, which exist in keto form, the main differences of calculated and experimental values are observed for dihedral angles. The most pronounced differences are in the cases of F–C(O)–CH_2–C(O)–F and Cl–C(O)–CH_2–C(O)–Cl. In both cases calculations predict the (sp, sp) conformer to be most preferred, whereas GED studies result in a mixture of (ac, sp) and (ac, ac) conformers with the predominance of the former. However, we note that the calculated energies of (ac, sp) and (sp, sp) conformers are rather similar for both molecules.

Table 5 summarizes calculated and experimental geometric parameters of the substituents (optimized parameters are given both for keto and enol forms). The calculated values of bond lengths and bond angles of a certain substituent are rather similar in different molecules and different tautomeric forms and are in a good agreement with the experimental values.

In most cases the symmetry of CX_3 groups in the enol form is C_S. We can note that the differences in r(C–H) in CH_3 groups are small (not more than 0.006 Å) as well as the differences in the CCH angles. Therefore, C_{3v} symmetry of the methyl groups could be assumed even for CH_3 in OCH_3 or *tert*-butyl groups. However, in the case of the CF_3 group the differences in r(C–F) indicate a large deviation from C_{3v} symmetry.

Table 5
Optimized and experimental geometrical parameters of the substituents in β-diketones (Å, °).

	Calculation[a]	Experiment[b]
CH_3		
r(C–H)	1.086 ÷ 1.094	1.090 ÷ 1.109
∠HCH	106.6 ÷ 111.0	108.0 ÷ 109.3
∠HCC_n[c]	109.2 ÷ 111.6	109.0 ÷ 111.6
r(C–Cn)	1.490 ÷ 1.511	1.470 ÷ 1.510
NH_2		
r(N–H)	1.003 ÷ 1.011	1.005 ÷ 1.013
∠HNH	117.3 ÷ 120.9	119.0 ÷ 120.8
∠HNCn	117.1 ÷ 122.3	118.0 ÷ 122.3
r(N–Cn)	1.351 ÷ 1.356	1.354 ÷ 1.364
$C(CH_3)_3$		
r(C–H)	1.088 ÷ 1.091	1.129(5)
r(C–C)	1.533 ÷ 1.544	1.558(4)
∠HCH	107.5 ÷ 108.5	108.8
∠HCC	109.3 ÷ 112.6	110.1(6)
∠CCC	109.2 ÷ 109.9	110.9
∠CCCn	108.3 ÷ 112.4	108.0(2)
r(C–Cn)	1.520 ÷ 1.535	1.526(4)
CF_3		
r(C–F)	1.325 ÷ 1.352	1.337 ÷ 1.341
∠FCF	107.6 ÷ 108.9	108.0 ÷ 108.3
∠FCCn	108.6 ÷ 112.0	110.6 ÷ 110.9
r(C–Cn)	1.519 ÷ 1.560	1.541 ÷ 1.546
OCH_3		
r(C–H)	1.085 ÷ 1.089	1.085 ÷ 1.098
∠HCH	109.1 ÷ 110.8	109.5 ÷ 110.0
∠HCO	105.0 ÷ 110.7	108.0 ÷ 108.4
∠COCn	115.8 ÷ 118.5	113.3 ÷ 116.6
r(C–O)	1.436 ÷ 1.441	1.437 ÷ 1.440
r(Cn–O)	1.343 ÷ 1.346	1.347 ÷ 1.355
r(C1–O)[d]	1.328	
X (F, Cl)		
r(Cn–F)	1.347 ÷ 1.366	1.349(4)
r(C1–F)[d]	1.316	
r(Cn–Cl)	1.819 ÷ 1.823	1.772(2)
r(C1–Cl)[d]	1.725	

[a] Optimized with B3LYP/aug-ccPVTZ (this work).
[b] Experimental values are from the GED studies: [19–22,41,43] – for CH_3, [25,26] – for CF_3, [39,43] – for NH_2, [34,41] – for OCH_3, [27] – for $C(CH_3)_3$ and [31,32] – for F, Cl.
[c] Cn – C1 or C2.
[d] The r(C1–O), r(C1–F) and r(C1–Cl) values are to the enol form.

3.2.3. NBO-analysis

3.2.3.1. Bond orders and charge analysis. The calculated Wiberg bond orders along with the net atomic charges for all studied β-diketones are summarized in Tables 6 and 7. Since the values for different keto conformers are very similar, only the values of energetically preferred conformer are given. The C–C and C–O bond orders in the enol form, as well as the values of the distances from Tables 2 and 3 show that these bonds do not correspond to exact single or double bonds. This confirms the existence of π-conjugation in the enol rings [3]. The bond orders in the keto forms correspond to the single C–C and double C═O bonds.

The analysis of the data in Tables 6 and 7 shows that in general the substituents exert a small influence on the net atomic charge distribution in the carbon–oxygen skeleton C1(O1)–C–C2(O2). Only the charges on C1 or C2 atoms depend on the nature of corresponding substituents – R1 or R2. Furthermore, the charges of the substituents are small and do not depend strongly on their nature and electronegativity. So, we hardly can explain tautomeric properties of β-diketones by the electronegativity of the substituents.

3.2.3.2. Electron delocalization. The delocalization of electron density between occupied Lewis type (bonds or lone pairs) NBO orbitals and formal unoccupied (antibonds) non-Lewis NBO orbitals corresponds to a stabilizing donor–acceptor interaction. The energy of these interactions can be estimated by the second order perturbation theory. Tables 8 and 9 collect the largest values of calculated second order interaction energies (E^2) between donor and acceptor orbitals in investigated molecules.

For the enol form the largest values correspond to the interactions related to the resonance in the enol ring, i.e. the interactions between π(C1–C) and π*(C2–O2) and between Lp(2)O1 and π*(C1–C). Figs. 2 and 3 present such kinds of interactions for the orbitals of acetylacetone. Furthermore, we can see (in Table 8 and Fig. 4) that the interaction between the lone pair of the other oxygen atom Lp(2)O2 and the O–H anti-bonding orbital σ*(O1–H1) yields a strong hydrogen bond.

On the other hand, NBO-analysis demonstrates that in the case of β-diketones with substituents from group II, which contain lone pairs at the atom connected to C1 or C2, a very strong interaction exists between the lone pair of the substituent Lp(2)R and the anti-bonding π*(C–O) natural orbital. Such kind of interaction can occur only in the case of a C═O double bond. Thus, this hyperconjugation stabilizes the keto form. Furthermore, we note that the interaction between the lone pair of oxygen Lp(2)O and the anti-bonding σ*(C–R) natural orbital is slightly stronger in the case of substituents from group II. Consequently, this interaction additionally stabilizes the R–C═O fragment if R contains a lone pair, in comparison to substituents without lone pairs. Figs. 5 and 6 present such interactions for malonyl dichloride. Thus, the presence of two substituents with electron lone pairs leads to strong preference of the keto tautomer compared to the enol form.

The lone pairs of the substituents possess influence also on the geometrical parameters of the molecules. Thus, it is very interesting to note the E^2 values of interactions between Lp(R1) and σ*(C1–O1) in the enol form which are significant only for R1 = F, Cl and OCH_3, which possess more than one lone pair at the atom

Table 6
Net atomic charges (q, ē) and Wiberg bond orders (Q) for enol and most preferable keto forms of symmetrically substituted β-diketones.

	R1 = H R2 = H	R1 = CH_3 R2 = CH_3	R1 = CF_3 R2 = CF_3	R1 = Cl R2 = Cl	R1 = F R2 = F	R1 = OCH_3 R2 = OCH_3	R1 = NH_2 R2 = NH_2
Enol 1							
q(C1)	0.298	0.466	0.363	0.411	0.811	0.721	0.590
q(C2)	0.375	0.532	0.444	0.508	0.844	0.753	0.624
q(C)	−0.463	−0.471	−0.422	−0.483	−0.559	−0.524	−0.542
q(O1)	−0.631	−0.655	−0.608	−0.629	−0.629	−0.676	−0.674
q(O2)	−0.610	−0.635	−0.556	−0.584	−0.609	−0.692	−0.702
q(R1)	0.176	0.035	0.023	0.059	−0.295	−0.154	0.005
q(R2)	0.127	0.008	−0.01	−0.051	−0.334	−0.181	0.015
q(H1)	0.506	0.506	0.514	0.516	0.522	0.515	0.509
Q(C1–C)	1.600	1.553	1.592	1.542	1.536	1.479	1.448
Q(C2–C)	1.212	1.189	1.178	1.185	1.175	1.199	1.193
Q(O1–C1)	1.199	1.173	1.191	1.174	1.191	1.152	1.157
Q(O2–C2)	1.642	1.588	1.675	1.663	1.670	1.503	1.454
Q(O1–H1)	0.634	0.615	0.636	0.630	0.632	0.595	0.585
Q(O2···H1)	0.093	0.110	0.080	0.076	0.078	0.121	0.142
	sc, ac	sc, sc	ac, sp	ac, sp	ac, sp	ac, sp	sc, ac
Ketone							
q(C1)	0.442	0.599	0.514	0.570	0.886	0.805	0.668
q(C2)	0.451	0.599	0.516	0.576	0.886	0.806	0.667
q(C)	−0.593	−0.579	−0.604	−0.600	−0.629	−0.577	−0.568
q(O1)	−0.509	−0.543	−0.447	−0.462	−0.491	−0.581	−0.643
q(O2)	−0.499	−0.543	−0.454	−0.464	−0.491	−0.581	−0.619
q(R1)	0.110	0.039	−0.029	−0.075	−0.344	−0.183	0.007
q(R2)	0.117	0.039	−0.026	−0.081	−0.347	−0.188	0.011
Q(C1–C)	0.989	0.959	0.979	0.979	0.979	0.967	0.977
Q(C2–C)	0.978	0.959	0.978	0.988	0.980	0.964	0.951
Q(O1–C1)	1.885	1.826	1.919	1.914	1.917	1.767	1.645
Q(O2–C2)	1.896	1.826	1.909	1.912	1.917	1.765	1.677
Q(O1···H)							0.020

Table 7
Net atomic charges (q, ē) and Wiberg bond orders (Q) for enol and most preferable keto forms of non-symmetrically substituted β-diketones.

	R1 = CH_3 R2 = F	R1 = CH_3 R2 = Cl	R1 = CH_3 R2 = OCH_3	R1 = CH_3 R2 = NH_2	R1 = CF_3 R2 = NH_2	R1 = $C(CH_3)_3$ R2 = NH_2
Enol 1						
q(C_1)	0.468	0.474	0.447	0.445	0.323	0.470
q(C_2)	0.843	0.518	0.760	0.629	0.629	0.632
q(C)	−0.501	−0.478	−0.468	−0.472	−0.420	−0.480
q(O1)	−0.648	−0.643	−0.663	−0.666	−0.636	−0.677
q(O2)	−0.605	−0.583	−0.669	−0.684	−0.667	−0.684
q(R1)	0.047	0.050	0.036	0.032	0.004	0.017
q(R2)	−0.346	−0.084	−0.178	0.002	0.025	0.002
q(H1)	0.510	0.508	0.509	0.508	0.513	0.507
Q(C1–C)	1.571	1.546	1.603	1.604	1.661	1.606
Q(C2–C)	1.168	1.198	1.134	1.121	1.088	1.122
Q(O1–C1)	1.154	1.158	1.139	1.150	1.161	1.136
Q(O2–C2)	1.689	1.680	1.570	1.509	1.527	1.506
Q(O1–H1)	0.659	0.661	0.647	0.624	0.619	0.618
Q(O2···H1)	0.061	0.059	0.076	0.101	0.101	0.107
	ac, sp	ac, sp	ac, sc	sc, ac	sc, ap	sc, ac
Ketone						
q(C1)	0.595	0.596	0.600	0.602	0.516	0.626
q(C2)	0.888	0.584	0.801	0.667	0.667	0.671
q(C)	−0.610	−0.596	−0.575	−0.585	−0.595	−0.587
q(O1)	−0.521	−0.518	−0.531	−0.571	−0.501	−0.580
q(O2)	−0.516	−0.486	−0.601	−0.616	−0.600	−0.614
q(R1)	0.005	0.003	0.003	0.005	−0.028	−0.003
q(R2)	−0.354	−0.103	−0.176	0.007	0.012	0.002
Q(C1–C)	0.963	0.955	0.957	0.993	1.013	0.985
Q(C2–C)	0.996	1.009	0.968	0.955	0.947	0.951
Q(O1–C1)	1.852	1.853	1.841	1.791	1.854	1.767
Q(O2–C2)	1.893	1.895	1.740	1.678	1.690	1.681
Q(O1···H)				0.019	0.014	0.016

connected with C1. This interaction can rationalize the shortening of the C1–X bond length in the enol form in comparison with C2–X or C–X in the keto tautomers (see Table 5). The presence of only one lone pair in case of R1 = NH_2 in malonamide does not allow

Table 8
Selected second order perturbation energies E^2 (kcal/mol) for enol form.

R1	π(C1–C) ÷ π*(C2–O2)	Lp2(O1) ÷ π*(C1–C)	π(C1–C) ÷ π*(C1–C)	Lp(R1) ÷ π*(C1–C)	Lp(R1) ÷ σ*(C1–O1)	Lp2(O2) ÷ σ*(C2–C)	Lp2(O2) ÷ σ*(C2–R2)	Lp2(O2) ÷ σ*(O1–H1)	Lp(R2) ÷ π*(C2–O2)	R2
H	31.86	47.73				11.77	18.81	22.14		H
CH_3	33.31	49.53				10.59	18.61	28.70		CH_3
CF_3	30.54	49.22				12.70	26.77	18.65		CF_3
Cl	30.71	49.12	7.95	18.71	8.37	12.69	42.70	17.64	19.89	Cl
F	32.35	52.08	10.17	27.22	11.37	12.59	39.14	17.73	29.78	F
OCH_3	35.61	48.46	10.92	40.48	8.47	9.82	27.33	31.24	48.60	OCH_3
CH_3	35.13	47.88				12.61	45.71	13.56	18.47	Cl
CH_3	33.29	47.83				12.73	40.76	14.05	28.60	F
CH_3	30.08	46.05				12.33	29.65	17.94	48.98	OCH_3
CH_3	28.19	47.87				11.18	22.30	25.35	61.75	NH_2
CF_3	23.06	48.00				11.75	22.45	25.34	65.30	NH_2
$C(CH_3)_3$	28.60	47.09				10.80	21.99	27.59	61.57	NH_2
NH_2	28.00	49.05		44.50		6.19	20.64	38.60	43.32	NH_2

Table 9
Selected second order perturbation energies E^2 (kcal/mol) for diketo forms.

R1	Lp2(O1) ÷ σ*(C1–C)	Lp2(O1) ÷ σ*(C1–R1)	Lp(R1) ÷ π*(C1–O1)	Lp2(O2) ÷ σ*(C2–C)	Lp2(O2) ÷ σ*(C2–R2)	Lp2(O1) ÷ σ*(N–H)	Lp(R2) ÷ π*(C2–O2)	R2
H	20.77	22.76		21.78	22.48			H
CH_3	23.17	20.51		23.17	20.51			CH_3
CF_3	21.74	31.24		23.55	31.43			CF_3
Cl	20.32	52.86	19.54	19.06	51.86		20.24	Cl
F	21.11	46.60	29.60	19.58	46.58		30.33	F
OCH_3	22.22	32.96	49.49	20.32	33.35		50.12	OCH_3
CH_3	23.46	20.57		18.48	53.83		18.76	Cl
CH_3	23.46	20.60		19.50	46.36		29.15	F
CH_3	23.70	20.33		20.20	32.50		48.54	OCH_3
CH_3	20.57	20.49		22.18	23.84	3.75	53.58	NH_2
CF_3	19.31	30.04		23.03	23.97	0.81	53.52	NH_2
$C(CH_3)_3$	20.35	20.11		22.37	23.75	2.73	53.36	NH_2
NH_2	19.24	24.47	57.06	22.49	23.76	3.39	32.39	NH_2

such kind of interaction and the C1–N bond length is not very different from *r*(C2–N).

As mentioned above, for β-diketones with R1 from group I and R2 from group II, only one enol form exists (enol I on Fig. 1). The NBO-analysis offers an explanation for this observation. Enol I has the same fragment R2–C═O as in the keto form, containing R2 with lone pairs. Thus, the same type of hyperconjugation as in keto form is possible, i.e. interaction between lone pair of a substituent (R2) with the anti-bonding natural orbital π*(C2–O2). The preference of the enol tautomer in all non-symmetrically substituted β-diketones could be connected with the presence of considerable π-resonance in the ring and strong hydrogen bonding.

We should note that in the case of non-symmetrically substituted β-diketones the prediction of exact tautomeric composition is not easy. Apparently, the interactions mentioned above should lead to a strong preference of the enol form. However, the experimental studies of acetoacetamide and methyl acetoacetate result in the existence of a mixture of both tautomers in the vapor. Different levels of quantum chemical calculations with B3LYP and MP2 approximations lead to contradictive results concerning the tautomeric composition (see above). Obviously, for reliable predictions of the exact abundance of tautomers the electron density distribution should be derived more precisely applying higher level calculations than B3LYP and MP2.

3.2.4. Intramolecular hydrogen bond in the enol form

The strength of intramolecular hydrogen bond in the enol form of β-diketones is widely discussed (see e.g. [58–61]). Several authors tried to explain the π-conjugation in enol ring by the strong hydrogen bond [62,63]. The supposition about the influence of electronegativity of the substituents on the strength of a hydrogen bond is very popular [64,65]. The authors of [3,66] have pointed out that no easy way for direct measurement of the energy of a hydrogen bond, E(OHO), exists. Usually the calculated difference in energy between the open and closed enol form is considered as E(OHO). Emsley [3] notes that the best experimental source for estimating differences in E(OHO) is the well-tested linear correlation between the hydrogen bond energy and the IR shift $\Delta\omega$ (OH).

The Table 10 summarizes the calculated values which characterize the hydrogen bond in the enol forms of the molecules under investigation. Strong correlations between several values exist. Thus, the lengthening of the *r*(O···O) distance is accompanied by a shortening of the *r*(O1–H1) bond length and lengthening of the *r*(O2···H1) distance is paralleled with a decrease of the bond order *Q*(O2···H1). Furthermore, the values of E^2(Lp(2)O2 → σ*(O1–H1)) are decreasing and this confirms weakening of the hydrogen bond in this sequence. The increase of frequencies ω(O–H) in this row is also evidence for strengthening of the O–H bond with simultaneous weakening of the intramolecular hydrogen bond. At the same time, the values of net atomic charges of both oxygen atoms and of enolic H1 and of central C do not correlate with values, which characterized the hydrogen bond. Moreover, the strength of the hydrogen bond does not depend on the electronegativities of substituents. According to the data from Table 10 the nature of substituents affects slightly only the charges of neighboring atom C1 or C2 and, obviously, have no long-distance influence on the properties of the hydrogen bond in contrast to the opinion of the authors [45,64]. Furthermore, Emsley [3] supposes that the strength of the hydrogen bond determines the keto ↔ enol equi-

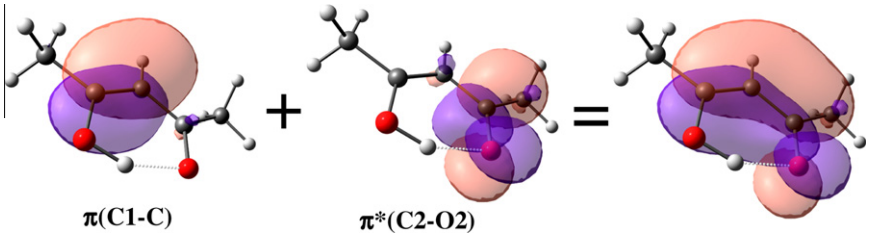

Fig. 2. The hyper conjugation between π(C1–C) and π*(C2–O2) in acetylacetone.

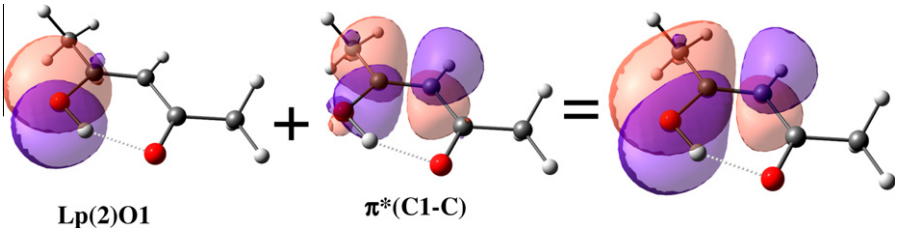

Fig. 3. The hyper conjugation between lone pair of O1 and π*(C1–C) in acetylacetone.

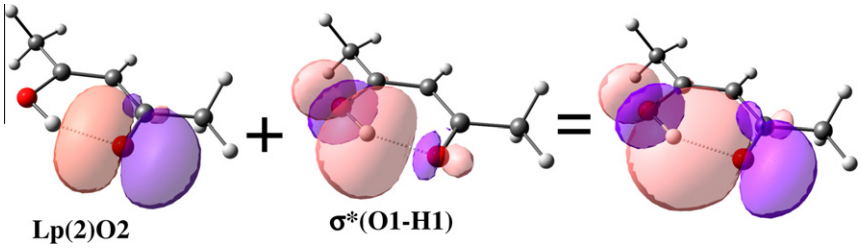

Fig. 4. The hyper conjugation between lone pair of O2 and σ*(O1–H1) in acetylacetone yields the strong hydrogen bond.

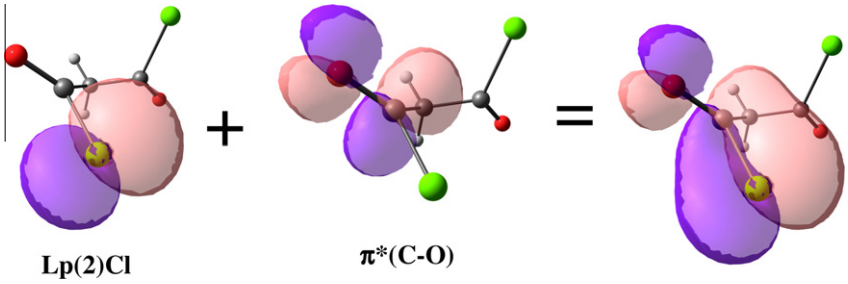

Fig. 5. The hyper conjugation between lone pair of Cl and π*(C–O) in malonyl dichloride.

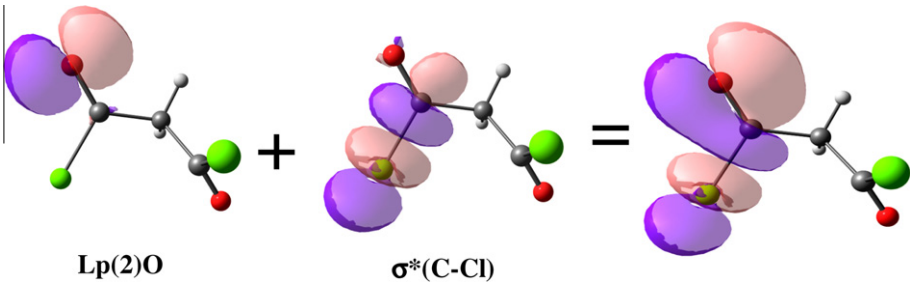

Fig. 6. The hyper conjugation between lone pair of O and σ*(C–Cl) in malonyl dichloride.

Table 10
The values characterizing hydrogen bond in the enol form of β-diketones.[a]

R1	R2	r(O1···O2)	r(O1–H1)	r(O2···H1)	Q(O2···H1)	q(R1)	q(R2)	q(O1)	q(O2)	q(H1)	q(C)	ω(OH)	$\Delta E = E_{keto} - E_{enol}$
NH_2	NH_2	2.418	1.022	1.547	0.142	0.005	0.015	−0.674	−0.702	0.509	−0.542	2737.89	−6.06
OCH_3	OCH_3	2.522	1.015	1.590	0.121	−0.154	−0.181	−0.676	−0.692	0.515	−0.524	2867.06	−6.15
CH_3	CH_3	2.533	1.006	1.615	0.110	0.035	0.008	−0.655	−0.635	0.506	−0.471	2990.24	6.43
$C(CH_3)_3$	NH_2	2.536	1.004	1.616	0.107	0.017	0.002	−0.677	−0.684	0.507	−0.480	3028.06[b]	2.76
												3031.19	
CF_3	NH_2	2.545	1.005	1.639	0.101	0.004	0.025	−0.636	−0.667	0.513	−0.420	3044.28	5.57
CH_3	NH_2	2.550	1.002	1.638	0.101	0.032	0.002	−0.666	−0.684	0.508	−0.472	3066.60	3.14
H	H	2.571	1.000	1.675	0.093	0.176	0.127	−0.631	−0.610	0.506	−0.463	3093.41	8.71
CF_3	CF_3	2.579	0.995	1.700	0.080	0.023	−0.01	−0.608	−0.556	0.514	−0.422	3197.97	8.72
Cl	Cl	2.590	0.997	1.707	0.076	0.059	−0.051	−0.629	−0.584	0.516	−0.483	3189.61	−2.75
CH_3	OCH_3	2.595	0.992	1.706	0.076	0.036	−0.178	−0.663	−0.669	0.509	−0.468	3249.26	5.38
F	F	2.602	0.998	1.722	0.078	−0.295	−0.334	−0.629	−0.609	0.522	−0.559	3193.59	−3.97
CH_3	Cl	2.626	0.987	1.760	0.059	0.050	−0.084	−0.643	−0.583	0.508	−0.478	3361.82	6.77
CH_3	F	2.634	0.987	1.764	0.061	0.047	−0.346	−0.648	−0.605	0.510	−0.501	3353.15	6.72

[a] r – interatomic distances, Å; Q – Wiberg bond orders; q – net atomic charges, ē; ω – harmonic frequencies, cm^{-1}; $\Delta E = E_{keto} - E_{enol}$ for most preferable keto form, kcal/mol.
[b] Both frequencies have the vibrational modes with large contributions of O–H and C–H stretches .

librium, stabilizing the enol form. The data in Table 10 do not support this assumption. So, according to the calculated values the strongest hydrogen bond is in the enol tautomer of malonamide which exists exclusively in the diketo form.

4. Conclusion

In our research we are trying to understand the problem of keto–enol tautomerism of β-dicarbonyl compounds. According to the experimental and theoretical data we can conclude that the reason for preference of enol or diketo tautomer is the nature of the substituents. NBO-analyses performed in this study show that the electronegativities of the substituents have no pronounced influence on the keto–enol equilibrium, whereas the presence or the absence of electron lone pairs on substituents rule keto or enol preference. Thus, the substituents, which we refer to the group I (H, CH_3, $C(CH_3)_3$, CF_3) have no lone pairs on the atom connected with carbon–oxygen skeleton, and favour the enol tautomer, whereas the substituents from group II (F, Cl, NH_2 or OCH_3) which possess one, two, or three lone pairs, favour the diketo form. For non-symmetrically substituted β-diketones with one substituent favouring the keto and the other one the enol form we expect the existence of a mixture of both tautomers with the preference of the enol form. However, a priory predictions of exact tautomeric composition are very difficult. Whereas the B3LYP method and the MP2 approximation with large enough basis sets provide sufficiently correct predictions of the main tautomeric form and of structural parameters of β-diketones, the level of theory for exact predictions of tautomeric compositions, obviously, should be higher.

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