AB INITIO STUDY OF THE STRUCTURE OF ENOLIC

AND KETONIC FORMS OF β-DIKETONES WITH THE

GENERAL FORMULA R″COCH$_2$COR′ (R′ AND R″ = H, CH$_3$, CF$_3$)

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Geometric parameters, values of force constants and vibration frequencies for different geometric configurations of enolic and ketonic forms of molecules of β-diketones, R″COCH$_2$COR′ (R″ and/or R′ are H, CH$_3$, CF$_3$) have been computed by the *ab initio* method MO LCAO SCF using wide bases of Cartesian Gaussians. The enolic form of the considered molecules is most energetically favorable. Values of isomerization energy, the height of internal rotation barriers, and energies of the intramolecular hydrogen bond were obtained for it. The stabilization of the enolic form was shown to be caused by the presence of the intramolecular hydrogen bond in the chelate ring. The effect of a substituent on the computed values of molecular parameters was examined. The comparison with the available experimental data testifies to a sufficiently high reliability of the data obtained.

Keywords: β-diketones, enol, ketone, quantum chemical computations, structure, vibration analysis, potential function, conformers, intramolecular hydrogen bond.

The structure of molecules of β-diketones with the general formula R″COCH$_2$COR′ has been investigated by various experimental methods. The majority of the works was devoted to the structure study of the enolic form of the compounds in question. Our previously performed [1, 2] analysis of the available in the literature data for the molecules R″COCH$_2$COR′ with symmetric radicals (R″ = R′) has shown that the information on the structure of enolic forms of these compounds is rather incomplete and contradictory. The results of examination of spectra point to the planar asymmetric structure of the chelate ring for the molecules under study. The authors of the most part of electron-diffraction works argue in favor of the planar symmetric structure of the chelate ring. The electron-diffraction investigation of the ketone form structure of the compounds in question has been carried out only for the molecule of acetylacetone in the work [3].

There are only the data for the molecule of methylmalonaldehyde in the literature [4, 5] for the molecules R″COCH$_2$COR′ with asymmetric radicals (R″ ≠ R′). In the work [4] based on the study of IR spectrum of methylmalonaldehyde molecules, isolated in the Ar and Xe matrix, the authors have come to the conclusion about the simultaneous existence of two isomers differing in the position of CH$_3$ group relative to the chelate moiety. According to the data of [4], the isomer in which the group CH$_3$ takes the place of the radical R″ is prevailing (Fig. 1*a*). The authors of the work [5], when interpreting the results of the experiment based on the laser control of proton motion in methylmalonaldehyde molecule, have preferred another isomer in which the group CH$_3$ occupies the position of the radical R′ (see Fig. 1*a*).

In the previous works [1, 2], we have performed *ab initio* calculations for the molecules with symmetric radicals (R″ = R′). Both enolic and ketonic forms were investigated for the molecule of malonic dialdehyde (R″ = R′ = H) [1], while
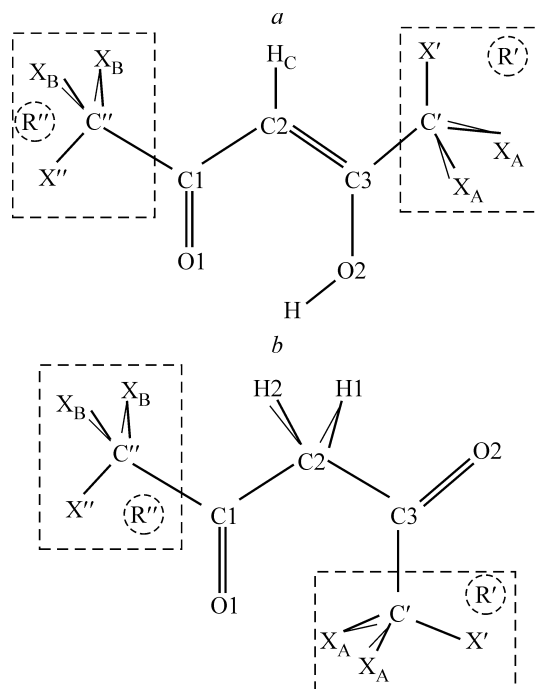
Fig. 1. Notation of atoms and substituents R′ and R″ in the geometric configurations of the enolic (*a*) and ketonic (*b*) forms of R″COCH$_2$COR′ molecules (R′ and R″ = H, CH$_3$, CF$_3$).

for the molecules of acetylacetone (R″ = R′ = CH$_3$) and hexafluoroacetone (R″ = R′ = CF$_3$) only enolic [2]. *Ab initio* study of the structure of enolic forms for various derivatives of malonic dialdehyde (3-21G basis) has been performed in the paper [6]. For the molecule of methylmalonaldehyde, the authors of [6] considered two isomers of the enolic form differing in the position of the methyl group. There were obtained for them the geometrical parameters, the energy of intramolecular hydrogen bond, and the height of the barrier on the way of proton migration inside the chelate ring [6].

The present work has been carried out to continue our previous research [1, 2]. The purpose of this contribution is to study the geometrical structure, barriers of the internal rotation in the enolic and ketonic forms of the molecules with the general formula R″COCH$_2$COR′, where R″ and/or R′ are H, CH$_3$, CF$_3$ (when R″ = R′ = H it is malonic dialdehyde (MDA), R″ = R′ = CH$_3$ it is acetylacetone (AA), R″ = R′ = CF$_3$ it is hexafluoroacetone (HFAA), R″ = H and R′ = CH$_3$ it is methylmalonaldehyde (MMA), R″ = CF$_3$ and R′ = H it is trifluoromalonaldehyde (TFMA), R″ = CF$_3$ and R′ = CH$_3$ it is trifluoroacetylacetone (TFAA)).

COMPUTATION DETAILS

All calculations have been performed with the version PC GAMESS [7] of the program software GAMESS [8] employing the electron density functional theory (version DFT/ B3LYP [9-11]). Valence three-exponent Huzinaga–Dunning bases, (10s6p/5s3p) for C, O, F and (5s/3s) for H [12, 13], were used in all computations, supplemented with one-exponents sets of polarization d-(C, O, F) [14] and p-functions (H)* [15]. Second-order Möller–Plesset perturbation theory (MP2) was also implemented to calculate the molecule MMA. The approximation of the "frozen" core was not used in MP2 calculations.

Optimization of geometric parameters of all the considered configurations was performed by the gradient method. The force field was obtained, and the frequencies of normal vibrations and the intensities of bands in IR spectra were

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*Values of exponent indices for polarization functions equal: 0.72 (C), 1.28 (O), 1.62 (F), 1.0 (H).

TABLE 1. Geometric Parameters and Values of Mülliken Charges of the Constituents ($q(R')$, $q(R'')$) and the Chelate Moiety (q_σ, q_π) of the Most Favorable Energetically Configurations of the Enolic Form of $R''COCH_2COR'$ Molecules According to the DFT Computation

Parameter	AA	MMA		MDA	TFMA		HFAA	TFAA	
	$R'=CH_3$; $R''=CH_3$	$R'=CH_3$; $R''=H$	$R'=H$; $R''=CH_3$*	$R'=H$; $R''=H$	$R'=H$; $R''=CF_3$	$R'=CF_3$; $R''=H$**	$R'=CF_3$; $R''=CF_3$	$R'=CH_3$; $R''=CF_3$	$R'=CF_3$; $R''=CH_3$***
	C_s	C_s	C_s	C_s	C_s	C_s	C_1	C_1	C_s
$R_e(C2–C3)$	1.372	1.373	1.361	1.364	1.364	1.360	1.360	1.374	1.357
$R_e(C1–C2)$	1.440	1.432	1.449	1.437	1.434	1.444	1.440	1.427	1.456
$R_e(C3–C')$	1.493	1.492	—	—	—	1.524	1.526	1.491	1.523
$R_e(C1–C'')$	1.511	—	1.510	—	1.553	—	1.552	1.553	1.506
$R_e(C3–O2)$	1.324	1.325	1.322	1.320	1.318	1.317	1.316	1.323	1.319
$R_e(C1–O1)$	1.248	1.242	1.243	1.239	1.231	1.236	1.228	1.235	1.246
$R_e(C2–H_C)$	1.080	1.080	1.081	1.080	1.079	1.078	1.078	1.079	1.079
$R_e(C1–H'')$	—	1.102	—	1.102	—	1.100	—	—	—
$R_e(C3–H')$	—	—	1.085	1.085	1.084	—	—	—	—
$R_e(C'–X')$	1.089	1.088	—	—	—	1.345	1.343	1.088	1.347
$R_e(C'–X_A)$	1.093	1.093	—	—	—	1.344	1.343	1.093	1.345
$R_e(C''–X'')$	1.090	—	1.088	—	1.331	—	1.329	1.332	1.088
$R_e(C''–X_B)$	1.092	—	1.093	—	1.352	—	1.350	1.353	1.094
$R_e(O2–H)$	1.008	1.003	0.999	0.998	0.991	1.001	0.993	0.995	1.004
$\alpha_e(O1C1C2)$	121.5	123.9	121.1	123.4	124.6	123.1	124.3	125.0	120.8
$\alpha_e(C1C2C3)$	120.6	120.2	120.2	119.4	119.3	118.8	118.5	119.9	119.3
$\alpha_e(C2C3O2)$	121.8	121.5	124.5	124.2	124.9	124.7	125.3	122.1	124.9
$\alpha_e(C''C1C2)$	119.6	—	118.7	—	116.9	—	116.8	116.7	118.6
$\alpha_e(C'C3C2)$	124.1	124.5	—	—	—	123.0	122.6	124.0	122.8
$\alpha_e(H''C1C2)$	–	117.4	—	117.6	—	117.6	—	—	—
$\alpha_e(H_CC2C3)$	119.4	120.1	119.3	120.0	119.8	120.8	120.5	119.8	120.2
$\alpha_e(H'C3C2)$	–	—	122.3	122.5	122.0	—	—	—	—
$\alpha_e(X'C'C3)$	111.5	111.5	—	—	—	111.4	111.3	111.5	111.6
$\alpha_e(X_AC'C3)$	109.7	109.7	—	—	—	110.8	110.6	109.6	110.9
$\alpha_e(X''C''C1)$	112.8	—	109.9	—	112.1	—	111.9	112.1	109.9
$\alpha_e(X_BC''C1)$	109.1	—	110.3	—	110.3	—	110.0	110.4	110.2
$\alpha_e(HO2C3)$	106.1	106.9	106.0	105.4	107.6	106.3	107.4	107.8	105.6
$\chi(X'C'C3O2)$	180	180	—	—	—	180	180	180	180
$\chi(X''C''C1O1)$	180	—	0	—	0	—	1.4	4.5	0
$q(R')$	0.044	0.056	0.164	0.171	0.183	0.002	0.017	0.076	–0.012
$q(R'')$	0.023	0.108	0.032	0.112	–0.027	0.126	–0.009	–0.039	0.052
q_σ	–0.009	–0.140	–0.158	–0.288	–0.151	–0.135	0.002	0.002	–0.000
q_π	–0.058	–0.024	–0.038	0.005	–0.005	0.007	–0.010	–0.039	–0.040

Note. Measurement units: values of internuclear distances (R_e) are in Å; valence (α_e) and dihedral (χ_e) angles are in deg; Mülliken charge (q) is in ē parts; $\chi(O1C1C2C3) = \chi(O2C3C2C1) = \chi(HO2C3C2) = 0$.

*$h = 0.9$ kJ/mol.

**$h = 6.9$ kJ/mol.

***$h = 6.3$ kJ/mol.

TABLE 2. Relative Energies of the Geometric Configurations Determining the Heights of Internal Rotation Barriers and Isomerization Energies of the Enolic Form of MMA, TFMA, AA, HFAA, TFAA Molecules

	MMA (X′, X″ = H)				TFMA (X′, X″ = F)			
χ(HO2C3C2)	0	0	180	180	0	0	180	180
χ(X′C′C3O2)	180	0	180	0	180	0	180	0
h	0	4.8	62.8	70.8	6.9	12.5	62.8	70.8
	min	sp^1	min	sp^1	min	sp^1	min	sp^1
χ(HO2C3C2)	0	0	180	180	0	0	180	180
χ(X″C″C1O1)	180	0	180	0	180	0	180	0
h	1.3	0.9	62.8	60.5	0.6	0	50.7	47.7
	sp^1	min	sp^1	min	sp^1	min	sp^1	min
	AA (X′, X″ = H)				HFAA (X′, X″ = F)			
χ(HO2C3C2)	0	0	0	0	0	0	0	0
χ(X′C′C3O2)	180	0	180	0	180	0	180	0
χ(X″C″C1O1)	180	180	0	0	180	180	1.4	0
h	0	5.0	0.03	5.3	1.0	6.3	0	5.7
	min	sp^1	sp^1	sp^2	sp^1	sp^2	min	sp^2
χ(HO2C3C2)	180	180	180	180	180	180	180	180
χ(X′C′C3O2)	180	0	180	0	180	0	180	0
χ(X″C″C1O1)	180	180	0	0	180	180	0	0
h	69.3	77.5	67.3	75.7	48.3	49.4	44.9	46.4
	sp^1	sp^2	min	sp^1	sp^2	sp^3	sp^1	sp^1
	TFAA							
χ(HO2C3C2)	0	0	0	0	180	180	180	180
χ(H′C′C3O2)	180	0	180	0	180	0	180	0
χ(F″C″C1O1)	180	180	4.5	0	180	180	0	0
h	0.1	4.2	0	4.3	57.7	64.7	55.0	62.0
	sp^1	sp^1	min	sp^2	sp^1	sp^2	min	sp^1
χ(HO2C3C2)	0	0	0	0	180	180	180	180
χ(F′C′C3O2)	180	0	180	0	180	0	180	0
χ(H″C″C1O1)	180	180	0	0	180	180	0	0
h	7.4	13.2	6.3	12.3	66.9	68.6	64.0	65.9
	sp^1	sp^2	min	sp^1	sp^2	sp^2	sp^1	sp^1

Note. Notation and measurement units are given in the footnote to Table 1. The relative energies of configurations (h) are in kJ/mol. The values of h were computed relative to the total energy of the most energetically favorable configuration of the enolic form (see Table 1). Abbreviations min and sp^N determine the type of the point on PES corresponding to the given geometric configuration: min is the minimum; sp^N means the saddle point of the order N.

computed in the harmonic approximation for each considered structure by the numerical method realized in the program GAMESS [8] with the optimized geometrical parameters.

Geometric configurations with U-, S-, and W-shaped form of the moiety [OCCCO] were considered in the context of the MP2 method for the enolic form of the MMA molecule. The structures with the U-shaped [OCCCO] moiety turned out to be most energetically favorable. Therefore only geometric configurations with the U-shaped [OCCCO] moiety were examined in the DFT approximation for the enolic form of all the molecules R″COCH$_2$COR′ in question, except the MDA molecule (Tables 1, 2).

TABLE 3. Relative Energies of the Geometric Configurations with Symmetry C_S of the Ketonic Forms of MMA, TFMA, TFAA, AA, HFAA Molecules

χ_1	χ_2	χ_3	χ_4	MMA Type	h	TFMA Type	h
				MMA		**TFMA**	
0	0	–	180	sp^2	54.3	sp^2	55.1
0	0	–	0	sp^2	52.6	sp^2	50.3
180	180	–	0	sp^2	43.8	sp^2	50.7
180	180	–	180	sp^3	51.1	sp^3	65.9
0	180	–	0	sp^1	38.0	sp^2	57.3
0	180	–	180	sp^3	44.3	sp^3	78.9
180	0	–	0	sp^2	31.8	sp^2	35.8
180	0	–	180	sp^2	33.6	sp^2	40.0
				AA		**HFAA**	
0	0	180	180	sp^3	56.6	sp^3	50.6
0	0	0	0	sp^2	53.5	sp^2	40.9
0	0	0	180	sp^2	55.0	sp^2	45.8
180	180	0	0	sp^2	59.2	sp^2	87.9
180	180	180	180	sp^4	79.5	sp^4	131.8
180	180	0	180	sp^3	66.9	sp^3	100.0
0	180	0	0	sp^2	37.0	sp^2	50.0
0	180	180	0	sp^2	38.5	sp^2	54.8
0	180	0	180	sp^3	43.6	sp^3	72.9
0	180	180	180	sp^3	44.9	sp^3	77.9

TFAA

χ_1	χ_2	χ_3	χ_4	Type	h
0	0	180	180	sp^3	58.9
0	0	0	180	sp^3	57.3
0	0	180	0	sp^2	54.0
0	0	0	0	sp^2	52.4
180	180	0	0	sp^2	70.6
180	180	180	0	sp^3	79.2
180	180	0	180	sp^3	90.9
180	180	180	180	sp^4	103.9
0	180	0	0	sp^2	59.5
0	180	180	0	sp^2	61.0
0	180	0	180	sp^3	83.4
0	180	180	180	sp^1	84.6
180	0	0	0	sp^2	42.5
180	0	180	0	sp^3	49.3
180	0	0	180	sp^2	46.8
180	0	180	180	sp^3	53.7

Note. Notation and measurement units are given in the footnote to Tables 1, 2.
$\chi_1 = \chi(O2C3C2C1)$; $\chi_2 = \chi(O1C1C2C3)$; $\chi_3 = \chi(X'C'C3O2)$; $\chi_4 = \chi(X''C''C1O1)$; For the molecule of TFAA, X'=H, X''=F.

TABLE 4. Geometric Parameters and Relative Energies of the Equilibrium Configuration Having the Symmetry C_1 of the Ketonic Form of R″COCH₂COR′ Molecules According to the DFT Computation Data

Molecule	AA $R'=CH_3$; $R''=CH_3$	MMA $R'=H$; $R''=CH_3$	MDA $R'=H$; $R''=H$	TFMA $R'=H$; $R''=CF_3$	HFAA $R'=CF_3$; $R''=CF_3$	TFAA $R'=CH_3$; $R''=CF_3$
1	2	3	4	5	6	7
R_e(C2–C3)	1.535	1.521	1.515	1.530	1.524	1.536
R_e(C1–C2)	1.536	1.532	1.515	1.512	1.519	1.515
R_e(C3–O2)	1.211	1.204	1.205	1.200	1.196	1.208
R_e(C1–O1)	1.211	1.211	1.205	1.201	1.196	1.199
R_e(C3–C′)	1.509	—	—	—	1.562	1.507
R_e(C1–C″)	1.509	1.509	—	1.558	1.558	1.563
R_e(C2–H1)	1.090	1.089	1.100	1.089	1.093	1.097
R_e(C2–H2)	1.090	1.096	1.094	1.097	1.093	1.091
R_e(C3–H′)	—	1.106	1.109	1.105	—	—
R_e(C1–H″)	—	—	1.105	—	—	—
R_e(C′–X′)	1.088	—	—	—	1.327	1.088
R_e(C′–X$_A$)	1.095	—	—	—	1.351	1.093
R_e(C′–X$_A$)	1.093	—	—	—	1.350	1.094

TABLE 4. (Continued)

1	2	3	4	5	6	7
$R_e(C''–X'')$	1.088	1.088	—	1.329	1.326	1.329
$R_e(C''–X_B)$	1.093	1.094	—	1.350	1.349	1.349
$R_e(C''–X_B)$	1.095	1.094	—	1.351	1.354	1.353
$\alpha_e(O2C3C2)$	120.6	123.7	124.7	122.7	125.6	119.4
$\alpha_e(C3C2C1)$	108.4	110.6	114.4	111.9	111.6	113.7
$\alpha_e(O1C1C2)$	120.6	120.1	123.3	124.0	124.0	126.2
$\alpha_e(C'C3C2)$	116.3	—	—	—	114.2	117.5
$\alpha_e(C''C1C2)$	116.3	116.9	—	115.9	115.6	114.5
$\alpha_e(H1C2C3)$	108.0	109.4	107.2	106.4	108.1	110.5
$\alpha_e(H2C2C1)$	110.8	106.7	110.1	113.6	112.0	109.6
$\alpha_e(H'C3C2)$	—	114.7	114.6	115.2	—	—
$\alpha_e(H''C1C2)$	—	—	115.6	—	—	—
$\alpha_e(X'C'C3)$	110.2	—	—	—	111.9	109.9
$\alpha_e(X_AC'C3)$	109.3	—	—	—	109.9	109.8
$\alpha_e(X_AC'C3)$	110.3	—	—	—	109.8	110.1
$\alpha_e(X''C''C1)$	110.3	110.3	—	112.2	112.3	112.0
$\alpha_e(X_BC''C1)$	110.2	109.9	—	109.8	110.5	110.0
$\alpha_e(X_BC''C1)$	109.4	110.1	—	109.8	108.8	110.0
$\chi(O2C3C2C1)$	87.9	130.9	0.8	144.6	3.6	107.4
$\chi(O1C1C2C3)$	88.8	60.4	132.8	48.0	88.1	18.8
$\chi(C'C3C2C1)$	90.5	—	—	—	176.9	73.5
$\chi(C''C1C2C3)$	89.6	118.5	—	131.3	93.2	161.4
$\chi(X'C'C3O2)$	7.3	—	—	—	2.7	0.9
$\chi(X''C''C1O1)$	7.0	1.4	—	3.0	10.7	6.5
h	21.8	26.6	31.7	32.7	29.8	34.2

Note. Notation and measurement units are given in the footnote to Tables 1, 2. The values of h were computed relative to the total energy of the most energetically favorable configuration of the enolic form (see Table 1).

Similar to the enolic form, all geometric configurations having C_s symmetry with U-, W-, and S-shaped [OCCCO] moiety were considered in the DFT approximation for the ketonic form of all molecules R''COCH$_2$COR' under study, except the MDA molecule. The performed calculations of force fields have shown that all the considered structures of C_s symmetry meet the saddle points on the potential energy surface (PES) (Table 3). When searching for the equilibrium configuration, the geometrical parameters of the structure with symmetry C_s having the lowest energy and corresponding 1st order saddle point were taken as starting. The parameters of equilibrium configurations with C_1 symmetry of ketonic forms of the molecules under study are given in Table 4.

In the work [1], all possible configurations of the MDA molecule have been thoroughly examined by the MP2 method. Therefore only two geometric configurations of C_s and C_1 symmetry corresponding to enolic and ketonic forms respectively were calculated in the framework of DFT approximation.

DISCUSSION OF CALCULATION RESULTS

MP2 and DFT calculation results of the parameters for various geometric configurations of enolic and ketonic forms of the MMA molecule have indicated that the greatest differences in values for internuclear distances and valence

angles comprise 0.011 Å and 1.7° respectively. Relative disposition of all the considered geometrical configurations on the energy scale is retained when transiting from MP2 to DFT. Differences in relative energies (h), obtained in the approximations MP2 and DFT, do not exceed 0.7 kJ/mol and 4.6 kJ/mol for the geometric configurations with $h \leq 5$ and $h \approx 55\text{-}70$ kJ/mol respectively.

Thus, the results obtained by DFT and MP2 methods lead to close values of molecular parameters and relative energies in the examined compounds. We have carried out the calculations of properties for other compounds by the DFT method for it takes less computation time and computer resources. Therefore the data obtained with the DFT method will be discussed further here.

Equilibrium configurations. Geometrical parameters of the most energetically favorable configurations of the enolic form for all the molecules examined are listed in Table 1. The chelate moiety, [OCC(H)COH], is planar in all molecules. Depending on the type of the substituent, internuclear distances and valence angles of the chelate moiety vary within the limits 0.01-0.02 Å and 2-4 Å respectively. In accordance with the calculation, bond orders in the chelate moiety have the following values in ē units (see Fig. 1a): 1.49-1.58 (C2–C3), 1.08-1.20 (C2–C1), 1.29-1.33 (C3–O2), 1.77-1.86 (C1–O1), 0.76-0.80 (O2–H), 0.93-0.95 (C2–H_C). These values display that π-conjugation exists in the oxygen-carbon framework of the chelate moiety, and hence, Fig. 1a with its alternate single and double bonds is rather conventional.

Spatial orientation of substituents depends on the substituent position and nature. The groups CH_3 and CF_3 occupy the positions of R′ and R″, respectively, in the equilibrium configurations of the enolic forms of mixed β-diketones. In the position R′, CX_3 groups are arranged in such a way that the bond C′–X′ screens the bond C2=C3. At the same time, these groups in the position R″ are oriented so that the bonds C″–H″ and C″–F″ screen the bonds C1–C2 and C1=O1 respectively.

It is interesting to note that according to the DFT calculation data, the equilibrium configuration of the enolic form of HFAA and TFAA molecules, in contrast to other examined compounds, has the symmetry C_1 (Table 1). In the configuration of C_1 symmetry, the bond C″–F″, screening the bond C1=O1, comes out of the plane of the chelate moiety by 4.5° and 1.4° in TFAA and GFAA molecules respectively. The structure of C_s symmetry meets the 1st order saddle point on PES in HFAA and TFAA molecules. The relative energy of this configuration ($h = 0.026$ kJ/mol for TFAA and 0.00046 kJ/mol for HFAA) determines the height of the regrouping barrier between two equivalent structures having C_1 symmetry. In accordance with the data of the previous computation [2], however, performed by means of the MP2 method, the equilibrium configuration of the enolic form of the HFAA molecule is the structure of C_s symmetry. It should be noted that the results of both the present and the previous studies evidence a virtually free rotation of CF_3 group in the R″ position. Obviously, the computation of the potential function describing the internal rotation requires the employment of higher theoretical approximations.

The geometrical parameters for the equilibrium configurations having C_1 symmetry of ketonic forms of the considered molecules are listed in Table 4. When the substituent is changed, the variations of internuclear distances and valence angles of the oxygen-carbon framework do not exceed 0.02 Å and 6.2° respectively. The calculated values for the order of C=O and C–C bonds lie within the intervals of 2.12-2.19 ē and 0.87-0.93 ē respectively.

Analysis of electron density distribution in the equilibrium configurations of the enolic form of the molecules examined was performed basing on the magnitudes of Mulliken charges of the substituents ($q(R′)$ and $q(R″)$) and the chelate moiety ($q_\sigma + q_\pi$) given in Table 1. The values q_σ and q_π were obtained on the base of populations of corresponding atomic orbitals in molecular orbitals responsible for the generation of the system of σ- and π-bonds in the considered molecules. The computed charge values indicate that the chelate moiety carries excessive negative charge in all the compounds studied by us, i.e. it is the electron acceptor. Hence, the electron density flow from both substituents or from one of them into the chelate moiety is observed in all examined moieties. The substituents in the position R′ possess the greatest donor properties. In this case, even the group CF_3 traditionally attributed to acceptors possesses donor properties in all studied molecules, except the lying higher TFAA isomer. Only the substituent R″ = CF_3 is the acceptor. The obtained charge values show the donor properties of the substituents to diminish in the series H → CH_3 → CF_3. The obtained values of q_σ and q_π charges reveal that

the dominant part of the excessive electron density is distributed over the system of σ-bonds in the chelate moiety only in the case of those compounds, when hydrogen atom is in the place of one or both substituents. When the substituents are CH_3 and CF_3 groups, the excessive charge is concentrated almost totally in the system of π-bonds in the chelate moiety.

Analysis of the substituent nature effect (R″ and R′) on the geometrical parameters of the chelate ring of the enolic forms of the molecules examined was carried out on the data from Table 1. The values of geometrical parameters for the chelate ring change systematically depending on the substituent nature in the series $CH_3 \rightarrow H \rightarrow CF_3$. The value of the equilibrium internuclear distance R_e(C1–C2) grows or, on the contrary, diminishes when the substituent R′ or R″ is changed respectively. In both cases, the value of R_e(C1–C2) variation comprises 0.012-0.016 Å. The distance R_e(C2–C3), unlike R_e(C1–C2), decreases noticeably (by 0.013-0.015 Å) when the substituent R′ is changed. The change of the substituent R″ results in the growth of R_e(C2–C3) not more than by 0.003 Å. The equilibrium internuclear distances R_e(C1–O1) and R_e(C3–O2) decrease when both the substituents R′ and R″ are changed. Maximal variations of R_e(C1–O1) and R_e(C3–O2) amount to 0.018 Å and 0.008 Å respectively. The value R_e(C2–H$_c$) varies by not more than 0.002 Å, when the substituent is changed. The replacement of the substituent R″ most greatly affects the variation of R_e(O2–H). In the series R″ = $CH_3 \rightarrow H \rightarrow CF_3$, the value of R_e(O2–H) decreases by 0.008-0.013 Å.

Valence angles, as well as internuclear distances, vary systematically under the replacement of the substituent. The replacement of the substituent R′ results in the lessening of the valence angles α_e(O1C1C2), α_e(C1C2C3), α_e(HO2C3) and the growth of the value of α_e(O2C3C2). At the same time, under the replacement of the substituent R″, the values of α_e(O1C1C2), α_e(O2C3C2), α_e(HO2C3) increase, with the value of α_e(C1C2C3) decreasing. On the whole, the variations of the equilibrium values for the valence angles of the chelate ring do not exceed 4°.

The calculation results for the equilibrium configurations of the ketonic form (Table 4) indicate that under the replacement of the substituent in the oxygen-carbon framework [OCCCO] the internuclear distances and the valence angles, involving the carbon atom to which the substituent is bonded, vary most remarkably. Under the replacement of the substituent in the series $CH_3 \rightarrow H \rightarrow CF_3$, there occurs the decrease in the values of R_e(C–C) and R_e(C=O) by 0.017-0.021 Å and 0.010-0.012 Å respectively. The values of valence angles α_e(OCC) and α_e(CCC) increase by not more than 5.6°.

Often while studying the structure of molecules containing CX_3 groups, authors assume in the interpretation of experimental results that the substituents CX_3 possess the local symmetry C_{3v}. Our computations reveal (Table 1) that geometrical parameters of methyl groups in the enolic forms of AA, MMA, TFAA molecules in the substituents R′ and R″ differ insignificantly between themselves: the difference in bond lengths ΔR_e(C–H) and valence angles $\Delta\alpha_e$(HCH) does not exceed 0.005 Å and 1.8° respectively. In TFMA, TFAA, and HFAA molecules, the structure of the substituents CF_3 depends on their position. The structure of the substituent R′ = CF_3 in the HFAA molecule is close to a regular trigonal bipyramid (ΔR_e = 0.0 Å, $\Delta\alpha_e$ = 0.7°). However, the shape of another substituent R″ = CF_3 yet significantly differs from regular in all three molecules: ΔR_e = 0.021 Å, $\Delta\alpha_e$ = 1.9°.

Methyl groups in the equilibrium configurations of the ketonic forms (Table 4), as well as the enolic forms, are closest in shape to a regular trigonal pyramid. In AA, MMA, TFAA molecules, the values of ΔR_e(C–H) and $\Delta\alpha_e$(HCH) do not exceed 0.004 Å and 0.9° respectively. At the same time according to the computation results for TFMA, TFAA, and HFAA molecules, the difference in the values of internuclear distances R_e(C–F) and valence angles α_e(FCF) in CF_3 group comprises 0.020-0.023 Å and 2.0-2.4° respectively.

Internal rotation. Relative energies and types of the points on PES of geometric configurations of the enolic form of the examined compounds are presented in Table 2. The performed vibration analysis has revealed that vibration shape corresponding to the imaginary frequency points to the turn of CX_3 group towards the equilibrium structure. Thus, the relative energies of the structures meeting the first order saddle points on PES determine the height of the barriers of the internal rotation of CX_3 groups. Our calculations show the height of rotation barriers to weakly depend on the group nature and comprise for the substituents in the positions R″ and R′ 0.03-1.1 kJ/mol and 4.8-6.0 kJ/mol respectively. Therefore the

internal rotation of R′ substituent is more hindered when compared to the rotation of the substituent R″. Spatial orientation of one group slightly affects the rotation barrier height of the second group. Moreover, the relative energy of the configuration corresponding to a simultaneous turn of both groups (saddle points of the 2nd order) is close to the sum of values determining the height of rotation barriers for each group. Hence, the internal rotations of CX_3 are to a considerable extent mutually independent.

It should be noted that the obtained in the present work heights of the internal rotation barriers for CX_3 groups in AA and HFAA molecules are close to the estimations we have made earlier [2] using MP2, MP3, MP4, CISD, and CISD+Q approximations.

The analysis of the data obtained by us shows that the geometrical parameters of the enolic fragment change insignificantly at the turn of CX_3 groups: internuclear distances vary on average by 0.004 Å (at the most by 0.009 Å in the HFAA molecule), and valence angles by 0.1-0.6° (at the most by 1.3° in the TFAA molecule). The parameters of CX_3 groups change in the following way: internuclear distances R_e(C–H), regardless of the group position vary within the limits 0.001-0.004 Å, while R_e(C–F), on average, by 0.011 Å and 0.020 Å for the radicals R′ and R″ respectively.

Energy of the intramolecular hydrogen bond (E_{HB}). The geometric configurations with hydrogen atom situated outside the chelate moiety [OCCCO] (χ_e(HO2C3C2) = 180°, Table 2) were considered for the enolic form of all molecules examined by us (except MDA). In a number of theoretical works (see references in [1]), the difference of total energies of isomers with open (χ_e(HO2C3C2) = 180°) and closed (χ_e(HO2C3C2) = 0) chelate rings has been assumed as the energy of hydrogen bond. According to the data from Table 2, the value E_{HB} amounted to (kJ/mol): 67.3 for the AA molecule; 62.8 for MMA; 55.0 for TFAA; 47.7 for TFMA; 44.9 for HFAA. Earlier we have obtained in the approximation MP2 for the MDA molecule [1] the value E_{HB} = 50.0 kJ/mol.

The computed values of the order of O1···H bond point to the generation of the intramolecular hydrogen bond (IMHB) in the equilibrium configuration of the enolic form: 0.188 (AA), 0.179 (MMA), 0.145 (TFAA), 0.155 (MDA), 0.123 (TFMA), 0.131 (HFAA). The values of the internuclear distances O1···O2 of the equilibrium configurations, 2.529 Å (AA), 2.556 Å (MMA), 2.579 Å (TFAA), 2.582 Å (MDA), 2.609 Å (TFMA), 2.588 Å (HFAA), are also typical of the compounds with IMHB. The decrease in IMHB energy in the series AA → MMA → TFAA → MDA → TFMA → HFAA correlates with the increase in values R(O1···O2) and the diminution of the order value for the bond O1···O2.

It should be noted that the value of E_{HB} is remarkably higher than the values for the relative energies of the equilibrium configurations of the ketonic form (see Table 4) and, as the calculation data for the MMA molecule indicate, the values for the relative energies of the geometric configurations of the enolic form with the *W*- and *S*-shaped [OCCCO] moiety. Apparently, the generation of a strong IMHB in the configuration with the closed 6-member chelate ring is the reason for so significant energy stabilization of the enolic form of the considered compounds.

Comparison with the experimental data. In the works [1, 2], a detailed analysis of the available experimental data on the study of the enolic form structure of symmetric β-diketones of MDA, AA, and HFAA is carried out, and it is revealed that the results of theoretical calculations agree with the data obtained when interpreting NMR, microwave, IR, and RS spectra, as well as the results of electron diffraction examinations.

In the electron diffraction study [3] of the ketonic form structure of the AA molecule, a set of effective r_g-parameters has been obtained (t = 100-110°C). We have obtained the values R_e(C1–C2) ≈ R_e(C2–C3) = 1.535 Å and R_e(C1–O1) ≈ R_e(C3–O2) = 1.211 Å which agree with those observed by the authors of [3] values r_g(C–C) = 1.540±0.015 Å and r_g(C–O) = 1.225±0.010 Å. Moreover, the obtained in [3] values r_g(C–H) = 1.109±0.014 Å in methyl groups are close to the values listed in Table 4. Noticeable differences of our data from those given in [3] are observed for the values of valence and dihedral angles determining the overrun of C1=O1 and C3=O2 bonds out of the plane of C1–C2–C3 triangle. This difference is connected with the fact that the authors of [3] appear to use the values of the effective internuclear distances to determine the angle values.

TABLE 5. Theoretical and Experimental Values of Vibration Frequencies for the Isomers of the Enolic Form of the MMA Molecule According to the DFT Computation Data

Isomer: R′ = CH₃; R″ = H				Isomer: R′ = H; R″ = CH₃			
Calculation			Experiment [4]	Calculation			Experiment [4]
ω_i	A_i	Attribution		ω_i	A_i	Attribution	
3217	3	A', r(C–H$_c$)		3214	2	A', r(C–H$_c$)	
3139	10	A', r(C′–H′)		3181	32	A', r(C–H′) + r(O–H)	
3093	6	A'', r(C′–H$_A$)		3146	20	A', r(C″–H″)	
3063	258	A', r(O–H)	2972	3127	238	A', r(O–H) + r(C–H′)	3020
3039	1	A', r(C′–H$_A$)		3091	8	A'', r(C″–H$_B$)	
2973	146	A', r(C–H″)		3035	3	A', r(C″–H$_B$)	
1684	216	A', r(C=O) + r(C=C)		1688	325	A', r(C=O) + r(C=C)	1647
1642	394	A', α(HOC) + r(C=O)	1605	1627	208	A', α(HOC) + r(C=O)	1592
1490	20	A', χ(H$_A$) + α(C=C′H′)	1465	1489	84	A', α(C=CH$_c$) + α(C=CH′)	1457
1477	10	A'', χ(H′)		1482	11	A'', χ(H″)	
1460	113	A', α(HOC) + α(C=CH$_c$)	1428	1470	46	A', χ(H$_B$)	1425
1419	12	A', α(CC′H$_A$) + α(CC′H′)		1397	34	A', α(CC″H$_B$) + α(CC″H″)	
1405	58	A', α(C–CH″)		1383	50	A', α(CC″H″) + r(C=C)	1358
1378	149	A', r(C=C) + α(HOC) + r(C=O) + r(C–O)		1296	130	A', α(C=CH′) + r(C–O)	1266
1223	46	A', r(C–C′) + α(C=CH$_c$)	1180	1228	132	A', r(C–C″) + α(CC″H″) + r(C–C) + α(C=CH$_c$)	1203
1092	25	A', r(C–C) + α(C=CH$_c$)	1068	1121	35	A', α(C=CH$_c$) + r(C–O)	1093
1064	5	A'', α(CC′H$_A$) + χ(H′)		1052	18	A'', α(CC″H$_B$)	1028
1019	11	A', α(CC′H′) + α(CC′H$_A$)		1013	38	A'', ρ(H′) + χ(H)	985
1017	0	A'', ρ(H″)		991	34	A', α(CC″H″) + r(C–C″)	971
974	95	A'', χ(H)	928	933	57	A'', χ(H) + ρ(H′)	899
948	6	A', α(C=C–C) + α(O=C–C) + α(O–C=C)		920	8	A', α(C=C–C) + r(C–C)	
787	41	A'', ρ(H$_c$)	768	785	39	A'', ρ(H$_c$)	765
756	24	A', α(O=C–C) + r(C–C′)	716	726	4	A', α(O–C=C) + r(C–C″)	687
604	0	A'', χ_F + ρ(C′)		618	0	A'', χ_F + χ(H″) + ρ(C″)	
505	16	A', α(O–C=C) + α(O=C–C)		535	17	A', α(O=C–C) + α(O–C=C)	526
384	4	A', α(C=CC′)		374	1	A'', χ_F	
307	6	A'', χ_F		372	5	A', α(C–CC″)	
271	7	A', α(C–C=C)		251	4	A', α(C–C=C) + α(C–CC″)	
178	0	A'', χ_F + χ(H′) + χ(H$_A$)		131	1	A'', χ_F + χ(H″) + χ(H$_B$)	
125	1	A'', χ(H$_A$) + χ(H′)		17	0	A'', χ(H$_B$) + χ(H″)	

Note: ω_i is the vibration frequency (cm^{-1}); A_i is the vibration intensity (km/mol). In the vibration attribution, symmetry of the vibration mode and contributions of the natural vibrational coordinates to the potential energy are indicated. The contributions less than 15% are omitted. Coordinate notation: χ(H$_A$), χ(H′), χ(H$_B$), χ(H″) is the turn of the bonds C–H$_A$, C–H′, C–H$_B$, C–H″ relative to the bond C–C respectively; χ(H) is the turn of the bond H–O relative to the bond O–C; χ_F is non-planar deformation of the chelate moiety [OCCCO]; ρ(H$_c$), ρ(H″), ρ(C′), ρ(H′), ρ(C″) is the overrun of the corresponding atom out of the plane of the chelate moiety.
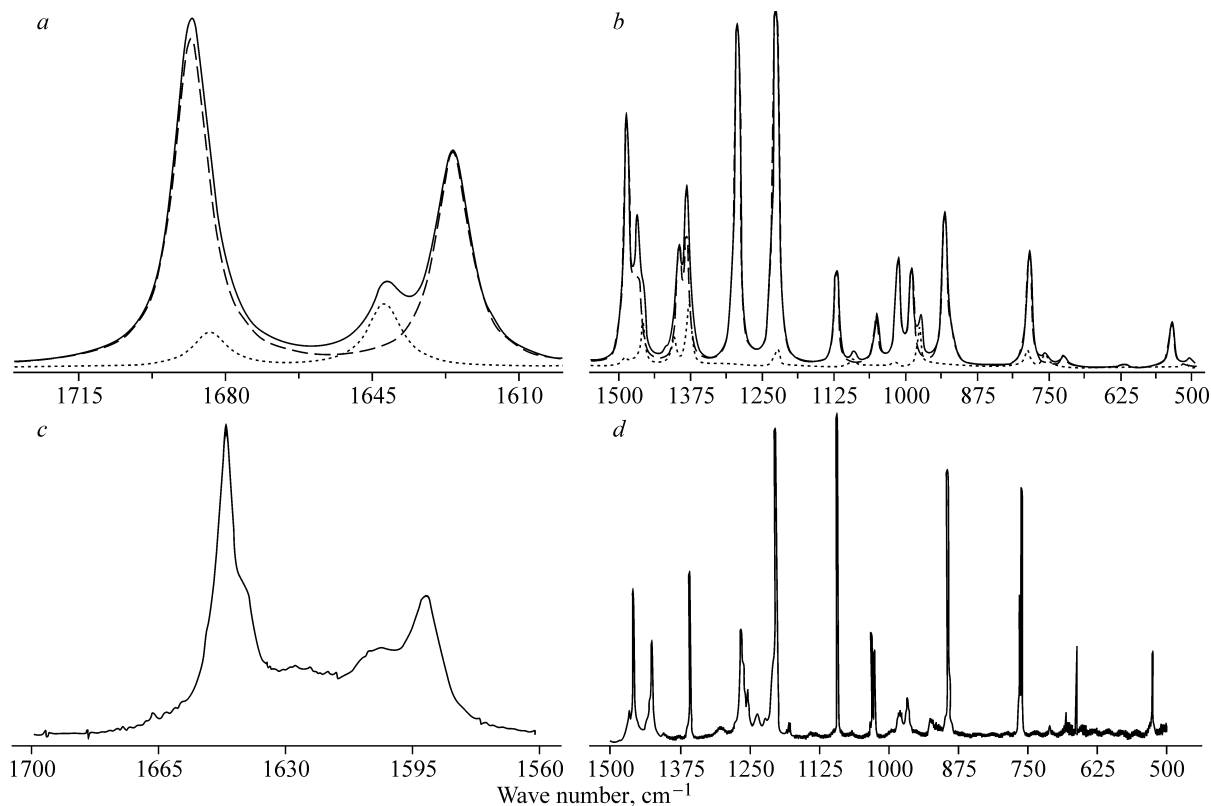
Fig. 2. Model (*a*, *b*) and experimental (*c*, *d*) IR spectra for the MMA molecule. Dashed and dotted lines in the model spectrum denote the spectra for the isomers MMA2 (R′=H, R″=CH₃) and MMA1 (R′=CH₃, R″=H) respectively. The experimental spectrum was taken from [4].

The interpretation of IR spectra for MMA molecules has been performed by the authors of the work [4] in the assumption of the existence of two isomers of the enolic form in vapors frozen in the Ar and Xe matrix. The attribution of the observed absorption bands was carried out in [4] with the employment of the estimated force field. Hence, the authors of [4] have come to the conclusion that the isomer MMA with R′=H and R″=CH₃ (further, MMA2) is dominant in comparison with the isomer with R′=CH₃ and R″=H (further, MMA1).

It is clear that the most probable mechanism of the transformation of one isomer into another lies in the intramolecular proton migration between the oxygen atoms of the chelate moiety. In the work [5], the experiment was carried out based on the laser control of the proton motion in the molecule of methylmalonaldehyde. According to the data from [5], the best interpretation of the results obtained is reached with a model potential function in which the deepest minimum corresponds to the isomer MMA1. The second minimum corresponding to the isomer MMA2 lies higher than the main one by 0.67 kJ/mol [5]. The results of our work agree with the data from [5]. According to the computations in the DFT approximation (Tables 1, 2), the relative energy of the isomer MMA2 is equal to 0.9 kJ/mol.

Thus, the results of the spectral investigation [4] and the data of the experiment [5] and theoretical calculations lead to different conclusions about the structure of the main isomer of the MMA molecule. To resolve this contradiction we have modeled the IR spectrum for the enolic form of the MMA molecule. To calculate the relative content of isomers in vapor, we have used the computed by DFT method values of the relative energy, geometric parameters, and vibration frequencies. Thermodynamic functions were calculated in the approximation "harmonic oscillator–rigid rotator." Our calculation of the equilibrium constant for the isomerization reaction, MMA1 → MMA2, at the temperature 100°C (the temperature of sample evaporation [4]) resulted in the following ratio of the isomers: MMA1:MMA2 = 1:6.3. The isomer MMA2 due to its higher entropy turned to be dominant in the vapor. Theoretical and experimental values for vibration frequencies of the MMA molecule are listed in Table 5. Fig. 2 illustrates the model (in modeling, the intensity of vibrations of the MMA2 isomer was

multiplied by 6.3) and experimental [4] IR spectra of the MMA molecule. The attribution of the experimental spectrum in Table 5 was performed basing on the comparison of the experimental and theoretical frequencies. The comparison indicates that the computed values are systematically higher than experimental: the mean deviation is 3.0%; maximal, 5.7%. This overestimation is connected with both systematic errors of theoretical values and a possible matrix shift of the measured values. It should be noted that we were not able to attribute two frequencies of 1628 cm^{-1} and 1304 cm^{-1}. The authors of [4] attributed these two bands to vibrations of the isomer MMA1. The results of our computations show that the band of 1304 cm^{-1} does not belong to the MMA molecule. According to our data, the band of 1628 cm^{-1} could be attributed to the vibration with the theoretical frequency of 1684 cm^{-1}. However, the frequency of 1684 cm^{-1} of the MMA1 isomer is close to the frequency of 1688 cm^{-1} of the MMA2 isomer attributed to the high intensive band of 1647 cm^{-1} in the experimental spectrum [4] (Fig. 2). Close values for the corresponding experimental frequencies are likely to be expected. Weak shading observed at the band of 1647 cm^{-1} in the experimental spectrum (Fig. 2) can serve as the corroboration for this assumption. On the whole, the experimental and theoretical spectra (Table 5 and Fig. 2) agree well. Furthermore, it should be noted that the obtained in [5] frequency of the fundamental transition of 276 cm^{-1}, attributed to the vibration O1···O2, is also very close to the predicted by us value of 271 cm^{-1} of the main isomer MMA1.

Such a good agreement of the theory and the experiment eliminates the illusory contradiction in the available theoretical and experimental data and testifies to the reliability of the results obtained by us.

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