

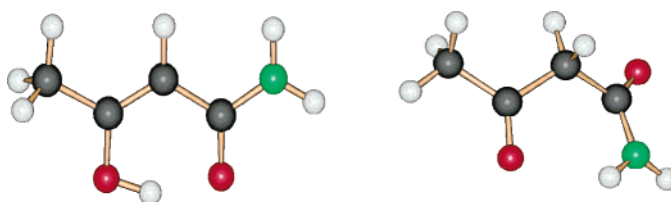
Tautomeric and Conformational Properties of Acetoacetamide: Electron Diffraction and Quantum Chemical Study

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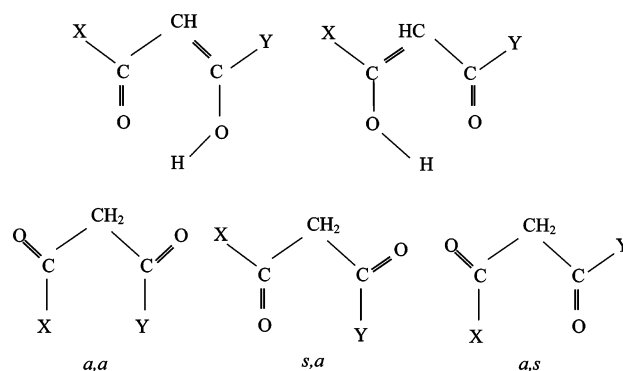


The tautomeric properties of acetoacetamide, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NH}_2$, have been investigated by gas electron diffraction (GED) and quantum chemical calculations (B3LYP and MP2 approximations with 6-31G(d,p) and 6-311++G(3df,pd) basis sets). GED results in a mixture of 63(7)% enol tautomer and 37(7)% diketo form at 74(5) °C. Only one enol form with the O–H bond adjacent to the methyl group ($\text{CH}_3\text{C}(\text{OH})=\text{CHC}(\text{O})\text{NH}_2$) and only one diketo conformer (with dihedral angles $\tau(\text{O}=\text{C}(\text{CH}_3)-\text{C}-\text{C}) = 31.7(7.5)^\circ$ and $\tau(\text{O}=\text{C}(\text{NH}_2)-\text{C}(\text{H}_2)-\text{C}(\text{O})) = 130.9(4.5)^\circ$) are present. The calculated tautomeric composition varies in a wide range depending on the quantum chemical method and basis set. Only the B3LYP method with small basis sets reproduces the experimental composition correctly.

Introduction

The keto–enol tautomerism of dicarbonyl compounds of the type $\text{XC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Y}$ has attracted great interest in the past few decades.¹ The preference of the enol or keto tautomeric form depends strongly on the substituents X and Y. According to gas-phase structural studies, the enol tautomer is present when both X and Y are H,^{2–4} CH_3 ,^{5–7} $\text{C}(\text{CH}_3)_3$,⁸ or CF_3 ⁹ (group I). Two enol forms can occur, with the O–H bond close to Y or

SCHEME 1. Enol Tautomers (Top) and Three Possible Conformers of the Diketo Tautomer (Bottom) of $\text{XC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Y}$ Compounds



close to X (see Scheme 1). On the other hand, the compounds with $\text{X} = \text{Y} = \text{F}$,¹⁰ Cl ,¹¹ OCH_3 ,¹² or NH_2 ¹³ (group II) exist in diketo form. For this tautomer different conformations are

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TABLE 1. Calculated Relative Energies and Gibbs Free Energies and Abundance of the Diketo Tautomer of Acetoacetamide

method	$\Delta E = E_{\text{keto}} - E_{\text{enol}}$ (kcal/mol)	$\Delta G^\circ = G^\circ_{\text{keto}} - G^\circ_{\text{enol}}^a$ (kcal/mol)	abundance of the diketo form ^a (%)
MP2/6-31G(d,p)	-2.02	-3.64	100
B3LYP/6-31G(d,p)	1.83	0.35	38
MP2/6-311++G(3df,pd)	1.64	-0.44	65
B3LYP/6-311++G(3df,pd)	2.62	1.28	14

^a At 347 K (74 °C).

feasible, depending on the relative orientations of the C=O bonds (Scheme 1; “s” stands for synperiplanar (sp) or synclinal (sc) and “a” for antiperiplanar (ap) or anticlinal (ac)¹⁴).

In a previous investigation¹⁵ we have studied the tautomeric and conformational properties of methyl acetoacetate, CH₃C(O)CH₂C(O)OCH₃ (MAA), a dicarbonyl compound which contains substituents from the two different groups. X = CH₃ favors the enol tautomer, whereas Y = OCH₃ favors the diketo form. In this case a gas electron diffraction (GED) study resulted in a mixture of 80(7)% enol and 20(7)% diketo tautomers. The predictions by the B3LYP calculations were in close agreement with the GED data, 92% (B3LYP/6-31G**) or 87% (B3LYP/6-31++G**) enol tautomer, whereas the MP2 calculations predicted a strong preference of the diketo form with only 1% (MP2/6-31G**) or 8% (MP2/6-311G(2df)) enol tautomer.

The present study deals with acetoacetamide, CH₃C(O)CH₂C(O)NH₂ (AA). In this dicarbonyl compound the substituents X = CH₃ and Y = NH₂ also belong to different groups. This makes the tautomeric properties of this compound highly interesting. An aqueous solution of AA contains a mixture of diketo and enol tautomers.¹⁶ The equilibrium constant $K_E = [\text{enol}]/[\text{keto}] = 0.11$ implies a strong preference for the diketo form (90%). Ab initio (HF/6-31G*) and molecular mechanics (MM2(87)) calculations¹⁷ were performed only for the diketo tautomer of AA. A conformational analysis was carried out by varying only the N–C–C–C dihedral angle in steps of 45° without full structural optimization. The lowest energy occurs at $\tau(\text{N–C–C–C}) = 45^\circ$.

To determine the tautomeric properties of acetoacetamide in the gas phase, we performed a GED study, which is supplemented by quantum chemical calculations. It turns out that this compound is better suited for a study of the tautomeric equilibrium than MAA, since quantum chemical calculations (see below) predict only one stable enol form and a single stable diketo conformer for this dicarbonyl compound, whereas one enol and three diketo conformers with very similar relative free energies were predicted in the case of MAA.¹⁵

Results

Quantum Chemical Calculations. All quantum chemical calculations were performed with the program set GAUSSIAN 03.¹⁸ The geometries of the enol and diketo tautomers of AA were optimized with the MP2 and B3LYP methods with small (6-31G(d,p)) and large (6-311++G(3df,pd)) basis sets. The relative energies ($\Delta E = E_{\text{keto}} - E_{\text{enol}}$) and relative free energies

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(14) sp corresponds to dihedral angles $\tau(\text{O=C–C–C})$ of $0^\circ \pm 30^\circ$, sc to $60^\circ \pm 30^\circ$, ac to $120^\circ \pm 30^\circ$, and ap to $180^\circ \pm 30^\circ$.

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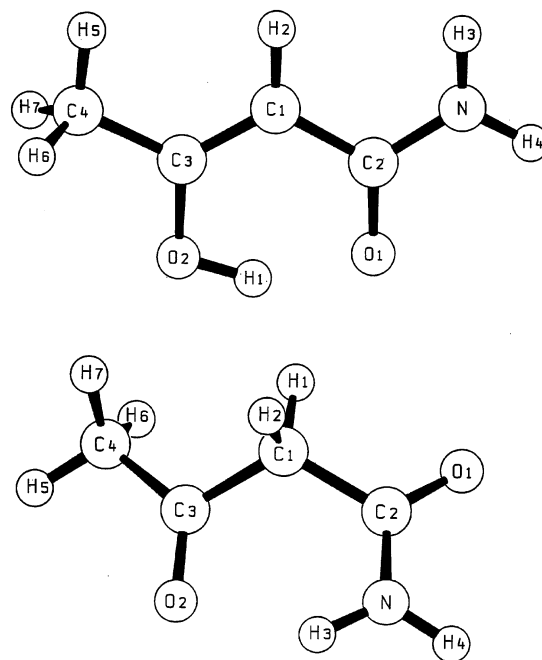


FIGURE 1. Molecular structures of enol (top) and diketo (bottom) forms of acetoacetamide.

($\Delta G^\circ = G^\circ_{\text{keto}} - G^\circ_{\text{enol}}$) obtained with the different computational methods are summarized in Table 1. ΔG° values and predicted abundances of the diketo tautomer are given for the temperature of the GED experiment (347 K). According to quantum chemical calculations, only one stable enol form with the O–H bond adjacent to the methyl group, CH₃C(OH)=CHC(O)NH₂, exists (see Figure 1). If a starting geometry with the O–H bond adjacent to the NH₂ group, CH₃C(O)CH=C(O)NH₂, is used, the O–H bond flips over to the acetyl group and the geometry optimization converges toward the enol form shown in Figure 1.

To find all possible diketo conformers, the potential energy surface was scanned with the B3LYP/6-31G** method. The

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torsional angles $\tau(\text{O1C2C1C3})$ and $\tau(\text{O2C3C1C2})$ were changed in steps of 20° with full optimization of all other parameters (see Figure 1 for atom numbering). There is only one deep minimum on the potential energy surface with $\tau(\text{O1C2C1C3}) = 140^\circ$ and $\tau(\text{O2C3C1C2}) = 40^\circ$. It should be noted that all geometric parameters optimized at different levels of theory are very close, excluding the torsional angles $\tau(\text{O1C2C1C3})$ and $\tau(\text{O2C3C1C2})$ in the diketo tautomer. Thus, $\tau(\text{O1C2C1C3})$ varies from 126.4° (MP2/6-311++G(3df,pd)) to 145.4° (B3LYP/6-311++G(3df,pd)), and $\tau(\text{O2C3C1C2})$ varies from 64.9° (MP2/6-311++G(3df,pd)) to 35.7° (B3LYP/6-311++G(3df,pd)). For comparison of calculated and experimental keto–enol equilibrium compositions, Gibbs free energies must be applied, instead of the relative energies. G° values include zero-point energies, temperature corrections, and entropies. For the differences, ΔG° , these contributions depend primarily on low-frequency vibrations, which differ appreciably for keto and enol tautomers. E.g., the lowest frequency for the diketo form is predicted to be 44 cm^{-1} and that for the enol form to be 83 cm^{-1} (B3LYP/6-311++G(3df,pd)). This causes differences between ΔE and ΔG° of up to 2 kcal/mol. Furthermore, a multiplicity of 2 has to be taken into account for the diketo tautomer (both OCCC dihedral angles may have positive or negative signs).

The predictions of quantum chemical calculations concerning the tautomeric equilibrium depend strongly on the computational method. The energy and free Gibbs energy differences vary from 2.62 (B3LYP/6-311++G(3df,pd)) to -2.02 (MP2/6-31G(d,p)) kcal/mol and from 1.28 (B3LYP/6-311++G(3df,pd)) to -3.64 (MP2/6-31G(d,p)) kcal/mol, respectively (see Table 1). Whereas the MP2 approximation with small basis sets predicts the presence of the diketo conformer only, B3LYP with large basis sets predicts a strong preference of the enol form.

The geometric parameters for the enol and diketo tautomers that were derived with the B3LYP/6-311++G(3df,pd) method are listed in Table 2, together with the experimental results. Parameters derived with the MP2 approximation (not shown) and large basis sets are very similar. Vibrational amplitudes and corrections, $\Delta r = r_{\text{hl}} - r_{\text{a}}$, were derived from theoretical force fields (B3LYP/6-311++G(3df,pd)) with the method of Sipachev, using the program SHRINK.¹⁹ The values for the enol form are listed in Table 3.

Structural Analysis. The experimental geometric structure and tautomeric properties of AA were determined with a combined GED/mass spectrometric method. The heaviest ion in the mass spectrum was $[\text{C}_4\text{H}_7\text{NO}_2]^+$ (see the Experimental Section). This demonstrates that monomers are present in the vapor at the conditions of the GED experiment. No ions were detected, which could arise from impurities. The experimental radial distribution function (Figure 2) was derived by Fourier transformation of the experimental intensities.

Comparison with calculated radial distribution functions demonstrates that the experimental radial distribution curve cannot be reproduced reasonably well with the diketo or enol tautomer alone (see Figure 2). The two calculated functions differ especially in the distance ranges 2.5–3.5 and 4.5–5.5 Å. The prominent peak in the diketo curve around 3.0 Å is due to $\text{N}\cdots\text{O}_2$, $\text{C}_2\cdots\text{O}_2$, and $\text{C}_3\cdots\text{N}$ nonbonded distances in this tautomer. In the least-squares analysis a mixture of both diketo and enol forms was considered. For both tautomers the differences between all C–H and N–H (and O–H in the enol

TABLE 2. Experimental and Calculated Geometric Parameters of the Enol and Diketo Tautomers of Acetoacetamide^a

parameter	enol		diketo	
	GED (r_{hl} , \angle_{hl}) ^b	B3LYP ^c	GED (r_{hl} , \angle_{hl}) ^b	B3LYP ^c
$r(\text{C1}-\text{C2})$	1.466(5)	1.451	1.545(5)	1.533
$r(\text{C1}-\text{C3})$	1.375(5) ^d	1.360	1.533(5) ^d	1.521
$r(\text{C3}-\text{C4})$	1.507(5) ^d	1.492	1.519(5) ^d	1.507
$r(\text{C2}-\text{O1})$	1.245(3)	1.245	1.222(4)	1.216
$r(\text{C3}-\text{O2})$	1.326(3) ^d	1.327	1.218(4) ^d	1.213
$r(\text{C2}-\text{N})$	1.354(5)	1.359	1.351(8)	1.353
$r(\text{C4}-\text{H5})$	1.092(6)	1.088	1.087 ^e	1.087
$r(\text{C4}-\text{H6})$	1.096(6) ^d	1.092	1.094 ^e	1.094
$r(\text{C4}-\text{H7})$	1.096(6) ^d	1.092	1.093 ^e	1.093
$r(\text{N}-\text{H3})$	1.008(6) ^d	1.004	1.012 ^e	1.012
$r(\text{N}-\text{H4})$	1.010(6) ^d	1.006	1.008 ^e	1.008
$r(\text{C1}-\text{H2})$	1.084(6) ^d	1.080	1.097 ^e	1.097
$r(\text{O2}-\text{H1})$	1.007(6) ^d	1.003		
$r(\text{C1}-\text{H1})$			1.088 ^e	1.088
$\angle\text{C2C1C3}$	119.9(2.1)	120.2	117.8(1.9)	118.6
$\angle\text{C1C2O1}$	121.6(2.2)	122.3	118.9(3.0)	119.9
$\angle\text{C1C3O2}$	121.6(2.2) ^d	122.4	121.4(3.0) ^d	122.4
$\angle\text{C1C3C4}$	123.8(2.8)	123.9	114.3(3.3)	116.0
$\angle\text{C1C2N}$	116.2(2.6)	117.8	115.4(2.5)	116.1
$\angle\text{H5C4C3}$	111.6 ^e	111.6	110.3 ^e	110.3
$\angle\text{H6C4C3}$	109.7 ^e	109.7	109.3 ^e	109.3
$\angle\text{H7C4C3}$	109.7 ^e	109.7	110.5 ^e	110.5
$\angle\text{H3NC2}$	122.2 ^e	122.2	119.3 ^e	119.3
$\angle\text{H4NC2}$	118.5 ^e	118.5	117.5 ^e	117.5
$\angle\text{H1O2C3}$	106.1 ^e	106.1		
$\angle\text{H1C1C3}$			111.2 ^e	111.2 ^f
$\angle\text{H1C1C2}$			107.0 ^e	107.0 ^f
$\tau(\text{O1C2C1C3})$	0.0 ^e	0.0	130.9(4.5)	145.4
$\tau(\text{O2C3C1C2})$	0.0 ^e	0.0	31.7(7.5)	35.7
$\tau(\text{C4C3C1O2})$	180.0 ^e	180.0	179.0 ^e	179.0
$\tau(\text{NC2C1O1})$	180.0 ^e	180.0	177.0 ^e	177.0
$\tau(\text{H5C4C3O2})$	180.0 ^e	180.0	6.6 ^e	6.6
$\tau(\text{H3NC2C1})$	0.0 ^e	0.0	15.3 ^e	15.3

^a Distances in angstroms and angles in degrees. For atom numbering see Figure 1. ^b Uncertainties in r_{hl} , $\sigma = (\sigma_{\text{sc}}^2 + (2.5\sigma_{\text{LS}})^2)^{1/2}$ ($\sigma_{\text{sc}} = 0.002r$, σ_{LS} = standard deviation in least-squares refinement); for angles $\sigma = 3\sigma_{\text{LS}}$. ^c 6-311++G(3df,pd) basis sets. ^d Difference from previous parameter fixed to calculated (B3LYP) value. ^e Not refined. ^f Average value.

form) bond lengths, between the C3–O2 and C2–O1 bond lengths, and among the C1–C2, C1–C3, and C3–C4 bond lengths, as well as the orientations of NH₂ and CH₃ groups, were constrained to calculated values (B3LYP/6-311++G(3df,pd)). For the enol tautomer overall C_s symmetry was assumed. The geometric parameters for enol and diketo tautomers, using B3LYP/6-311++G(3df,pd) results as starting parameters, were then refined by a least-squares procedure of the molecular intensities. Independent r_{hl} parameters were used to describe the molecular structure. Vibrational amplitudes were refined in groups with fixed differences. There were 13 correlation coefficients that had values larger than |0.7|. Most of them refer to correlations between parameters belonging to different tautomers. There were only four values larger than |0.8|: $r(\text{C}-\text{N})_{\text{keto}}/r(\text{C}-\text{N})_{\text{enol}} = -0.94$, $\angle(\text{C2}-\text{C1}-\text{C3})_{\text{enol}}/\angle(\text{C1}-\text{C2}-\text{O1})_{\text{enol}} = -0.96$, $\angle(\text{C1}-\text{C3}-\text{C4})_{\text{keto}}/\angle(\text{C1}-\text{C2}-\text{O1})_{\text{enol}} = -0.84$, $\angle(\text{C1}-\text{C3}-\text{C4})_{\text{keto}}/\angle(\text{C1}-\text{C3}-\text{C4})_{\text{enol}} = -0.87$.

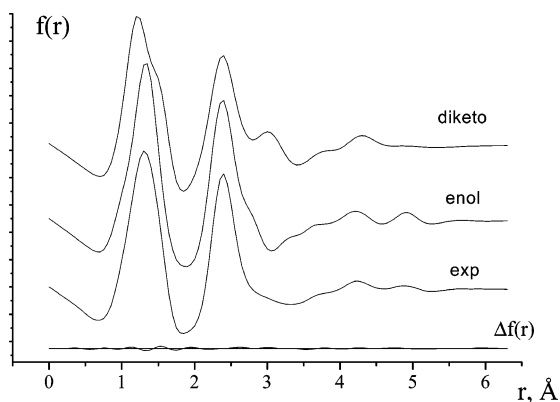
The best agreement factors resulted for a mixture of 63(7)% enol and 37(7)% keto forms with $R_f = 4.9\%$. This composition corresponds to the temperature of the effusion cell of 74(5) °C. Final results of the least-squares analysis are given in Tables 2 (geometric parameters) and 3 (vibrational amplitudes; the refined groups of variation are designated as *l1*, *l2*, etc.). The refined geometrical parameters are rather similar to those predicted by

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TABLE 3. Interatomic Distances r_{hl} , Vibrational Amplitudes l , and Vibrational Corrections $r_{\text{hl}} - r_{\text{a}}$ for the Enol Conformer (Excluding Nonbonded Distances Involving Hydrogen)^a

	r_{hl}^b (Å)	$l(\text{GED})^b$	$l(\text{B3LYP})^c$	$r_{\text{hl}} - r_{\text{a}}^c$
O2-H1	1.007(6)	0.072(6), 11 ^d	0.078	-0.00009
N-H3	1.008(6)	0.066(6), 11	0.072	0.0026
N-H4	1.010(6)	0.066(6), 11	0.072	0.0026
C1-H2	1.084(6)	0.070(6), 11	0.075	0.0019
C4-H5	1.092(6)	0.070(6), 11	0.076	0.0015
C4-H6	1.096(6)	0.071(6), 11	0.077	0.0016
C4-H7	1.096(6)	0.071(6), 11	0.077	0.0016
C2-O1	1.245(3)	0.035(6), 11	0.040	-0.0002
C3-O2	1.326(3)	0.039(6), 11	0.044	0.0006
C2-N	1.354(5)	0.039(6), 11	0.044	0.0009
C1-C3	1.375(5)	0.038(6), 11	0.043	0.0001
C1-C2	1.466(5)	0.043(6), 11	0.049	0.0017
C3-C4	1.507(5)	0.044(6), 11	0.050	0.0003
O1...N	2.276(63)	0.054(3), 12	0.054	0.0056
C1...O2	2.359(38)	0.054(3), 12	0.055	0.0028
C4...O2	2.385(76)	0.064(3), 12	0.064	0.0047
C1...O1	2.369(38)	0.056(3), 12	0.056	0.0049
C1...N	2.395(33)	0.061(3), 12	0.062	0.0030
C2...C3	2.460(37)	0.057(3), 12	0.057	0.0081
O1...O2	2.530(44)	0.102(3), 12	0.103	0.0116
C1...C4	2.544(39)	0.064(3), 12	0.065	0.0019
O2...C2	2.806(19)	0.106(10), 13	0.078	0.0111
C3...O1	2.807(19)	0.106(10), 13	0.078	0.0113
C3...N	3.655(32)	0.085(21), 14	0.063	0.0163
C2...C4	3.879(27)	0.100(21), 14	0.067	0.0125
O2...N	4.154(49)	0.120(19), 15	0.082	0.0252
C4...O1	4.314(27)	0.121(19), 15	0.084	0.0187
C4...N	4.939(39)	0.112(29), 16	0.081	0.0200

^a Values in angstroms. Error limits are 3σ values. For atom numbering see Figure 1. ^b r_{hl} , $l(\text{GED})$ = interatomic distances and vibrational amplitudes (respectively) derived from GED data. ^c $l(\text{B3LYP})$, $r_{\text{hl}} - r_{\text{a}}$ = vibrational amplitudes and vibrational corrections (respectively) derived from theoretical force fields (B3LYP/6-311++G(3df,pd)) with the method of Sipachev, using the program SHRINK.¹⁹ ^d Group number of amplitude.

**FIGURE 2.** Experimental and calculated radial distribution functions and difference curve for the mixture of diketo and enol forms.

the quantum chemical calculations (B3LYP/6-311++G(3df,pd)). Only the torsional angle $\tau(\text{O1C2C1C3})$ in the diketo tautomer differs from the calculated value by about 15° . However, as mentioned above, the range of calculated torsion angles in the diketo form is about 30° .

Discussion

The GED experiment for acetoacetamide, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NH}_2$, which is a dicarbonyl compound with two different substituents, CH_3 favoring the enol tautomer and NH_2 the diketo tautomer, results in a tautomeric mixture of 37(7)% diketo and

63(7)% enol tautomers in the gas phase at 74(5) °C. This composition corresponds to a free Gibbs energy difference $\Delta G^\circ = 0.37(15)$ kcal/mol and an equilibrium constant $K_E = [\text{enol}]/[\text{keto}] = 1.70(5)$. We can note that the B3LYP calculation with a small basis set reproduces the experiment perfectly. The value of the equilibrium constant K_E derived from GED differs considerably from that derived for an aqueous solution with $K_E = 0.11$,¹⁶ which corresponds to a strong preference of the diketo tautomer of 90%. Apparently, intermolecular interactions with water molecules stabilize the diketo form in aqueous solution.

As pointed out in the Introduction, the tautomeric properties of dicarbonyl compounds $\text{XC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Y}$ depend strongly on the substituents X and Y. For symmetrically substituted compounds with X and Y belonging to group I (H, CH_3 , $\text{C}(\text{CH}_3)_3$, or CF_3) only the enol form exists in the gas phase. On the other hand, for compounds with X and Y belonging to group II (F, Cl, NH_2 , and OCH_3) only the diketo tautomer is observed. We will attempt now to formulate a rule of thumb to predict of tautomeric properties of dicarbonyl compounds with specific substituents X and Y. An intuitive characterization of the substituents would be their electronegativity. Using the values χ_{BB} of Boyd and Boyd,²⁰ H (2.10), CH_3 (2.55), $\text{C}(\text{CH}_3)_3$ (2.55), CF_3 (2.71), Cl (3.00), NH_2 (3.12), OCH_3 (3.53), and F (4.00), the following rule can be formulated: substituents of group I with $\chi_{\text{BB}} < 2.8$ favor the enol tautomer, and substituents of group II with $\chi_{\text{BB}} \geq 3.0$ favor the diketo form. We are aware that this is a crude rule since group electronegativities depend on the method of their determination and may differ appreciably. Particularly, other electronegativity scales give values larger than 3.0 for the CF_3 group.

An alternative characterization of the substituents is the presence or absence of electron lone pairs. Substituents of group I (H, CH_3 , $\text{C}(\text{CH}_3)_3$, and CF_3), which favor the enol tautomer, do not possess any lone pair, whereas substituents of group II (NH_2 , OCH_3 , Cl, and F), which favor the diketo form, possess one, two, or three lone pairs. For the dicarbonyl compounds studied so far in the gas phase both types of characterization (electronegativity values χ_{BB} or the presence of lone pairs) lead to the same conclusions. A disagreement between the two types of characterization occurs for substituents with lone pairs and low electronegativity, such as SH or SR. The presence of electron lone pairs should favor the diketo form, but their electronegativity ($\chi_{\text{BB}} = 2.65$ for SH and SCH_3) is less than 2.8 and should favor the enol tautomer. So far, the tautomeric properties of dithiomalonic acid or derivatives of it have not been determined in the gas phase. Quantum chemical calculations for $\text{HSC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{SH}$ predict a strong preference of the diketo tautomer ($\Delta G^\circ = G^\circ_{\text{keto}} - G^\circ_{\text{enol}} = -2.21$ and -6.08 kcal/mol according to the B3LYP and MP2 methods with 6-31G(d,p) basis sets, respectively). Furthermore, ^1H and ^{13}C NMR spectra for *S,S'*-diethyl dithiomalonate, $\text{EtSC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{SEt}$, in CCl_4 solution result in the presence of the diketo form only.^{21,22} Provided that the quantum chemical calculations mentioned above for dithiomalonic acid and the NMR data for the liquid diethyl derivative represent the gas-phase tautomeric properties correctly, the latter characterization of substituents based on the presence or absence of electron lone pairs provides

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TABLE 4. Conditions of the GED Experiment

nozzle-to-plate distance (mm)	338.0	598.0
fast electron beam (μA)	1.46	0.75
accelerating voltage (kV)	73	74
(electron wavelength (\AA))	(0.043978(40))	(0.043639(20))
temperature of the effusion cell (K)	348(5)	348(5)
ionization voltage (V)	50	50
exposure time (s)	70–75	55–60
residual gas pressure (Torr)	2.1×10^{-6}	3.3×10^{-6}

TABLE 5. Mass Spectral Data of the Vapor of $\text{C}_4\text{H}_7\text{NO}_2$

ion	m/e	abundance (%)	ion	m/e	abundance (%)
$[\text{M}]^+{}^a$	101	28	$[\text{C}(\text{O})\text{NH}_2]^+$	44	44
$[\text{M} - \text{CH}_3]^+$	86	10	$[\text{H}_3\text{CC}(\text{O})]^+$	43	100
$[\text{M} - \text{CH}_3 - \text{NH}_2 - 2\text{H}]^+$	69	12	$[\text{C}(\text{O})\text{CH}_2]^+$	42	26
$[\text{NH}_2\text{C}(\text{O})\text{CH}_3]^+$	59	62			

^a $\text{M} = \text{C}_4\text{H}_7\text{NO}_2$.

a correct prediction of the tautomeric properties of the dithio-malonates, and has to be preferred to the electronegativity criterion. This is only a purely empirical rule, and we are unable to provide a convincing explanation for it. Apparently, conjugation between a lone pair of the substituent and the $\text{C}=\text{O}$ π -bond, i.e., a resonance structure of the type $\text{X}^+=\text{C}-\text{O}^-$ stabilizes the keto structure.

In the case of dicarbonyl compounds with one group I substituent and one group II substituent, a mixture of enol and diketo tautomers is expected. So far, only two such dicarbonyl compounds have been studied in the gas phase, methylacetoacetate, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{OCH}_3$, and acetoacetamide, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NH}_2$. Indeed, both of them exist as a mixture of enol and diketo tautomers. Only the enol form with the $\text{O}-\text{H}$ bond adjacent to the methyl group (group I substituent) is observed. Acetoacetamide possesses a slightly higher diketo contribution (37(7)%) than methylacetoacetate (20(7)%). This may be due to an additional stabilization of the diketo tautomer by a weak $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond.

Experimental Section

A commercial sample was used. The electron diffraction patterns and the mass spectra were recorded simultaneously using the techniques described previously.^{23,24} The conditions of the GED/MS experiment and the relative abundance of the characteristic ions

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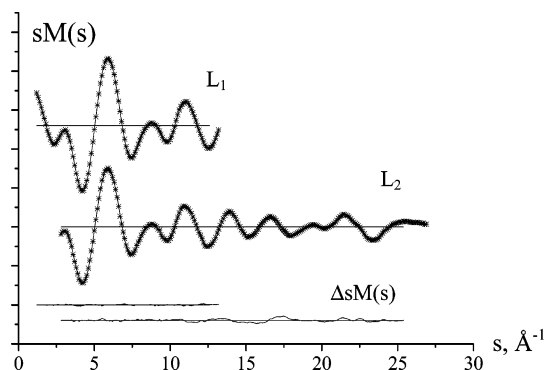


FIGURE 3. Experimental (dots) and calculated (solid line) modified molecular intensity curves and the residuals (experimental – theoretical) at two nozzle-to-plate distances ($L_1 = 598$ mm, $L_2 = 338$ mm).

of $\text{C}_4\text{H}_7\text{NO}_2$ are shown in Tables 4 and 5, respectively. The temperature of the stainless steel effusion cell was measured by a W/Re-5/20 thermocouple that was calibrated by the melting points of Sn and Al. The wavelength of electrons was determined from diffraction patterns of polycrystalline ZnO. The optical densities were measured by a computer-controlled microdensitometer.²⁵ The molecular intensities $sM(s)$ were obtained in the s ranges 2.8–26.9 and 1.2–13.2 \AA^{-1} for the short and long nozzle-to-plate distances, respectively ($s = (4\pi/\lambda)(\sin \theta/2)$, where λ is the electron wavelength and θ is the scattering angle). The experimental and theoretical intensities $sM(s)$ are compared in Figure 3.

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Supporting Information Available: Results of MP2 and B3LYP calculations with different basis sets: Cartesian coordinates, electronic energies, number of imaginary frequencies, zero-point corrections, thermal corrections to energies, enthalpies, and Gibbs free energies for enol and diketo conformers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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