J. Phys. Chem. A **2004,** *108,* 3593−3597 **3593**

Tautomeric and Conformational Properties of Methyl Acetoacetate, $\mathrm{CH_3OC(O){-}CH_2{-}C(O)CH_3}$: Electron Diffraction and Quantum Chemical Study

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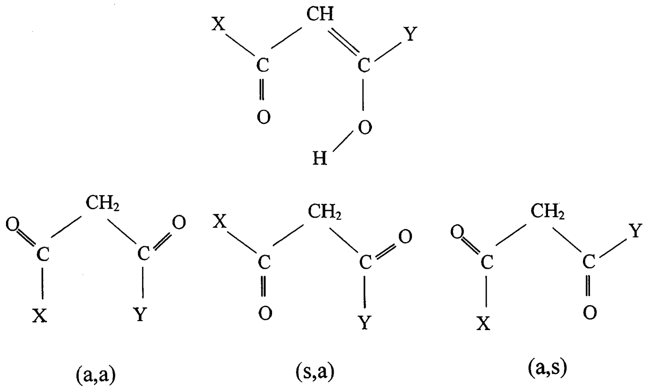
Received: January 23, 2004; In Final Form: February 17, 2004

The tautomeric properties of methyl acetoacetate, $\mathrm{CH_3OC(O){-}CH_2{-}C(O)CH_3}$, have been investigated in the gas phase by gas electron diffraction (GED), IR(matrix) spectroscopy, and quantum chemical calculations (the MP2 approximation with 6-31G** and 6-311G(2df) basis sets and the B3LYP method with 6-31G** and 6-31++G** basis sets). GED results in a mixture of 80(7)% enol tautomer and 20(7)% diketo form at 309(6) K. Only one enol form with the O−H bond adjacent to the methyl group, $\mathrm{CH_3OC(O){-}CH{=}C(OH)CH_3}$, is present. The GED analysis cannot distinguish between the three diketo conformers which are predicted by quantum chemical calculations. IR(matrix) spectra confirm the presence of a mixture of enol and keto forms with the enol tautomer strongly prevailing. Quantum chemical calculations with the MP2 approximation predict a very small contribution of the enol tautomer, in contrast to the experiments. B3LYP calculations, however, reproduce the experimental tautomeric mixture very closely.

Introduction

The keto−enol tautomerism of dicarbonyl compounds of the type $\mathrm{XC(O){-}CH_2{-}C(O)Y}$ has attracted great interest in the past decades.[1] The preference of the enol or keto tautomeric form depends strongly on the substituents X and Y. Gas phase structural studies result in enol tautomers when X and Y are H,[2−4] CH_3,[5−7] $C(CH_3)_3$,[8] or CF_3.[9] On the other hand, the keto tautomer occurs when X and Y are F,[10] Cl,[11] OCH_3,[12] or NH_2.[13] For this tautomer different conformations are feasible, depending on the relative orientations of the C═O bonds (Chart 1, "s" stands for synperiplanar (sp) or synclinal (sc) and "a" for antiperiplanar (ap) or anticlinal (ac)).[14] Methyl acetoacetate (MAA), $\mathrm{CH_3OC(O){-}CH_2{-}C(O)CH_3}$, is a β-dicarbonyl which contains substituents from the two different groups. CH_3 favors the enol form, whereas OCH_3 favors the keto tautomer. This makes the tautomeric properties of this compound highly interesting. According to ^{1}H NMR spectra, liquid MAA exists at 306 K exclusively in the keto form.[15] A similar result is obtained from ^{13}C NMR spectra.[16] On the other hand, vibrational spectra of the liquid are interpreted in terms of the enol form.[16] At 423 K a mixture of both tautomers with the keto form prevailing is observed in the ^{1}H NMR spectra of the liquid, and a free energy difference of $\Delta G^0 = G^\circ\,(\text{keto}) - G^\circ\,(\text{enol}) = -1.89 \pm 1.61$ kcal/mol is derived.[15] 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 $\Delta G^\circ = -0.08 \pm 1.45$ kcal/mol.[15] Unfortunately, the experimental uncertainty in this NMR study is large, and the study covers a wide range of tautomeric mixtures of enol/keto from 1:13 to 10:1. In the present study we report a gas phase electron diffraction study (GED) of MAA, which is supplemented by IR(matrix) spectra and by quantum chemical calculations.

CHART 1: Enol Tautomer (Above) and Three Possible Conformers of the Diketo Tautomer of $\mathrm{XC(O){-}CH_2{-}C(O)Y}$ Compounds (Below)



Quantum Chemical Calculations

All quantum chemical calculations were performed with the program set GAUSSIAN 98.[17] The geometries of the enol tautomer and of the possible conformers of the keto form of MAA were optimized with the MP2 approximation (6-31G** and 6-311G(2df) basis sets) and with the B3LYP hybrid method (6-31G** and 6-31++G** basis sets). Only conformers with the synperiplanar orientation of the O−CH3 bond relative to the C═O bond are considered below; conformers with antiperiplanar orientation are higher in energy by 6 kcal/mol or more. The dihedral angles, relative energies (ΔE), and relative free energies (ΔG°) obtained with the different computational methods are summarized in Table 1. Because no frequency calculation was performed with the MP2/6-311G(2df) method, the vibrational frequencies obtained with the MP2/6-31G** approximation were used for deriving ΔG^0 from ΔE.

According to quantum chemical calculations, only one stable enol form with the O−H bond adjacent to the methyl group,

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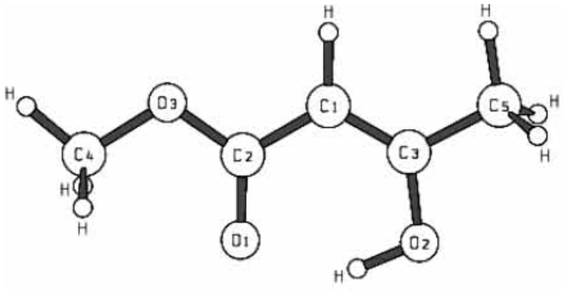
10.1021/jp049666w CCC: \$27.50

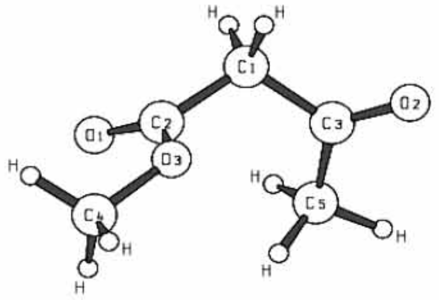
TABLE 1: Optimized Dihedral Angles τ_1 and τ_2, Relative Energies, and Gibbs Free Energies of the Enol Tautomer and Diketo Conformers of MAA (see Figure 1 for Atom Numbering)

	enol	diketo (ac, ac)	diketo (ac, sp)	diketo (sc, ac)
MP2/6-31G**				
τ_1 (C3C1C2O1)	0.0	118.5	98.7	65.2
τ_2 (C2C1C3O2)	0.0	135.2	−4.0	105.2
ΔE (kcal/mol)	0.0	0.79	0.52	0.50
$\Delta G°$ (kcal/mol)	0.0	−2.09	−2.19	−2.11
MP2/6-311G(2df)				
τ_1 (C3C1C2O1)	0.0	113.3	98.3	65.5
τ_2 (C2C1C3O2)	0.0	138.4	−1.2	103.0
ΔE (kcal/mol)	0.0	2.04	2.00	1.86
$\Delta G°$ (kcal/mol)^a	0.0	−0.84	−0.71	−0.75
B3LYP/6-31G**				
τ_1 (C3C1C2O1)	0.0	119.8	98.2	52.8
τ_2 (C2C1C3O2)	0.0	135.3	1.6	108.1
ΔE (kcal/mol)	0.0	5.63	5.42	4.73
$\Delta G°$ (kcal/mol)	0.0	2.08	2.25	2.00
B3LYP/6-31++G**				
τ_1 (C3C1C2O1)	0.0	*b*	93.7	56.7
τ_2 (C2C1C3O2)	0.0	*b*	5.7	104.7
ΔE (kcal/mol)	0.0	*b*	5.16	4.76
$\Delta G°$ (kcal/mol)	0.0	*b*	1.34	2.00

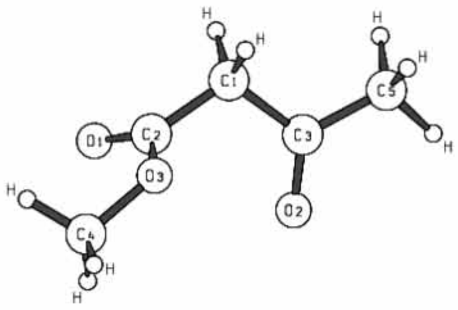
[a] Derived from ΔE using the vibrational frequencies calculated with the MP2/6-31G** method. [b] Not a stable conformer according to this method.



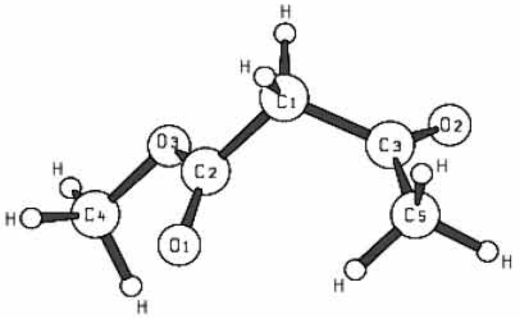
(a) enol tautomer



(b) (ac,ac) diketo tautomer



(c) (ac,sp) diketo tautomer



(d) (sc,ac) diketo tautomer

Figure 1. Molecular structures of enol tautomer (a) and diketo conformers (b), (c), and (d).

$CH_3OC(O){-}CH{=}C(OH)CH_3$, exists, which possesses a C1=C3 double bond along with a C3−O2 single bond (see Figure 1). If a starting geometry with the O−H bond adjacent to the methoxy group, $CH_3OC(OH){=}CH{-}C(O)CH_3$, is used, the O−H bond migrates from the ester group to the acetyl group and the geometry optimization converges toward the enol form shown in Figure 1. 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 (see Figure 1). 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, and according to these calculations the (sc, ac) form possesses the lowest energy among the diketo conformers. The diketo conformers are higher in energy than the enol tautomer. This energy difference depends strongly on the computational method. The energy of the (sc, ac) conformer relative to the enol form varies from 0.50 kcal/mol (MP2/6-31G**) to 4.76 kcal/mol (B3LYP/6-31++G**).

For comparison of calculated and experimental conformational properties, Gibbs free energies must be applied, instead of the relative energies. $\Delta G°$ values include zero-point energies, temperature corrections, and entropies. These contributions depend primarily on low-frequency torsional vibrations around the C−C and $O{-}CH_3$ bonds, which differ appreciably between keto and enol tautomers. For example, the lowest frequency for the (sc, ac) conformer is predicted to be 20 cm^{-1} and that of the enol form to be 85 cm^{-1} (MP2/6-31G**). This results in an entropy difference between these two structures of about 6 cal K^{-1} mol^{-1}, leading to $T\Delta S$ of about 1.8 kcal/mol. Furthermore, the free energy takes the different multiplicities (m) of the various forms into account: $m = 1$ for the enol (planar structure) and $m = 2$ for all diketo forms (nonplanar structures). The vibrational contributions and different multiplicities lead to rather large differences between relative energies ΔE and free energies $\Delta G°$. The data in Table 1 show that the MP2 method with small and large basis sets predicts a strong preference for the keto forms, whereas the B3LYP method predicts a preference for the enol tautomer.

The geometric parameters for the enol tautomer that were derived with the MP2/6-31G** and B3LYP/6-31++** methods are listed in Table 2, together with the experimental results. Parameters of the three diketo conformers obtained with the MP2/6-31G** approximation are given as Supporting Information (Table S1). Vibrational amplitudes and corrections were derived from theoretical force fields (MP2/6-31G*) with the method of Sipachev, using the program SHRINK.[18] The values for the enol form are listed in Table 3.

TABLE 2: Experimental and Calculated Geometric Parameters of the Enol Tautomer of Methyl Acetoacetate[a]

parameters	GED (r(h1))[b]	MP2/6-31G**	B3LYP/6-31G++**
r(C1−C2)	1.449(4)	1.448	1.446
r(C1=C3)	1.362(4)[c]	1.361	1.368
r(C3−C5)	1.493(4)[c]	1.492	1.496
r(C2=O1)	1.248(4)	1.241	1.242
r(C3−O2)	1.339(4)	1.342	1.336
r(C2−O3)	1.347(4)[c]	1.350	1.348
r(O3−C4)	1.437(4)[c]	1.440	1.440
r(C4−H)	1.098(7)	1.086[e]	1.092[e]
r(C5−H)	1.100(7)[c]	1.089[e]	1.094[e]
r(C1−H)	1.077[d]	1.077	1.081
r(O2−H)	0.988[d]	0.988	0.996
∠C2C1C3	120.0(1.4)	119.9	120.1
∠C1C2O1	121.6(2.3)	124.9	124.3
∠C1C3O2	126.7(1.9)	123.5	122.7
∠C1C2O3	115.1(1.7)	113.0	113.9
∠C1C3C5	122.4(2.1)	123.9	123.9
∠C2O3C4	113.3(1.5)	114.2	116.3
∠O3C4H	108.4(2.8)	108.6[e]	108.7[e]
∠C3C5H	109.3(3.3)	110.1[e]	110.3[e]
∠C3O2H	106.1[d]	106.1	107.0
abundance of enol, %	80(7)	1	87
$\Delta G^0 = G°$ (keto) − $G°$ (enol)	0.85(22)	−2.79 [f]	1.14 [f]

[a] Distances in angstroms and angles in degrees. For atom numbering see Figure 1. [b] Uncertainties for distances are $\sigma = (\sigma_{sc}^2 + (2.5\sigma_{LS})^2)^{1/2}$ ($\sigma_{sc} = 0.002r$, σ_{LS} = standard deviation in least-squares refinement); for angles $\sigma = 3\sigma_{LS}$. [c] Difference to previous parameter fixed to calculated (MP2) value. [d] Not refined. [e] Average value. [f] Weighted mean value.

TABLE 3: Interatomic Distances, Vibrational Amplitudes, and Vibrational Corrections for the Enol Conformer (Excluding Nonbonded Distances Involving Hydrogen)[a]

	distance	*l* (GED)	*l* (MP2)	Δ*r*
O2−H	0.988	0.082(6) *l*1	0.073	0.0011
C1−H	1.077	0.083(6) *l*1	0.074	0.0020
C4−H	1.098(7)	0.085(6) *l*1	0.075	0.0015
C5−H	1.100(7)	0.085(6) *l*1	0.075	0.0017
C2=O1	1.248(4)	0.045(6) *l*1	0.039	0.0003
C3−O2	1.339(4)	0.047(3) *l*2	0.043	0.0004
C2−O3	1.347(4)	0.048(3) *l*2	0.045	0.0004
C1=C3	1.362(4)	0.045(3) *l*2	0.042	0.0001
O3−C4	1.437(4)	0.051(3) *l*2	0.048	−0.0008
C1−C2	1.449(4)	0.049(3) *l*2	0.047	0.0006
C3−C5	1.493(4)	0.051(3) *l*2	0.048	−0.0001
O1···O3	2.283(8)	0.052(2) *l*3	0.051	0.0005
C2···C4	2.327(9)	0.062(2) *l*3	0.062	0.0026
O2···C5	2.335(14)	0.064(2) *l*3	0.063	0.0001
C1···O3	2.362(9)	0.061(2) *l*3	0.060	0.0083
C1···O1	2.357(10)	0.055(2) *l*3	0.055	0.0005
C1···O2	2.414(10)	0.055(2) *l*3	0.054	0.0021
C2···C3	2.435(12)	0.061(2) *l*3	0.060	0.0209
C1···C5	2.503(11)	0.063(2) *l*3	0.063	0.0058
O1···O2	2.627(15)	0.118(2) *l*3	0.117	0.0394
O1···C4	2.613(15)	0.093(2) *l*3	0.092	−0.0020
C3···O1	2.788(15)	0.086(8) *l*4	0.084	0.0250
C2···O2	2.892(16)	0.086(8) *l*4	0.085	0.0325
C3···O3	3.614(10)	0.058(8) *l*4	0.062	0.0268
C1···C4	3.652(9)	0.061(8) *l*4	0.065	0.0138
C2···C5	3.829(14)	0.082(8) *l*4	0.067	0.0231
O2···O3	4.230(16)	0.162(13) *l*5	0.085	0.0418
O1···C5	4.281(14)	0.110(13) *l*5	0.089	0.0314
C3···C4	4.761(13)	0.136(17) *l*6	0.075	0.0365
O3···C5	4.864(15)	0.110(17) *l*6	0.079	0.0288
O2···C4	5.085(19)	0.148(17) *l*6	0.117	0.0527
C4···C5	6.128(16)	0.144(45) *l*7	0.080	0.0433

[a] Values in angstroms. Error limits are 3σ values. For atom numbering see Figure 1.

Structure Analysis

The heaviest ion in the mass spectrum was $[C_5H_8O_3]^+$ (Table 5). This proves that monomers are present in the vapor at the conditions of the GED experiment. Model calculations for MAA demonstrate that the experimental radial distribution curve cannot be reproduced reasonably well with any diketo conformer (see Figure 2) especially in the distance range of 4.5−6.5 Å. The agreement factors (R_f) for diketo geometries and vibrational amplitudes derived with the MP2/6-31G** method are 19.5% (sc, ac), 18.7% (ac, sp), and 17.2% (ac, ac), whereas the enol tautomer results in R_f = 12.3% for the calculated structure.

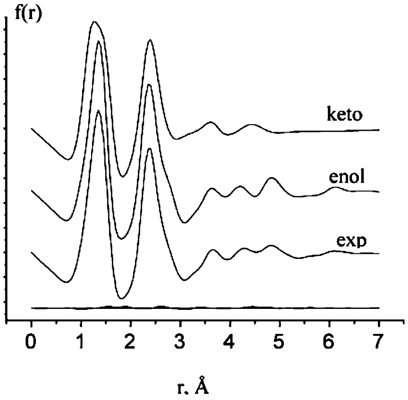


Figure 2. Experimental and calculated radial distribution functions and difference curve for mixture.

In the least-squares analysis only the geometry of enol tautomer was refined. The overall symmetry was constrained to C_s, and local C_{3v} symmetry with staggered orientation was assumed for the CH_3 groups. Differences between the C5−H and C4−H bond lengths, the C2−O3, O3−C4, and C3−O2 bond lengths, and the C1−C2, C1−C3, and C3−C5 bond lengths were restrained to calculated values (MP2/6-31G**). Preliminary geometric parameters for the enol tautomer from the MP2/6-31G** calculation were then refined by a least-squares procedure of the molecular intensities. Independent r(h1) parameters were used to describe the molecular structure. Vibrational amplitudes were refined in groups with fixed differences. The following correlation coefficients had values larger than |0.7|: *r*(C1−C2)/*r*(C2−O1) = −0.79, *r*(C1−C2)/*r*(C2−O3) = −0.85, *r*(C1−C2)/∠(C1−C2−O3) = −0.71,

∠(C2−C1−C3)/∠(C1−C2−O1) = −0.94, ∠(C2−C1−C3)/∠(C1−C3−O2) = −0.88, ∠(C1−C2−O1)/∠(C1−C3−O2) = 0.83, ∠(C2−C1−C3)/l_1 = 0.89, ∠(C1−C2−O1))/ l_1 = −0.89, ∠(C1−C3−O2)/ l_1 = −0.89. The fit of the molecular intensities improved if a small amount of any diketo conformer was added. The electron diffraction intensities are not sensitive to the type of diketo conformer chosen. The best agreement factors resulted for a composition of the mixture of 80(7)% enol and 20(7)% keto forms with R_f = 4.0% for the (ac, sp) conformer, 4.1% for the (ac, ac) conformer, and 4.2% for the (sc, ac) conformer. This composition corresponds to a temperature of the effusion cell and the gas of 309(6) K. In all cases the parameters for the enol tautomer are equal within their uncertainties. Final results of the least-squares analysis are given in Table 2 (geometric parameters) and Table 3 (vibrational amplitudes). The refined geometrical parameters for the enol conformer are rather similar to those predicted by the quantum chemical calculations.

IR(matrix) Spectrum

The IR(matrix) spectrum was recorded in the range of 4000−400 cm^{-1} with a Bruker IFS 66v spectrometer and with a resolution of 1 cm^{-1}. An Ar stream was passed over liquid MAA at −62 °C, and immediately after this the mixture of MAA with Ar was deposited through a spray-on nozzle at room temperature on an aluminum-plated copper mirror in a He-cooled cryostat at 15 K. Details of the matrix-isolation apparatus have been given elsewhere.[19] Because the conditions for preparing the MAA/Ar matrix are not well-defined, it is not known whether the enol−diketo equilibrium in the gas phase is established before deposition of the mixture in the matrix and, if so, what the corresponding temperature would be. Thus, from the matrix spectrum we cannot expect to obtain a tautomeric composition in quantitative agreement with the GED result. However, assignment of the strongest bands in the matrix spectrum in combination with calculated vibrational frequencies, band intensities, and the potential energy distribution provides evidence for the presence of both tautomeric forms in the matrix. The strongest band at 1252 cm^{-1} (vvs) corresponds to the ν(C−OH) vibration of the enol tautomer, which is predicted (MP2/6-31G*) at 1283 cm^{-1} with an intensity of 645 km/mol, by far highest intensity. Two strong bands at 1635 cm^{-1} (vs) and 1660 cm^{-1} (vs) are assigned to the strongly coupled ν(C=C) and ν(C=O) vibrations of the enol form. The corresponding calculated wavenumbers and intensities are 1660 cm^{-1} (330 km/mol) and 1695 cm^{-1} (351 km/mol). ν(O−H) in the enol form is predicted at 3436 cm^{-1} (MP2/6-31G**) and 3264 cm^{-1} (B3LYP/6-31++G**), respectively, with intensities of 316 and 226 km/mol. In the experimental spectrum the strongest band in this region occurs at 2960 cm^{-1} with medium intensity. The difference between the experimental and predicted wavenumbers of more than 300 cm^{-1} indicates that the computational methods do not reproduce the hydrogen-bonded system correctly. Several weak bands in the region of 2850−3050 cm^{-1} correspond to the various C−H stretches. Two weaker bands at 1720 cm^{-1} (m) and 1760 cm^{-1} (s) have no counterparts in the calculated spectrum of the enol form and can only be assigned to the two ν(C=O) vibrations of the diketo tautomer, which are predicted at 1779 cm^{-1} (100 km/mol) and 1813 cm^{-1} (370 km/mol) for the (ac, sp) conformer. These wavenumbers are very similar for the two other diketo conformers. Thus, the IR (matrix) spectrum confirms qualitatively the presence of a mixture of enol and diketo tautomers with the enol form strongly prevailing.

TABLE 4: Conditions of GED Experiment

nozzle-to-plate distance, mm	338	598
electron beam, μA	0.96	1.01
electron wavelength, Å	0.045 04(6)	0.045 44(4)
temperature of effusion cell, K	303(5)	315(5)
exposure time, s	120−150	45−55
residual gas pressure, Torr	6.5×10^{-6}	8.4×10^{-6}

TABLE 5: Mass Spectral Data (Ionization Voltage 50 V) of the Vapor of $C_5H_8O_3$

ion	m/e	abundance, %
$[M]^{+\,a}$	116	55.2
$[M-CH_3]^+$	101	39.0
$[M-2CH_3]^+$	86	9.5
$[M-OH-CH_3]^+$ $[M-OCH_3-H]^+$	84	74.0
$[M-OCH_3-CH_3]^+$	70	33.4
$[M-OCH_3-OH]^+$	68	100
$[C(O)OCH_3]^+$	59	54.1
$[M-C(O)OCH_3]^+$	57	18.8

[a] M = $C_5H_8O_3$.

Discussion

As mentioned in the Introduction, dicarbonyl compounds of the type XC(O)−CH_2−C(O)Y favor the enol form for X,Y = H, CH_3, $C(CH_3)_3$, or CF_3 and favor the diketo form for X,Y = F, Cl, OCH_3, and NH_2. Thus, electron-donating substituents stabilize the enol form and electron-withdrawing groups stabilize the diketo tautomer. Although the CF_3 group possesses electronegativity similar to that of chlorine, it is considered to be a π donor. Methyl acetoacetate, a dicarbonyl compound with one substituent favoring the enol form (CH_3) and the other one favoring the diketo form (OCH_3), occurs in the gas phase as a tautomeric mixture. The GED analysis results in a mixture of 80(7)% enol tautomer and 20(7)% diketo form. It is not possible to determine the individual conformation or conformational mixture of the diketo tautomer. This composition corresponds to a difference in free energies $\Delta G^0 = G°$ (keto) − $G°$ (enol) = 0.85(22) kcal/mol at 36(6) °C (nozzle temperature). $G°$ (keto) is a weighted mean value for all possible diketo conformers. This value is in agreement with the NMR result for the gas phase (0.08 ± 1.45 kcal/mol) within its large experimental uncertainty.[15] The MP2 calculations predict a strong preference for the diketo forms with only 1% (MP2/6.31G**) or 8% enol tautomer (MP2/6-311G(2df)). The predictions by the B3LYP calculations are in close agreement with the GED experiment: 92% (B3LYP/6-31G**) or 87% (B3LYP/6-31++G**) enol tautomer. The quantum chemical calculations (MP2 and B3LYP) reproduce the experimental geometric parameters of the enol tautomer very closely.

Experimental Section

The electron diffraction patterns and the mass spectra were recorded simultaneously using the techniques described previously.[20,21] The conditions of the GED/MS experiment and the relative abundance of the characteristic ions of $C_5H_8O_3$ are shown in the Tables 4 and 5, respectively. The substance was introduced into the effusion cell by means of an inlet system. 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 nozzle temperature and gas temperature are equal to that of the effusion cell. The wavelength of the electrons was determined from diffraction patterns of polycrystalline ZnO. The optical densities were measured by a computer-controlled MD-100 (Carl Zeiss, Jena) microdensito-

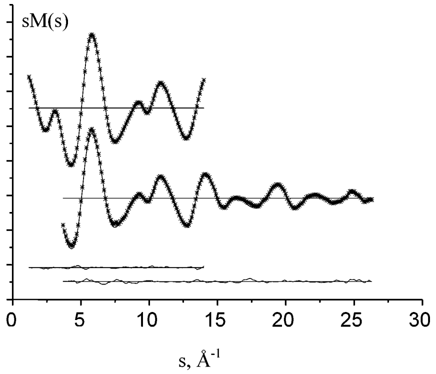


Figure 3. Experimental and calculated modified molecular intensities and residuals.

meter.[22] The background functions $G(s)$ were refined by the Fourier spectrum analysis of the intensity curves $I_{obs}(s)$. The molecular intensities $sM(s)$ were obtained in the s-ranges of 3.7−26.3 Å^{-1} and 1.2−14.0 Å^{-1} for the short and long nozzle-to-plate distance, respectively ($s = (4\pi/\lambda)\sin\theta/2$; λ is the electron wavelength and θ is scattering angle). The experimental and theoretical intensities $sM(s)$ are compared in the Figure 3.

Acknowledgment. We are grateful for financial support from the Russian Foundation for Basic Research (RFBR Grant N 01-03-33103). The authors thank Dr. Sonia Ulic and Professor Helge Willner (Universität Duisburg) for recording the IR(matrix) spectrum and Privatdozent Dr. H.-G. Mack for assistance in quantum chemical calculations. N.V.B. is grateful to the Deutsche Akademische Austauschdienst (DAAD) for a fellowship.

Supporting Information Available: Table S1: Calculated geometric parameters for diketo conformers. This material is available free of charge via the Internet at http://pubs.acs.org.

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