

# *Ab initio* Study of the Keto-Enol Equilibrium of Malonaldehyde

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**Summary.** The mechanism of the keto-enol tautomerism of malonaldehyde was studied by *ab initio* methods using 6-21G\*\* and 6-311G\*\* basis functions at the HF level. Two separate mechanisms were examined: through-space proton transfer in the  $\omega$ -shaped form and through-space proton transfer in a sickle-shaped form obtained from the  $\omega$  form by rotation. The transition state structure of the  $\omega$  form is non-planar, whereas that of the sickle form is planar. The sickle form is connected with a 2<sup>nd</sup> order saddle, indicating that there should exist a lower energy barrier, *i.e.* that the through-bond mechanism may be preferred. The calculated energy barriers of keto-enol tautomerism for the sickle form is twice as high as those for the omega form.

**Keywords.** Malonaldehyde; Keto-enol tautomerism; *ab initio* Calculations; Energy barriers.

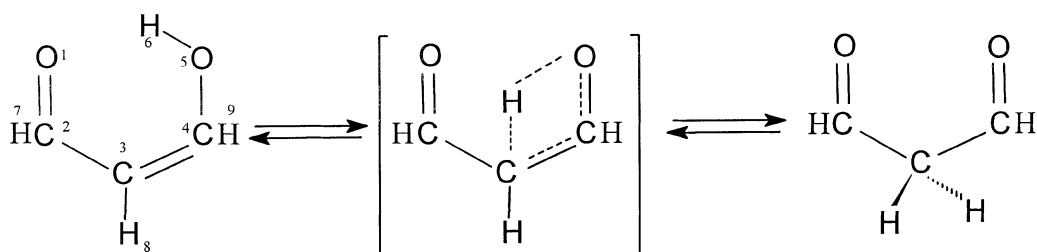
## Introduction

Malonaldehyde has been studied extensively being a comparatively small molecule with interesting properties. The interest in this molecule is connected mostly with its intramolecular hydrogen bond and the intramolecular proton transfer. AM1, MNDO [1–3], and *ab initio* [4–9] calculations have shown that the enol form is more stable than the diketo form due to additional stabilization by the H-bond in a cyclic ( $\omega$ -shaped) form. The two forms may interconvert through two possible mechanisms: through-space or through-bonds [10]. It has been proven theoretically that in the  $\omega$ -shaped form the proton transfer takes place through space [8, 11, 12].

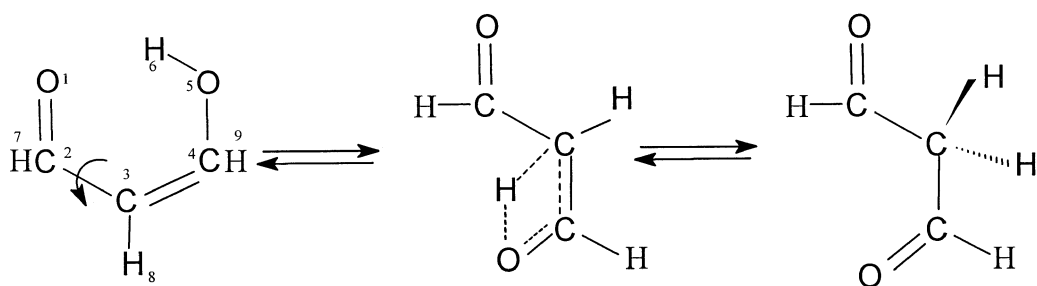
The molecular structure of malonaldehyde has been reported: CO = 1.23 Å, C–OH = 1.35 Å, H···O = 1.68 Å, O···O = 2.55 Å. [13, 14]. The through-space proton transfer mechanism is depicted in Scheme 1.

Besides the mechanism given in Scheme 1, where the through-space proton transfer occurs in the so-called  $\omega$ -shaped form, stabilized additionally by the H-bond O(1)···H(6), it is possible that the through-space proton transfer may occur after rotation around the C(3)–C(4) bond by 180° within the resulting sickle-shaped form (Scheme 2).

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Scheme 1



Scheme 2

## Results and Discussion

### Proton transfer in the $\omega$ -form (Scheme 1)

The resulting geometries from the optimization procedures and the QST jobs, implemented within Scheme 1, are given in Table 1.

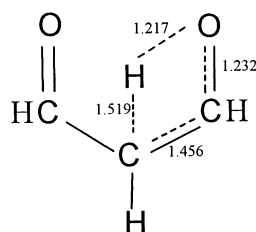
It can be readily seen from Table 1 that the expansion of the basis functions from 6-21G\*\* to 6-311G\*\* has a very modest effect on the calculated bond lengths (less than 0.01 Å) with the exception of the H-bond for which larger differences (0.1 Å) are observed. The agreement with the experimental bond lengths in the enol form [12, 14] (*vide supra*) is satisfactory (CO calcd. 1.205 Å, exp. 1.23 Å; C-OH calcd. 1.313 Å, exp. 1.35 Å; H $\cdots$ O calcd. 1.791 Å, exp. 1.69 Å) and slightly better with 6-21G\*\* than with 6-311G\*\*. The differences of the results with the two basis sets, however, are much greater for the valence angles, especially for the transition state, where differences for the dihedral angles of up to 40 degrees were observed.

The geometry of the transition state is non-planar. The internuclear distances which change most, are given in Scheme 3.

It can be seen from Scheme 3 that the H(6)–O(5) bond is lengthened and a new C(3)–H(6) bond is formed. This process is connected with a change in the hybridization state of both C(3) ( $sp^2 \rightarrow sp^3$ ) and O(5) ( $sp^3 \rightarrow sp^2$ ). The CH-bond in the transition state (1.5 Å) is much longer than common CH bonds (1.1 Å), whereas the OH bond in the transition state (1.2 Å) is close to the OH bond in the enol form (1.0 Å). The dihedral angles show that the proton transfer occurs by moving the proton out of the OCCCO plane – the dihedral angle H(9)C(4)C(3)H(6) is 180° in

**Table 1.** *Ab initio* calculated geometries of the  $\omega$ -shaped enol and diketone of malonaldehyde and the transition state of Scheme 1

Parameter	Transition State		Enol		Diketone	
	6-311G**	6-21G**	6-311G**	6-21G**	6-311G**	6-21G**
C=O	1.940	1.196	1.200	1.205	1.176	1.179
C2)–C(3)	1.459	1.470	1.455	1.457	1.514	1.521
C(3)–C(4)	1.456	1.465	1.341	1.342	1.514	1.520
C(4)–O(5)	1.232	1.234	1.310	1.313	1.176	1.179
(O)H ··· O	3.425	2.807	1.898	1.791	3.095	3.107
H(6)–O(5)	1.217	1.191	0.953	0.962	3.095	3.107
H–C(2)	1.096	1.102	1.093	1.098	1.099	1.103
H–C(3)	1.083	1.083	1.073	1.075	1.091	1.095
H–C(4)	1.081	1.085	1.076	1.080	1.099	1.103
H(6)–C(3)	1.5185	1.548	2.431	2.392	1.091	1.095
H–C(3)–C(2)	116.9	116.2	119.5	120.1	107.8	108.6
H–C(3)–C(4)	112.0	119.2	119.4	120.4	107.8	108.6
O=C(2)–C(3)=C(4)	–8.4	–7.1	0.0	0.0	0.0	0.0
O=C(2)–C(3)–H	–146.8	–147.6	180.0	180.0	–123.9	–123.4
H–C(2)–C(3)–H	35.4	35.1	0.0	0.0	56.1	56.6
C(2)–C(3)–C(4)–O	135.0	89.8	0.0	0.0	0.0	0.0
H–C(3)–C(4)–H	95.9	49.3	0.0	0.0	–56.1	–56.6
H–O–C(4)–C(3)	–6.5	–3.7	0.0	0.0	–123.9	–123.4
H–C(4)–C(3)–H(6)	173.6	176.8	180.0	180.0	56.1	56.6

**Scheme 3**

the enol form, becomes  $174^\circ$  in the transition form, and finally drops to  $56^\circ$  in the keto form. The calculated HF energies and the zero-point corrections were used to calculate the energy barrier of the enol  $\rightarrow$  diketone conversion *via* Scheme 1; it amounts to  $\Delta E^* = 322 \text{ kJ} \cdot \text{mol}^{-1}$ . Conversely, there is a lower barrier for the diketone  $\rightarrow$  enol conversion ( $\Delta E^* = 296 \text{ kJ} \cdot \text{mol}^{-1}$ ).

As stated before, there is one imaginary frequency for this transition state at  $\nu = -2074 \text{ cm}^{-1}$ . Table 2 lists the atomic displacements involved in this vibration. The largest displacement is that of H(6) which is the moving proton. The movement of H(8) should also be noted since it has to free room in order to accommodate H(6) at the C(3) atom ■.

**Table 2.** Amplitude displacements (in Å) of the atoms for the  $-2074\text{ cm}^{-1}$  vibration of the transition state from Scheme 1

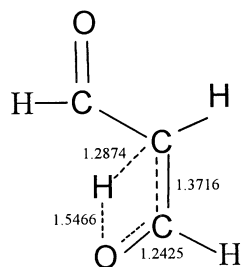
	Atom	X	Y	Z
1	O	0.00	0.00	0.00
2	C	0.01	0.00	0.01
3	C	-0.04	-0.01	0.03
4	C	-0.04	0.01	0.01
5	O	-0.01	0.03	-0.02
6	H	0.88	-0.45	-0.04
7	H	0.01	0.01	-0.01
8	H	0.06	0.04	-0.10
9	H	0.01	-0.02	-0.04

*Proton transfer in the sickle form (Scheme 2)*

Some important internuclear distances in the proton transfer transition state of Scheme 2 are given in Table 3. For the sake of comparison, Table 3 lists also the enol and diketo-form parameters. The relevant internuclear distances in the transition state are illustrated in Scheme 4. It should be noted that the QST2 program, which needs the geometries of the two minima only for detecting the transition state, did not work in this case. We had to resort to the QST3 program, which requires a 'reasonable' guess of the transition state geometry; three sets of coordinates were used as input. The reason for the QST2 failure is given below.

**Table 3.** *Ab initio* calculated geometries of the sickle-shaped enol and diketone and the 2<sup>nd</sup> order saddle point from Scheme 2

Parameter	2 <sup>nd</sup> order Saddle		Enol		Ketone	
	6-311G**	6-21G**	6-311G**	6-21G**	6-311G**	6-21G**
C(3)=C(4)	1.372	1.374	1.331	1.330	1.508	1.516
C(4)-O(5)	1.242	1.241	1.331	1.335	1.182	1.185
H(6)-O(5)	1.547	1.559	0.941	0.946	3.081	3.092
H-O(2)	1.095	1.099	1.100	1.106	1.091	1.095
H(6)-C(3)	1.287	1.278	2.536	2.531	1.088	1.092
H(8)-C(3)-C(2)	99.0	98.293	116.4	116.4	108.8	109.3
H(8)-C(3)-C(4)	140.1	141.2	118.2	118.4	108.9	109.5
C(3)-C(4)-O(5)	115.1	115.3	129.0	129.3	124.5	123.7
O=C(2)-C(3)-C(4)	180.0	180.0	180.0	180.0	180.0	180.0
O=C(2)-C(3)-H(8)	0.0	0.0	0.0	0.0	-57.3	-57.6
H(7)-C(2)-C(3)-H(8)	180.0	180.0	180.0	180.0	122.7	122.4
C(2)-C(3)-C(4)-O	0.0	0.0	0.0	0.0	0.0	0.0
H(8)-C(3)-C(4)-H(9)	0.0	0.0	0.0	0.0	57.3	57.7
H-O-C(4)-C(3)	0.0	0.0	0.0	0.0	-35.4	-34.7
H(9)-C(4)-C(3)-H(6)	180.0	180.0	180.0	180.0	-57.3	-57.7



Scheme 4

Unlike the non-planar transition state of the  $\omega$ -shaped enol-diketone interconversion, the transition structure of the sickle-shaped enol-diketone interconversion is planar. The proton transfer takes place in the XY plane, which is the molecular plane for the sickle enol form with  $C_s$  symmetry. By comparing Schemes 3 and 4, it can be seen that the trends in the variations of the bond-to-be-formed and bond-to-be-broken are exactly the opposite – in the two transition states the CH bond distance is much longer than the OH bond distance in Scheme 3, whereas the opposite holds for Scheme 4. This picture may be interpreted in terms of the hindered movement of the proton inside the ring of the  $\omega$ -form: to reduce repulsion with neighbouring non-bonded atoms, the moving proton migrates over the molecular plane. In the sickle form, the through-space proton transfer experiences less repulsion from the neighbouring non-bonded atoms.

It should be noted that our attempts to detect an ‘ordinary’ transition state (1<sup>st</sup> order saddle point, one imaginary frequency) connecting the two (enol-diketone) sickle-shaped forms failed. The frequency calculations with the QST3-obtained transition structure display two imaginary frequencies with negative wavenumbers:  $-1329$  and  $-816$   $\text{cm}^{-1}$ , corresponding to negative force constants of  $-1.6$  and  $-0.5$   $\text{mdyn}\cdot\text{\AA}^{-1}$ , respectively. Consequently, the structure obtained is a second-order saddle point. Possibly, this is the reason why the QST2 program with just the geometries of the two final states initially failed. The presence of a 2<sup>nd</sup> order saddle point indicates [17] that there should exist a barrier lower than the one obtained connecting the sickle-shaped enol and ketone. To unveil the nature of that lower energy barrier, we have examined in some detail the form of the two vibrations with negative wavenumbers.

The  $-1329$   $\text{cm}^{-1}$  vibration corresponds to a movement (amplitude  $0.86$   $\text{\AA}$ ) of the H(6) proton in the molecular plane towards the C(3) atom, whereas the  $-816$   $\text{cm}^{-1}$  vibration takes the H(6) proton out of the molecular plane. This may imply the start of the reverse rotation from the sickle-shaped form to the  $\omega$ -shaped form of the enol (see Ref. [18]). Thus, H(6) may ultimately be placed above the CCC plane, enabling its ‘through bond’ transfer to C(3) (for the full description of such a movement, see Ref. [10]).

Using the calculated HF energies and the zero-point corrections for the sickle-shaped forms we have calculated the barriers of enol  $\rightarrow$  diketone ( $\Delta E^* = 547$   $\text{kJ}\cdot\text{mol}^{-1}$ ) and diketone  $\rightarrow$  enol ( $\Delta E^* = 519$   $\text{kJ}\cdot\text{mol}^{-1}$ ) conversions. The second barrier is lower than the first one, but both barriers for the sickle form are twice as high as those for the  $\omega$ -form.

### Conclusions

It may be concluded that the through-space proton transfer in the  $\omega$ -shaped enol to yield the diketone form is much more favourable than the proton transfer in the sickle-shaped form. Moreover, the sickle-shaped enol can result from the more stable  $\omega$ -shaped enol only after rotation around a predominantly double bond, which is also energetically unfavourable, the rotational energy barrier being about  $\Delta E = 65 \text{ kJ} \cdot \text{mol}^{-1}$  [18]. Further, the transition state of the  $\omega$ -enol-diketone conversion is non-planar which can be explained in terms of avoided repulsion when the proton traverses the internal space defined by the  $\omega$ -form. Conversely, the structure connecting the sickle shape forms (a 2<sup>nd</sup> order saddle point) is planar and defines a much higher barrier. Hence, it seems likely that the through-bond proton transfer in the sickle form may be more favourable than the through-space mechanism.

### Methods

The *ab initio* calculations were performed at the restricted *Hartree-Fock* level using the basis functions 6-21G\*\* and 6-311G\*\* and the program GAUSSIAN 94 [5]. The HF method was used to optimize the structures of the enol and diketone forms. Frequency calculations were performed to prove that the resulting stationary points are minima (no imaginary frequencies). Further, we used the geometry of the two minima and the program QSR2, implemented within GAUSSIAN 94 [5], to find the transition state located between the two minima. In cases of complete failure (*vide infra*) of QSR2, the program QST3 was used, which requires as input a 'reasonable' guess for the transition state. Once again frequency calculations with the transition state geometry were performed in order to prove that it is a first order saddle point (one imaginary frequency) [15] and hence can be termed as ordinary transition state.

The use of two basis sets was supposed to provide information of how the change in basis set size may affect the geometry and the transition energies. The electron correlation, which is neglected in our study, is known to increase the rotational barriers by 0.5–1.0 kJ·mol<sup>-1</sup>, but its effect on the transition structures and energies should be more pronounced [16].

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