A Theoretical Study of Hydrogen Bonding in Malonaldehyde

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Abstract: We have used semiempirical (INDO and CNDO/2) and ab initio methods to calculate the potential energy curve of malonaldehyde as a function of the O–O distance. The ab initio results predict a potential curve with two (C_{2v} and C_s) minima separated by a barrier of 10.6 kcal/mol and confirm that the symmetry of a hydrogen bond is a function of the distance between the bridging atoms. The reliability of semiempirical results for this system is discussed.

I. Introduction

A considerable amount of theoretical work has been devoted to the study of hydrogen bonding.[1,2] Few papers dealt with intramolecular hydrogen bonds,[3] mainly because these appear in large systems. An exception, malonaldehyde (MA), with only five heavy atoms, has received much attention,[4-10] yet several aspects concerning hydrogen bonding in this system remain obscure.

The first problem is its molecular point group. CNDO/2 calculations, both with full geometry optimization[10] and optimizing only the position of the bridging hydrogen,[4] predicted an asymmetric planar (C_s) molecule, while a complete geometry (INDO) optimization[5] indicated a planar and symmetric (C_{2v}) molecule. Ab initio calculations based on INDO results[6] led to the same conclusion. Karlstrom et al.,[7] using an extended basis set, found that the equilibrium conformation corresponds to a planar and asymmetric structure. In either case no full geometry optimization was attempted.

A recent minimal basis set full geometry optimization[8] predicted a planar and asymmetric MA, with an O–O distance shorter than the one found by Karlstrom et al.[7]

Experimental information about the structure of this molecule is not definitive and, sometimes, contradictory.[11] Experimental structure determinations on a MA derivative (acetylacetone) are not conclusive either: some[12] predict C_{2v} symmetry, while others[13] predict C_s.

Experimental work[14-16] since the last theoretical calculations indicates that MA has C_s symmetry. Rowe et al.[14] analyzed the microwave spectra of isotopic species of MA and concluded that the molecule is planar and that its potential surface presents a symmetrical double minimum separated by a relative low barrier that allows rapid tunneling. These conclusions were confirmed by UV and X-ray photoelectron spectroscopy studies carried out by Seliskar et al.[15] and Brown,[16] respectively.

However, the symmetry of a hydrogen bond seems to be related to the distance between the two bridging atoms (the O–O distance, R_{O-O}). Most hydrogen bonds are asymmetric, with some exceptions such as $(FHF)^-$, $(H_2O_5)^+$, etc., where the distance R is small. It is generally accepted[6,17] that a value of $R < 2.5$ Å is a necessary condition to have a symmetric hydrogen bond.

In this paper the problems of the relative stability of the C_{2v} and C_s forms of MA, and the (possible) proton transfer process, are considered by theoretical calculations of the potential curve as a function of the O–O distance, with semiempirical methods (CNDO/2 and INDO), and by performing ab initio calculations using minimal and extended basis sets.

II. Calculations

A. Semiempirical.

In this section we present the potential energy curve of planar MA as a function of the O–O distance,

obtained carrying out a full geometry optimization (using the procedure developed by Rinaldi et al.[18]) for O–O distances from 2.1 to 2.7 Å, in steps of 0.05 Å. These calculations were performed using the INDO and CNDO/2 methods, whose results are shown in Figures 2 and 3, respectively.

The INDO calculation gives a potential energy curve with a minimum at $R_{O-O} = 2.28$ Å and an optimized geometry agreeing with that of Marsh et al.[5] However, to the left of the minimum ($R_{O-O} < 2.28$ Å) stable structures have C_{2v} symmetry but for $R_{O-O} > 2.28$ Å, i.e., to the right of the minimum, stable structures have C_s symmetry. We have determined that the potential energy curve is a superposition of two parabolas; one corresponds to the symmetric form ($R_{O-O \, min} = 2.28$ Å) and the other, with a minimum very close to the previous one ($R_{O-O \, min} = 2.3$ Å) and only 0.08 kcal/mol above it, corresponds to the asymmetric form.

The CNDO/2 results show a potential curve with a minimum at $R_{O-O} = 2.35$ Å, which corresponds to a C_s structure. The points of the curve for $R_{O-O} < 2.25$ Å correspond to C_{2v} structures. Again, the potential curve is the superposition of two curves. The C_{2v} one presents a minimum at $R_{O-O} = 2.31$ Å, 1.04 kcal/mol above the C_s minimum, in agreement with Kato et al.[10]

Thus, using these methods it is possible to find one or two conformations, depending on the selected O–O distance. If R_{O-O} is small enough (<2.3 Å) the structure found will have C_{2v} symmetry. If R_{O-O} is large enough (>2.3 Å) two structures, C_s and C_{2v}, can be found.

B. Ab Initio.

First, a full geometry optimization of MA, using a STO-3G minimal basis set,[19] for R_{O-O} between 2.1 and 2.7 Å, was performed.

To save computation time, at each R_{O-O} distance, the optimization process was divided into five steps: (a) optimization of the C–C bond lengths and the CCC angle; (b) optimization of the C–O bond lengths and the CCO angles, keeping constant the parameters optimized in (a); (c) optimization of the O–H distance and the COH angle starting from the results of (a) and (b); (d) optimization of all the C–H distances and the corresponding CCH angles; (e) starting with the results from (d), repetition of steps (a), (b) and (c) until no appreciable changes were observed in any of the geometrical parameters. Step (d) was not repeated, because the influence of the CH bond lengths and the CCH angles on the structure of the molecular framework must be very small. The potential energy curve calculated in this way is presented in Figure 4.

III. Discussion

Again, the total curve is the superposition of two parabolas. The C_{2v} curve presents a minimum ($E = -262.145\,31$ au) at $R_{O-O} = 2.29$ Å and the C_s one ($E = -262.155\,77$ au) at $R_{O-O} = 2.56$ Å.

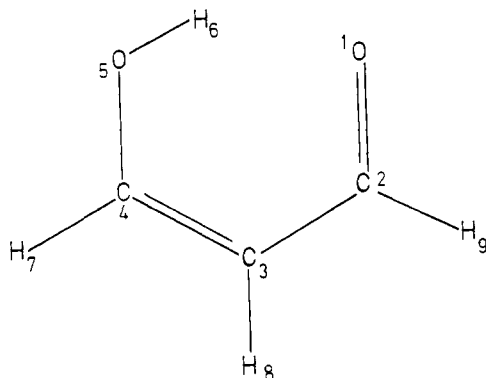These results qualitatively agree with those of Karlstrom
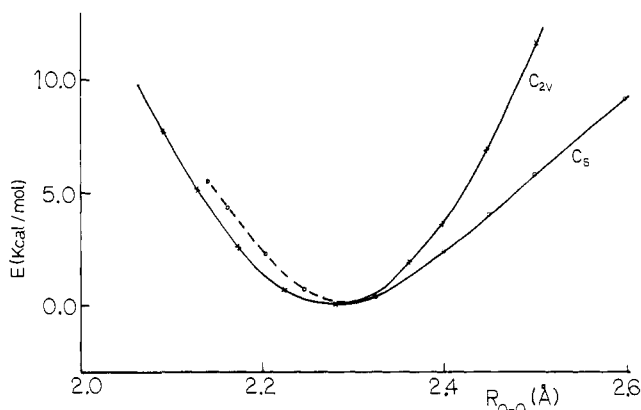
Figure 1. Numbering of atoms for malonaldehyde.

Figure 2. INDO potential energy curve for MA as a function of R_{O-O}. The dashed line corresponds to a C_s form with the C_3–C_4 bond length equal to 1.34 Å.
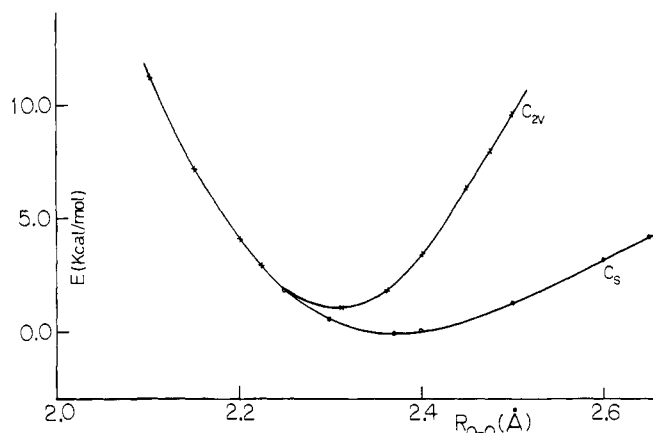

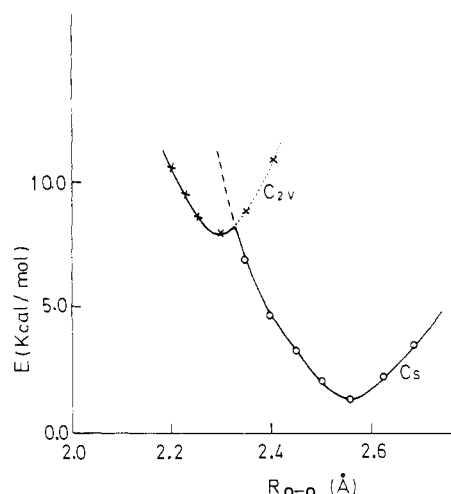Figure 3. CNDO/2 potential energy curve for MA as a function of R_{O-O}.

Figure 4. Ab initio (STO-3G minimal basis set) potential energy curve for MA as a function of R_{O-O}. Geometry was fully optimized for each O–O distance. The dotted line was obtained imposing C_{2v} symmetry and the dashed line is an extrapolation.

et al.,[7] but a shorter R_{O-O} distance is found. Our results, however, show that a minimal basis set full geometry optimization gives a significant energy difference between the C_{2v} and C_s forms, unlike previous results.[7] Nevertheless the barrier height (6.6 kcal/mol) is small enough to allow rapid tunneling through it, as postulated in the microwave study of Rowe et al.[14]

Recently, Del Bene et al.[8] questioned whether the kink they found (using a simple coordinate which smoothly converts the C_s form to the C_{2v} form) at the top of the curve for the proton transfer process of MA was a true minimum or a saddle point. According to our results it corresponds to a true minimum; that of the C_{2v} parabola. This can be proved by the fact that when the geometry of MA is optimized, imposing C_{2v} symmetry, the parabola obtained fits exactly the left upper part of the potential curve in Figure 4. The depth of the minimum depends, obviously, on how the C_{2v} and C_s curves intersect.

From Figure 4 it is also clear that for $R_{O-O} < 2.32$ Å the symmetric structure is stable and for $R_{O-O} > 2.32$ Å the asymmetric one is stable. This can explain why the only structure found using a INDO full geometry optimization is the C_{2v} one. It has been well established[1,2] that this semiempirical method underestimates the R_{O-O} distance, and therefore the minimum is located in a region where only the C_{2v} form is stable.

Although it is generally accepted[6,17] that the necessary condition to have a symmetric hydrogen bond is that $R_{O-O} < 2.5$ Å, we found in MA the C_s minimum for $R_{O-O} \simeq 2.5$ Å, but the C_{2v} one appears at $R_{O-O} < 2.3$ Å, confirming that the symmetry of a hydrogen bond is a function of the distance between the bridging atoms.

Figure 4 shows that for $R_{O-O} = 2.33$ Å two different structures (C_{2v} and C_s) coexist. The corresponding geometrical

parameters (see Table I) are quite different, although these two forms are practically degenerate in energy ($\Delta E = 0.06$ kcal/mol).

A detailed study of MA using an extended basis set is time consuming and almost prohibitive. However, we have considered it of interest to study this system, using a split-valence basis set (6-31G)[20] and the STO-3G optimized geometry, for two reasons: (a) to estimate[21] the influence of the basis set in the value of the barrier height; (b) to obtain reliable values of 1s binding energies (since this basis set represents very well the 1s orbitals) that would permit us to interpret the X-ray photoelectron spectrum of this compound.

With the new basis the calculated barrier is higher (10.6 kcal/mol) than the one obtained with the STO-3G basis set. Although no geometry optimization was carried out, this result seems to indicate that an improvement of the basis set would yield higher barriers.

In Table II we present the calculated energies (6-31G) of the lowest occupied orbitals of the two forms of MA, that correspond to the 1s binding energies of oxygen and carbon atoms, respectively. Our results give a separation between the two O_{1s} ionizations of 0.4 eV. Brown,[16] using X-ray photoelectron spectroscopy, observed a separation of 1.57 eV, but it is well known[22] that Koopman's theorem does not hold so well for core electron as for valence electron ionizations. On the other hand, the X-ray photoelectron spectrum consists of three peaks. Two of them are explained assuming a C_s struc-

Table I. Structure of the C_s and C_{2v} Forms of MA at R_{O-O} = 2.33 Å

	C_s	C_{2v}
Distances, Å		
C_2-O_1	1.256	1.292
C_4-O_5	1.340	1.292
C_3-C_2	1.430	1.402
C_3-C_4	1.341	1.402
O_5-H_6	1.010	1.179
C_2-H_9	1.100	1.100
C_3-H_8	1.080	1.070
C_4-H_7	1.090	1.100
Angles, deg		
$C_2C_3C_4$	120.9	115.2
$C_3C_2O_1$	116.4	121.3
$C_3C_4O_5$	119.0	121.3
$C_4O_5H_6$	106.0	101.8
$H_9C_2C_3$	121.2	121.0
$H_7C_4C_3$	119.9	121.0

Table II. Calculated (6-31G) Energies of the Lowest Occupied Orbitals for the C_s and C_{2v} Forms of Malonaldehyde

C_s		C_{2v}	
energy, eV	orbital symmetry	energy, eV	orbital symmetry
−306.18	A′	−306.01	A_1
−306.86	A′	−309.43	B_1
−309.51	A′	−309.43	A_1
−560.20	A′	−560.30	B_1
−560.60	A′	−560.30	A_1

ture of MA. The third one cannot be explained, although it seems clear that it does not arise either from the keto form or from impurities.[16] Our results (see Table II) indicate that three peaks should appear in the spectrum if the two forms (C_s and C_{2v}) were present, the more intense being those arising from the C_s form. This conclusion seems to be ratified by the fact that these three peaks appear in all compounds that are partially or totally enolized but do not appear in 3,3-dimethylacetylacetone,[16] which presents only the keto form, and since MA is a nonrigid molecule that belongs to the G_4 symmetry subgroup, its ground state would probably be better described by both C_s and C_{2v} forms connected by a rapid proton transfer.[23]

We have checked that variations of ±0.05 Å in the O–O distance do not affect our results. Therefore if geometry optimization were carried out we believe that our conclusions would still hold.

A greater difference was found between the two highest C_{1s} binding energies (for the C_s form) which should correspond to an experimental separation, in the X-ray photoelectron spectrum, larger than that corresponding to the O_{1s}, suggesting another experimental way of testing the geometry of MA. If only the C_s form is present the spectrum should show three peaks; two peaks if only the C_{2v} structure is stable and more than three peaks if both are present in some proportion.

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