Structure and Tunneling Dynamics of Malonaldehyde. A Theoretical Study

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Abstract: The geometry and harmonic vibrational frequencies of equilibrium malonaldehyde and of the transition state for the symmetric intramolecular hydrogen atom transfer have been determined at the SCF level of theory (using a slightly better than double-ζ basis set). All geometrical parameters were fully and simultaneously optimized by using SCF gradient techniques. Comparison of the equilibrium structure with the structure determined from microwave spectra shows good agreement in most respects, although there are a few differences. At the C_s equilibrium geometry and the C_{2v} transition state large scale configuration interaction (all single and double excitations) calculations were carried out to determine the barrier height for the symmetric hydrogen atom transfer; including a correction for quadruple excitations, this gives a classical or "bare" barrier height of 8.0 kcal/mol. A one-dimensional model for the tunneling dynamics of H-atom transfer leads to a tunneling splitting in the ground vibrational state of ~ 18 cm^{-1}, in relatively good agreement with the experimental value. It is noted, though, that the value of the splitting is sensitive to the potential surface parameters (i.e., bare height, frequencies) and that there is also uncertainty about the accuracy of the one-dimensional description of the tunneling.

I. Introduction

The structural and dynamical properties of malonaldehyde and related compounds are of considerable experimental and theoretical interest. The enol tautomer (see Figure 1) is more stable than the keto tautomer, mainly because of the presence of an intramolecular hydrogen bond.[1] However, the question of whether these molecules have an asymmetric (Figure 1a) or symmetric (Figure 1b) hydrogen bond has been a subject of considerable uncertainty. This question is of fundamental importance, since the asymmetric form has more interesting dynamical properties due to the possibility of tunneling between the two equivalent asymmetric structures.

The results of early experimental studies (carried out on several compounds related to malonaldehyde by substitution of different groups for the hydrogen atoms bonded to the carbons) using methods such as electron diffraction,[2,3] infrared spectroscopy,[4] and X-ray diffraction[5,6] were inconclusive. NMR studies[1,7,8] suggested that if the enols have C_s symmetry, there is rapid topomerization ($k \geq 10^6$ s^{-1}), so that they appear to have C_{2v} symmetry on the NMR time scale. Since the difference in stabilities between the two forms is small, the equilibrium structure could also depend on the physical state.

Oxygen inner shell binding energies obtained for malonaldehyde acetylacetone, and hexafluoroacetylacetone, by the use of X-ray photoelectron spectroscopy,[9] showed that these molecules have two distinctly different O_{1s} ionization energies, consistent with the asymmetric structure in which the two oxygens are nonequivalent. Even more conclusive, however, are microwave spectra of several isotopic species of malonaldehyde[10] which show that the molecule has a symmetrical double minimum potential surface with a relatively low barrier between the equivalent asymmetric minima, so that rapid tunneling occurs between them. Quenching of tunneling was shown to occur in species with unsymmetrical isotopic substitution, and the various spectra were analyzed to obtain the geometrical parameters.

Most previously published ab initio calculations on malonaldehyde[11-14] yield planar, asymmetrical structures. None of these studies, however, have reported vibrational frequencies for the asymmetric structure or for the symmetric transition state. The most reliably obtained barrier heights to proton exchange have been $\sim$10–11 kcal/mol. A semiempirical study[15] using the CNDO/2 method did carry out a vibrational analysis, but unfortunately this level of theory yields a nonplanar structure and transition state and a barrier height of only 1 kcal/mol. There have also been several previous treatments[16-18] of the proton tunneling, but due to lack of an accurate barrier height and a vibrational analysis these have been inconclusive.

The purpose of this paper is twofold: to determine the geometry and vibrational frequencies of the asymmetric equilibrium structure and of the symmetric transition state at a higher level of *ab initio* theory than previous work and then to use these results to make at least a preliminary calculation of the tunneling splitting in the ground vibrational state. Section II describes the ab initio calculations and their results and then makes a careful comparison of the theoretical geometry of the asymmetric equilibrium structure with that obtained from the microwave spectra.[10] The tunneling splitting is discussed in section III; the theoretical result is in reasonably good agreement with the experimental value, but it is pointed out that the calculated splitting depends sensitively on the accuracy of the potential surface parameters (i.e., barrier height, frequencies), in addition to there being uncertainty about the reliability of a one-dimensional treatment of the tunneling dynamics. Section IV concludes.

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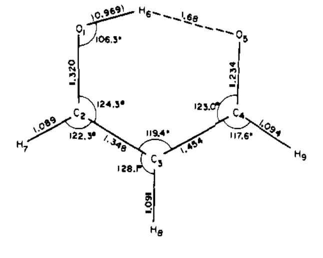
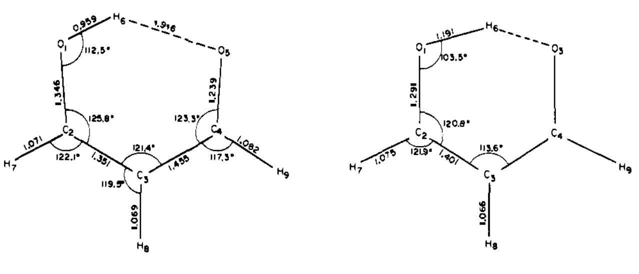


Experimental



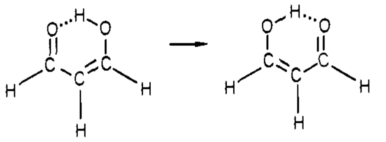
a) Cs structure (one of two equivalent structures)

b) C2v structure

Figure 1. Experimental[10] and theoretical structures for malonaldehyde and a theoretical structure for the transition state for the degenerate rearrangement of malonaldehyde. All bond distances are in angstroms.

II. Electronic Structure Considerations

In this work stationary point geometries and harmonic vibrational frequencies were predicted at the single configuration self-consistent field (SCF) level of theory.[19] Subsequently these geometries were used in conjunction with large-scale configuration interaction (CI) methods[20] to predict the height of the classical barrier for the degenerate rearrangement (eq II.1).



(II.1)

A nearly standard contracted gaussian basis set was used in the present research. This basis begins with the double-ζ (DZ) set of Huzinaga[21] and Dunning,[22] designated C,O(9s 5p/4s 2p), H(4s/2s). Although desirable, it was not feasible here to add a full set of polarization functions (d's on C and O; p's on H) to each atom. Therefore, following Karlström, Wennerström, Jönsson, Forsên, Almlöf, and Roos,[12] polarization functions were added only to the hydrogen atom that migrates during the rearrangement (eq II.1). For this set of p functions (p_x, p_y, p_z), a Gaussian orbital exponent $\alpha = 0.8$ was chosen. The final basis set has the same number of contracted Gaussian functions (61) as the earlier ab initio study by the Almlöf-Roos group.[12] However our primitive basis sets C,O(9s 5p), H(4s) are significantly larger than the C,O(7s 3p), H(3s) sets used in the earlier study, and the total energies reported here are accordingly lower. Nevertheless, one expects relative energies to be quite comparable.

In determining the structures of malonaldehyde and its rearrangement transition state, Karlström et al.[12] made several assumptions. These assumptions reduced the number of internal degrees of freedom considered from 21 to 9 (C_s malonaldehyde equilibrium geometry) and 5 (C_{2v} transition state) for the two stationary points. Potentially more serious, however, was the use of a serial optimization for the remaining geometrical parameters, with coupling between the chosen variables neglected. One of the justifications for the present study was the fact that all geometrical parameters were fully and simultaneously optimized using SCF gradient techniques.[23] In retrospect, it will be seen that the structural predictions of Karlström et al. are qualitatively reasonable. More significantly, the character of the resulting stationary points was unambiguously established here via harmonic vibrational analyses.[24]

Table I. Cartesian Coordinates for the Stationary Points on the Malonaldehyde Potential Energy Hypersurface

at-	C_s structure		C_{2v} structure	
om	x	y	x	y
O_1	−2.488 162 8	3.733 746 5	−2.182 923 4	3.820 941 1
C_2	−2.194 007 9	1.247 196 3	−2.241 067 8	1.382 555 0
C_3	0.036 768 0	0.003 925 3	0.0	−0.027 549 2
C_4	2.430 291 9	1.357 074 9	2.241 067 8	1.382 555 0
O_5	2.548 382 9	3.693 508 9	2.182 923 4	3.820 941 1
H_6	−0.906 156 4	4.656 285 8	0.0	4.369 104 2
H_7	−3.967 072 3	0.273 098 8	−4.067 392 1	0.493 509 0
H_8	0.049 054 9	−2.016 093 3	0.0	−2.042 566 1
H_9	4.141 505 7	0.236 258 8	4.067 392 1	0.493 509 0

[a] In atomic units. All z coordinates are zero. The atoms are numbered as shown in Figure 1.

Figure 1 illustrates the malonaldehyde stationary point geometries, and the associated atomic Cartesian coordinates are reproduced in Table I. For the equilibrium geometry, the very careful microwave studies of Wilson and co-workers[10] allow a detailed comparison with experiment. With two exceptions, the theoretical predictions are in good agreement with experiment. Specifically the differences between theoretical and experimental bond distances are +0.026 Å (C—O), +0.003 Å (C=C), +0.001 Å (C—C), +0.005 Å (C=O), −0.018 Å (C_2—H_7), −0.022 Å (C_3—C_8), and −0.012 Å (C_4—C_9). The O—H bond distance was assumed by Baughcum, et al.[10] to be 0.969 Å, and this value agrees satisfactorily with the 0.959 Å predicted in the present theoretical study. In the same vein the bond angle differences between theory and experiment are +1.3° (O—C=C), +2.0° (C=C—C), +0.3° (C—C=O), 0.2° (H_7C=C), and −0.3° (C—C—H_9). The theoretical value of 119.5° for the C=C—H_8 angle is in poor agreement with experiment (128.1°), but the latter authors[10] specifically state in Table V that "due to the positions of C_3 and H_8 close to the axis, this number is probably not accurate."

The theoretical value of C-O-H angle in Figure 1 is expected to be too large, by conceivably as much as 10°. This is a general result obtained when basis sets without polarization functions (e.g., d functions centered on oxygen) are used to describe angles around oxygen.[25] For the prototype water molecule, for example,[26] a double-ζ basis set yields $\theta_e(\mathrm{HOH}) = 112.6°$, as compared to the well-known experimental value 104.5°, $\Delta\theta_e$ being 8.1°. Thus we are not surprised that the predicted $\theta_e(\mathrm{COH_6}) = 112.5°$ is significantly larger than the experimental value[10] of 106.3°. That is, this discrepancy does not represent a conflict between theory and experiment but merely an instance in which the level of theory applied is deficient.

The comparison between the theoretical (1.916 Å) and experimental (1.68 Å) values of $r_e(H_6\cdots O_5)$, the difference being fully 0.24 Å, is less satisfactory. Note however that the above experimental distance refers to the H_6 isotopic species, while for the monodeuterated D_6 structure the $D_6\cdots O_5$ distance is significantly longer,[10] 1.708 Å. Better resolved from the microwave experiments is the nonbonded $O_1\cdots O_5$ distance, for which a rather narrow isotopic range of 2.553–2.576 Å is reported. The theoretical value predicted here for this distance is 2.685 Å, or about 0.1 Å longer than experiment. Although the comparison between

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Table II. Harmonic Vibrational Frequencies (in cm^{-1}) for Malonaldehyde (C_s) and the Transition State (C_{2v}) for Its Degenerate Rearrangement[a]

C_s		C_{2s}	
a	3969	a_1	3472
a'	3454	a_1	3388
a'	3430	b_2	3388
a'	3291	a_1	2058
a'	1825	a_1	1725
a'	1727	b_2	1652
a'	1582	b_2	1603
a'	1515	b_1	1453
a'	1477	a_1	1447
a'	1355	b_2	1378
a'	1185	b_2	1210
a''	1147	a_1	1162
a''	1139	b_1	1133
a'	1030	a_1	1129
a'	947	a_1	1015
a''	869	b_1	854
a''	838	a_1	691
a'	520	b_2	598
a''	465	b_1	472
a'	261	a_2	398
a''	257	b_2	1853i

[a] Note by way of convention that for the C_{2v} transition state, the out-of-plane normal modes are labeled a_2 and b_1.

theory and experiment for this O···O distance is still unsatisfactory, it is notably improved over that found for the hydrogen-bonded $H_6 \cdots O_5$ distance.

Perplexingly, the minimum basis SCF values of the $H_6 \cdots O_5$ distance is malonaldehyde, 1.65[11] and 1.66 Å,[14] are in good agreement with the experimental range, 1.68–1.71 Å. Roos's value[12] of 1.78 Å, however, is closer to that predicted here. Closer yet is the $H_6 \cdots O_5$ distance of 1.878 Å predicted with the nearly double-ζ 4-31G basis (SCF level of theory) by George, Bock, and Trachtman.[28] Thus one observes the curious correlation that agreement between theory and experiment deteriorates monotonically as the level of theory is improved. It is clear that higher levels of theory should be applied to the malonaldehyde geometrical structure. A full double-ζ plus polarization SCF treatment is the logical next step in this direction.

The force constant matrices used to determine the vibrational frequencies were obtained by taking numerical differences of analytic gradients. The perturbing steps were taken to be 0.01 bohr in each unique direction of perturbation. The ensuing harmonic vibrational frequencies are given in Table II. Perhaps the most important result seen in Table II is the definitive conclusion that, at this level of theory, malonaldehyde is predicted to be planar. The lowest out-of-plane vibrational frequency is substantial, 257 cm^{-1}. This result does not agree with the semiempirical report by Kato, Kato, and Fukui[15] that one out-of-plane vibrational mode has a negative force constant. However, our theoretical prediction is consistent with Wilson's experimental conclusion[10] that malonaldehyde is "planar or essentially planar". In an analogous manner, the presence of a single imaginary vibrational frequency for the C_{2v} structure proves that it is a true transition state. This finding would appear to rule out the suggestion by Del Bene and Kochenour[11] that the C_{2v} might represent a very shallow minimum of the potential energy hypersurface.

At the self-consistent field (SCF) level of theory adopted here, the classical or "bare" barrier height is 11.4 kcal. To obtain a realistic prediction of the rearrangement barrier height, it was deemed essential to consider the effects of electron correlation.[29] This was done via configuration interaction (CI) including all single and double excitations relative to the SCF reference configuration. Note that the core or 1s-like molecular orbitals (the five lowest occupied and five highest unoccupied) were omitted from the CI procedure. With this restriction there were 37 528 $^1A_1$ configurations for the C_{2v} transition state and 74 740 $^1A'$ configurations for the C_s equilibrium geometry. These variational correlated wave functions were determined via the shape-driven graphical unitary group approach.[20] The CI wave functions were determined at the predicted SCF stationary point geometries.

Table III. Total Energies (in hartrees) for Malonaldehyde and Its Transition State for Degenerate Rearrangement

	malonaldehyde	transition state	bare barrier, kcal
SCF	−265.571 98	−265.553 79	11.4
CISD	−266.014 72	−266.001 24	8.5
Davidson corrected for unlinked clusters	−0.060 45	−0.061 24	8.0[a]

[a] An estimate of the activation energy is obtained via transition-state ideas by subtracting from this value the 3.0-kcal difference in zero-point vibrational energy between malonaldehyde and its transition state.

Single and double excitation CI reduces the above-discussed SCF barrier of 11.4 to 8.5 kcal. A further correction[30] for the effects of quadruple excitations (unlinked clusters) reduces the classical barrier to 8.0 kcal, our final theoretical prediction. If zero-point vibrational energies of the equilibrium geometry and of the transition state are included, then the effective barrier height lies 5.0 kcal above the ground state of malonaldehyde. The total energies obtained at the various levels of theory are given in Table III.

Although there is no direct experimental determination of the barrier, our 8.0-kcal barrier may be compared with earlier theoretical predictions. The minimum basis set (STO-3G) studies of Del Bene and Kochenour[11] and of Bouma, Vincent, and Radom[14] yield classical barriers of 6.6 and 10.3 kcal/mol, respectively. Since the methods used were apparently identical, we assume that the Radom result is the correct one, while the incomplete geometry optimization by Del Bene and Kochenour leads to difficulty. The correct STO-3G barrier of 10.3 kcal is in good agreement with the present SCF classical barrier of 11.4 kcal.

The SCF classical barrier predicted by Karlström et al.[12] was 11.5 kcal, in close agreement with the present research. This is of course expected since the Karlström basis set is (see above) nearly as large as that adopted here. In their second paper, Karlström, Jönsson, Roos, and Wennerström[13] used approximate natural orbitals to reduce the number of configurations (74 740; see above) appearing in the single and double excitation CI. When electron correlation was thus taken into account, the SCF barrier of 11.5 kcal was lowered to 10.0 kcal, in reasonable agreement with the present CI value of 8.5 kcal. Therefore, we conclude that general agreement (at comparable levels of theory) is found between the three most recent theoretical studies of the malonaldehyde rearrangement barrier height.

III. Tunneling Splitting in the Ground Vibrational State

Here we consider a simple one-dimensional description of the splitting in the ground vibrational state of malonaldehyde (and its symmetric isotopic variants) that results from tunneling of the hydrogen atom between the two oxygen atoms. A more rigorous treatment of this, based on the reaction path Hamiltonian[31] model of polyatomic dynamics, is in progress;[32] this approach includes, in an approximate fashion, the effect of all the other degrees of freedom on the tunneling motion.

The situation is a classic example of splitting due to tunneling in a symmetric double-well potential, and for small splittings this is given within the WKB approximation by[33]

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$$\Delta E = \frac{\hbar\omega_F}{\pi} e^{-\theta} \qquad \text{(III.1)}$$

where ω_F is the classical vibrational frequency in one of the wells and θ is the WKB barrier penetration integral. If the barrier is approximated by an Eckart potential function,[34] then θ is given by

$$\theta = \frac{2\pi}{\hbar\omega_i} \left(V_{eff} - \sqrt{E_0 V_{eff}}\right) \qquad \text{(III.2)}$$

where V_{eff} is the effective one-dimensional barrier height, E_0 is the energy relative to the bottom of the potential wells, and ω_i is the imaginary frequency at the top of the barrier.

In approximating the tunneling as one dimensional, one must identify which mode of the "reactant" (i.e., C_s symmetry) is the reaction coordinate, the Fth degree of freedom in present language. ($F = 3N - 6$ is the total number of vibrational degrees of freedom.) We then assume that the other $(F - 1)$ vibrational modes contribute adiabatically[35] in determining the effective one-dimensional barrier. For the ground vibrational state one thus has

$$V_{eff} = V_0 + \sum_{k=1}^{F-1} \frac{1}{2}(\hbar\omega_k^{\ddagger} - \hbar\omega_k) \qquad \text{(III.3a)}$$

$$E_0 = \frac{1}{2}\hbar\omega_F \qquad \text{(III.3b)}$$

where $\{\omega_k\}$ and $\{\omega_k^{\ddagger}\}$ are the reactant (C_s) and transition state (C_{2v}) frequencies, respectively, and V_0 the "bare" barrier height discussed in Section II. For the results discussed below we used the "best" theoretical value for V_0, the quadruples corrected CI value

$$V_0 = 7.96 \text{ kcal/mol} = 2784 \text{ cm}^{-1} \qquad \text{(III.4)}$$

It is also clear that within the one-dimensional picture one should choose the O–H stretch of the reactant as the reaction coordinate, the frequency of which (cf. Table II) is 3969 cm^{-1}; thus

$$\hbar\omega_F = 3969 \text{ cm}^{-1} \qquad \text{(III.5)}$$

From the frequencies in Table II one then obtains

$$\sum_{k=1}^{F-1} \frac{1}{2}(\hbar\omega_k^{\ddagger} - \hbar\omega_k) = 957 \text{ cm}^{-1} \qquad \text{(III.6)}$$

With the values given by eq III.4–III.6 it is a simple matter to use eq III.1–III.3 to compute the splitting, and one obtains $\Delta E = 40$ cm^{-1}, about twice the quoted experimental value[10] of ~21 cm^{-1}. It is well-known, however, that vibrational frequencies determined at the double-ζ SCF level of theory are too large,[36] typically on the order of 10%. If one scales all the frequencies of reactant and transition state (including the imaginary frequency of the transition state) down by 10%, then the above equations give $\Delta E = 18$ cm^{-1}, in much better agreement with experiment.

This degree of agreement is quite encouraging—particularly in light of the fact that previous calculations[16] obtained a value of less than 1 cm—but one must be somewhat cautious in making too much of it. Thus although the one-dimensional model is qualitatively reasonable for the present system, one does not know how much the other degrees of freedom will change the result quantitatively; it is not clear, for example, that the $(F - 1)$ vibrational modes other than the reaction coordinate behave adiabatically—perhaps a sudden approximation would describe them better. As mentioned above, work is in progress to help answer these questions.

Also, even within the one-dimensional model it is seen that the splitting is relatively sensitive to the potential surface parameters: a 10% decrease in the frequencies reduced the splitting by about a factor of 2. It is also clear that the splitting depends critically on the barrier height; a 1 kcal/mol increase (decrease) in it decreases (increases) the splitting by somewhat more than a factor of 2, and it is unlikely that the present quantum chemistry treatment is reliable to this degree of accuracy. At present, therefore, one may say that the theoretical description of the tunneling splitting is in reasonable shape, but that to obtain a highly reliable theoretical value for it will require even more accurate calculations for the relevant parts of the potential energy surface, even if the one-dimensional model for the dynamics turns out to be adequate.

Having calculated the full $3N \times 3N$ Cartesian force constant matrices, it is a simple matter to compute the vibrational frequencies for other symmetric isotopic variants and then the tunneling splitting via eq III.1–III.4. (As discussed in ref 33, eq III.1 applies only to the symmetric case.) For isotopic substitutions that do not involve the active hydrogen H_6—e.g., D_7D_9, $^{13}C_2{}^{13}C_3{}^{13}C_4$—the result is essentially unchanged from the all hydrogen case. If the active hydrogen is replaced by deuterium—as in D_6, D_6D_8—III.1–III.4 give $\Delta E \approx 3$ cm^{-1} if the frequencies are unscaled and $\Delta E \lesssim 1$ cm^{-1} if all frequencies are reduced by 10%. Reference 10 quotes a value of $\Delta E \approx 3$ cm^{-1} for the isotope D_6D_8, which in this case agrees with the results of the one-dimensional model better if the frequencies are unmodified.

IV. Concluding Remarks

Malonaldehyde, along with its isotopic variants and chemical derivatives, has become the prototypical system of intramolecular hydrogen bonding. This is due to the considerable amount of accurate experimental data now available and also to the fact that computational quantum chemistry is progressing to the stage that reasonably accurate ab initio calculations are possible for it. The tunneling splitting in the symmetric species also provides an excellent test for dynamical theories of intramolecular dynamics.

This paper represents significant progress in the theoretical description of malonaldehyde: the geometries of the stationary points on the potential energy surface have been located precisely, the barrier height for hydrogen atom transfer has been determined at a higher level of *ab initio* theory, vibrational frequencies have been calculated, and with these potential surface parameters it is seen that the simplest one-dimensional model gives a reasonable value for the tunneling splitting. As noted in the paper, though, even more accurate and reliable theoretical treatments are desirable, and these are worthy topics for future research.

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(33) This well-known result is given in many places. See, for example, the approach in W. H. Miller, *J. Phys. Chem.*, **83**, 960 (1979) and references therein.

(34) See, for example, H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, 1966.

(35) See, for example, D. G. Truhlar and A. Kuppermann, *J. Am. Chem. Soc.*, **93**, 1840 (1971).

(36) See, for example, Y. Yamaguchi and H. F. Schaefer, III, *J. Chem. Phys.*, **73**, 2310 (1980).