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Structures and Proton Transfer of Malonaldehyde and Its Chloroderivatives.

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The semiempirical PM3 method has been used for a study of the optimized geometries of malonaldehyde and its chloro-derivatives, in order to obtain information on the proton transfer and proton tunneling. The calculated bond lengths and bond angles are in fairly good agreement with the experimental and ab initio values. The proton transfer and proton tunneling are suggested to be promoted upon electronic excitation to the S_1 state. Substitution of a chlorine atom reduces these rates, which depend on the substituted positions.

1. Introduction

Hydrogen bonds play important roles in chemical and biological systems. Many molecules with adjacent acidic and basic functional groups are capable of undergoing proton transfer through intramolecular hydrogen bond. Malonaldehyde is a typical molecule having intramolecular hydrogen bond, showing keto-enol tautomerism. An appreciable amount of experimental works has been done for malonaldehyde in the ground electronic state. Equilibrium geometry has been determined by its microwave spectrum.¹⁾ The existence of a double minimum potential for the two equivalent planar asymmetric forms with C_s symmetry has been confirmed by many spectroscopic studies. Rapid proton tunneling occurs between the two forms. The tunnelling barrier and tunneling splitting were determined to be 2150 cm^{-1} (25.7 kJ/mol) and 21 cm^{-1} , respectively from the microwave spectral data.¹⁾²⁾

Ab initio calculations have been performed to obtain information on the structural and dynamical properties of malonaldehyde and related compounds.^{3) - 8)} The agreement between the theoretical and experimental geometries was quite satisfactory, though the slightly different results were reported depending on the basis sets and methods used for the calculations. The best agreement with the experimental geometry was obtained with the high-level ab initio 6-61G**/second order Møller-Plesset perturbation theory (MP2) calculations by Frish et al.³⁾ It has been pointed out that the introduction of the electronic correlation is important in the calculations. However, the double zeta + polarization/MP2 (DZP/MP2) geometry⁴⁾ was close to the DZP/selfconsistent theory (DZP/SCF) predictions of Frish et al.,³⁾ although the correlation was not taken into account in the DZP/MP2 calculations. This was due to the smaller dimensions of the basis set used, especially by the lack of d polarizations on carbon atoms.

Proton transfer barrier has been estimated in the electronic ground state. The clas-

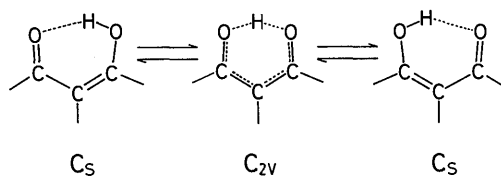
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sical or bare barrier height between the two equivalent forms with C_s symmetry was reported to be 47.7 kJ/mol at the SCF level of calculation, in which a nearly standard contracted Gaussian basis set was used.⁵⁾ A correction for the effects of quadruple excitations, however, reduced the barrier to 33.5 kJ/mol⁵⁾ which was close to the experimental value.¹⁾²⁾ Recently, Rios and Rodriguez reported the barrier to be 32.5 kJ/mol at the 3-21G level of calculations.⁸⁾ They further analyzed the substituent effect on the intramolecular hydrogen bond of malonaldehydes.⁸⁾ The hydrogen bond is strengthened by electron-donating substituents and weakened by electron-withdrawing substituents.

Many experimental and theoretical works on malonaldehyde stated above are limited to its electronic ground state. The proton affinities of adjacent acidic and basic functional groups, which contribute to the intramolecular proton transfer, change upon electronic excitation, leading to the excited-state intramolecular proton transfer (ESIPT). This is closely related to the development of the information storage devices and proton transfer lasers. Ab initio calculations give the good description of the equilibrium geometry and proton transfer barrier of malonaldehyde. They are time-consuming and too expensive for calculating optimized geometry. The recent semiempirical MOPAC method has been reported to evaluate well molecular geometries and hydrogen bond strength.⁹⁻¹⁴⁾ The present work was undertaken to get information on the dynamical aspects of ESPT of malonaldehyde and its chloro-derivatives, by using semiempirical MOPAC calculations.

2. Calculations

The MOPAC package (Ver. 6.01) furnished by Japan Chemistry Program Exchange was used. In this study, we used the PM3 approach for determining the minimum-energy molecular geometries of all the possible configurations, since it has been said to provide the better estimation of the molecular geometry than the AM1 method, especially in the presence of hydrogen-bonding interactions. Calculations were performed for the C_s and C_{2v} symmetric keto-enol forms (**Scheme 1**) of malonaldehyde (MA) and chloro-substituted derivatives (1-chloromalonaldehyde (1-Cl-MA), 2-chloromalonaldehyde (2-Cl-MA), 3-chloromalonaldehyde (3-Cl-MA)) on a FACOM-M1800 computer in Kyushu University Computer Center. In order to obtain reliable energy values, all optimization were carried out taking into account, at least partially, the energy correlation and configuration interactions.



Scheme 1

3. Results and Discussion

3.1 Geometries in the electronic ground states

Table 1 shows the bond lengths and bond angles for the optimized geometry of MA.

Table 1 Comparison of geometries of malonaldehyde in the ground electronic state.

	PM3 ^a	AM1 ^a	6-31G**/MP2 ^b	DZP/SCF ^c	DZP/MP2 ^d	exp ^e
O-H	0.965	0.970	0.994	0.957	0.956	0.969
O···H	1.823	2.077	1.694	1.880	1.908	1.68
O···O	2.642	2.849	2.589		2.703	2.553
C-O	1.333	1.353	1.328	1.314	1.326	1.320
C-H ₃	1.096	1.108	1.083	1.077	1.071	1.089
C=C	1.369	1.362	1.362	1.348	1.353	1.348
C-H ₂	1.095	1.103	1.077	1.073	1.068	1.091
C-C	1.454	1.443	1.439	1.458	1.459	1.454
C-H ₁	1.099	1.112	1.098	1.092	1.088	1.094
C=O	1.227	1.243	1.248	1.210	1.217	1.234
H-O-C	109.0	110.2	105.4	109.4	109.7	106.3
O-C=C	124.9	127.0	124.5	126.1	126.1	124.5
C=C-C	121.4	125.0	119.5	120.8	121.3	119.4
C-C=O	121.6	123.7	123.5	124.0	123.8	123.0
C=C-H ₃	124.7	123.6	122.5	121.2	121.4	122.3
C=C-H ₂	119.7	118.7	120.0	119.5	119.4	128.1
C-C-H ₁	118.5	115.7	117.6	116.4	117.6	117.6

^aThis work. ^bRef. 3. ^cRef. 3. ^dRef. 4. ^eRef. 1.

For comparison, the data obtained by the AM1 approach and ab initio calculations, and experimental data are also listed. The optimized geometry calculated by the present AM1 method is the same as that obtained by other previous AM1 calculations,^{9,10} in which the AMPAC package furnished by Q.C.P.E. was used. The optimized geometry estimated from the PM3 method is in fairly good agreement with the geometries determined by the experimental method and by ab initio calculation at 6-31G**/MP2 level, except for the O···H and O···O distances, and the C=C-H₂ bond angle. It might be concluded that the MOPAC PM3 approximation can evaluate the molecular geometry within acceptable accuracy. The deviation in the O···H and O···O distances from the experimental values is mainly due to the inherent underestimate of the hydrogen bond strength in the semiempirical calculations. Both the O···O and O···H distances obtained from the PM3 calculations are shorter than those from the AM1 method. It would be better to use the PM3 approach to deduce the geometry of MA by using the semiempirical calculations.

The best agreement with experimental data has been obtained with ab initio 6-31G**/MP2 calculations.³ The difference between the theoretical calculations lies clearly in the estimation of the O···H and O···O distances. The validity of the estimation is determined how much calculated O···H and O···O values are close to the experimental ones. The data in **Table 1** mean that the PM3 calculation can describe the equilibrium geometry of malonaldehyde better than or as well as ab initio calculations at DZP/SCF³ and DZP/MP2⁴ levels.

Table 2 lists the bond lengths and bond angles for chloromalonaldehydes calculated by the the PM3 method. **Table 2** involves the structural data obtained from the ab initio calculations,⁸ for comparison. The Cl atom has been known to act as the electronwithdrawing group and/or the electron-releasing group due to its conjugative effect. The

Table 2 Geometries of chloromalonaldehydes in the ground electronic state.

	PM3 ^a			ab initio ^b		
	1-Cl-MA	2-Cl-MA	3-Cl-MA	1-Cl-MA	2-Cl-MA	3-Cl-MA
O-H	0.965	0.967	0.967	0.975	0.981	0.971
O···H	1.856	1.833	1.821	1.923	1.820	1.741
O···O	2.670	2.652	2.643	2.687	2.620	2.567
C-O	1.331	1.332	1.341	1.335	1.336	1.318
C=C	1.368	1.371	1.369	1.338	1.331	1.331
C-C	1.450	1.460	1.457	1.430	1.440	1.445
C=O	1.220	1.224	1.225	1.177	1.227	1.231
H-O-C	109.7	109.3	108.2	113.5	112.0	110.5
O-C=C	125.0	124.2	125.7	126.7	124.4	126.8
C=C-C	120.7	122.5	120.9	118.7	122.2	118.0
C-C=O	124.2	120.7	121.4			

^aThis work. ^bRef. 8.

electron-withdrawing effect of the Cl atom results in the weakening the hydrogen bond. Conversely, when the Cl atom is substituted at the position which is favorable for the conjugation, the hydrogen bond is strengthened by the electron-releasing effect. The geometries of chloromalonaldehydes in the PM3 calculation are not so different from malonaldehyde, but the clear distinctions are observed. In 1-Cl-MA and 2-Cl-MA, the O···O and O···H distances longer than those in the parent compound manifest the prevalence of the electron-withdrawing effect. The effect is more remarkable in 1-Cl-MA, which is shown by the larger increase in the O···O and O···H distances, compared with 2-Cl-MA. The situation in 3-Cl-MA differs from the other chloromalonaldehydes. The Cl atom withdraws charge from the hydroxyl oxygen. On the other hand, the Cl atom occupies the position rather favorable for the conjugation of the lone-pair electrons to the C=C double bond. This must result in two opposite effects on the hydrogen bond. No appreciable change in the O···O and O···H distances is probably due to the balance between the two opposite effects.

Prevalence of the electron-withdrawing effect over the electron-donating one is obtained also in the ab initio calculations on 1-Cl-MA and 2-Cl-MA.⁸⁾ The optimized geometries deduced from the PM3 and ab initio calculations are also similar for these compounds, although the appreciably large difference is seen in the O···H separation (0.067 Å) in 1-Cl-MA. Meanwhile substitution at the carbon atom adjacent to hydroxyl group resulted in the shortening of O···O and O···H separations in the ab initio calculation,⁸⁾ it does not result in any appreciable change of the O···O and O···H distances in the present work. This results suggest that the electron-releasing effect due to the conjugation tends to be reflected more markedly to the strength of the hydrogen bond in the ab initio calculation than in the PM3 calculation. The reason for this is not clearly understood.

3.2 Geometries in the S₁ states

Malonaldehyde has been reported to show excited state intramolecular proton transfer (ESIPT).¹⁵⁾ It is very interesting to know the geometries of MA and its chloro-derivatives

Table 3 Geometries of malonaldehydes in the S_1 state.

	MA	1-Cl-MA	2-Cl-MA	3-Cl-MA
O-H	0.980	0.985	0.986	0.973
O...H	1.682	1.712	1.707	1.852
O...O	2.537	2.562	2.562	2.639
C-O	1.284	1.282	1.285	1.272
C=C	1.521	1.513	1.500	1.458
C-C	1.416	1.422	1.418	1.459
C=O	1.262	1.254	1.255	1.224
H-O-C	110.3	111.8	111.0	114.1
O-C=C	122.4	122.0	121.5	123.7
C=C-C	117.6	117.5	119.6	121.0
C-C=O	121.0	122.9	120.6	119.8

in the electronic excited states (S_1), from the point of view clarifying the dynamical properties of proton transfer and proton tunneling. However, there is no such report on the S_1 states. **Table 3** shows structural data for the optimized geometries of MA and the chloro-derivatives. For malonaldehyde, compared with the geometry in the ground electronic state, the O-H bond becomes longer, and the O...O and O...H distances are shortened. This suggests that the intramolecular hydrogen bond of MA is strengthened upon electronic excitation. Electronic excitation results also in the shortening of C-C and C-O bonds, and the lengthening of C=C, C=O and O-H bonds. Correspondingly, bond angles change in C-C=C, O-C=C, O=C-C and H-O-C. The same trends are observed in the geometries of 1-Cl-MA and 2-Cl-MA, suggesting that their intramolecular hydrogen bonds are strengthened upon electronic excitation. The hydrogen bonds, however, are not stronger than in MA, which is clearly shown by comparison of the O...O and O...H distances.

3-Chloromalonaldehyde shows a different behavior. The O...O distance is almost the same as that in the ground state. The O...H distance increases by 0.031 Å upon excitation, which is in the reverse direction compared with 1-Cl-MA and 2-Cl-MA. These are coincident with the increase of the C-O bond length and no change in the C=O bond length. Probably, the hydrogen bond is weakened in the S_1 state of 3-Cl-MA. Highest occupied molecular orbital is anti-bonding π orbital in MA, 1-Cl-MA and 2-Cl-MA, while it is anti-bonding C-Cl orbital in 3-Cl-MA. This is the reason why the geometry change of 3-Cl-MA upon excitation differs from other compounds.

3.3 Barrier for proton transfer

Malonaldehyde is a typical molecule showing intramolecular proton transfer. Proton transfer occurs through the transition state with a C_{2v} configuration. The barrier for proton transfer is estimated from the energy difference between the C_s and C_{2v} configurations. Then, the energies for optimized geometries with the C_{2v} symmetry were estimated for MA and its monochloro derivatives. 1-Chloromalonaldehyde is converted to 3-Cl-MA via proton transfer. The transfer is assumed to proceed through the common transition state in which a hydroxylic proton is equidistant from two oxygen atoms.

The calculated barrier heights are listed in **Table 4**. For malonaldehyde, the classical

Table 4 Barrier heights for proton transfer (Units: kJ/mol).

State	MA	1-Cl-MA	2-Cl-MA	3-Cl-MA
S ₀	110.0	117.8	112.8	106.8
S ₁	49.5	60.1	56.7	69.0

or “bare” barrier height in the ground state was calculated to be 47.7 kJ/mol by using the SCF level of theory, but it was shown to be reduced to 33.5 kJ/mol by a correction for the effects of quadruple excitations (unlinked clusters).⁵⁾ Rios and Rodriguez reported the theoretical value of 32.5 kJ/mol for the barrier for proton transfer.⁸⁾ These values are close to the experimental value (25.7 kJ/mol^{1),2)}. The PM3 calculation used in this work gives 110 kJ/mol for the proton transfer barrier of MA. This barrier height is larger by a factor of three than those obtained by ab initio calculations. For chloromalonaldehydes, barrier heights are in the range of 107 to 118 kJ/mol and the effects by substituting a chlorine atom are quite small. Rios and Rodriguez reported 60.9 kJ/mol, 36.6 kJ/mol, and 44.1 kJ/mol for 1-Cl-MA, 2-Cl-MA, and 3-Cl-MA, respectively, which were estimated from ab initio calculations at the 3-21 level. These data mean that the semiempirical PM3 method gives the higher barriers for proton transfer than those obtained by ab initio calculations. This is the case in the AM1 method. A major reason for this would be the inherent underestimation of the hydrogen bond strength in the semiempirical methods. Change from the C_s structure to the C_{2v} structure in the transition state requires the shortening of the O···O and O···H distances and correspondingly, the narrowing of O=C-C, C=C-O, and O-H···O angles. This structural change causes the strain in the molecules, but strengthen the intramolecular hydrogen bond. The former will be released partially by the latter. The PM3 method doesn't evaluates accurately the relaxation of the strain by an increase of the intramolecular hydrogen bond in the transition state.

Excited state intramolecular proton transfer and proton tunneling are assumed to occur also in chloromalonaldehydes. The present PM3 method was found to give larger barrier heights than the ab initio estimations in the ground electronic state. It would be better to use the high-level ab initio calculation for evaluating the barriers for proton transfer. Sophisticated ab initio calculations, however, are too time-consuming and too expensive to calculate the optimized geometry and its energy. It is even difficult to perform the calculations of excited states. It might be assumed that the semiempirical methods gave the qualitative order of barrier heights for ESIPT. Hence, we carried out the semiempirical calculations to on barrier heights in the S₁ states of MA and its chloro-derivatives. In **Table 4** are shown the barrier heights in the S₁ states. The potential barrier of MA decreased to about a half of that in ground state. Vibrational levels of MA are splitted due to rapid proton tunneling between the two equivalent structures with C_s symmetry. Seliskar and Hoffmann reported that the vibrationless level of the S₁ state showed a 7 cm⁻¹ decrease relative to the zero vibrational level in the ground electronic state by exciting the 3540 Å band system of MA.¹⁵⁾ A decrease in the tunneling splitting suggests a reduction in the rate of proton tunneling. In the PM3 calculations (**Table 3**), the O···O and O···H distances decrease upon electronic excitation. The lowering of both the O···O, O···H distances and the

barrier height imply that proton tunneling is promoted in the S_1 state, which is inconsistent with the experimental results. The reason for this discrepancy is not clear right now. Tropolone and 9-hydroxy-phenalenone are typical molecules showing the vibrational splitting due to rapid proton tunneling. The tunneling splittings of these molecules have been reported to increase in the S_1 states.^{17)–19)} Further theoretical and experimental works are required to clarify this contradictory results on MA.

In monochloro derivatives, their potential barriers for proton transfer decrease also in their S_1 states. All the values of barrier heights are higher than that of MA. This is due to the weakening of intramolecular hydrogen bond upon substitution of a chlorine atom. Both proton transfer and proton tunneling are suppressed by the chlorine atom substitution on MA in both the S_0 and S_1 states. The effect is most strongly appeared in 3-Cl-MA. 2-Chloromalonaldehyde in the S_1 state has the shorter O \cdots O and O \cdots H distances comparing with the ground state. Their shortening and lowering of the barrier suggest an increase in the rate of proton transfer and the magnitude of tunneling splitting in the S_1 state. 1-Chloromalonaldehyde is converted to 3-Cl-MA via proton transfer. By taking the barrier of 1-Cl-MA to 3-Cl-MA process as that of forward process, we found a forward and a reverse barrier of 60.0 kJ/mol and 67.0 kJ/mol in the S_1 states, respectively. The O \cdots O distance is shorter in 1-Cl-MA than in 3-Cl-MA. This leads to the conclusion that the forward process occurs more easily than the reverse process. It should be noted that 1-Cl-MA is less stable in the ground state than 3-Cl-MA, but their relative stability is reversed in the S_1 state.

We have been studying the proton tunneling of chlorinated tropolones, which are prototype molecules having an intramolecular hydrogen bond. Electron-releasing due to the conjugative effect increased the excited-state tunneling splittings of symmetrically-substituted tropolones, such as 5-chloro- and 3,5-dichlorotropolones. This results are reasonably explained by considering both the O \cdots O distances and the barriers for proton transfer which are estimated from the PM3 calculations. In this case, calculated potential barriers for proton transfer would be larger than the experimental barriers, because of the underestimate of the hydrogen bond strength inherent in the semiempirical calculations. The results obtained in this work, however, could give qualitative information about proton transfer of malonaldehydes in the S_1 state.

Table 5 indicates the partial atomic charges on the carbonyl oxygen and hydroxylic oxygen. Electronic excitation make the carbonyl oxygen more negative and the hydroxylic oxygen less negative in MA, 1-Cl-MA, and 2-Cl-MA. Meanwhile, in 3-Cl-MA, charges on the two oxygen atoms become less negative upon excitation and a reduction in

Table 5 Partial atomic charges on carbonyl and hydroxylic oxygen atoms.

Group	Electronic State	MA	1-Cl-MA	2-Cl-MA	3-Cl-MA
O=C	S_0	-0.348	-0.348	-0.324	-0.334
	S_1	-0.465	-0.459	-0.460	-0.285
O-H	S_0	-0.246	-0.248	-0.251	-0.249
	S_1	-0.062	-0.092	-0.120	-0.046

the degree of electro-negativity is more striking in the hydroxylic oxygen than in the carbonyl oxygen. As a whole, partial charge difference between the two oxygen atoms increases in the S_1 state of MA and its chloro-derivatives. The differences are in the order of $MA > 1-Cl-MA > 2-Cl-MA > 3-Cl-MA$. Potential barriers increases in the order $MA, 2-Cl-MA, 1-Cl-MA, 3-Cl-MA$. The charge differences are a measure of the basicity differences of the two oxygen atoms, which reflect directly the electronic effects of the chlorine atom. They have not always good correlation with the proton transfer barriers.

4. Conclusion

The semiempirical PM3 calculations have been performed for determining the optimized geometries of MA and its chloro-derivatives. Estimated bond lengths and bond angles were in fairly good agreement with the experimental values. However, the $O\cdots O$ and $O\cdots H$ distances were overestimated due to the inherent underestimation of the hydrogen bond strength. Barrier heights for proton transfer decreased upon electronic excitation in all the molecules studied here. Both the proton transfer and proton tunneling were suggested in their S_1 states.

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