Molecular Orbital Studies of Hydrogen Bonds. VIII. Malonaldehyde and Symmetric Hydrogen Bonding in Neutral Species

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Abstract: Semiempirical and ab initio molecular orbital calculations are carried out for the enol form of malonaldehyde. The distance between the bridging atoms $R_{X\cdots Y}$ is found to be the most critical factor for a symmetric hydrogen bond. From theoretical calculations on malonaldehyde and FHF, and from comparison with ionic species, two working hypotheses are proposed for a neutral species to have a symmetric hydrogen bond. They are (1) $R_{X\cdots Y} < 2.3$ Å and (2) the existence of a conjugated backbone structure.

I. Introduction

Theoretical studies of hydrogen bonding have become a very active area of research in the last decade or so. Ab initio calculations have been carried out for a variety of hydrogen bonding systems, with great success in predicting geometries and binding energies.[1,2] The energy decomposition analysis of the calculated interaction energy has been used to study the origin of the hydrogen bonding: the electrostatic energy plays the most important role in determining the mode of approach, while three energy components (electrostatic, exchange repulsion, and delocalization) are nearly equally important in the equilibrium geometry of the complex.[1,3-5]

There is a series of intra- and intermolecular hydrogen bonding systems of particular interest, which form very strong hydrogen bonds with the proton located symmetrically between the two bridging atoms, say X and Y. In normal hydrogen bonding, the proton is σ-bonded to one bridge atom, say X, with a bond distance only a few hundredths longer than the isolated X-H distance, and the Y···H distance is substantially longer than the X-H distance; typically $R_{XH} \sim 1$ Å, $R_{X\cdots Y} \sim 2.8$ Å, and $R_{H\cdots Y} \sim 1.8$ Å. We call this situation "asymmetric hydrogen bonding". In contrast, the linear bifluoride anion $(FHF)^-$, for instance, has a very short F···F distance (2.26 Å) and its hydrogen atom is located symmetrically between the two fluorine atoms.[6] We call this "symmetric hydrogen bonding". This system was also examined theoretically by McLean and Yoshimine using an ab initio SCF method with a large Slater type basis set.[7] Their calculations indicate that the most stable geometry of bifluoride is symmetric, with $R_{F\cdots F}$ between 4.2 and 4.3 Bohr (2.22 to 2.28 Å), in excellent agreement with experiment. A hydrated proton, $(H_5O_2)^+$, also exhibits the symmetric hydrogen bonding, with the O···O distance around 2.45 Å.[8] Ab initio studies on this species[9] give good agreement with experiment. It is noted that in both $(FHF)^-$ and $(H_5O_2)^+$ the situation is somewhat complicated by the fact that in some crystalline environments the hydrogen bonding becomes asymmetric.[8b]

Another system exhibiting symmetric hydrogen bonding is the hydrogen maleate ion HOOC—CH=CH—COO$^-$.[10] Here again the O···O distance is very short, 2.437 Å, and the hydrogen-bonded proton is located symmetrically on the line between the two bridge oxygen atoms. Ab initio calculations by the author's group[4,11] demonstrate that the ground state potential energy curve for the motion of the proton on the line between the two bridge oxygen atoms has a single minimum at the midpoint, in agreement with experiment. Calculations predict that in lower excited states the hydrogen bonding will be asymmetric, in contrast to the ground state. This is explained[11] by reasoning that upon excitation an electron is moved from the hydrogen bonding area O···H···O to the nonbonding area OC—CH=CH—CO and, as a result, the now neutral O···H···O region loses the strong electrostatic environment to keep the proton at the midpoint. This suggestion is consistent with the fact that all the experimentally known symmetric hydrogen bonds occur in anions and cations, but not in neutral systems. Although the situation is somewhat obscured by environmental effects, it is generally considered that $R_{X\cdots Y} <$ 2.5 Å is a necessary condition for having a "symmetric" hydrogen bond.[8,9,12] Furthermore, even though we do not discuss the case, there are systems which have a short X···Y distance and whose H potential curve has a single minimum near, but not exactly at, the midpoint of XY, with X-H and Y-H distance substantially longer than normal.[8b] These systems should be considered to be of the same class as the "symmetric" hydrogen bonding systems mentioned above.

It should be noted that all the above examples involved charged species. This is reasonable, since the charge is needed to have a stronger electrostatic interaction, resulting in a short X···Y bond distance, hence a symmetric hydrogen bond. Therefore, we would not expect to find many, if any, neutral systems possessing symmetric hydrogen bonds. To the authors' knowledge, there is no such experimentally established case.

There is one neutral molecule being studied at present, however, which appears to exhibit symmetric hydrogen bonding. Preliminary results of microwave spectroscopy suggest that the enol form of malonaldehyde is a symmetric molecule, with the hydrogen-bonded proton located symmetrically between the two bridge oxygen atoms. Its dimethyl derivative, acetylacetone, also has a symmetric hydrogen bond, according to an electron diffraction study.[14] The questions then arise as to whether or not a theoretical study of these compounds will predict symmetric hydrogen bonding and, if so, what may be learned concerning the origin of such behavior. There are two theoretical studies directly relevant to these questions. The first of these studies,[15] by Schuster, employed the semiempirical SCF procedure CNDO/2 to calculate the potential surface of the hydrogen bonded proton of malonaldehyde for a fixed geometry of the molecular backbone, determined from average geometrical parameters of similar organic molecules (i.e., all bond angles equal 120°, $R_{CO} = 1.30$ Å, $R_{CC} = 1.40$ Å, and $R_{CH} = 1.08$ Å, giving a bridge O···O separation of 2.43 Å). His results predicted that the hydrogen bonded proton is oriented asymmetrically, with a bond length to one bridge

Table I. Optimum Position of the Hydrogen Atom in Various Semiempirical Calculations

	System studied				
Run	Compd	Method	Geometry	O . . . O distance, A	Position of hydrogen atom
1[a]	Acetylacetone	INDO	Completely optimized	2.279	Symmetric
2	Malonaldehyde	INDO	From run 1	2.279	Symmetric
3	Malonaldehyde	CNDO/2	From run 1	2.279	Symmetric
4	Malonaldehyde	CNDO/2	CCC, CCO angles 120°	2.416	Asymmetric

[a] From ref 16.

oxygen of 1.13 Å, and a distance of 1.33 Å to the other bridge oxygen. His calculations also showed that the energy barrier between the two minima, i.e., the energy barrier for proton transfer, is quite low (ΔE = 0.5 kcal/mol). Quite different results were presented in an INDO study of acetylacetone by Gordon and Koob.[16] Starting with a very asymmetric molecular geometry, they varied all $3N - 6$ degrees of freedom independently to obtain the most stable geometry. This geometry optimization resulted in a symmetric molecular geometry, including a symmetric hydrogen bond. To reinforce the indication that the hydrogen bond is symmetric, they moved the hydrogen bonded proton toward one of the bridge oxygens, while keeping the rest of the molecule essentially fixed, and found that any such proton movement results in a significant increase in the energy.

As the two studies presented above gave contradictory results, it was felt that an investigation should be made of the difference between these studies in order to determine which factor(s) led to the contradictory results. To summarize, the differences between these studies lie in: (1) the compounds considered, (2) the computational methods, and (3) whether or not the geometry was optimized. A study of these differences served as the starting point for this study, and the results will be presented in section II.

Ab initio studies have been shown to yield more reliable results in calculations of equilibrium molecular geometries in general[18] and of hydrogen bonded systems in particular[2,3a] than do semiempirical methods, and when one is interested in the origin of the interaction, only ab initio methods give a physically meaningful insight into it.[3a,4] In this paper ab initio molecular orbital methods are used to study the conditions which a neutral system must satisfy in order to have symmetric hydrogen bonds. These conditions are then compared with those for ionic systems. Results of ab initio studies for malonaldehyde will be presented in section III. In section IV, $(FHF)^-$ and FHF will be compared in ab initio calculations as an example of corresponding ionic and neutral systems, respectively. Working hypotheses for symmetric hydrogen bonding in a neutral system will be discussed in section V.

II. Semiempirical Results for Malonaldehyde

The first step of the present study is to examine the contradictory findings of Schuster[15] and Gordon and Koob,[16] in an effort to determine which of the three differences noted above contributed most to the opposing results. The differences are systematically removed as follows.

(A) **Compound.** The difference in the compounds studied was removed by replacing the methyl groups of the fully optimized geometry[16] for acetylacetone with protons at a bond distance of 1.08 Å, giving malonaldehyde with an O···O distance of 2.279 Å (run 2 of Table I). An INDO calculation[18] of the potential surface for the hydrogen bonded proton was then performed, by varying the position of that proton, while holding the rest of the geometry fixed. The calculated potential surface of the hydrogen bonded proton has a single minimum on the C_{2v} axis, at 0.28 Å from the O···O line, very close to the fully optimized minimum for acetylacetone.[16]

(B) **Computational Method.** The potential surface of the hydrogen bonded proton was next recalculated with CNDO/2, using the same geometry as above. A single minimum was obtained, this time at 0.25 Å from the O···O line (run 3 of Table I). The energy of this minimum is 5.0 kcal/mol below the minimum energy obtained in ref 15.

(C) **Geometry Optimization.** The geometry of the molecule was then changed to one quite close to that assumed in ref 15, by making the CCC and CCO bond angles equal to 120°. This caused the O···O distance to increase to 2.416 Å. While holding the rest of the geometry fixed, the potential surface of the hydrogen bonded proton was calculated using CNDO/2 (run 4 of Table I). The result is a double-minimum surface, predicting an asymmetrically hydrogen bonded proton about 0.10 Å off the C_{2v} axis and about 0.20 Å from the O···O line (giving an OH distance of about 1.1 Å). This geometry is very close to that determined in ref 15 and is about 2.5 kcal/mol higher in energy than the result of run 3 above.

The above results clearly demonstrate that a lack of geometry optimization caused the prediction of an asymmetric orientation by Schuster. Since the basic result of this geometry optimization is to decrease the O···O distance, it is most likely this parameter governs the shape of the potential surface. The cutoff for having a symmetric orientation then lies between an O···O separation of 2.28 and 2.42 Å.

To lend more support to the contention that the gross shape of the hydrogen bonded proton potential surface is governed chiefly by the interatomic O···O distance, and to determine the sensitivity of the potential surface to CCC and CCO angle variations, further INDO potential surfaces were calculated for geometries with all the bond distances and the O···O distance fixed but with different CCC and CCO angles. The fully optimized INDO geometry of malonaldehyde obtained by Marsh, Thomas, and Gordon[19] has a O···O distance of 2.282 Å with $\angle$CCC = 113.21° and $\angle$CCO = 122.78°. This geometry was found to have a single minimum for the hydrogen bonded proton on the C_{2v} axis and at 0.294 Å from the O···O line. The CCC angle was then increased to 118.00° and the CCO angle was decreased to 119.04° to maintain the O···O distance of 2.282 Å. The hydrogen bonded proton potential surface for this second geometry gives a single minimum at 0.285 Å from the O···O axis, with an energy only 1.4 kcal/mol above the fully optimized result. Thus, little change in the potential surface of the hydrogen bonded proton resulted from the changes in angles, and it may be inferred that this is due to keeping the O···O distance constant. In addition, these calculations demonstrate the relative insensitivity of the potential surface to variations in the CCC and CCO angles, so that in further calculations, when the O···O distance is changed just by changing the CCO angle, the resultant change in the potential surface can be attributed to the change in O···O distance only.

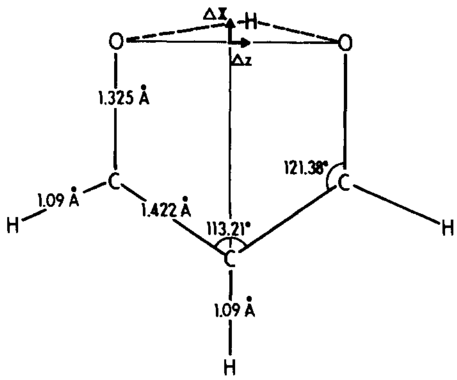


Figure 1. Assumed geometry of malonaldehyde for ab initio calculations and the definition of Δx and Δz, the deviation of the position of the hydrogen bonded proton from the midpoint between two bridge oxygen atoms.

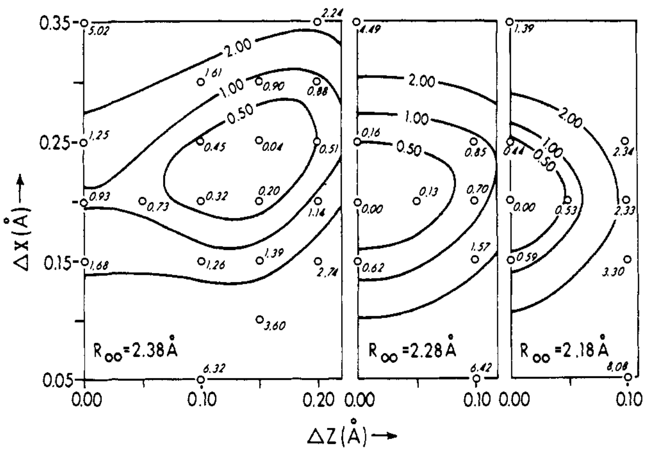


Figure 2. Calculated potential energy surfaces for the motion of the hydrogen bonded proton in malonaldehyde for three different values of R_{OO}, the O···O distance.

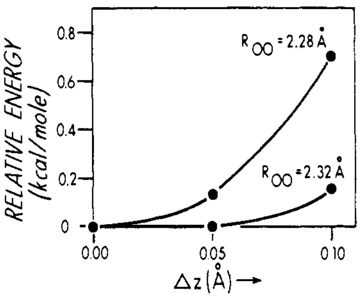


Figure 3. Calculated potential energy curves for the motion of the hydrogen bonded proton in malmaldehyde. This indicates R_{OO} = 2.32 Å is the cutoff distance between symmetric and asymmetric hydrogen bonding.

III. Ab Initio Results for Malonaldehyde

Because the semiempirical CNDO/2 and INDO methods tend to underestimate the hydrogen bonding O···O distance,[2,3a] ab initio calculations are in order before the relationship between the O···O distance and the location of the potential minima for the hydrogen bonded proton in malonaldehyde can be more quantitatively understood.

Since no experimental geometry for malonaldehyde is known, and since it was felt that an ab initio geometry optimization would be prohibitively costly, a *probable* optimum ab initio geometry was determined from previous ab initio calculations on smaller systems[20] and the fully optimized INDO geometry.[19] The CC and CO bond lengths were taken to be the averages of ab initio single and double bond lengths, respectively. The validity of this averaging procedure is supported by the fact that the INDO optimum CC and CO bond lengths[19] almost exactly match averages of INDO CC and CO single and double bond lengths.[21] All CH bond lengths were set at 1.09 Å. Furthermore, the CCC angle was fixed at 113.21°, as determined from INDO calculations,[19] and the CCO angle was varied to achieve different O···O distances. The CCH angles were taken from the INDO results[19] and when the CCO angle was changed by θ, the opposing CCH angle was changed by $-\theta/2$.

Since the optimum INDO O···O distance was determined to be 2.28 Å, ab initio scans of the hydrogen bonded proton potential surface were run for O···O distances of 2.18, 2.28, and 2.38 Å. Figure 1 shows the geometry used for the O···O distance of 2.28 Å, together with the position of the hydrogen bonded proton indicated by Δx and Δz over which a two-dimensional scan was made. The SCF calculations were carried out using a version of the GAUSSIAN 70 program,[22] with an STO-3G minimal basis set with scaling factors and coefficients determined by Hehre, Stewart, and Pople.[23]

Results of these scans are shown in Figure 2. As is evident from the figure, O···O distances of 2.18 and 2.28 Å yield single minimum potentials, while the 2.38 Å O···O distance gives a double minimum potential. Both single minima occur at 0.20 Å from the O···O line. The lower single minimum (−262.13910 hartree), achieved for the 2.28 Å O···O separation, is 3.8 kcal/mol below the single minimum for the 2.18 Å O···O separation (−262.13295 hartree), and is 1.1 kcal/mol below the double minimum (−262.1373 hartree) for the 2.38 Å O···O separation, located roughly 0.14 Å off the C_{2v} axis and 0.23 Å from the O···O line (giving an R_{OH} of about 1.08 Å).

In order to determine the O···O distance cutoff for a single minimum, the energies for the three scans at a common point (Δz = 0.10 Å, Δx = 0.20 Å) were fit to a quadratic form, which gave a cutoff O···O distance of 2.32 Å. To demonstrate that 2.32 Å is actually the cutoff point for having a single minimum, SCF calculations were carried out along the line Δx = 0.20 Å, since the other single minima occurred on this line. The results of these calculations are shown in Figure 3, from which it is evident that an O···O separation of 2.32 Å yields a very broad and flat single minimum which rises only 0.15 kcal/mol at 0.10 Å from the minimum (compared to 0.70 kcal/mol in the case of the 2.28 Å O···O distance and 2.33 kcal/mol for the 2.18 Å O···O distance). This cutoff of 2.32 Å is significantly less than the experimental O···O separation of 2.437 Å in the hydrogen maleate anion, as described in section I.

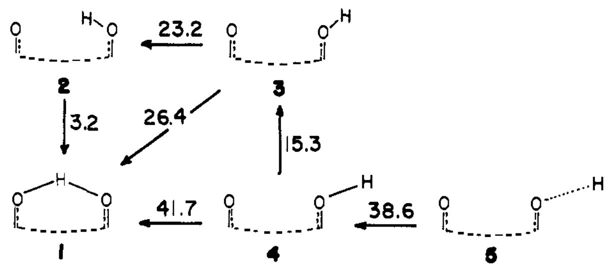
An attempt was then made to understand the origin of the single and double minimum potential surfaces through the charge distributions for the various structures studied. The net charges on the hydrogen bonded proton (H_1) and the two bridge oxygens (O_1 and O_2) for the different geometries studied and for various values of Δz are given in Table II. [Note that H_1 moves closer to O_1 as Δz increases.] Since the charge variations for each geometry are rather small (compare, for example, the variations in the maleate anion[11]), and since there is little qualitative difference between the results for the 2.28 and 2.38 Å O···O separations, little information concerning the origin of the gross shape of the potential surface can be gained from studying these net charges. However, two obvious trends should be noted. First, as the O···O separation increases, the magnitudes of the net charges decrease, probably due to decreased atomic interaction. Second, as Δz increases, the magnitudes of the charges on H_1 and O_1 increase due to

Table II. Charge Variations in Malonaldehyde

O···O distance, Å	Δx, Å	Δz, Å	Charge, e H	Charge, e O_1	Charge, e O_2
2.18	0.20	0.00	+0.320	−0.322	−0.322
		0.05	+0.320	−0.327	−0.317
		0.10	+0.322	−0.332	−0.312
2.28	0.20	0.00	+0.305	−0.312	−0.312
		0.05	+0.306	−0.314	−0.309
		0.10	+0.306	−0.317	−0.306
2.38	0.20	0.00	+0.294	−0.303	−0.303
		0.05	+0.293	−0.304	−0.302
		0.10	+0.293	−0.304	−0.299
		0.15	+0.294	−0.306	−0.295
		0.20	+0.297	−0.310	−0.292

bond formation, while the magnitude of the charge on O_2 decreases, due to a lessened interaction with the proton.

In order to obtain some insight into the origin of the hydrogen bonding energy in the symmetric equilibrium geometry of malonaldehyde, calculations were performed on the following hydrogen bonded and nonbonded geometries for an O···O separation of 2.28 Å: **1** OH distance 1.158 Å, direction cis; **2** OH distance 0.99 Å, direction cis; **3** OH distance 0.99 Å, direction trans; **4** OH distance 1.158 Å, direction trans; **5** OH distance 1.362 Å, direction trans. The results are shown schematically in the following diagram.



The geometry **1** is the equilibrium, symmetrically hydrogen bonded geometry (Δz = 0 Å and Δx = 0.20 Å) which gives ∠COH = 102.0°. All the following geometries assume this value of ∠COH. The geometry **2** has a shorter OH distance of 0.99 Å, an equilibrium distance for nonhydrogen bonded OH. The difference in energy between **1** and **2**, 3.2 kcal/mol, is the extra stabilization energy of symmetric hydrogen bonding over asymmetric hydrogen bonding. **3** is a nonhydrogen bonded structure which is obtained from the hydrogen bonded geometry **2** by rotating the OH bond by 180° about the CO axis. Since this is presumably the most stable, nonhydrogen bonded geometry with the symmetric backbone structure,[24] the energy difference between **1** and **3**, 26.4 kcal/mol, can qualitatively be called "the total hydrogen bond energy" of malonaldehyde. It is recognized that this energy is substantially larger than that of a standard intermolecular hydrogen bond energy, 5 to 10 kcal/mol. "The total hydrogen bond energy" is the sum of 3.2 kcal/mol, mentioned above, and 23.2 kcal/mol, the **1**–**2** difference, which itself includes the cis–trans isomerization energy as well as the asymmetric hydrogen bonding energy. Similarly, one can regard "the total hydrogen bond energy", 26.4 kcal/mol, as the difference between the energy loss, 15.3 kcal/mol, due to the O–H stretching (**4**–**3**), and the large stabilization energy, 41.7 kcal/mol, of the O–H stretched molecule due to the symmetric hydrogen bonding and the cis–trans isomerization.

IV. Comparison between $(FHF)^-$ and FHF

In hydrogen bonding in ions, it is estimated experimentally[8,12] as well as theoretically[9,2] that the XY distance, the distance between two heavy atoms binding to the hydrogen atom, must be less than 2.5 Å in order for the "symmetric" structure (with a long X–H bond and a Y–H bond of the same or similar length) to be more stable than the "asymmetric" structure (with a normal X–H bond length). One can speculate that for a small XY separation, the electrostatic and polarization interactions in the ionic moiety are so strong that the loss of the energy due to the weakening of the X–H bond is more than compensated for. On the other hand, for hydrogen bonding in a neutral species, if any symmetric structure can be stable, such a critical distance would be much smaller, because of the lack of the large charge distribution in the interaction region.

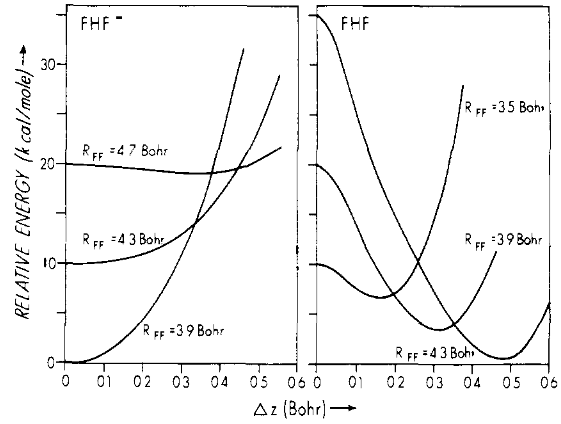


Figure 4. Calculated potential energy curves for the motion of the proton in collinear $(FHF)^-$ and FHF. Δz is the deviation of the proton from the midpoint between two fluorine atoms. The energy has been shifted arbitrarily for each curve.

The existence of the backbone conjugation seems to have little effect in the hydrogen bonding of an ionic species. In the hydrogen maleate ion, ab initio calculations indicate[11] that the replacement of the CH═CH backbone by a hypothetical nonconjugative CH_2–CH_2 group (of the same C–C bond length and C–C–C bond angle as CH═CH, thus keeping the O···O distance unchanged) would not change the stable symmetric hydrogen bonding. Of course, FHF^- and hydrated protons have symmetric hydrogen bonding despite the lack of any backbone structure which forces the X···Y distance within the critical value. On the other hand, in a neutral species, the existence of the backbone structure and the conjugation through it may be of more importance.

In order to examine the differences between ionic and neutral hydrogen bonds, and to compare with malonaldehyde on the role of backbone conjugation, we have carried out ab initio calculations for ionic $(FHF)^-$ and neutral FHF in the collinear form. Though very accurate calculations for both $(FHF)^-$ and F_2H have been published,[7,25] a different region of the potential energy surfaces than is available is needed, and furthermore we want to compare them with calculations for similar accuracy. A 4-31 split-shell Gaussian basis set with a standard set of parameters[26] is used in the standard SCF procedure for the closed shell $(FHF)^-$ and in the generalized restricted Hartree-Fock procedure for the open shell FHF ($^2\Sigma$).[27] For a few selected values of the FF distance, the potential energy curve, relative to Δz = 0, is plotted as a function of Δz in Figure 4. For the anion the FF distance of the change over from symmetric to asymmetric hydrogen bonding is calculated to be 4.5 Bohr (~2.4 Å), which is in good agreement with the previous calculation.[7] The most stable structure is symmetric with $R_{FH} \sim 2.15$ Bohr (1.14 Å), which is again in agreement with the previous result of $R_{FH} \sim 2.2$ Bohr. For the neutral FHF, the calculation indicates that the structure is asymmetric (double minimum) even for $R_{FF} \sim 3.5$ Bohr (1.85 Å) which is almost as small as twice the HF distance of the isolated HF. Furthermore, the isolated FH + F is calculated to be more stable than any FHF complex studied here.

V. Discussion

The principal conclusion of this work is that the $O\cdots O$ separation is the main determining factor for the symmetric feature of the potential surface of the hydrogen bonded proton in malonaldehyde. Ab initio calculations with the STO-3G basis set predict an $O\cdots O$ distance cutoff of about 2.3 Å, below which a single minimum, "symmetric" hydrogen bonding can be obtained. Since no extensive geometry optimization which includes backbone structural changes has been carried out in this ab initio study, we cannot make a conclusive prediction as to whether or not the malonaldehyde should have a symmetric hydrogen bonding structure. We can say, however, that ab initio calculations do support such a possibility, provided the $O\cdots O$ distance is actually smaller than about 2.3 Å.[28] Our predicted $O\cdots O$ distance is very close to this critical value, suggesting that malonaldehyde appears to be on the border line between the symmetric and asymmetric forms. This conclusion can be compared with the prediction of an INDO study that after a complete optimization of the geometry, the symmetric hydrogen bonding structure with $R_{O\cdots O} = 2.28$ Å is the most stable. At present, the experimental result is not yet well established, and further experimental studies are urged for better understanding of this unique neutral system with a possible symmetric hydrogen bond.

Even though theoretical as well as experimental information is still limited, it would be worthwhile to suggest working hypotheses for conditions necessary for "symmetric" hydrogen bonding in a neutral system, based on what has been presented here. The conditions proposed by the authors are: (1) that the $X\cdots Y$ distance is less than about 2.3 Å,[28] and (2) that the system has a conjugated backbone structure.

The smaller the $X\cdots Y$ distance, the more likely the hydrogen bond will be "symmetric". This is because a strong electrostatic moiety is essential for symmetric hydrogen bonding and in a neutral system this is very sensitive to the $X\cdots Y$ distance. The example of FHF suggests that it may be rather difficult to bring two neutral components of the complex to the distance required above, as the exchange repulsion would be substantial at this small distance. Therefore, the intramolecular hydrogen bonding system, as opposed to the intermolecular system, would be more advantageous in that the backbone structure would appropriately bring the interacting groups into the proper neighborhood. In an ionic system, as was seen in hydrogen maleate, the existence of the backbone conjugation was not an essential factor. In the neutral system, however, it is expected, though as yet untested,[29] that such a conjugation would become an essential factor by providing an extra stabilization energy in the symmetric bonding.

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References and Notes

(1) K. Morokuma and L. Pederson, *J. Chem. Phys.*, **48**, 3275 (1968).
(2) For review, P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).
(3) (a) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971); (b) S. Iwata and K. Morokuma, *J. Am. Chem. Soc.*, **95**, 7563 (1973).
(4) K. Morokuma, S. Iwata, and W. A. Lathan, "The World of Quantum Chemistry", R. Daudel and B. Pullman, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1974, pp 277–316.
(5) See also, R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *Theor. Chim. Acta*, **20**, 331 (1971).
(6) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **20**, 704 (1952).
(7) A. D. McLean and M. Yoshimine, *IBM J. Res. Dev., Suppl.*, **12**, 206 (1968).
(8) (a) A. F. Beecham, A. C. Hurley, M. F. Mackey, V. W. Maslen, and A. McL. Mathieson, *J. Chem. Phys.*, **49**, 3312 (1968); (b) J. M. Williams and S. W. Peterson, *Spectrosc. Inorg. Chem.*, **2**, 1 (1971).
(9) (a) W. P. Kraemer and G. H. F. Diercksen, *Chem. Phys. Lett.*, **5**, 463 (1970); (b) P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, **92**, 6101 (1970); (c) M. D. Newton and S. Ehrenson, *ibid.*, **93**, 4971 (1971).
(10) (a) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **29**, 948 (1958); (b) S. F. Darlow and W. Cochran, *Acta Crystallogr.*, **14**, 1250 (1961).
(11) S. Iwata, K. Morokuma, and A. D. Isaacson, "Molecular Orbital Studies of Hydrogen Bonds. VII. Ground and Excited States of Hydrogen Maleate", to be published.
(12) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968.
(13) E. B. Wilson, 28th Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June, 1973, abstract p 29; W. F. Rowe and E. B. Wilson, private communication.
(14) A. H. Lowrey, C. George, P. D'Antonio, and J. Karle, *J. Am. Chem. Soc.*, **93**, 6399 (1971).
(15) P. Schuster, *Chem. Phys. Lett.*, **3**, 433 (1969).
(16) M. S. Gordon and R. D. Koob, *J. Am. Chem. Soc.*, **95**, 5863 (1973).
(17) W. A. Lathan, L. A. Curtiss, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971); M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).
(18) Program used is P. A. Dobosh, CNINDO, Program No. 141, Quantum Chemistry Program Exchange, Indiana University.
(19) F. S. Marsh, B. G. Thomas, and M. S. Gordon, *J. Am. Chem. Soc.*, submitted for publication.
(20) W. A. Lathan, L. A. Curtis, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
(21) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968).
(22) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Program No. 236, Quantum Chemistry Program Exchange, Indiana University.
(23) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(24) The equilibrium geometry of the nonhydrogen bonded malonaldehyde would probably have a nonsymmetric backbone structure with a bond length alteration. But this is not the topic of the present paper.
(25) S. V. O'Neil, P. K. Pearson, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, **58**, 1126 (1973).
(26) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(27) (a) S. Y. Chang, E. R. Davidson, and A. Vincow, *J. Chem. Phys.*, **52**, 5596 (1970); (b) S. Iwata and K. Morokuma, unpublished work and programs.
(28) The STO-3G set is known to give internuclear separation 5–10% too small in many cases. Therefore, the calculated cutoff of about 2.3 Å may be an underestimate. Since the generally established criterion for the ionic system is 2.5 Å, and the smaller the distance the more likely the system is to be symmetric, a cutoff of 2.3 Å is proposed for the neutral species.
(29) Ir studies of matrix isolated neutral hydrogen bonded radicals ClHCl, BrHBr, and IHI (P. N. Noble and G. C. Pimental, *J. Chem. Phys.*, **41**, 3165 (1968); V. Bondybey, G. C. Pimental, and P. N. Noble, *J. Chem. Phys.*, **55**, 540 (1971); P. N. Noble, *ibid.*, **56**, 2088 (1972)) suggest symmetric hydrogen bonds for these systems. However, the microwave study of the water dimer (T. R. Dyke and J. S. Muenter, *ibid.*, **57**, 5011 (1972); **60**, 2929 (1974)) indicates the ir result of the complex geometry (M. van Thiel, E. D. Becker, and G. C. Pimental, *ibid.*, **27**, 486 (1957)) is inconclusive.