that the orbitals are more localized than suggested by the values of $|F(\Omega,\Omega)/\bar{N}(\Omega)|$. For instance, the value for $\langle\mu_1|\mu_1\rangle_\Omega \times 100$ in the CH bond loge is 82%. This figure is definitely more compatible with the electron pair concept than is the figure of 69% which is obtained from $|F(\Omega,\Omega)/\bar{N}(\Omega)|$. It should be noted, however, that the value of $\langle\mu_1|\mu_1\rangle_\Omega$ in the F_2 bond loge is as low as 0.30. It is also important to note that Bader and Stephens found[1a] that no single region of the space of the valence density of CH_4, NH_3, H_2O, or Ne exhibits a minimum in its fluctuation.[6]

For a closed shell system, the relationship between $\langle\mu_1|\mu_1\rangle_\Omega$ and $|F(\Omega,\Omega)/\bar{N}(\Omega)|$ is

$$\langle\mu_1|\mu_1\rangle_\Omega^2 = \frac{\bar{N}(\Omega)}{2}|F(\Omega,\Omega)/\bar{N}(\Omega)| - \sum_{i\neq 1}\langle\mu_i|\mu_i\rangle_\Omega^2 \quad (7)$$

From the above relationship, if $\bar{N}(\Omega) \leq 2$, then $\langle\mu_1|\mu_1\rangle_\Omega < |F(\Omega,\Omega)/\bar{N}(\Omega)|^{1/2}$. However, if $\bar{N}(\Omega)$ is close to 2, which is usually the case, and if $|F(\Omega,\Omega)/\bar{N}(\Omega)|$ is not extremely small, then the following simple approximate relationship must hold because $\langle\mu_1|\mu_1\rangle_\Omega^2 \gg \langle\mu_i|\mu_i\rangle_\Omega^2$ $(i \neq 1)$:

$$\langle\mu_1|\mu_1\rangle_\Omega \approx |F(\Omega,\Omega)/\bar{N}(\Omega)|^{1/2} \quad (8)$$

Tables I-III confirm the validity of eq 8. Consequently, for many loges, $\langle\mu_1|\mu_1\rangle_\Omega$ should yield a significantly higher number than $|F(\Omega,\Omega)/\bar{N}(\Omega)|$; witness $|F(\Omega,\Omega)/\bar{N}(\Omega)|^{1/2}$ for the bond loges of BH_4^-, NH_3, and H_2O.

In conclusion, we have emphasized that it is worthwhile to investigate the extent of pair localization in a molecule in terms of orbitals as well as in terms of the localizability of the Fermi hole.

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(6) Descriptions of valence loges for these systems are given on p 17 and 18 of ref 1a.

Correlation Effects on Barriers to Proton Transfer in Intramolecular Hydrogen Bonds. The Enol Tautomer of Malondialdehyde Studied by ab Initio SCF–CI Calculations

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Abstract: Ab initio MO-LCAO-SCF-CI calculations have been performed on the enol tautomer of malondialdehyde, the parent compound for β-dicarbonyls. The molecule contains an intramolecular hydrogen bond, the potential of which is found to be of the double-well type. Previous calculations of the barrier height performed on the SCF level yielded a value of 48 kJ/mol. The present study includes correlation effects which reduce the barrier height to 42 kJ/mol.

The enol tautomers of β-dicarbonyl compounds are usually stabilized by a strong intramolecular hydrogen bond. A much debated question has been if this hydrogen bond is strong enough to result in a single minimum potential for the proton or if it is of the double minimum type. The two possibilities are illustrated in Figure 1 for the parent β-dicarbonyl compound malondialdehyde (MA). In order to study the problem regarding the shape of the hydrogen bond potential we recently performed a series of ab initio MO-LCAO-SCF calculations of MA.[2] The results from this study clearly indicated that this compound has a C_s symmetric structure with a double minimum potential. Independently Isacson and Morokuma[3] have reached the opposite conclusion, that the C_{2v} form is the most stable, also from an MO-LCAO-SCF calculation. The source of this discrepancy is probably that Isacson and Morokuma only performed a very restricted geometry optimization of the C_s form which prevented them from finding the C_s minimum structure.

There exists as yet very little experimental data on the structure of MA, but the analogous compound 2,4-pentanedione (acetylacetone) has been extensively studied. The results of different techniques are however incompatible. In two studies using electron diffraction[4,5] acetylacetone was found to have C_{2v} symmetry while both ir[6] and NMR[7] studies have shown acetylacetone to have an asymmetric hydrogen bond.

In our previous SCF study of MA[2] it was concluded that the most serious error in the calculation might be due to the neglect of correlation effects. Studies of smaller systems such as $H_3O_2^-$, HF_2^-, and $H_5O_2^+$ have shown that correlation effects can be of considerable importance for the shape and barrier height of hydrogen bond potentials.[8,9] Very accurate CI calculations on $H_3O_2^-$ using an extended basis set and accounting for 75% of the total valence shell correlation energy[8b] actually yielded a proton transfer barrier of only 0.6 kJ/mol while the corresponding value obtained on the SCF level of approximation was 6.0 kJ/mol. Very similar results were obtained in

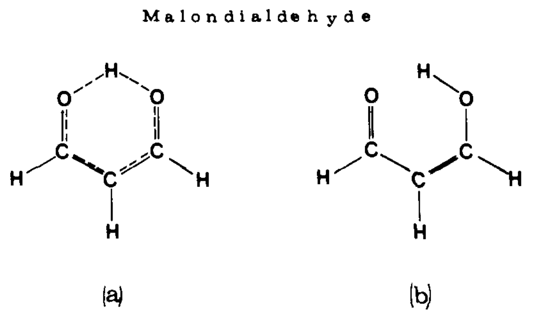

Figure 1. Possible structural representations of the enol tautomer of malondialdehyde: (a) C_{2v}, symmetric; and (b) C_s, symmetric form.

a parallel study[8a] but with a basis set comparable to the one used in the present series of calculations. The magnitude of the correlation effects on the barrier height is closely related to the difference in the OH bond distance between the symmetric and asymmetric forms. The reason for this is obviously the incapability of the SCF approximation to correctly describe the partial dissociation of the OH bond which takes place in the proton transfer reaction.

In view of the importance of correlation effects on hydrogen bond potentials and also the contradictory results of different experiments, we have considered an SCF-CI study of MA to be of great value in order to obtain more conclusive results. The development of the direct configuration method[10] has made such calculations feasible even for systems as large as MA.

Computational Method

The configuration interaction calculations were based on the SCF results of ref 2 and were performed with the direct configuration interaction method (CIMI method) using the MOLECULE-CI program system.[10b] In the CIMI method one determines the CI vector in an iterative procedure which avoids the construction of a Hamiltonian matrix. Instead the increment vector in each iteration is obtained directly from a given list of molecular one- and two-electron integrals. The process is very fast and it is therefore possible to include a large number of configurations in the CI expansion.

The double ζ type basis set used in the SCF calculations of ref 2 resulted in 61 contracted Gaussian basis functions and, thus, in 19 occupied and 42 virtual orbitals. A CI expansion containing one reference state (the HF determinant) and including all single and double replacement states of correct symmetry would have 162 569 terms for the C_s form of MA. Neglecting replacements in the 1s core orbitals reduces this number to around 70 000. However, this number was still too large for the available computer facilities and a further reduction in the size of the expansion was found to be necessary.

Two different methods were used for the selection of important configurations. First a selction procedure was attempted which was based on physical arguments. The idea was that the difference in correlation energy between the C_s and the C_{2v} forms of MA should arise mainly from the difference in OH bond lengths for the two structures. Thus only those orbitals (occupied and virtual) that had a substantial amplitude in the O-H···O region were used to construct the replacement states. Although the orbitals for the two different conformations of MA are rather similar it turned out to be very difficult to make selections of orbitals which made the CI expansions for the two forms equivalent. The results obtained with this selection procedure must therefore be regarded as uncertain with respect to the barrier height.

To avoid the difficulty with the arbitrary selection of orbitals but also to improve the convergence of the CI expansion an alternative method which leads to a consistent choice of orbitals was considered. As is well known,[11] in a certain sense the optimal convergence properties of the CI expansion are obtained if the configurations are built with the exact natural orbitals of the system. In practice these orbitals are unknown until the Schrödinger equation has been solved. There are however good indications that the use of approximate natural orbitals (ANO's) obtained from a second-order perturbation calculation also gives a CI expansion with considerably improved convergence properties.[10b] In second-order perturbation theory the virtual part of the first-order density matrix can be written as a closed expression in molecular one- and two-electron integrals.[10b] It can therefore easily be calculated independently of the size of the corresponding CI vector. A new orbital space can then be constructed where the occupied part consists of the closed shell HF orbitals while the virtual part is taken as the diagonal basis for this density matrix. It has been demonstrated that the relative importance of these ANO's in the CI expansion is closely related to the corresponding occupation numbers.[10b] The size of the CI expansion can therefore be reduced in a consistent way by including only ANO's with occupation numbers larger than a given threshold. A thorough discussion of the effects of such truncations in the ANO basis on energy differences and different molecular properties will be given elsewhere.[12] In the present study ANO's constructed according to the scheme sketched above and with two different truncation limits have been used to reduce the size of the CI expansion.

Computations and Results

The previous SCF calculations on MA were taken as a starting point for the CI calculation. These SCF calculations showed a double minimum potential for the hydrogen bond with the C_s form of MA being 48 kJ/mol more stable than the C_{2v} form. In calculating the correlation energy correction to the potential it was found too expensive (in terms of computer time) to reoptimize the geometry. Consequently CI calculations were performed for only three geometries. These were (a) the optimal SCF C_s structure ($k = 0$); (b) the optimal SCF C_{2v} structure ($k = 1$); (c) the midpoint between these two structures obtained by a linear interpolation in all geometry parameters ($k = 0.5$).

Correlation effects will lead to slight changes in all geometry parameters for the system. Implicit in the procedure given above, therefore, is the assumption that these geometry changes are the same, with respect to improvement in total energy, for all the three structures except for the particular degree of freedom represented by the reaction coordinate k.

Three types of CI expansions were constructed for each of the three geometries a, b, and c, except for case c where only the two expansions based on ANO's were considered. In the first of these (CI1) 10 occupied and 19 virtual orbitals with large amplitudes in the O-H···O area were selected by inspection. The expansion comprised all single and double replacements in this space (9557 and 4832 configuration state functions for the C_s and C_{2v} forms, respectively). The two other series of calculations were made with selected ANO's chosen as the virtual orbital space. All single and double replacements from the 14 valence orbitals (1s core orbitals were in all cases left uncorrelated) to a set of 30 (CI2) and 14 (CI3) virtual ANO's, respectively, were considered. The smallest occupation numbers for these orbitals in the approximate natural orbital expansion were 1.0×10^{-3} and 6.2×10^{-3}, respectively. The number of terms in the expansions in the C_s (C_{2v}) form were 47 712 (23 971) and 10 856 (5480), respectively.

The results of the calculations are summarized in Table I. Some computation times are given in Table II. As can be seen from Table I the two ANO expansions yield similar energy differences while the first expansion shows quite a different

Table I. Calculated SCF and Correlation Energies for the Three Different Geometries (in Atomic Units)

	k = 0.0	k = 0.5	k = 1.0
SCF[a]	−265.26657	−265.25766	−265.24808
CI1	−0.16980		−0.19070
CI2	−0.45665	−0.45871	−0.45920
CI3	−0.35842	−0.35888	−0.35552
SCF + CI2	−265.72322	−265.71637	−265.70728

[a] From ref 2.

Table II. Computation Times (Central Processing Time in Minutes) for the SCF and the Largest CI Calculations for the C_{2v} (23 971 Configurations) and C_s (47 712 Configurations) Symmetric Forms of MA

	C_s	C_{2v}
SCF calcd	44	20
Calcn of integrals over symmetry adapted basis functions	34	16
Calcn of ANO's	60	24
Transformation to MO integrals	50[a]	13[a]
CI calcd	181 (29)[a,b]	140 (22)[b]

[a] These calculations were performed on a Univac 1110 computer in Bergen, Norway. The other calculations were performed on a Univac 1108 computer in Lund, Sweden. [b] Values within parentheses give the CPU time for one iteration in the CI process.

and more dramatic effect. The truncation of the CI2 expansion is very small, in fact the ANO's not included in the virtual space correspond to a summed occupation number of only 4.0 × 10^{-3} which is only ~1% of the total occupation of the virtual space. This means that within the orbital basis used only a very small and (for different geometries) probably very similar amount of correlation energy is neglected. From previous test calculations we can estimate the error in the hydrogen bond potential due to the truncation of the ANO expansion in the CI2 calculations to be less than 1.0 kJ/mol.[10b,12] Obviously the results of the CI1 calculation must therefore be an artefact arising from nonequivalent CI expansions. This illustrates the difficulty in using localization criteria to select an appropriate orbital basis in CI calculations.

A new hydrogen bond potential can be obtained from the SCF potential and the calculated correlation energies (CI2), fitted to a polynomial of fourth degree in k, symmetric with respect to the C_{2v} structure. Figure 2 shows the calculated correlation energy and Figure 3 the resulting hydrogen bond potential as functions of the reaction coordinate k. An absolute energy minimum is obtained for k = 0.07 and the energy difference between the C_s and C_{2v} forms is found to be 42 kJ/mol. Finally the optimal structure corresponding to k = 0.07 is shown in Figure 4.

Discussion

From the results obtained in the most extensive calculation (CI2) it seems clear that the correlation effects lower the barrier in the hydrogen bond potential, but the effect is not very dramatic. It is very unlikely that the accumulated errors in the calculations are so large that the barrier of 42 kJ/mol is an artefact. In our previous SCF calculation estimated error bounds were presented. Through the present CI calculation the uncertainty due to correlation effects has been reduced considerably and the energy difference between the C_s and the C_{2v} forms of MA should be within 42 ± 10 kJ/mol. It should be noted that this energy difference refers to the minimum in the potential energy curve. In the actual molecules one has to correct for the zero-point vibrational energies. An unperturbed OH stretching vibration has a zero-point energy of ~22 kJ/mol which shows that the actual barrier to topomerization in MA is considerably smaller than 42 kJ/mol.

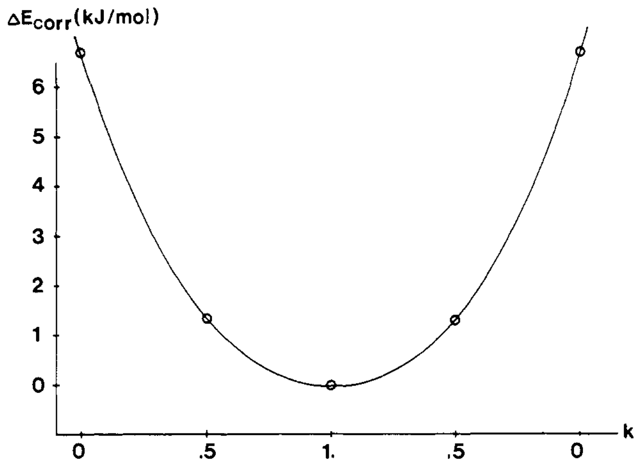

Figure 2. Calculated change in the correlation energy as a function of the reaction coordinate k.

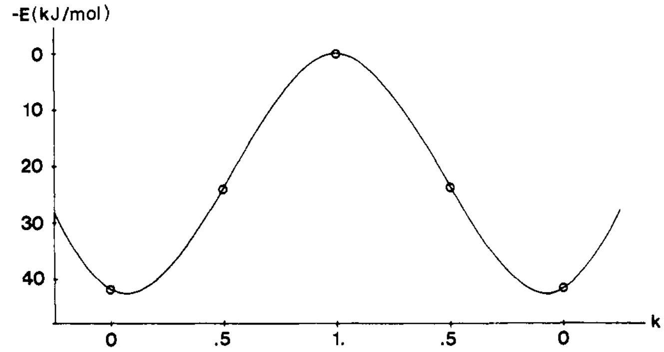

Figure 3. Calculated hydrogen bond potential including correlation effects.

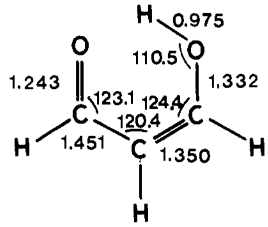

Figure 4. Calculated optimal geometry corresponding to k = 0.07.

Wilson et al.[13] have recently presented an analysis of microwave spectra of a number of isotopic species of malondialdehyde. They concluded that there is strong evidence for a double minimum potential function for the hydrogen-bonded hydrogen. The barrier was expected to be relatively low resulting in a rapid tunneling between the two topomeric forms. The O···O distance was found to be 2.55 Å. The theoretical value obtained in the present work is 2.60 Å. As expected, the measured value for the O···O distance, which is vibrationally averaged, is slightly shorter than the calculated value which refers to the bottom of the potential well.

As mentioned before, the relative error in the CI2 calculation is very small. Thus the CI3 expansion, in which 86% of the total occupation number of the virtual space is included in the ANO space, gives a reasonable estimate of the relative correlation energies with an error of around 10 kJ/mol. However, even if the numerical error caused by the larger truncation of the virtual space is rather small, one obtains a qualitatively

Table III. Correlation Effect on Molecular Properties

	Dipole moment, D	q,[c] kHz	Asymmetry parameter	Deviation from bond direction,[a] deg
		$k = 0$		
SCF	3.22	311	0.12	4.5
CI2	3.15	314	0.12	4.5
		$k = 0.5$		
SCF	3.35	127	0.25	13.5
CI2	3.28	129	0.26	12.8
		$k = 1$		
SCF	3.48	56	0.33	90[b]
CI2	3.40	58	0.42	90[b]

[a] Deviation of the direction of the largest principal component of the electric field gradient tensor from the bond direction. The largest component is turned clockwise relative to the hydrogen bond defined as in the C_s symmetric form in Figure 1. [b] The out-of-plane component is the largest. [c] Quadrupole coupling constant for the hydrogen bonded hydrogen atom.

incorrect result in this calculation, the correlation energy increasing instead of decreasing the barrier height (cf. Table I). More detailed investigations[12] also indicate that it is necessary to include ANO's with occupation numbers down to around 1.0×10^{-3} in order to obtain results with an accuracy of 1.0 kJ/mol compared to a full calculation including all single and double replacement states in the total virtual space.

In a molecule as large as MA a considerable amount of the total correlation energy is due to determinants with more than two excitations relative to the SCF wave function. The most important contribution from the determinants with more than two replacements is due to so called unlinked clusters. Their contribution to the correlation energy can be estimated from the renormalization equation

$$E_{\text{u.c.}} = (1 - C_0{}^2)E^{(2)}$$

where $E^{(2)}$ represents the correlation energy obtained from double excitations and C_0 is the coefficient of the SCF determinant in the CI expansion. From this formula the error in the barrier height due to the neglect of the contributions from unlinked clusters is estimated to 0.5 kJ/mol.

The magnitude of the correlation energy contribution to the hydrogen bond potential is, as was mentioned previously, closely related to the difference in OH distance between the symmetric and asymmetric structures. Thus in $H_5O_2{}^+$ the lowering of the barrier height due to correlation was found to be 10 kJ/mol[9] corresponding to a maximum OH distance of 1.37 Å (in the symmetric form) while the corresponding values for $H_3O_2{}^-$ are 5.4 kJ/mol and 1.17 Å, respectively.[8b] MA falls in between these two systems with a maximum OH distance of 1.18 Å and a correlation contribution of 6.0 kJ/mol.

In Table III calculated SCF and CI values for the quadrupolar coupling constant and the dipole moment are presented. Differences between the SCF and the CI results are small in all cases. This is in good agreement with the results of the population analysis which show only small changes between the SCF and CI first-order density matrices.

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