Monatshefte für Chemie 131, 107–115 (2000)

Monatshefte für Chemie
Chemical Monthly

Ab initio Study of Malonaldehyde Rotamers

Vassil B. Delchev[1] and **Georgi S. Nikolov**[2,*]

[1] Department of Physical and Theoretical Chemistry, University of Plovdiv, BG-4000 Plovdiv, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria

Summary. Malonaldehyde rotamer geometries were optimized using *ab initio* calculations at the HF level with STO-3G** and 6-21G** basis sets. The most stable rotamer is the ω-shaped one with cyclic structure and intramolecular hydrogen bond. The most unstable rotamer is that obtained by rotation of the ω-rotamer around the CO single bond by 180° due to the loss of the additional stabilization contributed by the intramolecular H-bond. The energy barriers separating the different rotamers vary between 13 and 233 $\text{kJ} \cdot \text{mol}^{-1}$. The structure of the transition states is non-planar with rotation angles varying between 72 and 98°.

Keywords. Malonaldehyde; Rotamers; *ab initio* Calculations; Transition states.

Introduction

β-Diketones have been studied extensively by theoretical methods because of their interesting properties connected with the keto-enol conversion. The simplest representative of these compounds stems from malonaldehyde. So far, the theoretical studies have been carried out mainly with semiempirical methods such as AM1 or MNDO [1–3] and less frequently by *ab initio* methods [4–8]. The molecular structures of malonaldehyde is known [9, 10], some of the geometry parameters being $\text{CO} = 1.23\,\text{Å}$, $\text{C-OH} = 1.35\,\text{Å}$, $\text{OH} = 0.97\,\text{Å}$, $\text{O}\cdots\text{O} = 2.55\,\text{Å}$, $\text{H}\cdots\text{O} = 1.68\,\text{Å}$, and $\angle\text{OCCC} = 0°$.

Several planar conformers are possible for malonaldehyde (Fig. 1). Rotamer **A** has been proved [1] to be the most stable one, and its extraordinary stability is related to the formation of an intramolecular H-bond and a cyclic pseudoaromatic structure. The relative stability of the other rotamers is not known. Since some of the rotamers may play an important role in keto-enol conversions, it is interesting to know their properties in detail.

Results and Discussion

In agreement with literature data [9, 10], rotamer **A** was found to be the most stable one with $E_{\text{HF}} = -262.160958$ a.u. The reason for that fact is the formation of an

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[*] Corresponding author

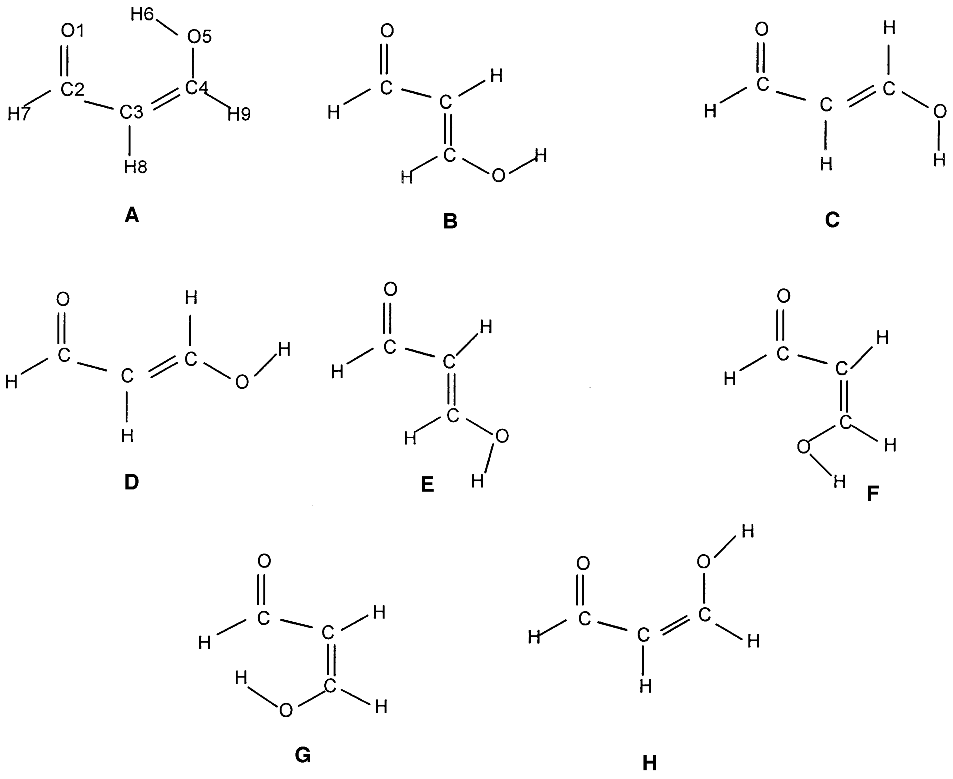

Fig. 1. Eight rotamers of malonaldehyde with a planar structure

Table 1. Ground state energies of the rotamers and energy barriers of the respective rotations

Rotamer	E_{HF}/a.u.		Energy barrier/kJ · mol^{-1}	
A	−262.160958	**A**→**H** 64.9	**A**→**C** 214.1	**A**→**G** 65.4
B	−262.147972	**B**→**G** 231.7		
C	−262.147705	**C**→**A** 179.3	**C**→**D** 28.1	
D	−262.144889	**D**→**C** 20.5		
E	−262.144298	**E**→**F** 233.4		
F	−262.143938	**F**→**G** 18.4	**F**→**F** 232.5	
G	−262.143910	**G**→**A** 20.5	**G**→**B** 221.2	**G**→**F** 18.4
H	−262.141430	**H**→**A** 13.4		

intramolecular hydrogen bond (*vide infra*). The most unstable rotamer is **H** with $E_{HF} = -262.1414303$ a.u. in which the H-bond is ruptured, but the conjugation in the OCCCO fragment is retained. This proves that the stability of **A** is due to the H-bond. The energies of all rotamers and the energy barriers of the respective rotations are given in Table 1.

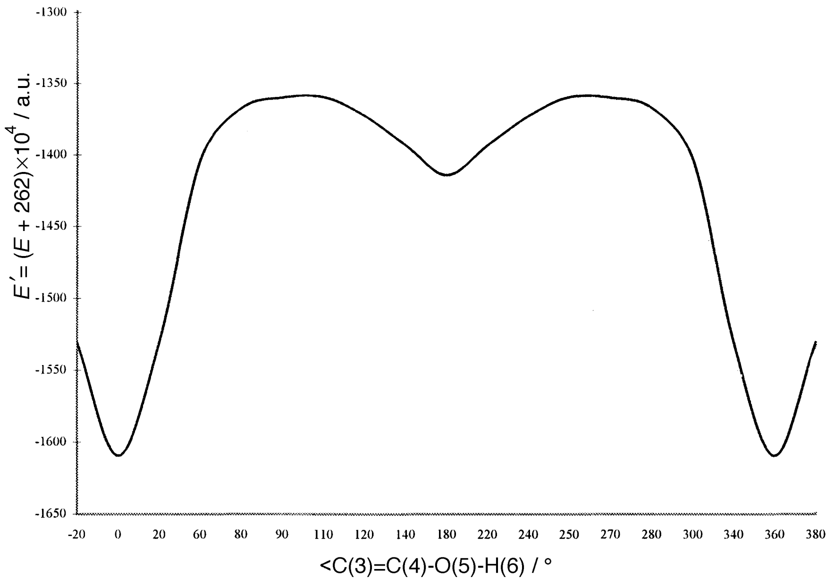

Fig. 2. $\mathbf{A}\rightleftharpoons\mathbf{H}$ conversion

$\mathbf{A}\rightleftharpoons\mathbf{H}$ *Conversion*

The transition $\mathbf{A}\rightleftharpoons\mathbf{H}$ occurs through rotation around the bond O(5)–C(4) or by varying the dihedral angle H(6)O(5)C(4)C(3) from 0° to 180°. The dependence of the energy on this dihedral angle is shown in Fig. 2.

The energy difference between the two rotamers is $\Delta E = 52\,\mathrm{kJ\cdot mol^{-1}}$, the transition state is at $E_{\max} = -262.1363$ a.u., and the dihedral angle amounts to 105.2°. Rotamer **A** has C_s symmetry and is of weak pseudoaromatic nature: H(6)-O(5) = 0.97 Å, H(6)···O(1) = 2.37 Å, C(4)-C(3) = 1.334 Å, and C(3)-C = 1.484 Å. The first C bond is close to a double bond (1.33 Å), and the second is close to a single bond (1.54 Å) (see *e.g.* Ref. [11]). It should be noted that the calculated length of the hydrogen bond (2.68 Å) is much bigger than the experimental value (1.68 Å [9, 10]); this may be the reason for the weakly expressed conjugation in the cyclic form **A**.

The energy barrier of the $\mathbf{A}\rightarrow\mathbf{H}$ transition is five times ($65\,\mathrm{kJ\cdot mol^{-1}}$) higher than that for the reverse $\mathbf{H}\rightarrow\mathbf{A}$ transition ($13\,\mathrm{kJ\cdot mol^{-1}}$). Actually, the $\mathbf{A}\rightarrow\mathbf{H}$ transition involves the rupture of the H-bond and, consequently, is not a pure rotation.

$\mathbf{A}\rightleftharpoons\mathbf{C}$ *Conversion*

The transition $\mathbf{A}\rightleftharpoons\mathbf{C}$ is characterized by a higher energy barrier than $\mathbf{A}\rightleftharpoons\mathbf{H}$. The energy variation with the C(2)C(3)C(4)C(5) dihedral angle is given in Fig. 3. The transition state occurs at 95.5° with $E_{\max} = -262.0797$ a.u., and the barrier is highly asymmetric ($214\,\mathrm{kJ\cdot mol^{-1}}$ for $\mathbf{A}\rightarrow\mathbf{C}$ and $179\,\mathrm{kJ\cdot mol^{-1}}$ for $\mathbf{C}\rightarrow\mathbf{A}$ (see Table 1).

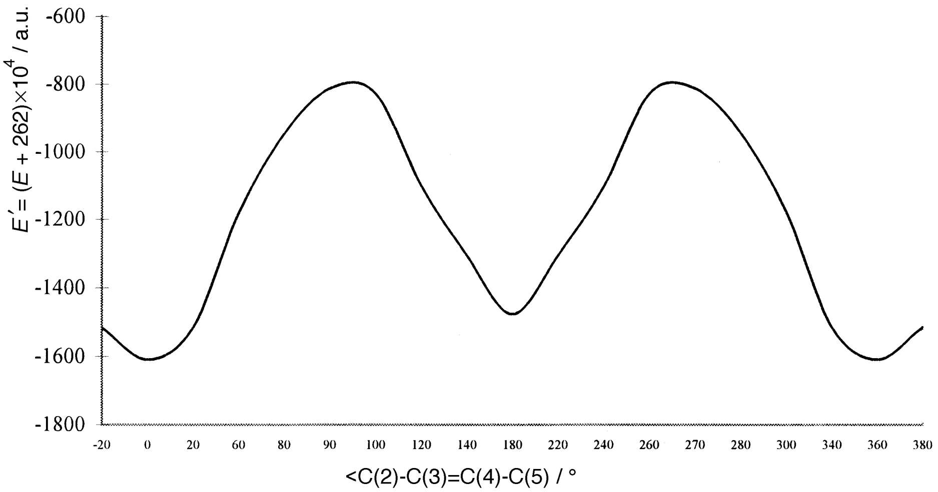

Fig. 3. $\mathbf{A} \rightleftharpoons \mathbf{C}$ conversion

Compared with the $\mathbf{A} \rightarrow \mathbf{H}$ transition, $\mathbf{A} \rightarrow \mathbf{C}$ requires much more energy which is related to the rotation around the predominantly double bond C(3)C(4) and the movement of a larger fragment. The high barrier for the reverse rotation may be explained along similar lines.

$\mathbf{C} \rightleftharpoons \mathbf{D}$ *Conversion*

Figure 4 depicts the energy variation connected with the interconversion $\mathbf{C} \rightleftharpoons \mathbf{D}$. The barrier is characterized by $E_{\max} = -262.1371$ a.u. and an angle of 85.5°. The energy barriers are comparatively low ($\mathbf{C} \rightarrow \mathbf{D}$: 28, $\mathbf{D} \rightarrow \mathbf{C}$: $20\,\mathrm{kJ \cdot mol^{-1}}$, see

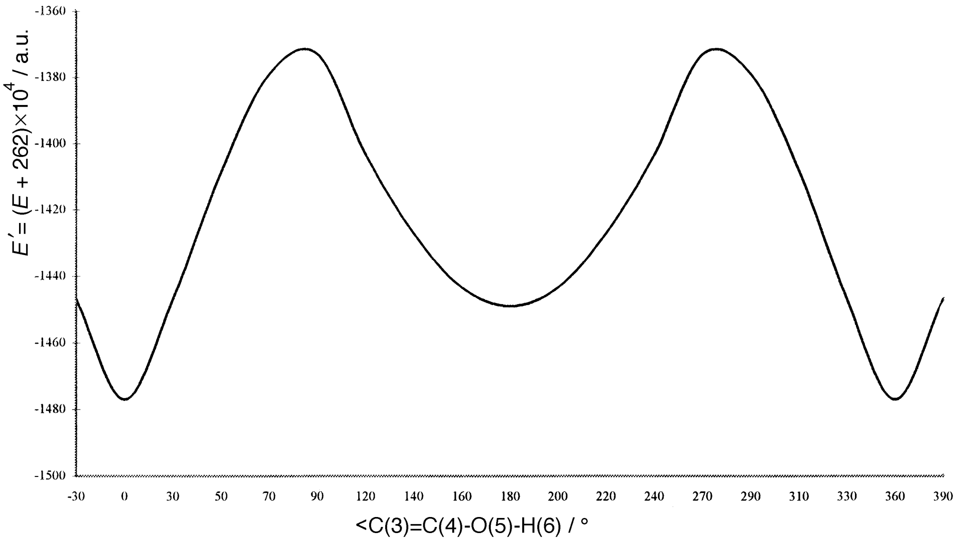

Fig. 4. $\mathbf{C} \rightleftharpoons \mathbf{D}$ conversion

Table 1). The energy difference between the two rotamers is $\Delta E = 7\,\mathrm{kJ \cdot mol^{-1}}$, rotamer **C** being more stable than **D**.

A $\rightleftharpoons$ **G** *Conversion*

The interconversion **A**$\rightleftharpoons$**G** is connected with a rotation around the C(4)C(3)C(2)O(1) angle (Fig. 5). The transition state for **G**→**A** is at $E_{\mathrm{max}} = -262.1361$ a.u. and at an angle of 81.5°. The energy difference between the two rotamers is $\Delta E = 45\,\mathrm{kJ \cdot mol^{-1}}$ in favour of **A**. This shows that rotamer **G** is unstable which may be due to the large distance between the hydroxy hydrogen and the carbonyl oxygen (O(1)···H(6) = 3.81 Å) compared to **A** (O(1)···H(6) = 2.37 Å).

It should be noted that the barrier to the **A**→**G** transition ($65\,\mathrm{kJ \cdot mol^{-1}}$) is much lower than that for the **A**→**C** transition ($214\,\mathrm{kJ \cdot mol^{-1}}$), which is to be expected taking into account that **A**→**G** involves a rotation around a predominantly single and **A**→**C** around a predominantly double CC bond.

Rotamer **G** is interesting in view of providing a probability for H(6) proton transfer to C(3), resulting in the keto form [12]. The transition state shows a negative frequency; the corresponding vibrations are shown in Fig. 6. The wave number is

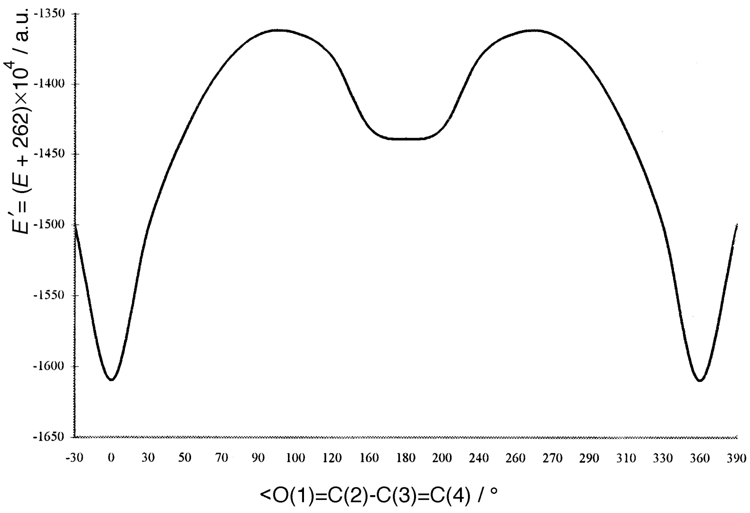

Fig. 5. **A**$\rightleftharpoons$**G** conversion

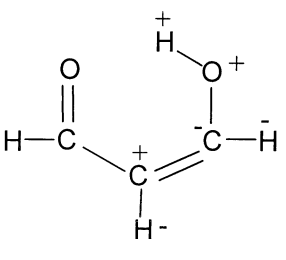

Fig. 6. Form of the imaginary vibration with a negative frequency ($-180\,\mathrm{cm^{-1}}$) converting rotamer **A** to rotamer **G**; +: movement above the CCC plane, −: movement below the CCC plane

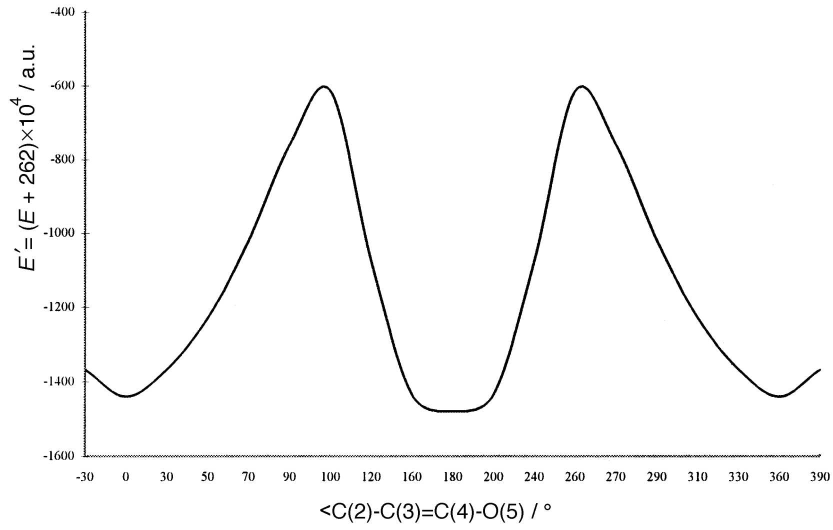

Fig. 7. **G**$\rightleftharpoons$**B** conversion

$-180\,\mathrm{cm}^{-1}$, and the IR intensity and force constant were $11.57\,\kappa\mathrm{M}\cdot\mathrm{mol}^{-1}$ and $-0.064\,\mathrm{mdyn}\cdot\text{Å}^{-1}$, respectively. The transition state has an energy of -265.39210 a.u. and C_1 symmetry.

G $\rightleftharpoons$ **B** *Conversion*

Figure 7 shows the energy variation with the C(2)C(3)C(4)O(5) dihedral angle. The energy difference between the two rotamers is $\Delta E = 11\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ in favour of rotamer **B**. Due to rotation around the partially double bond C(3)C(4), the energy barriers are high (Table 1). The transition state occurs at 98.7° with $E_{\mathrm{max}} = -262.0598$ a.u.

G $\rightleftharpoons$ **F** *Conversion*

The transition of **G** into **F** (Fig. 8) has a low energy barrier ($E_{\mathrm{max}} = -262.1369$ a.u.) which occurs at 77.1°. Due to the small ground state energy difference of **G** and **F** ($\Delta E = 0.08\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$), the energy barrier is symmetric and low ($18\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$).

F $\rightleftharpoons$ **E** *Conversion*

A barrier of $E_{\mathrm{max}} = -262.0555$ a.u. at 98.0° was found in both directions. Figure 9 shows the energy variation with the dihedral angle C(2)C(3)C(4)O(5). It can be seen from this Figure that the barrier is symmetric. The energy difference for the ground states of the two rotamers is very low ($\Delta E = 0.92\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$), but slightly greater than that for **G**$\rightleftharpoons$**F**. The rotamer **F** is more unstable than **E**, possibly because of a larger steric hindrance.

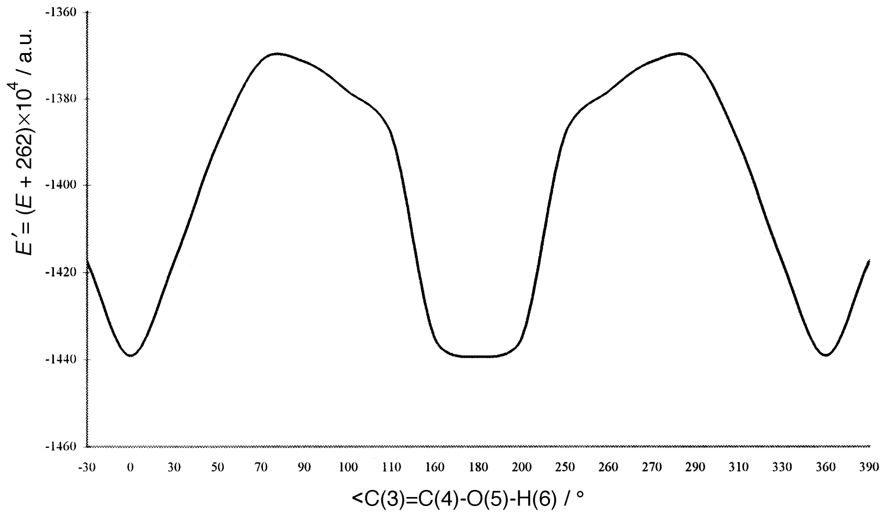

Fig. 8. $\mathbf{G \rightleftharpoons F}$ conversion

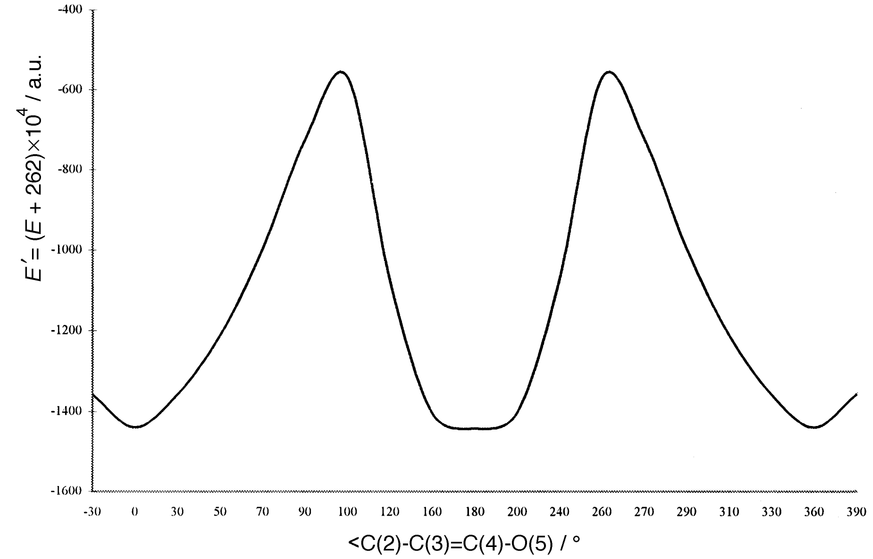

Fig. 9. $\mathbf{F \rightleftharpoons E}$ conversion

Conclusions

Although the low basis set used in the calculations and the neglection of electron correlation make the absolute values unreliable, it is believed that conclusions reached and trends observed on a comparative basis may provide useful information about the relative stability of the malonaldehyde rotamers [13]. The effect of electron correlation is usually small, typically in the order of 0.5–1.0 $\mathrm{kJ \cdot mol^{-1}}$. Electron correlation with few exceptions (mainly compounds with lone electron pairs) increases the rotation barriers [13].

The effect of the basis set is more pronounced than that of the electron correlation [13, 14]. Whereas the barrier heights slightly increased with higher basis sets, the locations of the energy barriers were found to depend strongly on the basis set used. Thus, for example, the energy barrier maximum for the **A**$\rightarrow$**G** conversion occurs at 98° with the basis 6-21G** and at 81° with STO-3G**. The quoted values of the angles at which the energy barriers occur were obtained with STO-3G**.

The most stable rotamer is **A** due to its intramolecular hydrogen bond. As noted previously [6], this bond is highly asymmetric and has a double minimum. Rotamer **H**, which involves a rotation bringing H(6) out of the position of H-bond, is the most unstable one. This is strong evidence that the stability of **A** is due to the H-bond and not to the orientation of the other atoms with respect to each other.

There is a notable trend in the energies of the malonaldehyde rotamers depending on the distance H(6)$\cdots$O(1) – the smaller the distance, the lower the energy. With increasing H(6)$\cdots$O(1) distance, the energy increases up to a certain distance and then decreases again.

For a small number of rotamers (**F**$\rightleftharpoons$**G**, **F**$\rightleftharpoons$**E**), a symmetric barrier was found, and the reason for such a shape of the barrier is due to the close values of the ground state energies of the separate rotamers **F**, **G** and **E**. The highest barrier was found for the conversion **E**$\rightarrow$**F** ($233\,\mathrm{kJ \cdot mol^{-1}}$), and the lowest barrier for **H**$\rightarrow$**A** ($13\,\mathrm{kJ \cdot mol^{-1}}$). The other rotations display a highly asymmetric barrier, the asymmetry becoming stronger with larger energy differences of the two rotamers on the two sides of the barrier.

Methods

The geometries of the eight rotamers were fully optimized by *ab initio* methods [5] at the HF level using STO-3G** and 6-21G** basis sets. The calculated geometries were used in subsequent frequency calculations to prove that the rotamers correspond to energy minima in the full ($9\times3=27$ *Cartesian* coordinates, $27–6=21$ internal coordinates) coordinate hyperspace. The absence of negative frequencies proved that the stationary points found correspond to such minima. The QST2 (using two rotamer geometries) and QST3 (using two rotamer geometries and a guess of the transition state), implemented within the GAUSSIAN 94 programme, were used to find the transition states (geometry and energy) between pairs of rotamers. Again frequency calculations were used to prove that the transition states correspond to saddle points with one negative frequency. The frequency calculations also provided the zero-point energy corrections.

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Received January 18, 1999. Accepted (revised) August 4, 1999