Tetrahedron Vol 45, No 7, pp 2083 to 2098, 1989
Printed in Great Britain

0040-4020/89 $3 00+ 00
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AN *ab-initio* STUDY OF THE ELECTRONIC STRUCTURE AND CONFORMATIONAL PREFERENCES OF MALONYL RADICAL

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(*Received in UK* 18 *January* 1989)

Abstract: In this paper we describe the results obtained in *ab-initio* UHF-MO computations, at the 3-21G level, on the radical of the malonic acid $CH(COOH)_2$. This radical can exist either as a π or a σ radical and in various conformations. We have found that in all cases the π radical is significantly more stable than the σ radical. A qualitative perturbation molecular orbital (PMO) analysis has been used to rationalize the conformational preferences in the case of the π radical. It has been found that these preferences are mainly due to the presence of various hydrogen bonds which involve an OH group and the adjacent oxygen atom.

1. Introduction

The importance of free radicals in organic synthesis has been widely recognized during the last thirty years and a large amount of experimental investigations has been carried out on these species[1]. In addition to these experimental studies, where new and powerful techniques as electron spin resonance (ESR) have been applied [2], also many theoretical approaches have been used to obtain a better understanding of the properties of these chemical species[3].

In the present paper we report the results of a theoretical study on a very interesting radical species, the malonyl radical $\dot{C}H(COOH)_2$. This radical and the radicals from malonic acid and its derivatives (malonic esters, emiesters and malonamide) have been extensively investigated from an experimental point of view and their importance in chemical synthesis and physical organic chemistry has been demonstrated[4-10]. It is well known for example the involvement of malonyl radicals in the Ce(IV)-catalyzed oxidation of malonic acid by acidic bromate (the Belousov-Zhabotinskii oscillating reaction)[4]). The importance of this radical has also been demonstrated in the oxidation of malonic acid promoted by manganese(III) sulphate[5] and in some interesting reactions of malonic acid and its derivatives with olefins which are promoted either by Mn(III)[6] or by peroxides[7]. In recent investigations on the synthetic utility of malonyl radicals[10] it has been discovered that these radicals, generated by Mn(III), can be efficiently trapped by electron-rich aromatic hydrocarbons either in inter-molecular or intra-molecular processes. This reaction, which can be schematically represented, in the inter-molecular case, as:

$$\mathrm{ArH} + \mathrm{R'\text{-}CH(COOR)_2} + 2\mathrm{Mn(III)} \text{ ----> }$$
$$\text{ ----> } \mathrm{Ar\text{-}CR'(COOR)_2} + 2\ \mathrm{Mn(II)} + 2\mathrm{H^+}$$

is of particular interest because the result of the attack of malonyl radicals on aromatic compounds could in principle lead to intermediates for antiinflammatory products.

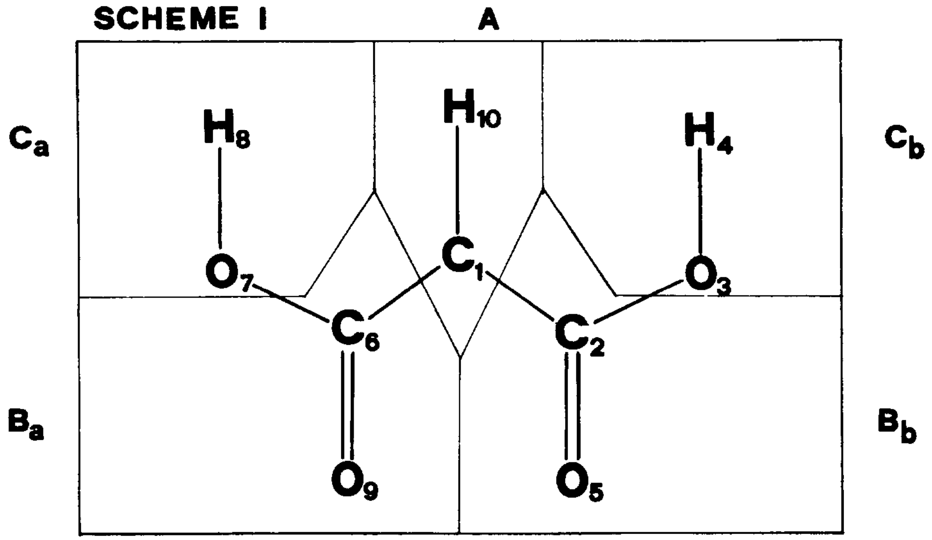
Because of the increasing interest for these chemical species in synthetic studies, it seemed wortwhile to perform a detailed ab-initio study of their properties. In this study we have used an unrestricted Hartree-Fock (UHF)[11] treatment and an extended 3-21G basis set [12]. We have discussed the electronic nature and the preferred structures of these radicals which can exist in various conformations. A simple PMO model[13], where we have considered only the most relevant electronic interactions occurring in these systems, has been used to rationalize the main results of *ab-initio* computations.

2. Computational procedure and results

Ab-initio UHF-MO computations have been carried out at the 3-21G level on various conformations of the radical of the malonic acid $\dot{\mathrm{C}}\mathrm{H(COOH)_2}$, which is shown in Scheme I.

All the computations have been performed with the Gaussian-82 series of programs [14] and all the various molecular geometries that we have investigated have been fully optimized using the gradient method [15].

SCHEME I



For this radical we have considered the various conformations shown in Figures 1, 2 and 3. All these conformations are planar and can be conveniently classified as belonging to one of the three following types:

1) a U structure where the two carbonyl groups are anti with respect to the C1-H10 bond (see Figure 1);

2) a S structure where one carbonyl group is syn and the other anti with respect to the C1-H10 bond (see Figure 2);

3) a W structure where both carbonyl groups are syn with respect to the C1-H10 bond (see Figure 3).

Furthermore within each type of structure we can have various conformations which differ only in the orientation of the two OH bonds. Both the O3-H4 and O7-H8 bonds can be in fact cis or trans with respect to the C1-C2 and C1-C6 bonds respectively. For this reason we have associated two indices with the main symbols U, S and W to denote a Cis (c) or a Trans (t) orientation of the two OH groups.

The molecular species that we have studied can exist either as a π or a σ radical, depending on the symmetry of the singly occupied molecular orbital (SOMO) which can be π or σ. In order to determine the real nature, π or σ, of this radical, we have performed the SCF computations on both types of radical for the two conformations U(cc) and U(tt). In both cases we have found that the π radical is significantly more stable than the corresponding σ radical (13.54 and 37.19 Kcal/mol for U(cc) and U(tt) respectively), as one can expect from the fact that in the σ radical the carbon C1 becomes very similar to a carbanionic center with two electrons in the 2p(π) orbital. Consequently all the remaining structures reported in Figures 1-3 have been investigated only as a π radical.

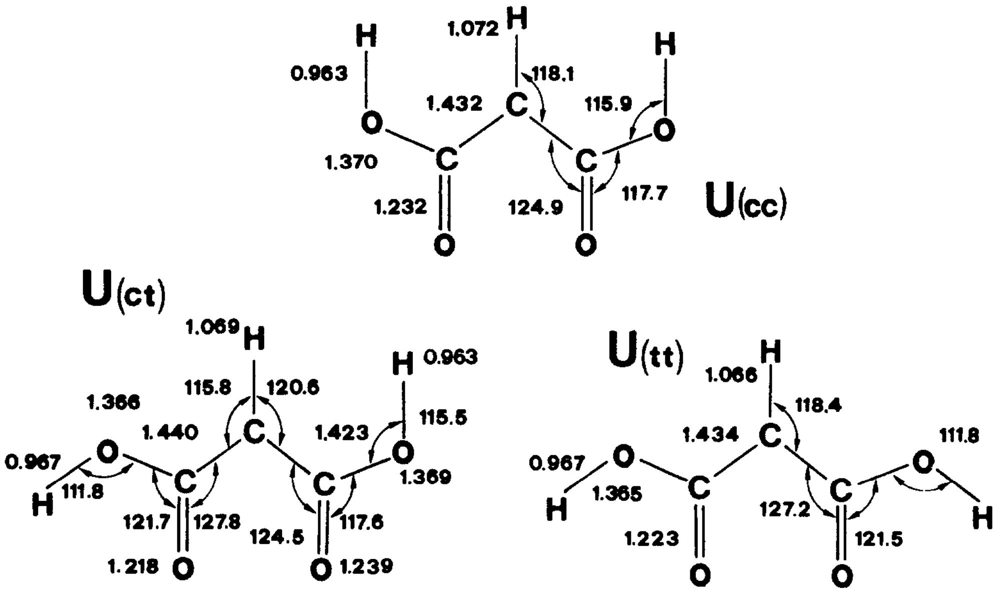


Figure 1. A schematic representation of the three U conformers together with the values of the geometrical parameters computed at the 3-21G level (Bond lengths are in angstroms and angles in degrees).

The results of the SCF computations are collected in Table I and II and Figures 1-3. In Table I we have reported the absolute and relative energies

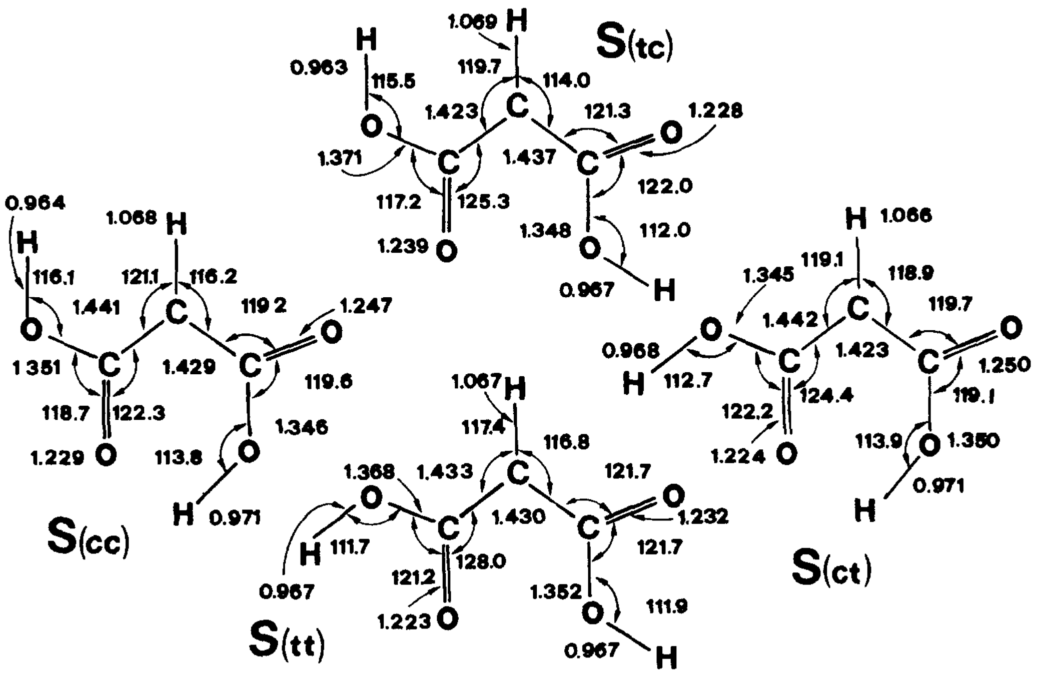


Figure 2. A schematic representation of the four S conformers together with the values of the geometrical parameters computed at the 3-21G level (Bond lengths are in angstroms and angles in degrees).

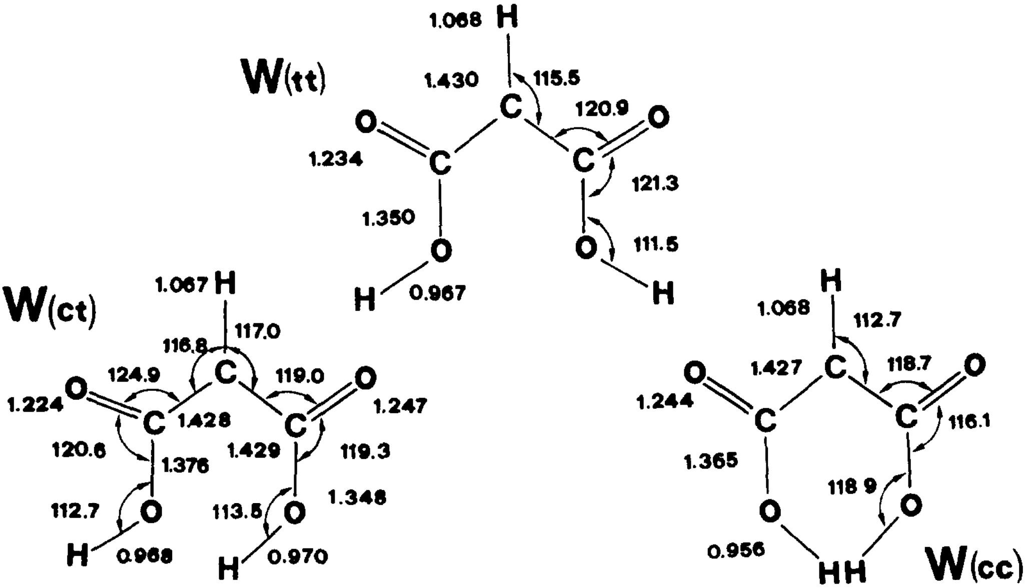


Figure 3. A schematic representation of the three W conformers together with the values of the geometrical parameters computed at the 3-21G level (Bond lengths are in angstroms and angles in degrees).

for the various conformations of the π radical, and in Figures 1-3 we have collected the corresponding optimum values of the various geometrical

TABLE I. Total energies (E) and relative energies (δE) computed with the UHF MO method and the 3-21G basis set for various conformations of the π radical.

	E(a)	δE(b,c)	
U(cc)	-412.44726	19.60	(17.24)
U(ct)	-412.46232	10.15	(7.79)
U(tt)	-412.47474	2.36	(0.00)
S(tc)	-412.46076	11.13	(11.13)
S(cc)	-412.46670	7.40	(7.40)
S(ct)	-412.47850	0.00	(0.00)
S(tt)	-412.47343	3.18	(3.18)
W(tt)	-412.47078	4.84	(4.41)
W(ct)	-412.47782	0.43	(0.00)
W(cc)	-412.43832	25.21	(24.79)

(a) Values in atomic units.
(b) Values in Kcal/mol.
(c) The relative energies δE are computed with respect to the most stable conformer S(ct). The values in parenthesis are computed with respect to the most stable conformer of each main structure.

TABLE II. Stabilizing effects(a) associated with the formation of an intra-fragment and an inter-fragment hydrogen bond in the π radical.

Intra-fragment H-bond	
U(ct) - U(cc)	-9.45
U(tt) - U(ct)	-7.79
S(tc) - U(cc)	-8.47
U(tt) - S(tc)	-8.77
S(ct) - S(cc)	-7.40
S(tt) - S(tc)	-7.95
S(tt) - U(ct)	-6.97
W(tt) - S(tc)	-6.29
W(ct) - S(cc)	-6.97
Inter-fragment H-bond	
S(cc) - U(cc)	-12.20
S(ct) - S(tc)	-11.13
S(ct) - U(ct)	-10.15
W(ct) - S(tc)	-10.70
W(ct) - U(ct)	-9.72

(a) Values in Kcal/mol.

parameters.

To analyze the relative stability of the various conformers, we have coupled the results of the *ab-initio* SCF computations to a qualitative Perturbation Molecular Orbital (PMO) approach [13a-d]. Following this method the molecular system under examination (composite system) is decomposed into a set of interacting fragments. The energy associated with the interaction between the various fragments to obtain the composite system is estimated on the basis of perturbation theory. To evaluate this energy one must consider all the relevant interactions between the orbitals belonging to different fragments following the rule that, when two orbitals combine, they give a lower energy bonding or in-phase combination and a higher energy antibonding or out-of-phase combination. The in-phase combination is dominated by the lower energy fragment orbital, while the most important component of the out-of-phase combination is the higher energy fragment orbital. Furthermore PMO theory tells us that the energy effect associated with an interaction between two doubly occupied orbitals ϕ_i and ϕ_j is destabilizing (the interaction is repulsive), while an interaction which involves a doubly occupied orbital ϕ_i and an empty orbital ϕ_j corresponds to a stabilization. These two energy effects can be evaluated respectively on the basis of the following two expressions:

$$
\begin{aligned}
\delta E^4(ij) &= 4S_{ij}(E_0 \cdot S_{ij}-H_{ij})/(1-S_{ij}^2)\\
&= 4S_{ij}^2(E_0-K)/(1-S_{ij}^2) \qquad (1)
\end{aligned}
$$

$$
\begin{aligned}
\delta E^2(ij) &= 2(H_{ij}-S_{ij}Ei)^2/(E_i-E_j)\\
&= 2Sij^2(K-Ei)^2/(E_i-E_j) \qquad (2)
\end{aligned}
$$

where E_i and E_j represent the energies of the two interacting orbitals ϕ_i and ϕ_j, S_{ij} represents their overlap integral, H_{ij} the corresponding matrix element and E_0 is the mean of the energies E_i and E_j. Expression (1) is obtained applying the variational method to the case of a four-electron/two-orbital interaction problem [16], while expression (2) is a well known result of perturbation theory [17]. From expression (1) we can see that, assuming $H_{ij}=K\cdot S_{ij}$, the destabilisation is proportional to the square of the overlap S_{ij} and the mean energy of the interacting orbitals, while expression (2) shows that the magnitude of the stabilization is approximately proportional to the square of S_{ij} and inversely proportional to the energy separation between the interacting orbitals.

3. Discussion: Conformational preference in the π radicals

In this section we shall try to explain the preferential stability observed for the various conformers of the π radical in terms of a qualitative PMO treatment. The fragmentation chosen for this analysis is shown in Scheme I. Following this scheme the composite system has been devided in five fragments: the two C==O fragments, the two OH fragments and the central C-H fragment. The π orbitals of the various fragments are shown in Figure 4. These orbitals are: for a C==O fragment a doubly occupied orbital πco and an empty orbital πco*, for an OH fragment a lone-pair n(π)

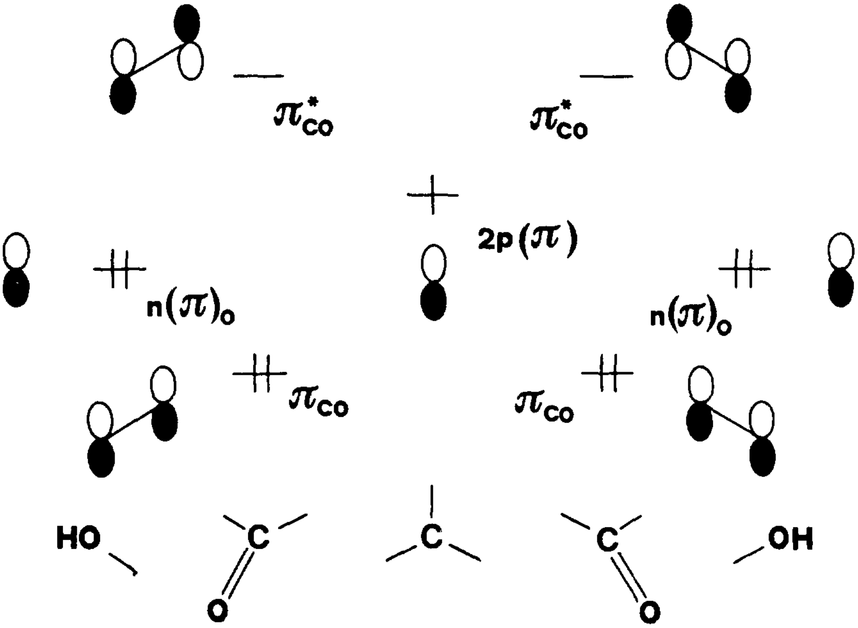


Figure 4. π fragment orbitals of the malonyl radical system.

and for the C-H fragment a singly occupied orbital 2p(π) on the carbon atom C1. The σ fragment orbitals which are relevant for our analysis are shown in Figures 5 and 6. They are: for a C==O fragment an oxygen lone-pair n(p), for an OH fragment an oxygen lone-pair n(sp), a doubly occupied bonding orbital σ_{OH} and an empty orbital σ_{OH}^* and for the central CH fragment a doubly occupied bonding orbital σ_{CH} and an empty orbital σ_{CH}^*.

The interactions of interest between the component fragments are:

i) σ-repulsive interactions (which can be associated with steric repulsions) between the σ-type lone-pairs of the oxygen atoms of the two carboxy groups COOH (n(p) and n(sp) lone-pairs). These interactions are illustrated in detail in Figure 5a for three different conformers.

ii) σ-interactions involving the orbitals associated with the two O-H bonds or the orbitals of one O-H bond and those of the central C-H bond. These interactions, which are shown in Figure 5b, can be repulsive, when two bonding doubly occupied orbitals are involved (σ_{OH}-σ_{OH} or σ_{OH}-σ_{CH} interaction), or attractive when they are associated with a bonding and an antibonding orbital (σ_{CH}-σ_{OH}^* or σ_{OH}-σ_{CH}^* interactions).

iii) σ-interactions involving the OH bond of an OH fragment and the oxygen atom of the other OH fragment or that of a C==O fragment; these interactions are schematically represented in Figure 6.

iv) Interactions involving the π orbitals of the two COOH carboxy groups and the singly occupied 2p(π) orbital on C1 (see Figure 4).

The repulsive interactions i) are almost negligible because of the large distance between the interacting oxygen atoms of the two carboxy groups: this distance is in all cases larger than 2.6 Å so that the corresponding overlap between the interacting oxygen lone-pairs is very small.

A similar situation occurs for interactions ii). In this case the hydrogen atoms of the central C-H bond and the O-H bonds in the U and S structures are too far away for being responsible of a significant interaction between the orbitals associated with these bonds. The distance H8-H10 is for example 2.249Å and 2.266Å in U(cc) and S(tc) respectively.

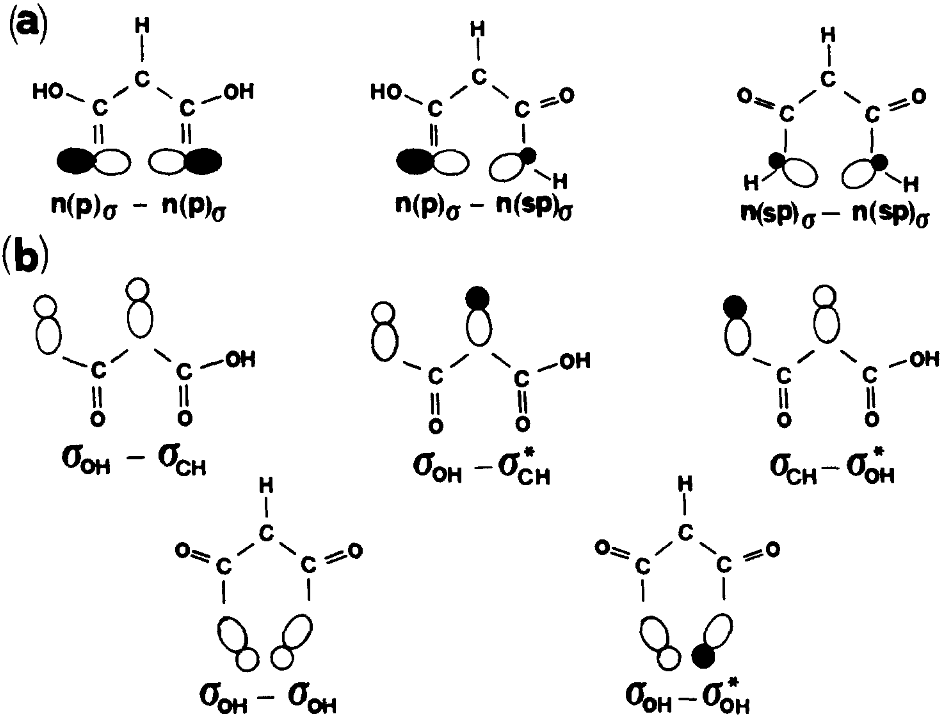


Figure 5. σ interactions involving the oxygen lone-pairs (a) and the orbitals associated with the OH and CH bonds (b)

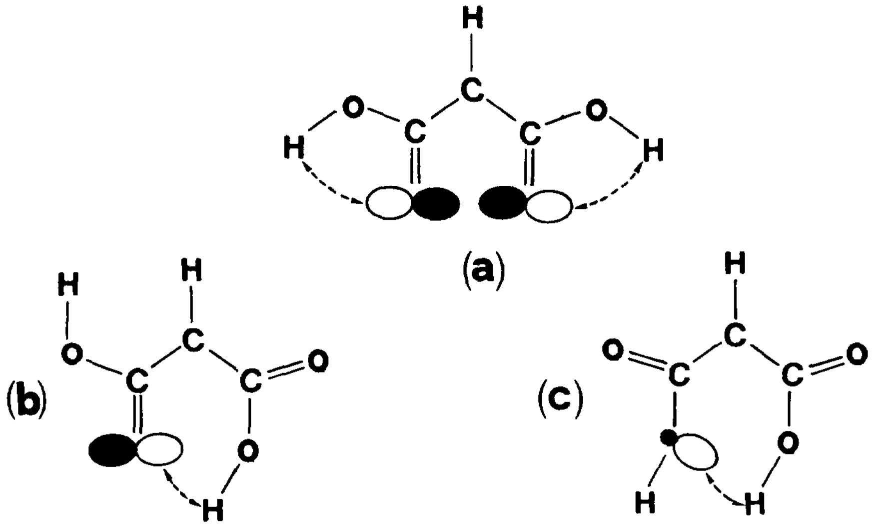


Figure 6. Schematic representation of the intra-fragment hydrogen bond (a) and of the two different types of inter-fragment hydrogen bonds (b and c)

Similar considerations apply to the hydrogen atoms of the two O-H bonds in the W structures, except W(cc): the H4-H8 distance, which is 4.514Å in W(tt) and 2.626Å in W(ct), becomes much shorter (1.794Å) in the W(cc) conformer, suggesting the possibility that this type of interaction plays an important role in this case.

Interactions iii),in principle, can be significantly affected by the orientation of the OH groups, which changes on passing from one conformer to another. The rotation of the OH groups around the C2-O3 or the C6-O7 bond is responsible for the appearance or disappearance of one or two hydrogen bonds involving an OH group and the adjacent oxygen atom. More precisely three different types of hydrogen bonds, schematically represented in Figure 6, can be found in these molecular systems:

a) An intra-fragment hydrogen bond involving the OH group and the C==O group of the same carboxy fragment (see Figure 6a).

b) An inter-fragment hydrogen bond which involves the OH group of one carboxy fragment and the carbonyl oxygen atom of the other COOH fragment (see Figure 6b). The orbitals involved in case a) and b) are the O-H bonding and anti-bonding orbitals and the n(p) σ oxygen lone-pair.

c) An inter-fragment hydrogen bond which arises from the interaction between the OH groups of two different carboxy fragments; this type of bond can be found only in the W(ct) structure and involves the O-H bonding and anti-bonding orbitals and the n(sp) σ oxygen lone-pair (see Figure 6c).

Finally we can examine the π-type interactions (iv). The analysis of the values of the optimized geometrical parameters shows that the relative positions of the carbon and oxygen atoms do not change very much along each main series, leaving the overlap between the fragment orbitals represented in Figure 4 almost unchanged. Consequently also the energy effects associated with these π interactions should not change very much, suggesting that the π energy remains of the same order of magnitude for each main structure U, S or W. On the other hand the rotations around the C1-C2 and the C1-C6 bonds which interconnect one main structure to another, change significantly the relative positions of the carbon and oxygen atoms and could cause a significant variation in π energy. To elucidate this last point and to roughly estimate the change in π energy, we can compare various conformers where it is plausible to assume that only the π interactions vary significantly. In the U(tt) and S(tt) conformers, for example, we have the same number and types of hydrogen bonds and, as previously pointed out, the repulsions involving the σ-type oxygen lone-pairs must be very small. The total energy difference between U(tt) and S(tt) is only 0.82 Kcal/mol, with U(tt) more stable than S(tt), suggesting that the energy effect associated with the π interactions remains of the same order of magnitude also when we compare two conformers belonging to different structures. The same evidence is provided when we compare other conformers which differ in the arrangement of the carbon and oxygen atoms but with the same relevant σ interactions. The energy values reported in Table I, for example, show that the difference between S(tt) and W(tt), both characterized by two intra-fragment hydrogen bonds, is still quite small, about 1.66 Kcal/mol. In a similar manner the energy difference between U(ct) and S(tc), which both have only one intra-fragment hydrogen bond, is 0.98 Kcal/mol. A further example is given by the two isomers S(ct) and W(ct), both characterized by the presence of one intra-fragment and one inter-fragment hydrogen bond: in this case the energy difference is almost negligible, about 0.43 Kcal/mol. Furthermore, in all cases, when we compare two conformers with the same σ interactions , the U conformers are more stable than the S conformers and these are more stable than the W conformers.

All these results suggest that:

v) The π interactions do not seem to be a key factor in determining the preferential stability of the various conformers: they remain in fact of the same order of magnitude either along the same series or passing from one series to another.

vi) Even if the energy effects associated with the π interactions are quite small, these interactions seem to be sligthly more stabilizing in the U conformers than in the S conformers and again sligthly more stabilizing in the S conformers than in the W conformers.

vii) Because the σ and π interactions i), ii) and iv) discussed so far are almost constant or negligible, it follows that the relevant interactions which control the preferential stability of the various conformers must be those associated with the hydrogen bonds (interactions iii)).

viii) We can use the energy difference between the various isomers to roughly estimate the stabilizing effect associated with the formation of each hydrogen bond.

An analysis of the total energy values collected in Table I has shown that, in all cases, the structures with one hydrogen bond are more stable than the structures where no hydrogen bond can be found and that the structures with two hydrogen bonds are always more stable than the structures with only one hydrogen bond. A further indication provided by this analysis is that an inter-fragment hydrogen bond seems to be more stabilizing than an intra-fragment one. This point is supported by various evidence: structure S(cc), where we have only one inter-fragment hydrogen bond, is more stable than structure U(ct) where there is only one intra-fragment hydrogen bond. In a similar manner the two structures S(ct) and W(ct), both characterized by one intra-fragment and one inter-fragment hydrogen bond, are more stable than structures S(tt) and W(tt), where we have two hydrogen bonds of intra-fragment type.

To obtain a rough idea of the stabilizing effect associated with the formation of one hydrogen bond, we have collected in Table II the energy differences between various conformers. The values reported in part a of this Table refer to structures which differ only in one intra-fragment hydrogen bond so that they provide a rough estimate of the energy effect associated with this type of bond. The values reported in part b of the same Table refer to structures which differ in one inter-fragment hydrogen bond and they represent a measure of the effect of this second type of bond. While the values reported in part a are all between 9.45 and 6.29 Kcal/mol, those reported in part b are sligthly larger (between 9.72 and 12.22 Kcal/mol) showing the larger stabilizing effect of an inter-fragment hydrogen bond with respect to an intra-fragment one. These values are in good agreement with the experimental values which show, for example, that, in carboxylic acids, the hydrogen bonds connecting one molecule with another are characterized by energy values in the range of 6 to 8 Kcal/mol [18].

It is also of interest to analyze the geometrical effects associated with the formation of hydrogen bonds in the malonyl radical systems. The comparison between the U(ct) and the U(cc) structure shows the geometrical effect of an intra-fragment hydrogen bond. While the geometry of the COOH fragment not involved in the formation of the hydrogen bond does not change very much, that of the other COOH fragment varies significantly: the O7-C6-O9 angle increases (from 117.7° to 121.7°) on going from U(cc) to U(ct) and the H8-O7-C6 angle decreases in the same direction (from 115.9° to 111.8°). In a similar manner, when we compare S(tc) to S(tt), we observe an increase in the O7-C6-O9 angle (117.2° and 121.2° in S(tc) and S(tt) respectively) and a corresponding decrease in the H8-O7-C6 angle (from 115.5° to 111.7°).

On the other hand, the major effect of the formation of an inter-fragment hydrogen bond corresponds to a shortening of the distance between the two oxygen atoms involved in this type of bond. The O9-O3 distance, for example, is 2.734Å in S(tc) where no inter-fragment hydrogen bond can be found and becomes 2.660Å and 2.676Å in S(cc) and S(ct) respectively in agreement with the formation of an hydrogen bond involving the O3,H4 and O9 atoms. This distance increases again in the S(tt) structure where the inter-fragment hydrogen bond disappears. In a similar way the O3-O7 distance changes from 2.604 to 2.688Å on going from W(ct) to W(tt).

Finally the W(cc) conformer, where no hydrogen bond can be found, is the only example where the interaction between the orbitals associated with the two OH bonds can play an important role. The two hydrogen atoms are in fact close enough (1.790Å) to determine a large repulsion between the two doubly occupied bond orbitals σ_{OH}. In agreement with this observation W(cc) is much higher in energy (7.55 Kcal/mol) than U(cc), the only other conformer without hydrogen bonds. This electron repulsion is also responsible for a significant increase of the O3-O7 distance which changes from 2.688Å and 2.604Å in W(tt) and W(ct) respectively to 3.227 Å in W(cc).

4. Conclusions

In this paper we have discussed the conformational behaviour observed in the case of the π radical of the malonic acid: $\dot{C}H(COOH)_2$. We have found that the repulsions associated with the interactions involving the σ lone-pairs of the oxygen atoms or the O-H and C-H bonds are not responsible for the various conformational preferences except in the case of the W(cc) structure where the repulsion between the two O-H bonds makes this conformer the least stable in the series. Also the π interactions are not relevant in determining these conformational preferences and their energy effect remains approximately the same in all structures.

The conformational preferences shown by the malonyl radical are mainly due to the existence of hydrogen bonds, which have a stabilizing effect: in fact the most stable conformers are those with the largest number of hydrogen bonds. We have distinguished three types of hydrogen bond: an intra-fragment and two different inter-fragment hydrogen bonds. In all cases we have found that the inter-fragment bonds are more stabilizing than the intra-fragment ones, the average stabilizing effect being in the first case about 7.8 Kcal/mol and in the second case about 10.8 kcal/mol.

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