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Hydrogen-Bonding Interactions in 2-Thiophen-3-ylmalonic Acid

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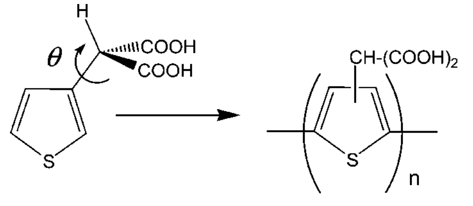
Formation of intra- and intermolecular hydrogen bonds in 2-thiophen-3-ylmalonic acid, the precursor of a polythiophene derivative bearing two carboxylic acid groups in the side chain, have been examined by Fourier transform infrared (FTIR) spectroscopy and ab initio quantum mechanical calculations. Interactions found in the FTIR spectra recorded for the melted and solid states are in good agreement with results provided by MP2/6-31+G(d,p) calculations on monomers and dimers, respectively. Specifically, inter- and intramolecular hydrogen bonds were detected in the solid and melted states, respectively. Calculations on dimers stabilized by intermolecular hydrogen bonds exclusively and by both intra- and intermolecular interactions indicated that the former structures are significantly more stable than the latter ones, which is fully consistent with experimental observations. On the other hand, intramolecular interactions in isolated monomers are favored in the melted state, which is dominated by a thermally driven entropic process.

SCHEME 1



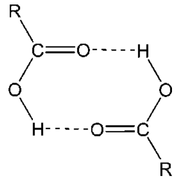
T3MA poly(2-thiophen-3-yl-malonic acid)

Introduction

Polythiophene, an important class of π-conducting polymers with interesting electronic and optical properties,[1] is an insoluble and infusible material due to the rigidity of the backbone and strong intermolecular interactions. Soluble forms of polythiophene can be prepared by introduction of substituents. Specifically, long alkyl side chains increase solubility in organic solvents,[2] whereas hydrophilic substituents may produce water-soluble polythiophenes.[3]

In recent years we have reported a number of studies devoted to preparing and/or modeling the structural and electronic properties of polythiophene derivatives bearing hydrophilic substituents.[4] Within this context, at present we are interested in poly(2-thiophen-3-ylmalonic acid), a polythiophene derivative bearing a substituent with two acid groups per structural unit (Scheme 1). The properties of this polymer, which is obtained through chemical polymerization of 2-thiophen-3-ylmalonic acid (T3MA),[5] are expected to depend significantly on the hydrogen-bonding interactions formed by the carboxylic acid side groups. Furthermore, hydrogen bonds are also responsible for the interactions recently found between the ester derivative of this polymer and specific nucleotide sequences of plasmid DNA.[5] The ability to form specific interactions makes this material particularly interesting. However, there are many hydrogen-bonding possibilities in poly(2-thiophen-3-ylmalonic acid), and the development of a model able to rationalize the electronic and structural properties of this polymer is therefore a complex task. This limitation has motivated the present study, in which we report a combined experimental and theoretical study of hydrogen bonding in T3MA.

SCHEME 2: Carboxylic Acid Dimers



The literature available on the structural and spectral properties of carboxylic acids is significant. It is well-known that formic acid and acetic acid exist as a ring structure (R = H and CH_3, respectively, in Scheme 2) with the two monomer units linked by hydrogen bonds, which add stability.[6] The dimerization energies of formic acid and acetic acid determined experimentally were 14.8 and 14.6 kcal/mol,[6a] respectively; a number of theoretical studies to provide a complete understanding of these systems were also reported.[7] On the other hand, the energy of dimerization determined for benzoic acid, which also adopts a ring structure (R = C_6H_5 in Scheme 2), was reported to be 16.2 kcal/mol,[8] indicating that introduction of the benzyl group produces a stabilizing effect in the interaction.

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On the other hand, aliphatic dicarboxylic acids, HOOC-(CH$_2$)$_n$-COOH (with $n = 0$ for oxalic acid, $n = 1$ for malonic acid, $n = 2$ for succinic acid, $n = 3$ for glutaric acid, etc.), with an odd member of methylene units show a peculiar arrangement with the carboxyl groups rotated in opposite directions and located in different planes.[9] This leads to an efficient molecular packing stabilized by intermolecular hydrogen bonds. In the specific case of malonic acid, different crystalline varieties were found depending on the temperature.[10] The room-temperature phase is a centrosymmetric triclinic crystal with two molecules per unit cell.[10c] Molecules are arranged in zigzag chains, with the hydrogen-bonded carboxyl groups forming two crystallographically and spectroscopically different rings that are nearly orthogonal. This generates chains of molecules connected by hydrogen bonds.

In T3MA, the bulky and electronically rich thiophene group is expected to influence the whole molecular arrangement. Specifically, the disposition of the carboxylic acid groups, which can be arranged to form intra- or/and intermolecular hydrogen bonds, may be altered significantly with respect to those observed in conventional mono- and dicarboxylic acids. In this work we concentrate on the inter- and intramolecular nature of hydrogen bonds formed by T3MA. The paper is organized as follows. The next section reports the experimental and theoretical methods used to develop the study. In the Results and Discussion section we examine the tendency of T3MA, which is insoluble in organic solvents, to form intra- and intermolecular hydrogen bonds in both the solid and the melted states using Fourier transform infrared (FTIR) spectroscopy. After this, we evaluate the formation of intra- or/and intermolecular hydrogen bonds in T3MA monomers and dimers using quantum mechanical calculations, and the results are compared with previous calculations on conventional carboxylic acids. Finally, the last section summarizes the conclusions of the work.

Methods

FTIR Spectroscopy. FTIR spectra were recorded on a FTIR 4100 Jasco spectrophotometer. Samples were placed in an attenuated total reflection (ATR) accessory (top plate) with a diamond crystal (Specac model MKII golden gate heated single reflection diamond ATR). The top plate was used with a computer controlled high-stability temperature controller (model West 6100+), which allows us to increase the temperature from 25 to 200 °C.

Quantum Mechanical Calculations. All calculations were carried out with the Gaussian03 computer program.[11] Molecular geometries of systems formed by one or two molecules of T3MA were derived from complete geometry optimizations by the MP2[12] method combined with the 6-31+G(d,p) basis set;[13] that is, the geometries of the monomers were not frozen during the geometry optimization of the dimers. No symmetry restriction was imposed during the optimizations of the complexes. In selected cases, which will be specified in the Results and Discussion section, geometries obtained at the MP2/6-31+G(d,p) level were reoptimized by use of the B3LYP[14] method combined with the same basis set. The basis set superposition error (BSSE)[15] was corrected by the counterpoise (CP) method.[16]

Results and Discussion

Hydrogen Bonds in Solid and Melted States. T3MA is soluble in polar solvents able to form hydrogen bonds but completely insoluble in nonpolar organic solvents like chloroform, carbon tetrachloride, benzene, etc. Accordingly, the tendency of this compound to form intra- and intermolecular hydrogen bonds was studied in the solid and melted states. Figure 1 shows the FTIR spectrum of T3MA recorded at room temperature (25 °C), in which several absorption bands related to hydroxyl (OH, 3095 cm^{-1}) and carbonyl groups (C=O, 1650−1750 cm^{-1}) are clearly identified. Regarding to the C=O stretching vibrations, the absorptions detected at 1751 and 1657 cm^{-1} correspond to the free state and the hydrogen-bonding association, respectively. Thus, the involvement of such group in hydrogen bonds is denoted by the shift to lower frequencies of the unassociated stretching vibration, and the magnitude of the shift grows with the strength of the interaction. In this case, the shift of 94 cm^{-1} was attributed to intermolecular hydrogen bonds, which are expected to be particularly strong in T3MA.

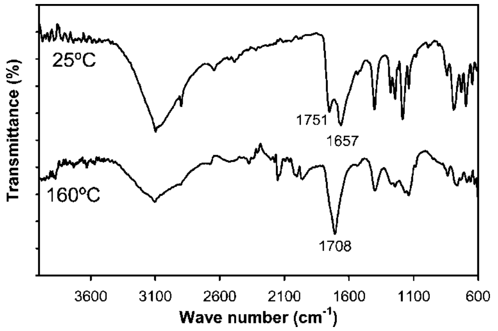
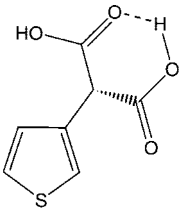


Figure 1. FTIR-ATR spectra recorded for 2-thiophen-3-ylmalonic acid (T3MA) at 25 °C (solid state) and 160 °C (melted state).

SCHEME 3



In order to check this hypothesis, intermolecular interactions were broken by heating the sample at 160 °C; the spectrum recorded at this temperature is included in Figure 1. As expected, the vibration at 1657 cm^{-1} is not detected in the melted sample, while a new band appears at 1708 cm^{-1}. This strong absorption, which is shifted by 43 cm^{-1} with respect to the free state, corresponds to intramolecular hydrogen bonds. It is worth noting that a similar red shift (60 cm^{-1}) was found in the FTIR spectra of monomeric malonic acid isolated in a solid argon matrix, allowing us to identify molecular conformations stabilized by an intramolecular hydrogen bond.[17] Thus, in spite of the thermal motion associated with this high temperature, which affects both the T3MA molecules as a whole and internal degrees of freedom as the dihedral angle θ (Scheme 1), intramolecular interactions involving the two carboxylic acids are formed because of the intrinsic thermodynamic stability of the resulting six-membered rings (Scheme 3). Furthermore, the shoulder detected at 1751 cm^{-1} is evidence for the presence of free carbonyl groups in the melted state.

Figure 2 shows the FTIR spectra recorded for T3MA at different temperatures between 25 and 160 °C. This provides a kinetic view of the formation of intramolecular interactions, which is evidenced by the apparition of the absorption band at 1708 cm^{-1} (shown by arrows), and the consequent disappearance of intermolecular interactions at 1657 cm^{-1} when the temperature grows.

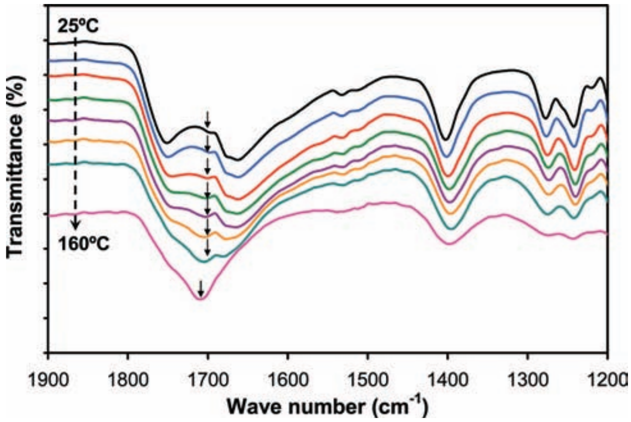


Figure 2. FTIR-ATR spectra recorded for 2-thiophen-3-ylmalonic acid (T3MA) at different temperatures between 25 °C (solid state) and 160 °C (melted state).

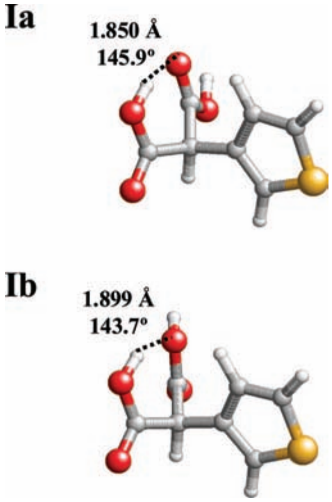


Figure 3. Relevant minimum energy conformations found for T3MA at the MP2/6-31+G(d,p) level. In the lowest energy conformation, the intramolecular hydrogen bond involves one carboxyl and one hydroxyl group (**Ia**), while the conformation with two hydroxyl groups forming a hydrogen bond (**Ib**) is destabilized by 3.1 kcal/mol. Hydrogen-bonding parameters, $d_{\mathrm{O}\cdots\mathrm{H}}$ (in angstroms) and $\angle\mathrm{O{-}H\cdots O}$ (in degrees), are indicated.

Intramolecular Hydrogen Bonds: Calculations on a Single Molecule. Figure 3 shows the two minimum-energy conformations calculated for a single molecule of T3MA. As can be seen, the two structures differ in the architecture of the six-membered hydrogen-bonded ring formed by the two carboxylic acid groups. Thus, in the lowest energy conformation, hereafter denoted **Ia**, the intramolecular hydrogen bond involves the carbonyl of one carboxylic acid and the hydroxyl of the adjacent carboxylic acid group, that is, $\mathrm{C{=}O\cdots H{-}O}$ with hydrogen-bonding parameters $d_{\mathrm{O}\cdots\mathrm{H}} = 1.850$ Å and $\angle\mathrm{O{-}H\cdots O} = 145.9°$. In contrast, the hydrogen bond of the second minimum (**Ib**), which is 3.1 kcal/mol less stable than **Ia**, is formed by two hydroxyl moieties, $\mathrm{C{-}O\cdots H{-}O}$, with $d_{\mathrm{O}\cdots\mathrm{H}} = 1.899$ Å and $\angle\mathrm{O{-}H\cdots O} = 143.7°$.

On the other hand, it is worth noting that the dihedral angle θ, which defines the spatial orientation of the malonic acid substituent with respect to the thiophene ring, is $-9.5°$ and $-178.3°$ for **Ia** and **Ib**, respectively. Minimum energy conformations with hydrogen-bonding patterns identical to those defined for **Ia** and **Ib** were detected for $\theta = 145.2°$ and $-126.7°$, respectively. However, from an energetic point of view these structures differ from those displayed in Figure 3 by less than 0.1 kcal/mol, indicating that the stability of the conformations found for a single molecule of T3MA must be exclusively attributed to the hydrogen-bonding scheme, being independent of the spatial orientation of the malonic side group.

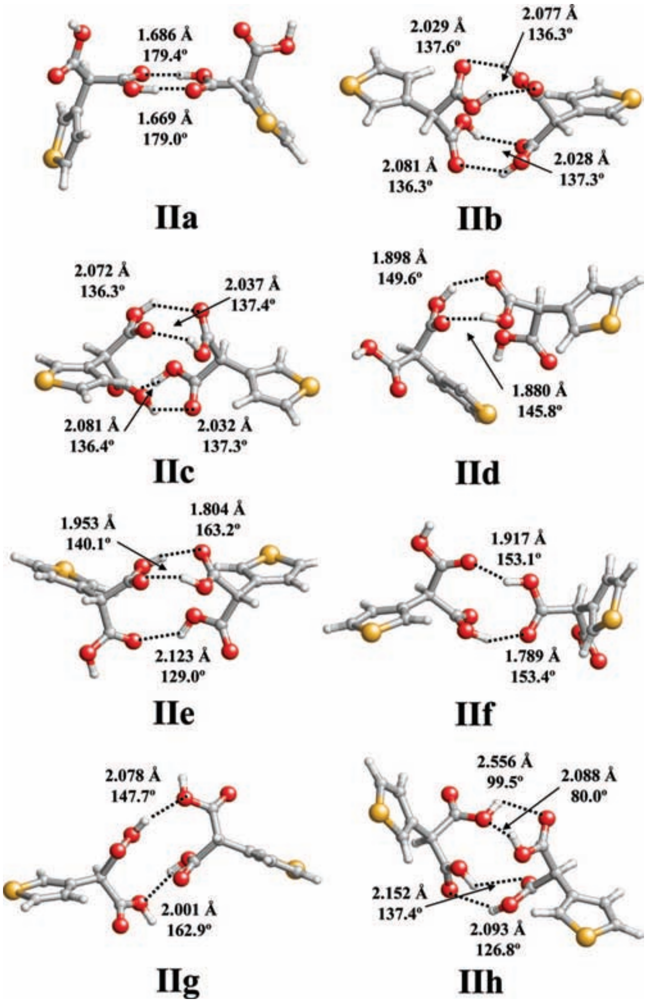


Figure 4. Structure of T3MA dimers stabilized by intermolecular hydrogen bonds calculated at the MP2/6-31+G(d,p) level. Hydrogen-bonding parameters $d_{\mathrm{O}\cdots\mathrm{H}}$ (in angstroms) and $\angle\mathrm{O{-}H\cdots O}$ (in degrees) are indicated.

The hydrogen bonds found for T3MA in the melted state (Figure 1) should be attributed to the hydrogen-bonding schemes showed in Figure 3, especially to that of the lowest energy conformation **Ia**. Thus, the kinetic study developed by FTIR spectroscopy (Figure 2) indicates that intermolecular hydrogen bonds disappear when the temperature grows and, therefore, the hydrogen bonds found at 160 °C should be associated with isolated molecules of T3MA and not with molecular complexes.

Dimers Stabilized by Intermolecular Hydrogen Bonds. A total of 150 dimers of T3MA with the four carboxylic acid groups arranged to form intermolecular hydrogen bonds were constructed, with varying spatial orientations and dihedral angles θ between the two molecules These starting geometries were submitted to complete geometry optimizations at the MP2/6-31+G(d,p) level. Only eight of the resulting structures were unique and were stabilized by at least two intermolecular hydrogen bonds; that is, structures with small geometrical differences and complexes stabilized by only one hydrogen bond were discarded. These structures are displayed in Figure 4, with hydrogen-bonding parameters [$\mathrm{O\cdots H}$ distance and $\mathrm{(C{-})O/(C{=})O\cdots H{-}O}$ angle] being indicated in all cases. Table 1 lists

TABLE 1: Relative, Dimerization,[a] and Binding Energies[b] Calculated for the Eight Dimers Stabilized by Intermolecular Hydrogen Bonds[c]

	ΔE (kcal/mol)		$\Delta E_{\mathrm{dimer}}$ (kcal/mol)		ΔE_{bind} (kcal/mol)	
dimer	−CP	+CP	−CP	+CP	−CP	+CP
IIa	0.0	0.0	−19.9	−15.2	−20.9	−16.2
IIb	0.4	3.3	−19.4	−11.9	−22.4	−14.8
IIc	0.4	3.3	−19.4	−11.9	−22.4	−14.9
IId	0.5	3.7	−19.3	−11.5	−21.1	−13.2
IIe	2.0	3.4	−17.8	−11.8	−20.9	−14.9
IIf	5.2	5.0	−14.7	−10.1	−16.4	−11.9
IIg	8.0	9.9	−11.9	−5.4	−13.1	−6.5
IIh	9.2	11.0	−10.7	−4.1	−15.7	−9.2

[a] $\Delta E_{\mathrm{dimer}}$ is the difference between the energy of the dimer and 2 times the energy of the monomer in its most stable arrangement (**Ia**). [b] ΔE_{bind} is the difference between the energy of the dimer and the energies calculated for the monomers when their geometries in the dimer are considered. [c] Structures of these dimers are shown in Figure 4.

the relative energies (ΔE) of the eight structures, which were calculated with and without basis-set superposition error (BSSE).

The lowest energy structure, **IIa**, shows two C═O···H—O hydrogen bonds with an arrangement similar to that found for dimers of formic acid, acetic acid, and benzoic acid (Scheme 2). Interestingly, two carboxylic groups define an eight-membered hydrogen-bonded ring in which both the lack of strain and the remarkable strength of the interactions are reflected by the hydrogen-bonding parameters: the angles ∠O—H···O are close to the ideal value (180°) and the distances $d_{\mathrm{H\cdots O}}$ are particularly short. Indeed, the hydrogen-bonding parameters displayed in Figure 4 for **IIa** are very similar to those reported for the formic acid dimer at the MP2/DZP level;[18] that is, ∠O—H···O = 177.8° and $d_{\mathrm{H\cdots O}} = 1.672$ Å. Furthermore, the distances between the oxygen atoms involved in the hydrogen bonding interactions, 2.667 and 2.684 Å, are very similar to those determined by gas electron diffraction for the dimer of acetic acid (2.684 Å).[19]

Inspection of Table 1 reveals that structures **IIb**, **IIc**, and **IId** are about 0.5 kcal/mol less stable than **IIa** when BSSE is not corrected. However, their relative energies increase to 3.3−3.7 kcal/mol after application of the CP correction. Interestingly, **IIb** and **IIc** involve four intermolecular hydrogen bonds defining two eight-membered rings, even though their geometric parameters reveal that these interactions are weaker than those found in **IIa**. On the other hand, the hydrogen-bonding scheme of **IId** is identical to that of **IIa**, even though the corresponding geometric parameters are significantly worse for the former dimer than for the latter one: ∠O—H···O is smaller by ~30° and $d_{\mathrm{H\cdots O}}$ is larger by ~0.21 Å. On the other hand, ΔE obtained for **IIe** after BSSE correction is 3.4 kcal/mol. This structure shows three hydrogen bonds with considerable differences in their geometric parameters; that is, ∠O—H···O and $d_{\mathrm{H\cdots O}}$ range from 129.0° to 163.2° and from 1.804 to 2.123 Å. Finally, the stability of structures **IIf**−**IIh** is remarkably low: ΔE is larger than 5 kcal/mol after CP correction is applied.

Table 1 includes the dimerization energy (ΔE_{dim}), which has been calculated as the difference between the energy of the dimer and 2 times the energy of the monomer in its most stable arrangement (**Ia**). Accordingly, ΔE_{dim} includes geometry relaxation of both the dimer and the monomer. It is worth noting that dimerization produces a strong stabilization, especially for dimers **IIa**−**IIf**: the values of ΔE_{dim} obtained for these complexes range from −19.9 to −14.7 kcal/mol without CP correction and from −15.2 to −10.1 kcal/mol with CP correction. Thus, the BSSE contribution varies between 24% and 40% for these dimers. On the other hand, the values of ΔE_{dim} with CP obtained for **IIg** and **IIh** are also favorable, although significantly higher (−5.4 and −4.1 kcal/mol, respectively). The BSSE contribution estimated for these complexes is about 55% and 61%, respectively.

The significant stability and hydrogen-bonding characteristics of **IIa** are fully consistent with the FTIR results obtained for T3MA at room temperature. Thus, in this complex two carbonyl groups are involved in strong intermolecular hydrogen bonds and the other two remain unassociated, explaining the absorptions detected at 1751 and 1657 cm^{-1}. However, caution is required because complexes formed by a large number of molecules linked through intermolecular hydrogen-bonding networks have not been considered in this theoretical study. Accordingly, although a hydrogen-bonding pattern close to that experimentally observed for formic, acetic, and benzoic acids[6,8] agrees with the FTIR spectrum of T3MA in the solid state, a structure formed by chains of hydrogen-bonded molecules similar to that found for malonic acid[9,10] cannot be ruled out.

On the other hand, binding energies (ΔE_{bind}), which neglect the geometry relaxation of the monomer, are also listed in Table 1. Obviously, the magnitude of BSSE contribution is similar to that described above for ΔE_{dim}. Interestingly, the values of ΔE_{bind} with CP increase from −16.2 (**IIa**) to −6.5 kcal/mol (**IIg**). These values are in good agreement with early published values for dimers of carboxylic acids arranged as in Scheme 2.[7a,c] Thus, ΔE_{bind} with CP reported for the formic acid dimer at the MP2/cc-pVDZ level was −10.4 kcal/mol (BSSE contribution of about 36%); the MP2 value at the basis set limit was −13.8 kcal/mol.[7c] On the other hand, values predicted at the B3LYP/6311++G(d,p) level for acetic acid and benzoic acid dimers are −14.3 and −14.9 kcal/mol, respectively.[7a]

It should be emphasized that the size of the system under study precludes frequency calculations at the MP2/6-31+G(d,p) level. However, in order to examine the influence of zero-point vibrational energies (ZPVE) in the dimerization and binding energies, we decided to check a strategy based on addition of the ZPVE, calculated by a method based on density functional theory (DFT), to electronic energies obtained at the MP2 level. Accordingly, the eight complexes showed in Figure 4 were reoptimized at the B3LYP/6-31+G(d,p) level. Unfortunately, the structures of these complexes were drastically modified during the reoptimization process. This is because the DFT methods describe the interaction between π-systems as repulsive while, as was demonstrated in a recent study devoted to examining π-stacked thiophene dimers, trimers, and tetramers,[20] the MP2 method reproduces satisfactorily the attractive non-covalent interactions between π-systems even when they are very weak. Thus, although B3LYP reoptimizations led to structures stabilized by hydrogen bonds between the carboxylic groups, the initial structures were in many cases rearranged to maximize the separation between the two thiophene rings. This feature is illustrated in Figure 5, which compares the molecular arrangements of **IId** before and after reoptimization. Due to the lack of agreement between MP2 and B3LYP structures, we decided to omit the analysis of ZPVE effect on the MP2 complexes.

Dimers Stabilized by both Intra- and Intermolecular Hydrogen Bonds. A total of 40 dimers of T3MA with the carboxylic acid groups arranged to form at least two hydrogen bonds, one intramolecular and one intermolecular, were constructed. After complete geometry optimization at the MP2/6-31+G(d,p) level, only 21 structures retained such initial criterion

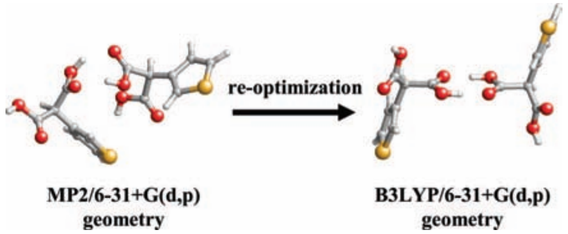


Figure 5. Comparison between the structures obtained at the MP2/6-31+G(d,p) and B3LYP/6−31+G(d,p) levels for dimer **IId**.

and were unique; that is, structures with small geometrical differences were not considered as significant and were discarded. The 13 dimers with relative energy smaller than 5 kcal/mol are depicted in Figure 6; the remaining structures are supplied as Supporting Information. On the other hand, Table 2 lists the values of ΔE, ΔE_{dim}, and ΔE_{bind} calculated for the 21 optimized structures.

As can be seen, the ΔE values are contained within an interval of 9.9 kcal/mol, which is reduced to 6.5 kcal/mol when the CP correction is applied. The significant influence of BSSE is also reflected in the relative energy order of the calculated dimers, which is completely different with and without CP. The lowest energy structure without CP correction corresponds to **IIIa**, which is stabilized by three O—H···O═C hydrogen bonds, two intramolecular and one intermolecular. However, this structure becomes 0.9 kcal/mol unfavored with respect to **IIIb** when BSSE is eliminated; the latter is the lowest energy structure when CP correction is applied. The hydrogen-bonding scheme of **IIIb** is very similar to that described for **IIIa** (Figure 6): two intramolecular and one intermolecular interaction of the O—H···O═C type, the most remarkable difference between such two structures being the C—H···O═C interaction detected in the former dimer. This weak interaction seems to provide an additional stabilization of ∼1 kcal/mol.

The next four structures (**IIIc, IIId**, **IIIe**, and **IIIf**) presents three hydrogen bonds of the O—H···O═C type, two intramolecular and one intermolecular. This common hydrogen-bonding pattern is responsible for their remarkable similarity in terms of relative stability (Table 2): the calculated ΔE values without and with CP range from 2.4 to 2.6 kcal/mol and from 1.1 to 1.5 kcal/mol, respectively. Dimers **IIIg**, **IIIh**, and **IIIi** are stabilized by one O—H···O—C intermolecular hydrogen bond withtwo intramolecular interactions of the O—H···O═C type (Figure 6). The CP-corrected ΔE values indicate that these structures are about 2−3 kcal/mol unfavored with respect to **IIIb**. The energetic characteristics of structures **IIIj** and **IIIk** are relatively similar, being less stable than the global minimum by 4.0 and 3.7 kcal/mol, respectively, once the BSSE has been corrected. However, the hydrogen-bonding schemes of these two dimers present significant differences. Specifically, the three interactions showed by **IIIj** are one intramolecular of the O−H···O−C type and two of O−H···O═C type, one intermolecular and one intramolecular. In contrast, the interactions found in **IIIk** are two intramolecular of the O−H···O═C type and one intermolecular of the O−H···O−C type. The ΔE values with CP calculated for **III*l*** and**IIIm** are 4.6 and 5.3 kcal/mol, respectively. Interestingly, these two dimers show intramolecular interactions with the same hydrogen-bonding pattern, the only difference between them being the pattern of the intermolecular interaction. This is O—H···O—C and O—H···O═C for **III*l*** and **IIIm**, respectively. Finally, ΔE of the remaining structures is higher than 5.0 kcal/mol, and their importance is relatively small. In spite of this, it should be noted that in some cases (**IIIn** and **IIIr**) the CP-corrected ΔE values decrease to about 3 kcal/mol.

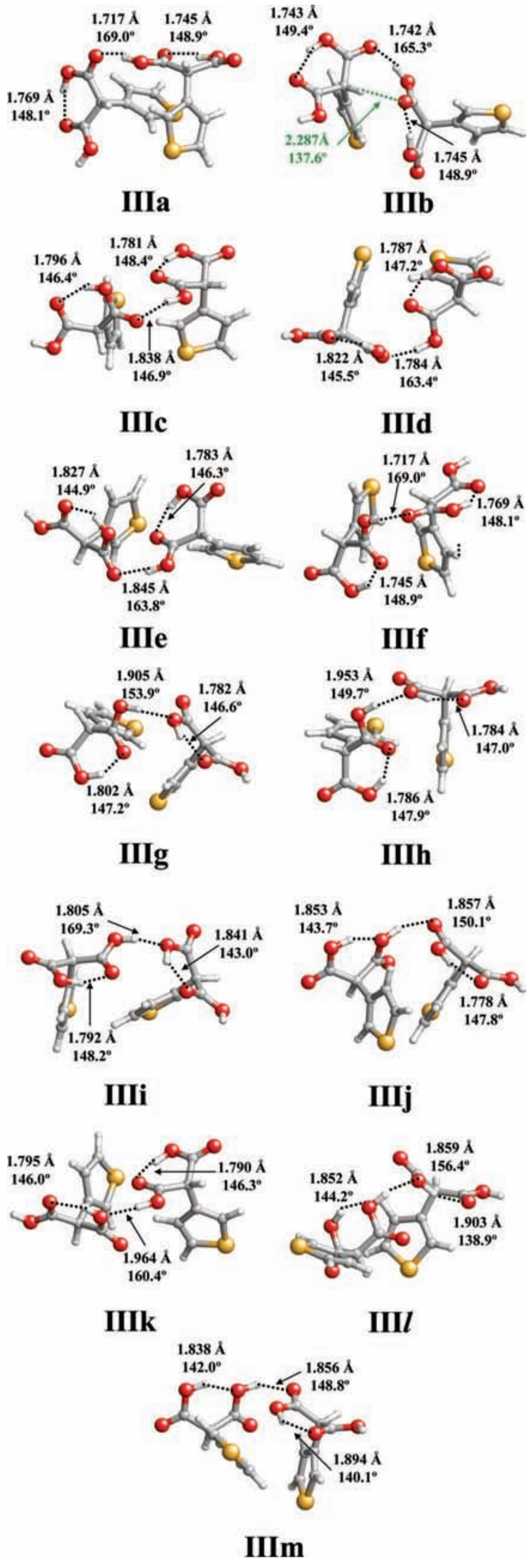


Figure 6. Structure of T3MA dimers stabilized by at least one intermolecular and one intramolecular hydrogen bond, calculated at the MP2/6-31+G(d,p) level. Hydrogen-bonding parameters $d_{\text{O}\cdots\text{H}}$ (in angstroms) and ∠O−H···O (in degrees) are indicated. C−H···O intermolecular interactions and geometric parameters are indicated in green.

TABLE 2: Relative, Dimerization,[a] and Binding Energies[b] Calculated for the 21 Dimers Stabilized by both Intra- and Intermolecular Hydrogen Bonds[c]

	ΔE(kcal/mol)		ΔE_{dimer} (kcal/mol)		ΔE_{bind} (kcal/mol)	
dimer	−CP	+CP	−CP	+CP	−CP	+CP
IIIa	0.0	0.9	−20.2	−10.0	−23.3	−13.1
IIIb	0.2	0.0	−20.0	−11.0	−22.9	−13.3
IIIc	2.4	1.5	−17.8	−9.4	−20.0	−11.6
IIId	2.4	1.1	−17.8	−9.8	−19.1	−11.1
IIIe	2.5	1.5	−17.7	−9.5	−18.9	−10.7
IIIf	2.6	1.4	−17.6	−9.5	−18.8	−8.8
IIIg	3.0	2.8	−17.2	−8.1	−18.9	−9.9
IIIh	3.2	3.1	−17.0	−7.9	−18.6	−9.4
IIIi	3.2	2.1	−17.0	−8.8	−18.8	−10.7
IIIj	3.8	4.0	−16.4	−7.0	−21.0	−11.6
IIIk	4.3	3.7	−15.9	−7.2	−17.4	−8.8
III*l*	4.9	4.6	−15.3	−6.3	−19.7	−10.7
IIIm	4.9	5.3	−15.3	−5.7	−21.5	−11.9
IIIn	5.3	2.9	−14.9	−8.1	−16.2	−9.4
IIIo	5.4	5.3	−14.8	−5.6	−20.7	−11.5
IIIp	6.0	4.8	−14.2	−6.2	−18.6	−10.1
IIIq	6.2	6.5	−14.0	−4.4	−18.4	−8.8
IIIr	7.3	3.4	−12.9	−7.6	−17.1	−11.8
IIIs	8.1	5.0	−12.1	−5.9	−17.3	−11.2
IIIt	8.2	3.9	−12.0	−7.0	−16.2	−11.2
IIIu	9.9	5.8	−10.3	−5.2	−14.6	−9.4

[a] ΔE_{dimer} is the difference between the energy of the dimer and 2 times the energy of the monomer in its most stable arrangement (**Ia**). [b] ΔE_{bind} is the difference between the energy of the dimer and the energies calculated for the monomers when their geometries in the dimer are considered. [c] Structures of these dimers are shown in Figures 6 and S1 (Supporting Information).

The ΔE_{dim} values (with respect to **Ia**) calculated without and with CP range from −20.2 to −10.3 kcal/mol and from −11.0 to −4.4 kcal/mol, respectively, indicating that dimerization is a favored process. Accordingly, the BSSE contribution is considerably larger for complexes stabilized by both intramolecular and intermolecular hydrogen bonds than for dimers that only involve intermolecular interactions. Specifically, the BSSE correction in the former complexes varies between 42% (**IIIt**) and 69% (**IIIq**). Comparison of the ΔE_{dim} values with CP correction displayed in Tables 1 and 2 reveals that the formation of complexes stabilized exclusively by intermolecular hydrogen bonds is significantly favored with respect to the dimers involving both intermolecular and intramolecular interactions. Thus, the energy difference between the most stable complex of each category, **IIa** and **IIIb**, is 4.2 kcal/mol. This feature is consistent with the FTIR spectrum recorded in the solid state (Figure 1), in which we found that T3MA molecules form only intermolecular hydrogen bonds. On the other hand, the trends followed by ΔE_{bind} values are very similar to those described for ΔE_{dim}: both the uncorrected and CP-corrected values are higher than those obtained for the structures stabilized only by intermolecular hydrogen bonds.

The overall results displayed in this work indicates that the stability of the systems investigated follows this order: dimers of T3MA stabilized by intermolecular hydrogen bonds > dimers involving both intermolecular and intramolecular interactions > individual monomers with intramolecular hydrogen bonds. Accordingly, it can be concluded that the intermolecular interactions detected by FTIR in the solid state are favored from an enthalpic point of view. In contrast, the intramolecular interactions determined in the melted state are the result of an entropically favored process, which is produced by thermal disruption of molecular associations.

Conclusions

The results obtained in this work by use of MP2/6-31+G(d,p) calculations and FTIR spectroscopy indicate that the carboxylic acid groups of T3MA tend to be involved in intermolecular hydrogen bonds at room temperature. Thus, the dimers of T3MA involving only intermolecular hydrogen bonds are more stable than those involving both inter- and intramolecular hydrogen bonds. Furthermore, the dimerization energies indicated that the formation of hydrogen-bonded complexes is considerably favored with respect to individual molecules. These results are fully consistent with those obtained for T3MA in the solid state, in which both carbonyl groups associated in intermolecular hydrogen bonds and in the free state were detected by FTIR. On the other hand, the FTIR spectrum recorded in the melted state indicated the formation of intramolecular hydrogen bonds at high temperatures. Thus, the stabilization of individual monomers with respect to complexes with hydrogen bonds should be attributed to an entropically driven process induced by temperature.

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Supporting Information Available: Coordinates and energy of all structures calculated in this work: monomers (**Ia** and **Ib**) and dimers (**IIa−IIh** and **IIIa−IIIu**) of T3MA. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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