

# Hydrogen-Bonded Dimers of CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH: Ab Initio Structures and Multivariate Analysis

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Structures and vibrational frequencies of relevant hydrogen-bonded dimers of 2-methoxyethanol are obtained at the 3-21G\*//AM1 level (the 3-21G\* basis set included polarization functions deliberately added to second period atoms) and the results analyzed by standard multivariate methods. Dimers built from the same pair of isolated monomers belong to the same homologous series. The most stable dimer is obtained from the most stable conformations of both monomers, has a 10-membered intermolecular ring with a boat-chair-boat conformation, and presents a zero dipole moment. In addition, the most stable dimers of the three homologous series have 10-membered rings with relatively symmetric conformations and zero or very low dipole moments. The energies of the monomers in these dimers—monomers with geometries frozen in the dimer—are close to the isolated and relaxed monomers energies. Generally speaking, OH···O and CH···O hydrogen bonds are found to contribute appreciably for the stability of the dimers. In particular, for the second most stable dimer, two of the three CH···O hydrogen bonds are shorter than the intramolecular OH···O bond for the isolated monomer. Multivariate analysis of all the results shows that the O···H—O angle is highly correlated with the H—O bond length and that the COC and OCC angles are also highly correlated for both monomers, hence confirming that each monomer in a dimer keeps essentially the same conformation it has in the isolated monomer. The first and second principal components include all the highly correlated variables and account for 45% of the total variance. 3-D plots of the three most important principal components confirm a strong structural resemblance both for 10-membered ring dimers of homomeric series, *i.e.*, formed by the same monomers, and for the more stable dimers in each homologous series. In addition, among the heteromeric dimers with seven membered rings, the ones whose first conformation is *G* or *G'* are less stable and located in a separate group.

## 1. Introduction

The two more stable conformers of 2-methoxyethanol, CH<sub>3</sub>-OCH<sub>2</sub>CH<sub>2</sub>OH (abbreviated C<sub>1</sub>E<sub>1</sub>), *tgg'* and *ggg'*, owe their stabilities to mainly O···H—O intramolecular hydrogen bonds, *tgg'* being 6–7 kJ mol<sup>-1</sup> more stable than *ggg'*.<sup>1</sup> In the liquid phase, FTIR and Raman spectra of C<sub>1</sub>E<sub>1</sub> show features ascribable to different degrees of aggregation through intermolecular hydrogen bonding.<sup>1</sup> The formation of intermolecular hydrogen bonded dimers is of fundamental importance for understanding the structure and dynamics of C<sub>1</sub>E<sub>1</sub> in the liquid phase.

C<sub>1</sub>E<sub>1</sub> is a good model system for assessing dimer formation, since its conformational degrees of freedom compete in energy with both intra- and intermolecular hydrogen bonding interactions. A comparison of the performances of various *ab initio* calculations previously carried out for the structures and vibrational spectra of C<sub>1</sub>E<sub>1</sub> led to the general conclusion that a 3-21G basis set which includes polarization functions deliberately added to second period atoms (hereafter referred to as 3-21G\* basis set) is the smallest basis set that adequately reproduces the structures and energies obtained from the more sophisticated levels of calculation with electronic correlation<sup>2</sup> for the more relevant conformers. Since the full optimization of the dimer structures with the 3-21G\* basis set was expensive enough in computational effort, the geometries of dimers were fully optimized at the AM1 level, in this work. Single point calculations were subsequently carried out at the 3-21G\* level,

since the 3-21G\*//AM1 calculation approximately reproduces the conformational energies of the monomer. Vibrational frequencies were evaluated at the level of the energy minimization calculation, *i.e.*, at the AM1 level. The most relevant structural parameters and the OH stretching frequencies were analysed by standard multivariate methods.

## 2. Methods

*Ab initio* MO calculations at the 3-21G\*//AM1 level were carried out with the *Gaussian 92* program system.<sup>3</sup> The 3-21G\* basis set included *d* functions ( $\zeta = 0.8$ ) deliberately added to the C and O atoms. As is well-known, polarization functions properly describe the lone pair "tail" functions for the second period atoms. The absolute errors in bond lengths and bond angles with respect to the equilibrium geometrical parameters are less than 1 pm and 0.1°, respectively. Calculations of vibrational frequencies were carried out using the above program package and the AM1 derived force fields.

Dimers were built with the monomer conformations, *tgg'* and *ggg'*, and their enantiomers, *tg'g* and *g'g'g*. For simplification, this three-letter acronym which indicates the CO—C—OH axes in this order was compressed to a single upper case letter (*T* or *G*) with an apostrophe to specify an enantiomer, *e.g.*, *T*, *G*, *T'*, and *G'* stand for *tgg'*, *ggg'*, *tg'g*, and *g'g'g*, respectively.

Since dimeric structures of C<sub>1</sub>E<sub>1</sub> should result mainly from (O)H···O hydrogen bonds, two types of intermolecular rings were considered, namely, (i) a 10-membered ring in which the ether O atoms from both monomers act as H-bond acceptors and the hydroxyl H atoms as H-bond donors (Figure 1a)), and (ii) a seven membered ring with the ether O atom from one

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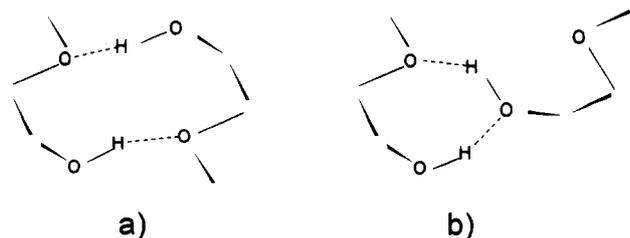


Figure 1. Ten- (a) and seven- (b) membered ring dimers of C<sub>1</sub>E<sub>1</sub> (schematic).

monomer and the hydroxyl O atom from the other acting as H-bond acceptors (Figure 1b)).

Test calculations for different hydrogen bonded dimers, in particular those with four membered rings resulting from the antiparallel alignment of OH bonds, are much less stable and so do not deserve consideration.

The notation adopted herein indicates the conformations of the monomers, followed by the size of the intermolecular ring in parentheses. Whenever necessary, the conformation of the intermolecular ring is indicated apart. For example, TT'(10) stands for a dimer made of T and T' monomers, forming a 10-membered ring. This dimer displays a boat-chair-boat conformation (BCB). For seven-membered ring dimers, the first monomer is always chosen to involve the ether O atom as H-bond acceptor, e.g., the T monomer for TG'(7) (see Figure 1-b)).

For any distinct pair of monomers, each of the geometries shown in Figure 1 was fully optimized at the AM1 level, yielding a total of 13 different dimers. While the existence of other stable dimers should not be entirely excluded, the structures considered in our study are representative and enable the deduction of important structural trends.

The following partition of the total energy of a dimer,

$$E = E_1 + E_2 + E_h \quad (1)$$

is adopted, where  $E_1$  and  $E_2$  represent the energies of monomers 1 and 2 whose geometries are "frozen" in the dimer and  $E_h$  is the total intermolecular hydrogen bonding energy. The energies of the relaxed isolated monomers are represented by  $E_1^0$  and  $E_2^0$ . Dimers which correspond to the same  $E_1^0 + E_2^0$  value belong to the same homologous series. Two of the three series of dimers are formed by *homomeric dimers* ( $E_1^0 = E_2^0$ ), the other includes *heteromeric dimers* ( $E_1^0 \neq E_2^0$ ).

The data were collected in a  $13 \times 21$  matrix, where each row corresponds to an individual dimer, and each column to a particular variable (energy, dipole moment, geometrical parameter, or vibrational frequency). Standard multivariate analysis was performed using a version of the ARTHUR computer program adapted to personal computers.<sup>4</sup> Before computing the principal components (PC's), the data were scaled so that all the variables had zero average and the same variance. R-type PC's<sup>5,6</sup> were obtained by diagonalization of the  $X^T X$  product matrix, where X is the scaled data matrix. Sample character-

istics were normalized to the PC variances and the variable characteristics were normalized to one.

### 3. Results and Discussion

**Energies and Structures of Dimers.** Using the above-mentioned notation, Table 1 considers the effect, of two important operations, a mirror reflection,  $R$ , and an exchange of conformations between monomers,  $X$ , on a dimer. Since these operations commute, their product order is irrelevant. A dimer and its enantiomer both have the same structure and energy, as they are assumed to be isolated.

As can be seen in Table 1,  $R$  leads to the same enantiomer only for homomeric 10-membered ring dimers built from enantiomers. In turn, when  $X$  is applied to a 10-membered ring dimer (homomeric or heteromeric), the same enantiomer is always obtained. Hence, for 10-membered ring dimers, the order of the conformations is irrelevant. On the other hand, applying  $X$  to a heteromeric seven-membered ring dimer leads to a new one. In addition,  $X$  has the same effect as  $R$  when either of these operations is applied to homomeric seven membered ring dimers formed by enantiomers.

Table 2 presents energies, OH stretching frequencies, dipole moments, and geometrical parameters for relevant dimers of C<sub>1</sub>E<sub>1</sub>. In this table several comparisons involving the dimers and the isolated monomers are established. The following general conclusions can be easily drawn: (i) all the considered dimers are stable in relation to their isolated monomers; (ii) the monomers in the dimers are less stable than the isolated monomers, as can be easily seen from  $E_1 - E_1^0$  and  $E_2 - E_2^0$  values; (iii) the latter unstabilizing term is overcome by the total hydrogen bonding energy; (iv) the most stable dimer, TT'(10), results from the most stable conformation of both monomers, has a 10-membered ring with a BCB conformation, the more stable conformation for cyclododecane,<sup>7,8</sup> and presents a zero dipole moment; (v) among heteromeric dimers, the most stable one, TG(10) is ca. 9 kJ mol<sup>-1</sup> above TT'(10), and shares with it a few common structural features, namely, size (10) and conformation (BCB) of the ring, and a very low dipole moment; (vi) among dimers formed from monomers with G and/or G' conformations, the more stable one, GG'(10), is almost 17 kJ mol<sup>-1</sup> above TT'(10), has the same ring size, a CCC conformation, and a zero dipole moment; (vii) all the considered dimers present negative OH stretching frequency shifts consonant with longer OH bond lengths and comparatively short O...H contact distances; (viii) the intramolecular OH...O contact distances for the most stable isolated conformers increase in the dimers whereas the intermolecular OH...O contact distances are comparatively short (see also Figure 2); (ix) all the studied dimers present between one and four appreciably short CH...O contact distances; (x) the above-mentioned trends observed for the OH stretching frequency shifts and the hydrogen contact distances suggest the occurrence of hydrogen bonds whose cooperativity enables us to explain the dimers stability as referred to in (i).

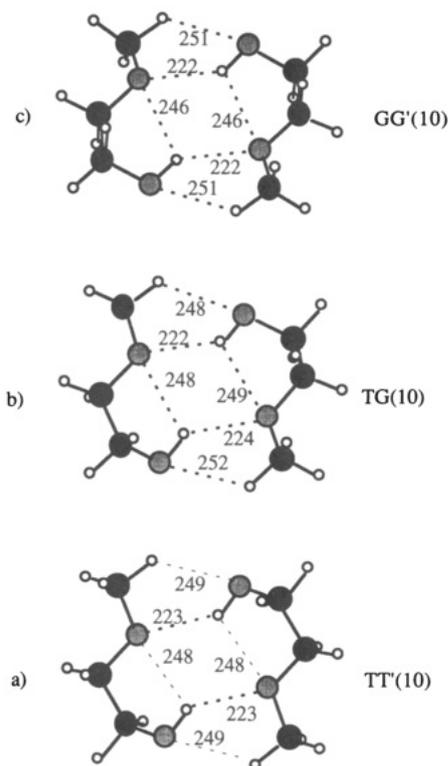
TABLE 1: Effect of Mirror Reflection ( $R$ ) and Exchange of Conformations ( $X$ ) on a C<sub>1</sub>E<sub>1</sub> Dimer

operation	homomeric dimer		heteromeric dimer	
	7-membered ring	10-membered ring	7-membered ring	10-membered ring
$AB \xrightarrow{R} A'B'$ (mirror reflection)	different enantiomer (e.g. TT'(7) → T'T(7))	different enantiomer (e.g. TT(10) → T'T'(10))	different enantiomer (e.g. TG'(7) → T'G(7))	different enantiomer (e.g. TG'(10) → T'G(10))
$AB \xrightarrow{X} BA$ (exchange of conformations)	different enantiomer (e.g. TT'(7) → T'T(7))	same enantiomer (e.g. TT'(10) → T'T(10))	new dimer (e.g. TG'(7) → G'T(7))	same enantiomer (e.g. TG'(10) → G'T(10))
	same enantiomer (e.g. TT(7) → TT(7))			

**TABLE 2: Energies, OH Stretching Frequencies, Dipole Moments, and Geometrical Parameters for Relevant Dimers of C<sub>1</sub>E<sub>1</sub>**

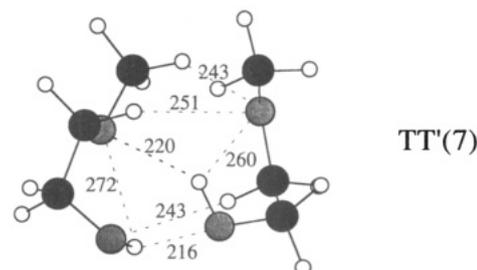
	TT'(10)	TT'(7)	TT(10)	TT(7)	TG(10)	TG'(7)	TG(7)	TG'(10)	GT(7)	GT(7)	GG'(10)	GG'(7)	GG(10)
energies/kJmol <sup>-1</sup>													
$E(\text{dimer}) - E(\text{TT}'(10))^a$	0.0	1.9	3.5	9.4	8.6	8.9	9.8	11.0	11.2	31.0	16.6	19.7	33.1
$E_1 - E_1^{0b}$	1.2	7.8	0.8	2.9	1.9	5.8	3.1	1.5	4.8	25.	1.0	4.7	4.9
$E_2 - E_2^{0b}$	1.2	5.5	0.8	3.5	1.2	3.4	3.1	2.4	3.8	2.7	1.0	3.3	4.9
$E_1^0 - E_1^0$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.1	7.1	7.1	7.1	7.1
$E_2^0 - E_2^0$	0.0	0.0	0.0	0.0	7.1	7.1	7.1	7.1	0.0	0.0	7.1	7.1	7.1
$-E_h$	46.6	55.6	42.4	41.2	45.7	51.5	47.8	44.2	48.6	48.0	43.8	46.6	35.1
frequency shifts/cm <sup>-1</sup>													
$\nu(\text{OH}(1)) - \nu(\text{OH}(1))^{\circ c}$	-29	-32	-28	-30	-22	-30	-25	-23	-34	-23	-24	-27	-28
$\nu(\text{OH}(2)) - \nu(\text{OH}(2))^{\circ c}$	-28	-19	-30	-22	-27	-10	-27	-26	-24	-23	-37	-20	-34
$\mu/\text{D}$	0.0	3.1	0.5	3.9	0.5	3.0	2.1	2.6	1.9	2.7	0.0	1.3	0.8
distances/pm													
O(1)••H(1) <sup>d</sup>	248	272	247	259	249	264	255	250	260	254	246	240	256
O(2)••H(2) <sup>d</sup>	248	260	247	260	248	241	246	253	257	254	246	252	256
O(1)••H(2)	222	220	222	223	222	218	221	224	220	226	222	225	223
H(1)••O(2)	222	216	222	215	224	217	227	226	222	229	222	213	233
C <sub>methyl</sub> H(1)••O(2)	249	243	246	247	248	255	256	—	—	—	251	—	247
C <sub>methylene</sub> H(1)••O(2)	—	251	—	—	—	—	—	238	—	240	—	—	252
O(1)••HC <sub>methyl</sub> (2)	249	—	246	—	252	249	246	—	254	—	251	—	247
O(1)••HC <sub>methylene</sub> (2)	—	243	—	—	—	—	256	—	243	238	—	250	252
OH(1)–OH(1) <sup>e</sup>	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.3	0.2	0.3	0.2	0.2
OH(2)–OH(2) <sup>e</sup>	0.3	0.3	0.3	0.3	0.3	0.1	0.3	0.2	0.3	0.3	0.3	0.1	0.2
angles/deg													
O–H(1)••O(2)	142	149	141	95	144	175	138	148	149	129	143	167	136
O(1)••H–O(2)	142	141	141	125	142	135	145	145	135	144	142	115	136

<sup>a</sup>  $E(\text{TT}'(10)) = -1\,399\,870\text{ kJ mol}^{-1}$ . <sup>b</sup>  $E_T^0 = -699\,913\text{ kJ mol}^{-1}$ ;  $E_G^0 = -699\,906\text{ kJ mol}^{-1}$ . <sup>c</sup>  $\nu(\text{OH}(T))^{\circ} = \nu(\text{OH}(\text{isolated } T)) = 3481\text{ cm}^{-1}$ ,  $\nu(\text{OH}(G))^{\circ} = \nu(\text{OH}(\text{isolated } G)) = 3471\text{ cm}^{-1}$ . <sup>d</sup> O••H (isolated T) = 245 pm, O••H (isolated G) = 242 pm. <sup>e</sup> OH(isolated T) = 96.6 pm; OH(isolated G) = 96.7 pm.



**Figure 2.** Structures of most stable dimers in each homologous series of dimers for C<sub>1</sub>E<sub>1</sub>: (a) dimers built from monomers with T and/or T' conformations; (b) dimers made of monomers with T (or T') and G (or G') conformations; (c) dimers formed by monomers with G and/or G' conformations (see text).

It is interesting to note that all the above dimers, TT'(10), TG(10), and GG'(10), have 10-membered rings with relatively symmetric conformations (Figure 2) and zero or very low dipole moments (Table 2). In addition, their energy differences indicate that  $E_1 - E_1^0$  and  $E_2 - E_2^0$  are much smaller than  $E_h$ . In turn, the latter energy has roughly the same magnitude for all these dimers. In fact, these seem to be quite general trends,



**Figure 3.** Structure of TT'(7) dimer (see text).

easily confirmed by inspection of Table 2, with the single exception, GT(7).

Among the four dimers of the first series, the first three account for more than 90% of the total dimers population. While TT'(10) and TT(10) present similar structural parameter values, the latter has a BCC conformation and is less symmetric than the former whose conformation is BCB. In addition, TT(10) has a larger dipole moment and a slightly lower  $E_h$  value (Table 2). The same trends are found for TT'(7) and TT(7), with the latter being less symmetric (boat conformation, B) than the first of these (chair conformation, C). Hence, dimers formed by different enantiomers are more symmetric and have lower dipole moments than those built from the same enantiomer.

Comparing now TT'(7) and TT'(10), the first of these dimers is less stable, in consonance with a much higher dipole moment, and has higher  $E_1 - E_1^0$  and  $E_2 - E_2^0$  values whose sum exceeds the difference between the  $E_h$  values of these dimers (see Table 2). In addition, while TT'(7) is less symmetric than TT(10)—it has a much higher dipole moment—its relative stability is favored by the occurrence of stronger intermolecular H bonds of both types (OH••O and CH••O), as is confirmed by a higher  $E_h$  value and shorter H-bond distances (Figure 3 and Table 2). It is interesting to notice that TT'(7) owes its relative stability mainly to three CH••O hydrogen bonds, two of which are even shorter than the intramolecular OH••O bond for the isolated T monomer (Figure 3 and Table 2).

Finally for the dimers of the first series, TT(7) presents the highest dipole moment, has long intramolecular H-bond contact

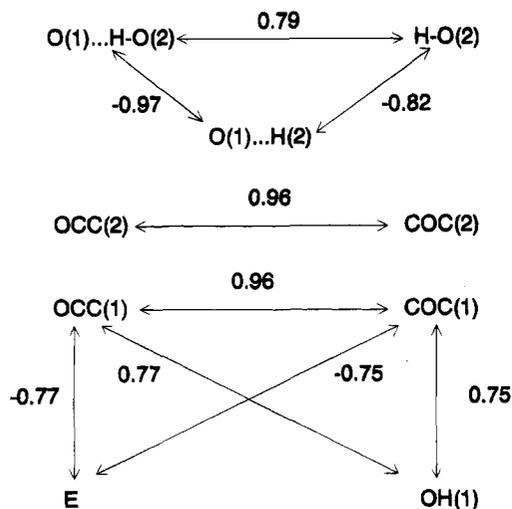


Figure 4. Correlations between structural parameters (only correlation coefficients greater than 0.70 are shown).

distances and appreciably bent H-bond angles (hence, with a low  $E_h$  value), and exhibits a single CH $\cdots$ O attractive interaction (Table 2). These features enable one to understand why TT(7) is energetically positioned among the dimers of the second series (the heteromeric series).

Considering now the heteromeric dimers, *i.e.*, TG(10), TG'(7), TG(7), TG'(10), GT'(7), and GT(7), the first five have energies closely spaced around 10 kJ mol<sup>-1</sup>. In addition, for dimer pairs with seven-membered rings generated mutually by an exchange of conformations, the ones in which the T monomer involves the ether O atom as H-bond acceptor, *i.e.*, the first conformation is T or T', are more stable (Table 2). For example, TG(7) and TG'(7) are more stable than GT(7) and GT'(7), respectively.

Among all the dimers of the three series considered here, only GT(7) in the heteromeric series presents  $E_1 - E_1^0 = E_G - E_G^0$  of the same magnitude as  $E_h/2$  (see Table 2). This is an interesting feature, since it points to a G conformation in the dimer appreciably different from the conformation of the isolated G monomer.

The dimers of the third series are made of G or G' conformations for the monomers, and are situated above 16 kJ

TABLE 3: Loadings for the Five More Relevant Principal Components

variable	principal component				
	1	2	3	4	5
OCC(1)	0.37				
COC(1)	0.36				
OH(1)	0.34				-0.37
OH(2) $\cdots$ O(1)	-0.33			0.26	
O(1) $\cdots$ H(2)	0.31				
OH(2)	-0.31				
$E$	-0.29		-0.28		-0.31
COC(2)		0.46			
OCC(2)		0.43			
$\nu$ (OH(2))		-0.36			
OH(1) $\cdots$ O(2)		0.33		-0.28	-0.27
$E_2 - E_2^0$			0.39		
COH(1)			0.38		
$E_1 - E_1^0$			0.30		
$\nu$ (OH(1))			-0.29	-0.25	
COH(2)			0.28		
O(2) $\cdots$ H(1)				0.43	0.37
$\mu$				-0.41	
$E_h$				-0.40	-0.31
% variance	26	19	17	11	9

mol<sup>-1</sup>. Hence, only the more stable of these dimers, GG'(10), deserves some consideration, especially because it has a 10-membered ring and is formed by different enantiomers. In fact, these features are consistent with general trends which have been already mentioned and discussed for the first homologous series.

**Multivariate Analysis.** Various dimer characteristics were considered, namely total energies ( $E$ ), values of  $E_i - E_i^0$  and  $E_h$ , dipole moments, OH stretching frequencies, relevant bond lengths, bond angles, and hydrogen bonding contact distances and angles. After determining the principal components (Table 3), correlations between different parameters were evaluated, and high correlation coefficients, above 0.70, are presented in Figure 4. From these coefficients it can be inferred that the O $\cdots$ H—O angle is highly correlated with the H—O bond length, and that the COC and OCC angles are also highly correlated for both monomers. In fact, a plot of OCC vs. COC angles (Figure 5) confirms that each monomer in a dimer keeps essentially the same conformation it has in the isolated monomer. In addition, from Figure 4 it can be concluded that

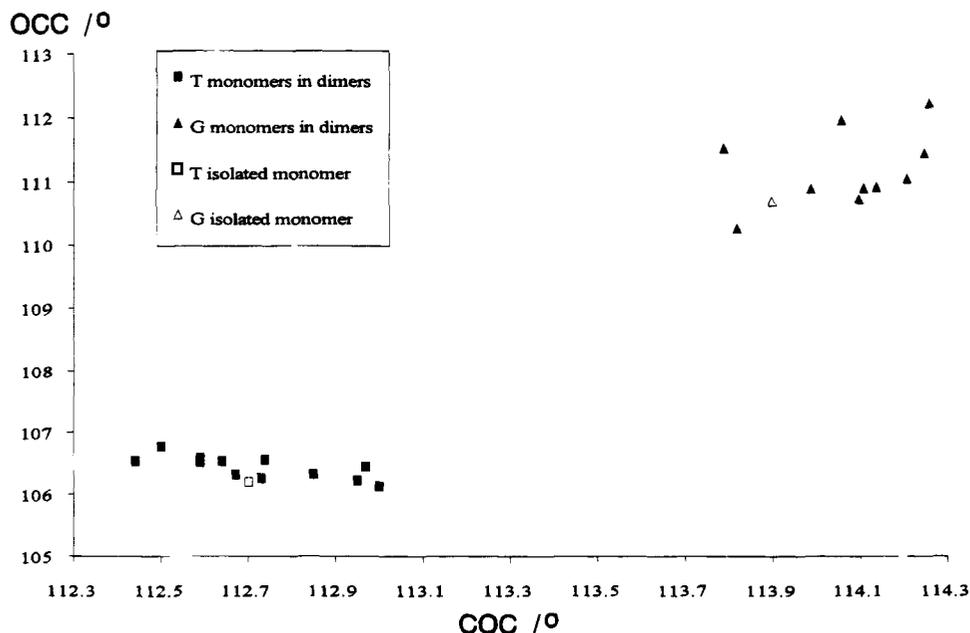
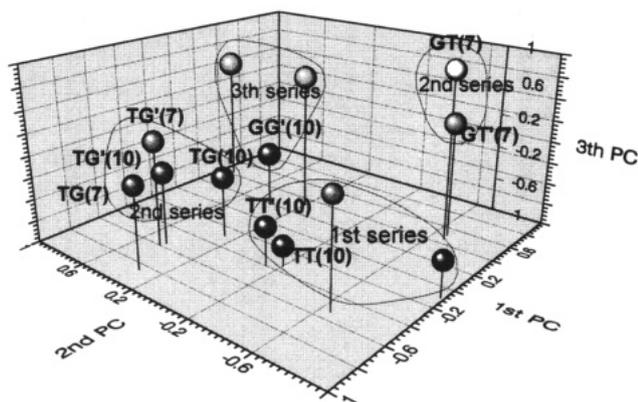


Figure 5. OCC (°) vs COC (°) for dimers of C<sub>1</sub>E<sub>1</sub>.

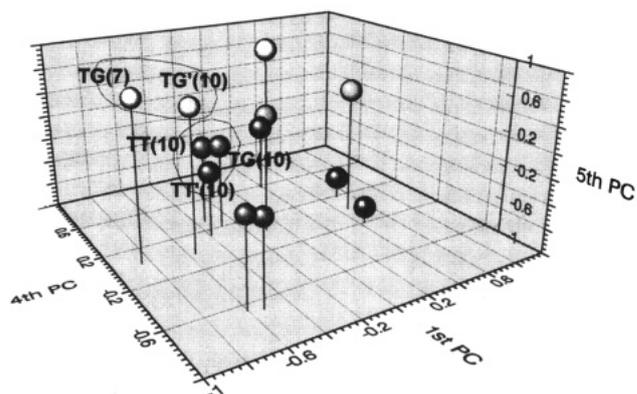


**Figure 6.** 3-D plot of first, second, and third PC's.

these angles correlate strongly also with the OH bond length and negatively correlate with the energy of the dimer.

Five PC's describe over 80% of the total data variance (Table 3). In addition, the first and second PC's include all the variables with large positive and negative correlation coefficients and account for 45% of the total variance. Principal component loadings with similar magnitudes and equal signs indicate variables that are highly and positively correlated. On the other hand, similar magnitudes but opposite signs occur for variables that are negatively correlated. For example, as indicated by the first principal component loadings of opposite signs for the  $O(1)\cdots H(2)$  distance and the  $O-H(2)\cdots O(1)$  angle, the H-bond distance decreases as the  $OH(2)\cdots O(1)$  angle increases, as can be expected in hydrogen bonding situations. A 3-D plot of the three more important PC's, which account for 62% of the total variance, is presented in Figure 6. Proximity of two points on this graph implies structural similarity. Hence, the first general observation from Figure 6 confirms that dimers included in the same homologous series have strong structural resemblance, in particular, for both homomeric series. Within the first homomeric series, it is clear that 10-membered ring dimers, *i.e.*,  $TT'(10)$  and  $TT(10)$ , are the most similar ones. In fact, this very close resemblance is confirmed by inspection of the structural parameters in Table 2. As previously mentioned, among those pairs of heteromeric dimers with seven membered rings generated mutually by an exchange of conformations, the ones in which the first conformation is T or T' are more stable. This finding is also confirmed by the multivariate analysis, as shown in Figure 6, where the dimers started by a G or G' conformation are located in a separate group, away from the group of the other heteromeric dimers.

The first PC is largely described by structural parameters from the first monomer as well as by intermolecular structural variables and the total dimer energy. The second PC is characterized by the COC and OCC angles and the OH stretching frequency of the second monomer. The third PC has important contributions from the relaxation energies, the COH angles and the OH stretching frequency of the first monomer. As shown in Figure 6 the most stable 10-member ring dimers,  $TT'(10)$  and  $TT(10)$ , are in the middle of the graph, having first



**Figure 7.** 3-D plot of first, fourth, and fifth PC's.

and second component scores not too far from zero. This indicates that the parameters involved in these principal components, OCC(1), COC(1), OCC(2), COC(2) angles, OH distances and  $O-H\cdots O$  angles have intermediate values whereas the higher energy dimers have more extreme values for these parameters. Also these more stable dimers have large negative values for the PC<sub>3</sub> scores corresponding to low  $E_2 - E_2^0$ ,  $E_1 - E_1^0$  and COH angle values.

In order to unveil additional similarities not shown clearly by Figure 6, the fourth and fifth PC's have to be considered (Figure 7). For instance, within the heteromeric series,  $TG(7)$  and  $TG'(10)$  are confirmed as similar dimers by these PC's. On the whole, the first five PC's show that  $TG(10)$  is very similar to  $TT'(10)$  and  $TT(10)$  and that  $GG'(10)$  shows some resemblance with the latter three dimers. Once again, this points clearly to an important common feature with much structural relevance, namely, the occurrence of 10-membered intermolecular rings.

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## References and Notes

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