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## On the structures of the methanol trimer and their cooperative effects

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### Abstract

A previously non-described trimer with a C–H...O hydrogen bond has been characterized as minimum at several computational levels. This conformer allows a complete assignment of the experimental infrared cavity ringdown laser absorption spectrum (IR-CRLAS) in the O–H stretch region. B3LYP/6-311++G(d,p) charge densities of the methanol dimer and trimers analyzed with the atoms in molecules (AIM) theory indicate the hydrogens of the methyl group play a significant role on the stabilization of these clusters. On the contrary, their cooperative effects can be numerically reduced to those exhibited by the OH groups.

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### 1. Introduction

The dimer and the trimer of methanol have been the subject of multiple experimental and computational studies [1–22]. Most of the studies hitherto carried out considered a single minimum for the dimer, with an open chain structure (Fig. 1). Nevertheless, a cyclic dimer, much weaker than the open one, was proposed on the basis of B3LYP/6-31++G(2d,2p) calculations [22]. Three different minima (T1, T2, and T4, Fig. 1) had been found for the trimer by means of full geometry optimization at diverse computational levels comprising: HF/6-311++G(2d,2p) [9], MP2/6-311+G(d,p) [10],

B3LYP/6-311+G(d,p) [10]. The experimental i.r. spectrum in the O–H stretch region [19] has been explained by considering one planar cyclic trimer with a slight asymmetry (T1) [10], but also considering three structures for the trimer: T1, an open chain (T4) and a bowl conformer with symmetric ring structure (T2) [20]. The magnitude of the cooperative effects was assigned from the formation energies and harmonic frequencies of trimers and dimer [9]. Nevertheless, the origin of these cooperative effects was not investigated. Therefore, in this work we have analyzed the charge density of the methanol dimer and trimer within the framework of the AIM theory [23,24] in order to get insight about the electronic origin of the cooperative effects displayed by the trimers. This theory has been successfully applied to explain features of similar clusters and adducts [25–28]. Also, we have

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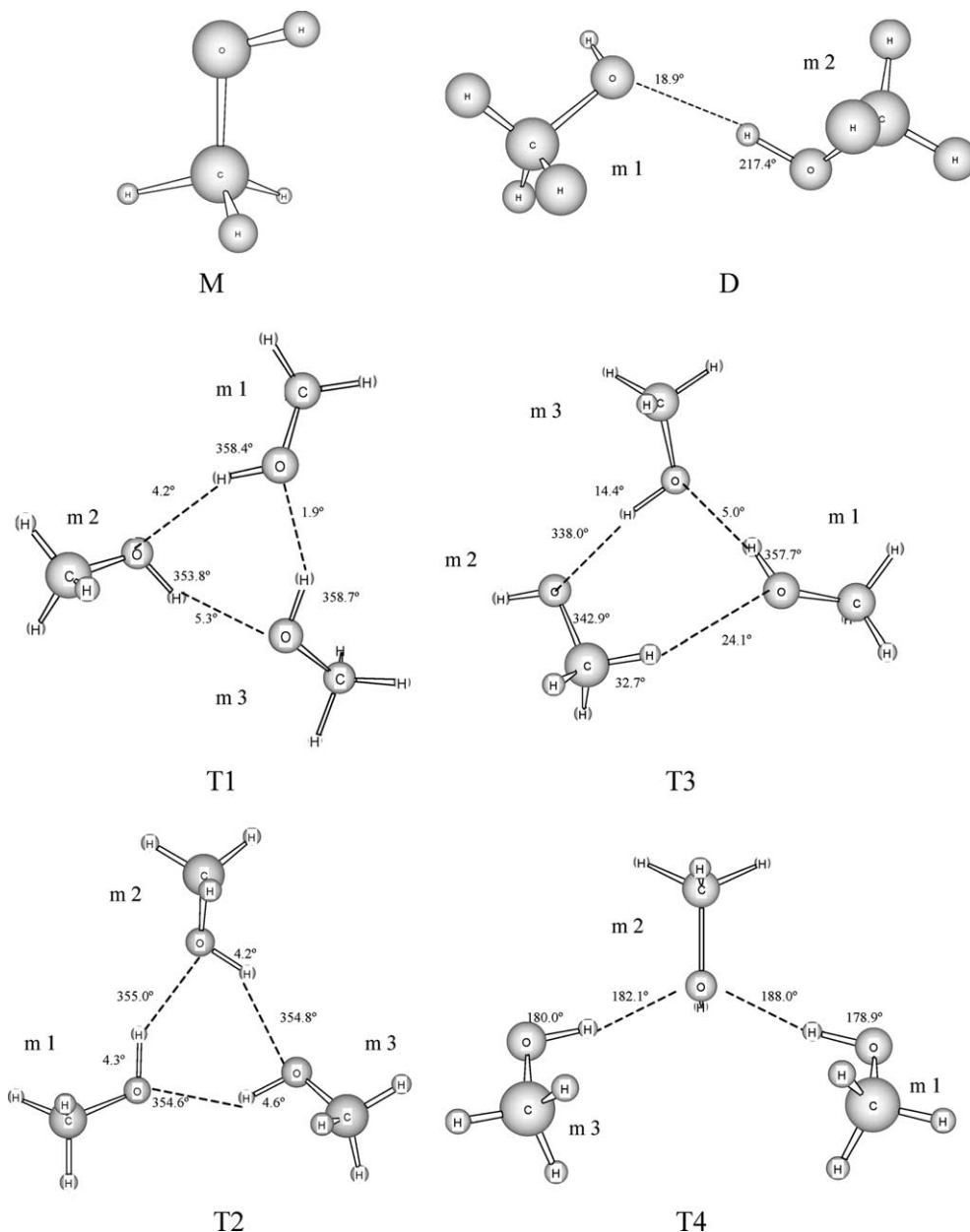


Fig. 1. Plot of the B3LYP/6-311++G\*\* optimized geometries obtained for the monomer (M), dimer (D), and trimers (T1–T4) of methanol. Values of the main dihedral angles are indicated near the corresponding central bond.

found that the energy hypersurface of the trimer contains four minima. This fact is confirmed at several computational levels and allows an improved assignment of the vibrational spectra of the O–H stretch mode.

## 2. Computational details

We have carried out a detailed exploration of the potential energy hypersurfaces of the dimer and trimer of methanol at the B3LYP/6-311++G(d,p)

computational level with the GAUSSIAN 98 [29] program. The charge densities for methanol and the minima obtained for dimer and trimer were analyzed with the AIMPAC [30] package of programs. This work is mainly concerned with atomic electron populations,  $N(\Omega)$ , and atomic energies,  $E(\Omega)$ , as well as with the properties of the bond critical points (BCP) of the electron charge density.

Dimerization and trimerization energies were obtained taking into account ZPVE and counterpoise corrections (CP) [31]. The effect of the BSSE correction on the optimized geometry was explored by considering a corrected potential energy surface [32]. No meaningful modifications were noticed in the geometries or in the CP energy corrections. Thus, in what follows we refer to the standard optimization geometries and CP corrected dimerization and trimerization energies. G3 energies were obtained for all the cyclic trimers, yielding relative values that are in close agreement (discrepancies lower than  $0.3 \text{ kJ mol}^{-1}$ ) with those obtained at the B3LYP/6-311++G(d,p) (Table 1).

The vibrational frequencies employed to calculate ZPVE corrections were obtained at the B3LYP/6-311++G(d,p) level, but those employed for assigning the infrared spectrum were obtained at the B3LYP/cc-pVTZ level.

The cooperative effect on the energy of formation,  $E_{\text{no pair}}$ , was obtained with (Eq. (1)), where  $\Delta E_{123}$  corresponds to the difference between the energy of the trimer and the three monomers, each of them in the same geometry adopted in the trimer and calculated with the total trimer basis set.  $\Delta E_{12}$ ,  $\Delta E_{13}$  and  $\Delta E_{23}$  are the same differences for the corresponding dimers, all of them calculated in the geometry of the trimer and with its entire basis set. The AIM theory allows us to break down the

cooperative effect into atomic contributions (Eq. (2))

$$E_{\text{no pair}} = \Delta E_{123} - (\Delta E_{12} + \Delta E_{13} + \Delta E_{23}), \quad (1)$$

$$\begin{aligned} E_{\text{no pair}} &= \sum \Delta E_{\text{no pair}}(\Omega) \\ &= \sum [\Delta E_{123}(\Omega) - (\Delta E_{12}(\Omega) + \Delta E_{13}(\Omega) \\ &\quad + \Delta E_{23}(\Omega))]. \end{aligned} \quad (2)$$

### 3. Structure and bonding

Fig. 1 shows the optimized structures obtained for the dimer and trimers of methanol at the B3LYP/6-311++G(d,p) level, whose energies are listed in Table 1 that also includes G3 energies for the cyclic trimers. We have extensively looked for the existence of cyclic dimers. We found a  $C_{2h}$  structure with  $O \cdots H-O$  hydrogen bonds (HB) that presented two imaginary frequencies both at the B3LYP/6-311++G(d,p) and B3LYP/6-31++G(2d,2p) surfaces. Another  $C_{2h}$  structure with  $C-H \cdots O$  HBs (that give rise to a six-membered ring), with one imaginary frequency was also obtained.

The most stable trimer (T1) presents one methyl group (m2) in approximate antiperiplanar arrangement with regard to the other two, what agrees with previous theoretical studies [10,14,16,17,20] and experimental evidences [19–21]. In the second most stable structure, T2, all the methyl groups are in approximate synperiplanar arrangement [10]. Both T1 and T2 present three  $O \cdots H-O$  hydrogen bonds. As conformer T3, characterized by a  $C-H \cdots O$  hydrogen bond (Table 2), had not been previously found, we have

Table 1

Total B3LYP/6-311++G(d,p),  $E$ , and G3,  $E^{G3}$ , molecular energies (in a.u.), dimerization and trimerization energies,  $\Delta E$  (in  $\text{kJ mol}^{-1}$ ), and cooperative contributions to the trimerization energy in cyclic conformers, as computed from total energies,  $E_{\text{no pair}}$ , and by adding their atomic components,  $\Sigma E(\Omega)_{\text{no pair}}$ , (in  $\text{kJ mol}^{-1}$ )

	$E$	$E^{G3}$	$\Delta E$	$E_{\text{no pair}}$	$\Sigma E(\Omega)_{\text{no pair}}$
M	−115.76500				
D	−231.53928		−15.8		
T1	−347.32226	−346.91121	−49.9	−10.4	−12.0
T2	−347.32096	−346.91029	−47.8	−9.9	−12.3
T3	−347.31731	−346.90751	−39.5	−6.8	−9.4
T4	−347.31103		−26.4		

Table 2

Main B3LYP/6-311++G(d,p) BCP properties for HBs in the structures here studied

	$R(\text{O}-\text{H})$	$10^3 \rho(r_c)$	$10^3 \nabla^2 \rho(r_c)$	$10^3 H(r_c)$
D	1.904	26.9	99.4	2.0
T1	1.879 <sup>a</sup>	29.4 <sup>a</sup>	103.5 <sup>a</sup>	1.2 <sup>a</sup>
	1.880 <sup>a</sup>	29.2 <sup>a</sup>	103.9 <sup>a</sup>	1.3 <sup>a</sup>
	1.898 <sup>a</sup>	27.7 <sup>a</sup>	99.8 <sup>a</sup>	1.6 <sup>a</sup>
T2	1.898 <sup>a</sup>	27.3 <sup>a</sup>	100.0 <sup>a</sup>	1.8 <sup>a</sup>
	1.898 <sup>a</sup>	27.3 <sup>a</sup>	99.9 <sup>a</sup>	1.8 <sup>a</sup>
	1.896 <sup>a</sup>	27.4 <sup>a</sup>	100.3 <sup>a</sup>	1.7 <sup>a</sup>
T3	1.834	31.8	109.8	0.8
	1.845 <sup>a</sup>	30.9 <sup>a</sup>	115.0 <sup>a</sup>	1.4 <sup>a</sup>
	2.449 <sup>b</sup>	9.6 <sup>b</sup>	29.1 <sup>b</sup>	0.9 <sup>b</sup>
T4	1.957 <sup>c</sup>	24.5 <sup>c</sup>	88.6 <sup>c</sup>	2.0 <sup>c</sup>
	1.960	24.4 <sup>c</sup>	88.1 <sup>c</sup>	2.0 <sup>c</sup>

<sup>a</sup> HB between hydroxylic H and O bonded to a H donor.

<sup>b</sup> C–H...O HB.

<sup>c</sup> HB between hydroxylic H and a double acceptor O.

also optimized it at higher computational levels (MP2/6-311++G(d,p) and QCISD/6-311++G(d,p)). All the frequencies were real at the three levels confirming T3 as a true minimum. The cyclic structure was confirmed by locating a (3,+1) critical point for the charge density (Fig. 2) with the three theoretical levels. Finally, the previously reported linear conformer, T4 [10] has also been found as a minimum in this work, though with lower stability than T3.

Table 2 lists the main BCP properties of the HBs found in methanol trimers. It can be observed ( $\rho(r_c)$  and  $R$  values) that HBs are reinforced in all the cyclic structures with regard to that in the dimer, whereas it is depleted in the open chain trimer T4, where the oxygen atom of the m2 monomer is a double acceptor. Finally, the C–H...O bond present in T3 is significantly weaker. Positive  $\nabla^2 \rho(r_c)$  and  $H(r_c)$  values indicate, that as it is a normal rule for HBs [25,26], these bonds are more associated with closed shell rather than with electron pair shared interactions.

The BCP properties (Table 3) indicate that, in the dimer, the O–H bond weakens and the C–O bond strengthens in the donor monomer (m1), whereas the C–O bond weakens and the O–H remains practically unaffected in the acceptor monomer (m2). As a sign of cooperativity [9], it can be observed that the BCP properties of the O–H bonds change more in the cyclic trimers,

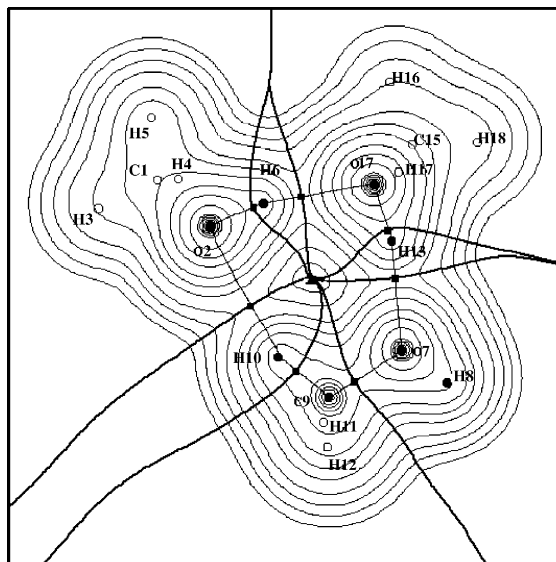


Fig. 2. Plot of the B3LYP/6-311++G\*\* electron charge density in the plane defined by the three BCP hydrogen bonds in the T3 trimer. ■ and ▲ denote, respectively, BCPs and ring critical points. Thick lines correspond to the projection of the zero flux surfaces, defining the atoms in the molecule, in the plane. Bondpaths are the lines connecting the nuclei. Projections of atoms outside the plane are represented by ○, whereas those in plane are indicated by ●.

while the variations experienced by those of C–O bonds are much smaller (the contrary is found for the monomer m3 of T3 that is involved in the C–H...O HB).

The cluster formation affects very slightly the C–H bonds. Thus the variations experienced by the bond lengths never overpass 0.003 Å, and those of  $\rho(r_c)$  only exceed  $2.10^{-3}$  a.u. in the C–H bond involved in the HB in T3 ( $3.7 \times 10^{-3}$  a.u.).

#### 4. Vibrational frequencies

The infrared cavity ringdown laser absorption spectrum (IR-CRLAS) of the methanol trimer obtained by Provencal et al. [20] in the O–H stretch region ( $3420\text{--}3520\text{ cm}^{-1}$ ) can be described as five neat peaks (two strong and three weak) and one shoulder or very weak peak (Table 4). According to their interpretation the two strong peaks and the weak peak at  $3432.1\text{ cm}^{-1}$  can be assigned to the three frequencies of T1, whereas

Table 3

Main BCP properties (in a.u.) and bond lengths (in Å) for O–H and O–C bonds in the diverse monomers of the structures here studied

		OH				CO			
		$r(\text{OH})$	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$	$r(\text{CO})$	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$
M		0.961	0.3697	−2.5036	−0.7026	1.423	0.2523	−0.4641	−0.3292
D	m1	0.1	−0.21	−1.38	−0.05	0.9	−0.79	5.51	1.38
D	m2	0.9 <sup>a</sup>	−1.19 <sup>a</sup>	1.20 <sup>a</sup>	0.82 <sup>a</sup>	−0.6 <sup>a</sup>	0.51 <sup>a</sup>	−3.91 <sup>a</sup>	−0.81 <sup>a</sup>
T1	m1	1.4 <sup>b</sup>	−2.00 <sup>b</sup>	6.12 <sup>b</sup>	2.37 <sup>b</sup>	0.0 <sup>b</sup>	−0.18 <sup>b</sup>	1.68 <sup>b</sup>	0.35 <sup>b</sup>
T1	m2	1.5 <sup>b</sup>	−1.94 <sup>b</sup>	5.35 <sup>b</sup>	2.21 <sup>b</sup>	0.1 <sup>b</sup>	−0.13 <sup>b</sup>	1.66 <sup>b</sup>	0.22 <sup>b</sup>
T1	m3	1.4 <sup>b</sup>	−2.04 <sup>b</sup>	6.49 <sup>b</sup>	2.45 <sup>b</sup>	0.0 <sup>b</sup>	−0.10 <sup>b</sup>	1.58 <sup>b</sup>	0.17 <sup>b</sup>
T2	m1	1.4 <sup>b</sup>	−1.89 <sup>b</sup>	4.84 <sup>b</sup>	−2.09 <sup>b</sup>	0.1 <sup>b</sup>	−0.04 <sup>b</sup>	1.58 <sup>b</sup>	0.04 <sup>b</sup>
T2	m2	1.4 <sup>b</sup>	−1.90 <sup>b</sup>	4.87 <sup>b</sup>	−2.10 <sup>b</sup>	0.1 <sup>b</sup>	−0.05 <sup>b</sup>	1.53 <sup>b</sup>	0.04 <sup>b</sup>
T2	m3	1.4 <sup>b</sup>	−1.89 <sup>b</sup>	4.88 <sup>b</sup>	−2.09 <sup>b</sup>	0.1 <sup>b</sup>	−0.05 <sup>b</sup>	1.58 <sup>b</sup>	0.04 <sup>b</sup>
T3	m1	1.3 <sup>c</sup>	−1.88 <sup>c</sup>	6.23 <sup>c</sup>	2.18 <sup>c</sup>	−0.6 <sup>c</sup>	0.47 <sup>c</sup>	−3.38 <sup>c</sup>	−0.73 <sup>c</sup>
T3	m2	0.0	−0.18	−1.32	−0.07	1.5	−1.45	10.24	2.55
T3	m3	1.4 <sup>b</sup>	−1.91 <sup>b</sup>	4.47 <sup>b</sup>	1.97 <sup>b</sup>	0.1 <sup>b</sup>	−0.12 <sup>b</sup>	0.82 <sup>b</sup>	0.26 <sup>b</sup>
T4	m1	0.6 <sup>d</sup>	−0.96 <sup>d</sup>	0.81 <sup>d</sup>	0.59 <sup>d</sup>	−0.4 <sup>d</sup>	0.34 <sup>d</sup>	−2.64 <sup>d</sup>	−0.52 <sup>d</sup>
T4	m2	0.2 <sup>c</sup>	−0.42 <sup>c</sup>	−1.48 <sup>c</sup>	0.14 <sup>c</sup>	1.8 <sup>c</sup>	−1.49 <sup>c</sup>	9.03 <sup>c</sup>	2.72 <sup>c</sup>
T4	m3	0.7 <sup>d</sup>	−0.96 <sup>d</sup>	0.84 <sup>d</sup>	0.60 <sup>d</sup>	−0.4 <sup>d</sup>	0.34 <sup>d</sup>	−2.58 <sup>d</sup>	−0.51 <sup>d</sup>

Values for isolated monomer are absolute, whereas those for the remaining structures are relative to those and multiplied by 10<sup>2</sup>.<sup>a</sup> Monomer with donor hydroxylic H.<sup>b</sup> Monomers with donor hydroxylic H and acceptor O.<sup>c</sup> Monomers with donor hydroxylic H. The O accepts a methylic H.<sup>d</sup> Monomers with donor hydroxylic H bonded to a double acceptor O.<sup>e</sup> Monomers with a double acceptor O.

Table 4

Wavenumbers (in cm<sup>−1</sup>) and intensities (in km mol<sup>−1</sup>) for the frequencies of methanol trimer

Experimental	Theoretical			
Provencal et al. [20]	B3LYP/cc-pVTZ			B3LYP/6-311+G(d,p)
	This work			Mó et al. [10]
	T1	T2	T3	T1
3503.7 (436) <sup>a</sup>			3609 (671)	3625
3494.6 (218) <sup>a</sup>		3588 (792)		3623
		3589 (789)		
3473.2 (1200) <sup>a</sup>	3582 (828)			3612
3467.1 (1327) <sup>a</sup>	3576 (849)			3600
3454.5 (218) <sup>a</sup>		3556 (567)		
3432.1 (255) <sup>a</sup>	3510 (12)			3546
(unobserved)		3526 (7)	3842 (39)	

Theoretical values are shown in the same line that the experimental peak to whom they are assigned.

<sup>a</sup> Relative intensities estimated from Fig. 7 of [20].

the remaining signals are due to T2, though they state that the very weak peak at 3454.5 cm<sup>−1</sup> cannot be conclusively assigned. The presence of a third trimer T3, allows us to make a different assignment that solves at least two shortcomings of the previous one. Thus, according to our B3LYP/cc-pVTZ frequency calculations (Table 4), the

signal at 3454.5 cm<sup>−1</sup> can be assigned to the 3556 cm<sup>−1</sup> frequency of T3, that presents a strong intensity that could make it observable (though very weakly) in spite of the small population of the conformer. Also, the frequency of 3609 cm<sup>−1</sup> presented by T3 can be used to get a better assignment of the weak signals at 3494.6 and 3503.7 cm<sup>−1</sup>

(with significantly different intensities and frequencies) that were previously assigned to the two nearly degenerate frequencies of T2 (3588 and 3589  $\text{cm}^{-1}$ ) that also present very similar intensities. We propose these two peaks can be the result of the superposition of three active frequencies.

The frequencies calculated in this work indicate larger redshifts for T1 and T2 than for T3 where cooperative effects should be lower because of the replacement of one  $\text{O-H}\cdots\text{O}$  HB by a  $\text{C-H}\cdots\text{O}$  HB.

### 5. Atomic properties and cooperative effects

The variations experienced by  $E(\Omega)$  and  $N(\Omega)$  in the dimer and trimer formation display good linear relationships when we distinguish between O atoms, hydroxylic hydrogens, C atoms and methyl hydrogens (Fig. 3). This indicates that the cluster

stabilization is due to the charge rearrangement. It can also be observed that the variations experienced by these properties for the set of the three methyl hydrogens are of the same order than those presented by O or hydroxylic H. Thus, methyl hydrogens play an important role in the cluster formation.

The cooperative effects in methanol trimers were studied in previous works centering on the OH unit and in the variations experienced by vibrational frequencies, dipole moments, bond lengths, and charge density at the BCPs.  $E_{\text{no pair}}$  was always obtained from molecular energies [9,10,15].

The values obtained for trimerization energies, include an important  $E_{\text{no pair}}$  contribution (Table 1). It can be observed that  $E_{\text{no pair}}$  values obtained from molecular energies and by summing the corresponding atomic contributions differ by less than 2.6  $\text{kJ mol}^{-1}$ . Though these discrepancies are around the same that many atomic  $E_{\text{no pair}}(\Omega)$

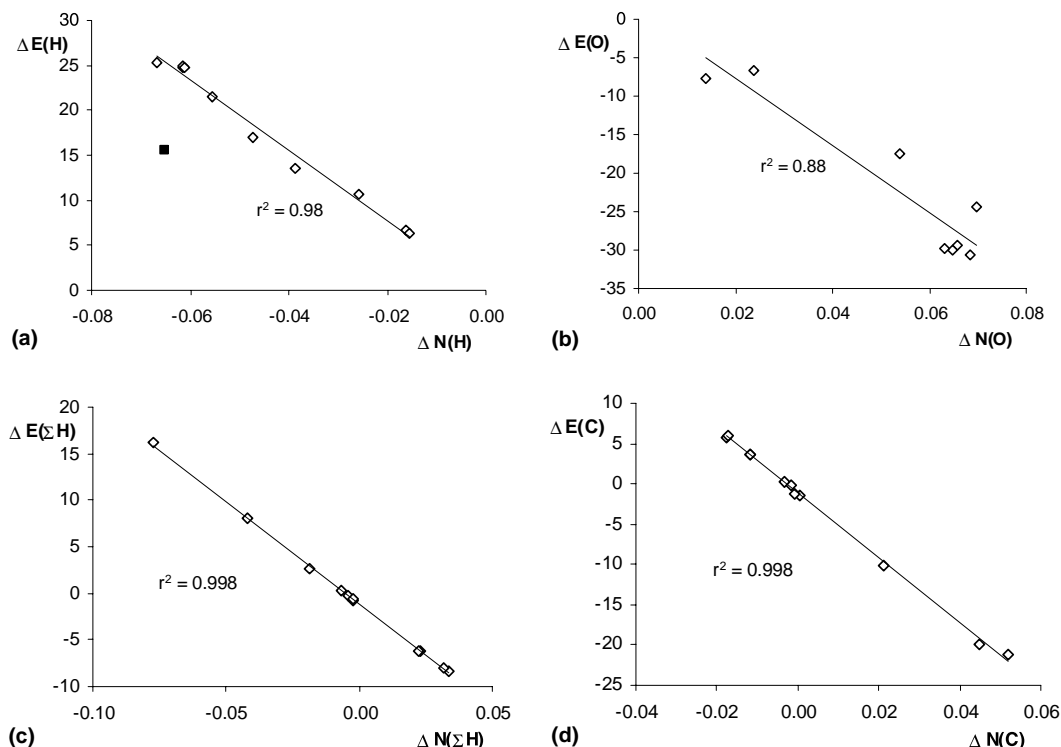


Fig. 3.  $\Delta E(\Omega)$  vs.  $\Delta N(\Omega)$  plots for diverse atoms (hydroxylic hydrogen (a), oxygen (b), carbon (c), and summation of the methyl hydrogens (d)) of the monomers of the methanol trimers. The variation experienced by the methyl hydrogen involved in the  $\text{C-H}\cdots\text{O}$  bond is represented by ■ in (a). All  $\Delta N(\Omega)$  values are in a.u. and all  $\Delta E(\Omega)$  values are in  $\text{kcal mol}^{-1}$ .

Table 5  
Atomic,  $E_{\text{no pair}}(\Omega)$ , and monomer contributions to cooperative energy

	$E(\text{O}_2)$	$E(\text{H}_6)$	$E(\text{C}_1)$	$E(\text{H}_3)$	$E(\text{H}_4)$	$E(\text{H}_5)$	$E(\text{m1})$
<i>Monomer m1</i>							
T1	−10.4	3.7	−0.2	−1.1	1.8	0.6	−5.7
T2	−8.2	4.2	−1.3	−1.1	1.7	0.9	−3.8
T3	−5.5	3.5	1.4	−1.5	−0.1	1.6	−0.6
	$E(\text{O}_7)$	$E(\text{H}_8)$	$E(\text{C}_9)$	$E(\text{H}_{10})$	$E(\text{H}_{11})$	$E(\text{H}_{12})$	$E(\text{m2})$
<i>Monomer m2</i>							
T1	−7.2	4.4	0.1	−1.1	1.8	1.0	−1.1
T2	−9.2	4.4	−0.9	−1.1	1.7	0.9	−4.2
T3	9.3	1.3	−3.5	6.3 <sup>a</sup>	1.3	0.8	15.3
	$E(\text{O}_{14})$	$E(\text{H}_{13})$	$E(\text{C}_{15})$	$E(\text{H}_{16})$	$E(\text{H}_{17})$	$E(\text{H}_{18})$	$E(\text{m3})$
<i>Monomer m3</i>							
T1	−9.1	3.9	−1.1	−1.2	1.7	0.5	−5.3
T2	−8.8	4.3	−1.3	−1.1	1.6	0.9	−4.3
T3	−18.7	0.2	−6.2	−0.6	0.1	1.0	−24.2

All values in  $\text{kJ mol}^{-1}$ .

<sup>a</sup> Methyl H involved in HB.

contributions, they are about the same as those obtained between the total molecular energy and the summation of atomic energies in the molecule. Also, they only represent a 15% for T1  $E_{\text{no pair}}$ . Both facts allow, at least, a qualitative interpretation of  $E_{\text{no pair}}(\Omega)$  values (Table 5).

The atomic contributions to the non-pair energy listed in Table 5 led us to conclude that, in the three cyclic trimers, the total cooperative energy can be obtained by adding the contributions of the three OH groups (−14.7, −13.3, and −9.5  $\text{kJ mol}^{-1}$  for T1, T2, and T3, respectively). Nevertheless, it has to be taken into account that all the atoms in the methyl groups display non-vanishing  $E_{\text{no pair}}(\Omega)$  values. In fact, all the methyl hydrogens in gauche present positive  $E_{\text{no pair}}(\Omega)$  values, whereas those in anti have negative  $E_{\text{no pair}}(\Omega)$  values. If we exclude the monomer m1 in T3, all the carbon atoms display negative contributions to this quantity.

Overall, the additional stabilization due to cooperative effects is mainly originated in the charge gained by the oxygen when it acts simultaneously as donor and acceptor ( $N(\text{O})$  is 9.121 a.u. in T2 and varies from 9.120 to 9.123 a.u. in T1, whereas it only reaches 9.109 a.u. in the donor oxygen and 9.069 a.u. in the oxygen acceptor in D).

The specific structure of the trimer T3 is also reflected by its  $E_{\text{no pair}}(\Omega)$  values. Thus,  $E_{\text{no pair}}(\Omega)$

is positive for the oxygen of m2 (that is only involved in one HB) and much more negative than in T1 and T2 for the oxygen of m3. The important decrease of  $N(\text{H}_{10})$  (−0.064 a.u.) due to its participation in the  $\text{C-H}\cdots\text{O}$  HB is also related to the exceptionally positive value of  $E_{\text{no pair}}(\text{H}_{10})$ .

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