AIM characterization of hydrogen bonds in dimers of methoxymethane

3 AUTHORS, INCLUDING:

Ricardo Mosquera
University of Vigo
144 PUBLICATIONS **1,812** CITATIONS

AIM characterization of hydrogen bonds in dimers of methoxymethane

A. Vila[a], R.A. Mosquera[b,*], J.M. Hermida-Ramón[c]

[a]*Departamento de Física Aplicada, Universidade de Vigo, Facultade de Ciencias do Campus de Ourense, E 32004 Ourense, Spain*
[b]*Departamento de Química Física, Universidade de Vigo, Facultade de Ciencias do Campus de Vigo, E 36200 Vigo, Spain*
[c]*Departamento de Química Física, Universidade de Santiago de Compostela, Facultade de Química, E 15700 Santiago, Spain*

Abstract

The minimum energy structures of the methoxymethane dimers have been analyzed by means of the atoms in molecules theory (AIM) by employing HF/6-311++G(d,p) wave functions. The position and properties of the bond critical points, and the variation of several integrated properties of the O and H atoms (electronic population, atomic energy, module of the dipole moment and atomic volume) from the monomer to the dimer, clearly show the presence of C–H···O hydrogen bonds in the five minima of the dimer. The binding energies for every minimum were also obtained and their order has been interpreted in terms of the AIM results. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio calculations; AIM theory; Dimerization; Methoxymethane

1. Introduction

Molecular association plays a paramount role in the study of pure fluids and their mixtures. In fact, many efforts have been expended along the time on describing it in a long series of systems, modeling its effects on several properties, or developing theories to explain and predict the formation, structure, and properties of molecular aggregates [1]. From a physical point of view, molecular association is the result of all the specific interactions involved in a given system. Thus, hydrogen bond and van der Waals interactions have been considered as the origin of the stability of many molecular aggregates. In spite of the substantial differences between covalent bonds

and van der Waals interactions, molecular orbital calculations are so adequate to describe the latter as the former. Supermolecule calculations [2–4], which consider the aggregation complex (supermolecule) as a set of nuclei, and electrons and the energy involved in its formation as the difference between the energy of the complex and the addition of the energy of the isolated monomers, became a standard procedure for the study of dimers, trimers and larger molecular associations [5–6]. On the other hand, the Atoms in Molecules Theory (AIM) [7] provides a universally applicable tool for the classification of the bonding interactions that take place in any molecular system, even inside a supermolecule [8]. It also allows, without invoking any arbitrary criterion, a unique division of a molecule into disjoint subsystems that verify the theorems of Quantum Mechanics and correspond to the atoms inside the molecule. The average value of any property can be calculated for each of these

* Corresponding author. Tel.: +34-98-681-2298; fax: +34-98-681-2382.

E-mail address: mosquera@uvigo.es (R.A. Mosquera).

subsystems; thus, AIM theory can be employed to monitorize how the properties of each atom in the monomer are affected by the formation of the dimer or cluster considered [9].

In the present paper, and continuing a systematic study of the properties of alkyl ethers [10], we attempt to analyze the changes on the atomic and bond properties of the methoxymethane molecule upon dimerization. We have also considered the properties of the intermolecular bond critical points, looking for their relationship with the dimerization energies. Special attention has been paid to characterize the nature of the C–H···O contacts in order to confirm if they can be considered as hydrogen bonds (HB) as was previously proposed [11]. This characterization was carried out on the basis of several charge density based criteria [12,13]. C–H···O HBs are usually classified among the denominated weak hydrogen bonds. According to Jeffrey [14], this term includes all those HBs whose binding energy is between 1 and 4 kcal mol^{-1}, though other limits for the binding energy (i.e. 2.4 and 12 kcal mol^{-1}) have been proposed [15]. So, this term contains HBs like those in the gas phase adducts of HX (X = F, Cl, Br, CN) with N_2, CO, OCS, or CO_2 [16] (with binding energies of about 3 kcal mol^{-1}), the C–H···O=C bond in the dimer of the acetic acid [17], or the HC≡CH···O=CH$_2$ bond in this gas phase adduct, whose binding energy was computed as 1.15 kcal mol^{-1} at the MP2/D95++(d,p) level [18]. Though the potential role of the C–H bond as HB donor was originally proposed in 1937 by Glasstone [19], there was a long-standing controversy on the existence of the C–H···O hydrogen bond. Nowadays this controversy is clearly resolved accepting it as part of the non-conventional hydrogen bonds (recently reviewed by Alkorta et al. [20]). Several detailed revisions on C–H···O hydrogen bond have been recently published [13,14,21–23].

2. Computational details

The topological analysis and the evaluation of all local properties were performed using MORPHY98 [24]. The integrations over the atomic basins were carried out using the AIMPAC program series[1] [25] with HF wave functions obtained with the GAUSSIAN 94 program [26], employing the 6-311++G(d,p) [27] basis set. The geometry optimization was carried out in two steps: first an HF/6-31G(d) [28] optimization of the five stationary points obtained in a previous exploration of the potential hypersurface of the dimer [11], followed by a full HF/6-311++G(d,p) optimization. The harmonic vibrational frequencies were also calculated at the HF/6-311++G(d,p) computational level in order to characterize the optimized stationary points as minima or first-order (or higher-order) saddle points, and to evaluate the corresponding zero point vibrational energy (ZPVE). The ZPVEs were scaled down by the empirical factor 0.89, which accounts for the overestimation of vibrational frequencies at the theoretical level here employed [29].

The total energies, E, of the five minima found for the methoxymethane dimer are listed in Table 1, along with the corresponding values of the scaled ZPVEs. The energy of dimerization (D_e) of each minima was obtained as the difference shown in Eq. (1), where $E((CH_3OCH_3)_2)$ is the energy of the dimer after BSSE correction:

$$D_e = E((CH_3OCH_3)_2) - 2 \cdot E(CH_3OCH_3) \qquad (1)$$

The basis set superposition error (BSSE) in the energy of dimerization was corrected using the full counterpoise method [30]. The dimerization enthalpies at 0 K (ΔH_0^0) were obtained by adding to the D_e values defined above, the corresponding ZPVE corrections of the monomer and the dimer. Table 1 also displays the integration errors expressed as differences between total properties and those obtained by summation of the properties of the fragments $[\Sigma N(\Omega) - N$ or $\Sigma E(\Omega) - E]$. The values obtained for these magnitudes warrant that the partition of the total molecular properties into atomic properties has been carried out with an enough degree of accuracy. Only the small variations undergone by the electron population of several non-hydrogen atoms between the monomer and some of the dimer structures (**III–V**) can be significantly affected by integration errors. The following atomic properties were integrated for all the oxygen and hydrogens interconnected by

---

[1] Contact bader@mcmail.cis.mcmaster ca.

Table 1
Total energies, E; zero point vibrational energies, ZPVE; basis set superposition error, BSSE; dimerization energies, D_e; dimerization enthalpies ΔH_0^0 at 0 K and errors in the integrated energies and populations for the different methoxymethane dimers

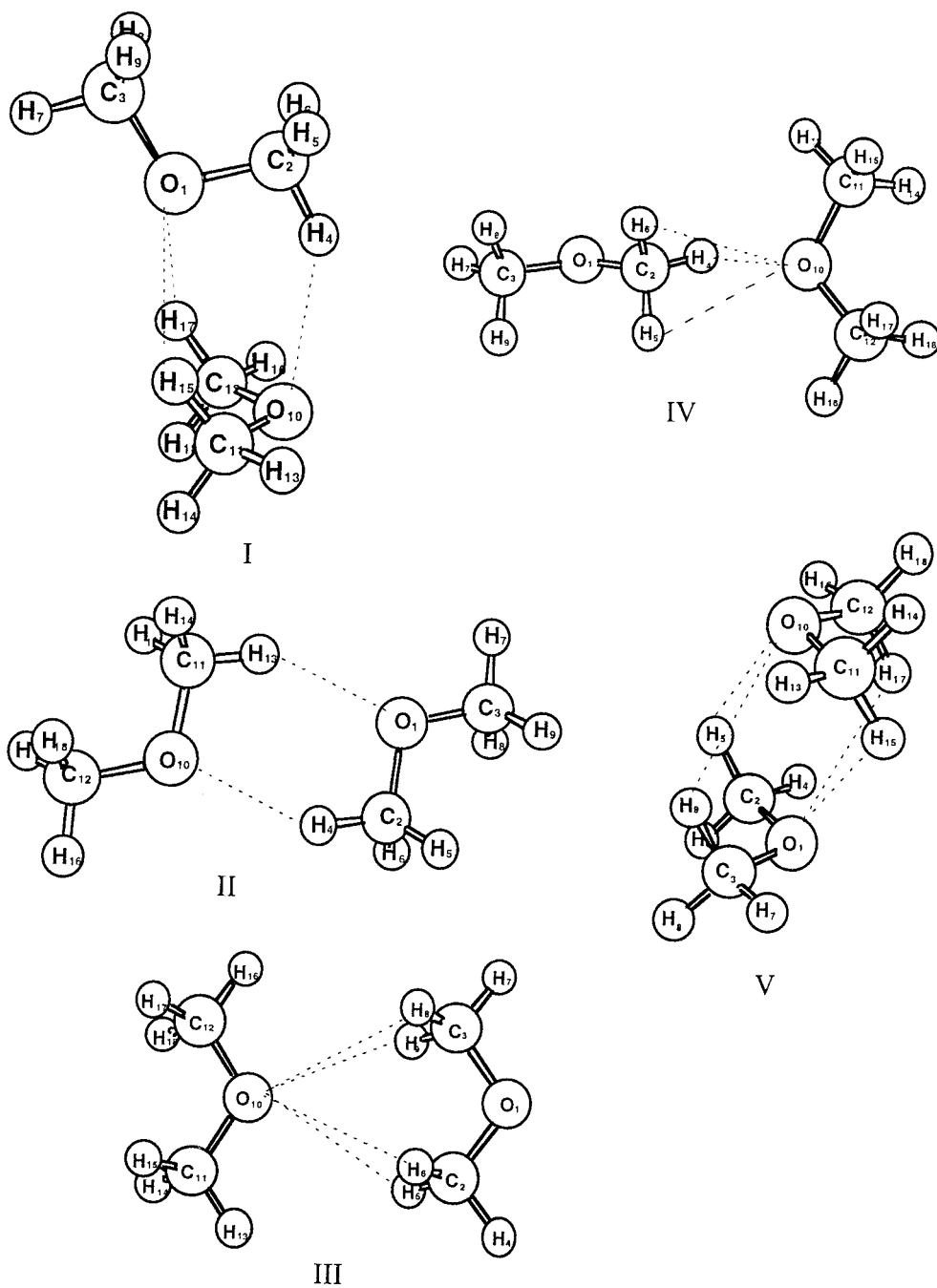| Compound	E (a.u.)	ZPVE (kJ mol^{-1})	BSSE (kJ mol^{-1})	D_e (kJ mol^{-1})	ΔH_0^0 (kJ mol^{-1})	$E - \Sigma\, E(\Omega)$ (kJ mol^{-1})	$N - \Sigma N(\Omega)$ (a.u.)
(CH$_3$)$_2$O	$-$154.11231	222.73	–	–	–	1.36	0.0016
I	$-$308.22653	447.73	1.32	$-$4.98	$-$2.71	4.73	0.0063
II	$-$308.22655	447.64	0.93	$-$5.05	$-$2.87	0.81	0.0014
III	$-$308.22538	445.85	0.32	$-$1.95	$-$1.56	3.47	0.0042
IV	$-$308.22568	446.16	0.70	$-$2.76	$-$2.06	5.09	0.0051
V	$-$308.22582	447.14	1.18	$-$3.13	$-$1.45	1.52	0.0017

Fig. 1. Nomenclature and arrangement of the monomers in the five minima (**I–V**) found in the HF/6-311++G(d,p) potential surface of methoxymethane dimer.

Table 2
Intermolecular coordinates (Å and degrees) for the different structures of methoxymethane dimmer

Compound	R(O10–O1)	A(O10–O1–C2)	D(O10–O1–C2–C3)	A(C11–O10–O1)	D(C11–O10–O1–C2)	D(C12–O10–C11–O1)
I	3.758	74.8	179.9	78.4	−121.4	71.8
II	3.936	69.7	−179.9	69.7	−179.9	−179.8
III	4.764	59.3	5.6	122.5	−4.5	179.9
IV	4.939	3.9	−174.3	121.2	107.4	−159.7
V	4.107	74.1	92.9	74.1	180.0	92.9

intermolecular bondpaths in every one of the minima obtained for the dimer: atom electron population $N(\Omega)$, electronic energy $E(\Omega)$, module of the dipole moment of the fragment $\mu(\Omega)$, and atomic volume $v(\Omega)$ of the region bounded by the interatomic surface and the contour defined by an electron charge density of 0.001 a.u. The intermolecular bonds were characterized in terms of the properties at the bcp, viz. the eigenvalues of the Hessian matrix for the electron charge density, λ_i, bond ellipticity ϵ, (defined as $\epsilon = (\lambda_1/\lambda_2) - 1$ where $|\lambda_1| > |\lambda_2|$ are the two negative eigenvalues of the above Hessian matrix), charge density, ρ_c, the laplacian of the charge density, $\nabla^2\rho_c$, the total energy density, H_c, and the distances from every nucleus to the bcp, r_H and r_O.

3. Results and discussion

3.1. Structures

The optimized structures for the five minima found in the HF/6-311++G(d,p) potential surface of methoxymethane dimer are shown in Fig. 1 and the corresponding intermolecular coordinates are summarized in Table 2. In the lowest-energy structure, labeled as **II**, the two methoxymethane molecules and the two C–H···O interactions lie in the same plane. Because of the symmetry of this conformation, a binding energy of some 2.5 kJ mol^{-1} can be unambiguously assigned to each hydrogen bond. The conformation **I**, that was calculated to be only 0.07 kJ mol^{-1} less stable than conformation **II**, can be considered roughly isoenergetic at this level of calculation. It should be noted, however, that the ordering of the stationary points **II** and **I** could change by using electron correlation and/or by augmenting the basis functions. In spite of their similar binding energy, a

significant shortening (0.18 Å) in the intermolecular distance O_1–O_{10} is found on going from structure **II** to structure **I**. Two of the donor hydrogens in structure **I** are out of the monomer COC plane (*gauche* hydrogens) and another one is in-plane (*trans* hydrogen). The three hydrogen bonds in structure **I** are not equal and hence we cannot strictly assign a binding energy per hydrogen bond. Structure **III** corresponds to a parallel arrangement of two methoxymethane molecules lying almost in the same plane where the O_1–O_{10} intermolecular distance is noticeable higher than that obtained in the two most stable structures. The four HBs in structure **III** are equivalent and a binding energy of some 0.5 kJ mol^{-1} per HB can be considered. Though this binding energy is quite small, this interaction clearly verifies geometrical and charge density criteria assigned to a hydrogen bond. Structure **IV** corresponds to a spatial arrangement of the two monomers where O_1, C_2 and O_{10} are nearly aligned ($\alpha = 3.9°$). The three C–H···O contacts can not be deemed as equivalent, either. Finally, for structure **V**, the distance between the two oxygen atoms is noticeable shorter than that obtained for structures **III** and **IV**. Structure **V** presents up to four hydrogen bonds that can be considered as equivalent; therefore we can assign a binding energy of some 0.8 kJ mol^{-1} to each one. Once again this interaction fulfills the remaining criteria here considered for hydrogen bonds.

The optimized structural parameters for the monomer and the five dimers of methoxymethane are presented in Table 3. The electron diffraction data for $(CH_3)_2O$ [31] ($r_{CO} = 1.410$ Å and $\alpha_{COC} = 111.7°$) compare well with the calculated geometrical parameters optimized at the HF/6-311++G(d,p) level. As regards the intramolecular coordinates, inspection of Table 3 shows that the geometry of each monomer remains almost unchanged upon

Table 3
Selected geometrical parameters of methoxymethane and its five dimers here studied. (distances in Å and angles in degrees)

	$(CH_3)_2O$	I	II	III	IV	V
R(C2–O1)	1.391	1.394	1.395	1.392	1.394	1.394
R(C2–O1)	1.391	1.391	1.391	1.392	1.399	1.392
A(C2–O1–C3)	114.1	114.1	114.1	113.9	114.0	113.9
R(C11–O10)		1.393	1.395	1.392	1.392	1.394
R(C12–O10)		1.393	1.391	1.392	1.392	1.392
A(C11–O10–C12)		113.8	114.1	114.0	114.1	113.9

dimerization. The largest variation of the geometry takes place in the region of the donor monomer that involves the greatest number of C–H···O bonds (C_2–O_1 in the **IV** structure or C_2–O_1 and C_{11}–O_{10} in the tandem hydrogen bonded structure **II**).

3.2. Bond properties

The number of critical points of all types is governed by a fundamental theorem of the topology, the Poincaré–Hopf relationship [32], which establishes that the number of nuclei n, bond critical points b, ring critical points r, and cage critical points c, are related by Eq. (2).

$$n - b + r - c = 1 \tag{2}$$

Dimerization of methoxymethane, as shown in Fig. 1, brings about the creation of more than one new intermolecular bond critical point; thereby the Poincaré–Hopf relationship demands the creation of at least one ring critical point. Thus, the planar cluster, labeled as **II**, presents two intermolecular bond critical points and one ring critical point as illustrated by Fig. 2.
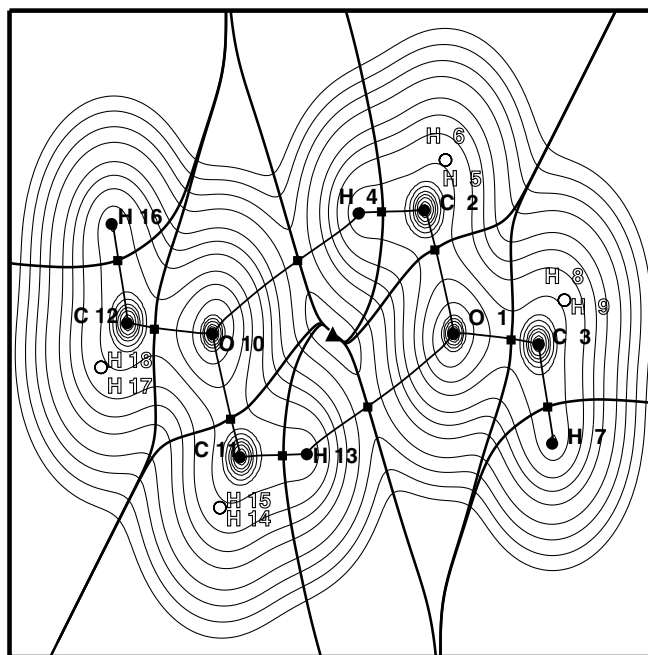
Fig. 2. Superposition of the contour lines (thin) of the charge density with the molecular graphs (bold) and interatomic surfaces (bold) of the most stable minimum (**II**) of the dimer of dimethoxymethane. Nuclei are represented by (●) and the symbols (■) and (▲) represent the locations of bond and ring critical points, respectively. Nuclei in the plane of the plot are shown in bold type, whereas those which are out of the plane are shown in open face.

Table 4
Calculated properties at the HB critical point for the five dimer structures and for conventional HB adducts and other C–H···O HBs (all values in a.u.)

Compound	Bond	λ_1	λ_2	λ_3	ρ_c	$\nabla^2\rho_c$
I	H15,17–O1	−0.0026	−0.0024	0.0171	0.0031	0.0121
	H4–O10	−0.0037	−0.0037	0.0224	0.0042	0.0148
II	H13–O1, H4–O10	−0.0046	−0.0042	0.0265	0.0050	0.0177
III	H5,6–O10	−0.0004	−0.0003	0.0049	0.0009	0.0042
	H8,9–O10	−0.0007	−0.0005	0.0064	0.0011	0.0052
IV	H4–O10	−0.0014	−0.0007	0.0138	0.0024	0.0116
	H5,6–O10	−0.0013	−0.0006	0.0082	0.0014	0.0064
V	H5,9–O10, H15,17–O1	−0.0018	−0.0017	0.0128	0.0022	0.0092
FH···OH$_2$[ac]	FH–O	−0.0425	−0.0399	0.2094	0.0276	0.1260
FH···ClH[ac]	FH–Cl	−0.0067	−0.0062	0.0423	0.0072	0.0294
NCH···OH$_2$[bc]	NCH–O	−0.0227	−0.0208	−0.1016	0.0181	0.0581
CH$_4$···OH$_2$[bc]	CH$_3$H–O	−0.0041	−0.0038	0.0249	0.0041	0.0170

[a] Ref. [12].
[c] Values computed with HF/6-311++G(d,p)//HF/6-31G(d) wave functions.
[b] Ref. [33].

In the light of the local properties at the C–H···O intermolecular bond critical points in the five dimers of methoxymethane under investigation (Table 4), the weak character of these interactions can be clearly established:

(a) For all the intermolecular bond critical points we note that the two negative eigenvalues of the Hessian, λ_1, λ_2, have very small magnitudes, which reflects the low concentration of charge density at the bond critical point. The values obtained for these quantities at the same computational level for conventional HBs, such as those presented by FH···OH$_2$ [12] or NCH···OH$_2$ [33] adducts, are around 10–20 times the largest values reported here (Table 4). Nevertheless, the values obtained for dimers **I** and **II** are quite close to those previously computed for the C–H···O hydrogen bond of the CH$_4$···OH$_2$ complex [33] and to the more conventional HB of the FH···ClH system [12]. The decrease that can be observed for λ_1 and λ_2 between structures **I–II** and **III–V** can be compared to the one observed between FH···OH$_2$ and FH···ClH. This can be used to support that all the CH···O interactions presented in the five structures of the CH$_3$OCH$_3$ dimer are hydrogen bonds though they have different strength.

It is also noteworthy the similar magnitude of the two negative curvatures, that indicates the uni-formity of charge density around the intermolecular bond critical points. Consistently with the binding energy ordering, the largest values of the negative curvatures correspond to the intermolecular bond critical points of the most stable dimer **II**.

(b) The computed values of the positive curvature, λ_3, were found to be very small, but similar to those previously obtained in C–H···O intermolecular interactions [13,33]. According to Bader [7], the small value of this curvature indicates that it is easy to "move" the position of the critical point along the bondpath and therefore the bond and its properties are more affected by changes in the molecule. In agreement with the values of the binding energy at this level of calculation, λ_3 values are larger for structures **I** and **II** than in the less stable conformers **III–V**.

(c) The ellipticity of the bond, ϵ, also provides a measure for its structural stability. However, the very small negative eigenvalues of the Hessian at the bond critical point discard any reasonable interpretation of the computed values.[2]

(d) The low values obtained for the charge density, ρ_c, at the intermolecular bond critical points also

---

[2] The values of the ellipticity of the intermolecular bonds studied in this work vary from 0.002 to 1.622. This large variation comes only from the very poor significance of the very small λ_1 and λ_2 values and is not susceptible of any interpretation.

Table 5
Mutual penetration of hydrogen and oxygen atoms in HBs (all values in Bohr)

Compound	Bond	r_O^0	r_O	Δr_O	r_H^0	r_H	Δr_H	$\Delta r_O + \Delta r_H$
I	H15,17–O1	3.369	3.264	0.105	2.769	2.407	0.362	0.467
	H4–O10	3.534	3.109	0.425	2.774	2.212	0.562	0.987
II	H13–O1, H4–O10	3.731	3.038	0.693	2.692	2.103	0.589	1.282
III	H5,6–O10	3.445	3.212	0.233	2.836	2.561	0.275	0.508
	H8,9–O10	3.447	3.213	0.234	2.834	2.562	0.272	0.506
IV	H4–O10	3.452	3.204	0.248	2.712	2.321	0.391	0.639
	H5,6–O10	3.452	3.305	0.147	2.719	2.326	0.393	0.540
V	H5,9–O10, H15,17–O1	3.527	3.261	0.266	2.899	2.589	0.310	0.576

reflect the weak character of these bonds. These values fall in the range 0.0008–0.0052 a.u. and are similar to those previously found in intermolecular C–H···O bonds [13,33]. The values of the charge density at the intermolecular bond critical points are found to parallel those of the binding energy, the stabilization of the cluster is reflected in increased ρ_c values (structures **I** and **II**). Correlations between the binding energy and the sum of the charge densities at the intermolecular bond critical points, $\Sigma\rho_c$, have been previously established yielding a linear correlation coefficient greater than 0.99 [13]. For the calculations reported here, the fit is significantly worse (linear correlation coefficient of 0.91). It is reasonable to expect this relationship to improve by using electron correlation.

It has been found that ρ_c presents, in all the structures, larger values for the HBs involving H in trans arrangement than those HBs where the H is in gauche disposition. This indicates the larger strength of the former HBs.

(e) The small and positive values of $\nabla^2\rho_c$ indicate that a small charge concentration takes place along the bond-path linking the two nuclei. It can be observed that as ρ_c increases, the positive curvature of ρ at the critical point increases in value and the magnitudes of the two negative curvatures simultaneously undergo a decrease, thus $\nabla^2\rho_c$ values increase. Hence, the behavior of $\nabla^2\rho_c$ is parallel to that exhibited by ρ_c. $\nabla^2\rho_c$ values in the C–H···O bonds of structures **III** and **V** are abnormally low if compared with those previously obtained for another C–H···O hydrogen bonds [13,33].

(f) The total energy density at the bond critical point, H_c, has also proven to be a useful parameter to complement the Laplacian in the analysis of bond types [34]. Due to the small H_c values (ranging from 3×10^{-4} to 5×10^{-4}), no distinction can be made between the intermolecular interactions in the five conformers of methoxymethane dimer.

(g) Hydrogen bonding can also be monitorized in terms of the mutual penetration of the van der Waals envelopes of the hydrogen and acceptor atoms [12]. For every C–H···O interaction, we have computed the difference between the nonbonded radii (r_O^0 and r_H^0) and the corresponding bonded radii (r_O and r_H). The nonbonded radii were estimated as the distance from the nucleus to the 0.001 a.u. contour of the charge density, in the direction of the intermolecular C–H···O interaction. Except for the structure **II** (see Table 5), the hydrogen atom was found to penetrate more than the oxygen. In agreement with the binding energy ordering, the largest mutual penetration of H and O atoms takes place in the most stable structure **II**, followed by the almost isoenergetic structure **I**. For the remaining structures, **III–V**, the computed mutual penetration is about half of that found in the structure **II**.

3.3. Atomic properties

In order to study the possible distortion of the isolated molecule charge density experimented upon the dimerization, the electron population of the atoms in the isolated monomer (Table 6) and the different conformers of the dimer were computed. The hydrogen atom in the COC plane of the free monomer was

Table 6
Integrated atom properties in CH_3OCH_3. (all values in a.u. (Hydrogens a and b are in and out of the heavy atom plane, respectively))

	$N(\Omega)$	$E(\Omega)$	$\mu(\Omega)$	$v(\Omega)$
O	9.274	− 75.5761	0.142	86.95
C	5.256	− 37.3378	0.643	48.76
H[a]	1.011	− 0.6358	0.125	36.99
H[b]	1.047	− 0.6473	0.134	38.81

found to be less populated by 0.0037 a.u. than the out of plane ones. This is consistent with the explanation of the anomeric effect through a charge transfer from a lone pair to the trans C–H bond [35,36].

Hydrogen bonding has been interpreted as the result of the penetration of H and O nonbonded densities, which results in a charge transfer from the donor to the acceptor atoms [12]. This loss of charge of the hydrogen (accompanied by a decrease in its atomic volume and dipolar polarization) and the concomitant energetic destabilization are shown in Table 7. Donor hydrogen atoms in trans with regard to the COC plane (structures **II** and **I**) undergo the largest vari-

Table 7
Atomic properties of the hydrogen atoms involved in HBs relative to those of the free monomer. (all values in au. H column contains the nomenclature of the hydrogens)

Compound	H	$\Delta N(H)$	$\Delta E(H)$	$\Delta\mu(H)$	$\Delta v(H)$
I	15,17	−0.025	0.0085	−0.009	−0.26
	4	−0.026	0.0093	−0.011	−0.22
II	4, 13	−0.038	0.0139	−0.016	−0.39
III	5, 6	−0.006	0.0018	−0.003	−0.17
	8, 9	−0.004	0.0011	−0.001	−0.12
IV	4	−0.005	0.0015	−0.001	−0.16
	5, 6	−0.003	0.0007	−0.001	−0.17
V	5, 9, 15, 17	−0.005	0.0013	−0.002	−0.13

ations in the atomic properties, accounting for the above-mentioned higher binding energy of these two clusters and the higher ρ_c values of these C–H···O bonds. Though for **III**–**V** structures, $\Delta N(H)$ values (Table 7) are of the same order of magnitude than the total integration error (Table 1), these variations in the electron population can be considered reliable. This reliability is supported on the fact that the atomic properties of all hydrogens were always integrated with $L(H)$ values smaller than 10^{-5} a.u. This warrants that $N(\Omega)$ values are obtained with absolute errors much smaller than 10^{-3} a.u. [10].

Our calculations indicate (Table 8) that the donor C enlarges its electron population in the structures **I** and **II** of the dimer. On the other hand, the acceptor oxygens also enlarge their electron population, though these changes are smaller than those experimented by the donor C. The generalization of these trends to structures **III** and **V** cannot be safely established because $\Delta N(O)$ and $\Delta N(C)$ values for these structures fall inside the limits of the integration errors.

It is also noteworthy that each of the monomeric units remains nearly neutral upon dimerization. The charges of all the monomers add up to an average value of 0.002 a.u. (the maximum value attained was that of 0.006 a.u., in the monomer corresponding to O_{10} in structure **I**). As these values are lower than the total error in the integration of $N(\Omega)$, we cannot conclude the existence of a small charge transfer between the two monomers.

4. Conclusions

We have performed a detailed charge density analysis of the five minima in the potential surface of methoxymethane dimer. From the preceding

Table 8
Atomic populations of the carbon and oxygen atoms in the five dimers of methoxymethane, relative to those of the free monomer (all values in a.u.)

Compound	$\Delta N(O1)$	$\Delta N(C2)$	$\Delta N(C3)$	$\Delta N(O10)$	$\Delta N(C11)$	$\Delta N(C12)$
I	0.004	0.018	−0.001	0.003	0.008	0.010
II	0.005	0.023	−0.002	0.005	0.023	−0.002
III	0.001	−0.000	0.001	0.002	0.003	0.003
IV	0.003	0.005	−0.007	0.003	0.002	0.002
V	0.001	0.011	0.001	0.001	0.011	0.001

discussion, the following conclusions can be drawn:

1. At the HF/6-311++G(d,p) level, the most stable structure of methoxymethane dimer results from a planar arrangement of the two monomers, which presents two intermolecular contacts lying in the same plane. An isoenergetic structure displays a perpendicular arrangement with three C–H···O interactions (**I**).

2. Upon dimerization, the geometry of the monomers remains nearly unperturbed.

3. Local properties at the H–C···O intermolecular bond critical points are closely related to the binding energy. There is a good linear correlation between the binding energy and the sum of the charge densities at the hydrogen bond critical points, for all structures under study.

4. There is no overall charge transfer from one monomeric unit to the other, within the limits of the integration error.

References

[1] J.P. Wolbach, S.Y. Sandler, Int. J. Thermophys. 18 (1997) 10 001.
[2] P. Hobza, R. Zaradnik, Intermolecular Complexes, Elsevier, Amsterdam, 1998.
[3] J.H. van Lenthe, J.G.C. van Dunijneveldt-van de Ridjt, F.B. van Dunjneveldt, Adv. Chem. Phys. 124 (1987) 521.
[4] P. Hobza, R. Zaradnik, Chem. Rev. 88 (1988) 871.
[5] A.J. Stone, Modelling of molecular structures and properties, in: J.-L. Rivail (Ed.), Studies in Physical and Theoretical Chemistry, vol. 71, Elsevier, Amsterdam, 1990.
[6] A.J. Stone, The Theory of Intermolecular Forces, Clarendon Press, Oxford, 1996.
[7] R.F.W. Bader, Atoms in Molecules, A Quantum Theory, International Series of Monographs in Chemistry, vol. 22, Oxford University Press, Oxford, 1990.
[8] R.F.W. Bader, J. Phys. Chem. A 102 (1998) 7314.
[9] J. Hernández-Trujillo, R.F.W. Bader, J. Phys. Chem. A 104 (2000) 1779.
[10] A. Vila, E. Carballo, R.A. Mosquera, Can. J. Chem. 78 (2000) 1535.
[11] J.M. Hermida-Ramón, M.A. Ríos, Chem. Phys. 262 (2000) 423.
[12] M.T. Carroll, R.F.W. Bader, Mol. Phys. 65 (1988) 695.
[13] U. Koch, P.L.A. Popelier, J. Phys. Chem. 99 (1995) 9747.
[14] G.A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, New York, 1997.
[15] F. Hibbert, J. Emsley, Adv. Phys. Org. Chem. 26 (1990) 255.
[16] A.C. Legon, D.J. Millen, Chem. Rev. 86 (1986) 635.
[17] L. Turi, J.J. Dannenberg, J. Phys. Chem. 97 (1993) 7899.
[18] L. Turi, J.J. Dannenberg, J. Phys. Chem. 97 (1993) 12197.
[19] S. Glasstone, Trans. Faraday Soc. 33 (1937) 200.
[20] I. Alkorta, I. Rozas, J. Elguero, Chem. Soc. Rev. 27 (1998) 163.
[21] G.R. Desiraju, Acc. Chem. Res. 29 (1996) 441.
[22] T. Steiner, E.B. Starikov, A.M. Amado, J.J.C. Teixeira-Dias, J. Chem. Soc., Perkin Trans. 2 (1995) 1321.
[23] P. Seiler, L. Isaacs, F. Diederich, Helv. Chim. Acta 79 (1996) 1047.
[24] MORPHY98, a topological analysis program written by PLA Popelier with a contribution from RGA Bone (UMIST, Engl., EU).
[25] AIMPAC: a suite of programs for the Theory of Atoms in Molecules, in: R.F.W. Bader and coworkers (Eds.), McMaster University, Hamilton, Ont., Canada, L8S 4M1.
[26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M. A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, GAUSSIAN 94, Revision C.3, Gaussian, Inc., Pittsburgh PA, 1995.
[27] K. Krishnan, J.S. Binkley, J.S. Seeger, J.A. Pople, J. Chem. Phys. 80 (1984) 3265.
[28] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
[29] J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, L.A. Curtis, J. Chem. Phys. 90 (1989) 5622.
[30] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.
[31] U. Blukis, P.H. Kasai, R.J. Myers, J. Chem. Phys. 38 (1963) 2753.
[32] K. Collard, G.G. Hall, Int. J. Quantum Chem. 12 (1977) 623.
[33] G.L. Sosa, N. Peruchena, R.H. Contreras, E.A. Castro, J. Mol. Struct. (THEOCHEM) 401 (1997) 77.
[34] D. Cremer, E. Kraka, Angew. Chem. 26 (1984) 627.
[35] G.F. Smits, M.C. Krol, C. Altona, Mol. Phys. 65 (1988) 513.
[36] U. Salzner, P.v.R. Schleyer, J. Am. Chem. Soc. 115 (1993) 10 231.