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Computational Study of the Interaction in $(CH_3)_2X$ Dimer and Trimer (X = O, S)

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We used ab initio and density functional theory (DFT) methods to perform calculations on dimethyl ether and dimethyl sulfide dimers and trimers. A total of five minima were identified for each dimer that exhibited two different types of hydrogen bonds depending on whether the hydrogen atom involved was located in the molecular plane. The most stable dimer for dimethyl ether was found to be a structure where two molecules lie in two perpendicular planes and possess an interaction energy of −12.0 kJ/mol. On the other hand, the most stable structure in the dimethyl sulfide dimer exhibits two molecules in an antiparallel arrangement and an interaction energy of −17.2 kJ/mol. On the basis of the calculations, the ether tends to interact with the hydrogen atoms in the molecular plane whereas the sulfide interacts preferentially with hydrogen atoms outside it. The interaction with the atoms in the plane is similarly strong in both molecules; however, the sulfur atom interacts more strongly with the hydrogen atoms located outside the molecular plane; this results in the dimer of dimethyl sulfide being more stable than that of dimethyl ether. We examined three minima for the corresponding trimers, where pairwise nonadditive contributions were found to be negligible and mostly of the repulsive type. Also, no appreciable cooperative effects were observed. The most stable trimer for the ether was found to have an interaction energy of −24.8 kJ/mol and that for the sulfide one of −34.4 kJ/mol; consequently, the CH···S interaction is stronger than the CH···O interaction, both in the dimer and in the trimer.

1. Introduction

Molecular clusters are bound via weak interactions of the van der Waals type or via stronger interactions involving intermolecular hydrogen bonding.[1−3] A comprehensive knowledge of the characteristics of the interaction between molecules in clusters is crucial with a view to understanding various chemical and physical phenomena. Thus, a good knowledge of the interactions between molecules is an essential prerequisite for developing simple interaction potentials applicable to larger systems such as molecules of biological interest.

One important aspect of intermolecular interactions is the potential occurrence of nonadditive pairwise phenomena.[4,5] The interaction between more than two molecules is known not to be accurately described by interactions between molecule pairs alone as it also involves contributions from three, four, or even more molecules. In some cases, particularly in hydrogen-bonded clusters, nonadditive pairwise effects are cooperative, so their strength grows as additional molecules are incorporated into the cluster. Cooperativity in the interaction reflects in such properties as the interaction energy, electric dipoles, or vibrational frequencies, which vary in a gradual manner with an increase in the number of molecules in the cluster. For this to be the case, usually hydrogen bonds must be present and in an appropriate spatial arrangement. Thus, linear chained structures usually exhibit cooperativity in the interaction.[5−7]

Most studies of the interactions in molecular clusters have been conducted on molecules that unambiguously form hydrogen bonds (viz, species containing O, N, or F). Few authors, however, have examined the interaction in systems containing other atoms capable of forming hydrogen bonds. In this respect, the presence of sulfur in the molecule introduces some peculiarities in the interaction which have rarely been studied in depth. Recently,[8] we conducted a computational study of the interaction in methanethiol and found it to differ markedly from its oxygen-containing analogue (methanol). In fact, the presence of the sulfur atom was found to decrease cooperativity in the interaction, but not to a negligible level; also, it resulted in a more complex potential surface that contained an increased number of minima the stability of which arose from the presence of two types of similarly strong bonds, viz, S−H···S and C−H···S.

Further to our studies on sulfur-containing molecular clusters, in this work we examined the interaction in the sulfur derivative

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of dimethyl ether. This species can form hydrogen bonds via the hydrogen atoms in its methyl groups that are similar to those found in methanethiol; therefore, the interaction is primarily governed by C−H···S contacts. To obtain a reference for the analysis of the behavior of dimethyl sulfide, we also examined the clusters of dimethyl ether.[9,10]

This paper therefore analyzes the characteristics of the interaction in dimethyl ether dimer and trimer, and those of its sulfur derivative, by using ab initio and density functional theory (DFT) methods. The results for the dimers allowed us to identify the most favorable structures for the interaction and to determine their stability. On the other hand, the results for the trimers permitted us to assess cooperativity in the interaction and the significance of the contribution of nonadditive pairwise terms to it. Finally, a comparison of the results for dimethyl sulfide and dimethyl ether allowed us to identify the peculiarities of the effect of the sulfur atom on the intermolecular interaction.

2. Computational Details

The structures of the homomolecular dimers and trimers of dimethyl ether and dimethyl sulfide were optimized by using the PW91PW91[11,12]—that is, PW91 functional for exchange and correlation—and MP2 methods in conjunction with the 6-31+G* basis set. This basis set was employed in previous work on other weakly bound systems of similar strength to those studied here with acceptable results for the geometric parameters at a reasonable computational cost.[13−15] To explore different regions of the potential surface, we tested various starting geometries that were chosen in terms of the results previously obtained by one of the authors for dimethyl ether dimer and also on the basis of chemical intuition.[9] The optimization of the starting structures yielded various stationary points each of which was subjected to vibrational analysis to confirm that they are minimum energy structures.

We also calculated the interaction energies for the dimers using the MP4 method and performed additional calculations with the aug-cc-pvdz basis set to estimate the effect of the size of the basis set on the interaction energy. The optimized geometry at the MP2/6-31+G* level was used in both cases.

Each interaction energy was calculated as the difference between the energy for the cluster and that for the molecules in isolation, using the supermolecule method in every case. This procedure is known to be subject to basis set superposition error (BSSE);[16,17] to minimize it, we used the counterpoise method of Boys and Bernardi,[16−18] which calculates energies by using the entire basis set for the whole cluster:

$$\Delta E_{ij...} = E_{ij...}(ij...) - \sum_i E_i^{\text{complex}}(ij...) \tag{1}$$

where superscripts indicate the geometry to be employed and terms in parentheses the basis set used in the calculation.

Clustering distorts the molecular geometry relative to the isolated molecule. To evaluate this effect on the clustering energy, we calculated the deformation energy from

$$E^{\text{def}} = \sum_i (E_i^{\text{complex}}(i) - E_i^{\text{isolated}}(i)) \tag{2}$$

Also, to calculate the contribution of pairwise nonadditive terms in the trimers, we calculated the difference between the interaction energy and the combined interaction energies calculated for the different molecular pairs in the trimer (always with the basis set for the whole cluster to avoid BSSE):

$$E_{\text{nopair}}(ij...) = \Delta E_{ij...} - \sum_{i>j} \Delta E_{ij}(ij...) \tag{3}$$

All computations were done with the software Gaussian 98.[19]

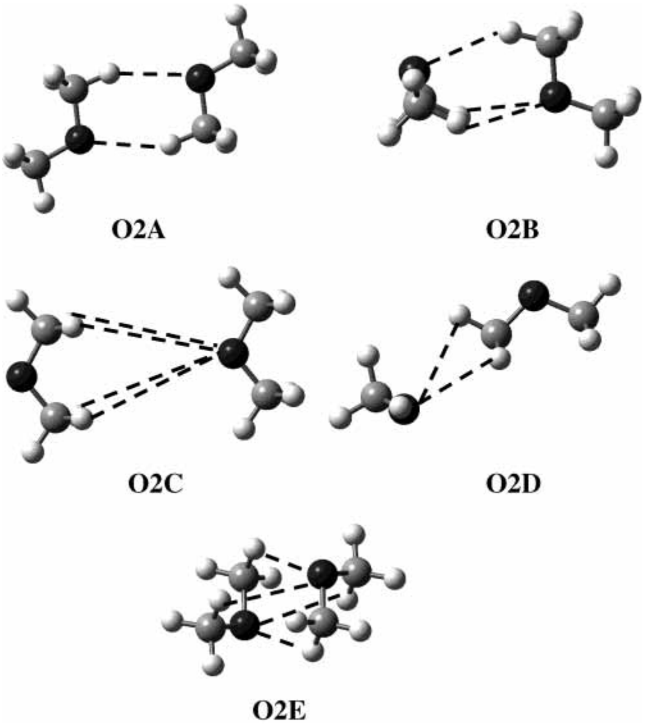

Figure 1. Structures of the minima of dimethyl ether dimer.

3. Results

3.1. Dimers. Figure 1 shows the structures of the minima identified for dimethyl ether dimer. A total of five different structures corresponding to actual minima on the potential surface were located, which is consistent with previous results of Hermida-Ramón.[9] These five structures were minima with both methods employed in this work. It must be indicated here that calculations employing the B3LYP functional[20,21] were also performed, but the results were less satisfactory that those obtained with PW91PW91 (different number of minima, underestimated interaction energies, etc.).

The structures of Figure 1 fulfill two conditions, namely: (a) they can establish C−H···O contacts and (b) their molecular dipoles possess favorable orientations. Both requirements are met, at least partly, by the five structures. Dimethyl ether is a moderately polar molecule (1.31 D),[22] so most of its interaction will be of the dipole−dipole type and give rise to structures with near-aligned dipoles (e.g. in **O2A**, **O2C**, and **O2E**). In addition to the dipole interaction, the dimer can establish C−H···O contacts, which are present in the five structures—in some cases, they correspond to very distorted arrangements, however. Dimethyl ether dimer can also form C−H···O hydrogen bonds, which, however, can be of two types depending on whether the hydrogen atom involved lies in the molecular plane (**O2A**) or outside it (**O2E**). The former is normally the sole hydrogen bond in which the oxygen atom is involved; in the latter, the oxygen atom takes part simultaneously in various bonds. We shall henceforward use H_P to designate the hydrogen atoms lying in the molecular plane and H_{OP} those located outside it, and hence distinguish between hydrogen bonds of the $C-H_P\cdots O$ and $C-H_{OP}\cdots O$ types.

Table 1 shows the values of selected geometric parameters for the minima of Figure 1. Minimum **O2A** is a structure with

TABLE 1: Selected Geometric Parameters for the Minima of Dimethyl Ether Dimer[a]

	PW91PW91					MP2				
	O2A	**O2B**	**O2C**	**O2D**	**O2E**	**O2A**	**O2B**	**O2C**	**O2D**	**O2E**
R_{OO}	3.706	3.619	4.373	4.739	3.887	3.617	3.478	4.024	4.553	3.342
Θ_{XOO}	125.9	131.6	173.1	59.3	80.0	125.7	132.0	179.9	60.4	81.7
	125.9	68.9	8.4	157.6	78.6	125.8	65.4	0.1	114.7	81.7
Φ_{XOOX}	180.0	−176.9	−30.2	179.1	145.2	179.6	−180.0	31.7	180.0	179.8
$R_{O\cdots H}$	2.474	2.780	3.529	3.201	3.612	2.413	2.572	2.989	2.993	2.864
	2.473	2.750	3.453	3.078	3.541	2.411	2.572	2.981	2.992	2.865
		2.593	3.207	3.084	2.927		2.507	2.984	2.876	2.862
			3.071		2.924			2.982		2.862
$\Theta_{O\cdots HC}$	152.1	132.5	96.6	86.5	118.7	150.9	134.7	104.2	87.2	118.6
	152.1	133.2	95.6	92.8	120.5	151.0	134.8	104.6	87.2	118.6
		144.2	115.6	92.9	130.0		141.9	104.4	93.5	118.6
			118.5		131.1			104.5		118.6
μ	0.00	1.57	3.03	2.35	0.80	0.00	1.97	3.56	1.73	0.00
$\mu'^{\,b}$	0.00	1.43	2.77	2.11	0.80	0.00	1.75	3.22	1.47	0.00

[a] Distances given in Å, angles in deg. X denotes an imaginary atom on the bisector of the COC angle lying between the two methyl groups. [b] μ' is the vector combination of molecular dipole moments (given in D).

two $C-H_P\cdots O$ hydrogen bonds with its dipoles in an antiparallel arrangement. The angle between the axes of the two molecules (taken to be the lines connecting the oxygen atom with the midpoint between the methyl groups) is nearly 180°, which reflects the presence of two antiparallel dipoles stabilizing the dimer. The oxygen atoms are 3.6−3.7 Å apart, depending on the computational method, and the distance of the hydrogen bonds is 2.4−2.5 Å. Also, the bond angle is rather nonlinear (in the region of 150°).

In minimum **O2B**, the two molecules lie in perpendicular planes and form up to three hydrogen bonds. One is similar to those observed in **O2A** ($C-H_P\cdots O$), whereas the other two correspond to the simultaneous interaction of the oxygen atom with the two hydrogen atoms outside the molecular plane ($C-H_{OP}\cdots O$). The three hydrogen bonds are longer than in the previous minimum; thus, the shortest ($C-H_P\cdots O$) has a distance of 2.5−2.6 Å and the other two ($C-H_{OP}\cdots O$) are virtually identical in length (2.6−2.8 Å). The two types of bond are rather nonlinear (particularly those of the $C-H_{OP}\cdots O$ type).

In **O2C**, the two molecules have their dipoles aligned and lie one behind the other. The distances between the oxygen atoms are much longer (up to 4.4 Å with DFT), and so are those of the $C-H_{OP}\cdots O$ contacts (up to 3.5 Å). In structure **O2D** the distances are also large, reaching 4.7 Å with DFT.

In structure **O2E**, the molecules have antiparallel dipoles and occupy superimposed planes, similarly to acetone dimers.[23] It should be noted that MP2 provides an essentially symmetric structure with four near-equivalent $C-H_{OP}\cdots O$ bonds at 2.9 Å, whereas PW91PW91 provides a less symmetric structure with two short hydrogen bonds (2.9 Å) and two long ones (3.6 Å).

Dimethyl sulfide dimers are similar to dimethyl ether dimers. The five minima identified for the former are shown in Figure 2 and the values of selected geometric parameters for each given in Table 2. The main difference from dimethyl ether is that, because the sulfur atom is larger than the oxygen atom, intermolecular distances are substantially longer in the sulfide. Thus, the $S\cdots S$ distance in **S2A** is 3.9−4.5 Å and the hydrogen bond distances are in the region of 3.1 Å. Deviations from linearity in the hydrogen bonds are more marked than those in dimethyl ether, which suggests that the sulfur atom has a lower tendency to form linear hydrogen bonds with the hydrogen atoms in the molecular plane. Also, unlike the MP2 structure, that obtained with the PW91PW91 method is not symmetric; this reflects the general tendency of MP2 to provide more symmetric structures for the studied clusters. Structure **S2B** is similar to that in dimethyl ether. However, unlike dimethyl ether, the longest of the three hydrogen bonds formed is that involving the hydrogen atom in the molecular plane ($C-H_P\cdots S$), which suggests that the sulfur atom interacts preferentially with the hydrogen atoms outside the plane. The other structures exhibit no significant differences from those in dimethyl ether. It should be noted that no significant differences in molecular geometry with respect to the isolated molecules were detected; consequently, the interaction cannot be very strong—not so strong as to cause any appreciable deformation in the molecules.

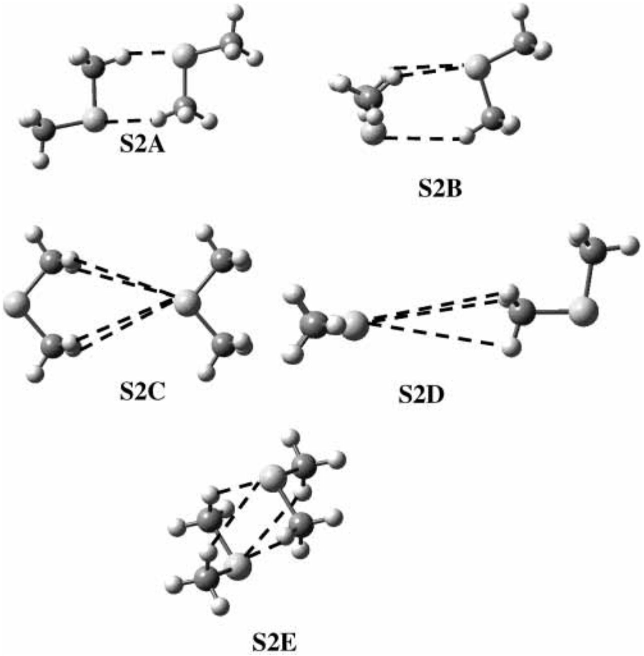

Figure 2. Structures of the minima of dimethyl sulfide dimer.

The geometric results presented in Tables 1 and 2 are obtained by optimization on an uncorrected potential surface, the counterpoise procedure being only applied to the final structure, so they are affected by BSSE. To estimate the effect of BSSE on the structures of the minima, MP2 calculations were performed on a corrected potential surface by using the method developed by Simón et al.[24] for selected minima. As expected, on the corrected surface intermolecular distances are slightly longer than the values shown in Tables 1 and 2 (about 0.1−0.2 Å). However, the characteristics of the minima are the same and the effect of BSSE on geometries or energies is not significant, so we believe that it is not necessary to perform such a more demanding type of calculation for this systems.

TABLE 2: Selected Geometric Parameters for the Minima of Dimethyl Sulfide Dimer[a]

	PW91PW91					MP2				
	S2A	**S2B**	**S2C**	**S2D**	**S2E**	**S2A**	**S2B**	**S2C**	**S2D**	**S2E**
R_{SS}	4.450	4.143	5.080	5.676	4.262	3.876	4.016	4.885	5.513	4.043
Θ_{XSS}	117.7	64.4	179.7	178.2	65.3	120.6	64.7	154.6	176.6	67.7
	98.8	123.8	1.0	50.8	65.3	120.6	126.8	4.9	52.9	67.7
Φ_{XSSX}	151.5	175.9	145.9	21.8	180.0	180.0	−179.6	161.0	−171.7	−179.9
$R_{S\cdots H}$	3.253	3.158	3.667	3.639	3.275	3.083	3.138	3.656	3.516	3.161
	3.061	3.144	3.667	3.640	3.275	3.083	3.050	3.606	3.527	3.161
		3.090	3.636	3.592	3.272		3.049	3.354	3.425	3.161
			3.626		3.270			3.284		3.161
$\Theta_{S\cdots HC}$	120.6	137.5	107.7	92.7	137.8	128.9	136.6	105.8	91.7	134.0
	150.3	137.9	107.5	92.9	137.8	128.9	136.7	106.5	91.1	134.0
		144.7	109.7	95.2	137.9		139.3	108.8	90.6	134.0
			110.1		137.9			110.8		134.0
μ	0.87	1.75	3.76	3.38	0.00	0.00	1.91	3.64	3.34	0.00
μ' [b]	0.94	1.74	3.49	3.16	0.00	0.00	1.83	3.43	3.13	0.00

[a] Distances given in Å, angles in degrees. X denotes an imaginary atom on the bisector of the CSC angle lying between the two methyl groups. [b] μ' is the vector combination of molecular dipole moments (given in D).

TABLE 3: Interaction Energy for the Minima of Dimethyl Ether and Dimethyl Sulfide Dimers[a]

		dimethyl ether					dimethyl sulfide				
		O2A	**O2B**	**O2C**	**O2D**	**O2E**	**S2A**	**S2B**	**S2C**	**S2D**	**S2E**
PW91PW91	ΔE (kJ/mol)	−9.03	−8.76	−4.26	−4.73	−6.16	−7.82	−9.98	−4.13	−3.32	−9.76
	D_0	−6.11	−5.86	−1.21	−3.44	−4.09	−5.37	−8.54	−3.18	−0.32	−7.75
	ΔH^{298} (kJ/mol)	−3.20	−2.96	1.56	0.46	−0.58	−2.20	−4.58	−1.43	2.36	−4.35
	E_{def}	0.18	0.22	0.11	0.13	0.19	0.12	0.17	0.05	0.00	0.26
MP2	ΔE (kJ/mol)	−8.64	−9.01	−3.69	−3.87	−6.82	−5.91	−8.59	−3.95	−2.32	−9.67
		[−8.60]	[−8.94]	[−4.12]	[−4.20]	[−6.98]	[−5.42]	[−7.90]	[−3.48]	[−2.29]	[−8.60]
		(−10.33)	(−11.95)	(−6.54)	(−6.08)	(−11.45)	(−10.53)	(−14.13)	(−7.76)	(−4.78)	(−17.19)
	D_0	−6.21	−5.95	−2.21	−2.35	−4.23	−4.67	−6.55	−3.16	−1.56	−6.76
	ΔH^{298} (kJ/mol)	−3.28	−3.53	1.25	1.01	−1.24	−3.33	−3.26	0.91	2.59	−4.33
	E_{def}	0.18	0.10	0.11	0.04	0.28	0.04	0.11	0.04	0.01	0.03

[a] Numbers in brackets were obtained at the MP4/6-31+G* level. Numbers in parentheses were obtained at the MP2/Aug-cc-pvdz level.

Tables 1 and 2 also show the calculated dipole moments for the different structures, as well as those obtained by combining the dipoles for the individual molecules (calculated for the cluster geometry, using the basis set for the cluster). As can be seen, some structures are nonpolar, or nearly so, whereas others are highly polar. Thus, structures **2A** and **2E** have a near-zero dipole moment as the molecular dipoles oppose each other. The PW91PW91 method provides nonzero dipole moments for minimum **S2A** in the sulfide and **O2E** in the ether by the effect of the method yielding less symmetric structures. In any case, these are structures with a relatively low dipole moment (less than 1 D). On the other hand, **2B** and, especially, **2C** and **2D** have large dipole moments as their molecular dipoles are aligned and exhibit an additive contribution to the resulting dipole.

The difference between the calculated value and that obtained as the vector combination of the individual dipoles reflects the significance of inductive effects in these structures. The presence of a polar molecule alters the charge cloud of the neighboring molecule and generates an induced dipole that contributes to the total dipole moment. Obviously, this type of contribution must be more substantial in highly polar and polarizable molecules. The two molecules studied in this work are similarly polar (1.3 and 1.5 D for dimethyl ether and dimethyl sulfide, respectively);[22,25] however, the sulfide is more readily polarizable by virtue of the presence of the sulfur atom,[26] so it should in principle be more prone to exhibit this type of phenomenon. For these effects to be appreciable, however, an appropriate geometry is required. The molecules in the sulfide cluster are more distant than those in the ether cluster, so the electric field produced by the neighboring molecule is weaker and the resulting inductive effect smaller in the former. Also, the probably large induced dipole moments of two symmetric structures such as **2A** and **2E** does not reflect in the final result, which, on symmetry grounds, should be zero. As can be seen from Tables 1 and 2, there are some discrepancies between the calculated values and those obtained as the combined individual dipoles, especially for dimethyl ether dimer. However, the differences are generally small—they hardly exceed 6% of the total dipole moment in dimethyl sulfide dimer. Usually, this type of phenomenon is related to cooperativity in the interaction, so one can expect small cooperative effects to be present. Obviously, the largest inductive effects will correspond to the linear structures **2C** and **2D**, where the molecular dipole moments are mutually enhanced. In these structures, the dipole moment increases by up to 15% in the dimethyl ether dimer.

Table 3 shows the interaction energies for dimethyl ether minima. Both MP2 and PW91PW91 provide similar results for the interaction between two molecules of dimethyl ether. Thus, the PW91PW91 method provides an energy value of −9.0 kJ/mol for structure **O2A**—the most stable at this computational level. The second most stable structure, **O2B**, is only 0.3 kJ/mol less stable than **O2A**. On the basis of the interaction energies for these structures, each C−H···O contact with a hydrogen atom in the molecular plane contributes −4.5 kJ/mol, whereas each with a hydrogen atom outside the plane contributes only −2.1 kJ/mol. Structures **O2C** and **O2D** depart from this trend as a result of the relative position of the C−H···O atoms being substantially different from those in the previous structures. For **O2E** an interaction energy of −6.2 kJ/mol is obtained.

The situation is slightly different when examined in the light of the MP2/6-31+G* results. In this case, the most stable structure is **O2B**, with an interaction energy of −9.0 kJ/mol. The second most stable structure is **O2A**, which is only 0.4 kJ/mol less stable than **O2B**. On the basis of these values, each

$C-H_P\cdots O$ contact contributes −4.3 kJ/mol to the interaction energy, whereas each $C-H_{OP}\cdots O$ contributes −2.3 kJ/mol.

The inclusion of zero point energy or thermal effects does not introduce significant changes, apart from some modifications in the order of stability of structures with similar interaction energies.

To determine the effect of the computational method on the results, we performed MP4/6-31+G*//MP2/6-31+G* calculations to determine the interaction energies for the dimers. The results, shown in Table 3, were similar to those obtained with the MP2, with differences less than 0.5 kJ/mol in all instances.

Also, to assess the effect of the size of the basis set, we performed calculations at the MP2/aug-cc-pvdz//MP2−6-31+G* level. The results, shown in Table 3, reveal that the use of a larger basis set introduces substantial additional stabilization. In fact, most of the structures are −2 to −3 kJ/mol more stable—and up to −4.6 kJ/mol in the case of **O2E**. Structure **O2B** continues to be the most stable (−11.95 kJ/mol), but now followed by **O2E** (only 0.5 kJ/mol less stable) and **O2A** (1.1 kJ/mol less stable). At this computational level, each hydrogen bond involving a hydrogen atom in the molecular plane contributes −5.2 kJ/mol to the interaction energy, whereas one with a hydrogen atom outside the plane contributes −3.4 kJ/mol.

Let us now examine the results obtained for the sulfide dimers. As can be seen from Table 3, the interaction is similar in magnitude to that in the ether dimers. However, structure **S2A** is less stable than in dimethyl ether, which suggests that $C-H_P\cdots X$ hydrogen bonds are less favorable in the presence of sulfur than in oxygen. The PW91PW91 method provides a **S2E** structure that is appreciably more stable in the sulfide dimer, with an interaction energy of −9.8 kJ/mol. Therefore, the formation of $C-H_{OP}\cdots X$ bonds is more favorable in the sulfur-containing dimer. With the MP2 method the most stable structure corresponds to **S2E**, the interaction energy for which (−9.7 kJ/mol) also exceeds that of dimethyl ether dimer.

The use of the MP4 method introduces no appreciable differences in the results; if any, it provides slightly less negative interaction energies. On the other hand, expanding the basis set increases the stability of all structures (by a factor of up to 2 relative to the smaller basis set). Thus, the interaction energy for **S2A** is −10.5 kJ/mol, which is very similar to that for the ether, whereas the values for **S2B** and **S2E** are substantially higher (−14.1 and −17.2 kJ/mol, respectively). Therefore, the interaction is similar in both molecules when the structure concerned forms $C-H_P\cdots X$ contacts; in those structures forming hydrogen bonds with the hydrogen atoms outside the plane, however, the interaction is stronger in the sulfur-containing derivative. One can therefore conclude that the oxygen atom establishes $C-H_P\cdots O$ contacts preferentially, whereas the sulfur atoms tend to establish $C-H_{OP}\cdots S$ contacts. These results are similar to those obtained for methanethiol clusters,[8] which, unlike methanol clusters, tend to form $C-H\cdots S$ bonds rather than $S-H\cdots S$ bonds.

On the basis of the results obtained at this computational level, dimethyl ether dimer is 5.3 kJ/mol less stable than dimethyl sulfide dimer. In the latter, each contact with a hydrogen atom in the molecular plane contributes to the interaction energy to a similar extent (−5.3 kJ/mol) as in dimethyl ether; however, each hydrogen bond with a hydrogen atom outside the plane contributes −4.4 kJ/mol and the bond is thus stronger than in dimethyl ether dimer, which only contributes −3.4 kJ/mol. In summary, the balance of the contributions of the different types of $C-H\cdots X$ contacts results in dimethyl sulfide dimer being more stable than dimethyl ether dimer.

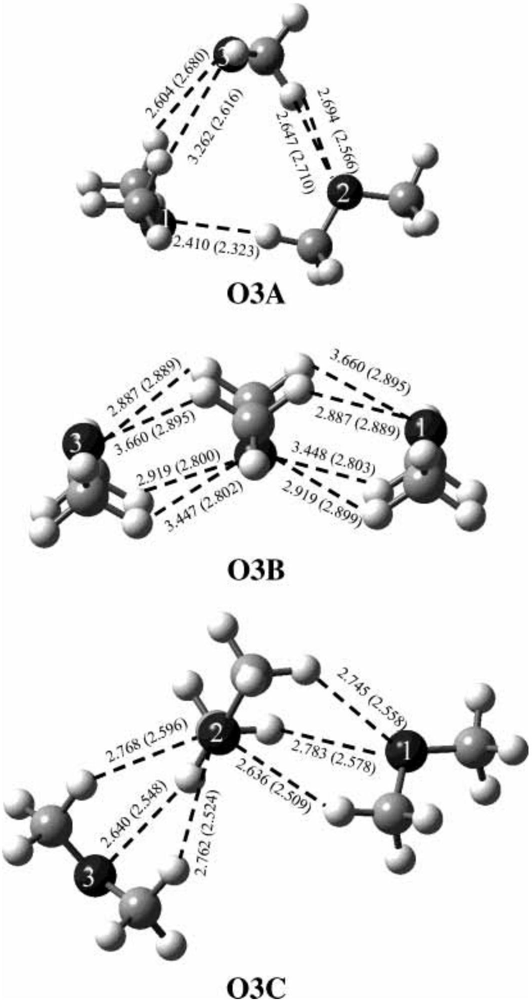

Figure 3. Structures of the minima of dimethyl ether trimer. Distances are given in Å. Values in parentheses were obtained with the MP2 method.

3.2. Trimers. The structures identified for dimethyl ether and dimethyl sulfide trimers are shown in Figures 3 and 4, respectively. As can be seen, the structures are combinations of others previously obtained for the dimer, albeit distorted as required to accommodate the interaction of the three molecules. Thus, structures **3A** exhibit contacts similar to those observed in **2B** and **2A** (or in **2C** and **2D**); minima **3B** clearly exhibit interactions of the type observed in **2E**; and minimum **3C** consists of chained **2B** structures forming 90° angles between successive molecules (i.e. a sort of chained structure).

The geometric characteristics of dimethyl ether and dimethyl sulfide trimers, some of which are summarized in Figures 3 and 4, warrant little comment. Overall, they are similar to those for the dimers. Thus, there are two different types of $C-H\cdots X$ contacts depending on whether the hydrogen atom involved is in the molecular plane. These contacts exhibit distances similar to those in the dimers; also, their $C-H\cdots X$ angles are rather nonlinear (100−150°). The structure most directly comparable with some in the dimers is obviously **3B**, where the molecules are arranged similarly as in **2E**. The values provided by the MP2 method reveal that the molecules are slightly closer to one another than in the dimer, even though the hydrogen bond distances are similar.

Tables 4 and 5 show the calculated dipole moments and those obtained as combinations of the individual molecular dipoles.

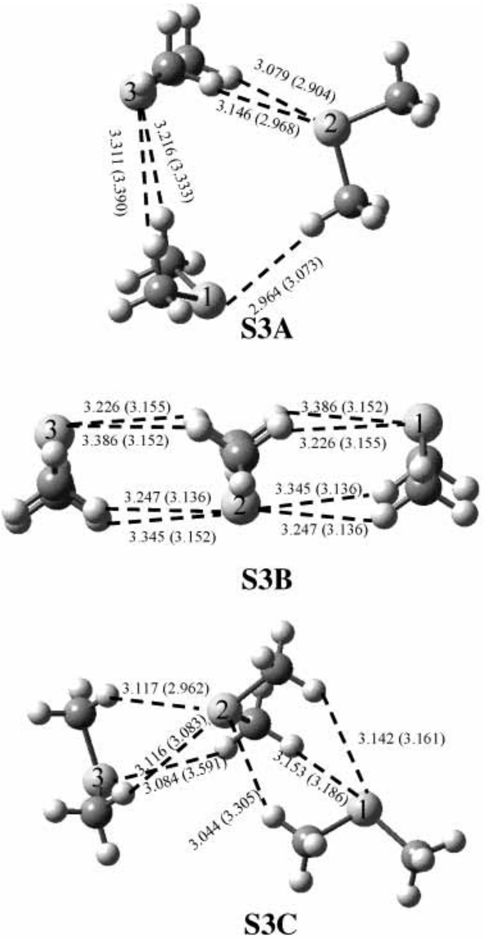

Figure 4. Structures of the minima of dimethyl sulfide trimer. Distances are given in Å. Values in parentheses were obtained with the MP2 method.

TABLE 4: Interaction Energy and Dipole Moment for the Minima of Dimethyl Ether Trimer[a]

	PW91PW91			MP2		
	O3A	**O3B**	**O3C**	**O3A**	**O3B**	**O3C**
ΔE (kJ/mol)	−17.71	−12.33	−16.84	−16.48 (−24.84)	−13.00 (−22.88)	−17.55 (−24.49)
D_0	−12.61	−7.28	−11.26	−10.19	−6.03	−11.79
ΔH^{298} (kJ/mol)	−6.35	−1.03	−5.31	−5.67	−1.97	−6.68
E_{def}	0.57	0.41	0.45	0.37	0.51	0.32
E_{nopair}	−0.54	−0.09	1.37	−0.80	0.12	0.31
ΔE_{12}	−6.35	−6.19	−8.78	−6.20	−6.75	−8.99
ΔE_{13}	−5.06	−6.14	−8.64	−3.60	−6.75	−8.83
ΔE_{23}	−5.76	0.09	−0.79	−5.88	0.39	−0.04
μ	1.21	0.87	1.88	1.76	1.53	2.07
μ' [b]	1.16	0.89	1.66	1.64	1.59	1.72

[a] Numbers in parentheses were obtained at the MP2/Aug-cc-pvdz level. [b] μ' is the vector combination of molecular dipole moments (given in D).

Most of the trimer minima exhibit a dipole moment similar to that for the isolated molecule, which suggests that the dipole moments of two molecules cancel each other. This is particularly outstanding in trimers **3B**, where two molecules are in an antiparallel arrangement. The dipole moment provided by PW91PW91 for structure **O3B** of the ether is rather different from the MP2 value, which is a result of PW91PW91 providing a distorted structure exhibiting partial cancellation of its dipole moments. At no time was an increase in dipole moment for the cluster associated to a cooperative inductive contribution detected, except in chained structure **O3C** of dimethyl ether, where a significant increment is observed. Rather, the combination of dipole moments usually exceeded the calculated value, which indicates that the induced dipole moment opposes the total dipole moment. This situation suggests that any cooperative phenomena of the type usually associated to inductive interactions must be negligible in the two types of cluster, especially in those formed by sulfide molecules.

TABLE 5: Interaction Energy and Dipole Moment for the Minima of Dimethyl Sulfide Trimer[a]

	PW91PW91			MP2		
	S3A	**S3B**	**S3C**	**S3A**	**S3B**	**S3C**
ΔE (kJ/mol)	−18.35	−18.91	−19.08	−14.41 (−29.07)	−18.97 (−34.39)	−16.49 (−32.58)
D_0	−13.86	−14.02	−14.5	−13.63	−13.47	−11.53
ΔH^{298} (kJ/mol)	−6.95	−10.31	−8.05	−4.30	−8.39	−6.14
E_{def}	0.23	0.52	0.16	0.75	0.71	0.52
E_{nopair}	−0.38	−0.20	1.05	−0.38	−0.21	−0.13
ΔE_{12}	−6.22	−9.65	−9.93	−8.51	−9.65	−5.21
ΔE_{13}	−5.25	−9.64	−9.90	−2.20	−9.65	−6.83
ΔE_{23}	−6.51	0.58	−0.30	−3.32	0.54	−4.31
μ	2.01	1.68	2.15	3.19	1.74	1.63
μ' [b]	1.95	1.72	2.15	3.21	1.78	1.65

[a] Numbers in parentheses were obtained at the MP2/Aug-cc-pvdz level. [b] μ' is the vector combination of molecular dipole moments (given in D).

Table 4 shows the energies for the minima of dimethyl ether trimer. Overall, the results are similar to those for the dimer. The most stable structure for dimethyl ether trimer is **O3C**, with an interaction energy of −17.6 kJ/mol, followed by **O3A** (only 1 kJ/mol less stable). As in the dimer, the most stable structures are those that form hydrogen bonds with hydrogen atoms in the molecular plane. Minimum **O3B** is the least stable, with an interaction energy of −13.0 kJ/mol. This is slightly less than twice the energy for **O2E**, which indicates that the presence of the third molecule somehow hinders the interaction between pairs of molecules. The use of the larger basis set aug-cc-pvdz provided more negative values for the interaction energy—which reached −24.8 kJ/mol in the most stable structure (**O3A**). The larger set reduced the energy differences between structures, to such an extent that they differed by less than 2 kJ/mol among the three minima.

Table 5 shows the results for dimethyl sulfide trimer, the most stable structure of which is **S3B**, with an interaction energy of −19.0 kJ/mol with the MP2 method. This is consistent with the results for the dimer as dimethyl sulfide dimers tend to establish contacts with the hydrogen atoms outside the molecular plane. The other two structures have slightly less negative interaction energies (viz, −14.4 kJ/mol for **S3A** and −16.5 kJ/mol for **S3C**). Again, the use of the aug-cc-pvdz basis set resulted in more negative values for the interaction energy, which amounted to −34.4 kJ/mol for the most stable structure (**S3B**). On the basis of the data in Tables 4 and 5, the trimers of dimethyl sulfide are more stable than those of dimethyl ether. The energy differences never exceeded 1.5 kJ/mol with the 6-31+G* basis set; with the larger set, however, the sulfide trimers were much more stable, with energy differences of up to 11.5 kJ/mol. These results suggest that the interaction energy of dimethyl sulfide is more markedly affected by the size of the basis set, so, a larger set would probably provide even greater stability differences between the trimers of the two species.

Tables 4 and 5 also show the interaction energies resolved into the interacting molecular pairs. Structures **3A** exhibit three attractive interactions, the strongest of which corresponds to the 1−2 pair, which forms a $\mathrm{C{-}H_P\cdots X}$ hydrogen bond. The anomalously high energy for the 1−2 interaction in the sulfide is a result of the structure calculated by the MP2 method being more compact and allowing for secondary interactions that contribute to the interaction between this molecular pair. Structures **3B** exhibit two equivalent attractive interactions between each molecule on its ends and the central one. The interaction between the terminal molecules, with its dipoles arranged in parallel, is of the repulsive type—but very small by the effect of the large distance between them. Finally, structures **3C** exhibit two markedly attractive interactions between its pairs of adjacent molecules, which are arranged similarly as in dimer **2B**. The interaction between nonadjacent molecules is slightly attractive. The situation is different in the sulfide as its structure is distorted and not exactly equivalent to two chained **2B** dimers, so the interactions between the three pairs of molecules are all attractive and similar in magnitude.

The sum of these three contributions gives the pairwise additive energy; also, the difference from the interaction energy gives the contribution of the interaction between trios of molecules. As can be seen from Tables 4 and 5, such a contribution is minimal and confirms that nonadditive effects in these systems are very small. In fact, the contribution of the interaction between molecular trios is slightly attractive or even repulsive at some minima.

4. Conclusions

We conducted a computational study of dimethyl ether and dimethyl sulfide dimers and trimers, using the PW91PW91 and MP2 methods in conjunction with the 6-31+G* basis set. The two methods located various stationary points on the potential surfaces for the clusters for which the interaction energies and various other properties were calculated. We also used the MP4 method and the aug-cc-pvdz basis set to estimate any deficiencies in the computational methods used and the dependence of the results on the size of the basis set.

A total of five minima were located on the potential surfaces for the dimers of both species that allowed us to identify two different types of C−H···X contact depending on whether the hydrogen atom involved was inside or outside the molecular plane. Both types of contact result in markedly nonlinear bond angles (100−150°). The most stable structure for dimethyl ether dimer forms a hydrogen bond with a hydrogen atom in the molecular plane and two others with hydrogen atoms outside such a plane; the resulting interaction energy is −9.0 kJ/mol (−12.0 kJ/mol with the aug-cc-pvdz basis set). On the other hand, the most stable structure for the dimethyl sulfide dimer is one with the two molecules in an antiparallel arrangement and establishing four contacts with hydrogen atoms outside the molecular plane; its interaction energy is −9.7 kJ/mol (−17.2 kJ/mol with the aug-cc-pvdz basis set). Dimethyl ether molecules tend to form hydrogen bonds with the hydrogen atoms in the molecular plane, whereas those in dimethyl sulfide favor those with hydrogen atoms outside the plane.

The corresponding trimers exhibit three minima, the most stable of which has an interaction energy of −17.6 kJ/mol for dimethyl ether (−24.5 kJ/mol with aug-cc-pvdz). The interaction energy for the most stable structure in the dimethyl sulfide trimer has an interaction energy of −19.0 kJ/mol (−34.4 kJ/mol with aug-cc-pvdz). Therefore, at the highest computational level used in this work, the trimer of dimethyl sulfide is 9−10 kJ/mol more stable than that of dimethyl ether.

Overall, the trimers exhibit no significant cooperative effects; thus, nonadditive pairwise contributions hardly exceed 1 kJ/mol in the most favorable cases. Therefore, one cannot expect clusters of these molecules to exhibit appreciable cooperativity in their interaction.

As a general conclusion, the results confirm the tendency of the sulfur atom to interact more strongly than the oxygen atom with the hydrogen atoms in the methyl groups.

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Supporting Information Available: Tables of Cartesian coordinates for the optimized stuructures of dimethyl ether and dimethyl sulfide dimers and trimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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