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Methanethiol Dimer and Trimer. An ab Initio and DFT Study of the Interaction

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Clusters consisting of two and three methanethiol molecules were subjected to HF, DFT/B3LYP, and MP2 calculations using the aug-cc-pvdz/cc-pvdz basis set. Overall, five structures corresponding to minima on the potential surface for methanethiol dimer were located that allowed the identification of interactions of the S−H···S and C−H···S types. While the latter type of interaction prevails in the dimer, the former is only observed in two of the five minima. Overall, the S−H···S contacts present angles that depart considerably from linearity. The use of a method that considers intermolecular electron correlation is indispensable with a view to obtaining accurate results. In fact, the HF and DFT/B3LYP methods provided significantly longer intermolecular distances than the MP2 method and underestimated interaction energies by more than 50%. The interaction energy of the most stable minimum was −11.2 kJ/mol with the MP2 method and was associated with the two interactions between the sulfur atom and the hydrogen atoms in the methyl group. Five possible minima for methanethiol trimer were also examined. The predominating interaction in these structures was of the S−H···S type, which was found to occur in all five minima and was accompanied by interactions with the methyl groups that contributed to stabilizing the clusters. The interaction energy for the most stable structure was −28.1 kJ/mol. The contribution of nonadditive pairwise terms to the interaction was fairly low, but significant (ca. 6% of the overall interaction energy). The analysis of vibration modes revealed the dimer to exhibit no specially significant frequency shifts, which suggests that no S−H···S hydrogen bonds are established. However, the structures that present S−H···S contacts exhibited red shifts of ca. 60 cm^{-1}. The situation with the trimer was different: all structures exhibited S−H···S interactions, which resulted in red shifts of ca. 80−90 cm^{-1}, suggesting the presence of a cooperative phenomenon. Other vibration modes exhibited virtually no shifts; by exception, the frequency of the H$_s$-S−C−H$_p$ torsion underwent a marked blue shift (about 130 cm^{-1} for the dimer and up to 200 cm^{-1} for the trimer).

1. Introduction

Molecular clusters consisting of a variable number of molecules are usually bound by weak interactions of the van der Waals type or stronger interactions such as hydrogen bonds. Acquiring as deep a knowledge as possible about molecular clusters is crucial with a view to understanding a wide variety of chemical and biochemical processes.[1−3] One special feature of clusters consisting of more than two molecules is the presence of nonadditive pairwise contributions to the interaction energy. Such contributions usually have effects such as introducing a further increase in the interaction energy, altering the dipole moments of the clusters or changing the vibration frequencies especially involved in the interaction. These effects usually increase with increasing number of molecules in the cluster, so they are frequently referred to as cooperative phenomena, which are especially important in hydrogen-bonded clusters.[4−7] Most studies dealing with cooperativeness involve hydrogen-bonded substances; by contrast, few have addressed substances forming no hydrogen bonds or others where the presence of such bonds cannot be unequivocally established.

Thus, a number of studies about cooperativeness in methanol clusters have been performed to determine the significance of nonadditive pairwise terms,[8−16] the contribution of which amounts to as much as 15−20% of the interaction energy for the trimer.[9,11,14,15] Recently, the authors reported on the interaction of methylamine clusters;[17] this substance can be assimilated to methanol containing an amino rather than a hydroxyl group. The contribution of nonadditive pairwise terms to the interaction energy for the trimer was calculated to be in the region of 11%. In continuation of previous research, in this work we examined clusters of methanethiol, a sulfur derivative of methanol, to determine the characteristics of the interaction. The methanethiol molecule is moderately polar[18,19] and possesses a dipole moment slightly lower than that for methanol but higher than that for methylamine. Therefore, as with methanol and methylamine, the interaction between methanethiol molecules is expected to be governed by the electrostatic contribution, which is associated to the interaction between permanent multipoles in the molecules. Molecular beam electric deflection (MBED) experiments have shown methanethiol dimer and trimer to be polar, which rules out the occurrence of structures with a zero dipole moment.[20] However, this fact does not allow one to exclude cyclic configurations as such structures can be constructed with a nonzero dipole. To the authors' knowledge, the only available reference to the theoretical study of methanethiol clusters was published recently;[15] it studied cooperativeness in alkanols and examined methanethiol clusters for comparison. However,

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cluster structures were optimized using the HF/6-31G** method only and the corresponding energies were obtained from single point calculations at a higher computational level. The HF method is known to provide poor geometric estimates of molecular clusters owing to its deficiencies in considering the contribution of dispersion. Usually, introducing correlation results in significantly shortened intermolecular distances (particularly in weakly bonded clusters). On the other hand, in the above-mentioned reference, specific (cyclic) configurations for the clusters were assumed that were not shown to correspond to specific minima on the potential surface. For these reasons, we believed a new, deeper study of the potential surface of methanethiol clusters was in order.

2. Computational Details

This paper reports the results of DFT/B3LYP[21] and ab initio calculations performed using the HF and MP2 methods on clusters consisting of two or three methanethiol molecules. Calculations were done using the aug-pvdz/cc-pvdz basis set (i.e. diffuse functions in the hydrogen atoms were excluded); however, additional calculations with the aug-cc-pvtz basis set were used to estimate the effect of expanding the basis set on the resulting interaction energy. Also, MP4 calculations were also performed to obtain the interaction energy of the clusters. In both cases, the geometry was obtained from MP2 calculations with the aug-cc-pvdz/cc-pvdz basis set.

The three above-mentioned methods (HF, DFT/B3LYP and MP2) were used to conduct a systematic search for minima on the potential surface of the dimer and trimer, and to examine the results thus obtained with a view to establishing the characteristics of the interaction between methanethiol molecules. The use of the MP2 method and the comparison of its results with those of the other two methods allowed us to estimate the effect of dispersion on the characteristics of the interaction. All calculations were done using the Gaussian 98 software suite.[22]

The structures of methanethiol dimers and trimers were fully optimized using the methods described above. To examine various regions of the potential surface, different starting geometries were chosen in terms of chemical intuition—and also based on the use of a simple potential function consisting of a Lennard-Jones function incorporating a molecular multipole distribution.[3] The optimized structures provided various stationary points each of which was subjected to vibrational analysis in order to ascertain whether it corresponded to a minimum on the potential surface.

Interaction energies were obtained as the difference between the energy of the cluster and the combined energies of the molecules in isolation, using the supermolecule method.[1,23] This procedure is known to be subject to a major error: the BSSE.[1,23,24] To avoid it, interaction energies were obtained using the counterpoise method of Boys and Bernardi,[25] which calculates energies using the basis set of the whole cluster:

$$\Delta E_{ij...} = E_{ij...}(ij...) - \sum_i E_i(ij...) \qquad (1)$$

As usual, this correction was applied a posteriori, i.e., only at the optimization end point. The BSSE is known to alter the potential surface,[26] which can result in slight changes in intermolecular distances and small variations in interaction energies. However, these effects are usually small and, to our minds, should have no appreciable effect on the conclusions drawn from our calculations. The formation of the cluster introduces a distortion in the molecular geometry relative to the molecules in isolation. We assessed such an effect on the clustering energy from the deformation energy:[27,28]

$$E_{\mathrm{def}} = \sum_{\mathrm{i}} (E_i^{\mathrm{complex}} - E_i^{\mathrm{isolated}}) \qquad (2)$$

where superscripts indicate the geometry employed in the calculation.

TABLE 1: Calculated Properties for the Methanethiol Molecule

	HF	B3LYP	MP2	expt[b]
$R_{\mathrm{S-C}}$	1.824	1.840	1.832	1.814
$R_{\mathrm{S-H}}$s	1.339	1.357	1.350	1.335
$R_{\mathrm{C-Hp}}$	1.088	1.097	1.099	1.092
$R_{\mathrm{C-H}}$	1.087	1.097	1.099	1.092
$\Theta_{\mathrm{Hs-S-C}}$	98.1	97.0	96.8	96.5
$\Theta_{\mathrm{Hp-C-H}}$	109.0	109.0	108.9	109.8
$\Theta_{\mathrm{H-C-H}}$	110.5	110.5	110.5	109.8
μ (D)	1.744	1.606	1.619	1.517

[a] Distances are given in angstroms and angles in degrees. [b] References 18 and 19.

To determine the contribution of noncooperative terms in the clusters consisting of three molecules, we calculated the nonadditive pairwise contribution to the interaction as the difference between the interaction energy and the combined energies of interaction calculated for the different molecular pairs in the trimer, using the basis set for the whole cluster to avoid the BSSE,

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

Finally, other factors potentially providing valuable information about the cooperative character of the interaction were considered. Thus, we analyzed distortions in the molecular geometry caused by the interaction and frequency shifts associated to normal modes especially involved in the interaction, and compared the dipole moments with those obtained as the combination of the individual values for the isolated molecules. The charge distribution can change appreciably by effect of the interaction and, in polar molecules, the change is usually associated to an inductive mechanism where the charge distribution of a molecule is altered by the neighboring molecule and vice versa.[3,27,29] Provided the molecules are favorably oriented, this type of mechanism is the usual origin of some cooperative phenomena.

3. Results

This section presents the results obtained in the study of clusters consisting of two and three methanethiol molecules. The results for the dimer are examined first, followed by those for the trimer and a brief discussion of the frequency shifts observed.

3.1. Methanethiol Dimer. Table 1 shows the results obtained as regards the optimized geometry of the isolated methanethiol molecule using the methods described in the Introduction. Such results were used as references to determine the effect of the interaction on the molecular geometry of the clusters. As with methanol, the isolated molecule of methanethiol possesses a C_s structure where the hydrogen atom in the plane and that of the S−H group are in a trans conformation (see Figure 1).[18,19] The calculations reproduce the experimental values quite accurately and expose the typical lengthening of bonds by effect of the inclusion of electron correlation. On the other hand, methanethiol has a dipole moment of 1.52 D as determined experimentally

TABLE 2: Structure of the Minima for Methanethiol Dimer[a]

	2A			**2B**			**2C**			**2D**			**2E**		
	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
$R_{\mathrm{C-S1}}$	1.824	1.840	1.833	1.825	1.841	1.832	1.826	1.843	1.834	1.826	1.842	1.832	1.824	1.840	1.831
$R_{\mathrm{H-S1}}$	1.340	1.362	1.353	1.339	1.357	1.349	1.339	1.356	1.349	1.339	1.356	1.350	1.339	1.361	1.353
$R_{\mathrm{C-S7}}$	1.825	1.841	1.833	1.824	1.840	1.832	1.826	1.843	1.834	1.826	1.842	1.832	1.825	1.841	1.833
$R_{\mathrm{H-S7}}$	1.339	1.357	1.350	1.339	1.357	1.350	1.339	1.356	1.349	1.339	1.356	1.350	1.338	1.358	1.351
$\theta_{\mathrm{C-S1\cdots S}}$	83.7	84.0	80.2	80.6	79.8	77.8	63.9	61.6	58.7	66.5	63.1	69.8	80.4	81.5	74.3
$\theta_{\mathrm{C-S7\cdots S}}$	107.8	104.8	105.9	79.3	77.9	76.9	63.0	61.6	58.7	66.5	63.1	69.8	106.1	104.7	76.5
$\varphi_{\mathrm{C-S\cdots S-C}}$	117.4	111.6	115.8	−124.0	−120.4	−89.8	180.0	180.0	180.0	−120.4	−123.9	−93.0	−151.6	−155.6	−93.7
$r_{\mathrm{S\cdots S}}$	4.499	4.126	4.007	4.304	4.043	3.763	5.005	4.776	4.647	4.871	4.674	4.112	4.502	4.128	3.939
$r_{\mathrm{H\cdots S1}}$	4.009	3.646	3.352	3.505	3.252	2.996	3.539	3.219	3.000	3.480	3.156	2.941	3.868	3.639	3.031
$r_{\mathrm{H\cdots S7}}$	*3.219*[b]	*2.801*	*2.686*	3.514	3.243	2.979	3.539	3.219	3.000	3.480	3.156	2.941	*3.240*	*2.798*	*2.782*
$\theta_{\mathrm{X-H\cdots S1}}$	121.2	122.8	127.2	139.9	138.4	132.1	149.7	152.5	153.6	151.9	154.8	143.4	124.0	118.0	133.3
$\theta_{\mathrm{X-H\cdots S7}}$	*159.5*	*163.8*	*164.4*	135.0	133.4	131.1	149.7	152.5	153.6	151.9	154.8	143.4	*156.8*	*164.9*	*142.2*
μ	0.953	1.181	0.989	1.556	1.487	2.162	0	0	0	0.040	0.118	0.733	1.449	1.425	2.128
μ'[c]	0.880	1.020	0.881	1.580	1.540	2.267	0	0	0	0.053	0.130	0.807	1.452	1.316	2.263

[a] Distances are given in angstroms, angles in degrees, and dipole moments in debye. [b] Values in italics correspond to a SH···S contact. [c] Obtained as vector sum of the molecular dipole moments.

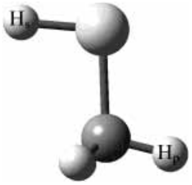

Figure 1. Methanethiol molecule.

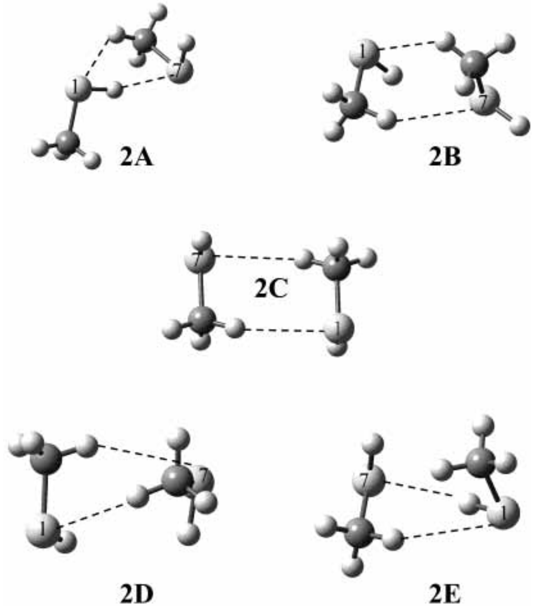

Figure 2. Minima for methanethiol dimer.

(1.62 D with the MP2 method);[18,19] this value is similar to, but slightly smaller than, that for the methanol molecule, so, in principle, the interaction between methanethiol molecules should be governed by the electrostatic contribution. Accordingly, the characteristics of methanethiol dimer should be similar to those of methanol dimer. In fact, in previous work the structures of methanethiol clusters were chosen on the grounds of their similarity to those of methanol clusters.[15] However, the incorporation of a sulfur atom results in a rather different situation. In fact, methanol dimer exhibits a single minimum on the potential surface that corresponds to a structure exhibiting a virtually linear hydrogen bond.[8−16,30] On the other hand, up to five different structures for methanethiol were identified in this work (see Figure 2), one of which (**2A**) is similar to that of methanol dimer. It should be noted that all five minima were identified by the three methods used.

All the structures examined exhibit interactions between the sulfur atom and the hydrogen atoms in the methyl group or in the S−H group of the other molecule. Structure **2A**, which is equivalent to that observed in methanol dimer,[8−16,30] exhibits a near-linear S−H···S hydrogen bond. However, an additional interaction involving the hydrogen atoms in the methyl group —one that will provide additional stabilization and does not occur in methanol clusters— is possible. All other structures exhibit the C−H···S interaction predominantly; in fact, some such structures exhibit no S−H···S interaction, but only that involving the hydrogen atoms in the methyl group. Table 2 shows selected geometric characteristics of the minima for methanethiol dimer.

As can be seen, the intermolecular distances are quite long as a result of the size of the sulfur atom. It should be noted that the incorporation of electron correlation results in substantial shortening of intermolecular distances (e.g. 0.5−0.8 Å in those between the sulfur atoms). Consequently, the procedure used in ref 15 can lead to significant errors as the minima on the HF and MP2 potential surfaces are relatively distant, so isolated MP2 calculations on the HF-optimized geometry can produce gross errors. Considerable shortening (0.5−0.8 Å) is also apparent from the distances between the atoms involved in an X−H···S interaction.

Overall, the structures provided by the MP2 method are more compact than those obtained with the other two methods. This is apparent from the C−H···S distances, some of which are substantially shorter than those provided by the DFT/B3LYP method. This might be the result of the contribution of dispersion, which is only considered by the MP2 method and tends to bring the methyl groups closer to the other molecule.

The sole structure clearly exhibiting the S−H···S interaction is that designated **2A**. The H···S intermolecular distance in this structure is 2.7 Å as calculated with the MP2 method; also, the angle of the S−H···S contact, while departing considerably from linearity, is still in the region of 160°. Structure **2E** can also exhibit this interaction, with an H···S distance of ca. 2.8 Å. In this case, the HF and DFT/B3LYP methods predict an angle about 160°, whereas the MP2 method predicts a much more marked deviation (viz. an angle of 142°). The other structures cannot establish an S−H···S interaction, but only those with the hydrogen atoms of the methyl group. The distances in the C−H···S bond contacts present in all the structures studied are

TABLE 3: Selected Thermodynamic Properties of the Minima for Methanethiol Dimer (kJ/mol)[a]

		ΔE^a	E_{def}	D_0	ΔH	ΔG
2A	HF	−3.33	0.01	−1.39	1.97	10.30
	B3LYP	−4.94	0.05	−2.06	0.33	25.30
	MP2	−9.55 (−8.04)[b] [−11.73][c]	0.16	−6.61	−4.22	17.54
2B	HF	−3.80	0.03	−1.78	1.47	23.32
	B3LYP	−3.94	0.07	−1.37	1.31	27.77
	MP2	−11.22 (−8.56) [−14.08]	0.18	−8.39	−6.18	24.85
2C	HF	−3.02	0.02	−1.21	2.23	22.42
	B3LYP	−3.34	0.05	−1.01	1.84	26.51
	MP2	−8.35 (−7.63) [−10.40]	0.05	−5.88	−3.15	21.37
2D	HF	−3.25	0.02	−1.34	2.00	23.47
	B3LYP	−3.65	0.06	−1.55	1.48	27.77
	MP2	−10.47 (−9.14) [−13.42]	0.34	−7.92	−5.46	23.11
2E	HF	−3.11	0.01	−1.17	2.19	18.73
	B3LYP	−4.66	0.05	−2.14	0.56	22.99
	MP2	−10.28 (−8.62) [−13.61]	0.20	−7.18	−5.42	27.00

[a] $T = 298.15$ K. [b] Values in parentheses obtained with the MP4 method. [c] Values in brackets obtained with the aug-cc-pvtz basis set.

all close to 3.0 Å with the MP2 method; however, the angles depart significantly from linearity (they range from 130 to 150°).

The interaction usually causes slight changes in intramolecular geometry. Thus, the O−H bond distance in the donor molecule of methanol dimer is lengthened by effect of the interaction.[8−15] On the other hand, methanethiol exhibits virtually no difference in intramolecular distances between the dimer and the isolated molecule. Only minima **2A** and **2E** exhibit a slight lengthening in the S−H distance (0.003 Å) by effect of the S−H···S interaction. In all other cases, the distance does not change or even decreases slightly with clustering. Also, C−S bond distances change slightly—but scarcely significantly—and deviations from the C_s symmetry of the molecule of only 2−3° in the H_sSCH_p torsional angle are observed.

Table 2 compares the calculated dipole moments with those obtained as the vector combinations of those for the molecules in the dimer configuration. Except for structure **2C**, all minima are polar (particularly **2B** and **2E**), which is consistent with the MBED predictions.[20] Usually, a significant increase with respect to the vector combination is observed that suggests the presence of a substantial inductive contribution —often associated to cooperative phenomena.[3,11,14,29] In methylamine dimers, the dipole moment increases by up to 20%.[17] In methanethiol dimers, the change is much smaller. Only in structure **2A**, which is that closest to a hydrogen bonding interaction, is an increase in dipole moment as large as 11% observed. In the other polar structures, the interaction decreases the dipole moment with respect to the vector combination of dipoles by 5−9%. These results suggest that the total induced dipole moment for methanethiol dimer opposes its permanent dipole moment. Usually, cooperativeness is associated to a situation where induced dipole moments strengthen the permanent dipole, so the cooperative phenomenon must be scarcely significant in the interaction between methanethiol molecules.

Table 3 shows selected energy parameter values for the structures of Figure 2. As can be seen, the interaction between methanethiol molecules is relatively weak: in fact, it amounts to only −11 kJ/mol for the most stable structure. This is much lower than the value for methanol dimer (−22 kJ/mol)[14,15] but similar to that for methylamine dimer (−13 kJ/mol).[17] As can be seen from Table 3, the results of the HF and DFT/B3LYP methods are considerably different from those of the MP2 method. The last are up to three times greater, which exposes the importance of using a method incorporating—at least partly—the contribution of dispersion. These results depart from those reported by Sum and Sandler,[15] who obtained an interaction energy of ca. −8 kJ/mol using a similar computational level but the HF/6-31G** method to optimize geometries. Also, these authors considered a single structure for the dimer that was similar to **2A**.

Our five minima exhibit very similar interaction energies that differ by less than 3 kJ/mol at most. The most stable structure is **2B**, followed by **2D** and **2E**, which possess virtually the same interaction energy. Surprisingly, the hydrogen-bonded structure is only more stable than **2C**—the least stable of the five—with the MP2 method. On the other hand, such a structure is the second in the stability sequence and the most stable in it with the HF and DFT/B3LYP method, respectively. This differential behavior of the MP2 method exposes the significance of dispersion, particularly in the structures involving interactions with the hydrogen atoms of the methyl groups.

The incorporation of the zero-point energy or thermal correction has no effect on the stability of the minima; however, only the MP2 methods provides stable dimers at 298 K. If the entropic factor is considered, the situation changes: structures **2B** to **2E** are now more compact than **2A**, which is much more open. For this reason, the entropy decrease resulting from the formation of the dimer is smaller for **2A**, which is thus the most favorable structure at 298 K.

Based on the results presented above, no contribution asociated to a hydrogen bond in methanethiol dimer can be considered as the corresponding structure is not clearly observed. In any case, the closest structure is **2A**, which, however, also exhibits a secondary C−H···S interaction. Finally, it should be noted that the deformation energies are scarcely significant in these systems, accounting for barely 1−2% of the total interaction energy.

Table 3 also shows the results obtained at the MP2/aug-cc-pvtz//aug-cc-pvdz level in order to estimate the effect of expanding the basis set. As can be seen, using an expanded basis set led to increased stabilization of the dimer (by 2−3 kJ/mol) but to no change in the stability sequence. Based on these results, the computational level used underestimated the interaction energy by about 20% (i.e., the level of calculation employed is still far from complete basis set limit). The MP4 results are also shown in Table 3. The cluster was more unstable, partly as a result of the differential position of the minimum on the MP2 and MP4 surfaces and partly as a consequence of the interaction energy being overestimated by the MP2 method. Overall, the limited size of the basis set used and the overestimation of the interaction energy due to the particular method employed partially countered their mutual effects.

3.2. Methanethiol Trimer. Like the dimer, methanethiol trimer has been the subject of little research as regards its interaction. To the authors' knowledge, the sole existing paper on the subject was recently published;[15] as noted earlier, structures were optimized at the HF/6-31G** level and none was checked to correspond to a specific minimum on the potential surface. Also, only a single, cyclic, structure was considered for the trimer, by analogy with that observed in methanol trimer.[8−14,16]

As noted in the previous section, the potential surface for methanethiol dimer is much more complex than that for methanol dimer: it exhibits up to five maxima. Accordingly, the potential surface for the trimer must be even more complicated. By optimizing different starting structures, we identified the five shown in Figure 3 as the most stable for methanethiol trimer. All corresponded to minima on the potential surface, as shown by the vibrational analysis conducted using the HF and DFT/B3LYP methods. Taking into account the size

TABLE 4: Structure of the Minima for Methanethiol Trimer[a]

	3A			3B			3C			3D			3E		
	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2	HF	B3LYP	MP2
R_{S-H}	1.340	1.361	1.351	1.339	1.357	1.352	1.340	1.363	1.355	1.340	1.362	1.354	1.339	1.357	1.351
	1.340	1.361	1.351	1.340	1.363	1.356	1.340	1.362	1.356	1.340	1.362	1.353	1.340	1.363	1.352
	1.340	1.361	1.351	1.340	1.363	1.355	1.340	1.362	1.353	1.339	1.357	1.350	1.340	1.363	1.354
$r_{H\cdots S1}$	*3.312*	*2.856*	*2.970*	*3.253*	*2.778*	*2.725*	*3.233*	*2.824*	*2.647*	3.402	3.105	3.018	*3.231*	*2.786*	*2.872*
							4.800	4.249	3.208						
$r_{H\cdots S7}$	*3.312*	*2.856*	*2.970*	*3.742*	*4.538*	*2.872*	*3.333*	*2.865*	*2.807*	*3.261*	*2.836*	*2.688*	*3.211*	*2.752*	*2.651*
				3.604	3.143	3.193	4.977	4.666	3.064						
$r_{H\cdots S13}$	*3.312*	*2.856*	*2.970*	*3.187*	*2.731*	*2.656*	*3.232*	*2.779*	*2.693*	*3.274*	*2.783*	*2.825*	*5.281*	*5.025*	*2.977*
				4.753	4.219	3.380	4.962	4.648	3.900	3.682	3.704	2.997	3.415	3.107	3.007
													4.549	3.997	3.140
$\theta_{X-H\cdots S1}$	*158.5*	*160.4*	*135.0*	*163.4*	*170.8*	*145.4*	*159.8*	*160.7*	*154.9*	153.6	156.0	136.3	*168.3*	*170.9*	*141.8*
							111.1	112.4	128.2						
$\theta_{X-H\cdots S7}$	*158.5*	*160.4*	*135.0*	*119.3*	*97.3*	*134.0*	*155.2*	*158.2*	*145.2*	*161.9*	*164.8*	*167.9*	*161.6*	*166.6*	*159.1*
				135.6	166.0	104.5	108.0	105.5	128.3						
$\theta_{X-H\cdots S13}$	*158.5*	*160.4*	*135.0*	*157.9*	*170.4*	*155.0*	*160.6*	*162.9*	*150.2*	*156.4*	*163.6*	*138.5*	*87.4*	*85.2*	*115.0*
				107.4	105.3	126.2	98.0	94.1	106.5	140.3	136.9	131.3	172.1	170.0	128.4
													114.8	115.8	132.7
μ	4.180	3.978	2.683	1.607	0.709	1.709	1.415	1.360	1.555	2.434	1.605	2.567	1.221	1.027	2.370
μ' [b]	4.332	4.193	2.985	1.739	1.182	1.929	1.475	1.463	1.730	2.448	2.019	2.226	1.305	1.275	2.607

[a] Distances are given in angstroms, angles in degrees, and dipole moments in Debye. Numbers in italics correspond to a SH···S contact. [b] Obtained as vector sum of the molecular dipole moments.

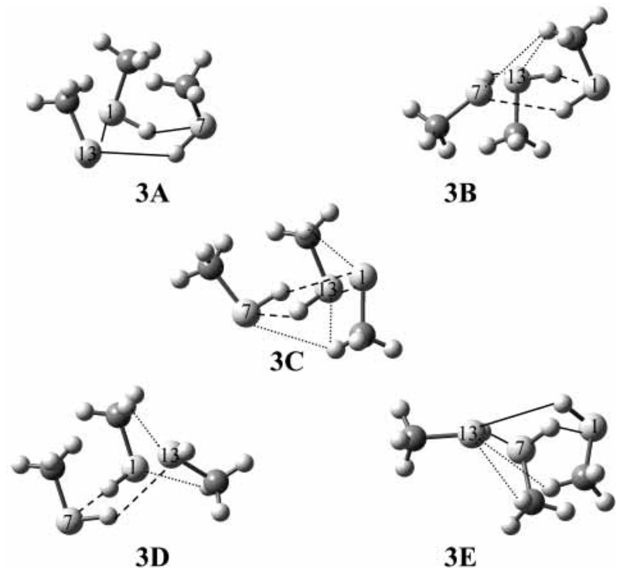

Figure 3. Minima for methanethiol trimer.

of the system, the MP2 method was not used to calculate the corresponding frequencies.

Table 4 shows the most salient geometric features of the structures of Figure 3. The five minima exhibit an identical pattern: the three thiol groups arrange themselves in a virtually cyclic configuration. The only structure departing from this trend is **3D**, where a thiol group points outward of the cycle (which is closed by interactions with the methyl groups). Surprisingly, the interaction in methanethiol trimer is established via the thiol groups, whereas that in the dimers occurs predominantly via the methyl groups. However, all trimer structures except **3A** exhibit several interactions of the sulfur atom with the methyl groups that favor clustering.

Structure **3A** corresponds to a cyclic configuration with three identical S−H···S bonds. This description is appropriate for the structures provided by the HF and DFT/B3LYP methods, where the interaction occurs via the S−H···S contact, with an angle about 160° and the hydrogen atom in the plane defined by the sulfur atoms. On the other hand, the MP2 method introduces a major deviation with respect to this structure: it leads to a more strained S−H···S interaction, with angles of 135° and a deviation of 30° with respect to the plane defined by the sulfur atoms. Probably, this phenomenon results from the contribution of dispersion; in fact, the methyl groups in the MP2-optimized structure are much closer to each other and their closeness is favored over the S−H···S interaction. The S···S and S···H bond distances are not shorter than in the dimer, but rather slightly longer by effect of the molecules in structure **3A** being in a more strained configuration. As a result, the S−H···S interaction must be weaker than in the dimer.

The other minima found exhibit several C−H···S interactions in addition to S−H···S interactions, which complicates their analysis. Structures **3B** and **3C** are very similar to each other and differ exclusively in the positions of the methyl groups with respect to the central ring formed by the S−H groups. Structure **3B** is somewhat more distorted and its S−H groups are more distant from the plane of the sulfur atoms. These minima correspond to that identified by Sum and Sandler[15] (viz. a cyclic trimer with two methyl groups on one side of the ring formed by the S−H groups and the third methyl group on the opposite side). Several structures exhibit shorter S−H···S distances relative to the dimer; however, comparisons are made difficult by the fact that each molecule in the trimer exhibits a different distance. Also, the C−H···S intermolecular distances are longer than in the dimer in most cases. As regards intramolecular distances, the trimer exhibits longer S−H distances in the groups involved in S−H···S interactions, the elongation being up to 0.006 Å with respect to isolated molecule and 0.003 Å with respect to the values observed in the dimer. This phenomenon is similar to that associated to cooperativeness in the hydrogen bonding interaction.

All trimer structures are highly polar, with a dipole moment of 2−3 D or even greater. This is consistent with previous MBED findings of Odutola et al.[20] As with the dimer, however, the dipole moment would be higher if the charge clouds had no mutual effect; in fact, the net result is a decreased dipole moment relative to the vector combination of the molecular dipoles.

Table 5 shows selected thermodynamic parameters for methanethiol trimer as calculated using the different methods. MP2 properties which required a vibrational analysis were obtained by using the DFT/B3LYP frequencies. The most stable

TABLE 5: Selected Thermodynamic Properties of the Minima for Methanethiol Trimer (kJ/mol)[a]

		ΔE^b	E_{nonpair}	E_{def}	ΔE_{12}	ΔE_{13}	ΔE_{23}	D_0^c	ΔH^c	ΔG^c
3A	HF	−6.96	−0.62	0.03	−2.13	−2.13	−2.13	−0.85	2.70	57.83
	B3LYP	−11.40	−2.10	0.15	−3.10	−3.10	−3.10	−1.00	2.20	69.18
	MP2	−24.79 (−21.40) [−30.89]	−1.47 (−1.14)	1.55	−7.77	−7.77	−7.77	−14.40	−11.19	55.78
3B	HF	−8.61	−0.57	0.07	−2.36	−2.84	−2.84	−2.47	1.10	53.85
	B3LYP	−12.96	−2.10	0.27	−2.28	−4.33	−4.44	−2.74	0.72	62.89
	MP2	−28.06 (−23.29) [−35.92]	−1.80 (−1.38)	0.48	−7.27	−9.19	−9.79	−17.84	−14.38	47.79
3C	HF	−8.53	−0.62	0.03	−2.91	−2.94	−2.05	−2.07	1.29	54.95
	B3LYP	−13.48	−2.19	0.20	−4.12	−4.28	−2.89	−3.48	0.04	59.40
	MP2	−28.13 (−23.37) [−35.69]	−1.57 (−1.27)	0.45	−9.48	−9.61	−7.48	−18.13	−14.61	44.75
3D	HF	−8.34	−0.33	0.05	−1.65	−3.52	−2.84	−2.09	1.37	57.66
	B3LYP	−11.72	−1.34	0.25	−2.91	−3.20	−4.25	−1.90	1.83	62.53
	MP2	−26.84 (−22.70) [−33.48]	−0.88 (−0.61)	0.42	−7.04	−10.84	−8.09	−17.02	−13.30	47.41
3E	HF	−7.89	−0.51	0.03	−2.78	−1.60	−2.99	−1.64	1.82	56.22
	B3LYP	−12.29	−1.68	0.18	−4.25	−1.84	−4.54	−2.49	−1.26	67.95
	MP2	−26.92 (−22.78) [−33.54]	−1.53 (−1.15)	0.39	−7.22	−8.93	−9.24	−17.13	−15.89	53.32

[a] $T = 298.15$ K. [b] Values in parentheses obtained with the MP4 method; values in brackets obtained with the aug-cc-pvtz basis set. [c] MP2 values obtained with DFT/B3LYP frequencies.

structure was that corresponding to minimum **3C** (−28 kJ/mol); in any case, the energy differences between minima never exceeded 3 kJ/mol. Incorporating the zero-point energy resulted in no significant change in the stability sequence; by contrast, the thermal correction clearly favored structure **3E**, which became the most stable at 298 K.

As with the dimer, the MP2 results differed appreciably from those of the other two methods; the latter underestimated the interaction energy by more than 50%. As noted earlier, the difference can be ascribed to dispersion, which may play a prominent role in this type of cluster. Using an isolated MP2 calculation on the HF/6-31G** geometry provided an interaction energy of ca. −21 kJ/mol, which introduced an error of about 25% in the interaction energy. This effect was largely due to the fact that the minimum on the MP2 potential surface occurred at distances 0.6−0.7 Å closer than in the HF minimum. The results provided by the aug-cc-pvtz basis set exhibited a trend similar to that of the minimum and introduced additional stabilization (ca. 7−8 kJ/mol), i.e., roughly 20% of the interaction energy was lost with the smaller basis set. The MP4 results exhibited a trend similar to that in the dimer: they resulted in values that were 4−5 kJ/mol less negative than those provided by the MP2 method.

Table 5 shows the contribution of nonadditive terms to the interaction energy as obtained from eq 3. As can be seen, the contribution was quite small, so cooperativeness in the interaction must be very low. However, the effect is much greater (up to 3 times) than that predicted in ref 15 and cannot be neglected. In fact, the contribution to the three-body interaction energy is about 6% of the interaction energy at the MP2 level (and up to 16% at the DFT/B3LYP level), which is less than in other clusters (11% in methylamine trimer as calculated at a similar computational level) but not negligible.

The formation of the trimer from the dimer is accompanied by a change in interaction energy of −17 kJ/mol, whereas the formation of the dimer involves an interaction energy of −11 kJ/mol (i.e., the formation of the trimer involves an additional stabilization of −6 kJ/mol). On the other hand, the interaction energy per molecule in the trimer is about −9.4 kJ/mol and thus much higher than in the dimer (−5.5. kJ/mol). Consequently, the formation of the trimer involves additional stabilization, which, however, cannot be unequivocally ascribed to cooperativeness as a greater number of interactions are established that contribute to stabilize the cluster. An analysis of the interaction of molecular pairs reveals that all exhibit a similar interaction energy that is lower than in the dimer by effect of the orientation between molecule pairs in the trimer being less favored. All three molecules orientate in such a way that all interactions are atractive, with interaction energies ranging from −7 to −11 kJ/mol in all cases.

TABLE 6: Frequency Shifts (cm^{-1}) and Relative Intensity of S−H Stretching Vibration

	HF		B3LYP		MP2	
	$\Delta\nu$	I/I_0^a	$\Delta\nu$	I/I_0^a	$\Delta\nu$	I/I_0^a
2A	−4.1	1.0	−64.6	23.3	−54.6	79.1
	0.1	0.6	2.8	0.4	−6.6	0.2
2B	0.5	1.5	−7.6	2.1	−6.1	2.7
	1.1	0.7	−6.8	0.5	−4.3	0.5
2C	−0.1	0.0	−1.7	1.9	−4.6	0.0
	−0.1	1.8	−1.7	0.0	−4.5	1.9
2D	0.3	0.1	−4.4	0.2	−2.8	0.4
	0.5	1.7	−4.1	1.7	−2.1	0.7
2E	−3.7	0.7	−62.4	23.5	−40.7	30.9
	−0.1	0.8	2.8	0.6	−6.2	1.4
3A	−4.2	0.0	−73.2	0.0		
	−3.4	1.2	−67.0	32.7		
	−3.4	1.2	−67.0	32.7		
3B	−5.9	1.1	−85.3	33.8		
	−3.5	2.0	−75.6	42.5		
	0.8	0.5	0.1	0.5		
3C	−6.3	0.8	−87.2	24.6		
	−5.0	1.9	−67.5	27.0		
	−3.4	0.9	−58.8	27.3		
3D	−5.0	1.0	−70.4	19.2		
	−2.4	0.9	−63.2	31.2		
	0.4	1.3	−1.8	1.1		
3E	−6.7	1.3	−86.7	32.2		
	−5.5	2.2	−75.3	37.8		
	−0.4	0.7	−2.4	0.6		

[a] I_0 is the intensity of the band in the isolated molecule.

3.3. Frequencies. The interaction frequently shifts the vibration frequencies for the clusters with respect to those for the molecules in isolation.[16] In some cases—particularly in modes closely involved in the interaction—shifts can be as large as several hundred reciprocal centimeters, especially if hydrogen bonding is present. Based on the foregoing, the interaction between methanethiol molecules conforms to no specific pattern involving hydrogen bonding (at least in the dimer), so any frequency shifts will necessarily be small. Tables 6 and 7 shows selected shifts and the relative intensity with respect to the original band in the isolated molecule.

The S−H stretching frequency will obviously be affected only in those structures involving S−H···S contacts. As a result, the

TABLE 7: Frequency Shifts (cm^{-1}) and Relative Intensity of H_sSCH_p Torsion

	HF		B3LYP		MP2	
	$\Delta\nu$	$I/I_0{}^a$	$\Delta\nu$	$I/I_0{}^a$	$\Delta\nu$	$I/I_0{}^a$
2A	8.0	0.8	41.4	1.2	29.9	1.4
	53.0	1.5	122.3	1.3	132.8	1.0
2B	7.3	1.0	27.6	1.3	11.7	1.0
	16.3	1.8	37.3	2.0	25.7	2.2
2C	1.0	0.0	11.1	0.0	6.4	0.0
	12.6	2.3	28.5	2.3	30.7	2.3
2D	−4.4	2.1	−6.4	2.0	−19.7	2.1
	16.6	0.1	21.3	0.1	25.4	0.2
2E	6.9	1.6	15.9	1.4	22.9	1.4
	50.2	0.6	111.3	0.5	107.8	1.8
3A	33.3	1.9	106.9	2.7		
	33.3	1.9	106.9	2.7		
	95.2	0.8	212.1	0.5		
3B	15.6	1.7	37.4	1.4		
	54.3	1.3	121.6	1.8		
	76.4	1.1	187.4	0.4		
3C	36.4	0.1	94.4	2.9		
	43.8	0.6	105.3	2.9		
	107.6	0.1	216.1	0.0		
3D	8.9	0.4	25.5	0.4		
	39.4	2.3	103.2	2.3		
	86.1	1.3	175.4	1.3		
3E	13.9	1.3	47.4	1.6		
	39.9	1.7	107.1	1.6		
	91.5	0.7	193.4	1.6		

[a] I_0 is the intensity of the band in the isolated molecule.

dimer exhibits no appreciable shift except in structures **2A** and **2E**. The frequencies corresponding to the S−H stretching of the donor molecule are predicted to be red shifted by up to −60 cm^{-1} in both structures, their intensities being increased by a factor of about 20 with the DFT/B3LYP method. By contrast, the other minima exhibit shifts of 2−7 cm^{-1} at most.

On the other hand, all trimer minima show significant red shifts, which amount to more than −85 cm^{-1} in several structures; also, the intensity of the bands are up to 30 times higher than in the isolated molecule. Based on these results, the S−H···S interaction is scarcely favorable in the dimer, so three of the minima found exhibit no hydrogen-bonding characteristics. On the other hand, this is the preferential interaction in the trimer, which behaves similarly to other species forming hydrogen bonds.

The analysis of other vibration modes provided no remarkable results as, overall, frequency shifts were very small. The stretching frequencies for the hydrogen atoms in the methyl group were rather insensitive to the interaction and remained at values highly similar to those in the isolated molecules. However, there were substantial blue shifts in the H_sSCH_p torsional frequency as motion is more hindered in the cluster. The dimer exhibited shifts of up to 130 cm^{-1} and the trimer of up to 200 cm^{-1}. In any case, these values should be taken cautiously since the approximations involved in calculating harmonic frequencies can introduce significant errors, especially in anharmonic and large amplitude motions, though we believe the principal conclusions are valuable.

4. Conclusions

In this work, we used the HF, DFT/B3LYP and MP2 methods with the aug-cc-pvdz/cc-pvdz basis set to perform computations on methanethiol clusters consisting of two and three molecules.

In contrast to methanol dimer, which exhibits a single minimum on its potential surface, methanethiol dimer was found to exhibit five minima. All five possess similar interaction energies, that for the most stable form being −11 kJ/mol. Accurately predicting the interaction in methanethiol dimer entails incorporating electron correlation (particularly intermolecular effects). For this reason, the HF and DFT/B3LYP methods grossly underestimate the interaction between molecules in the clusters.

Only two of the five minima exhibit a configuration allowing an interaction similar to hydrogen bonding between the thiol groups to occur. In the other minima, the molecules arrange themselves in such a way that interactions between the sulfur atom and the methyl group are favored. Only the molecular structures that exhibit a hydrogen-bonded configuration appear to be deformed. In fact, the deformation energy accounts for barely 2% of the total interaction energy.

An overall five structures corresponding to as many minima on the potential surface for methanethiol trimer were studied, the most stable of which presents an interaction energy of −28 kJ/mol. All trimer minima depart considerably from the behavior of the dimer structures. In fact, all exhibit S−H···S interactions plus additional interactions between the sulfur atom and the methyl group that help stabilize the clusters.

The energy of formation of the trimer from the dimer exceeds the dimerization energy, and so does the energy per molecule. However, this cannot be clearly ascribed to cooperativeness as the trimer establishes an increased number of S−H···S and C−H···S interactions that defy analysis.

The contribution of nonadditive phenomena to the interaction energy of methanethiol trimer is quite small but not negligible; in fact, it amounts to 6% —a value similar to, but slightly smaller than, that observed in methylamine trimer—of the total interaction energy in some structures.

The vibrational analysis reveals that the frequencies for the dimer are scarcely shifted from those for the isolated molecules; the sole appreciable effect is a red shift in the dimer structures involving a S−H···S contact. On the other hand, the trimer structures exhibit systematic shifts in the S−H stretching mode, which may be associated to hydrogen-bonding interactions. Also, the intensity of the bands is up to 30 times higher than in the isolated molecules. In addition to the S−H stretching band, the H_sSCH_p torsional mode undergoes a strong blue shift as motion is much more markedly hindered through coordination. The shifts in the torsional frequencies are even greater in the trimer.

In summary, the interaction in methanethiol dimer exhibits no clear-cut hydrogen-bonding character whereas that in the trimer is typical of hydrogen bonding, even though it is difficult to observe owing to its weakness.

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