

FULL PAPER

## SCO Trimers as High-energy Materials? A Density Functional Study

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**Abstract** Density functional calculations using the hybrid B3LYP functional have been carried out on the fragmentation reaction of cyclic SCO trimers. Analogous calculations for CO<sub>2</sub> and HNCO have also been performed for comparison. The energies of the different trimers relative to those of the isolated monomers as well as the energy barriers to fragmentation have been calculated. For all the calculations, a reaction path in which three bonds are simultaneously broken has been considered. It has been found that the fragmentation of cyclic SCO trimers is a rather facile process. The same statement applies to the cyclic CO<sub>2</sub> trimer but not to the HNCO one. In addition, the latter is much more stable than three free HNCO monomers, which is not the case for SCO and CO<sub>2</sub>.

**Keywords** Density functional, Cyclic trimers, Fragmentation reaction, Activation energy

### Introduction

The interest in cyclic SCO trimers arises from the possibility that, usually, the high-pressure modifications of a compound lead to higher coordination numbers of the atoms involved than the corresponding low-pressure forms. For instance in graphite, the C-atoms of this low-pressure modification have a coordination number of three, whereas the high-pressure modification, namely diamond, shows a coordination number of four. Therefore, it might be possible to have high-pressure modifications for CO<sub>2</sub> and O=C=S with coordination numbers of three (trigonal planar C) or four (tetrahedral C) comparable to SiO<sub>2</sub>. If this is the case,

such compounds could be of considerable interest for their use as high-energy materials [1]. If there is a way to keep the compound in the solid high-pressure form and to control its depolymerization at normal pressure, an enormous increase in volume would be obtained leading exclusively to gaseous products which are, in the case of CO<sub>2</sub>, non-toxic. The trimeric structures discussed here could thus be of large interest for technical applications (air-bag, explosives, ...).

To our knowledge, only two theoretical studies have been reported on the structure and energetics of main group element cyclic trimers [1,2]. The second one presents the results obtained from semiempirical calculations for the (CO<sub>2</sub>)<sub>3</sub> cyclic trimer, whereas the first one is a more extensive study which reports both semiempirical and *ab initio* results for (CO<sub>2</sub>)<sub>3</sub> polymers and oligomers. In the latter, comparison with other species is also reported. As far as the analogous

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**Table 1** Optimized structural parameters for CO<sub>2</sub> trimers (cyclic and TS) and CO<sub>2</sub> monomer at different levels of theory

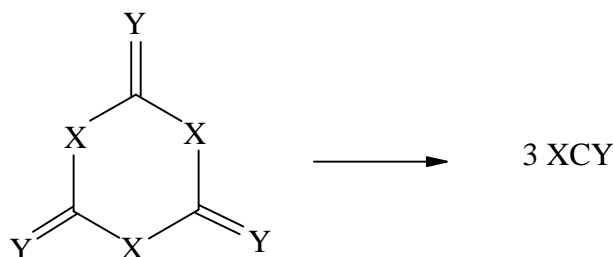
cyclic	B3LYP/6-31G*	MP2/6-31G*	MP2/6-31G*[1]
d <sub>C=O</sub> /d <sub>C-O</sub> (Å)	1.184/1.371	1.192/1.375	1.192/1.375
α <sub>O=C-O</sub> (°)	122.2	122.1	122.1
α <sub>O-C-O</sub> (°)	115.7	115.8	
α <sub>C-O-C</sub> (°)	124.3	124.1	
Energy (au)	-565.66695	-564.22248	-564.22248
+ZPE (au)	-565.62588	-564.18161	-564.18406
<b>TS</b>			
d <sub>C-O</sub> (Å)	1.172/1.248	1.182/1.260	1.181/1.260
d <sub>C...O</sub> (Å)	1.707	1.684	1.684
d <sub>C...C</sub> (Å)	2.681	2.664	
α <sub>OCO</sub> (°)	141.6	140.7	140.7
Energy (au)	-565.63157	-564.18865	-564.18865
+ZPE (au)	-565.59425	-564.15153	-564.15376
E <sub>a</sub> (kcal·mol <sup>-1</sup> ) [a]	<b>22.2</b>	<b>21.2</b>	<b>21.2</b>
+ZPE (kcal·mol <sup>-1</sup> )	<b>19.8</b>	<b>18.9</b>	<b>19.0</b>
<b>CO<sub>2</sub></b>			
d <sub>C=O</sub> (Å)	1.190	1.180	
α <sub>OCO</sub> (°)	180	180	
Energy (au)	-188.57935	-188.10775	
+ZPE (au)	-188.56973	-188.09624	
3*E(CO <sub>2</sub> ) (au)	-565.73805	-564.32325	
+ZPE (au)	-565.70919	-564.28872	
ΔE (au) [b]	-0.07110	-0.10077	
(kcal·mol <sup>-1</sup> )	-44.6	-63.2	
+ZPE (au)	-0.08331	-0.10711	
(kcal·mol <sup>-1</sup> )	-52.3	-67.2	

[a] E<sub>a</sub>=E(TS)-E(cyclic)

[b] ΔE=3\*E(CO<sub>2</sub>)- E(cyclic)

dimeric systems are concerned, calculations have been recently performed by Pyykkö [3].

On the basis of the results obtained in those previous studies and with the object of a better understanding of the structure and energetics of cyclic SCO trimers, it was tempting to use Density Functional Theory (DFT) for the present study. Figure 1 illustrates the general reaction investigated in this work.



**Figure 1** Fragmentation reaction of the cyclic (XCY)<sub>3</sub> trimer into three non-interacting XCY monomers (X=S or O and Y=O or S, for SCO and OCS, respectively; X=Y=O for CO<sub>2</sub>; X=NH and Y=O for HNCO)

## Computational details

Density functional calculations with the hybrid B3LYP [4] exchange-correlation functional have been performed using the Gaussian94 program [5]. The 6-31G\* basis set has been used for all the atoms and all the stationary points have been characterized by vibrational frequencies analysis. In some cases, correlated MP2/6-31G\* calculations have been performed for comparison.

## Results

First, the results obtained for the (CO<sub>2</sub>)<sub>3</sub> trimers are discussed and compared to those reported by Lewars [1] as well as to our own MP2/6-31G\* calculations. Second, the results obtained for the SCO trimers are presented. In this case, two different structures have been investigated depending on the relative position of the S and O atoms in the trimeric structures. To our knowledge, no theoretical study has been reported on these compounds. Third, the DFT results for the HNCO trimers are reported and compared to previous works.

In each case, the geometries of all the possible trimeric structures have been optimized and characterized by vibra-

tional frequencies analysis. Then, the activation energy for fragmentation has been calculated. Finally, the relative energies between the stationary points of the potential energy surface have been evaluated.



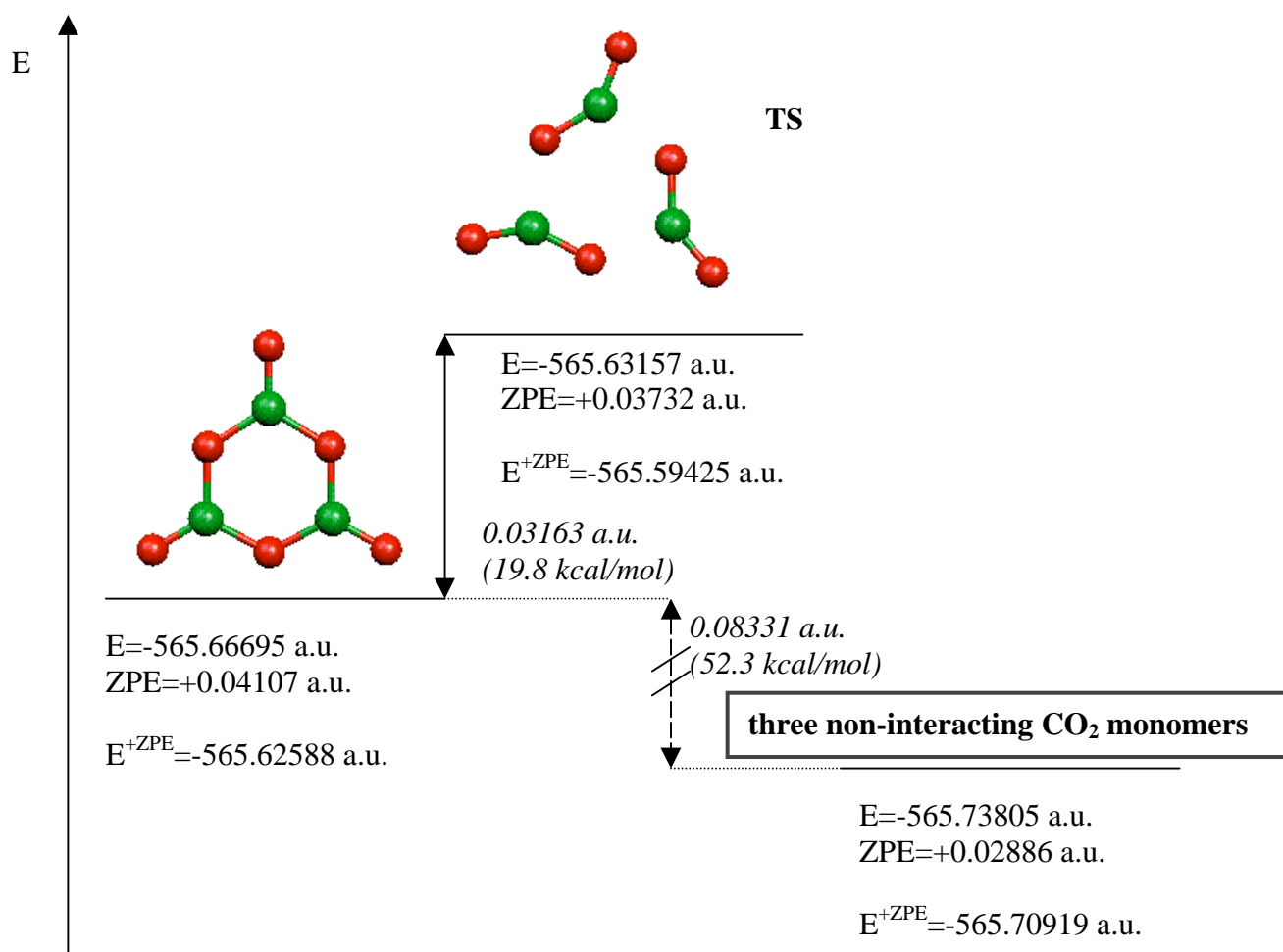
**Structural Features** The geometries and energies of the different structures encountered along the reaction path of the dissociation reaction of the cyclic  $(\text{CO}_2)_3$  structure are presented here. Indeed, the cyclic  $(\text{CO}_2)_3$  trimeric structure and the transition state (TS) connecting the previous structure with three non-interacting  $\text{CO}_2$  monomers have been investigated. As stated before, Density Functional Theory calculations have been performed using the hybrid B3LYP functional and the 6-31G\* basis set. For comparison, calculations have also been done at the correlated MP2 level and with the same basis set. The results obtained at the two levels of calculation are sum-

marized in Table 1. Figure 2 shows the structures and energies obtained at the B3LYP/6-31G\* level.

For the cyclic trimer, all the geometrical parameters but the C=O distance are similar at the two levels of calculation. The C=O distance is about 0.01 Å longer at the MP2/6-31G\* level of calculation. Our results are in good agreement with previously reported results which, together with our own preliminary calculations, validate the choice of the B3LYP/6-31G\* level in this work.

As in the case of the cyclic structure, our results for the TS structure are in good agreement with those of Lewars and both agree so as to a planar structure for the transition state of the reaction.

The TS has been characterized by vibrational frequencies analysis at both levels of calculation and one unique imaginary frequency corresponding to the fragmentation of the cyclic trimer into three  $\text{CO}_2$  monomers has been found in each case. Its value is 602i  $\text{cm}^{-1}$  at both levels of calculation, whereas the uncorrected value of 673i  $\text{cm}^{-1}$  and the corrected



**Figure 2** Potential energy surface of the fragmentation reaction of the cyclic  $(\text{CO}_2)_3$  trimer at the B3LYP/6-31G\* level of theory

**Table 2** Optimized structural parameters for SCO and OCS trimers (cyclic and TS) and SCO monomer at the B3LYP/6-31G\* level of theory

cyclic	(SCO) <sub>3</sub>	(OCS) <sub>3</sub>
$d_{C=X (X=O,S)}/d_{C-Y (Y=S,O)}$ (Å)	1.203/1.803	1.613/1.365
$\alpha_{X-C-Y}$ (°)	116.4	122.2
$\alpha_{Y-C-Y}$ (°)	127.3	115.5
$\alpha_{C-Y-C}$ (°)	112.7	124.5
Energy (au)	-1534.53613	-1534.49426
+ZPE (au)	-1534.50551	-1534.46197
<b>TS</b>	<i>in-plane</i>	<i>out-of-plane</i>
$d_{C-X}/d_{C-Y}$ (Å)	1.177/1.678	1.594/1.250
$d_{C...Y}$ (Å)	2.217	1.696
$d_{C...C}$ (Å)	3.404	
$\alpha_{XC-Y}$ (°)	139.7	139.8
Energy (au)	-1534.50004	-1534.45693
+ZPE (au)	-1534.47200	-1534.42868
$E_a$ (kcal·mol <sup>-1</sup> ) [a]	<b>22.6</b>	<b>23.4</b>
+ZPE(kcal·mol <sup>-1</sup> )	<b>21.0</b>	<b>20.9</b>
<b>SCO</b>		
$d_{C=O/C=S}$ (Å)	1.165/1.575	
$\alpha_{SCO}$ (°)	180	
Energy (au)	-511.53555	
+ZPE (au)	-511.52639	
3*E(SCO) (au)	-1534.60665	
+ZPE (au)	-1534.57917	
$\Delta E$ (au) [b]	-0.07052	-0.11239
(kcal·mol <sup>-1</sup> )	-44.3	-70.5
+ZPE (au)	-0.07366	-0.11720
(kcal·mol <sup>-1</sup> )	-46.2	-73.5

[a]  $E_a = E(TS) - E(cyclic)$

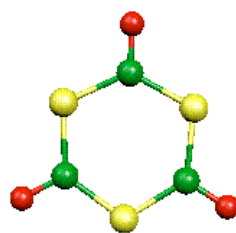
[b]  $\Delta E = 3 * E(SCO) - E(cyclic)$

(by a scaling factor of 0.94) value of 633i cm<sup>-1</sup> were obtained at the MP2/6-31G\* level [1].

**Energetic Features** The activation energy, calculated as the difference between the energy of the TS and that of the cyclic structure, is 22.2 and 21.2 kcal·mol<sup>-1</sup> at the B3LYP/6-31G\* and MP2/6-31G\* levels of theory, respectively. These values do not take into account the ZPE correction to the energy. Adding ZPE corrections, the activation energies are

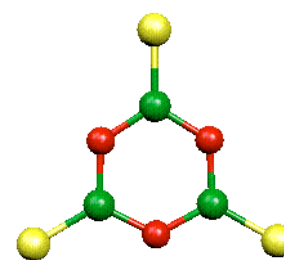
19.8 and 18.9 kcal·mol<sup>-1</sup> at the B3LYP/6-31G\* and MP2/6-31G\* levels, respectively. These values are in nice agreement with the 19.0 kcal·mol<sup>-1</sup> previously reported at the MP2/6-31G\* level of calculation. It is noteworthy that different values were obtained for the activation energy depending on the method of calculation [1]. In particular, the calculated activation energies range from 41.1 kcal·mol<sup>-1</sup> at the AM1 level to 36.6 and 28.0 kcal·mol<sup>-1</sup> at the HF/3-21G and HF/6-31G\* levels, respectively, and 19.0 kcal·mol<sup>-1</sup> at the MP2

**Figure 3** Cyclic (SCO)<sub>3</sub> (a) and (OCS)<sub>3</sub> (b) trimeric structures



cyclic (SCO)<sub>3</sub>

(a)



cyclic (OCS)<sub>3</sub>

(b)

level. Because of the agreement between our DFT calculations and the correlated MP2 results, we believe that both these methods provide the most reliable values for the activation energy of the reaction of interest.

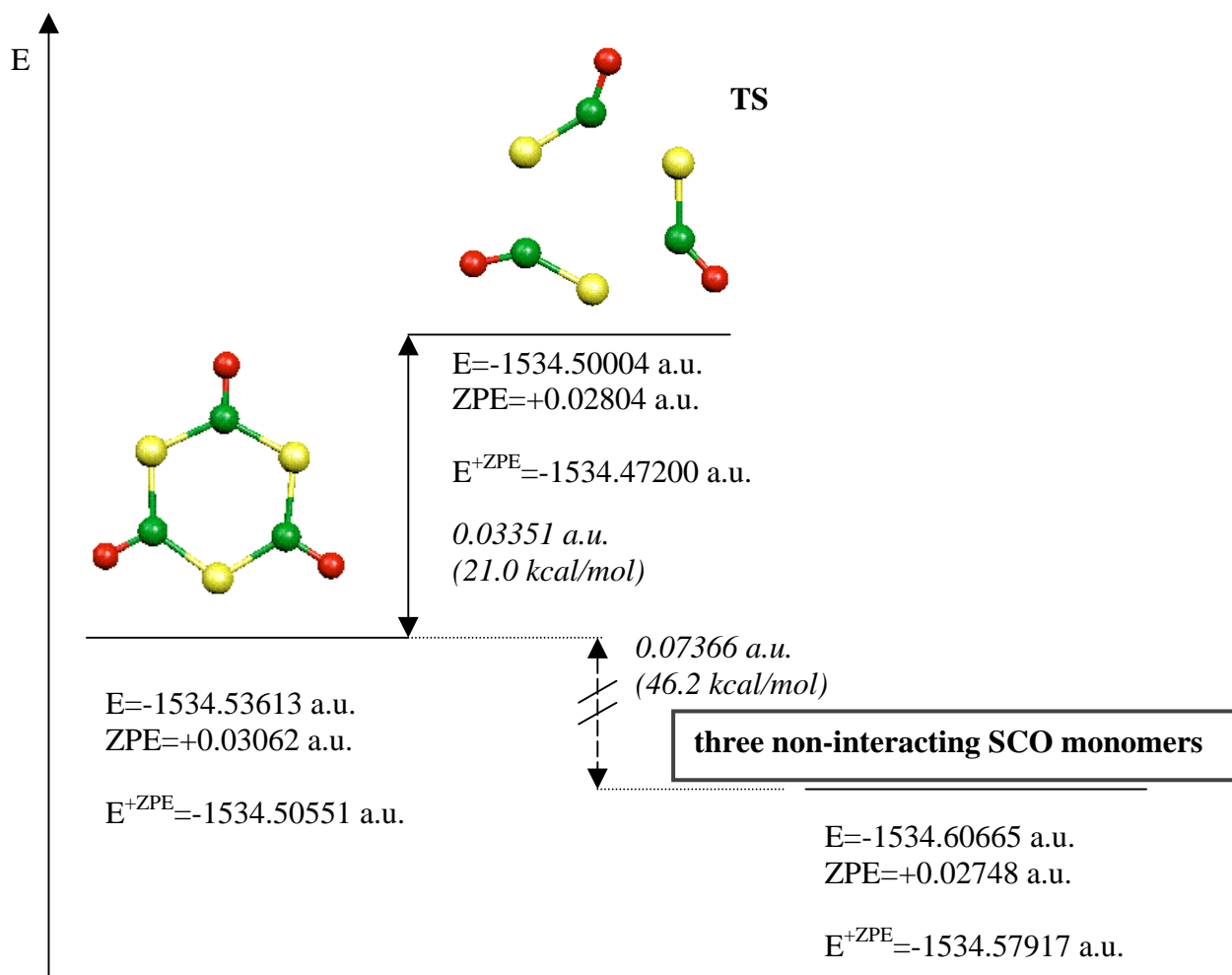
Since this energy corresponds to the breaking of three equal C-O bonds so as to lead to three CO<sub>2</sub> molecules, the ZPE-corrected activation energy per CO<sub>2</sub> molecule is thus 6.6 and 6.3 kcal·mol<sup>-1</sup> at the B3LYP/6-31G\* and MP2/6-31G\* levels, respectively. As previously reported, such values are rather small when compared to those of other well-known systems (i.e. cyclohexane, cyclohexene), which indicates that (CO<sub>2</sub>)<sub>3</sub> fragmentation into three CO<sub>2</sub> monomers is a rather facile process.

As depicted in Table 1 and Figure 2, at the B3LYP/6-31G\* level of theory and including ZPE corrections to the energies, the cyclic (CO<sub>2</sub>)<sub>3</sub> structure is 52.3 kcal·mol<sup>-1</sup> less stable than the corresponding three non-interacting CO<sub>2</sub> monomers, which stands for an exothermic reaction.

(SCO)<sub>3</sub>

**Structural Features** The geometry of the cyclic SCO trimer, as well as the structure of the transition state of the fragmentation reaction, have been calculated at the B3LYP/6-31G\* level of theory. In contrast to (CO<sub>2</sub>)<sub>3</sub> which leads to a single cyclic structure, two possible isomers arise from the combination of three SCO monomers. These two structures are shown in Figure 3. From simple considerations of bond strength, (SCO)<sub>3</sub> is expected to be more stable than (OCS)<sub>3</sub>.

The geometries of both those cyclic systems have been optimized and the stationary points of the potential energy surface corresponding to their respective fragmentation into three SCO monomers have been calculated. The results have been compared to each other and to the results reported above for (CO<sub>2</sub>)<sub>3</sub>. Table 2 displays the geometrical features of all the calculated structures and Figures 4 and 5 summarize both fragmentation reactions.



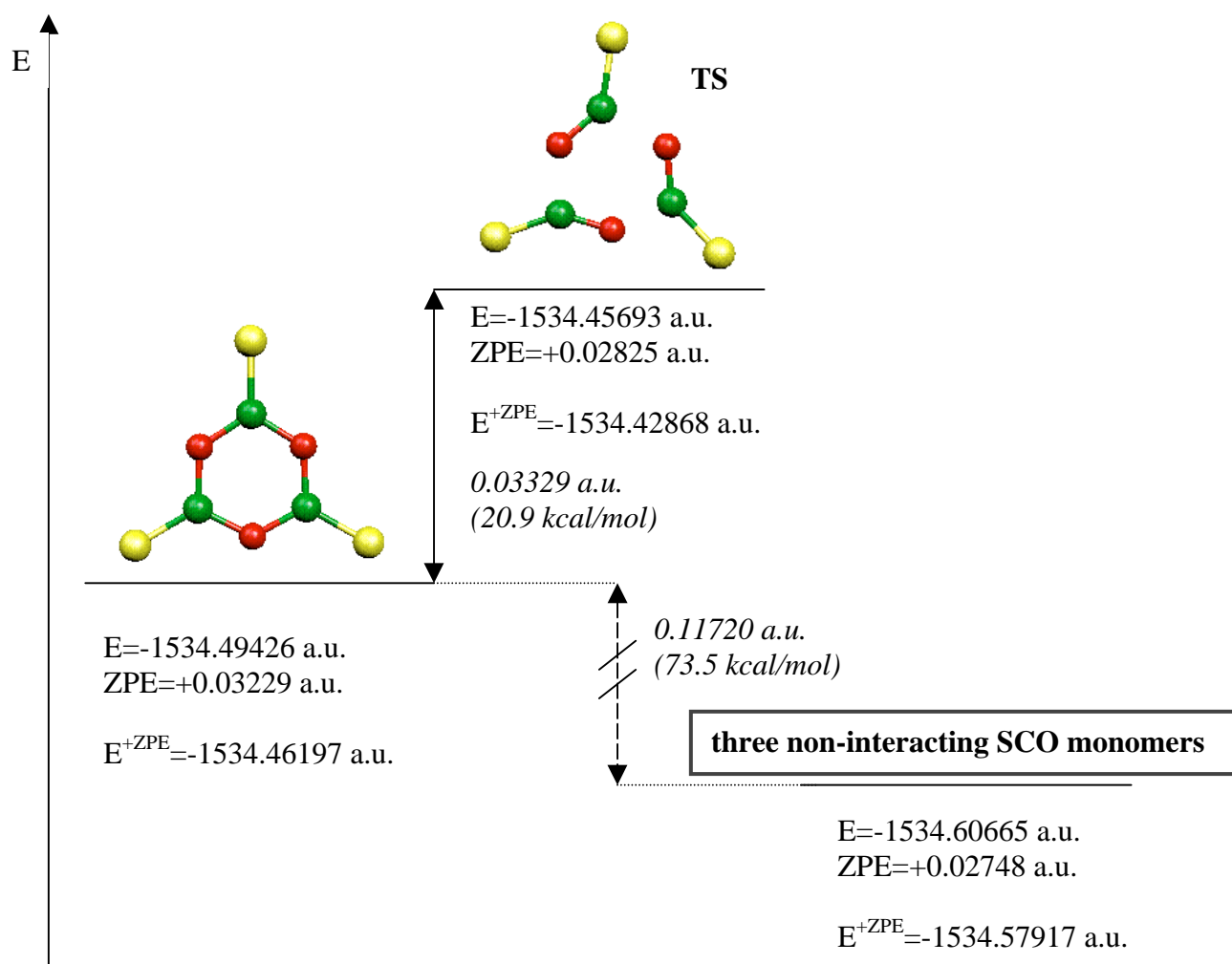
**Figure 4** Potential energy surface of the fragmentation reaction of the cyclic (SCO)<sub>3</sub> trimer at the B3LYP/6-31G\* level of theory

In the  $(\text{SCO})_3$  cyclic structure, the C=O bond length is 1.203 Å and thus, 0.019 Å longer than that of the analogous  $(\text{CO}_2)_3$  system. The C-S distance is 1.803 Å, which makes the whole structure more expanded than the analogous  $(\text{CO}_2)_3$ . The S-C-S angle is slightly larger than that in the  $(\text{CO}_2)_3$  system, whereas the O=C-S angle is slightly smaller and so does the C-S-C angle. The latter, 112.7°, is however larger than the corresponding C-S-C angle for the linear system  $(\text{CH}_3)_2\text{S}$  (99.1°) [6].

In the  $(\text{OCS})_3$  cyclic structure, the C=S bond length is 1.613 Å and therefore shorter than in the previous system, indicating a double bond character in this case (this value is close to that observed for C=S in  $\text{CS}_2$ , namely 1.56 Å) [6]. The C-O distance is 1.365 Å, which is very close to the corresponding value in the analogous  $(\text{CO}_2)_3$  structure. The characteristic valence angles are almost identical to those observed in  $(\text{CO}_2)_3$  and, therefore, the only major difference between  $(\text{CO}_2)_3$  and  $(\text{OCS})_3$  is the replacement of a C=O by a C=S bond.

From an energetic point of view,  $(\text{SCO})_3$  is 26.3 and 27.3 kcal·mol<sup>-1</sup> more stable than  $(\text{OCS})_3$ , without and with ZPE corrections, respectively. This energy difference may be explained by the larger bond energy of the C=O bond versus C-O and C=S bonds. It is known that the preferred structure for the thioethers is that with C=O double bond rather than C=S double bond [7].

The calculated vibrational frequencies for both these cyclic structures are reported in Table 3. The main differences are seen in the stretching modes corresponding to the C=X and C-Y bonds (X=O,S; Y=S,O in  $(\text{SCO})_3$  and  $(\text{OCS})_3$ , respectively). The corresponding frequencies are always higher for C=O and C-O than for C=S and C-S, respectively. This correlates well with the results reported previously for  $(\text{CO}_2)_3$  [1]. The in-plane bending mode ( $2a_1'$ ) also exhibits a higher value for O-C-O than for S-C-S. The frequencies of the out-of-plane bending modes leading to the motion between in-plane and boat conformation ( $1e''$  and  $2e''$ ) are almost equal in both cases. The values for the motion between in-plane



**Figure 5** Potential energy surface of the fragmentation reaction of the cyclic  $(\text{OCS})_3$  trimer at the B3LYP/6-31G\* level of theory

**Table 3** Calculated vibrational frequencies for the cyclic (SCO)<sub>3</sub> and (OCS)<sub>3</sub> structures at the B3LYP/6-31G\* level of theory

mode	ν((SCO) <sub>3</sub> ) (cm <sup>-1</sup> )		ν((OCS) <sub>3</sub> ) (cm <sup>-1</sup> )		Δν(cm <sup>-1</sup> ) [a]
1a <sub>1</sub> '	1786	R <sub>C-O</sub>	1381	R <sub>C-S</sub>	+405
2a <sub>1</sub> '	510	α <sub>SCS</sub>	851	α <sub>OCO</sub>	-341
3a <sub>1</sub> '	408	ring-breathing	462	ring-breathing	-54
1a <sub>2</sub> '	693	R <sub>C-S</sub>	1022	R <sub>C-O</sub>	-329
2a <sub>2</sub> '	452	α <sub>OCS</sub> (rotation)	474	α <sub>SCO</sub> (rotation)	-22
1a <sub>2</sub> ''	489	oop bending [b] (plane ↔ chair)	612	oop bending [b] (plane ↔ chair)	-123
2a <sub>2</sub> ''	102	“	79	“	+23
1e'	1764	R <sub>C-O</sub>	1289	R <sub>C-S</sub>	+475
2e'	986	R <sub>C-S</sub>	1173	R <sub>C-O</sub>	-187
3e'	532	R <sub>C-S</sub>	883	R <sub>C-O</sub> /R <sub>C-S</sub>	-351
4e'	337	R <sub>C-S</sub>	454	α <sub>OCO</sub>	-117
5e'	258	α <sub>SCS</sub>	217	α <sub>SCO</sub>	+41
1e''	574	oop bending [b] (plane ↔ boat)	581	oop bending [b] (plane ↔ boat)	-7
2e''	50	“	51	“	-1
<b>ZPE (a.u.)</b>	<b>0.03062</b>		<b>0.03229</b>		
<b>(kcal·mol<sup>-1</sup>)</b>	<b>19.2</b>		<b>20.3</b>		

[a]  $\Delta\nu(\text{cm}^{-1}) = \nu((\text{SCO})_3) - \nu((\text{OCS})_3)$

[b] where oop stands for out-of-plane

and chair conformation (1a<sub>2</sub>'' and 2a<sub>2</sub>'') are somewhat different. The lowest modes in e' symmetry correspond to in-plane bending modes and to single-bond stretching. The 4e' mode for (SCO)<sub>3</sub> and the 5e' mode for (OCS)<sub>3</sub> are analogous. In the former, the stretching C-S contribution dominates, whereas in the latter the bending S-C-O motion does. Finally, the mode corresponding to the ring fragmentation is 1a<sub>2</sub>'. Again, the associated vibrational frequency is lower for C-S (693 cm<sup>-1</sup>) than for C-O (1022 cm<sup>-1</sup>), which is in agreement with the value previously reported for (CO<sub>2</sub>)<sub>3</sub> fragmentation (958 cm<sup>-1</sup>) [1].

As far as the TS structures are concerned, a planar structure analogous to that obtained for (CO<sub>2</sub>)<sub>3</sub> is observed for (SCO)<sub>3</sub>. In contrast, the TS structure for the fragmentation of (OCS)<sub>3</sub> is no longer planar. The optimized structures for those both TS are presented in Figures 4 and 5, respectively.

For the TS structure that corresponds to the fragmentation of (SCO)<sub>3</sub>, the C=O distance is 1.177 Å, which is very close to the corresponding value in the case of (CO<sub>2</sub>)<sub>3</sub>. The C-S distance is 1.678 Å and thus, closer to a C=S bond than to a C-S one for the atoms belonging to the same SCO monomer, which agrees with the expected evolution of the fragmentation reaction. The corresponding C-S distance between the atoms of two different monomers is 2.217 Å. The C-C

distance between two monomers is 3.404 Å and the O-C-S angle is 139.7°, i.e. 23.3° larger than in the cyclic structure.

As regards the TS for the fragmentation of (OCS)<sub>3</sub>, a non-planar system has been obtained. The C=S distance is 1.594 Å, whereas the C-O distances are 1.250 and 1.696 Å between two atoms belonging to the same and to different monomers, respectively. The valence angle S-C-O is 139.8°, i.e. 17.6° larger than that in the cyclic analogue.

As all the other structures calculated here, the TS structures have been characterized by vibrational frequencies analysis. In both cases, a unique imaginary frequency is obtained with a value of 495i cm<sup>-1</sup> and 618i cm<sup>-1</sup> for (SCO)<sub>3</sub> and (OCS)<sub>3</sub>, respectively. These values correlate well with those reported in Table 3 for the modes responsible for fragmentation of the cyclic structure (1a<sub>2</sub>'). Indeed, the corresponding mode has a lower frequency for the breaking of a C-S bond than for that of a C-O bond. This is in agreement with the bond strength order, namely the C-O bond is stronger than the C-S bond.

**Energetic Features** The activation energy, i.e. the energy difference between the TS and the cyclic structure, has been calculated for each case. ZPE corrections to the energies have been included. For (SCO)<sub>3</sub> and (OCS)<sub>3</sub>, the values for the

**Table 4** Optimized structural parameters for HNCO trimeric structures (cyclic and TS) and HNCO monomer at the B3LYP/6-31G\* level of theory

	cyclic	Exp. [8]	B3LYP/6-31G*	HF/3-21G [1]
	$d_{C=O}/d_{C-N}$ (Å)	1.224/1.371	1.211/1.392	
	$d_{N-H}$ (Å)	—	1.012	
	$\alpha_{O=C-N}$ (°)	122.9	123.5	
	$\alpha_{N-C-N}$ (°)	115.4	113.0	
	$\alpha_{C-N-C}$ (°)	124.6	127.0	
	$\alpha_{H-N-C}$ (°)	117.7	116.5	
	Energy (au)		-506.12707	
	+ZPE (au)		-506.04620	-500.48963
	<b>TS</b>			
	$d_{C=O}/d_{C-N}$ (Å)		1.179/1.260	
	$d_{C...N}$ (Å)		2.059	1.700 [a]
	$\alpha_{OCN}$ (°)		158.2	
	$\alpha_{H-N-C}$ (°)		114.1	
	Energy (au)		-505.98539	
	+ZPE (au)		-505.91494	-500.31954 [a]
	$E_a$ (kcal·mol <sup>-1</sup> ) [b]		<b>88.9</b>	
	+ZPE (kcal·mol <sup>-1</sup> )		<b>82.4</b>	<b>106.9</b>
	<b>HNCO</b>			
	$d_{C=O}/d_{C-N}$ (Å)		1.174/1.219	
	$d_{N-H}$ (Å)		1.009	
	Energy (au)		-168.67750	
	+ZPE (au)		-168.65621	-166.79187
	3*E(HNCO) (au)		-506.03250	
	+ZPE (au)		-505.96863	-500.37561
	$\Delta E$ (au) [c]		+0.09457	
	(kcal·mol <sup>-1</sup> )		+59.3	
	+ZPE (au)		+0.07757	+0.11402
	(kcal·mol <sup>-1</sup> )		+48.7	+71.5
[a] C...N “broken” bond constrained at 1.700 Å				
[b] $E_a = E(TS) - E(cyclic)$				
[c] $\Delta E = 3 * E(HNCO) - E(cyclic)$				

energy barrier are 21.0 and 20.9 kcal·mol<sup>-1</sup>, respectively. As in the case of (CO<sub>2</sub>)<sub>3</sub>, the fragmentation energy per monomer is ~7 kcal·mol<sup>-1</sup>, which indicates that the fragmentation of the cyclic structures into three non-interacting SCO monomers is again a facile process.

As in the previous case, the ZPE corrected energies of both (SCO)<sub>3</sub> and (OCS)<sub>3</sub> cyclic structures are higher (46.2 and 73.5 kcal·mol<sup>-1</sup>, respectively) than that of three non-interacting SCO monomers, which indicate that the fragmentation reactions studied here are exothermic processes.

### (HNCO)<sub>3</sub>

**Structural Features** First, the geometry of the cyclic (HNCO)<sub>3</sub> trimer or cyanuric acid has been optimized at the B3LYP/6-31G\* level of theory. Then, the TS for the fragmentation reaction of cyanuric acid into three HNCO monomers has been found. Finally, the structure of the HNCO monomer has been calculated. Figure 6 shows the different structures characterized along the fragmentation reaction and Table 4 displays the numerical values of the optimized geometrical features.

The calculated geometry for cyanuric acid is in good agreement with experimental data. No systematic overestimation neither underestimation is observed either for bond lengths or valence angles.

In this case, a planar structure has been again obtained for the TS of the fragmentation reaction. The C=O bond decreases from 1.211 in the cyclic structure to 1.179 Å in the TS structure. The same effect occurs on the C-N bond, which varies from 1.392 to 1.260 Å. This behavior is in agreement with the expected evolution of the studied reaction. Indeed, these bond lengths are closer to their respective values in HNCO monomers (Table 4). The “broken” C...N distance is 2.059 Å and therefore closer to the corresponding distance of the TS of (SCO)<sub>3</sub> fragmentation than to those of the TS of (CO<sub>2</sub>)<sub>3</sub> and (OCS)<sub>3</sub> fragmentations. The OCN valence angle increases from 123.5 to 158.2°, whereas the HNC angle slightly decreases from 116.5 to 114.1°.

Vibrational frequencies analysis of the TS structure shows a unique imaginary frequency (491i cm<sup>-1</sup>) corresponding to the fragmentation motion. This value is closer to that obtained for the fragmentation of a C-S bond than to that corresponding to the fragmentation of a C-O bond. Again, the right trend of bond strengths is reproduced.



**Energetic Features** In contrast to the previous cases, the activation energy for the fragmentation reaction of cyanuric acid is 82.4 kcal·mol<sup>-1</sup> including ZPE corrections. This energy leads to a value of ~27.5 kcal·mol<sup>-1</sup> per HNCO monomer, which is almost four times higher than the corresponding values for (CO<sub>2</sub>)<sub>3</sub>, (SCO)<sub>3</sub>, and (OCS)<sub>3</sub>. Previous calculations at the HF/3-21G level led to an activation energy of 106.9 kcal·mol<sup>-1</sup> [1]. It is therefore to note that, the fragmentation reaction of cyanuric acid is not such a favorable process as the fragmentation of the other cyclic trimers presented in this work.

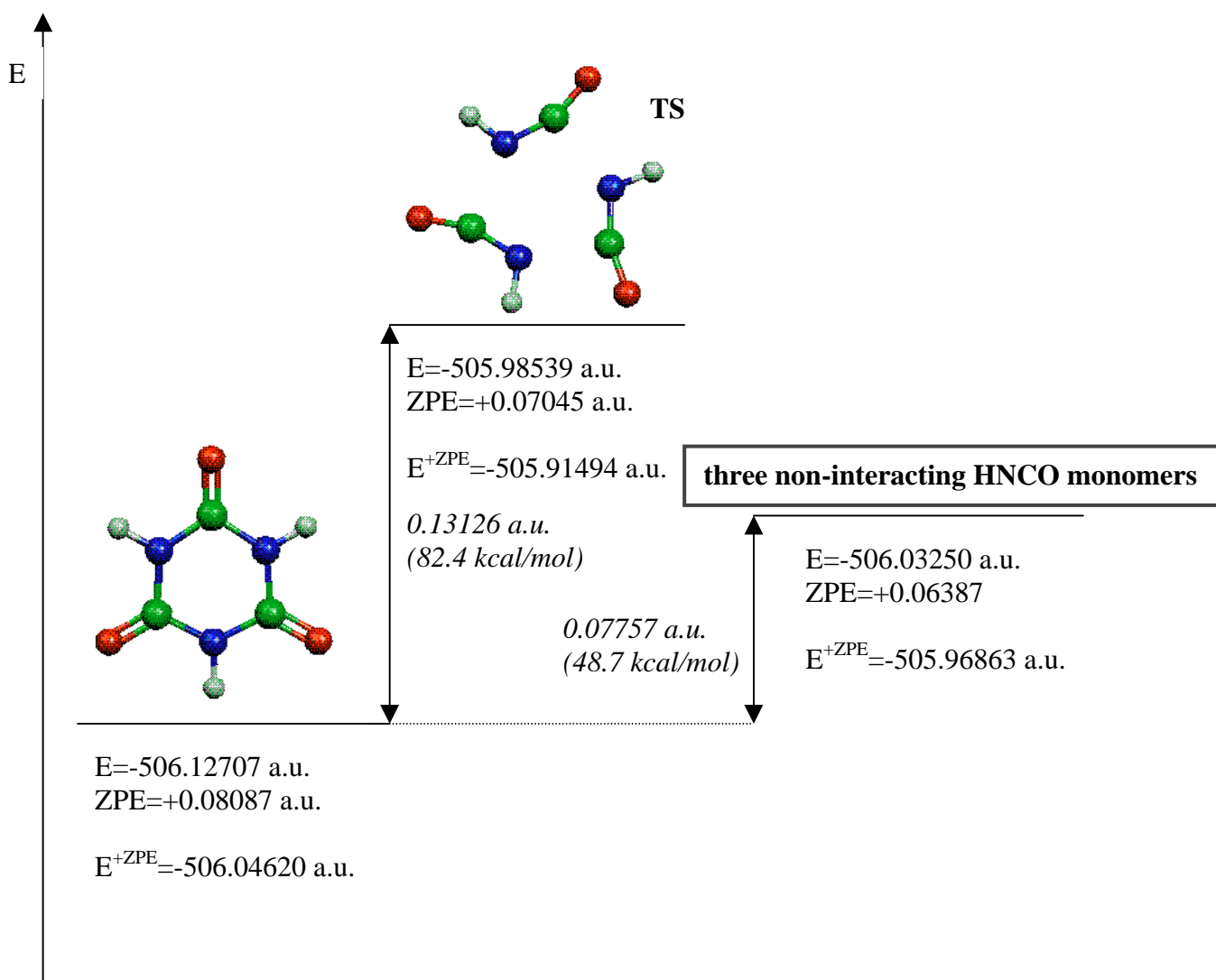
The energy difference between the (HNCO)<sub>3</sub> cyclic structure and that of three non-interacting HNCO monomers is 48.7 kcal·mol<sup>-1</sup> including ZPE corrections. However, as illustrated in Figure 6, the cyclic structure is now more stable than three free monomers, which means that the process is endothermic. This is in contrast with the previous systems

and, together with the large activation energy calculated for (HNCO)<sub>3</sub> fragmentation, stands for an unfavorable fragmentation reaction.

## Conclusions

In this work, DFT calculations using the hybrid B3LYP functional have provided useful information for a better understanding of the structure and energetics of main group element trimers.

The calculations presented here show that both (SCO)<sub>3</sub> and (OCS)<sub>3</sub> systems may undergo a fragmentation reaction. Indeed, the calculated activation energy for the reaction is low when compared to that of other known systems. In addition, the reaction is favored by the higher stability of three



**Figure 6** Potential energy surface of the fragmentation reaction of the cyclic (HNCO)<sub>3</sub> trimer at the B3LYP/6-31G\* level of theory

non-interacting SCO monomers when compared to the corresponding cyclic structures. Finally, even if both  $(\text{SCO})_3$  and  $(\text{OCS})_3$  fragmentation reactions are exothermic, the latter is more exothermic than the former by almost  $30 \text{ kcal}\cdot\text{mol}^{-1}$ .

A similar behavior is observed for the cyclic  $(\text{CO}_2)_3$  trimer, the reaction being as exothermic as that of  $(\text{SCO})_3$ . However, the fragmentation reaction of the cyclic  $(\text{HNCO})_3$  trimer is not such a favorable process. Indeed, the activation energy of the reaction is very high and the cyclic structure is much more stable than three free HNCO monomers. In this case, an endothermic process is observed.

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