J. Am. Chem. Soc. **2000,** *122,* 5367−5370

Search for New Allotropic Forms of Carbon Dioxide and Carbon Disulfide: A Density Functional Study of CX_2-Based Oligomers (X = O, S)

Gilles Frapper* and Jean-Yves Saillard

Contribution from the LACCO UMR 6503-CNRS, Université de Poitiers, 86022 Poitiers Cedex, France, and LCSIM UMR 6511-CNRS, Université de Rennes 1, 35042 Rennes Cedex, France

Received October 4, 1999

Abstract: Polymeric phases for carbon dioxide and carbon disulfide are predicted on the basis of density functional calculations. Poly-$COO_{2/2}$ containing three-coordinated carbon atoms is calculated to be 22 kcal/mol less stable than free molecular CO_2, while its sulfur analogue poly-$CSS_{2/2}$ is 19 kcal/mol higher in energy than free CS_2. Another polymeric carbon disulfide phase based on $CS_{4/2}$ tetrahedra is calculated to be only 2 kcal/mol higher in energy than the trithiocarbonate-based polymer poly-$CSS_{2/2}$. A three-dimensional CO_2 silica-like compound may be derived from the corresponding $CO_{4/2}$-based polymeric model which is higher in energy than free CO_2 by 40 kcal/mol. Besides these solid-state compounds containing an extended network, four- and six-membered rings $(CX_2)_n$ ($n = 2, 3$) have been calculated to be less stable than their corresponding monomers by less than 15 and 24 kcal/mol for X = S and O, respectively. The planar cyclic oligomers of CS_2 should be feasible and could be the precursors in the synthesis reaction of the one-dimensional poly-$CSS_{2/2}$ phase.

Introduction

The search for new allotropic or polymorphic phases of known compounds is a fascinating area, which can lead to materials exhibiting unusual properties and are also often attractive from both the fundamental and the aesthetical points of view. Typical examples can be found in the area of condensed phases of small molecular species which have been prepared by using various experimental techniques: ring-opening-polymerization, for example, polyphosphazene $-(NPCl_2)_x-$,[1] pressure-induced polymerization of molecular crystals, for example, cyanogen C_2N_2,[2] or thermally controlled polymerization, for example, S_2N_2.[3] A way to design new stable or metastable polymers or materials based on existing molecular species is to use the predictive ability of quantum chemical methods. We recently predicted by using this approach the existence of a polymeric phase of carbon monoxide,[4] which has been thereafter synthesized under high-pressure by Lipp and co-workers.[5] Continuing our search for new condensed phases derived from simple molecules, we investigate below the possibility for carbon dioxide (CO_2) and its isoelectronic species carbon disulfide (CS_2) to exist in the form of extended networks. As this work was in progress, quartz-like CO_2 has been characterized at high pressure.[6] Independently, a theoretical investigation using ab initio molecular dynamic simulations on pressure-induced solid CO_2 has confirmed these experimental findings.[7]

The topology of a chemical species made of one or several triatomic 16-valence electrons AX_2 units is directly related to the coordination number (C.N.) of the central atom A. For example, C.N. = 2 in molecular CO_2 **1**, C.N. = 3 in the ring compound $(CNCl)_3$ **2**, C.N. = 4 in the $BeCl_2$ polymer **3** as well as in several members of the SiO_2 silica family. In these examples, the octet rule is satisfied for all the atoms, which is not always the case in some silica phases such as stishovite where Si is hypervalent with C.N. = 6.[8] In the case of CS_2, two different coordination numbers have been shown to exist: C.N. = 2 in the molecular state **4** and CN = 3 in the high-pressure polymeric phase, the so-called Bridgman's black disulfide $(CS_2)_x$ **5**.[9] The literature describes this polymer as connected trithiocarbonate ($S_2C{=}S$) groups with S−S cross-linked structure.[10] This polymeric form of a 16-valence triatomic species bridges the gap between molecular CO_2 and the three-dimensional SiO_2 phases.

One may ask if carbon dioxide may polymerize as carbon disulfide CS_2 having the structural type **5** (thereafter called poly-$CXX_{2/2}$) or if CS_2 could exist in a form similar to **3**, that is, with four-connected carbon atoms, that is, poly-$CX_{4/2}$. A DFT investigation on the possibility of existence of extended networks for such 16-valence-electrons CX_2 (X= O, S) species is detailed thereafter.

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* To whom correspondence should be addressed. Fax: 33 (0)5 49 45 34 99. E-mail: gilles.frapper@campus.univ-poitiers.fr.

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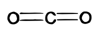

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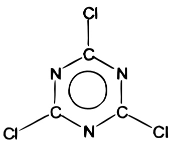

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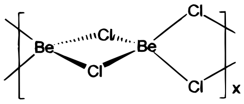

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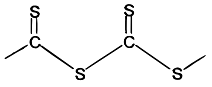

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Methods and Modeling

All of the geometry optimizations were carried out with the use of the Gaussian 94 package at the B3LYP level, using the 6-31G** basis set (B3LYP/6-31G** calculations).[11] Harmonic vibrational frequencies and zero-point vibrational energies (ZPVE) were computed at this level. All of the optimized structures where characterized as true minima. The total energies considered in this study were obtained by running single-point calculations on the optimized geometries with the larger 6-311++G** basis set (B3LYP/6-311++G**//B3LYP/6-31G** calculations, ZPVE corrected). Detailed results are given in Supporting Information.

The energy per CX_2 repeat unit of an infinite polymer has been calculated by using the finite difference method[12] which consists of calculating the total energies E_n of saturated oligomers $R(CX_2)_nR$ of increasing length. When n increases, the difference function $\Delta E_n = (E_{n+1} - E_n)$ is expected to tend to the polymer energy per repeat unit. The asymptotic value of ΔE_n is considered to be reached when the difference energy is less than 1 kcal/mol. In the following, we define as δE the difference between ΔE_n and the energy of the free triatomic molecular CX_2 species. Therefore, a negative (positive) δE value indicates that the extended structure is more (less) stable than the free triatomic molecule. In the case where cyclic $(CX_2)_n$ models where considered, $\delta E'$ was computed as being the difference between $(1/n) \times E[(CX_2)_n]$ and the energy of the triatomic molecular CX_2 species.

Results and Discussion

Cyclic Oligomers with C.N. = 3. The four- and six-membered $(CX_2)_n$ cyclic species have been calculated (X = O **6a**−**7a**, X = S **6b**−**7b**) as well as their corresponding CO_2 **1** and CS_2 **4** monomers. Their structures are based on the CS_2 dimer **6b** which has been proposed to polymerize into the $-(CS_2)_x-$ polymer **5**,[10b−d] and on the structurally characterized isoelectronic six-membered rings $C_3N_3Cl_3$ **2** or $B_3O_3F_3$ molecules.[13,14] The optimized structures and their relative energies $\delta E'$ of the $(CX_2)_n$ compounds ($n = 1-3$) are shown in Figure 1. All of the calculated models were found to be planar. The only unusual geometrical parameters are the rather short C···C nonbonding distances in the four-membered rings which lie in the range of 1.759−2.360 Å. Those values are lower than twice the van der Waals radius of carbon (3.7 Å[15]). Such unusually short nonbonding distances have been shown to exist in 1,3-disubstituted four-membered rings such as in cyclodisiloxane,[16] as well as in the B_2C_2 rhombuses existing in the two-dimensional B_2C network of the YB_2C phase.[17] Theoretical analysis have shown that this peculiar feature can be explained by using the σ-bridged-π bonding model.[18] This is a pure σ-type (in-plane) effect whose strength depends on the electronegativity difference between the two types of atoms constituting the ring. Besides these structural peculiarities of the four-membered ring, the geometrical parameters found for the $(CX_2)_n$ ($n = 1-3$) series lie in the range of expected values.

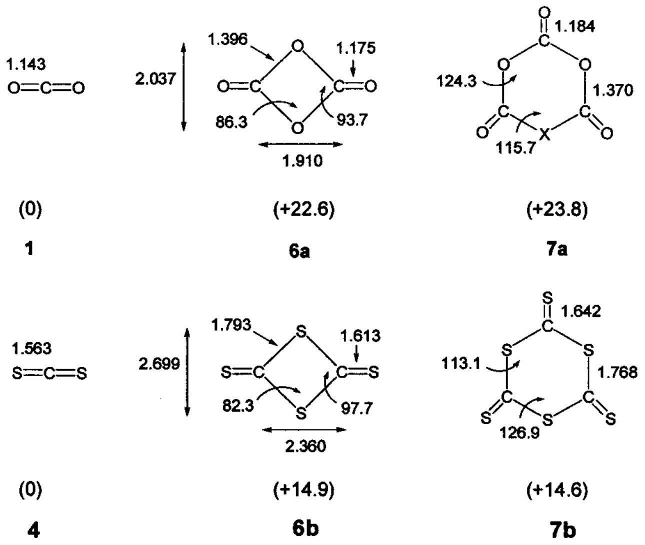

Figure 1. Optimized structures of $(CX_2)_n$ compounds ($n = 1-3$). **1**: CO_2 ($D_{\infty h}$); **6a**: C_2O_4 (D_{2h}); **7a**: C_3O_6 (D_{3h}); **4**: CS_2 ($D_{\infty h}$); **6b**: C_2S_4 (D_{2h}); **7b**: C_3S_6 (D_{3h}). Selected parameters are given (distances in Å and angles in degrees). In parentheses are given the relative energies per CX_2 repeat unit of the $(CX_2)_n$ species with respect to the free CX_2 monomer at the B3LYP/6-311+G*//B3LYP/6-31G* level of theory ($\delta E' = E(CX_2)_n/n - E(CX_2)$, in kcal/mol).

C_2S_4 **6b** and C_3S_8 **7b** are computed to be less stable than free CS_2 by less than 15 kcal/mol (per CS_2 unit) while their oxygen analogues C_2O_4 **6a** and C_3O_6 **7a** are less 24 kcal/mol (per CO_2 unit) higher in energy than free CO_2 (see Figure 1). Changing X into O in $(CX_2)_n$ rings increases $\delta E'$ by 9 kcal/mol, because of the larger ring strain in the oxygen species. Although less stable than their free monomers, oligomers of CS_2 (and perhaps even of CO_2) should be feasible, and these calculations support the hypothetical existence of C_2S_4 during the polymerization process of molecular CS_2 in $-(CS_2)_x-$.[10b−d]

$(CS_2)_n$ ($n = 2-4$) Systems Presenting S−S Bonds. The peculiarity of sulfur is its ability to easily make S−S bonds. This is why we have investigated hypothetical oligomers of CS_2, namely C_2S_4 **8a**−**b**, C_3S_6 **9a**−**b**, and C_4S_8 **10**, in which both sulfur−sulfur and carbon−carbon bonds are present (see Figure 2). C_2S_4 **8a** is higher in energy by 6.8 kcal/mol than its isomer

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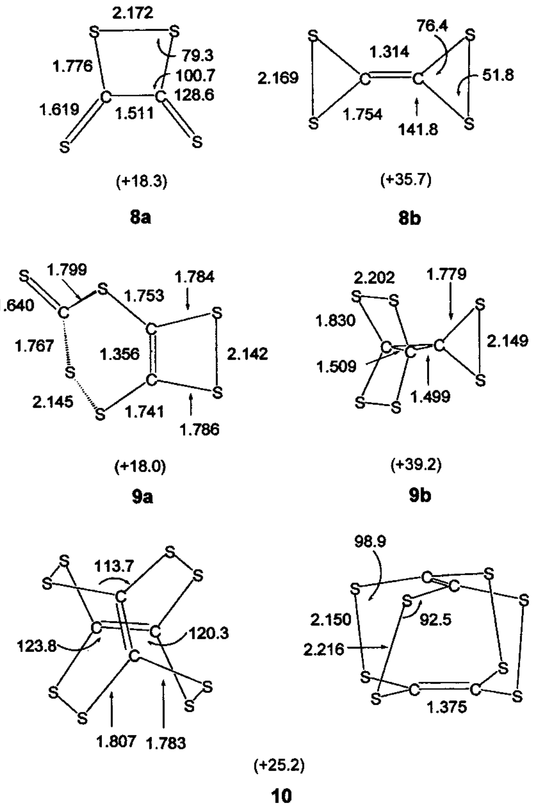


Figure 2. Optimized structures for C_{2v} **8a** and D_{2h} **8b** C_2S_4 isomers, C_1 **9a** and C_{2v} **9b** C_3S_6 isomers and D_2 **10** C_4S_8 compound. Selected parameters are given (distances in Å and angles in degrees). In parentheses are given the relative energies per CS_2 repeat unit of the $(CS_2)_n$ species with respect to the free CS_2 monomer monomer at the B3LYP/6-311+G*//B3LYP/6-31G* level of theory ($\delta E' = E(CS_2)_n/n - E(CS_2)$, in kcal/mol).

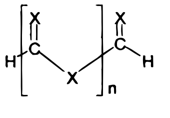
6b. The C_2S_4 core in **8a** has been claimed to be present in the architecture of carbon disulfide clusters anions, $(CS_2)_n^-$.[19] Structure **8b** with two strained three-membered rings is found to be rather unstable. Compound **9a**, a C_3S_6 molecule made of fused four- and six-membered rings, is calculated to be 10.1 kcal/mol higher in energy than the six-membered ring **7b**, while the fish-like strained compound **9b** is much less stable. The C_4S_8 model **10** presents a non-eclipsed geometry of D_2 symmetry with a nonbonded carbon–carbon distance of 2.648 Å between two C_2S_4 linked units. C_4S_8 is calculated to be less stable than free CS_2 ($\delta E' = 25$ kcal/mol). It is also less stable than the cyclic oligomers. Due to the exposed carbon atoms, this molecule must be highly reactive vis-à-vis a chemical attack.

Extended Structures with C.N. = 3. We discuss now the possibility of existence of extended networks made of the assembly of 16-electron CX_2 (X = O, S) monomers, starting with the investigation of poly-$CXX_{2/2}$ structure type **5**.[20] This model is derived from the structures of the characterized black $-(CS_2)_x-$ compound and from that of the metaborate $LiBO_2$ where similar one-dimensional BO_2^- chains are present.[21] To model the poly-$CXX_{2/2}$ system and evaluate its stability with respect to the free monomer, the finite difference method, based on calculations on polymers of increasing length,[12] was used (see above). Calculations have been done on the $H(C_{n+1}X_{2n+1})H$ series with X = O **11a** and S **11b**. Each oligomer structure has a starting all-trans conformation, that is, with the X–C–X–C dihedral angle (τ) along the chain set to 180° (a cis conformation is associated with $\tau = 0°$). This choice of the starting conformation before geometry optimization allowed us to get a homogeneous set of ΔE_n values within each series of compounds, avoiding the variation irregularities due to the peculiar conformational preference of each individual oligomer. We would like to mention here that rotation around the single bonds of the studied oligomers is very easy and is mostly dictated by packing forces in a real material and that prediction of the conformational structure of the poly-$(CXX_{2/2})_x$ was not our goal in using such molecular modeling approach. Table 1 summarizes the computational data on the oligomers **11**. Detailed structural parameters and the energies are given in Supporting Information. We discuss briefly below the major geometrical features of the calculated oligomers. Selected molecular structures are shown in Figure 3.

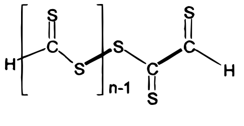
Table 1. Relative Energies δE^a (in kcal/mol) with Respect to Free CX_2 for CX_2-based Oligomers $H(C_{n+1}X_{2n+1})H$ **11** and $H_2(C_{n+1}X_{2n})H_2$ **12** (X = O, S)

n	11a	11b	11c	12a	12b
1	+21.4	+17.4		+34.3	+17.8
2	+22.1	+17.7	+20.3	+40.1	+20.6
3	+22.2	+18.6		+40.3	+20.7

[a] Relative energy per CX_2 repeat unit of the oligomers with respect to the free CX_2 monomer [$\delta E = E_{n+1} - E_n - E(CX_2)$]. The energies are calculated at the B3LYP level using the 6-311++G** basis set at the optimized B3LYP/6-31G** geometry (ZPVE corrected). See Supporting Information.



11a (X = O), **11b** (X =S)



11c

The optimized structures of the $H(C_{n+1}X_{2n+1})H$ models (X = O, S; $n = 1-4$) adopt (or are very close to) the C_2 symmetry, which renders equivalent both halves of each chain. They are nonplanar and exhibit typical C–X and C=X bond lengths (C–O = 1.365–1.396 Å; C=O = 1.187–1.191 Å; C–S = 1.767–1.804 Å; C=S = 1.616–1.622 Å).[8,15] The carbon atoms always maintain their expected (locally planar) sp^2 hybridization. Consequently, the conformation of the studied oligomers can be simply described by the series of the dihedral angles τ ($152 < \tau < 154°$ for X = O and $129 < \tau < 156°$ for X = S, see Figure 3). Turning the discussion to the variation of δE upon n (Table 1), one can see that for $n = 4$ the oscillations due to the small size effect are damped, and the asymptotic value of δE is nearly reached. At our level of calculations (B3LYP/6-311++G**//B3LYP/6-31G**, ZPVE corrected), poly-$CXX_{2/2}$ is computed to be less stable than the free CX_2 monomer by 22 and 19 kcal/mol (per CX_2 unit), for X = O and S, respectively.

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(19) Maeyama, T.; Oikawa, T.; Tsumura, T.; Mikami, N. *J. Chem. Phys.* **1998**, *108*, 1368. Their HF geometry optimization of $C_2S_4^-$ lead to a C_{2v} structure similar to **8a**, which they calculated to be the most stable form. Inversely, our UB3LYP/6-311++G** calculations show that the D_{2h} conformation of $C_2S_4^-$, similar to **6b**, is a local minimum lying 6.2 kcal/mol below the C_{2v} isomer.

(20) We have also investigated the hypothetical polymeric systems poly-$BFO_{2/2}$ and poly-$CClN_{2/2}$ derived from the existing six-membered ringd $C_3N_3Cl_3$ **3** and $B_3O_3F_3$ by ring-opening polymerization. Calculations have been done on (i) the $H(B_{n+1}O_nF_{n+1})H$ series, (ii) the $[H(C_{n+1}N_nCl_{n+1})H]^+$ cationic species, and (iii) the neutral $H(C_nN_nCl_n)H$ series. The calculated values of δE indicate that the polymerization process of the cyclic trimer, $nB_3O_3F_3 \rightarrow (BOF)_{3n}$, is almost thermoneutral. Poly-nitrile $-(CN_{2/2}Cl)_x-$ is found to be isoenergetic with the experimentally characterized $C_3N_3Cl_3$ cyclic compound, rendering this hypothetical helical polymer an interesting target for synthesis (manuscript in preparation).

(21) Note that $B_3O_6^{3-}$ isostructural and isoelectronic to $B_3O_3F_3$ is known as, for example, in $Na_3B_3O_6$. See ref 8a, p 1070–1071.

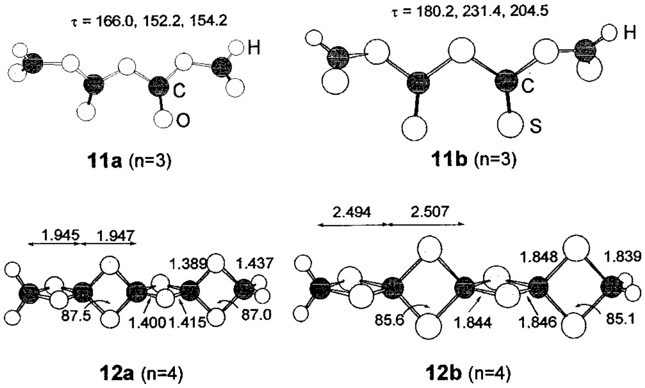
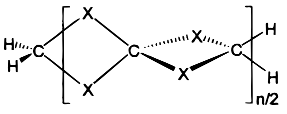


Figure 3. Optimized structures for HC_4O_7H **11a** (C_2), HC_4S_7H **11b** (C_1), $H_2(C_5O_8)H_2$ **12a** (D_{2h}) and $H_2(C_5S_8)H_2$ **12b** (D_{2h}) oligomers. Selected parameters are given (distances in Å, bond angles and dihedral angles along the H−C−X−C chain (τ) in degrees).

These values compare well with those obtained for cyclic oligomers (see Figure 1). On the basis of the rather small difference between both δE values (less than 3 kcal/mol) and on the fact that poly-CS_2 exists, one may conclude that the polymerization of CO_2 to the extended one-dimensional −O−C(=O)−O-containing network should be feasible, at least from a thermodynamical point of view.

Because the sum of one S−S and one C−C bond energies is nearly equal to two C−S bond energies,[15] one may be tempted to consider an alternative one-dimensional polymer analogue to **5**, namely **11c**. The increment energy δE for this model **11c** is calculated to be of the same order of magnitude as that for the one found in regular Bridgman's $(CS_2)_x$ **5** (see Table 1).

Extended Structures with C.N. = 4. We now turn the discussion to the possibility for poly-CX_2 to have a four-coordinated carbon atom leading to the design of a compound having connected CX_4 tetrahedra.[22,23] Let us remember that a high-pressure quartz-like CO_2 phase has been recently characterized[6] and that several carbonate-like CO_2 phases have been theoretically predicted to be stable at high pressure.[7] In this contribution, we consider the one-dimensional $H_2(C_{n+1}X_{2n})H_2$ series of oligomers **12**. The structure of these models is directly related to that of **3**. Such a structure for 16-electron AX_2 species is well-known, as in fibrous SiO_2 or SiS_2.[8a] In Table 1 are listed the relative energies δE calculated for the $H_2(C_{n+1}X_{2n})H_2$ oligomers with X = O, **12a**, and S, **12b**. Figure 3 shows the optimized molecular structures of the $H_2(C_5O_8)H_2$ and $H_2(C_5S_8)H_2$ oligomers. The only unusual structural parameters are the rather short C···C distances calculated between two nonbonded carbon atoms, less than 2 Å in $H_2(C_{n+1}O_{2n+1})H_2$ oligomers, as found also in the cyclic C_2X_4 dimers (see **6a**−**b**). Again, this is due to the σ-bridged-π orbitals effect described by Allen and others.[18] Poly-$CO_{4/2}$ (C.N. = 4) is computed to be less stable than the free CO_2 monomer (C.N. = 2) by 40 kcal/mol, and 18 kcal/mol less stable than poly-$COO_{2/2}$ (C.N. = 3) which contains O−C(=O)-O groups. Clearly, CO_2 phases in which carbon is four-coordinated are disfavored at standard pressure. The calculated energy differences are not very high, and one may think that they are probably overestimated, due to the simplification of three-dimensional silica-like phases by the one-dimensional models **12a**. On the other hand, we note that at low pressure the energy difference between molecular and extended CO_2 phases is calculated by Serra et al. to be ∼47 kcal/mol, a value somewhat larger (although of the same order of magnitude) than our δE value calculated for **12a**.[24] Let turn our discussion to the isostructural model of $BeCl_2$ **3** based on CS_4-tetraedra (see model **12b** with X = S). Poly-$CS_{4/2}$ (C.N. = 4) is evaluated to be only 2 kcal/mol less stable than poly-$CSS_{2/2}$ **11b** (C.N. = 3). On the basis of these results, one may conclude that an hypothetical condensed CS_2 phase may present four-connected carbon atoms as in the experimentally characterized $C(SR)_4$ molecules (e.g., R = Ph).[25]



12a (X = O), **12b** (X= S)

Summary and Future Prospectives

Density functional (B3LYP) calculations have been carried out on a series of oligomer-made 16-valence electron triatomic repeat units to investigate the stability of polymeric and condensed allotropics forms of CO_2 and CS_2. The planar cyclic compounds $(CS_2)_n$ (n = 2, 3) have been calculated to be thermodynamically slightly more stable than the existing one-dimensional chain $-(CSS_{2/2})_x-$ containing trithiocarbonate ($S_2C{=}S$) groups. These results reinforce the hypothesis that four-membered ring C_2S_4 may be a suitable precursor during the CS_2 polymerization. With four-coordinated carbon atoms, poly-$CS_{4/2}$ made of CS_4 shared tetrahedra is calculated to be almost isoenergetic to poly-$CSS_{2/2}$ and 19 kcal/mol higher in energy per CS_2 repeat unit than molecular carbon disulfide. This model, which mimics a silica-like CS_2 structure, suggests that such phases might some day be synthesized. The oxygen analogue compounds are higher in energy than the sulfur ones as compared to their free CX_2 (X = O, S). The one-dimensional poly-$COO_{2/2}$ containing three-coordinated carbon atoms is calculated to be lower in energy by 18 kcal/mol (per CO_2 unit) than the three-dimensional poly-$CO_{4/2}$ and 22 kcal/mol higher in energy than free CO_2.

We are currently using the same theoretical approach to investigate the stability of hypothetical polymeric forms of molecular species such as carbon sulfide and sulfur dioxide.

Acknowledgment. All calculations have been performed on a SP2 computer at the Centre Informatique National de l'Enseignement Supérieur (CINES) which is acknowledged for allocations of computer time (project No. c981019). We are grateful to John Akapulco for the drawings.

Supporting Information Available: B3LYP/6-31G** total energies (hartrees), zero-point vibrational energies (kcal/mol), and B3LYP/6-311++G**//B3LYP/6-31G** single-point total energies (hartrees) for all compounds discussed in the text. Vibrational frequencies for all $(CX_2)_n$ (n = 1−3) **1**, **4**, **6**−**7** and C_4S_8 **10** compounds and geometrical parameters for all $R(CX_2)_nR$ oligomers **11**−**12** with X = O and S are summarized (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9935714

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[22] Such $CO_{4/2}$ motif is present in very few structurally characterized molecular compounds: (a) Boulos, L. S.; Hennawy, I. T. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *84(1)*, 173. (b) Palomo, C.; Alzpurua, J. M.; Garcia, J. M.; Picard, J. P.; Dunogues, J. *Tetrahedron Lett.* **1990**, *vol. 31*, 13, 1921. (c) Jutzi, P.; Eikenberg, D.; Möhrke, A.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 753.

[23] Note that orthocarbonate $C(OR)_4$ compounds are known. See for example: Narasimhamurthy, N.; Manohar, H.; Samuelson, A. G.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1990**, *112*, 2937 and references therein.

[24] Chiarotti, G. L. Private communication. See also Figure 2 in ref 7.

[25] Von Katsuo, K. *Acta Crys.***1972**, *B28*, 606.