



The exceptions to the Walsh rules: Linear and cyclic structures of EX_2 (E = C, Si, Ge, Sn, Pb and X = O, S, Se)



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ABSTRACT

The stable minima of the EX_2 molecule (E = C, Si, Ge, Sn, Pb, and X = O, S, Se) with linear and cyclic structures were calculated at CCSD(T) and B3LYP levels. Most of dioxides favor linear structure following Walsh rules. However, lead dioxide is stabilized as cyclic structure. For sulfides, both cyclic SnS_2 and PbS_2 are found to be lower in energy while CS_2 and SiS_2 keep linear structure as most stable formula. As for selenides, more cyclic structures are located in lower energy than linear structures. The great difference between the linear and cyclic structures was mainly caused by relativistic effects, where greater size difference between valence *s* and *p* orbital in heavier atoms have lower tendency to form *sp* hybrid orbital. Finally the cyclic structure was analyzed in detailed according to NBO data and selected molecule orbital.

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1. Introduction

Compounds of the heavier main group elements are known to exhibit unusual structures compared with first-row molecules. A typical example is the heavy-atom analogues of acetylene that possess peculiar equilibrium geometries [1–6]. The unusual structures of E_2H_2 (E = Si–Pb) have been explained in terms of interactions between EH fragments in different electronic states [7]. Some heavier analogues of the HCN–HNC system also have different geometries from the first-row molecules. HPSi has a bent geometry, in contrast to the linear isovalent first-row compounds HCN, HNSi, and HCP [8]. The HCN–HNC system and the heavier analogues are potential targets to be detected in interstellar space and are experimentally interesting compounds to synthesize and characterize spectroscopically [9].

The global minimum of sixteen-electron triatomics is predicted to be linear by the Walsh rules [10]. Indeed, for molecules containing first-row elements (for example CO_2 , N_2O), this is a well-established principle [11]. Regarding heavier elements, though, the situation is often complicated. For the sixteen-electron triatomic molecules, most of linear forms are the global minimum but that cyclic isomers exist as local minima [12]. The energy difference between linear and cyclic structures decreases upon inclusion of heavier elements, suggesting that cyclic forms are sufficiently stable to make them plausible candidates for laboratory detection

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[13–16]. For example most group 14 element oxides favor linear structure, however, cyclic PbO_2 has been observed in low temperature argon matrix [17,18]. For group 14 element sulfides the CS_2 molecule is linear in gas phase but in low temperature argon matrix cyclic CS_2 was trapped as an intermediate [19]. In addition, both SiS_2 and GeS_2 were identified as linear structure in low temperature matrices [15,20], but recently in the gas phase cyclic SiS_2 was detected by rotational spectroscopy [12]. Thus, it is not surprising that exceptions to the Walsh rules have been encountered in the case of heavy element compounds.

In this work, the stable minimum structures of the EX_2 molecule (E = C, Si, Ge, Sn, Pb, and X = O, S, Se) were calculated with CCSD(T) and B3LYP levels. The calculated vibrational frequencies were compared with experimental values and the difference of bond formation between linear and cyclic structure were discussed in detail. The exceptions to the Walsh rules are discussed as well.

2. Computational methods

All calculations were performed using the Gaussian 03 program package [21]. Geometries of all structure were calculated by hybrid density functional theory (DFT) using the Becke's three parameter hybrid functional combined with the Lee, Yang, and Parr (LYP) correlation functional denoted as B3LYP [22] and were also optimized at the CCSD (T) level [9]. The 6-311++G (3df, 3pd) basis sets for C, Si and O, S, Se [23,24]. Ge, Sn and Pb were described by the SDD pseudopotential [17,23]. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed as true

minima by vibrational analysis. Natural bond order (NBO) analysis as implemented in the Gaussian 03 was also done to explore the bonding in new molecules.

3. Result and discussion

3.1. EO_2 ($E = C, Si, Ge, Sn, Pb$)

At B3LYP level, the linear CO_2 is $144.0 \text{ kcal mol}^{-1}$ lower in energy than cyclic CO_2 , which is the biggest energy difference for this oxides group (Fig. 1). The energy differences for heavier homologues become less to 58.4 (Si), 20.8 (Ge), 1.3 (Sn); however, the linear PbO_2 turns into energetically higher ($17.5 \text{ kcal mol}^{-1}$) lying than the cyclic PbO_2 isomer. At the CCSD(T) level of theory, very similar relative energies are given as shown in Fig. 1. This stability trend is in consistent with the result of Zyubina [25]. The geometry and energy of transition state structure were shown in Fig. S1 and Table S1 (supporting material). The computed activation barrier is $160.3 \text{ kcal mol}^{-1}$ from $lin-CO_2$ to $cyc-CO_2$; however, the energy barriers are reduced to 109.7 (Si), 73.7 (Ge), 50.7 (Sn), and 41.0 (Pb) kcal mol^{-1} . The reverse procedure from $cyc-CO_2$ to $lin-CO_2$ has activation energy of $10.3 \text{ kcal mol}^{-1}$, suggesting $cyc-CO_2$ should be experimentally inaccessible. Notice the calculated reverse activation energies are about 50 kcal mol^{-1} for the rest of oxides in this group, thus cyclic PbO_2 is more stable in energy than linear one.

Experimentally it is well known that CO_2 exists as a linear structure [26], and SiO_2 [27], GeO_2 [27], SnO_2 [28], and PbO_2 [17] with linear structures were observed in low temperature matrices. Interestingly in laser-ablated Pb atom reaction with O_2 , the cyclic PbO_2 was trapped in low temperature matrix, which had been identified from infrared spectroscopy [17,18].

3.2. ES_2 ($E = C, Si, Ge, Sn, Pb$)

The sulfide homologues exhibit some common energy stabilities compared with the oxide molecules. Based on B3LYP calculations the linear CS_2 is $74.4 \text{ kcal mol}^{-1}$ lower in energy than cyclic CS_2 , but this energy is reduced to $20.0 \text{ kcal mol}^{-1}$ for Si and $0.7 \text{ kcal mol}^{-1}$ for Ge. However, the cyclic structure for SnS_2 and PbS_2 is more stable (Fig. 2). The CCSD(T) calculations gave very similar results. The geometry and energy of transition state structure were shown in Fig. S2 and Table S2 (supporting material). Notice the energy differences between linear and cyclic structures for most sulfides are very close, suggesting that both structures are expected to observe experimentally.

The stable structure for CS_2 is found to be linear, however, the linear CS_2 can be isomerized to cyclic structure using 193 nm laser excite in low temperature matrices [19]. Recently in the gas phase cyclic SiS_2 was detected by rotational spectroscopy [12]. In addition the linear SiS_2 and GeS_2 were also observed [15,20], but rest of sulfides for these group elements are not identified so far. Based

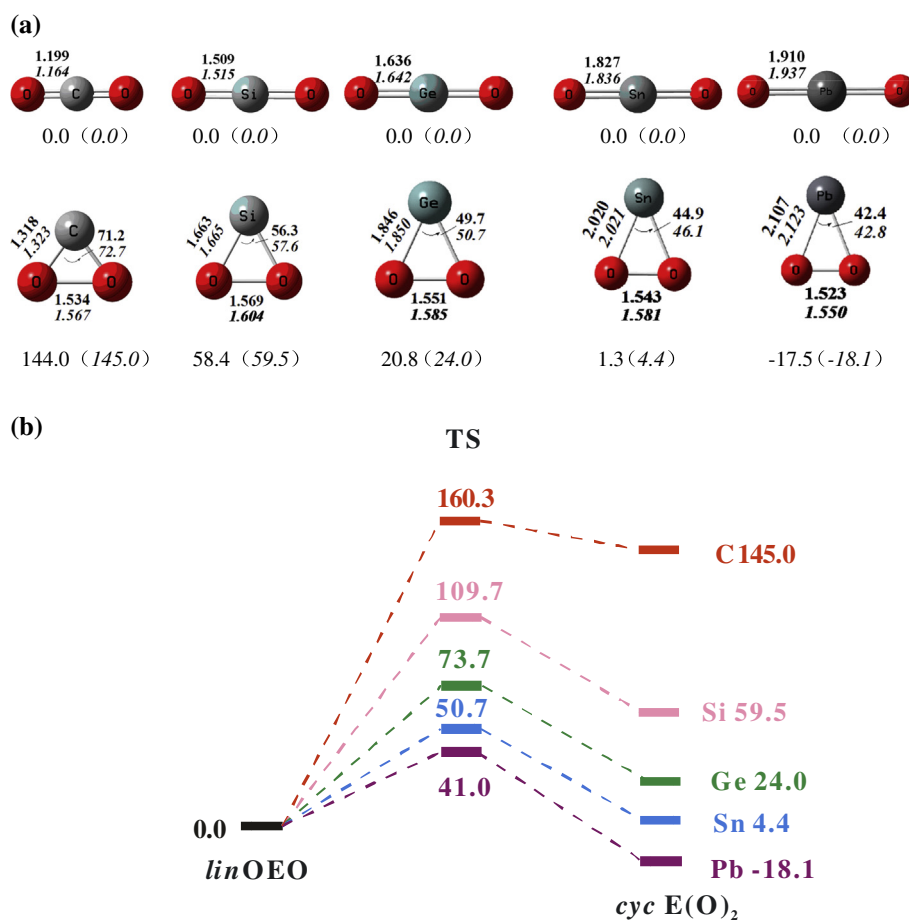


Fig. 1. (a) Optimized geometries of the stationary points on the PES of the (O, E, O) system ($E = C$ to Pb) at the B3LYP/6-311++G(3df,3pd)/SDD level. Relative energies in kcal mol^{-1} , bond lengths in Å, and bond angles in degrees. CCSD(T)/6-311++G(3df,3pd)/SDD values are given in parentheses. (b) Energy-profile diagram (reaction coordinate versus relative energy) of the (O, E, O) system at the CCSD(T)/6-311++G(3df,3pd)/SDD level.

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