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A Computational Study of the Formation and Dimerization of Benzothiet-2-one

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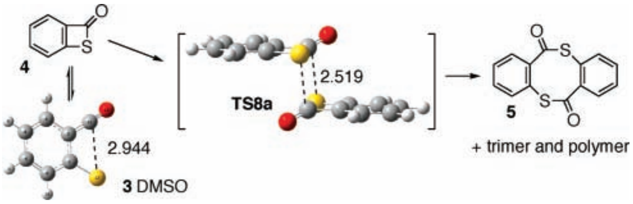
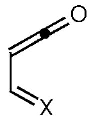
ABSTRACT



A computational B3LYP/6-31G(d,p) study of the formation of benzothiet-2-one (4) from benzothiophenedione (2) and its subsequent dimerization to 5 was performed. The proposed intermediate ketene 3 has no gas-phase barrier to ring closure to 4. Three transition structures for dimerization were located. The geometry of the lowest energy one (TS8a) has a geometry corresponding to a two atom + two atom, face-to-face addition of the two thiolactone moieties. The orbital interactions suggest that the reaction is pseudopericyclic.

Thioacylketenes (**1a**)[1] have been less studied than the isoelectronic oxoketenes[2] (**1b**) and imidoylketenes[3] (**1c**). Attempted conversion of **2** to the benzo-fused analogue **3** has led only to benzothiet-2-one (**4**).[4] Wentrup et al.[4c] subjected **2** to flash vacuum pyrolysis and isolated **4** at low temperatures (eq 1). Although **3** was suggested to be the first formed intermediate, the authors were unable to detect it. Gently warming **4** above −40 °C gave **5**. Trimeric and polymeric materials were also obtained; the authors suggest these are formed by nucleophilic attack on **4** and **5**. Compound **5** has also been recognized as a potential cleft in molecular recognition studies.[4d,e]



1a X = S
1b X = O
1c X = NH

There are two puzzling and interrelated aspects of this chemistry: (1) why was the ketene **3** not observed? Cheletropic decarbonylation of **2** would be expected to lead to **3**, and even a modest stabilization would allow it to be observed under matrix isolation conditions. (2) How is the product **5** formed? A concerted dimerization of **4** would appear to be a [2σs + 2σs] cycloaddition; such reactions are uncommon,

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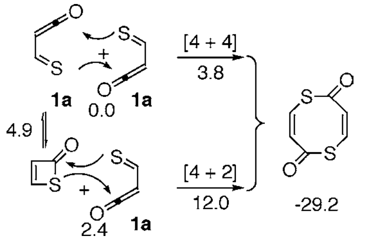
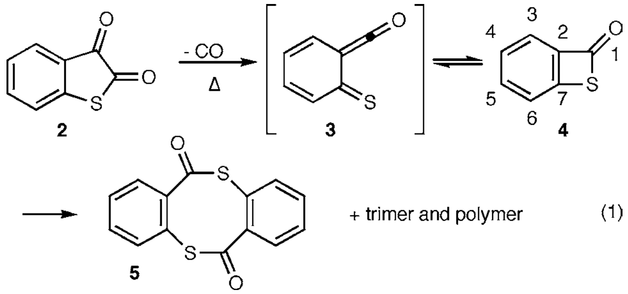
not surprisingly because they are forbidden by the Woodward−Hoffmann rules.[5] Concerted [4s + 4s] and [4a + 4a] cycloadditions are likewise forbidden. However, pseudopericyclic[6] [4 + 4] cycloadditions of imidoylketenes are known,[3g] and a [4 + 4] dimerization of thioformylketene (**1a**) was calculated to be the lowest energy pathway for dimerization (Scheme 1).[1f] A pseudopericyclic [4 + 4] dimerization of **3** in this case seems unlikely since **3** has not been observed even under matrix isolation conditions. To answer these questions, we undertook a computational study of these reactions at the B3LYP/6-31G(d,p) level of theory.[7]

Scheme 1. Calculated Energetics (B3LYP/6-31G(d,p) + ZPVE, kcal/mol) of the Dimerization of **1a** (From Ref 1f)





Benzothiophenedione (**2**) is calculated to be planar, and its thermal cheletropic decarbonylation is isoelectronic with decarbonylations of furandiones. The experimental X-ray geometries of the latter are distorted along the calculated planar, pseudopericyclic reaction coordinate.[8] However, in the calculated transition structure (**TS6**) for decarbonylation of **2**, the forming carbon monoxide is significantly out of plane (Figure 1). This geometry corresponds to the Woodward and Hoffmann "linear pathway",[5,9] but it leads directly to ring-closed **4** as the product.

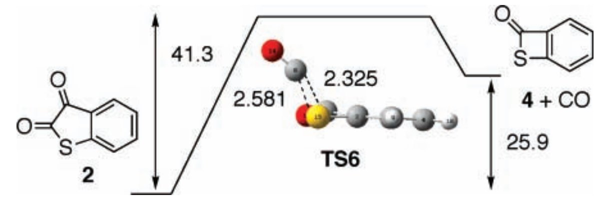


Figure 1. Calculated energetics of the cheletropic decarbonylation of **2** to give **4** and CO via **TS6**. A side view of **TS6** is shown. Relative energies are in kcal/mol at the B3LYP/6-31G(d,p) + ZPVE level. Distances are in angstroms. Sulfur atoms are yellow, oxygens are red, carbons are gray, and hydrogens are white.

A search was made for **3**, the ring-opened isomer of **4**. The C−S distance was constrained, and the rest of the molecule was optimized. There was no minimum on the potential energy surface, although a relatively flat region was found with a C1−S distance of about around 2.9 Å, approximately 12 kcal/mol above **4**. The data are graphed in Figure S1. For a more accurate picture of the energetics, the G3MP2B3 method was used (hybrid G3MP2 energies at the B3LYP geometries). Likewise, at this level, there was a relatively flat region around the C1−S distance of 2.9 Å and approximately 14−15 kcal/mol above **4**, but there was no barrier for the ring closure. This C1−S distance is slightly shorter than the 3.130 Å calculated for **1a**.[1f] All of the structures in the constrained optimization are planar; this suggests that the barrierless ring closure is pseudopericyclic. This is consistent with low barriers calculated for isoelectronic electrocyclizations of oxoketenes[2] and imidoylketenes.[3] While low barriers are often found for pseudopericyclic reactions,[6] the absence of any barrier for ring closure of **3** likely reflects the increased aromaticity of **4**. The zwitterionic resonance structure **3a** suggests that solvation might stabilize **3**. Indeed, when the geometry optimization was carried out using a polarizable continuum model, with the dielectric constant for DMSO, a minimum for **3** was found.[10] Similarly, two dimeric gas-phase structures containing two molecules of **3** were found, **7a** and **7c** (see Figure 2). Presumably, the partial charges from one molecule of **3** stabilize the other sufficiently to maintain the ring-opened structures. These are calculated to be 19.8 and 20.1 kcal/mol less stable than two molecules of **4**. However, since the estimate for the energy of a single molecule of **3** is approximately 12 kcal/mol higher

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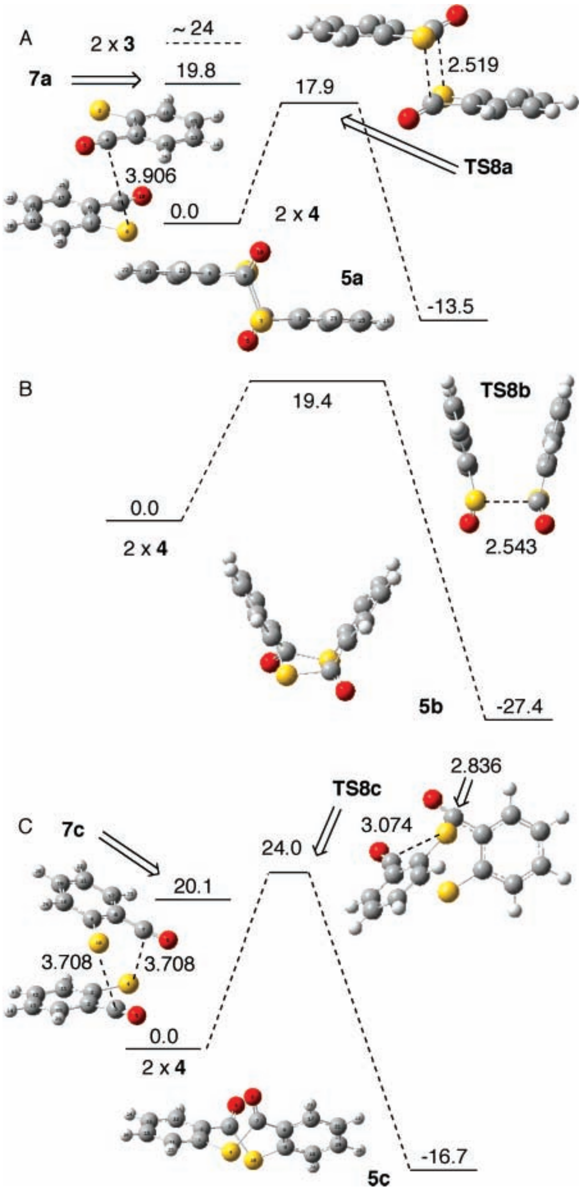
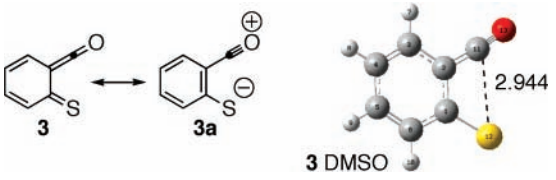


Figure 2. Calculated energetics of the dimerization of **3** or **4** to give **5**. Energies are in kcal/mol at the B3LYP/6-31G(d,p) + ZPVE level and are relative to two isolated molecules of **4**. See Figure 1 for key.

than **4** (see discussion above), these complexes of **3** (**7a** and **7c**) are stabilized relative to two isolated ring-opened structures.



Three transition structures were located for the formation of the dimeric compound **5**. Following the intrinsic reaction coordinate (IRC) from these transition states gave three conformations of **5**. The observed conformation of **5** is a tub-shaped structure **5b**, which has been of interest as a molecular cleft.[4d,e] The structures and relative energies of these molecules are shown in Figure 2 and Table 1.

Table 1. Energies (RE, kcal/mol) of Calculated Structures: For **2**, **TS6**, and **4** + CO, Energies Are Relative to **2** and For All Other Structures, Energies Are Relative to Two Molecules of **4**

	RE B3LYP/6-31G(d,p)[a]	RE + ZPVE[b]	low frequency[c]
2	0.0	0.0	80.9
TS6	43.8	41.0	253.4i
4 + CO	29.2	25.9	129.3
two **4**	0.0	0.0	129.3
5a	−14.8	−13.5	40.0
5b	−29.4	−27.4	43.0
5c	−18.4	−16.7	40.6
7a	21.1	19.8	11.3
7c	21.2	20.1	16.2
TS8a	18.3	17.9	309.5i
TS8b	20.0	19.4	315.2i
TS8c	25.0	24.0	128.4i

[a] B3LYP/6-31G(d,p) geometry optimized. [b] From (a) with unscaled zero-point vibrational energy (ZPVE) corrections. [c] Low or imaginary frequencies (cm^{-1}).

The lowest energy transition structure **TS8a** is for the face-to-face addition of two parallel molecules of **4** in an anti conformation. The C1−S bond is breaking; it is 2.349 Å, which is shorter than the distance in **3** (2.944 Å in DMSO) but longer than that in **4** (1.928 Å). The barrier for the dimerization is calculated to be 17.9 kcal/mol. This is consistent with the experimental observation that dimerization occurs above −40 °C.[4c] The IRC leads to the [4 + 4] product **5a** in the same anti conformation, which is 13.5 kcal/mol more stable than two molecules of **4**. The second transition structure, **TS8b**, is only slightly higher in energy, 19.4 kcal/mol above two molecules of **4**. The geometry of this is similar, in that the two molecules are again interacting face-to-face, but the two rings are syn to each other and distorted away from parallel. This leads to the observed tub geometry of the product, **5b**;[4d,e] this is calculated to be the most stable conformation of **5**, 27.4 kcal/mol below two molecules of **4**. The third transition structure, **TS8c**, has the highest barrier, 24.0 kcal/mol, and leads to the twisted conformation **5c**. Its geometry is analogous to that found for the [4 + 4] cyclodimerization of **1a**.[1f] In this structure, the thiolactone has already opened (C1−S = 3.047 Å). From each molecule of **3**, an in-plane lone pair from one sulfur adds to the in-plane π* of the other ketene. Most of the barrier is the cost of opening **4** to **3**; the barrier from **7c** is only 3.9 kcal/mol.

The geometry of the lowest energy transition structure **TS8a** is unusual. At first inspection, it appears to involve the overlap of the two symmetric π-systems, which, in the Woodward−Hoffmann formalism, is a forbidden cycloaddition.[5] It seems unlikely that this is indeed a forbidden transition structure, if only because such calculations require non-dynamical electron correlation methods (e.g., multiconfigurational SCF).

A closer examination of the relevant orbitals of **4** provides an explanation. The LUMO and first two occupied orbitals of **4** are shown in Figure 3A. As might be expected, the LUMO has π^* character on the ketene carbonyl. The HOMO has p-lone pair character on the sulfur and no coefficient on the ketene carbonyl. Thus, the HOMO−LUMO interactions between the molecules correspond to nucleophilic addition of one sulfur to the carbonyl π^* of the other, but there is no closed loop of interacting orbitals. The next highest occupied orbital (HOMO-1) can be considered to be formed from the interaction of an in-plane sulfur lone pair with the in-plane π^* of the ketene. The nucleophilic addition of sulfur to the carbonyl would increase the electron density at the oxygen, which would in turn break the thiolactone C−S bond. Since HOMO-1 does not overlap with the HOMO, the two systems are orthogonal (Figure 3B); therefore, the reaction is pseudopericyclic and allowed regardless of the number of electrons involved. An alternative formulation of the pseudopericyclic mechanism would be to conceptually separate the concerted bond forming and breaking. The new C−S bonds could be formed, prior to opening the thiolactone, leading to a zwitterionic structure (Figure 3C). This drawing is not meant to imply that such a structure is expected; it is intended solely as a simple, conceptual way to recognize a pseudopericyclic reaction.

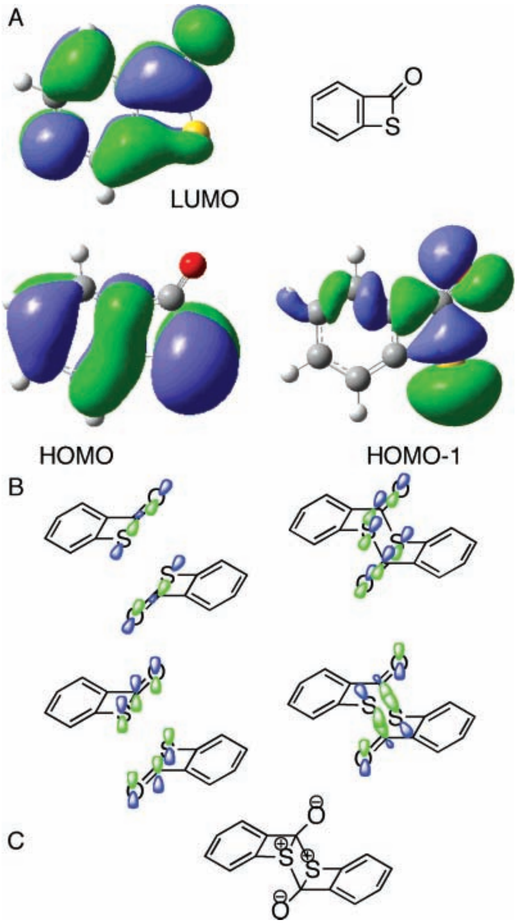


Figure 3. (A) Frontier molecular orbitals of **4**. (B) Orthogonal orbital interactions in the cyclodimerization of two molecules of **4** to give **5**. (C) Conceptual separation of the concerted bond forming and breaking steps, illustrating the pseudopericyclic separation of orthogonal orbitals.

Following the IRC from **TS8c** leads to the dimeric complex **7c**, which is 3.9 kcal/mol below **TS8c**. Thus reaching this transition structure appears to involve first ring opening of two molecules of **4** to form two molecules of **3**, stabilized by their mutual charge attractions. From here, the dimerization could occur. However, since **7a** and **7c** are higher in energy than either **TS8a** or **TS8b**, they cannot be on the lowest energy pathway for dimerization. Rather, **TS8a** and **TS8b** are reached directly from two molecules of **4**. This is consistent with the geometries of **TS8a** and **TS8b**, in which the thiolactone C1−S bond is only partially broken.

In summary, decarbonylation of **2** proceeds via a nonplanar, pericyclic transition structure **TS6** to directly form **4**. The ring-opened ketene **3** is not an intermediate in the gas phase, although it can be stabilized by a dielectric field as a model for a polar solvent. Likewise, **3** is stabilized in the dimeric complexes **7a** and **7c**. Cyclodimerization of **4** is calculated to proceed via a transition structure **TS8a** that superficially resembles a [2σs + 2σs] process. However, the orbitals suggest that this is a pseudopericyclic reaction, in which the breaking and forming bonds are orthogonal.

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Supporting Information Available: Computational details, absolute energies, Cartesian coordinates, and selected frontier molecular orbital surfaces of **TS8c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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