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A Theoretical Study of the [4 + 4] Dimerization of Thioformylketene

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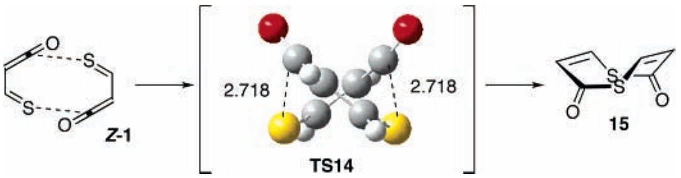
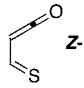
ABSTRACT



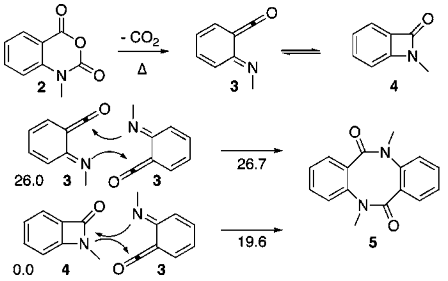
A theoretical study (B3LYP and G3MP2B3) of the dimerization of thioformylketene (1) was performed. Four pathways—two [4 + 2] pathways with thioformylketene (1), one [4 + 4] pathway with 1, and one [4 + 2] pathway involving 1 and thietone (11)—were considered. Interestingly, the [4 + 4] pathway with 1 had the lowest barrier (3.8 kcal/mol). The geometry of the transition state TS14 is unusual, with the forming bonds in the plane of the ketene. This suggests that the reaction is pseudopericyclic.

Not surprisingly, concerted [4 + 4] cycloadditions are rare; after all, the thermal [4s + 4s] and [4a + 4a] pathways are forbidden by the Woodward−Hoffmann rules,[1] and a [4s + 4a] transition state geometry would be difficult to achieve. There is another alternative, however, via a transition state that lacks cyclic orbital overlap. Such pathways have been described as pseudopericyclic; qualitatively such reactions (1) cannot be forbidden, (2) may have low barriers with nonaromatic transition states, and (3) the transition states may be planar.[2] The density functional theory study that follows, on the [4 + 4] dimerization of thioformylketene (**1**), although currently unknown, provides several examples of such pathways.


Z-1

A few experimental examples of formal [4 + 4] cycloadditions are known. For example, pyrolysis of **2**[3] gives the known[4] dianthranilide **5** (Scheme 1). Formally, this is the head to tail [4 + 4] dimer of the imidoylketene **3**. Interestingly, although isoelectronic acylketenes tend to form [4 + 2] dimers,[5] such products are not formed from **2**. Density functional theoretical (B3LYP/6-31G(d,p)+ZPVE) calculations on this and related model systems predict that a [4 + 4] pathway for dimerization of **3** is allowed and has a remarkably low (0.7 kcal/mol) barrier.[3a] The ring-closed azetinone **4** is much more stable (13.0 kcal/mol). Thus, the overall barrier height for the formation of **5** from two molecules of **4** is 26.7 kcal/mol. However, a [4 + 2] transition structure for the direct addition of **3** and **4** is of lower overall energy (19.6 kcal/mol) and thus would be expected to be experimentally favored.

Scheme 1. Energies (kcal/mol, B3LYP/6-31G(d,p) + ZPE) Are Relative to Two Molecules of **4**, from Ref 3



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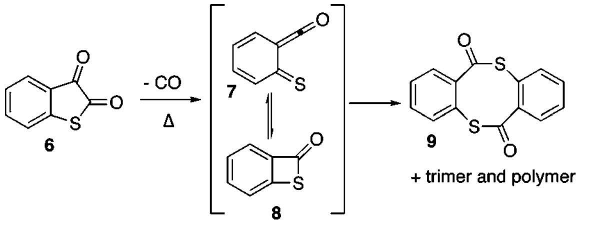
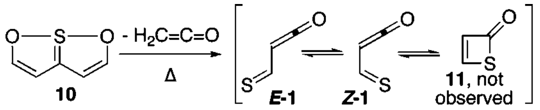
Thioacylketenes are isoelectronic with oxoketenes and imidoylketenes and undergo similar reactions.[6,7] Wentrup et al.[6a] subjected **6** to flash vacuum pyrolysis and isolated benzothiet-2-one **8** at low temperatures (eq 1). Although **7** was suggested to be the first formed intermediate, the authors were unable to detect it. This is presumably because the planar, pseudopericyclic ring closure to **8** is facile and is favored at equilibrium by the greater aromaticity of **8**, in analogy to **3** and **4**. Gently warming **8** above −40 °C gave **9**, formally a [4 + 4] dimer of **7**. A trimer and polymeric material were also obtained; the authors suggest these are formed by nucleophilic attack on **8** and **9**.



(1)

Open chain thioacylketenes have been observed, although the equilibrium with the thietone is affected by substitution.[7] Pedersen, Wong, and Flammang have studied the flash vaccum pyrolysis of **10**[7c] (eq 2). Among the products are both the s-*Z* and s-*E* forms of the parent thioformylketene (**1**). Because the ketene **1** is observed instead of **11** and because **9** is observed from dimerization of **8**, we anticipated that the lowest energy pathway for formation of **15** might be the direct [4 + 4] dimerization of **1**. Although **1** has been observed in matrixes, we are not aware of attempts to isolate any products from conditions where dimerization of **1** might have occurred.

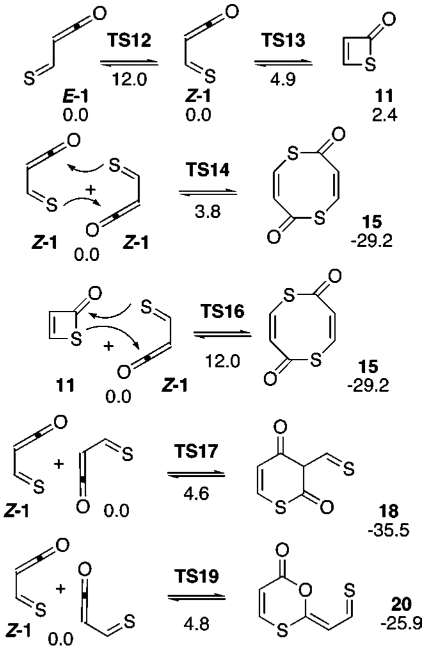


(2)

The two conformations (*s-Z* and *s-E*) of **1** are calculated to be of similar energy (within 0.03 kcal/mol at the G3(MP2) level).[7c] The calculated energy differences between ring opened and closed isomers vary widely depending on the substituents and on the level of theory used.[7e] However, B3LYP/6-31G(d) and G3(MP2) are in reasonable agreement that **1** is more stable than **11** and that the barrier for ring closure of **1** is low, around 6−7 kcal/mol.[7c]

Here we wish to report a computational study of the dimerization of **1**. We have considered four pathways for the dimerization (Scheme 2). All calculations were carried out using Gaussian03.[8] Optimizations of all structures were performed with the B3LYP[9] hybrid functional using the 6-31G(d,p) basis set.[10a] Structures ***Z*-1**, **11**, and **TS13** were optimized at the B3LYP/aug-cc-pVQZ level.[10b] Single-point energies were also calculated for selected structures at the B3LYP/aug-cc-pVQZ level.[10b] Energies for all structures were also calculated using the G3MP2 method at the B3LYP/6-31G(d) geometries (G3MP2B3).[11] Geometry-optimized structures for transition structures **TS14**, **TS16**, **TS17**, and **TS19** are shown in Figure 1; **TS12** and **TS13** are in Figure

Scheme 2. Reactions Calculated in This Work[a]



[a] Energies in kcal/mol at the G3MP2B3 level of theory.

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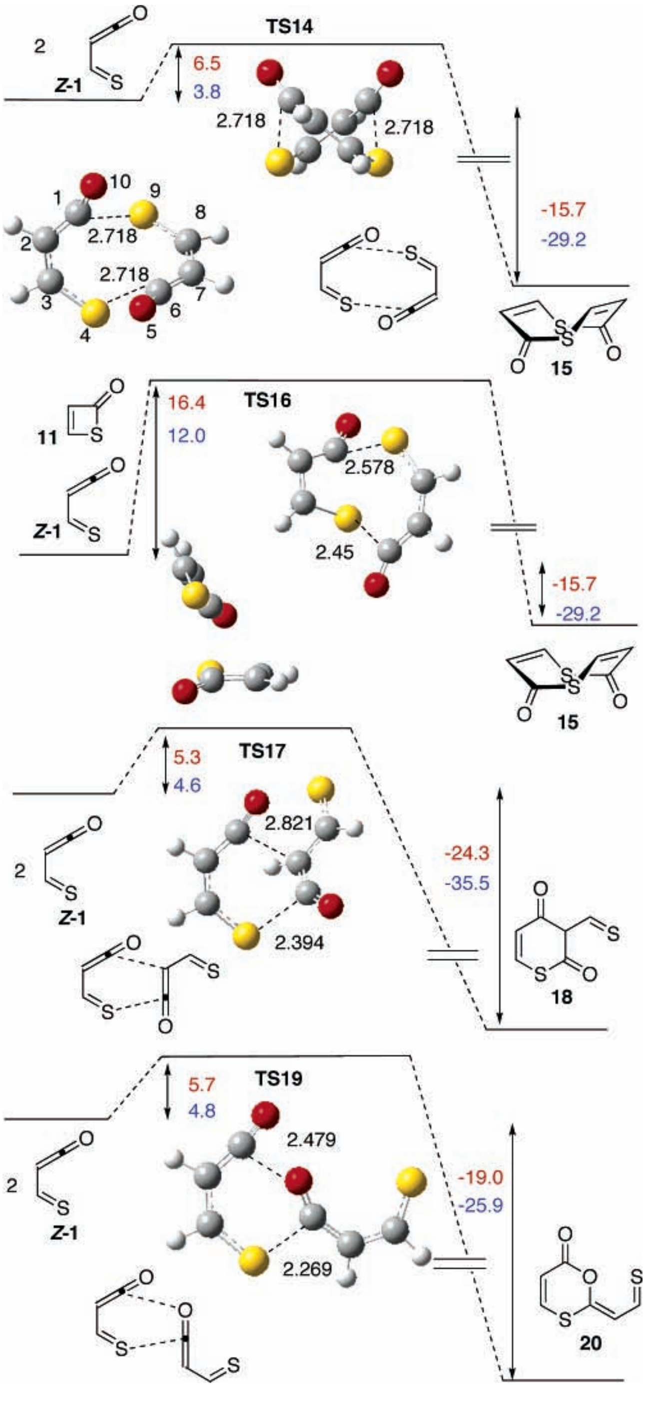


Figure 1. Calculated energetics of the [4 + 4] dimerization of ***Z*-1** to give **15** via **TS14** and of the [4 + 2] dimerizations of ***Z*-1** to give **18** and **20** via **TS17** and **TS19** respectively. Two views of **TS14** and views of **TS16**, **TS17**, and **TS19** are provided (B3LYP/6-31G(d,p) optimized geometries). Relative energies are in kcal/mol at the B3LYP/6-31G(d,p) + ZPVE level (red) and the G3MP2B3 level in (blue). Distances in Å.

S1. Relative energies and low or imaginary frequencies are given in Table 1. Optimized geometries, absolute energies, and other computational details are provided in the Supporting Information. In view of the wide variability of the calculated relative energies as a function of the level of theory,[7e] the energies discussed below are at the G3MP2B3 level, which is expected to be very reliable.[11] There is little difference between the relative energies calculated at the various levels. The B3LYP/6-31G(d,p)-optimized and B3LYP/aug-cc-pVQZ single-point energies are within 2 kcal/mol of each other. Geometry optimization at the B3LYP/aug-cc-pVQZ level does not alter the relative energies. G3MP2B3 energies are generally within a few kcal/mol of the B3LYP/6-31G(d,p) ones.

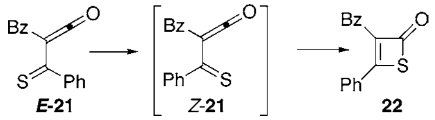
Table 1. Relative Energies (RE, kcal/mol) of Calculated Structures[a]

	RE B3LYP/ 6-31G(d,p)[b]	RE + ZPVE[c]	RE aug-cc-pVQZ[d]	RE G3MP2B3[e]	low freq[f]
***Z*-1**	0.0	0.0	0.0 (0.0)	0.0	123.4
***E*-1**	0.0	−0.3	−0.6	0.0	128.5
11	5.5	5.6	5.5 (5.5)	2.4	213.0
TS12	16.1	15.1	15.1	12.0	381.8i
TS13	6.2	6.9	6.0 (6.4)	4.9	183.4i
TS14	5.9	6.5	7.4	3.8	155.8i
15	−18.7	−15.7		−29.2	45.7
TS16	15.7	16.4	17.2	12.0	209.1i
TS17	4.2	5.3	6.0	4.6	139.7i
18	−27.9	−24.3		−35.5	42.5
TS19	4.5	5.7	6.1	4.8	128.5i
20	−22.7	−19.0		−25.9	38.4
24	−4.1	−3.5		−4.3	10.2

[a] For ***E*-1**, **11**, **TS12**, and **TS13** energies are relative to ***Z*-1**. For all other structures, energies are relative to two ***Z*-1**. [b] B3LYP/6-31G(d,p) geometry optimized. [c] From *b* with zero-point vibrational energies (ZPVE) corrections. [d] B3LYP/aug-cc-pVQZ/B3LYP/6-31G(d,p) energies (values in parentheses are from B3LYP/aug-cc-pVQZ geometry optimizations). [e] G3MP2B3 energies. [f] Low or imaginary frequencies (cm^{-1}) for the B3LYP/6-31G(d,p) structures.

The equilibrium between **1** and **11** would be expected to be of significance to the mechanism of formation of **15**, similar to the situation with the imidoylketene **3**, where the [4 + 2] cycloaddition of **3** and **4** to form **5** has a lower calculated barrier than the [4 + 4] dimerization of **3** (Scheme 1). Our results are in good agreement with Pedersen et al.'s prior work;[7c] the two conformations of thioformylketene (***E*-1** and ***Z*-1**) are very close in energy and, indeed, are equal at the G3MP2B3 level, while **11** is 2.4 kcal/mol higher in energy. Thus, a [4 + 4] dimerization of ***Z*-1** might be possible. The barrier for ring opening of **11** to ***Z*-1** is only 2.5 kcal/mol. Such a low barrier is not uncommon for pseudopericyclic reactions.[2] Interestingly, the barrier for interconversion of ***E*-1** and ***Z*-1**, simply by bond rotation, is much higher, 12.0 kcal/mol.

This result may be of chemical significance; Wentrup et al. have observed an IR stretch in an Ar matrix attributed to ketene **21** that is stable up to −80 °C.[7d] Above this temperature, it is converted to the thietone **22**. In the current study, the calculated barriers (***E*-1**, ***Z*-1**, and **11**) suggest that the *E* conformation of **21** is the observed ketene and the reason that **21** can be observed at all is the high barrier to bond rotation from ***E*-21** to ***Z*-21**. The pseudopericyclic cyclization of ***Z*-21** to **22** is likely to be too facile for ***Z*-21** to be stable at −80 °C.



***E*-21** *Z*-**21** **22**

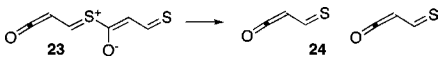
Two [4 + 2] pathways for the dimerization of thioketene **1**, one [4 + 4], and the [4 + 2] cycloaddition of **1** and **11** were considered as in Scheme 2. It is remarkable that the lowest barrier height for the dimerization of thioketene **1** to give **15** is via a [4 + 4] pathway (**TS14**) that is only 3.8 kcal/mol above two thioformylketenes (**1**) at the G3MP2B3 level. The unusual geometry of this transition structure **TS14** (Figure 1) holds the explanation. In this the forming bonds are in the plane of the ketene, as is common for pseudopericyclic reactions of ketenes.[2] The molecular planes of the two ketenes are rotated nearly 90° relative to each other. The dihedral angle between atoms C2, C3, S4, and C6 in **TS14** (Figure 1) is 20.6° and that between atoms S4, C6, C7, and C8 is 43.5°. These correspond primarily to the in-plane sulfur lone pair (S4) from one molecule attacking the π* (close to the plane of the ketene) from the other molecule. This geometry can be viewed as a compromise between an ideal planar, pseudopericyclic geometry and the ideal geometries for the nucleophilic addition of the sulfur in-plane lone pair to the in-plane π* of the ketene.

The symmetry of this transition structure (**TS14**) is what would be expected for a 4a + 4a transition state, which is forbidden by the Woodward−Hoffmann rules.[1] The geometry of the TS, however, was not anticipated by Woodward and Hoffmann; it does not correspond either to suprafacial nor antarafacial geometries on the ketenes. Rather, there is no cyclic orbital overlap at all; the reaction is pseudopericyclic[2] and therefore is allowed. An NBO surface of the HOMO of **TS14** and also a qualitative diagram of the orbitals involved are provided in the Supporting Information (see Figures S1 and S2). Electron flow in the out-of-plane π-systems compensates for what would otherwise lead to charge accumulation.

The dimerization of **1** and thietone **11** to give **15** by a [4 + 2] pathway (**TS16**) has a higher barrier of 12.0 kcal/mol. This can nevertheless be understood as pseudopericyclic as well, because bond formation occurs primarily in the plane of the ketene **1** (Figure 1). Thus, the new bonds do not overlap with the π-system in **1**.

The energy barriers for the alternative [4 + 2] dimerizations of **1** are only 4.6 kcal/mol (across C═C) and 4.8 kcal/mol (across C═O). For these structures as well, the reaction can be understood as pseudopericyclic as the bond formation occurs primarily in the plane of **1**. Although these are also quite low barriers, these computational results suggest that the [4 + 4] addition (**TS14**) would be the preferred pathway for the formation of **15** from **1**. Interestingly, the barrier for this [4 + 4] dimerization to give **15** is lower even though it is not as exothermic (−29.2 kcal/mol) as the [4 + 2] dimerization to give **18** (−35.5 kcal/mol). The dimerizations are sufficiently exothermic (25.9 to 35.5 kcal/mol) that they are not expected to be in equilibrium with the ketenes at room temperature.

To explore a stepwise pathway, an attempt was made to locate a structure corresponding to **23**. Although zwitterionic intermediates are found in the addition of imines to ketenes,[2f] no bound stucture was located. Instead, a bimolecular complex was found, 4.3 kcal/mol more stable than two isolated molecules of ***Z*-1**.



23 **24**

In summary, a theoretical study of the dimerization of the thioformylketene (**1**) was performed at the B3LYP/6-31G(d,p) and G3MP2B3 levels. Unlike the imidoylketene analogues in which a [4 + 2] pathway is favored,[3a] the current study suggests that the preferred pathway is a [4 + 4] cycloaddition via a pseudopericyclic reaction mechanism. Although pericyclic [4s + 4s] and [4a + 4a] cycloadditions are forbidden,[1] all pseudopericyclic reactions are allowed.[2] The unusual geometry in which the forming bonds are in-plane and the low energy barrier of only 3.8 kcal/mol are in agreement with the well-known characteristics of pseudopericyclic reactions.

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

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