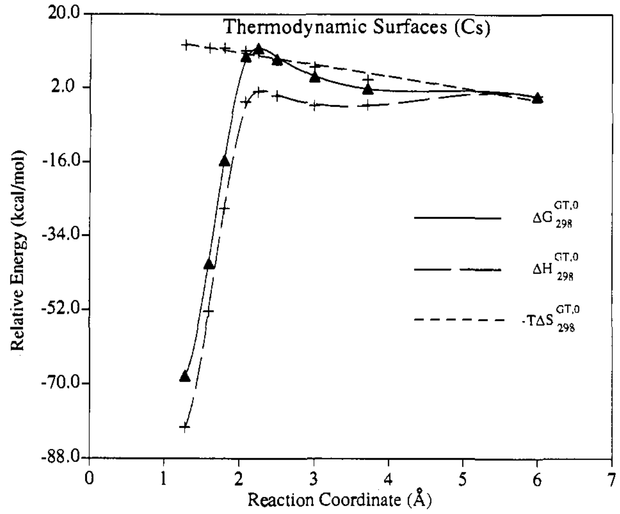


Figure 2. Computed activation profiles.

The results for the potential energy in Figure 1 at the 6-31G(d) level reveal a shallow minimum (−0.8 kcal/mol) at 3.71 Å for the π-complex and the transition state at 2.08 Å, 13.3 kcal/mol above the reactants. The MP2 corrections dramatically flatten the barrier to only 1.7 kcal/mol at 2.25 Å and deepen the minimum to −1.7 kcal/mol at 3.5 Å. Optimization at the MP2(FULL)/6-31G(d) level yields a barrier of only 0.6 kcal/mol shifted to 2.38 Å and a π-complex in a 2.0 kcal/mol depression at 3.25 Å. Fortuitously, Houk's 3-21G results are qualitatively similar to the MP2/6-31G(d) curve owing to an apparent cancellation in the strong basis set and correlation dependencies. The 3-21G TS is shifted in to 2.01 Å with a height of −1.3 kcal/mol, and the minimum for the π-complex occurs at 2.65 Å with a depth of −2.2 kcal/mol.[3]

The computed activation profiles[1,2] for $\Delta G^{GT,0}$, $\Delta H^{GT,0}$, and $-T\Delta S^{GT,0}$ are shown in Figure 2 using the MP2/6-31G(d)//6-31G(d) energies and 6-31G(d) derived frequencies. The enthalpy curve is quite flat to the 1.1 kcal/mol maximum at 2.25 Å, while the $-T\Delta S^{GT,0}$ curve rises nearly linearly along the reaction path. Loss of translational entropy is largely responsible for the substantial free-energy barrier of 11.7 kcal/mol. Interestingly, the abrupt drop in the enthalpy profile near 2.25 Å causes the positions of the variational and conventional transition states to essentially coincide; the enthalpy and free energy are both lower at 2.08 and 2.50 Å than 2.25 Å, so the inward shift for the VTS appears to be less than ca. 0.1 Å. It is reasonable to assume that this is a general feature for carbene additions and, consequently, a weakness in Houk's model.[3]

The present results suggest the following modified explanation of the experimental data. For halocarbene reactions with alkenes, π-complexes are not free-energy minima, though they may have broad, shallow wells in the enthalpy profiles. Such wells are more likely for monosubstituted than polysubstituted alkenes. The VTS occurs at the onset of covalent bonding where the enthalpy curve exhibits a precipitous drop. For alkenes more reactive than ethylene and carbenes comparable to or more reactive than CCl_2, this point will usually be at negative enthalpies and lead to negative activation energies. Furthermore, the entropy control of selectivity arises from the comparatively flat $\Delta H^{GT,0}$ profile approaching the VTS in comparison to the more strongly variant $T\Delta S^{GT,0}$ curve. Consequently, change in the position or looseness of the VTS typically has a greater effect on $T\Delta S^{GT,0}$ than $\Delta H^{GT,0}$.[9]

Registry No. CCl_2, 1605-72-7; $H_2C{=}CH_2$, 74-85-1.

Supplementary Material Available: Full geometrical specifications for the stationary points (6 pages). Ordering information is given on any current masthead page.

---

(8) Translations and rotations were projected out before diagonalization of the hessian matrix. Vibrations with imaginary or low (<500 cm^{-1}) frequencies were treated as rotations ($E_v = 1/2$ RT). In addition, for computing the free energy of activation profile an additional degree of freedom was removed from the hessian matrix for motion along the reaction coordinate.[1,2] This amounted to neglecting one of the low-frequency vibrations.

(9) Gratitude is expressed to the National Science Foundation for support of this work.

Spontaneous Solid-State [8 + 8] Dimerization of Cycloheptatrienethione: The First Example of a Nontopochemically Controlled Reaction in the Ground State

Takahisa Machiguchi,* Toshio Hasegawa, and Shunji Itoh

Department of Chemistry, College of
Liberal Arts and Science, Saitama University
Urawa, Saitama 338, Japan

Hiroshi Mizuno

Department of Molecular Biology
National Institute of Agrobiological Resources
Tsukuba Science City, Ibaraki 305, Japan

Received May 20, 1988
Revised Manuscript Received January 6, 1989

Solid-state organic chemistry[1,2] and particularly the field of topochemically controlled reactions have recently been developed in photoinduced reactions.[1d] This paper describes a newly discovered example of a ground-state nontopochemically controlled reaction of cycloheptatrienethione (**1**) in the crystalline state leading to a novel [$8\pi + 8\pi$] cyclodimer with a specific stereochemistry.

We have recently reported the synthesis,[3] properties,[3,4] and X-ray structural analysis (performed at −40 °C) of **1**,[5] a deep red crystalline but appreciably labile substance (mp 20 °C). Although crystalline **1** can be stored below −40 °C for many days, it was found that **1** dimerizes slowly at 0 °C in the solid state in the dark within a few days.

The initially formed product is obtained as amorphous solid (powder X-ray diffraction) which gives pale yellow prisms, mp 73 °C dec, on recrystallization (ether, 98%) without any change in the IR and NMR spectra. Combustion analysis and mass spectra indicate the molecular formula $C_{14}H_{12}S_2$ for the product **2**. The NMR (^1H and ^{13}C) spectra are fully consistent with its being a head-to-tail type of [8 + 8] dimer,[6] **2**. The stereochemistry of **2** was established to be the syn configuration based on X-ray diffraction method (Figure 1).[7] Monitoring the solid-state re-

---

(1) For reviews see: (a) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217-225. (b) Curtin, D. Y.; Paul, I. C.; Duesler, E. N.; Lewis, T. W.; Mann, B. J.; Shiau, W. *Mol. Cryst. Liq. Cryst.* 1979, *50*, 25-42. (c) Cavezzotti, A.; Simonetta, M. *Chem. Rev.* **1982**, *82*, 1-13. (d) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433-481. (e) *Organic Chemistry in Anisotropic Media*; Scheffer, J., Ed.; Tetrahedron Symposia-in-Print No. 29, Pergamon: Oxford, 1987.

(2) (a) Kitaigorodsky, A. I. In *Physical Chemistry: Molecular Crystals and Molecules*; Loebl, E. M., Ed.; Academic: New York, 1973; Vol. 29. (b) Thomas, J. M.; Morsi, S. E.; Desvergne, J. P. In *Advances in Physical Organic Chemistry: Topochemical Phenomena in Organic Solid-State Chemistry*; Gold, V., Bethell, D., Eds.; Academic: London, 1977; Vol. 15, pp 63-151. (c) *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987.

(3) Machiguchi, T.; Otani, H.; Ishii, Y.; Hasegawa, T. *Tetrahedron Lett.* **1987**, *28*, 203-206.

(4) Machiguchi, T.; Hasegawa, T.; Otani, H.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1375-1376.

(5) Machiguchi, T.; Mizuno, H.; Hasegawa, T.; Ishii, Y.; Otani, H. *Chem. Lett.* **1987**, 1893-1896.

(6) Cf. Oda, M.; Kayama, Y.; Kitahara, Y. *J. Chem. Soc., Chem. Commun.* **1971**, 505-506.

(7) Crystal data for **2**: monoclinic, space group = *C*2/*c*, $a = 16.836$ (2) Å, $b = 9.534$ (1) Å, $c = 16.499$ (1) Å, $\beta = 114.25$ (1)°, $V = 2414.7$ (4) Å^3, $Z = 8$, $D_{calcd} = 1.345$ g cm^{-3}. Reflections (2037) were measured of which 1624 were classed as observed. The structure was solved by the direct method using MULTAN84:[8] $R = 0.068$.

0002-7863/89/1511-1920$01.50/0 © 1989 American Chemical Society

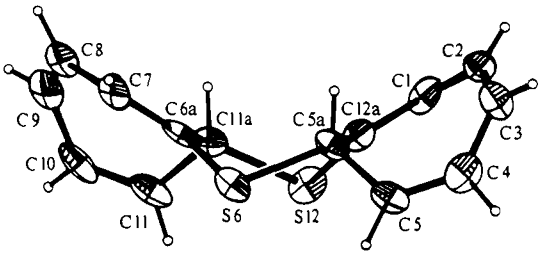
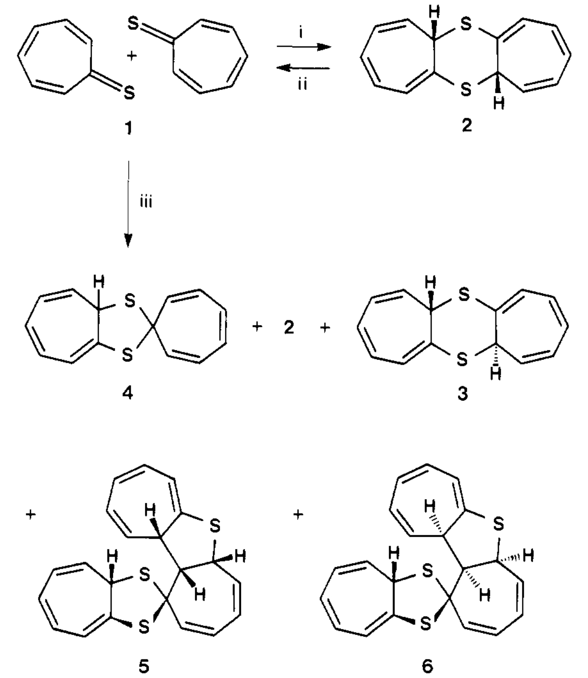


Figure 1. An ORTEP plot of the structure of syn dimer **2** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg) are as follows: S(12)–C(12a) 1.761 (6), C(12a)–C(1) 1.348 (8), C(1)–C(2) 1.442 (9), C(2)–C(3) 1.328 (9), C(3)–C(4) 1.431 (9), C(4)–C(5) 1.345 (9), C(5)–C(5a) 1.487 (8), C(5a)–C(12a) 1.480 (8), S(6)–C(5a) 1.840 (6); S(12)–C(12a)–C(1) 119.3 (4), S(12)–C(12a)–C(5a) 120.4 (4), C(5a)–C(12a)–C(1) 120.0 (5), C(12a)–C(1)–C(2) 124.3 (6), C(1)–C(2)–C(3) 126.1 (6), C(2)–C(3)–C(4) 126.6 (6), C(3)–C(4)–C(5) 124.1 (6), C(4)–C(5)–C(5a) 120.3 (6), C(5)–C(5a)–C(12a) 108.4 (5), C(12a)–C(5a)–S(6) 114.6 (4), C(5)–C(5a)–S(6) 108.7 (4).

Scheme I[a]



[a] (i) In the crystalline state, 0 °C, 2 days ($t_{1/2}$ ca. 1 h). (ii) At room temperature in solutions [MeCN, EtOH, CHCl$_3$, benzene, or CCl$_4$ ($t_{1/2}^{25\,°C}$ 8.7, 15.0, 26.7 min, 4.8 or 15.3 h, respectively)] or at the mp of **2** in the molten state. (iii) In the molten state by heating at 30 °C, 4 h ($t_{1/2}$ ca. 3 min), or at 0 °C, 1 day, under the influence of ultrasounds.

action by ^{1}H NMR (intermittent dissolution in part in CDCl$_3$ and measuring at −45 °C) revealed **2** being the sole product throughout the reaction.

Crystals of **1** have a packing arrangement[5] which is suitable to a full 16π pericyclization. Topochemical postulate[1,2] predicts a product having the anti geometry rather than a syn one (Figure 2). Nevertheless, crystalline **1** formed easily an unexpected syn dimer (**2**) without any sign of melting under the conditions throughout the cyclodimerization. Differential scanning calorimetry of the monomer crystals indicated dynamically (heating rate, 2 or 10 °C min^{-1}) no phase transition occurred in the temperature range −40 to +10 °C and showed isothermally (0 °C) a broad exothermic peak (0.3–3 h) due to the cyclodimerization.

When crystals of **1** were melted by heating (30 °C) or by ultrasonic irradiation (0 °C), the molten-phase reaction proceeded nonstereoselectively giving a mixture of dimers, syn **2** (35%) and anti **3** (7%), and an [8 + 2] cycloadduct **4** (2%), and trimers **5** (45%) and **6** (10%). Monitoring the reaction by ^{1}H NMR (CDCl$_3$, −45 °C) revealed the presence of a rapidly formed intermediate **4** which exceeded 20% of the reaction mixture at early stages of the reaction. The dimers (**2**–**4**) do not isomerize to each other at 0 °C. Thus, there is apparently little possibility of an initial formation of topochemically expected **3** in the solid-state reaction of **1**.

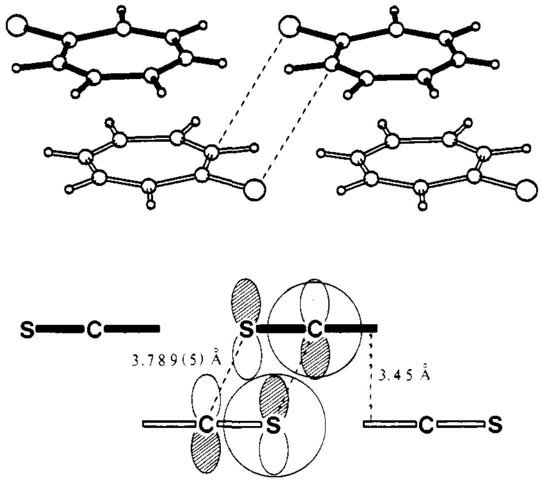


Figure 2. A drawing of the packing arrangement in the crystals of **1**. A schematic view illustrating the short contact of orbital interaction between C-2 and S (dotted lines) in an adjacent molecule and van der Waals radius (circles) are also given.

Although a fully optimized MNDO calculation[9] shows that the syn dimer (ΔH_f = 90.6 kcal mol^{-1}) is more stable than the anti dimer (ΔH_f = 95.2 kcal mol^{-1}), the reason for the exclusive formation of syn **2** remains at present unsolved. If this solid-state dimerization of **1** to **2** proceeds concertedly, the stereochemistry of **2** is consistent with a symmetry-forbidden $[{}_{\pi}8_{a} + {}_{\pi}8_{a}]$ type cycloaddition[10] by the superjacent orbital control[11] between the HOMO and NLUMO of **1**.[12]

The syn dimer **2** monomerized easily at the mp or in solution at room temperature. The kinetics of the cycloreversion in five solvents (MeCN, EtOH, CHCl$_3$, benzene, or CCl$_4$) were of the first-order reaction, and $\Delta H^{\ddagger}$ obtained were 19.2–22.1 kcal mol^{-1} and $\Delta S^{\ddagger}$ between −6.8 and −3.4 eu. These data suggest that the cycloreversion proceeds in a concerted manner.[13]

In conclusion, we have discovered a molecule whose crystalline reactivity is especially conspicuous for the exclusive formation of a nontopochemical product in the ground state. The [8 + 8] dimerization of **1** contrasts sharply with the [6 + 6] and several types of dimerization of tropone in solutions on photolysis.[14]

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles, listing of spectral data (mp, IR, UV-vis, ^{13}C NMR, ^{1}H NMR, and MS) for the reported compounds, and FMO interpretation (8 pages). Ordering information is given on any current masthead page.

---

(8) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN84. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York, England, and Louvain, Belgium, 1984.

(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

(10) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

(11) (a) Berson, J. A.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 8917–8918. (b) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406–414. (c) Paddon-Row, M. N.; Gell, K.; Warrener, R. N. *Tetrahedron Lett.* **1975**, 1975–1978.

(12) Machiguchi, T.; Hoshi, T.; Yoshino, J.; Kitahara, Y. *Tetrahedron Lett.* **1973**, 3873–3876.

(13) (a) Wassermann, A. *Diels-Alder Reactions*; Elsevier: New York, 1965. (b) Kwart, H.; King, K. *Chem. Rev.* **1967**, *67*, 415–447. (c) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807.

(14) (a) Mukai, T.; Tezuka, T.; Akasaki, Y. *J. Am. Chem. Soc.* **1966**, *88*, 5025–5026. (b) Kende, A. S. *Ibid.* **1966**, *88*, 5026–5027. (c) Kende, A. S.; Lancaster, J. E. *Ibid.* **1967**, *89*, 5283–5284. (d) Tezuka, T.; Akasaki, Y.; Mukai, T. *Tetrahedron Lett.* **1967**, 1397–1402, 5003–5008.