Interconversion and Reactions of *In*- and *Out*-Isomers of a Triarylphosphine-Containing Cyclophane

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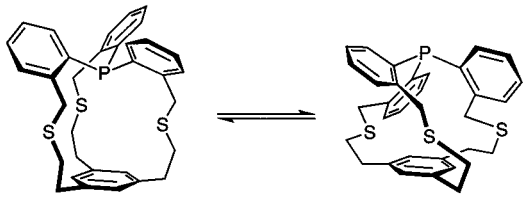
Abstract: The conformational isomerizations of an *in*-cyclophane containing a triarylphosphine poised above a basal aromatic ring (compound **1**) were studied by various experimental and computational methods. When the *in*-isomer **1** was heated at temperatures great enough to invert the triarylphosphine, the corresponding *out*-isomer (**2**) was not observed, but this isomer was trapped by heating with sulfur to give an *out*-phosphine sulfide (**4**). The X-ray structures of **1** and **4** were determined, and **1** was found to adopt an unusual, compact conformation, rather than the more extended conformation observed in a related system. The sulfuration of **1** is 10000 times slower than the corresponding sulfuration of triphenylphosphine, and the rate-determining step for the former reaction appears to be the phosphine inversion ($\Delta G^{\ddagger}_{inv} = 34.8$ kcal/mol). Desulfurization of **4** with hexachlorodisilane at room temperature smoothly returned the *in*-cyclophane **1**, with no intermediate **2** detected, indicating that the reverse phosphine inversion has a low barrier. The relative energies of the various conformations of these cyclophanes were evaluated by a wide range of computational methods, with comparisons to experimental geometries and stabilities where possible. Molecular mechanics and semiempirical MO calculations proved inadequate for these systems, but ab initio and hybrid density functional methods gave reasonable results.

Introduction

In/out isomerism[1] confers a greater difference in reactivity for the two isomers than any other type of stereoisomerism. Where medium rings are involved, the *in*-isomer is generally unreactive due to steric encumbrance, but the *out*-isomer may show reduced *or* enhanced reactivity, usually depending on the relative strain in the reactant and product. In recent years we have prepared more than a dozen cyclophanes possessing a variety of functional groups projected toward an aromatic ring, including methines,[2] phosphines,[3,4b] silanes,[3b] and fluorosilanes.[4] In each of these cases, molecular mechanics or semiempirical molecular orbital calculations correctly predicted that the *in*-geometry would be preferred, usually by a substantial margin, over the corresponding *out*-isomer. Although on one occasion we have observed an *out*-isomer in theses studies,[4b] in no case have *both* the *in*- and *out*-isomers been prepared or even detected. Most recently, however, we reported the preparation of the *in*-phosphine **1**, for which the *in*-geometry was established by ^{1}H NMR studies and, more significantly, by the X-ray structure of its trisulfone derivative.[4b] AM1 calculations suggested that the *in*-isomer is only 1.3 kcal/mol more stable than the *out*-isomer **2**;[4b] thus a 9:1 *in:out* equilibrium mixture of the two isomers should exist, and such a mixture might be obtained by heating **1**. Naturally, we wished to compare these *in*- and



1 **2**

out-isomers, if possible, and this simple idea led to an interplay of experimental and computational studies, reported herein, which feature unusual reactions of the cyclophanes and an interesting test of modern computational methods.

Results and Discussion

Inversion and Sulfuration of Phosphine 1. Phosphines have high, but not insurmountable, barriers to inversion. Baechler and Mislow[5] found that the free energy of activation for the inversion of trialkyl phosphines ($\Delta G^{\ddagger}_{inv}$) is ca. 36 kcal/mol, for dialkyl aryl phosphines ca. 33 kcal/mol, and for alkyl diaryl phosphines ca. 30 kcal/mol. The trend suggests that the barrier for triaryl phosphines should be ca. 27 kcal/mol, but this was not determined. However, the heating of phosphine **1**, even

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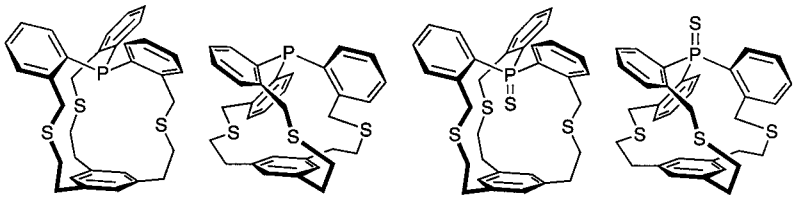
Table 1. Computational Data for Cyclophanes **1**−**4**[a]



1 **2** **3** **4**

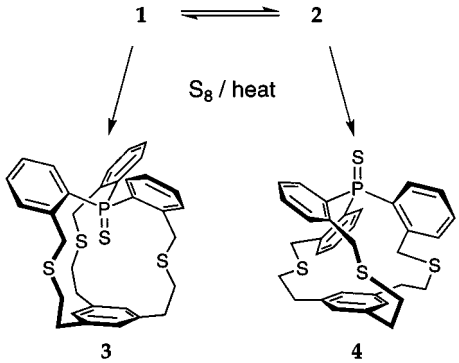
level	**1**	**2**	$\Delta\Delta H_{f(2-1)}$ or $\Delta E_{(2-1)}$	**3**	**4**	S_8	ΔE_{sulf}
MMFF	**145.95** (C_3-e)	**165.65** (C_3)	19.7	**184.31** (C_3-e)	**170.64** (C_3)		
	147.69 (C_3-s)	171.55 (C_1)		196.73 (C_3-s)	183.09 (C_1)		
AM1	124.50 (C_3-e)	**125.75** (C_3)	2.4	112.02 (C_3-e)	**109.78** (C_3)	15.31 (D_{4d})	−15.5
	123.39 (C_3-s)	128.08 (C_1)		**104.90** (C_3-s)	111.58 (C_1)		
HF/STO-3G	−**2770.114262** (C_3-e)	−2770.068620 (C_3)	28.0[b]	−**3163.209506** (C_3-e)	−3163.188259 (C_3)	−3145.462377 (D_{4d})	66.5[b]
	−2770.108255 (C_3-s)	−**2770.069578** (C_1)		−3163.195534 (C_3-s)	−**3163.191013** (C_1)		
HF/3-21G(*)	−2787.941654 (C_3-e)	−**2787.909696** (C_3)	21.1[b]	−**3183.614740** (C_3-e)	−3183.604326 (C_3)	−3165.330070 (D_{4d})	1.3[b]
	−**2787.943304** (C_3-s)	n.m.[c] (C_1)		−3183.602242 (C_3-s)	−**3183.607510** (C_1)		
HF/6-31G(d)	−**2802.132891** (C_3-e)	−**2802.100519** (C_3)	20.3[b]				
	−2802.130040 (C_3-s)	n.m.[c] (C_1)					
B3PW91/-6-31G(d)	−2812.648945 (C_3-e)						
	−**2812.652174** (C_3-s)						
B3PW91/cc-pVDZ	−2812.797573 (C_3-e)	−**2812.772941** (C_3)	18.5[b]			−3184.327043 (D_{4d})	−70.8[b]
	−**2812.802386** (C_3-s)	n.m.[c] (C_1)			−3210.956146 (C_1)		

[a] Except as noted, for the MMFF and AM1 calculations, enthalpies of formation (ΔH_f) are given in kcal/mol, and for the ab initio and HDFT calculations, energies (E) are given in au (1 au = 627.503 kcal/mol); where more than one conformation was calculated, the energy of the more stable conformation is **bold**. [b] Relative energies are given in kcal/mol. [c] The C_1 conformation is not a minimum at this level (optimization yields the C_3 conformation).

at 200 °C for several days, failed to produce any of the *out*-isomer **2** as judged by ^{1}H NMR. Such heating would have overcome even a 40 kcal/mol barrier to inversion. The NMR spectrum of a closely related *out*-methylsilane[4b] suggests that the methylene resonances of **1** and **2** should be very different; if so, as little as 1% **2** should have been detectable.

For this reason we suspected that the AM1 estimate of the energy difference between **1** and **2** (1.3 kcal/mol[4b]) was in error.[6] We have found that even low-level ab initio calculations give better estimates of the relative energies of strained aromatic compounds than empirical and semiempirical methods,[7] so the energies of **1** and **2** were evaluated at the HF/STO-3G level (see Table 1). These calculations gave a strikingly different estimate of the relative energies: **1** was calculated to be 28.0 kcal/mol more stable than **2**! The discrepancy of 27 kcal/mol between the AM1 and ab initio estimates is very large when one considers that **1** and **2** are merely conformational, not constitutional, isomers which contain only "ordinary" bonds. If the HF/STO-3G estimate is accurate, then it is impossible to produce significant amounts of **2** in a simple thermal isomerization.

However, a second, more interesting experiment was now suggested. If **2** is inaccessible, then it might be possible to prepare the *in*-phosphine sulfide **3** by heating **1** with sulfur under forcing conditions. At first, **1** was heated with excess sulfur in refluxing toluene, but no reaction was observed. However, when **1** was heated with sulfur in CS_2 at 185 °C in a sealed tube, a substantial amount of a new phosphine sulfide was formed as judged by MS analysis. Unfortunately, the ^{1}H NMR spectrum of the product suggested that the *out*-isomer **4** had been formed, and this was confirmed by subsequent X-ray analysis (see Figure 1). Thus, the *in*-phosphine **1** *can* be inverted under these conditions, and as **2** is formed it is captured as the phosphine sulfide **4**.



3 **4**

The reaction of triphenylphosphine with sulfur has been extensively studied. Bartlett and Meguerian found that the reaction of triphenylphosphine with sulfur in benzene is first order in both phosphine and sulfur and relatively fast at room temperature ($k_{25°C} = 4.4 \times 10^{-3}$ M^{-1} s^{-1}).[8] Davis verified this result and determined the activation energy for the reaction to be 16.5 kcal/mol.[9] Nucleophilic attack of the phosphine on S_8 to form a phosphonium polysulfide is the likely first and rate-determing step in this reaction.[8]

The reaction of cyclophane **1** with sulfur stands in stark contrast to those findings. Kinetic studies were conducted in sealed NMR tubes containing benzene-d_6 solutions of **1** and sulfur, and the reaction was monitored by ^{1}H NMR. The reaction is first order in **1** with a half-life of 36 h at 145 °C ($k_{145°C} = 5.3 \times 10^{-6}$ s^{-1}), and the rate is *independent* of sulfur concentration. These results suggest that phosphine inversion

(6) As is shown later, when additional conformations of **1** and **2** are taken into account, the AM1 difference grows to 2.4 kcal/mol (Table 1), still a very small value.

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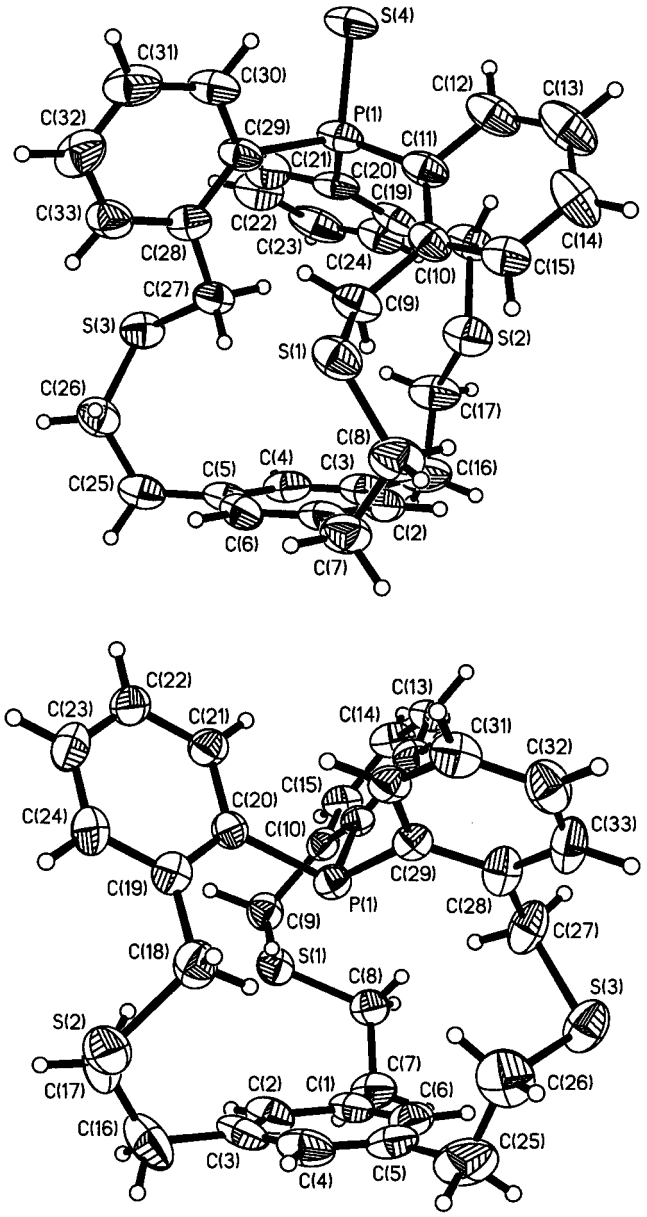

Figure 1. Molecular structures of the cyclophanes **4** (above) and **1** (below). Thermal ellipsoids have been drawn at the 50% probability level.

is the rate-determining step in the sulfuration of **1**. As the *out*-phosphine **2** forms at high temperature, it is immediately captured as the sulfide in an extremely rapid bimolecular reaction with sulfur. Furthermore, by using the Eyring equation (and assuming a transmission coefficient of 1), we may estimate $\Delta G^{\ddagger}_{inv}$ for **1** → **2** to be 34.8 kcal/mol.

Desulfurization of Compound 4. The ready availability of the *out*-sulfide **4** suggested that the *out*-phosphine **2** might be prepared by a mild desulfurization of **4**, provided that the barrier for the inversion of **2** is high enough. Since $\Delta G^{\ddagger}_{inv}$ for **1** → **2** is known (ca. 35 kcal/mol), a knowledge of the relative energies of **1** and **2** would yield the activation energy for the reverse reaction. If **2** is no more than 10 kcal/mol less stable than **1**, then $\Delta G^{\ddagger}_{inv}$ for **2** → **1** would be at least 25 kcal/mol, and the isolation of **2** would be relatively easy.

Mislow and co-workers have reported the use of hexachlorodisilane for the reduction of phosphine sulfides to phosphines with retention of configuration.[10] Their conditions call for heating the sulfide and Si_2Cl_6 in refluxing benzene for 6 h. We found that stirring **4** with Si_2Cl_6 in benzene at room temperature for 24 h smoothly and quantitatively converted **4** to the *in*-phosphine **1**. This reaction was conveniently monitored by ^{1}H NMR, but at no point in the reaction were any species observed other than **4** and **1**, suggesting that the barrier for **2** → **1** is quite low. Thus, the difference in energy between **1** and **2** must be substantially greater than 10 kcal/mol, in qualitative agreement with the HF/STO-3G calculations, but more information is required to map accurately the sulfuration/desulfuration reaction coordinate.

X-ray Structure of Phosphine 1. The large difference between the cyclophane energetics calculated by semiempirical and ab initio methods led us to wonder (a) which method gives the more accurate geometry for **1** and (b) would the differences in the structures elucidate the source of the energetic discrepancy. For these reasons we determined the X-ray structure of cyclophane **1**, which is illustrated in Figure 1. This structure was quite a surprise. Up to this point, it had been assumed that **1** adopts a conformation similar to that of its trisulfone, for which the X-ray structure is known.[4b] Indeed, both **1** and the trisulfone possess approximate C_3 symmetry in the crystal. However, **1** adopts a "short" conformation in which the torsion angles for the 4-atom chains linking the basal aromatic ring with the triarylphosphine [e.g. C(7)−C(8)−S(1)−C(9); see Figure 1] range from 99° to 116°, which is much more compact than the "extended" conformation seen in the trisulfone in which these torsion angles range from 152° to 159°. The net result is that the distance from the phosphorus to the mean plane of the basal aromatic ring in **1** is only 4.03 Å, more than 1 Å closer than in the trisulfone (5.40 Å). The finding of this second, "short" conformation of **1** led to a reevaluation and extension of the computational studies on these cyclophanes.[11]

Computational Studies. During the course of the experimental work, the energies and geometries of various conformations of the cyclophanes **1**−**4** were examined by molecular mechanics (MMFF), semiempirical (AM1), and low-level ab initio (HF/STO-3G) calculations, and the results of these and subsequent higher-level calculations are summarized in Tables 1 and 2.

The three low-level methods were generally in poor agreement, and particularly so with regard to the preferred conformation of cyclophane **1** and the relative energies of its *in*- and *out*-isomers (**1** and **2**). First, the short and extended C_3 conformations of **1** (designated C_3-s and C_3-e, respectively; see Figure 2) proved to be separate potential minima in all three types of calculation. However, only AM1 indicated the observed C_3-s conformation to be the more stable of the two (Table 1), yet the AM1 geometry was the worst of the three when compared to the observed X-ray structure (Table 2). Second, even when the various conformations of **1** and **2** are taken into account, the estimates of the relative energies of **1** and **2** by the three methods (19.7, 2.4, and 28.0 kcal/mol; Table 1) are widely scattered. Finally, the low-level results for phosphine sulfide **4** were also flawed; both the MMFF and AM1 methods indicate that a C_3 conformation is preferred for **4**, but its X-ray structure reveals a distinctive (and computationally distinct) C_1 conformation (Figure 1). Clearly, more extensive computational studies would be required to define the conformational preferences and energetics of these cyclophanes.

(10) Zon, G.; DeBruin, K. E.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7023−7027.

(11) The X-ray structure of **1** contains two independent molecules. The first, well-ordered molecule adopts the C_3-e conformation as discussed; however, one component of the disordered second molecule appears to be an unusual "leaning" C_1 conformation, indicating that other, low-symmetry conformations are accessible.

Table 2. Comparison of Experimental and Calculated Geometries for Compounds **1** and **4**[a]

level	**1** (C_3-s)[b] rms dev[c]	**1** (C_3-s)[b] max dev[c]	P-to-basal ring	**4** (C_1) rms dev[c]	**4** (C_1) max dev[c]	P-to-basal ring
expt (X-ray)			4.03			6.07
MMFF	0.209	0.347	4.22	0.126	0.360	6.19
AM1	0.272	0.488	4.57	0.320	0.790	6.14
HF/STO-3G	0.195	0.353	4.12	0.118	0.212	6.12
HF/3-21G(*)	0.203	0.375	4.22	0.094	0.178	6.18
HF/6-31G(d)	0.214	0.416	4.32			
B3PW91/6-31G(d)	0.197	0.399	4.22			
B3PW91/cc-pVDZ	0.195	0.400	4.20	0.103	0.218	6.20

[a] All distances are given in angstroms. [b] The X-ray structure possesses only approximate C_3 symmetry; the calculated structures have exact C_3 symmetry. [c] The function OFIT in SHELXTL was used to determine the best fit of the experimental and calculated geometries and the deviations of the atomic positions; all non-hydrogen atoms were employed for the fitting.

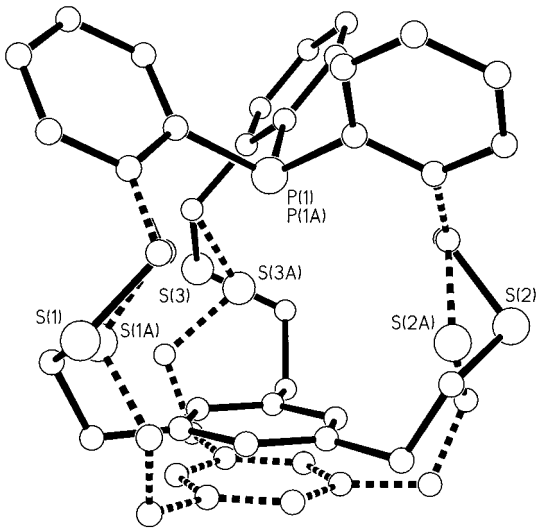

Figure 2. Comparison of the calculated (B3PW91/cc-pVDZ) structures for the C_3-s (solid line) and C_3-e (dashed line) conformations of cyclophane **1**.

Cyclophane **1** was examined most closely by higher-level ab initio methods and hybrid density functional theory (HDFT). A comparison of the C_3-s and C_3-e conformations of **1** at the highest level employed (B3PW91/cc-pVDZ) is illustrated in Figure 2. The triarylphosphine "tops" are virtually identical in the two structures; the differences reside entirely in the 4-atom linking chains and base. The HF/3-21G(*), B3PW91/6-31G-(d), and B3PW91/cc-pVDZ levels correctly indicate a preference for the C_3-s conformation (Table 1), and all three methods give structures in good agreement with the X-ray structure of **1** (Table 2). Indeed, the geometries produced by these three methods are very similar, and the somewhat larger deviations from the experimental structure are due to a distortion of the X-ray structure from ideal C_3 symmetry by crystal packing forces. Note, however, that an HF/6-31G(d) calculation of **1** proved to be anomalous; it prefers the C_3-e conformation, and the calculated geometry is significantly worse than the other three higher-level methods.

The relative energies of **1** and **2** as calculated by these methods are quite similar: **1** is more stable by about 20 kcal/mol. This value is in good agreement with the available experiments, and we suspect that the B3PW91/cc-pVDZ value of 18.5 kcal/mol is nearest the mark. The computed structures do not give an obvious explanation for the substantial difference in the energies of **1** and **2**. Neither structure shows unusually close nonbonded interactions, and the bond angles seem to be within normal limits, so the large energy difference must result from the accumulation of many small effects. In such situations, the computational methods chosen must deal with both bonds and nonbonded interactions quite accurately to give reliable estimates of conformational energies, and thus the ab initio and HDFT methods are clearly superior to molecular mechanics and semiempirical methods.

We note that both the HF/3-21G(*) and B3PW91/cc-pVDZ geometries for compound **4** are in excellent agreement with the X-ray structure (see Table 2). Interestingly, AM1, HF/STO-3G, and HF/3-21G(*) calculations indicate that the *in*-sulfide **3** should be 4−12 kcal/mol more stable than its *out*-isomer **4**. Unfortunately, the formation of **3** by direct sulfuration is sterically precluded, and attempted thermal isomerization of **4** simply leads to decomposition.

Finally, the widest discrepancies between the various computational methods are found for the energetics of the overall sulfuration reaction (ΔE_{sulf}, Table 1). The overall reaction is calculated to be strongly endothermic at the HF/STO-3G level ($\Delta E_{sulf} = +66.5$ kcal/mol; Table 1), nearly even at the HF/3-21G(*) level (+1.3 kcal/mol), and strongly exothermic at the B3PW91/cc-pVDZ level (−70.8 kcal/mol), but these large differences likely arise from inadequate treatment of S_8 by simple Hartree−Fock methods.

Conclusion. If one makes the assumption that the activation energy for the sulfurization of **2** is the same as that for triphenylphosphine (16.5 kcal/mol),[9] then the best available experimental and computational data yield the reaction coordinate diagram shown in Figure 3, which incorporates the energies for the phosphines **1** and **2**, the sulfide **4**, and S_8 at the B3PW91/cc-pVDZ level. This combination of computational and experimental estimates coincidentally gives very similar absolute energies for the transition states for the two steps of the sulfuration reaction. We suspect, however, that with a "tied-back" phosphine such as **2**, the second transition state is a bit lower than illustrated. The apparent barriers for **2** → **1** (16 kcal/mol) and **1** → **2** (35 kcal/mol) fall almost symmetrically on either side of the expected barrier for the inversion of an unencumbered triarylphosphine (27 kcal/mol); thus the arms of the cyclophane behave as sets of springs which restrain **1** from inverting but push **2** toward the reverse inversion. Finally, the low activation energy for isomerization of **2** to **1** indicates that any attempt to isolate the *out*-phosphine **2** will require a reagent that can efficiently desulfurize compound **4** at very low temperature.

Experimental Section

***out*-Phosphine Sulfide 4.** The *in*-phosphine **1**[4b] (14.0 mg, 0.025 mmol), sulfur (11.5 mg, 0.045 mmol S_8), and CS_2 (2 mL) were placed in a screw-capped tube, and the tube was heated in a 185 °C oil bath for 23 h. After cooling, the reddish-brown solution was fractionated by preparative TLC (silica gel GF; solvent, toluene) to give compound **3** as a white solid (6.0 mg, 0.010 mmol, 41%) as well as some unreacted starting material. Recrystallization of **3** from CH_2Cl_2−acetone gave

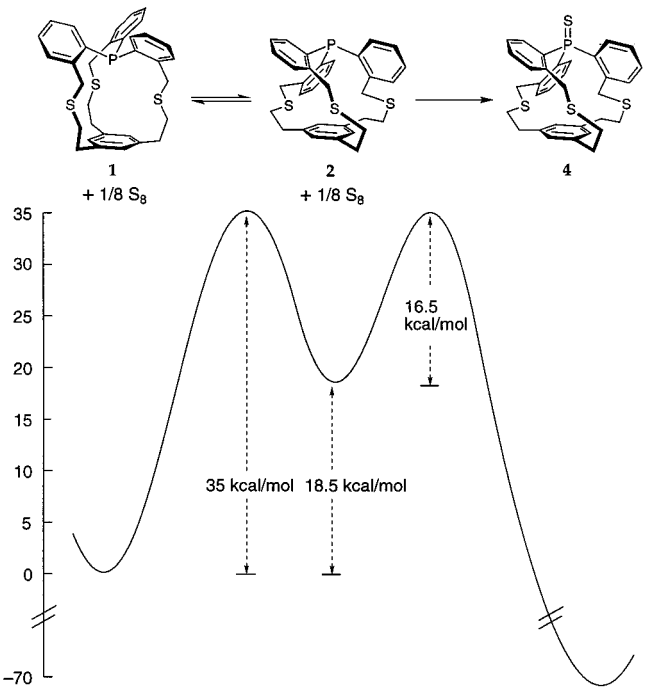

Figure 3. Proposed reaction coordinate diagram for the reaction of cyclophane **1** with sulfur.

crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.42 (m, 3 H), 2.78 (d, J = 14 Hz, 3 H), 2.79 (m, 3 H), 2.93 (m, 6 H), 3.23 (d, J = 14 Hz, 3 H), 6.94 (s, 3 H), 7.29 (dd, J = 7, 1 Hz, 3 H), 7.44 (m, 6 H), 8.52 (ddd, J = 17, 8 Hz, 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 35.5, 37.0, 37.1, 127.8 (d, J_{PC} = 14 Hz), 128.4, 130.4 (d, J_{PC} = 10 Hz), 131.7, 133.7, 136.7, 140.4 (d, J_{PC} = 8 Hz), 141.1; MS, m/z 588 (M^+, 10), 555 (M − SH, 10), 275 (100); exact mass 588.1205, calcd for $C_{33}H_{33}PS_4$ 588.1203.

X-ray Crystallographic Analysis of Compound 4: Formula $C_{33}H_{33}PS_4$; triclinic, space group $P\bar{1}$; a = 9.0388 (5) Å, b = 18.6943 (12) Å, c = 18.9445 (12) Å, α = 108.580 (2)°, β = 97.927 (2)°, γ = 102.693 (2)°, V = 2884.3 (3) Å^3, Z = 4, D_{calcd} = 1.356 g/cm^3. Mo Kα radiation (λ = 0.71073 Å) was employed for data collection (θ_{max} = 27.5°) at 170 K on a Nonius KappaCCD diffractometer. A total of 38433 reflections were indexed, integrated, and corrected for Lorentz and polarization effects (but not for absorption) by using the program DENZO,[12] and then were merged to 13134 reflections (R_{int} = 0.134) by using the program SCALEPACK.[12] The structure was solved by direct methods (SHELXTL[13]) and refined by full-matrix least-squares on F^2. Two molecules of **4** are included in the asymmetric unit. Molecule 1 is well ordered, but Molecule 2 displays a severe 3-fold disorder. Much effort was spent on attempts to model satisfactorily the disorder of Molecule 2, but these models gave poor geometries and required numerous restraints on the geometric and anisotropic thermal parameters. It was therefore decided to treat Molecule 2 in the manner of disordered solvent, so the SQUEEZE/BYPASS procedure[14] implemented in PLATON-96[15] was employed to account for all of the disordered cyclophane's electron density. With only Molecule 1 included in the instruction file for PLATON-96, the SQUEEZE option found a total electron count of 602.9 e in a volume of 1589.9 Å^3 for the region of the unit cell containing Molecule 2 (55% of the unit cell volume). This electron count corresponds to 1.94 $C_{33}H_{33}PS_4$ units (0.97 per asymmetric unit), an excellent result. The SQUEEZE-processed data were used for all subsequent refinement. All non-hydrogen atoms were refined anisotropically, with hydrogens riding [C−H = 0.95 or 0.99 Å, U(H) = 1.2U(C)]. The refinement converged to $R(F)$ = 0.0699, $wR(F^2)$ = 0.1553, and S = 1.191 for 5263 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.1427, $wR(F^2)$ = 0.1747, and S = 0.840 for 13134 unique reflections, 343 parameters, and 0 restraints. Full details are given in the Supporting Information.

X-ray Crystallographic Analysis of Compound 1: Formula $C_{33}H_{33}PS_3$; monoclinic, space group $P2_1/c$; a = 23.5487 (4) Å, b = 9.3568 (1) Å, c = 32.4855 (4) Å, β = 128.411 (1)°, V = 5608.7 (1) Å^3, Z = 8, D_{calcd} = 1.319 g/cm^3. Mo Kα radiation (λ = 0.71073 Å) was employed for data collection (θ_{max} = 22.5°) at 200 K on a Nonius KappaCCD diffractometer. A total of 85749 reflections were processed as described for **4** to yield 7379 unique reflections (R_{int} = 0.113). The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Two molecules of **1** are included in the asymmetric unit. Molecule 1 was well ordered and refined without difficulty, but Molecule 2 required a fairly complex two-site disorder model for satisfactory treatment. No geometric restraints were employed in the final crystallographic model, but it was necessary to restrain the thermal ellipsoids in Molecule 2 where the disorder brought two pairs of benzene rings close together but not coincident. All non-hydrogen atoms were refined anisotropically, with hydrogens riding [C−H = 0.95 or 0.99 Å, U(H) = 1.2U(C)]. The refinement converged to $R(F)$ = 0.0728, $wR(F^2)$ = 0.1512, and S = 1.418 for 5472 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.1023, $wR(F^2)$ = 0.1605, and S = 1.269 for 7378 unique reflections, 857 parameters, and 84 restraints. One reflection was suppressed.

Kinetic Studies. Kinetic studies of the sulfuration of **1** were conducted in sealed NMR tubes containing benzene-d_6 or CS_2 (as solvent), **1**, and sulfur. In a typical experiment, designed to determine the effect of sulfur concentration on the rate of reaction, three NMR tubes were prepared containing benzene-d_6 (1.0 mL), **1** (4.5 mg, 0.0081 mmol), and sulfur (3.2 mg, 0.012 mmol; 10.4 mg, 0.041 mmol; and 29.8 mg, 0.116 mmol). The tubes were placed in an oven held at 145 °C (at which $t_{1/2} \sim$ 36 h), and the tubes were removed at 6 to 12 h intervals to record the NMR spectra. At each time point, integration of the benzylic proton resonances at δ 3.2 and 3.7 was used to determine the ratio of **1** and **4** in the reaction mixture.

Computational Studies. Molecular mechanics calculations (MMFF[16]), semiempirical molecular orbital calculations (AM1[17]), and ab initio calculations at the HF/STO-3G level[18] were performed by using the SPARTAN program package (Version 5.0; Wavefunction, Inc., Irvine, California), and its built-in default thresholds for wave function and gradient convergence were employed. Frequency calculations were performed on the AM1-optimized equilibrium geometries to verify that these were true potential minima. GAUSSIAN 94, GAUSSIAN 98,[19] and GAMESS[20] were employed for the larger ab initio calculations at the HF/3-21G(*) and HF/6-31G(d) levels,[18] again employing the default convergence criteria, as well as for the hybrid density functional calculations at the B3PW91/6-31G(d) and B3PW91/cc-pVDZ levels.[21−23]

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Supporting Information Available: ^{1}H NMR spectra of compounds **1** and **4**, and crystal structure reports for compounds **1** and **4** (including full experimental details, tables of atomic coordinates, bond distances, bond angles, and thermal parameters, and selected figures) (PDF). An X-ray crystallographic file (CIF) is available through the Internet. This material is available free of charge via the Internet at http://pubs.acs.org.

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