Dynamic NMR Study of the Rotation around "Biphenyl-Type" Bonds in Polycyclic Sulfoxides

Samuel Braverman, Yossi Zafrani, and Hugo E. Gottlieb*

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

gottlieb@mail.biu.ac.il

Received September 25, 2001

In a recent paper, we reported on the base-catalyzed rearrangement of bis-propargylic sulfoxides that eventually leads to polycyclic products featuring an unsaturated, cyclic substituent such as cyclohexenyl or phenyl. Due to steric constraints, the latter is positioned roughly perpendicularly to the tricyclic core, and in most cases, two rotamers can be observed in the ground state. In the present work, we report on the synthesis and the products of both symmetrical and asymmetrical starting materials. We also measure, by NMR techniques, the rotation rate of the side chain for several such polycyclic sulfoxides. The barriers for this process, which is similar to a biphenyl rotation, are very strongly dependent on the nature of the substrate, ranging between <7 and 21.0 kcal·mol^{-1} for sulfoxides with two five-membered rings and two seven-membered rings, respectively. These barriers can be successfully simulated by molecular-mechanics calculations, and the geometries of the transition states are discussed.

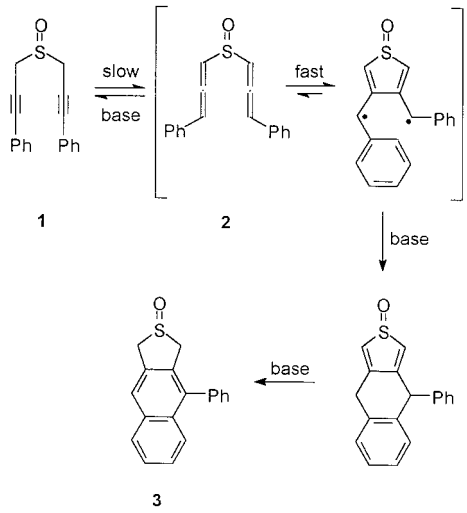
Introduction

In the past decade, considerable attention has been focused on cyclization reactions of diallenes or diacetylenes involving free-radical species.[1] The trigger for renewal of interest in this type of reaction was the elegant mode of action of the naturally occurring enediynes,[2] whose biological activity involves a diradical cycloaromatization.[3] Recently, we became interested in studying the effect of tandem cyclization and aromatization of some novel sulfur- and selenium-bridged propargylic systems, which, besides their potential biological activity, would also be of considerable mechanistic and synthetic interest.[4] During the course of our studies, we found that π-conjugated bis-propargylic sulfoxides and sulfones undergo facile isomerization to the corresponding diallenes, followed by tandem cyclization and aromatization via a probable diradical intermediate, in the presence of amine bases at room temperature (for the case of sulfoxides, see Scheme 1). To test the generality of the reactions reported in Scheme 1, we have examined the reactivity of other dipropargylic compounds such as **4b**.

Interestingly, we found that in the ^{1}H NMR spectrum of polycyclic sulfoxide **5b**, the olefinic proton appeared as two broad signals of similar intensity (see Figure S1, Supporting Information). This can be explained by postulating that, in the ground state, the cyclohexenyl ring is roughly perpendicular to the plane of the aromatic ring. Since the molecule contains a chiral sulfoxide moiety, this arrangement constitutes a second chiral element, and therefore, two diastereoisomers are possible. The latter can interconvert via a process similar to the well-known rotation of the aryl−aryl bond in biphenyls and can therefore be called diastereorotamers (see Scheme 2).

A dynamic NMR experiment (EXSY, Figure S1) showed that the barrier for this process is 18.1 kcal·mol^{-1}. We prepared in a similar fashion the five-membered ring equivalent **5a** and were quite surprised to find that the rotational barrier for this compound was too low to be measured by NMR (<7 kcal·mol^{-1}). While the rotation around the central bond in biphenyls has been well studied,[5] we could find only a few examples in the literature[6,7] for the equivalent process in simple olefin-

Scheme 1



1 2 3

(1) Selected reviews: (a) Nicolaou, K. C.; Smith, A. L. In *Modern Acetylene Chemistry*; Stang, P. J., Diedrich, F., Eds.; VCH: Weinheim, 1995; Chapter 7. (b) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D. Tetrahedron Report No. 399. *Tetrahedron* **1996**, *52*, 6453. (c) Wang, K. K., *Chem. Rev*. **1996**, *96*, 207. (d) Maier, M. E. *Synlett* **1995**, 13. (e) Magnuse, P., *Tetrahedron* **1994**, *50*, 1397. (f) Nicolaou, K. C.; Dau, W. M.; Tsay, S. C. Estevez, V. A. *Science* **1992**, *256*, 1172.

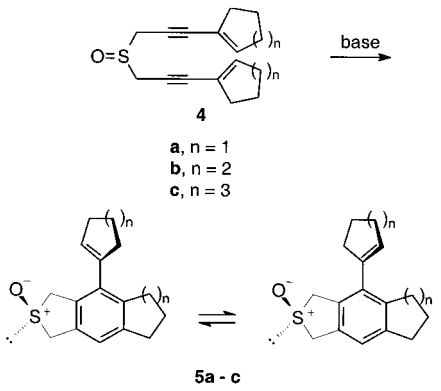
(2) For recent reviews, see: (a) Pogozelsky, W. K.; Tullius, T. D. *Chem. Rev*. **1998**, *98*, 1089. (b) Maier, M. E.; Bosse, Folkert, Niestroj, A. J. Eur. *J. Org. Chem*. **1999**, *1*, 1. (c) Thorson, J. S.; Shen, B.; Whitwam, R. E.; Liu, W.; Li, Y.; Ahlert, *J. Bioorg. Chem*. **1999**, *27*, 172.

(3) Nicolaou, K. C.; Dai, W. M. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 1387 and references cited therein.

(4) (a) Braverman, S.; Zafrani, Y.; Gottlieb, H. E. *Tetrahedron Lett.* **2000**, *41*, 2675. (b) Braverman, S.; Zafrani, Y.; Gottlieb, H. E. *Tetrahedron* **2001**, *57*, 9177.

10.1021/jo010947z CCC: $22.00
Published on Web 04/12/2002

Scheme 2



substituted benzenes. This dramatic substitutional effect encouraged us to investigate a series of unusual "biphenyl-like" polycyclic sulfoxides substituted by aromatic (**3**, **18e**, **19e**), cyclic (**5a**−**c**, **18a**, **19a**), and acyclic (**19d**) groups (Schemes 2 and 5). The synthesis of polycyclic sulfoxides such as **18a**,**d**,**e** and **19a**,**d**,**e** became possible by the use of mixed propargylic sulfoxides that can cyclize into two possible directions as shown in Scheme 5.

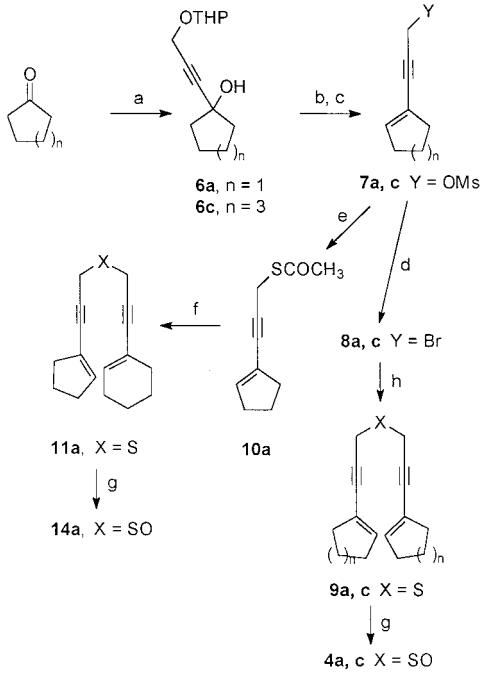
Results

Synthesis of Polycyclic Sulfoxides. The desired mixed propargyl sulfoxide **14a**, as well as symmetrical sulfoxides **4a**,**c**, was prepared by the procedure shown in Scheme 3. Thus, cycloalkanols **6a**,**c** were formed by treatment of the appropriate cycloalkanone with the lithiated tetrahydro-2-(3-propynyloxy)-2*H*-pyran and deprotected under methanolic acid conditions followed by tandem mesylation/elimination to afford **7a**,**c** in 78 and 61% overall yields, respectively. For symmetrical sulfoxides, these mesylates were treated with sodium bromide to give the propargyl bromides **8a**,**c** (81 and 27% yields). The latter were then reacted with sodium sulfide to furnish the corresponding sulfides **9a**,**c** in 62 and 98% yields, which were oxidized to sulfoxides **4a**,**c** (42% yield each). Asymmetrical sulfoxides **14a**,**d**,**e** were conveniently obtained by the reaction of the appropriate substituted propargyl bromides with propargyl thioacetates in the presence of potassium hydroxide, followed by oxidation with sodium periodate. Thus, reaction of mesylate **7a** with potassium thioacetate yielded propargyl thioacetate **10a** in 96% yield. In situ hydrolysis of the latter and nucleophilic displacement by the released thiolate anion on cyclohexenyl propargyl bromide afforded sulfide **11a** in 85% yield. Oxidation of the latter with sodium periodate gave sulfoxide **14a** in 50% yield. Similarly, sulfoxides **14d**,**e** were prepared in 29 and 39% yields, respectively, using thioacetate **12** as a starting material as shown in Scheme 4.

Asymmetrical sulfoxides **14a**,**d**,**e** undergo cyclization (see Scheme 5) in both possible directions, presumably as a function of the relative reactivity of diradicals intermediates **15a**,**d**,**e**. In general, when the latter involved a benzyl radical (e.g., **15d**,**e**), the preference was to recombine by intramolecular addition to a simple double bond rather than to a benzene ring; the preference is enhanced in a more polar solvent. Thus, reaction of sulfoxide **14d** with DBU in acetonitrile led exclusively to the corresponding sulfoxide **18d** in 74% yield, whereas a 85:15 mixture of **18d** and **19d** was formed in a less polar solvent, chloroform. Similarly, sulfoxide **14e**, when treated with DBU in chloroform, led to a 67:33 mixture of **18e** and **19e**, but only **18e** was obtained (89% yield) with DBU in acetonitrile. The reaction of sulfoxide **14a** with DBU in acetonitrile at room temperature led to **18a** and **19a** in a 16:84 ratio.

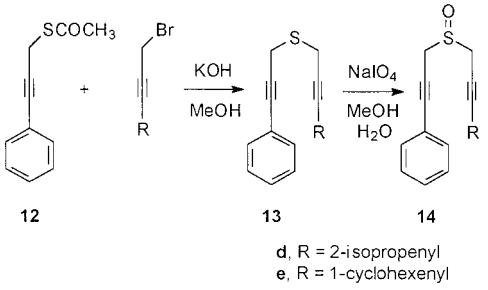
The ability to generate a variety of substituted cyclic sulfoxides, from both symmetrical and asymmetrical starting materials, allows us to investigate the changes in the side-chain rotation barrier (Scheme 2) as a function of different parameters, e.g., (a) the effect of ring size, using policyclic sulfoxides **5a**−**c**, which are derived from symmetrical starting materials; (b) the effect of the positioning of the different ring types ("fused" vs "perpendicular" rings) by examining sulfoxides **18a** and **19a**,

Scheme 3[a]



[a] Key: (a) $THPOCH_2CCH$, *n*-BuLi, TMEDA, THF, −78 °C; (b) CSA, MeOH, 25 °C; (c) Et_3N (3.5 equiv), CH_3SO_2Cl (2.5 equiv), ether, 0 °C; (d) NaBr, CH_3CN, 25 °C; (e) CH_3COSK, MeOH, 25 °C; (f) 3-(cyclohex-1-enyl)propargyl mesylate, KOH, THF−MeOH, 25 °C; (g) $NaIO_4$, H_2O−MeOH, 0 °C; (h) $Na_2S·9H_2O$, H_2O−MeOH, 0 °C.

Scheme 4

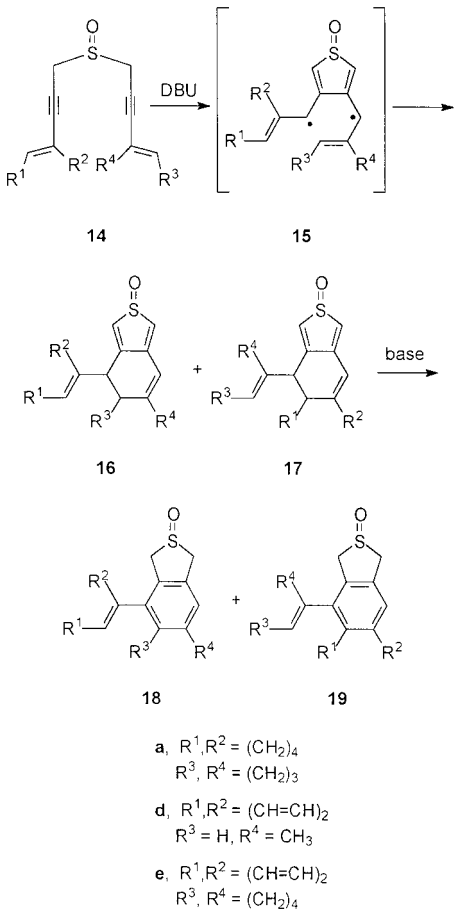


(5) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deerfield Beach, FL, 1985; Chapter 4.

(6) (a) Nasipuri, D.; Mukherjee, P. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 464. (b) Nasipuri, D.; Bhattacharya, P. K.; Furst, G. T. *J. Chem. Soc., Perkin Trans. 2* **1977**, 356. (c) Nasipuri, D.; Konar, S. K. *J. Chem. Soc., Perkin Trans. 2* **1979**, 269.

(7) (a) Anderson, J. E.; Hazlehurst, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1188. (b) Anderson, J. E.; Barkel, D. J.; Cooksey, C. J. *Tetrahedron Lett.*, **1983**, *24*, 1188.

Scheme 5



derived from the asymmetrical open-chain sulfoxide **14a**; and (c) the effect of ring shape (planar or nonplanar), as well as the effect of acyclic substituents, by investigating sulfoxides **3**, **18e**, and **19d**,**e**.

NMR Measurement of Rotational Rate Constants. As mentioned above, the main purpose of the preparation of the various cyclic sulfoxides was to compare the rotational barriers for the rotation of their "biphenyl-type" substituent. For the easier identification of these substrates in Tables 1−3, we decided on the following conventions:

The "biphenyl-type" substituent is called R and is abbreviated as 5, 6, or 7 for cyclopent-1-enyl, cyclohex-1-enyl, or cyclohept-1-enyl, respectively, or as Pr for prop-2-enyl. Ph is, of course, phenyl.

The carbocyclic ring fused to the central benzene moiety is abbreviated as 5, 6, or 7 for a five-, six-, or seven-membered ring, respectively. "Ph" indicates a fused benzene ring (i.e., the substrate is a substituted naphthalene).

As explained above, the cases in which R ≠ Ph give two sets of NMR signals at temperatures below coalescence. For several of these cyclic sulfoxides, we found that the most convenient way of measuring the rate constant for the rotation of the substituent is through the two-dimensional technique known as EXSY (exchange spectroscopy).[8] The resulting interferogram correlates via off-diagonal peaks the signals of two protons connected by an exchange process (Figures S1−S3, Supporting Information); the relative integral of these peaks is a function of an experimental parameter called "mixing time" and of the rate of interconversion. This technique was used for the olefinic proton signals of several of our diastereorotameric pairs, and the results are shown in Table 1. For other sulfoxides, namely **18a** and **19a** (see Table 2), the rotation rates were measured by a line shape analysis[9] of the coalescence of one pair of methylenes carbons α to the sulfur as a function of temperature.

The situation is different when R = Ph: in this case the rotamers are structurally identical. The pairs of ortho and meta carbons of the phenyl substituent, however, give separated signals in the low-temperature regime and their coalescence process can be followed by line shape analysis[9] (Table 2, Figure S4).

Table 1. Kinetic Results Obtained from Exchange Spectroscopy (EXSY)[a]

	R[b]	fused[b]	T (K)	t_m[c] (s)	$k_{m\rightarrow M}$[d] (s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})	K	ΔG_o (kcal mol^{-1})
19d	Pr	Ph	277.2	0.25	2.5	15.7 ± 0.1	1.29	0.12
19d	Pr	Ph	298.8	0.03	13.0	16.0 ± 0.1	1.13	0.07
19e	6	Ph	299.1	1.00	0.60	17.8 ± 0.1	1.05	0.03
5b	6	6	296.3	1.00	0.38	18.1 ± 0.1	1.18	0.10
5c	7	7	326.3	5.00	0.062	21.0 ± 0.1	1.01	0.01

[a] In $CDCl_3$. [b] See text for explanation of convention. [c] Mixing time. [d] Rate constant for the conversion from the minor to the major isomer.

Table 2. Kinetic Results Obtained from Lineshape Analysis

T (K)	$k_{m\rightarrow M}$[a] (s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})	K	ΔG_o (kcal mol^{-1})
	19a: R = 5, Fused = 6;[b,c] Signals Used: $^{13}CH_2$ α to S=O (ca. 59 ppm)			
175.4	5	9.5 ± 0.3	1.25	0.08
185.9	30	9.5 ± 0.1	1.15	0.05
196.4	90	9.6 ± 0.1		
206.9	240	9.7 ± 0.2		
217.5	600	9.8 ± 0.2		
228.0	1600	9.9 ± 0.2		
238.5	5000	9.8 ± 0.3		
	18a: R = 6, Fused = 5;[b,c] Signals Used: $^{13}CH_2$ α to S=O (ca. 59 ppm)			
206.9	15	10.9 ± 0.2	1.10	0.04
217.5	35	11.0 ± 0.1	1.20	0.08
228.0	200	10.8 ± 0.2	1.06	0.03
238.5	300	11.2 ± 0.2		
249.0	500	11.4 ± 0.2		
	18e: R = Ph, Fused = 6;[b,d] Signals Used: Ortho and Meta ^{13}CH's of Phenyl Group (ca. 128 ppm)			
327.5	4.8	18.2 ± 0.3		
339.8	9	18.5 ± 0.2		
344.3	15	18.4 ± 0.1		
349.8	27	18.3 ± 0.1		
361.0	60	18.3 ± 0.2		
	3: R = Ph, Fused = Ph;[b,d] Signals Used: Ortho and Meta ^{13}CH's of Phenyl Group (ca. 128 ppm)			
339.8	6	18.8 ± 0.3		
344.3	9	18.8 ± 0.2		
349.8	15	18.7 ± 0.1		
361.0	31	18.8 ± 0.1		
371.5	60	18.9 ± 0.2		
	20: R = 6, Fused = 6, Sulfone;[b,d] Signals Used: Benzylic CH_2 in Six-Membered Ring (ca. 2.6 ppm, AB → A_2)			
332.0	4	18.6 ± 0.2		
337.4	6	18.6 ± 0.2		
348.2	12	18.7 ± 0.1		
359.0	40	18.5 ± 0.1		
369.6	65	18.7 ± 0.1		

[a] Rate constant for the conversion from the minor to the major isomer. [b] See text for explanation of convention. [c] In CD_2Cl_2. [d] In DMSO-d_6.

(8) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935.

(9) Sutherland, I. O. In *Annual Reports in NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: London, 1971; Vol. 4, p 80.

For comparison purposes, we were interested in measuring the rotation rate for a sulfone. We chose to use **20**, the preparation of which has been reported previously.[4] For this material, the only asymmetric element is the "biphenyl-type" bond, and this implies that the protons of methylenes are diastereotopic in the low-temperature regime. Fast rotation of the cyclohexenyl substituent causes these protons to become isochronous, and this process also can be followed by line shape analysis[10] (Table 2).

An inspection of Table 2 suggests that $\Delta G^{\ddagger}$ values are, by and large, independent of the temperature, i.e., $\Delta S^{\ddagger} \approx 0$. It is thus possible to compare $\Delta G^{\ddagger}$ for different substrates, without taking into account the temperature at which the measurement was made. The barrier for sulfoxide **5a** could not be measured, as even at the lowest temperature we could reach with our instrument (170 K) only one set of unbroadened signals was observed in the NMR spectra.

Molecular Mechanics Estimates of Rotational Barriers. The free energies of activation for the rotation of the "biphenyl-like" substituent R cover a large range: from less than 7 kcal·mol^{-1} for **5a** to 21.0 kcal·mol^{-1} for **5c**. While the general trend might have been expected, we were quite surprised by the magnitude of the differences in $\Delta G^{\ddagger}$ values and decided to investigate further by estimating the rotational barriers via molecular mechanics. We used the PCModel package[11] (a MM2-based program), employing extensively its GMMX subroutine for finding global minima and therefore taking into account the various possible conformations of the nonaromatic rings. For each compound, we adopted the following procedure:

(a) After a first preliminary minimization, the program was allowed to find the low energy conformers with a cutoff of 1 kcal·mol^{-1}. Up to seven conformers were found for each of the rotamers. The energy difference between the global minima of the rotamer pair was usually smaller than 0.1 kcal·mol^{-1} (in one case up to 0.18 kcal·mol^{-1}), in line with the observation that the experimental equilibrium constants are very close to unity; see Tables 1 and 2. Such differences are within the expected error in the calculations, and indeed, no obvious correlation could be seen between experimental and calculated ΔG_o values; therefore, we do not wish to identify the structure of the major and minor rotamers.

(b) Starting from the low energy conformers for one of the rotamers, we fixed the dihedral angle defined by four sp^2-hybridized carbons forming the "biphenyl-type" bond to 0 and 180° (these are different when R ≠ Ph) and performed minimizations of the resulting structures. Preliminary calculations had shown that in the energy maxima these four carbons were within no more than a couple of degrees of planarity. We could find no regularity as to the preferred direction of rotation (0 or 180°). Often, these two angles and various conformations of the nonaromatic rings generated several maxima within a few hundred cal·mol^{-1} of the lowest energy one.

(c) The energy barrier for the rotation process was finally taken as the difference between the lowest energy transition state (found in step b) and the ground state of the minor isomer (step a).

(10) Alexander, S. J. *Chem. Phys.* **1962**, *37*, 967.
(11) PCMODEL version 7.50.00, Serena Software, Bloomington, IN.

Table 3. Comparison of Experimental and Molecular Mechanics Calculated Rotation Barriers

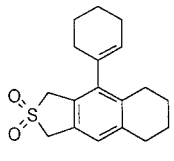
			rotational barrier, kcal mol^{-1}	
	R[a]	fused[a]	exptl	calcd
5a	5	5	<7	6.2
19a	5	6	9.7	10.1
18a	6	5	11.0	12.4
19d	Pr	Ph	15.8	13.2
19e	6	Ph	17.8	15.6
5b	6	6	18.1	17.7
18e	Ph	6	18.3	16.7
20	6[b]	6[b]	18.6	18.3
3	Ph	Ph	18.8	14.5
5c	7	7	21.0	20.4
	8	8		21.6

[a] See text for explanation of convention. [b] Sulfone.

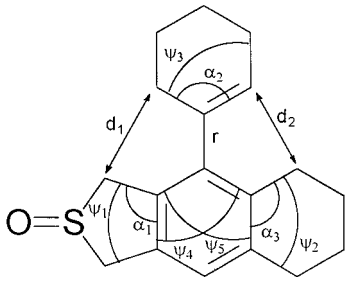
The calculated and experimental values of the barriers are compared in Table 3 and Figure 1.

Discussion

The effect of the substituents on the rotation barriers seems to be mainly steric, with relative sizes in the order 5 ≪ Pr < 6 < Ph < 7. We did not synthesize the compound with two eight-membered rings, but calculation of its barrier (Table 3) suggests that the increase is leveling off. The results also indicate that the nature of the substituent R is more important than that of the fused ring (e.g., the barriers are in the order **18a** > **19a** and **18e** > **19e**). Sulfone **20** has a barrier only slightly higher than its corresponding sulfoxide (**5b**).



20



5b

Table 3 and Figure 1 show that the molecular mechanics calculations predict successfully the barriers for all the compounds with only one aromatic ring. For compounds with a second benzene moiety (**18e**, **19d**, and **19e**), the calculated barrier is ca. 2 kcal mol^{-1} smaller than the experimental one; the position of the second ring (R or fused) is not so significant. For **3**, which has a third aromatic ring, the deviation is approximately double. The molecular mechanics parameters seem to underestimate the energetic cost involved in the loss of aromaticity introduced by deformation these rings in the transition state (see last item, below).

To obtain a better understanding of the molecular deformations involved in the rotation process, we inspected the calculated ground- and transition-state geometries of four representative cyclic sulfoxides (**3** and **5a**−**c**) comparing distances, planar angles (α_1−α_3), and dihedral angles (ψ_1−ψ_5). Our observations (more details can be found in Figure S5, Supporting Information) can be summarized as follows:

The "biphenyl-type" bond distance "*r*" (for this and the other geometric parameters, see structure **5b**, above) does not lengthen during the rotation process; in fact, there

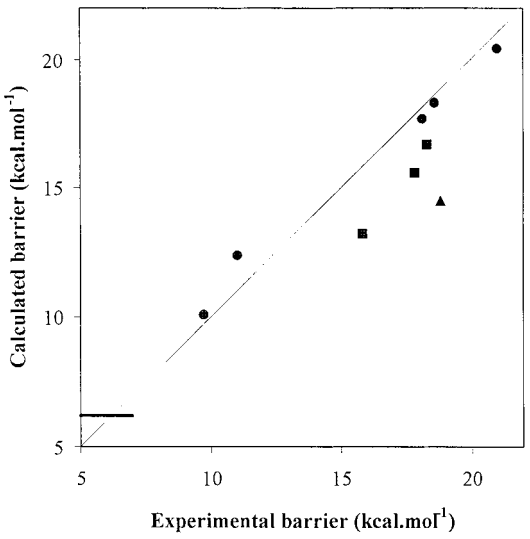


Figure 1. Experimental vs molecular-mechanics calculated rotation barriers. The squares and the triangle correspond to molecules with one and two peripheral aromatic rings, respectively, in which the calculation underestimates the barrier (see text). The bar at the bottom left of the figure refers to **5a**, for which, experimentally, only an upper limit can be ascertained.

seems to be a very slight *shortening* of this bond in the transition state (up to 0.02 Å for **5c**).

The distances d_1 and d_2 are quite invariant at 3.06 ± 0.04 and 2.94 ± 0.01 Å, respectively. These carbon−carbon distances seem quite short, and our feeling is that the molecules cannot accommodate any more crowding of the four peri carbons.

The planar angles decrease to let the rotating R group pass through. α_1 and α_3 are reduced by 2−4°, and in the six- and seven-membered rings α_2 is diminished by ca. 6°. It should be noted that, even in the ground state, these angles are much smaller in five- (111−115°) than in six- and seven-membered rings (120−123°). This explains why the barrier for **5a** is considerably lower than for the other systems examined (Table 3).

The brunt of the deformation is reflected in dihedral angles $\psi_2-\psi_5$. Typically, these are <2° in the ground state but are much larger in the transition state. For **5a**, the central aromatic ring shows distortions of up to 10°, and the deviations of planarity reach 30° for **5c**. The resulting loss of aromaticity, in addition to the close contacts of the peri carbons and their attached hydrogens, are probably responsible for the high rotation barriers in these cyclic sulfoxides.

As far as we can tell, this is the first report on the influence of ring size in the rotation around a "biphenyl-type" bond.

Experimental Section

General Methods. Tetrahydrofuran was distilled from Na and diethyl ether was dried over Na wires. Other commercially available chemicals were used without further purification.

NMR. ^{1}H and ^{13}C spectra were recorded in either $CDCl_3$ or other deuterated solvents (as indicated) and using TMS as internal standard. Chemical shifts are reported in δ and coupling constants in Hz. Sample temperatures were measured with a calibrated digital thermometer and are assumed to be correct to ±0.5 K. Rate constants were calculated from the volume integrals of the EXSY spectra with the equations of Perrin and Dwyer.[8] Line shape calculations were performed using computer programs based on the equations of Sutherland[9] (for two coalescing singlets) or of Alexander[10] (for the AB → A_2 case).

3-(Cyclopent-1-enyl)propargyl Mesylate (7a). To a stirred solution of tetrahydro-2-(2-propynyloxy)-2-*H*-pyran (2 g, 14.3 mmol) and TMEDA (1.65 g, 14.2 mmol) in dry THF (70 mL) at −78 °C was added 10.7 mL of 1.6 M BuLi. The reaction mixture was stirred for 30 min, and then a solution of cyclopentanone (1.2 g, 14.3 mmol) in dry THF (20 mL) was added. After 30 min of stirring at −78 °C, the solution was warmed to room temperature and stirred for a further 3 h. The reaction mixture was diluted with diethyl ether (300 mL) and washed with water (5 × 100 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give alcohol **6a** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.83 (t, J = 3.0 Hz, 1H), 4.33 and 4.25 (ABq, J = 15.5 Hz, each 1H), 3.88−3.80 (m, 1H), 3.58−3.51 (m, 1H), 1.96−1.54 (m, 14H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 96.7 (CH), 89.8 (C), 78.5 (C), 74.1 (C), 61.8 (CH_2), 54.2 (CH_2), 42.2 (2×CH_2), 30.1 (CH_2), 25.2 (CH_2), 23.3 (2×CH_2), 18.8 (CH_2).

With no purification, a solution of alcohol **6a** (2.5 g, 11.1 mmol) in methanol (100 mL) was treated by camphorsulfonic acid (0.51 g, 2.2 mmol) and stirred for 4 h at room temperature. The solution was neutralized by triethylamine (0.22 g, 2.2 mmol), and the solvent was removed under reduced pressure. The crude diol product (1.5 g, 10.7 mmol) and triethylamine (3.78 g, 37.5 mmol) were dissolved in dry diethyl ether (80 mL). After the mixture was cooled to 0 °C, a solution of methanesulfonyl chloride (3.1 g, 27 mmol) in dry diethyl ether (20 mL) was added, and the reaction mixture was stirred for 2 h before it was warmed to room temperature and stirred for further 3.5 h. The reaction mixture was then transferred to a separatory funnel, diluted with 100 mL of ether, and washed with water (3 × 100 mL), 3% HCl (100 mL), 3% $NaHCO_3$ (1 × 100 mL), and water (3 × 100 mL). After drying over anhydrous $MgSO_4$, filtration, and evaporation of the ether, the desired mesylate **7a** was obtained as a yellow oil (2.26 g, 78% overall yield), which was purified by column chromatography (silica gel, ethyl acetate−hexane, first 5:95 and then 20:80). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.16 (m, 1H), 5.00 (s, 2H), 3.13 (s, 3H), 2.46 (m, 4H), 1.93 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 140.7 (CH), 122.8 (C), 86.9 (C), 81.8 (C), 58.6 (CH_2), 38.9 (CH_3), 35.9 (CH_2), 33.3 (CH_2), 23.1 (CH_2). MS(EI): m/z 200 (M^+, 44.5), 137 (52.9), 123 (100). HRMS: calcd ($C_9H_{12}O_3S$) 200.0507, obsd 200.0509.

3-(Cyclohept-1-enyl)propargyl mesylate (7c) was obtained by the procedure mentioned above using **6c,** which was obtained as a viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.82 (t, J = 3.3 Hz, 1H), 4.32 and 4.26 (ABq, J = 15.5 Hz, each 1H), 3.86−3.78 (m, 1H), 3.57−3.50 (m, 1H), 2.02−1.96 (m, 2H), 1.85−1.50 (m, 16H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 96.5 (CH), 90.8 (C), 78.9 (C), 71.5 (C), 61.8 (CH_2), 54.2 (CH_2), 42.9 (2 × CH_2), 30.2 (CH_2), 28.0 (2 × CH_2), 25.3 (CH_2), 22.1 (2 × CH_2), 18.9 (CH_2).

Compound **7c** was obtained in 61% overall yield as viscous oil after separation by column chromatography (silica gel, ethyl acetate−hexane, first 5:95 and then 20:80). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.38 (t, J = 6.5 Hz, 1H), 4.97 (s, 2H), 3.12 (s, 3H), 2.34−2.30 (m, 2H), 2.22−2.20 (m, 2H), 1.76−1.72 (m, 2H), 1.58−1.51 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 142.7 (CH), 125.3 (C), 92.9 (C), 77.9 (C), 58.8 (CH_2), 38.9 (CH_3), 33.6 (CH_2), 31.8 (CH_2), 29.1 (CH_2), 26.3 (CH_2), 26.2 (CH_2). MS (CI): m/z 229 (MH^+, 9.4), 133 (100). HRMS: calcd ($C_{11}H_{17}O_3S$) 229.0898, obsd 229.0913.

3-(Cyclopent-1-enyl)propargyl Bromide (8a). A solution of sulfonate **7a** (1.9 g, 9.5 mmol) in acetonitrile (10 mL) was slowly added to a magneticaly stirred suspension of NaBr in acetonitrile (60 mL) at room temperature. After 48 h, the reaction mixture was diluted with diethyl ether and the organic layer was washed with water (3 × 100 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent gave 1.43 g of **8a** as a yellowish oil (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.11 (m, 1H), 4.09 (s, 2H), 2.43 (m, 4H), 1.91 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 139.9 (CH), 123.8 (C), 85.4 (C), 84.4 (C),

36.2 (CH_2), 33.4 (CH_2), 23.3 (CH_2), 15.8 (CH_2). MS(EI): *m/z* 184 (M^+, 18), 105 (100). HRMS: calcd (C_8H_9Br) 183.9887, obsd 183.9897.

3-(Cyclohept-1-enyl)propargyl bromide (8c) was obtained by the reaction of sulfonate **7b** with NaBr according to the above procedure, purified by column chromatography (silica gel ethyl acetate−hexane 5:95) as a colorless oil in 27% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.33 (t, J = 6.9 Hz, 1H), 4.08 (s, 2H), 2.33−2.29 (m, 2H), 2.21−2.17 (m, 2H), 1.74−1.71 (m, 2H), 1.59−1.49 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 141.9 (CH), 126.1 (C), 90.5 (C), 81.6 (C), 33.9 (CH_2), 32.1 (CH_2), 29.3 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 16.2 (CH_2). MS(EI): *m/z* 212 (M^+, 17.9), 133 (100). HRMS: calcd ($C_{10}H_{13}Br$) 212.0200, obsd 212.0194.

3-(Cyclopent-1-enyl)propargyl Thioacetate (10a). To a vigorously stirred solution of mesylate **7a** (1.5 g, 7.47 mmol) in methanol (50 mL) was added potassium thioacetate (1.7 g, 14.5 mmol) at room temperature. The reaction mixture was stirred for 30 min, diluted with diethyl ether, and washed with water (3 × 100 mL). After drying over anhydrous $MgSO_4$, filtration, and evaporation of the ether, the desired thioacetate **10a** was obtained as a yellow oil (1.3 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.02 (m, 1H), 3.81 (s, 2H), 2.43−2.36 (m, 4H), 2.35 (s, 3H), 1.90−1.85 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 194.0 (C), 138.2 (CH), 123.9 (C), 84.8 (C), 80.1 (C), 36.1 (CH_2), 33.1 (CH_2), 30.1 (CH_3), 23.1 (CH_2), 18.6 (CH_2). MS(EI): *m/z* 181 (MH^+, 100), 147 (48.3), 105 (51.9). HRMS: calcd ($C_{10}H_{13}OS$) 181.0687, obsd 181.0682.

Bis[3-(cyclopent-1-enyl)propargyl] Sulfide (9a). A solution of $Na_2S{\cdot}9H_2O$ (0.57 g, 2.37 mmol) in water (20 mL) was slowly added to a magnetically stirred solution of **8a** (0.59 g, 3.19 mmol) in methanol (30 mL) at 0 °C. After 2 h, the solution was warmed to room temperature and stirred for a further 2 h before ether was added. The organic layer was separated, washed with water (3 × 100 mL), and dried over $MgSO_4$. The solvent was evaporated to give 0.24 g of pure yellow oil (62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03 (m, 2H), 3.57 (s, 4H), 2.42 (m, 8H), 1.90 (dq, J = 7.5, 0.5 Hz, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 137.9 (CH), 124.1 (C), 85.6 (C), 80.6 (C), 36.3 (CH_2), 33.1 (CH_2), 23.2 (CH_2), 20.2 (CH_2). IR (neat): 2221, 1435 cm^{-1}. MS (CI): *m/z* 243 (MH^+, 35.9), 209 (45), 137 (41.4), 105 (100). HRMS: calcd ($C_{16}H_{19}S$) 243.1207, obsd 243.1200.

Bis[3-(cyclohept-1-enyl)propargyl] sulfide (9c) was prepared according to the above procedure as a yellow oil (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.26 (t, J = 6.9 Hz, 2H), 3.53 (s, 4H), 2.33−2.29 (m, 4H), 2.20−2.14 (m, 4H), 1.75−1.70 (m, 4H), 1.58−1.50 (m, 8H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 140.0 (CH), 126.6 (C), 86.8 (C), 81.8 (C), 34.3 (CH_2), 32.2 (CH_2), 29.2 (CH_2), 26.58 (CH_2), 26.57 (CH_2), 20.3 (CH_2). MS (CI): *m/z* 299 (MH^+, 62.3), 265 (22), 165(29.4), 133 (100). HRMS: calcd ($C_{20}H_{27}S$) 299.1833, obsd 299.1800.

3-(Cyclopent-1-enyl)-3′-(cyclohex-1-enyl) Dipropargyl Sulfide (11a). A solution of KOH (0.52 g, 9.3 mmol) in methanol (10 mL) was slowly added to a magnetically stirred solution of tihioacetate **10a** (0.84 g, 4.6 mmol) and 3-(cyclohexen-1-enyl)propargyl mesylate (1 g, 4.6 mmol) in tetrahydrofuran (30 mL) at room temperature. After 40 min, the reaction mixture was diluted with diethyl ether (100 mL) and washed with water (3 × 100 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give **16c** as a yellowish oil (1.02 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01 (quintet, J = 2.1 Hz, 1H), 5.95 (m, 1H), 3.49 (s, 2H), 3.47 (s, 2H), 2.38−2.34 (m, 4H), 2.04−2.02 (m, 4H), 1.82 (quintet, J = 7.5 Hz, 2H), 1.54−1.51 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 137.7 (CH), 134.8 (CH), 124.1 (C), 120.2 (C), 85.6 (C), 85.0 (C), 81.6 (C), 80.4 (C), 36.3 (CH_2), 33.0 (CH_2), 29.1 (CH_2), 25.4 (CH_2), 23.1 (CH_2), 22.1 (CH_2), 21.3 (CH_2), 20.0 (2 × CH_2). IR (neat): 2212, 1628, 1435 cm^{-1}. MS (CI): *m/z* 257 (MH^+, 100), 223 (80.6), 119 (96.7), 105 (79.6). HRMS: calcd ($C_{17}H_{21}S$) 257.1363, obsd 257.1352.

3-(Prop-2-enyl)-3′-phenyl dipropargyl sulfide (13d) was prepared according to the above procedure in 82% yield as a viscous yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45−7.41 (m, 2H), 7.30−7.28 (m, 3H), 5.29 (m, 1H), 5.22 (quintet, J = 1.5 Hz, 1H), 3.65 (s, 2H), 3.60 (s, 2H), 1.89 (dd, J = 1.5, 1.0 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 131.7 (2 × CH), 128.2 (3 × CH), 126.4 (C), 122.8 (C), 122.0 (CH_2), 84.6 (C), 83.5 (C), 83.2 (C), 70.1 (C), 23.4 (CH_3), 20.0 (CH_2), 19.9 (CH_2). IR (neat): 1611, 1490, 1355 cm^{-1}. MS (CI): *m/z* 227 (MH^+, 47.1), 193 (41.2), 115 (100). HRMS: calcd ($C_{15}H_{15}S$) 227.0894, obsd 227.0880.

3-(Cyclohex-1-enyl)-3′-phenyl dipropargyl sulfide (13e) was prepared according to the above procedure in 62% yield as viscous yellow oil, after separation by column chromatography (silica gel, ethyl acetate−hexane 2:8). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−7.44 (m, 2H), 7.33−7.30 (m, 3H), 6.13 (quintet, J = 1.8 Hz, 1H), 3.68 (s, 2H), 3.63 (s, 2H), 2.15−2.09 (m, 4H), 1.65−1.60 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 134.9 (CH), 131.7 (CH), 131.6 (CH), 128.1 (2×CH), 128.07 (CH), 122.9 (C), 120.3 (C), 85.2 (C), 84.7 (C), 83.1 (C), 81.6 (C), 29.2 (CH_2), 25.5 (CH_2), 22.2 (CH_2), 21.4 (CH_2), 20.2 (CH_2), 20.0 (CH_2). IR (neat): 2212, 1435, 1348, 1066 cm^{-1}. MS (CI): *m/z* 267 (MH^+, 88.4), 233 (41.5), 119 (80.2), 115 (100). HRMS: calcd ($C_{18}H_{19}S$) 267.1207, obsd 267.1183.

Bis[3-(cyclopent-1-enyl)propargyl] Sulfoxide (4a). To a magnetically stirred solution of $NaIO_4$ (0.176 g, 0.82 mmol) in 20 mL of water was added a solution of **9a** (0.2 g, 0.82 mmol) at 0 °C for 2 h. The mixture was warmed to room temperature and allowed to stir for 1 week. The solution was diluted with chloroform, washed with water (3 × 50 mL) and saturated NaCl, and then dried over $MgSO_4$. Evaporation of the solvent gave a mixture of products that was separated by column chromatography (silica gel, ethyl acetate−hexane 1:1) to give 85 mg of yellowish oil (42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.12 (quintet, J = 2.1 Hz, 2H), 3.98 and 3.81 (ABq, J = 16.0 Hz, each 2H), 2.47−2.42 (m, 8H), 1.90 (dquintet, J = 7.5, 0.5 Hz, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 139.6 (CH), 123.3 (C), 85.4 (C), 77.9 (C), 42.0 (CH_2), 36.0 (CH_2), 33.1 (CH_2), 23.0 (CH_2). IR (neat): 1448, 1345, 1061 cm^{-1}. MS (CI): *m/z* 259 (MH^+, 20.1), 209 (15.8), 153 (8), 137 (36.8), 105 (100). HRMS: calcd ($C_{16}H_{19}OS$) 259.1157, obsd 259.1162.

Bis[3-(cyclohept-1-enyl)propargyl] sulfoxide (4c) was prepared from **9c** by the procedure mentioned above and obtained in 42% yield as a yellowish viscous oil, after separation by column chromatography (silica gel, ethyl acetate−hexane 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.35 (t, J = 6.6 Hz, 2H), 3.93 and 3.76 (ABq, J = 16.0 Hz, each 2H), 2.34−2.30 (m, 4H), 2.21−2.16 (m, 4H), 1.75−1.72 (m, 4H), 1.57−1.49 (m, 8H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 141.6 (CH), 125.8 (C), 91.6 (C), 74.0 (C), 42.1 (CH_2), 33.9 (CH_2), 31.9 (CH_2), 29.1 (CH_2), 26.4 (CH_2), 26.3 (CH_2). IR (neat): 1446, 1067 cm^{-1}. MS (CI): *m/z* 315 (MH^+, 92.4), 299 (100), 265 (60.8), 133 (91.2). HRMS: calcd ($C_{20}H_{27}OS$) 315.1782, obsd 315.1760.

3-(Prop-2-enyl)-3′-phenyl dipropargyl sulfoxide (14d) was prepared from **13d** by the procedure mentioned above and obtained in 29% yield as a yellowish viscous oil, after separation by column chromatography (silica gel, ethyl acetate−hexane 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.44 (m, 2H), 7.33−7.30 (m, 3H), 5.38 (m, 1H), 5.30 (quintet, J = 2.1 Hz, 1H), 4.06 and 3.89 (ABq, J = 16.0 Hz, each 1H), 4.01 and 3.84 (ABq, J = 16.0 Hz, each 1H), 1.90 (dd, J = 1.5, 1.0 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 131.8 (2 × CH), 128.8 (CH), 128.2 (3 × CH), 125.6 (C), 123.4 (CH_2), 121.7 (C), 89.3 (C), 88.1 (C), 77.0 (C), 75.9 (C), 42.0 (CH_2), 41.9 (CH_2), 23.1 (CH_3). IR (neat): 1602, 1490, 1442, 1063 cm^{-1}. MS (CI): *m/z* 243 (MH^+, 21.6), 115 (100). HRMS: calcd ($C_{15}H_{15}OS$) 243.0843, obsd 243.0856.

3-(Cyclohex-1-enyl)-3′-phenyl dipropargyl sulfoxide (14e) was prepared from **13e** by the procedure mentioned above and obtained in 39% yield as a yellowish viscous oil, after separation by column chromatography (silica gel, ethyl acetate−hexane 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.45 (m, 2H), 7.34−7.31 (m, 3H), 6.18 (quintet, J = 1.8 Hz, 1H), 4.06 and 3.89 (ABq, J = 16.0 Hz, each 1H), 4.00 and 3.83 (ABq, J = 16 Hz, each 1H), 2.12−2.04 (m, 4H), 1.65−1.57 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 136.7 (CH), 131.9 (2 × CH), 128.8 (CH), 128.3 (2 × CH), 121.9 (C), 119.7 (C), 90.2 (C), 88.1 (C), 77.2 (C), 74.0 (C), 42.3 (CH_2), 42.0 (CH_2), 28.9 (CH_2), 25.6 (CH_2), 22.1 (CH_2), 21.3 (CH_2). IR (neat): 1489, 1442, 1066 cm^{-1}.

MS (CI): *m*/*z* 283 (MH^+, 21), 234 (35.6), 119 (100), 115 (87.8). HRMS: calcd ($C_{18}H_{19}OS$) 283.1157, obsd 283.1166.

3-(Cyclopent-1-enyl)-3′-(cyclohex-1-enyl) dipropargyl sulfoxide (14a) was prepared from **11a** by the procedure mentioned above and obtained in 50% yield as a yellowish viscous oil, after separation by column chromatography (silica gel, ethyl acetate−hexane 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.17 (m, 1H), 6.12 (m, 1H), 3.98 and 3.80 (ABq, J = 16 Hz, each 1H), 3.95 and 3.78 (ABq, J = 16 Hz, each 1H), 2.46−2.43 (m, 4H), 2.13−2.09 (m, 4H), 1.90 (quintet, J = 7.5 Hz, 2H), 1.64−1.60 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 139.6 (CH), 136.5 (CH), 123.4 (C), 119.6 (C), 90.0 (C), 85.4 (C), 78.0 (C), 74.0 (C), 42.0 (2 × CH_2), 36.1 (CH_2), 33.1 (CH_2), 28.8 (CH_2), 25.5 (CH_2), 23.1 (CH_2), 22.0 (CH_2), 21.2 (CH_2). IR (neat): 1431, 1060 cm^{-1}. MS (CI): *m*/*z* 273 (MH^+, 12.9), 255 (18.3), 223 (25.5), 119 (100), 105 (52). HRMS: calcd ($C_{17}H_{21}OS$) 273.1313, obsd 273.1303.

General Procedure for the Reaction of Sulfur-Bridged Propargylic Systems with DBU. To a solution of the desired sulfur-bridged propargylic system (1 mmol) in 10 mL of acetonitrile were added 1.5 equiv of DBU. After the mixture was stirred at room temperature for the appropriate time, chloroform was added, and the solution was washed with water (3 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The data for all cyclization products are listed below.

4-(Cyclopent-1-enyl)-3,5,6,7-tetrahydro-1*H*-2-thia-*s*-indacene 2-oxide (5a) was obtained from **4a** by the general procedure in 64% yield as a yellowish viscous oil, after separation by column chromatography (silica gel, ethyl acetate−methanol 12:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (s, 1H), 5.68 (quintet, J = 1.5 Hz, 1H), 4.26 and 4.10 (ABq, J = 15.0 Hz, each 1H), 4.22 and 4.06 (ABq, J = 15.0 Hz, each 1H), 2.89 (t, J = 9.0 Hz, 2H), 2.82 (t, J = 9.0 Hz, 2H), 2.54−2.48 (m, 4H), 2.08−2.01 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 145.2 (C), 142.8 (C), 141.3 (C), 134.1 (C), 132.9 (C), 130.6 (CH), 130.5 (C), 120.6 (CH), 58.8 (CH_2), 58.2 (CH_2), 35.9 (CH_2), 33.0 (CH_2), 32.8 (CH_2), 32.2 (CH_2), 25.6 (CH_2), 24.0 (CH_2). IR (neat): 1637, 1448, 1038 cm^{-1}. MS (CI): *m*/*z* 259 (MH^+, 59.5), 209 (100). HRMS: calcd ($C_{16}H_{19}OS$) 259.1157, obsd 259.1169.

4-(Cyclohept-1-enyl)-3,5,6,7,8,9-hexahydro-1*H*-2-thiacyclohepta[*f*]indene-2 oxide (5c) was obtained from **4c** by the general procedure in 33% yield as a yellowish viscous oil, after separation by column chromatography (silica gel, ethyl acetate 100%). These data refer to a mixture of two stable diastereorotamers which are easily distinguishable by the appearance of two aromatic singlets and two olefinic triplets, resulting from the orientation of the cycloheptenyl double bond with respect to the sulfinyl oxygen (see text). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 and 6.97 (2 × s, each 0.5H), 5.72 and 5.61 (2 × t, J = 6.3 Hz, each 0.5H), 4.29, 4.28, 4.15, 4.11, 4.10 and 3.99 (3 × ABq, J = 16.0 Hz, each 0.5H), 4.18 (s, 1H), 2.81−2.77 (m, 4H), 2.30−2.26 (m, 4H), 1.85−1.57 (m, 12H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.6 (C), 143.1 (C), 142.4 (C), 140.6 (C), 132.1 (CH), 131.7 (CH), 131.5 (C), 131.3 (C), 124.9 (CH), 124.8 (CH), 59.6 (CH_2), 59.5 (CH_2), 59.1 (CH_2), 36.6 (CH_2), 35.2 (CH_2), 35.1 (CH_2), 32.4 (CH_2), 32.1 (CH_2), 31.9 (CH_2), 31.4 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 28.1 (CH_2), 27.8 (CH_2), 27.2 (CH_2), 27.1 (CH_2), 26.8 (CH_2), 26.7 (CH_2). IR (neat): 1445, 1041 cm^{-1}. MS (CI): *m*/*z* 315 (MH^+, 88), 299 (100), 265 (97.5). HRMS: calcd ($C_{20}H_{27}OS$) 315.1782, obsd 315.1761.

6-Methyl-4-phenyl-1,3-dihydrobenzo[*c*]thiophene 2-oxide (18d) was obtained from **14d** by the general procedure in 74% yield as an orange viscous oil, after separation by column chromatography (silica gel, ethyl acetate−hexane 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44−7.33 (m, 5H), 7.17 (s, 1H), 7.15 (s, 1H), 4.32 and 4.17 (ABq, J = 16.0 Hz, each 1H), 4.27 and 4.11 (ABq, J = 16.0 Hz, each 1H), 2.40 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 140.6 (C), 140.0 (C), 138.8 (C), 135.8 (C), 130.0 (CH), 129.9 (C), 128.5 (2 × CH), 128.48 (2 × CH), 127.6 (CH), 126.1 (CH), 59.1 (CH_2), 58.4 (CH_2), 21.2 (CH_3). IR (neat): 1448, 1036 cm^{-1}. MS (CI): *m*/*z* 243 (MH^+, 32), 193 (100). HRMS: calcd ($C_{15}H_{15}OS$), 243.0844, obsd 243.0855.

Compound **19d** was prepared by the procedure mentioned above using chloroform as solvent and obtained in 8% yield together with **18d** (48%) as an inseparable mixture that was purified by column chromatography (silica gel, ethyl acetate−hexane 1:1, then ethyl acetate 100%). Due to the small amount of this product in the mixture, only partial NMR data are presented; the olefinic signals were well separated enough for a successful EXSY experiment (see text). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (m, 1H), 7.82−7.80 (m, 1H), 7.76 (br s, 1H), 7.49−7.48 (m, 2H), 5.55, 5.09 and 5.53, 4.99 (4 × s, each 0.5H), 4.46, 4.43, 4.41, 4.37, 4.35, 4.28, 4.18 and 4.05 (4 × ABq, J = 16.0 Hz, each 0.5H), 2.17 and 2.11 (2 × s, each 1.5H).

4-Phenyl-1,3,5,6,7,8-hexahydronaphtho[2,3-*c*]thiophene 2-oxide (18e) was obtained from **14e** by the general procedure in 89% yield as an orange viscous oil, after separation by column chromatography (silica gel, ethyl acetate−hexane 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45−7.32 (m, 3H), 7.23−7.20 (m, 1H), 7.12−7.08 (m, 2H), 4.29 and 4.13 (ABq, J = 16.0 Hz, each 1H) 3.95 and 3.75 (ABq, J = 16.0 Hz, each 1H), 2.83 (t, J = 6.3 Hz, 2H), 2.41 (t, J = 6.3 Hz, 2H), 1.79−1.63 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 140.3 (C), 139.2 (C), 138.0 (C), 135.3 (C), 131.7 (C), 131.2 (C), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 127.3 (CH), 126.1 (CH), 59.2 (CH_2), 58.7 (CH_2), 30.0 (CH_2), 27.9 (CH_2), 23.1 (CH_2), 22.6 (CH_2). IR (neat): 1448, 1036 cm^{-1}. MS (CI): *m*/*z* 283 (MH^+, 100), 233 (68.6). HRMS: calcd ($C_{18}H_{19}OS$) 283.1156, obsd 283.1166.

Compound **19e** was prepared by the procedure mentioned above using chloroform as solvent and obtained in 14% yield together with **18e** (30%) as an inseparable mixture that was purified by column chromatography (silica gel, ethyl acetate−hexane 1:1, then ethyl acetate 100%). Due to the small amount of this product in the mixture, only partial NMR data are presented; the olefinic signals were well separated enough for a successful EXSY experiment (see text). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93−7.89 (m, 1H), 7.83−7.80 (m, 1H), 7.76 (br s, 1H), 7.48−7.46 (m, 2H), 5.79 and 5.70 (2 × m, each 0.5H), 4.42, 4.41, 4.34, 4.33, 4.32, 4.31, 4.26 and 4.15 (4 × ABq, J = 16.0 Hz, each 0.5H), 2.31−2.25 (m, 2H), 1.75−1.68 (m, 4H). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 59.3, 59.2, 58.3, 57.9, 30.9, 29.9, 25.5, 25.4, 23.0, 22.2 (all CH_2 of two diastereorotamers).

4-(Cyclopent-1-enyl)-1,3,5,6,7,8-hexahydronaphtho[2,3-*c*]thiophene 2-oxide (19a) was obtained from **14a** by the general procedure as a mixture with **18a** in 30% yield as an orange viscous oil, after purification by column chromatography (silica gel, ethyl acetate−methanol 12:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.98 (s, 1H), 5.57 (m, 1H), 4.21, 4.10, 4.00 and 3.89 (2 × ABq, J = 16.0 Hz, each 1H), 2.78 (m, 2H), 2.63 (m, 2H), 2.53−2.48 (m, 4H), 2.03 (m, 2H), 1.76−1.70 (m, 4H). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 142.8 (C), 138.1 (C), 138.0 (C), 135.6 (C), 132.4 (C), 131.4 (C), 130.2 (CH), 125.8 (CH), 59.8 (CH_2), 59.0 (CH_2), 36.6 (CH_2), 33.5 (CH_2), 30.4 (CH_2), 27.5 (CH_2), 24.4 (CH_2), 23.7 (CH_2), 23.2 (CH_2). IR (neat): 1645, 1447, 1039 cm^{-1}. MS (CI): *m*/*z* 273 (MH^+, 68), 257 (14), 223 (100). HRMS: calcd ($C_{17}H_{21}OS$) 273.1313, obsd 273.1296.

4-(Cyclohex-1-enyl)-3,5,6,7-tetrahydro-1*H*-2-thia-*s*-indacene 2-oxide (18a). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (s, 1H), 5.57 (m, 1H), 4.22, 4.14, 4.00 and 3.95 (2 × ABq, J = 16.0 Hz, each 1H), 2.89 (t, J = 7.0 Hz, 2H), 2.80 (t, J = 7.0 Hz, 2H), 2.17−2.11 (m, 4H), 2.05 (m, 2H), 1.76−1.70 (m, 4H). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 145.5 (C), 142.8 (C), 139.7 (C), 136.7 (C), 133.7 (C), 131.3 (C), 127.0 (CH), 120.7 (CH), 59.6 (CH_2), 58.3 (CH_2), 33.3 (CH_2), 31.8 (CH_2), 29.1 (CH_2), 26.1 (CH_2), 25.6 (CH_2), 23.3 (CH_2), 22.6 (CH_2).

Acknowledgment. The financial support of this study by the Israel Science Foundation is gratefully acknowledged.

Supporting Information Available: ^{1}H (**5b**,**c** and **20**) and ^{13}C 1D-NMR spectra; EXSY spectra (**5b**,**c** and **19d**,**e**); ^{13}C line shape analysis for **18e**; full ^{1}H and ^{13}C assignment for **18a** and **19a**; geometrical parameters from molecular mechanics calculations (**3**, **5a**−**c**). This material is available free of charge via the Internet at http://pubs.acs.org.

JO010947Z