constant the ligand concentration. In all cases [Cu(II)] was ≳ 8[ligand]. In methanol solution where the extintion coefficient of the complex could be directly determined, binding constants were obtained without interpolation of the data. Under these conditions, the stoichiometry for all complexes was assumed to be 1:1 as confirmed by the spectroscopic (UV–vis) behavior either in water solution or in methanol. Only when the [Cu(II)]/[ligand] ratio is lower than unity are different stoichiometries apparent from the UV–vis analysis.

Fluorescence Quenching Experiments. Solutions of micellar or vesicular aggregates (2.5×10^{-4} M) were prepared in the presence of 1,8-anilinonaphthalenesulfonic acid (4.8×10^{-7} M); their fluorescence emission was determined at 500 nm (excitation wavelength 375 nm) on a Perkin Elmer MPF-66 instrument upon addition of different amounts of $Cu(NO_3)_2$.

Acknowledgment. Skillful technical assistance by E. Castiglione is gratefully acknowledged. P.S. thanks NATO for financial support (Grant for International Collaboration 0315/87).

Registry No. 1, 122899-66-5; 3, 122899-68-7; 4, 122924-10-1; 5, 122899-69-8; 6, 122899-70-1; Cu, 7440-50-8; $Br(CH_2)_2Br$, 106-93-4; $N(CH_3)_3$, 75-50-3; 4-hydroxy-2,6-bis(chloromethyl)pyridine, 122899-73-4; diethyl 4-((tetrahydro-2-pyranyl)oxy)-2,6-pyridinedicarboxylate, 122899-71-2; 4-hydroxy-2,6-bis(hydroxymethyl)pyridine, 122899-72-3; diethyl 4-((tetrahydro-2-pyranyl)oxy)-2,6-bis(hydroxymethyl)pyridine, 98828-63-8; 2,6-bis[(*n*-octylthio)methyl]-4-hydroxypyridine, 122899-74-5; 2,6-bis[(*n*-dodecylthio)methyl]-4-hydroxypyridine, 122899-75-6; 2,6-bis[(*n*-hexadecylthio)methyl]-4-hydroxypyridine, 122899-76-7; 2,6-bis[(methylthio)methyl]-4-hydroxypyridine, 122899-77-8; sodium thiomethoxide, 5188-07-8.

Supplementary Material Available: Figure S1 reporting the ANS fluorescence vs Cu(II) concentration for the different aggregates (1 page). Ordering information is given on any current masthead page.

Change in Conformational Preference between Dithia[3.3](1,4)naphthalenometacyclophanes and the Corresponding [2.2](1,4)Naphthalenometacyclophanes

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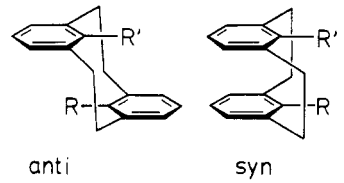
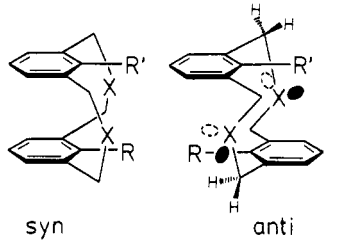
One of the unique properties of [2.2]metacyclophane is its preference for the stepped, anti conformation,[1] *anti*-**1**. Its isomer *syn*-**1** was recently prepared[2] by Mitchell et al. but found to isomerize readily to *anti*-**1** above 0 °C. The lower stability of *syn*-**1** is attributed to the unfavorable π–π interaction between the parallel benzene rings, although another mode of nonbonded interaction involving the intrusion of the H_i protons into the respective π-clouds of the opposite benzene rings is experienced in *anti*-**1**. The corresponding dithia- and diselena[3.3]metacyclophanes, however, were found to adopt preferentially the syn conformation, namely, *syn*-**4**[3] and *syn*-**7**,[4] respectively. The change in preference to the syn conformation is believed to be due to unfavorable torsional strain in the bridges in *anti*-**4** and *anti*-**7** with two bonds and two lone pairs always nearly eclipsed.[5] An interesting observation was that

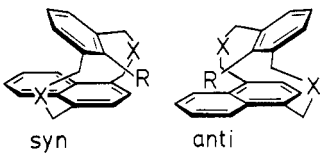


	R	R'
1	H_i	H_i
2	H_i	CH_3
3	CH_3	CH_3

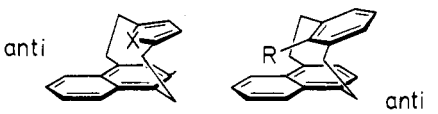


	X	R	R
4	S	H_i	H_i
5	S	H_i	CH_3
6	S	CH_3	CH_3
7	Se	H_i	H_i
8	Se	CH_3	CH_3

either ring contraction[6] or direct desulfurization[7] of *syn*-**4** and its derivatives afforded mainly *anti*-**1** and its corresponding derivatives. Photochemical deselenation[8] of *syn*-**7** also led to the isolation of only *anti*-**1**. The naphthalenometacyclophane **13** could, like **1**, exist in both syn and anti conformers experiencing similarly the respective nonbonded interactions. The related heterophanes **12** apparently adopt mainly the anti conformation;[9] only a very low yield of the syn conformer of **12** (X = S)[9b] was isolated. The dithiacyclophane **9**[10] has, however, been shown to exist, like **4**, in the syn conformation. Photodeselenation of the corresponding diselenacyclophane **10** was recently reported[8] to yield **13**, although there was no mention of the stereochemistry of either **10** or **13**. The above observation prompted us to investigate the photodesulfurization of *syn*-**9**. It would be interesting to determine whether an abrupt change in conformational preference similar to *syn*-**4** → *anti*-**1** is observed going from **9** to **13**.



	X	R
9	S	H_i
10	Se	H_i
11	S	CH_3



12 X = O, S, NH

13 R = H_i

14 R = CH_3

Irradiation[7a] of a solution of *syn*-**9**[10] in trimethyl phosphite with light at 254 nm gave, from TLC studies, only one isomer of **13** (mp 155–156 °C; identical with that reported[8]). Both cyclophanes **15**[11] and **17**[12] are known to be

(1) (a) Wilson, D. J.; Boekelheide, V.; Griffin, R. W. *J. Am. Chem. Soc.* **1960**, *62*, 6302. (b) Vögtle, F.; Neumann, M. v. P. *Angew. Chem., Int. Ed. Engl.* **1973**, *11*, 73. (c) Brown, C. J. *J. Chem. Soc.* **1953**, 3278.

(2) Mitchell, R. H.; Vinod, T. K.; Bushnell, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 3340.

(3) Anker, W.; Bushnell, G. W.; Mitchell, R. H. *Can. J. Chem.* **1979**, *57*, 3080.

(4) (a) Mitchell, R. H. *Can. J. Chem.* **1980**, *58*, 1398. (b) Bushnell, G. W.; Mitchell, R. H. *Can. J. Chem.* **1982**, *60*, 362.

(5) See, for example: Fukazawa, Y.; Aoyagi, M.; Itô, S. *Tetrahedron Lett.* **1979**, 1055.

(6) (a) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547. (b) Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 3881.

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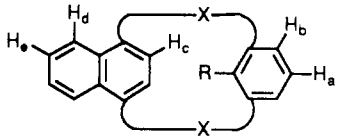
(8) Higuchi, H.; Tani, K.; Otsubo, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4027.

(9) (a) Wasserman, H. H.; Keehn, P. M. *Tetrahedron Lett.* **1969**, 3227. (b) Mizogami, S.; Osaka, M.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1974**, 799. (c) Rosenfled, S.; Keehn, P. M. *Tetrahedron Lett.* **1973**, 4921. (d) Corson, M.; Foxman, B. M.; Keehn, P. M. *Tetrahedron* **1978**, *34*, 1641.

(10) Lai, Y.-H. *J. Chem. Soc. Perkin Trans 2* **1989**, 643.

0022-3263/89/1954-5991$01.50/0

Table I. ^{1}H NMR Chemical Shifts for Naphthalenometacyclophanes with the Following General Formula

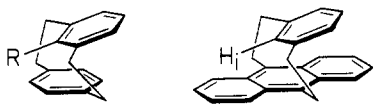


R = H_i, CH_3
X = CH_2SCH_2, CH_2CH_2

	cyclophane				
proton	*syn*-9[10]	*syn*-11	*anti*-11	*anti*-13	*anti*-14
H_i	5.51			3.95	
CH_3		1.90	0.86		0.30
H_a	6.3–6.6[a]	5.94[b]	6.98[c]	7.03[c]	6.90[c]
H_b		6.62[d]	7.21[e]	6.74[e]	6.68[e]
H_c	7.19	7.20	6.31	6.05	6.04
H_d[f]	7.92	7.86	8.11	8.09	8.07
H_e[f]	7.32	7.33	7.52	7.55	7.48
CH_2[g]	4.19[i]	4.05[i]	3.88[i]		
	4.33[j]	4.23[j]	4.53[j]	3.7–4.0 (2 H)[a]	3.7–3.9 (2 H)[a]
				2.0–2.8 (6 H)[a]	2.5–2.8 (6 H)[a]
CH_2[h]	3.32[i]	3.48[i]	3.40[i]		
	3.62[j]	3.62[j]	3.66[j]		

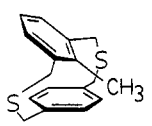
[a] A multiplet. [b] A triplet; δ_A of an AB_2 system. [c] A quartet; δ_A of an AB_2 system. [d] A doublet; δ_B of an AB_2 system. [e] An incompletely resolved doublet of doublets; δ_B of an AB_2 system. [f] An AA'BB' system. [g] Methylene protons adjacent to the (1,4)-bridged ring. [h] Methylene protons adjacent to the (1,3)-bridged ring. [i] δ_A of an AB quartet. [j] δ_B of an AB quartet.

conformationally rigid at room temperature. Located directly over the nonbridged rings, the H_i protons in *anti*-13 and 17 are expected to experience a much stronger shielding effect than that in 15. Thus a comparison of the chemical shifts of H_i protons in 13 (δ 3.95), 15 (δ 5.24) and 17 (δ 4.00) clearly confirms that the isolated isomer is indeed *anti*-13. Replacement of the H_i proton with a substituent in some metacyclophane derivatives is known to lead to variability in conformational preference.[13] A cyclization reaction between 1,4-bis(bromomethyl)-naphthalene[14] and 2,6-bis(mercaptomethyl)toluene[6a] in fact yielded a mixture of *anti*-11 and *syn*-11 similar to reported mixtures of anti and syn isomers obtained for 6[6a] and 8.[15] The methyl signal of *syn*-11 appeared at δ 1.90, identical with that reported for 18,[16] with that of *anti*-11 further

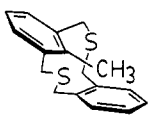


15 R = H_i
16 R = CH_3

17



18



19

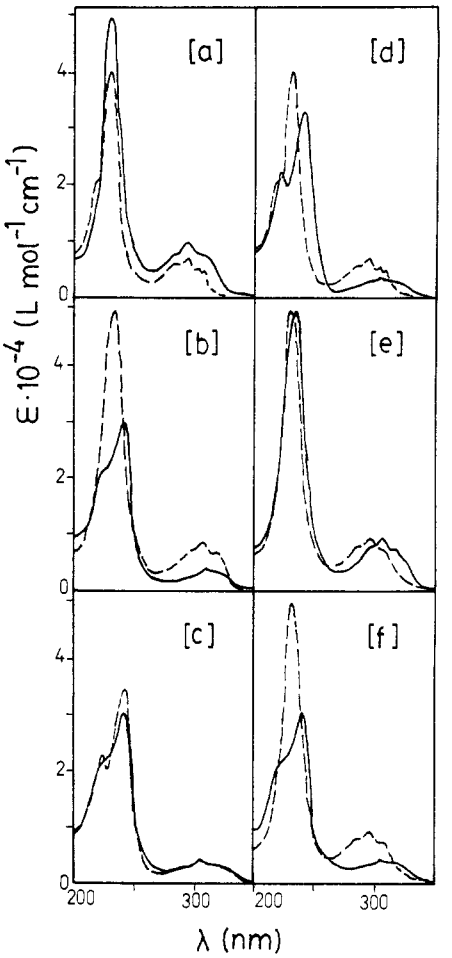


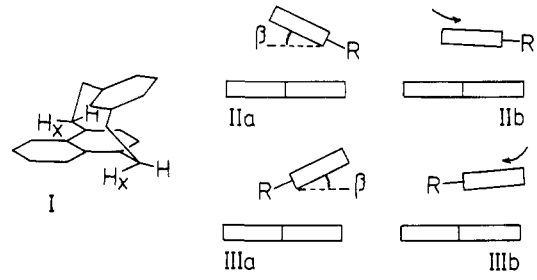
Figure 1. UV absorption spectra of cyclophanes 9, 11, 13, and 14: a, *syn*-9 (- - -), *syn*-11 (—); b, *anti*-11 (- - -), *anti*-14 (—); c, *anti*-13 (- - -), *anti*-14 (—); d, *syn*-9 (- - -), *anti*-13 (—); e, *syn*-11 (- - -), *anti*-11 (—); f, *syn*-11 (- - -), *anti*-14 (—).

shielded to δ 0.86 by the nonbridged ring. Photodesulfurization of *anti*-11 gave the parent *anti*-14 as expected; irradiation of a solution of *syn*-11 in trimethyl phosphite also led to the isolation of only *anti*-14, again indicating the abrupt change in conformational preference going from the [3.3]dithiacyclophane to the parent [2.2]-cyclophane system. Although the chemical shift of the "internal" substitutent (H_i, CH_3) in the meta-bridged ring could be readily used to assign the anti or syn stereochemistry of the above cyclophanes, those of the H_c, H_d, and H_e protons are also significantly different in the two conformations (Table I). The H_c protons, readily observed as a singlet in the NMR spectra, are clearly shielded (δ 6.0–6.3) by the meta-bridged ring in the anti conformers compared to those (ca. δ 7.2) in the syn conformers. On the other hand, the H_d and H_e protons that appeared as AA'BB' multiplets are in turn slightly shielded by the stacking meta-bridged ring in the syn conformation (Table I). The bridging methylene protons of *anti*-13 and *anti*-14 unexpectedly appear as two well-separated sets of multiplets in a 1:3 ratio (Table I). Molecular models show that in this rigid anti [2.2] conformation (see I), the H_x protons are held in close proximity to the nonbridged ring, thus experiencing additional deshielding effect consistent with two methylene protons observed at lower field. The degree of intrusion of a proton or a substituent into the π-cloud of a benzene ring in close proximity could readily be indicated qualitatively by the observed chemical shift. Comparing with the known conformationally rigid methyl-substituted dithia[3.3]cyclophanes *anti*-6 ($\delta(CH_3)$ 1.30),[6a]

(11) (a) Hefelfinger, D. T.; Cram, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 1073. (b) Cram, D. J.; Helgeson, R. C.; Lock, D.; Singer, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 1324.
(12) Sherrod, S. A.; da Costa, R. L.; Barnes, R. A.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1565.
(13) See, for example: (a) Vögtle, F.; Newmann, M. v. P. *Tetrahedron* **1970**, *26*, 5299. (b) Vögtle, F. *Liebigs Ann. Chem.* **1970**, *735*, 193.
(14) Lock, G.; Schneider, R. *Chem. Ber.* **1958**, *91*, 1770.
(15) Mitchell, R. H.; Weerawarna, K. S.; Bushnell, G. W. *Tetrahedron Lett.* **1987**, *28*, 5119.
(16) Boekelheide, V.; Tsai, C. H. *J. Org. Chem.* **1973**, *38*, 3931.

18 ($\delta(CH_3)$ 1.90),[16] and 19 ($\delta(CH_3)$ 1.30)[13a] and the [2.2]-cyclophanes *anti*-2 ($\delta(CH_3)$ 0.48),[17] *anti*-3 ($\delta(CH_3)$ 0.56),[6a] and 16 ($\delta(CH_3)$ 1.78),[16] it is evident that anti-11 (δCH_3 0.86) and *anti*-14 (δCH_3 0.30) have the most shielded methyl protons (highest degree of intrusion into the π-cloud) reported so far for the respective families of cyclophanes.

The detailed ^1H NMR data and the UV absorption spectra of 9, 11, 13, and 14 are given in Table I and Figure 1, respectively. These results collectively have illustrated two interesting conformational behaviors of the cyclophanes. Firstly, depending on the length and flexibility of the bridges and the steric demand of the "internal" substituent (H_i or CH_3) of the meta-bridged ring, the angle β in IIa and IIIa could vary by a tilting process of the meta-bridged ring. A decrease in angle β could be accompanied by a second simultaneous sliding process of the meta-bridged ring as shown in IIb and IIIb. In *syn*-9, due to the small steric demand of a proton, the meta-bridged ring could be tilted at a favorable angle β (IIa), thus minimizing the $\pi-\pi$ interaction between the two aromatic rings. This argument is supported by the fact that *syn*-11 and *anti*-11 were obtained only in a 1:2 ratio. The larger



spatial requirement of the methyl group in *syn*-11 results in a decrease in the angle β (IIa), thus increasing appreciably the unfavorable $\pi-\pi$ interaction. The result is a significant change in conformational preference to the anti conformation. The tilting tendency (varying β in IIa) could be readily observed by the change in chemical shift of the H_a proton. The H_a and H_b protons of *syn*-9 appear as a multiplet slightly shifted upfield at δ 6.5. Due to further tilting (smaller β; IIa) of the meta-bridged ring in *syn*-11, its H_a proton (δ 5.94) is forced closer to the central cavity of the nonbridged ring and thus experiences a larger shielding effect and is resolved from the H_b protons (δ 6.62). Going from 9 to 13 or 11 to 14 involves shortening the bridges. The steric demand of the H_i proton would result in further tilting of the meta-bridged ring (smaller β; IIa or IIIa) and thus closer stacking aromatic rings, hence more severe $\pi-\pi$ electronic interaction particularly in the syn conformation. Thus only *anti*-13 and *anti*-14 were isolated. The tilting process in the anti series could also be illustrated by the change in chemical shifts of the H_a, H_b, and H_c protons. In *anti*-11, with a relatively favorable angle β (IIIa), the H_a and H_b protons are projecting away from the naphthalene ring and appear in the normal "benzene region" (H_a at slightly higher field; Table I). The H_c protons (δ 6.31) are slightly shielded by the meta-bridged ring. In *anti*-14, the shorter bridges bring the two rings closer, resulting in a further upfield shift of the H_c protons (δ 6.04; Table I). The meta-bridged ring has to tilt further (smaller β; IIIa) with perhaps a concurrent sliding process (IIIb; meta-bridged ring is more parallel and moving further inward over the para-bridged naphthalene ring) to minimize the interaction between the methyl group and the opposite π-cloud going from *anti*-11 to *anti*-14. This places the H_b protons closer to the (1,4)-bridged ring and thus they appear now at a higher field (a common shielding effect observed for two stacking aromatic rings)[6a,18] than the H_a proton that is presumably still located outside the (1,4)-bridged ring. Due to the smaller steric demand of the H_i proton in *anti*-13, the meta-bridged ring could tilt at a larger angle β with less sliding (meta-bridged ring is projecting further outward from the para-bridged naphthalene ring), thus having the H_a and H_b protons relatively less shielded than those in *anti*-14 (Table I).

UV absorption spectroscopy has been employed to illustrate the face-to-face interaction between two benzene rings, which normally results in a bathochromic shift and broadening of absorption bands.[19] More closely stacked aromatic rings are expected to result in stronger interaction. This phenomenon is clearly observed in the comparison between *syn*-9 and *syn*-11 [Figure 1a; the latter has closer stacking rings due to tilting (smaller β; IIa) of meta-bridged ring resulting from a larger steric demand of the methyl group], *anti*-13 and *anti*-14 [Figure 1c; same reason as above], and *anti*-11 and *anti*-14 [Figure 1b; the latter has closer stacking rings due to shorter bridges]. A more interesting result is observed in the comparison between pairs of anti and syn isomers. The syn conformation, which usually describes a conformation with "overlapping" aromatic rings in cyclophanes, was initially expected to show a stronger face-to-face interaction. However, a large bathochromic shift and significant broadening of bands are observed [Figure 1d,f] for *anti*-13 and *anti*-14 when compared with the corresponding *syn*-9 and *syn*-11. Although going from *syn*-9/11 to *anti*-13/14 involves a shortening of the bridges, this may not be the only reason for the very significant interaction observed for the latter. We believe that the interaction between the "internal" substituent (H_i or CH_3) and the π-cloud in *anti*-13/14 is severe, and thus the tilting and sliding processes make the (1,3)- and (1,4)-bridged rings nearly parallel and almost overlapping. This anti conformation would then result in more significant $\pi-\pi$ interaction than that experienced in *syn*-9/11, which have favorably tilted (larger β) meta-bridged rings due to the longer and more flexible bridges. The above argument is further supported by a comparison of the UV spectra of *anti*-11 and *syn*-11, which now have identical bridges. In *syn*-11, the methyl group has more room to allow tilting at a larger angle β, similar to that of 18. As mentioned earlier, *anti*-11 would be expected to have a smaller angle β and a possible "inward" sliding of the meta-bridged ring, thus placing it over the (1,4)-bridged ring. Bathochromic shifts are clearly observed for both absorption bands of *anti*-11 at ca. 230 nm and ca. 300 nm [Figure 1e].

Variable-temperature ^1H NMR studies up to 150 °C have shown no indication for anti $\rightleftarrows$ syn interconversion in cyclophanes 11, 13, and 14. The sterically bulkier methyl group in 11 and 14 is expected to induce high interconversion barriers in these systems. This observation is consistent with absence of anti $\rightleftarrows$ syn interconversion reported for 6.[6a] A conformational study of 18 also revealed no meta-ring flipping.[20] The conformational flipping in 15 and 17, however, could be readily investigated.[12] The

(17) Blaschke, H.; Ramey, C. E.; Calder, I.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3675.

(18) (a) Mitchell, R. H.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 530. (b) Cram, D. J.; Dalton, C. K.; Knox, G. R. *J. Am. Chem. Soc.* **1963**, *85*, 1088.

(19) (a) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691. (b) Otsubo, T.; Kitasawa, M.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1515.

(20) Vögtle, F. *Tetrahedron Lett.* **1969**, 3193.

rate of meta-ring flipping in the latter was found to be 45 times faster with a $\Delta\Delta G^{\ddagger}$ of 2.6 kcal mol^{-1}. The most plausible explanation is the destabilization of the conformational ground state in **17** due to the $\pi-\pi$ repulsion of the stacking rings. The conformational ground states of *anti*-**13** and *syn*-**13** are expected to be similar to those of **15** and **17**, respectively. This would mean that *syn*-**13** is much less stable than *anti*-**13** due to the $\pi-\pi$ interaction. This is clearly consistent with the absence of *anti*-**13** → *syn*-**13** conversion in our dynamic NMR experiment and the change in conformational preference in going from *syn*-**9**/**11** to *anti*-**13**/**14** via desulfurization—a ring contraction reaction believed to involve ring-opening intermediate(s) thus resulting in the formation of the more stable anti [2.2]cyclophanes.

Experimental Section

All melting points were determined on a Synbron/Thermolyne MP-12615 melting point apparatus and were uncorrected. ^{1}H NMR spectra were determined in $CDCl_3$ on a JEOL FX90Q (90 MHz) Fourier transform spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. Infrared spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer. UV/vis spectra were determined in dichloromethane on a Shimadzu UV 240 graphicord spectrometer. Mass spectra were determined on a VG Micromass 7305 mass spectrometer at 70 eV using electron impact. Relative intensities are given in parentheses. Microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, National University of Singapore.

***anti*- and *syn*-9-Methyl-2,11-dithia[3.3](1,4)naphthalenometacyclophanes (11).** A solution of 2,6-bis(mercaptomethyl)toluene[6a] (0.996 g, 5.25 mmol) and 1,4-bis(bromomethyl)naphthalene[14] (1.648 g, 5.25 mmol) in benzene (150 mL) was added dropwise over a period of 2 h into a well-stirred solution of KOH (0.943 g, 16.81 mmol) in nitrogen-purged 95% ethanol (500 mL). After the addition, the mixture was further stirred for 15 h and the bulk of the solvent was then removed under reduced pressure. The residue was extracted with dichloromethane. The organic layer was washed with water, dried, and evaporated. The crude product was chromatographed on silica gel, using benzene/hexane (1:3) as eluant. Eluted first was *anti*-**11**: 141 mg (8%); mp 240–241 °C; ^{1}H NMR, see Table I; IR (KBr) 1580, 1500, 1440, 1400, 1240, 1210, 1180, 1110, 1030, 995, 960, 940, 910, 840, 820, 780, 760, 740, 710, 695, 675 cm^{-1}; UV λ_{max} 235 (ϵ 50500), 295 (7300), 306 (9500), 319 (7100) nm; MS ($M^{\cdot+}$) m/z 336 (61), 187 (47), 185 (30), 184 (18), 154 (100), 148 (11), 115 (11). Anal. Calcd for $C_{21}CH_{20}S_2$: C, 74.95; H, 5.99. Found: C, 75.20; H, 5.93.

Eluted next was a mixture of the anti and syn isomers: 146 mg (8%).

Eluted last was *syn*-**11**: 53 mg (3%); mp 237–238 °C; ^{1}H NMR, see Table I; IR (KBr) 1585, 1500, 1430, 1400, 1230, 1175, 1070, 1030, 940, 910, 840, 760, 730, 710 cm^{-1}; UV λ_{max} 230 (ϵ 50100), 285 (7900), 294 (9700), 303 (8200) nm; MS ($M^{\cdot+}$) m/z 336 (55), 187 (39), 185 (26), 184 (16), 154 (100). Anal. Calcd for $C_{21}H_{20}S_2$: C, 74.95; H, 5.99. Found: C, 74.40; H, 5.79.

***anti*-[2.2](1,4)Naphthalenometacyclophane (13).** A solution of the dithiacyclophane **9**[10] (190 mg, 0.59 mmol) in trimethyl phosphite (10 mL) was irradiated on a Rayonet photochemical reactor (Model RPR-100) at 254 nm for 18 h. The solution was then added to a mixture of 1 H HCl (100 mL) and cyclohexane (100 mL) and stirred thoroughly for 1 h. The organic layer was separated, washed with water, dried, and evaporated. The crude product was chromatographed on silica gel, using hexane as eluant, to yield colorless crystals of the cyclophane *anti*-**13**: 0.13 g (42%); mp 155–156 °C (lit.[8] mp 155.5–156.5 °C); ^{1}H NMR, see Table I; IR (KBr) 1570, 1430, 1380, 1355, 1160, 1145, 1075, 1010, 940, 920, 790, 770, 760, 700, 625 cm^{-1}; UV λ_{max} 222 (ϵ 27900), 241 (33500), 305 (br; 3900) nm; MS ($M^{\cdot+}$) m/z 258 (93), 243 (64), 230 (18), 104 (100), 103 (28).

***anti*-8-Methyl[2.2](1,4)naphthalenometacyclophane (14).** A solution of *anti*-**11** (80 mg, 0.24 mmol) in benzene (3 mL) and trimethyl phosphite (6 mL) was subjected to photodesulfurization conditions as described for the preparation of *anti*-**13**. Colorless crystals of *anti*-**14** were obtained: 20 mg (31%); mp 196–198 °C; ^{1}H NMR, see Table I; IR (KBr) 1570, 1445, 1350, 1165, 1145, 890, 870, 800, 760, 710 cm^{-1}; UV λ_{max} 224 (sh; ϵ 21000), 241 (30300), 305 (3900) nm; MS ($M^{\cdot+}$) m/z 272 (75), 257 (33), 118 (100). Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 93.12; H, 7.23.

The photodesulfurization was repeated with *syn*-**11** (40 mg, 0.12 mmol) to yield only *anti*-**14**: 20 mg (62%).

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Registry No. *syn*-**9**, 123487-52-5; *anti*-**11**, 123487-51-4; *syn*-**11**, 123538-43-2; *anti*-**13**, 116073-03-1; *anti*-**14**, 123487-53-6; 2,6-bis(mercaptomethyl)toluene, 41563-67-1; 1,4-bis(bromomethyl)naphthalene, 58791-49-4.

Stereochemical Studies of Simple Cyclooctyl Systems

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In an effort to utilize 1,5-cyclooctadiene (1,5-COD) as an inexpensive and readily available starting material for stereocontrolled synthesis, we have studied the functionalization of 1,5-cyclooctanedione, **1**, which can easily be prepared from 1,5-COD in three steps (Scheme I).[1,2] The selectivity of these reactions can be explained by the conformational preferences of the cyclooctyl system,[3] which are revealed by X-ray crystallographic analyses.

The X-ray crystal structure of 1,5-cyclooctanedione shows that in the solid state, the molecule exists in a boat–chair conformation.[4] The sp^2-hybridized carbon atoms of **1** are located at the flagpole positions of the eight-membered ring, thereby minimizing the strain which results from transannular interactions across the ring. If the bis(enolization) of **1** were to occur from the same conformation, high diastereoselectivity to produce a *E,E*-1,4-bis(enolate) would be expected. The most acidic protons are those which have the highest overlap of the C–H σ-bond with the carbonyl π-system, i.e. those nearly perpendicular to the plane of the C–O bond of the carbonyl at carbons 2, 4, 6, and 8. Enolization at positions 6 and 8 was considered unlikely since the strain involved with formation of a trans olefin in an eight-membered ring is on the order of 11 kcal/mol.[5]

In accord with these expectations, the bis(silyl ether) **2** was obtained in quantitative yield and as a single regio- and stereoisomer when 1,5-cyclooctanedione was subjected

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(2) The oxidation of *cis*-1,5-cyclooctanediol to 1,5-cyclooctanedione using PCC has recently been reported: Lyttle, M. H.; Streitwieser, A.; Miller, M. J. *J. Org. Chem.* **1989**, *54*, 2331.

(3) For a study of the diastereoselective transformations of cyclooctanones as well as other cyclic ketones, see: Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981.

(4) Miller, R. W.; McPhail, A. T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1527.

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