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# *Notes*

## Synthesis and Conformational Study of Isomers of 9-Methyl-2,11-Dithia[3.3](1,4)triphenylenometacyclophane and 2,23-Dithia[3.3](1,4)triphenylenophane

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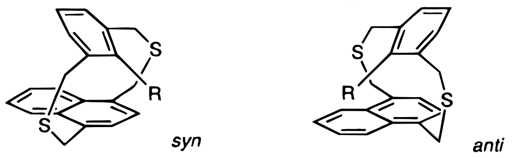
The dithianaphthalenophane **1** was reported to exist only as the *syn* isomer.[1] The *anti* and *syn* isomers of dithianaphthalenophane **2** were, however, obtained from a common synthetic reaction in an 8:3 ratio.[2] The main factor attributed to the change in conformational preference going from **1** (*syn* only) to **2** (*anti*-dominant) is the result of a less favorable $\pi-\pi$ interaction between the benzene ring and the nonbridged naphthalene ring in *syn* **2** compared to the nonbonded interaction involving the intrusion of the methyl group into the $\pi$-cloud of the nonbridged naphthalene ring in *anti* **2**.

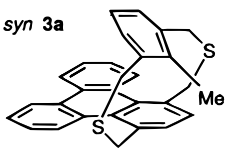
**1**, R = H ; **2**, R = $CH_3$



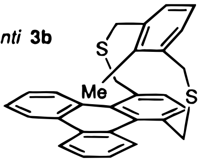
Results derived from theoretical and mathematical calculations[3] suggest that the aromaticity indices for each ring of naphthalene and the central ring of triphenylene are 0.7−0.8 and 0.2−0.4, respectively, relative to an aromaticity index of 1.0 for benzene. It would thus be of interest to determine whether the conformational preference would change going from **2** to dithiatriphenylenophane **3**. The $\pi-\pi$ interaction between the benzene ring and the less aromatic (decreasing in $\pi$-character) central triphenylene ring in *syn* **3** is expected to be less significant compared to a similar $\pi-\pi$ interaction in *syn* **2** as described earlier. In this paper we report the conformational study of isomers of 9-methyl-2,11-dithia-[3.3](1,4)-triphenylenometacyclophane (**3**) and 2,23-dithia-[3.3](1,4)triphenylenophane (**4**). It is noteworthy that before this work, there was no reported example of a triphenylenophane.

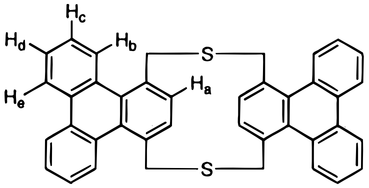
**Synthesis.** The synthesis of triphenylene from phenanthryne and furan has been reported.[4,5] Thus the reaction between phenanthryne, generated from treatment of 9-bromophenanthrene with sodium amide, and freshly distilled 2,5-dimethylfuran gave the Diels−Alder adduct

*syn* **3a**

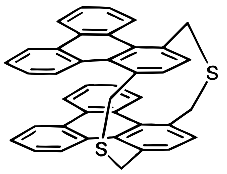


*anti* **3b**

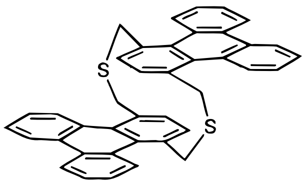




**4**

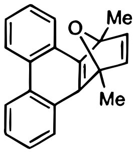


*syn* **4a**

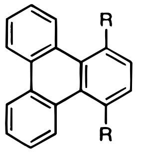


*anti* **4b**

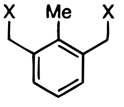
**5** in 30−65% yield. Deoxygenation of **5** using $Fe_2(CO)_9$[6] readily afforded 1,4-dimethyltriphenylene **6**. The dibromide **7** was isolated in an optimum yield of 65% by bromination of **6** with NBS in the presence of a catalytic amount of benzoyl peroxide. This reaction could, however, only be carried out on a relatively small scale (≤400 mg). Large scale reactions resulted in a lower yield of **7** and significant amounts of tri- and/or tetrabrominated products. Chromatographic separation of **7** from this mixture proved to be difficult. Treatment of **7** with thiourea followed by base hydrolysis of the intermediate thiouronium salt readily gave the dimercaptan **8**.



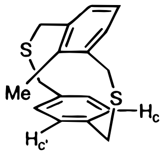
**5**



|  | R |
|---|---|
| **6** | Me |
| **7** | $CH_2Br$ |
| **8** | $CH_2SH$ |



|  | X |
|---|---|
| **9** | $CH_2Br$ |
| **10** | $CH_2SH$ |



**11**

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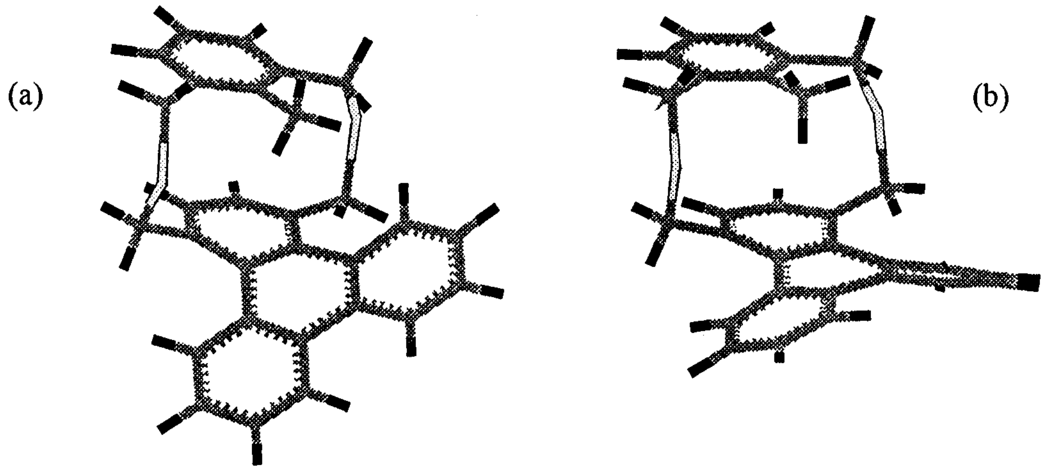

**Figure 1.** Optimized conformation for (a) "twist"-**3b** and (b) "bent"-**3b** derived from semiempirical molecular orbital PM3 calculations.

A cyclization reaction between **7** and **10**[7] under high dilution conditions[8] was first attempted. Results from chromatographic studies of the isolated product indicated the presence of only one isomer of **3**. This was assigned *syn* **3a** on the basis of NMR spectroscopic analysis (see later discussion). The low yield (*ca.* 30%) of *syn* **3a** obtained in this reaction could be due to steric hindrance at the methylene carbons in **7** that discouraged the nucleophilic approach of **10**. Thus a similar cyclization reaction between **8** and **9**[7] afforded a better yield (*ca.* 60%) of **3**. In addition, *syn* **3a** and *anti* **3b** were observed in a 8.5:1.5 ratio in the product mixture. The isomer *syn* **3a** could be readily isolated pure by recrystallization. A small sample of pure *anti* **3b** could, however, be obtained only from preparative TLC.

A low yield (<10%) of a highly insoluble product was isolated from a similar cyclization reaction between **7** and **8**. This was assigned *anti* **4b** on the basis of NMR spectroscopic analysis (see later discussion).

**Conformational Analysis.** The two aromatic moieties in **3** could be positioned in two ways represented by *syn* **3a** and *anti* **3b**, respectively (illustrated with planar rings for simplicity). As the presence of a substituent in the bay-region of a benzenoid is known to result in a significant twisting of the molecular framework, there are two possible conformations for each of *syn* **3a** and *anti* **3b**: the "twist" and the "bent" forms as illustrated for *anti* **3b** in Figures 1, parts a and b, respectively. Our semiempirical molecular orbital PM3[9] calculations show that in isolation, the relative stability of bent **3b**:twist **3a**:bent **3a**:twist **3b** is 0:3.8:4.4:9.8 kJ mol$^{-1}$, respectively. While the two conformers of **3a** have similar heats of formation, there is an appreciable difference in the relative stability between those of **3b**.

The $^1$H NMR spectrum of the major isomer of **3** shows a singlet at $\delta$ 2.09 for its methyl protons. With the available $^1$H NMR data (Table 1) for dithiacyclophanes **11**,[10] *syn* **2**, and *anti* **2**,[2] a comparison of the chemical shifts of their respective methyl signals readily confirms that the major isomer of **3** is *syn* **3a**. The methyl protons in *anti* **3b**, expected to be shielded by a combined ring current effect of the central and bridged triphenylene rings, are significantly shifted upfield to $\delta$ 0.85 similar to that observed for *anti* **2**. The stereochemistry of *syn* **3a** and *anti* **3b** could also be derived from a comparison of the chemical shifts of their $H_a$, $H_b$, and $H_c$ (Table 1). With the *meta*-bridged ring titlted at an angle with respect to the triphenylene moiety (Figure 2a,c; illustrated with planar rings for simplicity), the $H_a$,$H_b$ of *syn* **3a** and $H_c$ of *anti* **3b** are shielded by the central ring of triphenylene and the *meta*-bridged ring, respectively. The $H_a$,$H_b$ of *anti* **3b** and $H_c$ of *syn* **3a**, on the contrary, appear as "normal" benzene protons at $\delta$ 7−8 (Table 1). The other aromatic protons and the methylene protons of *syn* **3a** and *anti* **3b** were assigned, respectively, by a series of NOE experiments.

**Table 1. Proton Chemical Shifts of Selected Protons in Dithiacyclophanes 2,[2] 3, and 11[10]**

| | chemical shift ($\delta$) | | | | |
|---|---|---|---|---|---|
| proton(s) | *syn* **2** | *anti* **2** | **3a** | **3b** | **11** |
| $CH_3$ | 1.90 | 0.86 | 2.09 | 0.85 | 1.90 |
| $H_a$ | 5.94 | 6.98 | 5.71 | 7.11 | |
| $H_b$ | 6.62 | 7.21 | 5.87 | 7.24 | 6.8−7.2 |
| $H_c$ | 7.20 | 6.31 | 7.96 | 6.75 | 6.2−6.3[a] |

[a] $H_c$ are shielded by the 1,3-bridged ring; $H_{c'}$ overlaps with $H_a$, $H_b$.

In the $^1$H NMR spectrum of **3b** (or **3a**), there are only two sets of AB quartets and one set of signals for aromatic protons $H_c$, $H_d$, $H_e$, $H_f$, and $H_g$. This observation rules out the possibility of **3b** existing as a rigid twist **3b** (Figure 1a). In such a conformation, at least the two pairs of methylene protons and/or the aromatic protons $H_e$ in the bay-region are expected to be resolved. Thus the $^1$H NMR spectral data supports a rigid bent **3b** (Figure 1b) which was also found to be thermodynamically the most stable in the theoretical calculations. A less likely assumption is that the interconversion between the two mirror twist forms of **3b** is fast on the NMR time scale. This would still result in averaged signals corresponding to a structure similar to bent **3b**.

Results from the PM3 calculations indicate that bent *anti* **3b** is thermodynamically the most stable. The optimized structure of bent *anti* **3b** (Figure 1b) shows that the methyl protons are located over the $\pi$-cloud of the fused bond between the bridged and central rings.

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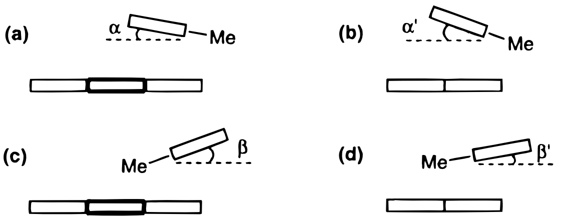


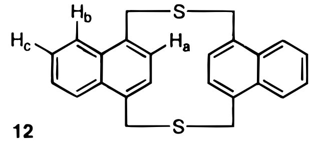
**Figure 2.** Side view showing tilting of *meta*-bridged ring in (a) *syn* **3a**, (b) *syn* **2**, (c) *anti* **3b**, and (d) *anti* **2**.

**Table 2. Proton Chemical Shifts of Selected Protons in Dithiacyclophanes 4b and 12,[12] 1,4-Dimethyltriphenylene 6, and 1,4-Dimethylnaphthalene 13[13]**

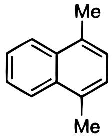
| | chemical shift ($\delta$) | | | | |
|---|---|---|---|---|---|
| proton(s) | **6** | **4b** | **13** | **12a** | **12b** |
| $H_a$ | 7.34 | 6.49 | 7.13 | 6.93 | 6.27 |
| $H_b$ | 8.47 | 8.41 | 8.0 | 7.86 | 8.10 |
| $H_c$ | 7.45 | 7.59 | 7.5 | 7.06 | 7.60 |
| $H_d$ | 7.45 | 7.68 | – | – | – |
| $H_e$ | 8.47 | 8.64 | – | – | – |

Thus these protons are believed to be shifted upfield ($\delta$ 0.85) due to a combined shielding effect of the two rings. Isolation of *syn* **3a** as the major isomer thus suggests that the cyclization reaction was likely to be kinetically controlled. The steric interactions arising from the intrusion of the methyl group into the triphenylene unit in the transition state leading to ring closure would account for the kinetically unfavored *anti* **3b**.

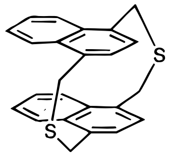
As for the conformation of the isolated dithia[3.3](1,4)-triphenylenophane **4**, there is no single proton probe in its $^1$H NMR spectrum which readily indicates its stereochemistry. A face-to-face interaction between two aromatic rings is, however, expected to result in mutual shielding of their ring protons.[11] This was observed[12] for all ring protons of *syn* **12a** whereas only $H_a$ of *anti* **12b** is shielded compared to ring protons of 1,4-dimethylnaphthalene **13** (Table 2).[13] Similarly a comparison (Table 2) between the spectra of the isolated isomer of **4** and 1,4-dimethyltriphenylene **6** clearly indicates that it is *anti* **4**. Only $H_a$ of *anti* **4** is significantly shielded. Assignment of the other protons in *anti* **4** was achieved by a series of NOE experiments.



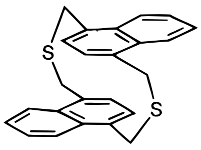
**12**



**13**



*syn* **12a**



*anti* **12b**

An examination of the $^1$H NMR data of conformers of **2** and **3** reveals an interesting conformational behavior of these dithiacyclophanes. The tilting angle (Figure 2) of the *meta*-bridged ring is dependent on two kinds of nonbonding interactions: the $\pi-\pi$ interaction between the stacked rings and the steric interaction due to the intrusion of the methyl group into the $\pi$-cloud of the adjacent ring in the *syn* and *anti* conformations, respectively. Going from *syn* **2** to *syn* **3a** (Table 1), there is an upfield shift of the signals of $H_{a,b}$ accompanied by a relatively less shielded $CH_3$ signal. Qualitatively, this is consistent with a smaller tilting angle ($\alpha < \alpha'$; Figure 2) in **3a**. This could be accompanied by an outward sliding of the *meta*-bridged ring thus moving the methyl group further away from the shielding zone of the *para*-bridged ring in **3a**. The chemical shifts of $H_{a,b}$ in *syn* **3a** are likely to be affected by the combined shielding effect of the two terminal nonbridged rings and the central ring.

**Conclusion.** Although *syn* **3a** was isolated as the major isomer in the synthesis, the cyclization reaction was likely to be kinetically controlled. Results from molecular orbital calculations have indicated that *anti* **3b** is thermodynamically the most stable isomer. This suggests that the $\pi-\pi$ interaction between the aryl rings concerned in *syn* **3a** is less favorable compared to the nonbonded interaction involving the intrusion of the methyl group into the triphenylene $\pi$-clouds in *anti* **3**, a phenomenon similar to that reported for naphthalenophane **2**. Thus a less aromatic central ring in triphenylene does not affect the conformational preference going from **2** to **3**.

## Experimental Section

Melting points are uncorrected. $^1$H NMR spectra were recorded in $CDCl_3$ on 300 or 500 MHz spectrometers with $Me_4Si$ as internal standard. Mass spectra were obtained using EI ionization at 70 eV. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

**1,4-Epoxy-1,4-dimethyl-1,4-dihydrotriphenylene (5).** A mixture of 9-bromophenanthrene (5.00 g, 19.5 mmol), sodium amide (3.80 g, 91.4 mmol), and freshly distilled 2,5-dimethylfuran (27.10 g, 282 mmol) in anhydrous THF (150 cm$^3$) was heated at reflux under nitrogen for 6 h. The mixture was concentrated and poured onto ice–water. Extraction with dichloromethane followed by chromatography of the residue on silica gel using hexane/dichloromethane (2:1) as eluent gave **5** as a colorless oil, 3.44 g (65%). $^1$H NMR $\delta$ 7.51–8.81 (m, 8 H), 7.05 (s, 2 H), 2.37 (s, 6 H); MS ($M^{\bullet+}$) $m/z$ 272 (62), 257 (20), 229 (100), 202 (20), 101 (10); $M_r$ calcd for $C_{20}H_{16}O$ 272.1201, found (MS) 272.1212.

**1,4-Dimethyltriphenylene (6).** A solution of **5** (3.00 g, 11.0 mmol) in benzene (100 cm$^3$) was treated with $Fe_2(CO)_9$[6] (4.80 g, 13.2 mmol). The mixture was stirred under nitrogen at 50–60 °C for 1 h. The reaction temperature was then raised to 90–100 °C and the mixture heated at reflux for 24 h. The mixture was cooled, and the insoluble iron-containing material was removed by filtration. The filtrate was evaporated to give a yellow solid. Chromatography on silica gel using hexane as eluent gave the desired product **6**, 2.25 g (80%). A sample was recrystallized from cyclohexane to give colorless crystals of **6**, mp 107–108 °C (lit.[14] 108–109 °C). $^1$H NMR $\delta$ 8.39–8.54 (AA″BB″, 4 H), 7.49–7.60 (AA″BB″, 4 H), 7.34 (s, 2 H), 2.95 (s, 6 H).

**1,4-Bis(bromomethyl)triphenylene (7).** *N*-Bromosuccinimide (0.60 g, 3.41 mmol) was added to a solution of **6** (0.40 g, 1.56 mmol) in $CCl_4$ (200 cm$^3$). A catalytic amount of benzoyl peroxide was added. The mixture was heated at reflux for 30 min by irradiation with a 200 W tungsten lamp. The mixture was then cooled and filtered. The filtrate was washed with aqueous $NaHCO_3$ and water, dried, and evaporated. The residue was chromatographed on silica gel using hexane/dichloromethane (3:1) as eluent to give a pale yellow solid, 0.41 g (64%). A sample recrystallized from bezene/cyclohexane afforded colorless crystals

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of **7**, mp 187−188 °C. $^1$H NMR $\delta$ 8.51−8.54 (AA″BB″, 4 H), 7.60−7.69 (AA″BB″, 4 H), 7.78 (s, 2 H), 5.03 (s, 4 H); MS ($M^{\bullet+}$) *m/z* 412 (5), 333 (10), 254 (100), 239 (65), 225 (10), 125 (45), 80 (32); IR (KBr) 1439, 1237, 1208, 822, 754, 731, 658, 550 cm$^{-1}$. Anal. Calcd for $C_{20}H_{14}Br_2$: C, 58.00; H, 3.38. Found: C, 57.93; H, 3.31.

**1,4-Bis(mercaptomethyl)triphenylene (8).** To a hot solution of thiourea (0.58 g, 7.63 mmol) in 95% ethanol (100 cm$^3$) was added **7** (0.90 g, 2.18 mmol). The mixture was heated at reflux for 1 h. The bulk of the solvent was removed under reduced pressure, and crystals of the corresponding bis(thouronium) salt of **7** were filtered. The salt was added to an aqueous solution (100 cm$^3$) of KOH (0.85 g, 15.2 mmol), and the mixture was heated at reflux for 6 h. The mixture was then cooled and made just acidic to litmus with concd $H_2SO_4$. The product was extracted into dichloromethane, and the organic layer was washed, dried, and evaporated. The residue was chromatographed on silica gel using dichloromethane as eluent to afford **8** as a white solid (0.64 g, 92%), mp 126−128 °C. $^1$H NMR $\delta$ 8.43−8.53 (AA″BB″, 4 H), 7.55−7.65 (AA″BB″, 4 H), 7.69 (s, 2 H), 4.36 (d, 4 H, *J* 6.5 Hz), 2.12 (t, 2 H, *J* 6.5 Hz); MS ($M^{\bullet+}$) *m/z* 320 (30), 285 (35), 253 (100), 239 (50), 225 (10), 119 (18); IR (KBr) 3060, 2920, 2850, 2546, 1493, 1430, 1378, 1245, 825, 756, 730 cm$^{-1}$. $M_r$ calcd for $C_{20}H_{16}S_2$ 320.0693, found (MS) 320.0681.

**9-Methyl-2,11-dithia[3.3](1,4)triphenylenometacyclophane (3).** (A) A solution of **7** (0.40 g, 0.97 mmol) and 2,6-bis(mercaptomethyl toluene (**10**)[7] (0.31 g, 0.97 mmol) in benzene (200 cm$^3$) was added dropwise over a period of 8 h into a well-stirred solution of KOH (0.17 g, 3.11 mmol) in nitrogen-purged 95% ethanol (600 cm$^3$). 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, washed, dried, and evaporated. The crude product was chromatographed on silica gel using hexane−dichloromethane (3:1) as eluent to yield *syn* **3a** (0.13 g, 31%). A sample recrystallized from benzene/cyclohexane gave colorless crystals of *syn* **3a**, mp 243−244 °C. $^1$H NMR $\delta$ 8.54 (br d, 2 H, *J* 8.1), 7.96 (s, 2 H), 7.96 (dd, 2 H, *J* 7.6, 1.2 Hz), 7.63 (ddd, 2 H, *J* 7.6, 7.6, 1.2 Hz), 7.49 (ddd, 2 H, *J* 7.6, 7.6, 1.2 Hz), 5.87 (d, 2 H, *J* 7.6 Hz), 5.71 (t, 1 H, *J* 7.6 Hz), 4.39, 4.44 (ABq, 4 H, *J* 15.6 Hz), 3.49, 3.52 (ABq, 4 H, *J* 14.0 Hz), 2.09 (s, 3 H); MS ($M^{\bullet+}$) *m/z* 436 (48), 317 (20), 285 (100), 253 (90), 239 (33); UV $\lambda_{\max}$ 242 ($\epsilon$ 42100), 278 ($\epsilon$ 81600) nm; IR (KBr) 3062, 2913, 1549, 1429, 1412, 1375, 917, 780, 759, 732, 596 cm$^{-1}$. Anal. Calcd for $C_{29}H_{24}S_2$: C, 79.77; H, 5.54. Found: C, 79.65; H, 5.36.

(B) The procedure was similar to that described in (A) by using a solution of **8** (0.60 g, 1.88 mmol) and 2,6-bis(bromomethyl)toluene **9**[7] (0.52 g, 1.88 mmol) in THF/benzene (1:1; 250 cm$^3$). Chromatography of the crude product on silica gel afforded a mixture of the two isomers of **3**, 0.48 g (58%). A relative ratio of 8.5:1.5 for *syn*-**3** to *anti*-**3** was obtained based on the integration ratio of their respective methyl protons in the $^1$H NMR spectrum of the mixture. Repeated washing of this mixture with ethanol gave pure *syn*-**3**. The washings were combined and evaporated. Preparative TLC of the residue on silica gel led to isolation of pure *anti*-**3**, mp 198−199 °C. $^1$H NMR $\delta$ 8.57 (br d, 2 H, *J* 7.6 Hz), 8.33 (br d, 2 H, *J* 7.6 Hz), 7.64 (br t, 2 H, *J* 7.6 Hz), 7.55 (br t, 2 H, *J* 7.6 Hz), 7.24 (d, 2 H, *J* 7.6 Hz), 7.11 (t, 1 H, *J* 7.6 Hz), 6.75 (s, 2 H), 4.09, 4.99 (ABq, 4 H, *J* 15.1 Hz), 3.37, 3.61 (ABq, 4 H, *J* 14.7 Hz), 0.85 (s, 3 H); MS ($M^{\bullet+}$) *m/z* 436 (34), 317 (24), 285 (92), 253 (100), 239 (30); UV $\lambda_{\max}$ 241 ($\epsilon$ 26100), 275 ($\epsilon$ 63300) nm. $M_r$ calcd for $C_{29}H_{24}S_2$ 436.1319, found (MS) 436.1328.

***anti*-2,23-Dithia[3.3](1,4)triphenylenophane (4b).** The procedure was similar to that described for the synthesis of **3** by using a solution of **7** (0.60 g, 1.46 mmol) and **8** (0.47 g, 1.46 mmol) in THF/benzene (1:1; 250 cm$^3$). The crude product was washed with repeated washed with benzene to give the dithiacyclophane **4b** as a white solid (65 mg, 8%), mp 270−272 °C. $^1$H NMR ($CD_2Cl_2$) $\delta$ 8.64 (dd, 4 H, *J* 7.6, 1.2 Hz), 8.41 (dd, 4 H, *J* 7.6, 1.2 Hz), 7.68 (ddd, 4 H, *J* 7.6, 7.6, 1.2 Hz), 7.59 (ddd, 4 H, *J* 7.6, 7.6, 1.2 Hz), 6.49 (s, 4 H), 4.16, 4.84 (ABq, 8 H, *J* 15.6 Hz); MS ($M^{\bullet+}$) *m/z* 572 (10), 317 (35), 285 (64), 253 (100), 239 (90), 226 (26); UV $\lambda_{\max}$ 231 ($\epsilon$ 4 900), 271 ($\epsilon$ 15 300) nm; IR (KBr) 3063, 1491, 1424, 1234, 1053, 757, 746, 730, 623 cm$^{-1}$. $M_r$ calcd for $C_{40}H_{28}S_2$ 572.1632, found (MS) 572.1638.

**Computational Details.** The initial geometries were generated using the MMX[15] force field with PCMODEL v4.0.[16] The semiempirical PM3[17] calculations were carried out with the MOPAC system (v6.0)[18] on a personal IRIS computer.

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