Synthesis and Conformational Study of the First Dithia[3]metacyclo[3](2,4)pyrrolophane and [2]Metacyclo[2](2,4)pyrrolophane. ^{1}H NMR Spectroscopic Evidence for a Novel Hydrogen-Bonding Phenomenon

Yee-Hing Lai,* K. F. Mok,† and Yuhua Ting

Department of Chemistry, National University of Singapore, Kent Ridge, Republic of Singapore 0511

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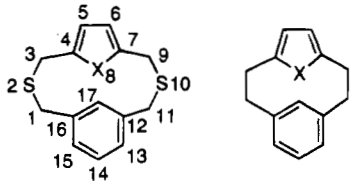
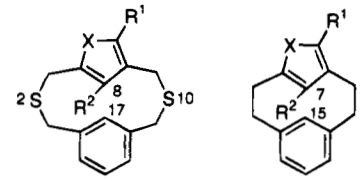
The first examples of a dithia[3]metacyclo[3](2,4)pyrrolophane and a [2]metacyclo[2](2,4)-pyrrolophane, namely **3g** and **4g**, respectively, were synthesized. The dithiacyclophane **3g** was found to adopt the *syn* conformation both in solid state and in solution. Results from the ^{1}H NMR spectroscopic study of **3g** suggest a novel hydrogen-bonding between a relatively "nonacidic" bridging methylene proton and the carbonyl oxygen of the "internal" ester group at C8. X-ray crystallographic data indicate an unexpectedly small inclination angle of the two aromatic rings in **3g** which would minimize the steric interaction between the *syn* ester group at C8 and H17. The [2$_2$]cyclophane **4g** was found to adopt the *anti* conformation both in solid state and in solution. Results from the ^{1}H NMR spectroscopic study of **4g** show that the methoxy protons of the "internal" ester group at C7 are still located in the shielding zone of the opposite *anti* benzene ring. X-ray crystallographic data indicate an unexpectedly large inclination angle of the two aromatic rings in **4g** which would minimize the steric interaction between the ester group at C7 and the opposite benzene ring.

A large number of cyclophanes have been shown to exhibit novel conformational behavior and other physical properties.[1] Among [*n*](1,3)cyclo[*n*]heterophanes which contain one furan, pyrrole, or thiophene ring, the [*n*](1,3)cyclo[*n*](2,5)heterophanes[2–5] **1a–c** and **2a–c** have



1 **2**

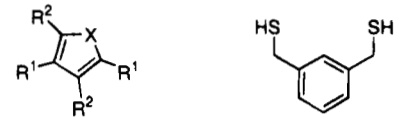
a : X = O
b : X = NH
c : X = S



3 **4**

	X	R^1	R^2
a	S	H	H
b	S	H	Br
c	S	CH_3	H
d	S	CH_3	Br
e	O	H	H
f	NH	H	H
g	NCH_3	CO_2CH_3	CO_2CH_3

been the most extensively studied. This is partly due to the fact that their corresponding precursors, namely 2,5-disubstituted 5-membered aromatic heterocycles, are synthetically more accessible. The dithia[3.3]phane **3a** and [2.2]phane **4a**,[6] and several of their derivatives,[5] were, however, the only such [*n*](1,3)cyclo[*n*](2,4)heterophanes reported before this work. Selectively 2,4-disubstituted furans and pyrroles, *e.g.*, **5a** and **5b** which could be used to prepare dithiacyclophanes **3e** and **3f**, respectively, would not be readily available synthetically. Competing reactions particularly at unprotected C5 and/or 1,4-addition reactions across C2/C5 would usually complicate most attempts in functional group transformation reactions at C2/C4.[7] We wish to report the synthesis and conformational study of the first examples of [*n*](1,3)cyclo[*n*](2,4)pyrrolophanes (n = 2,3), namely the dimethyl dicarboxylate derivatives **3g** and **4g**.



5 **6**

	X	R^1	R^2
a	O	CH_2Br	H
b	NH	CH_2Br	H
c	NH	CH_3	CO_2CH_3
d	NCH_3	CH_3	CO_2CH_3
e	NCH_3	CH_2Br	CO_2CH_3

† To whom correspondence concerning the crystallographic study should be addressed.

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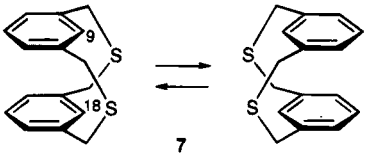
N-Methylation of dimethyl 3,5-dimethylpyrrole-2,4-dicarboxylate **5c**[8] via a slightly modified procedure[9] gave dimethyl *N*-3,5-trimethylpyrrole-2,4-dicarboxylate (**5d**) in an 87% yield. Irradiation of a mixture of **5d** and 2 equiv of *N*-bromosuccinimide with visible light in CCl_4 at solvent refluxing temperature afforded almost quantitatively the bis(bromomethyl)pyrrole **5e**. The coupling reaction of **5e** with bis(mercaptomethyl)benzene (**6**)[10] was carried out under high dilution conditions,[11] and the corresponding dithia[3](1,3)cyclo[3](2,4)pyrrolophane **3g** was isolated in 56% yield after chromatography. Pyrrolophane **3g** was found (see later discussion) to exist exclusively as the *syn* conformer.

The conformational study[12] of *syn* dithiacyclophane **7** has indicated ring flipping and bridge "wobbling" processes between pairs of *syn* conformers with no appreciable concentration of *anti* conformers. Dithiathiophenophanes **3a,c,d** were reported to be conformationally mobile at room temperature but whether both *syn* and *anti* conformers were present is uncertain.[5,6] Dithiathiophenophane **3b** seems to be conformationally more rigid but there was no clear indication whether *syn* or *anti* stereochemistry is preferred.[6] Comparison of the proton chemical shifts of H17 (δ 6.94) of **3g** (Figure 1a) and H9(H18) (δ 6.82)[12] of **7** suggests a *syn* conformation for **3g**. The H17 of **3g** is likely to be further deshielded by a "transannular" anisotropic effect of the carbonyl function. It was first indicated by Boekelheide[13] that electron-withdrawing groups increase the *syn:anti* ratio of dithia(1,3)cyclophanes. This was recently explained as being due to the stabilization of the *syn* conformer resulting from charge transfer or charge interaction across the rings.[14] The two methyl carboxylate groups in **3g** would thus encourage the two rings to be *syn*. This was confirmed to be the preferred conformation in the solid state by an X-ray crystallographic analysis of **3g** (Figure 1). The two aromatic rings are inclined (θ) only at 10.1° with respect to each other compared to a corresponding value of 20.6° for **7**.[12] The significantly larger steric demand of the "internal" ester group at C8 in **3g** is expected to account for the the relatively smaller ring inclination angle in this *syn* dithia[3_3](1,3)cyclophane. This minimizes the steric interaction between the ester group at C8 and H17 on the opposite benzene ring. There is, however, no significant deviation in the plane of either aromatic ring in **3g**. The five- and six-membered rings are staggered almost ideally from an aerial view (Figure 1b). The sulfur atoms are "*anti*" with respect to each other. The "external" carbonyl group at C6 is almost coplanar (torsional angle = 5.0°) with the pyrrole (aromatic) ring. This is expected to allow maximum π-electron delocalization as observed in earlier reported systems.[15] On the contrary, the "internal" carbonyl group at C8 is significantly tilted at a torsional angle of 28.6° to the pyrrole ring to minimize steric interactions.



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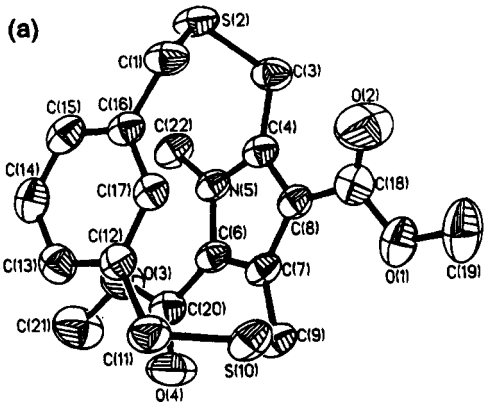

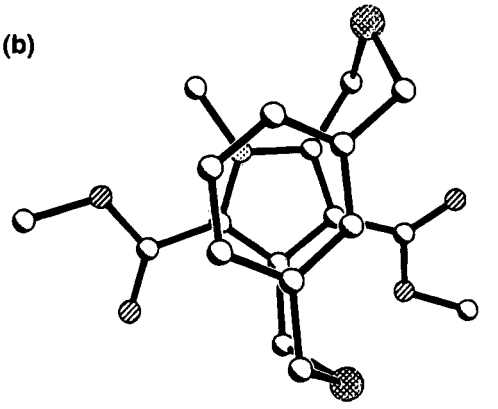

Figure 1. (a) Crystal structure (ORTEP) and (b) aerial view of dithiacyclophane **3g**.

Table 1. Assignment of Methylene Protons in Dithiacyclophane (3g)

proton	chemical shift (δ)	coupling constant (Hz)
$1\text{-}H_{ax}/1\text{-}H_{eq}$	3.95, 3.67	15.0
$3\text{-}H_{ax}/3\text{-}H_{eq}$	5.15, 3.20	14.4
$9\text{-}H_{ax}/9\text{-}H_{eq}$	4.54, 4.01	14.1
$11\text{-}H_{ax}/11\text{-}H_{eq}$	3.86, 3.73	16.6

The sulfur atoms are "*anti*" with respect to each other. The "external" carbonyl group at C6 is almost coplanar (torsional angle = 5.0°) with the pyrrole (aromatic) ring. This is expected to allow maximum π-electron delocalization as observed in earlier reported systems.[15] On the contrary, the "internal" carbonyl group at C8 is significantly tilted at a torsional angle of 28.6° to the pyrrole ring to minimize steric interactions.

The ^{1}H NMR spectrum of **3g** indicates that the same conformation is also preferred in solution. The methylene protons appear as four sets of AB quartets (Table 1), three of which are in the expected range of δ 3.7−4.0. One of the AB quartets, however, is shifted unexpectedly and significantly at δ_A 3.20 and δ_B 5.15. An analysis[16,17] of the deshielding effect of a carbonyl group indicates that strong deshielding of >1 ppm is observed for rigidly fixed protons[18] in close proximity to a cone whose axis is along the carbonyl function. The deshielding of a methyl or

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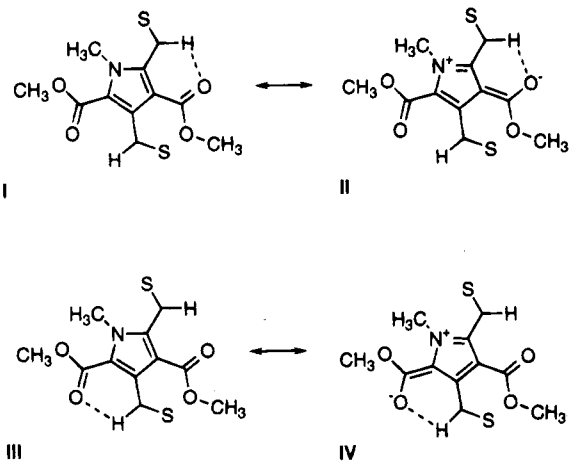
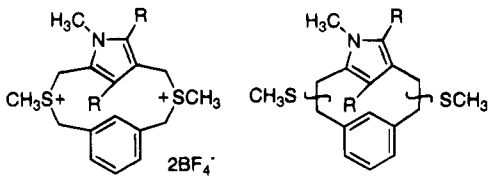


Figure 2. Partial structures of dithiacyclophane **3g** to illustrate the hydrogen bonding phenomenon.

methylene proton at different points in close proximity to a carbonyl function of an ester[19] or a ketone[20] have, however, been shown to be ≤0.4 ppm in many examples. The O2–$H3_{ax}$ distance (2.359 Å) is slightly longer than that of O4–$H9_{ax}$ (2.221 Å) in **3g** (Figure 1), and both the C3–$H3_{ax}$ and C9–$H9_{ax}$ bonds are held somewhat in the plane of the pyrrole ring. With the C18–O2 carbonyl group (28.6°) deviating significantly more than that of C20–O4 (5.0°) from the pyrrole ring, the deshielding effect on $H9_{ax}$ is expected to be relatively larger than that experienced by $H3_{ax}$. In an NOE experiment, irradiation at the *N*-methyl signal at δ 3.37 (shielded by the opposite *syn* benzene ring) clearly enhanced the aromatic signals of H14 and H15 and the doublet at δ 3.20 which corresponds to $H3_{eq}$. The other protons were assigned on the basis of a ^{1}H NMR COSY spectrum and several other NOE experiments. Thus, $H3_{ax}$ is unexpectedly shifted 0.6 ppm further downfield than $H9_{ax}$ (Table 1).

Examples of hydrogen bonding involving a sp^3 CH group are rare[21] but well supported by spectroscopic[22] and crystallographic[23] evidence. Qualitatively, $H3_{ax}$ and $H9_{ax}$ in **3g** are "benzylic" protons adjacent to a sulfur atom. The O2–$H3_{ax}$ and O4–$H9_{ax}$ distances are also reasonably short contacts for intramolecular hydrogen bonding.[23] In addition, the basicity of either carbonyl oxygen in **3g** would be increased due to conjugation with the pyrrole ring (refer to resonance structures **II** and **IV**; Figure 2). Thus, a novel hydrogen bonding between the carbonyl oxygen of the ester group at C8 and $H3_{ax}$ would be expected to result in a relatively larger observed deshielding. Indirectly, such a hydrogen bonding would also lead to a significant upfield shift of $H3_{eq}$ due to an increase in electron density on C3. In fact $H3_{eq}$ (δ 3.20) is shifted 0.8 ppm upfield relative to $H9_{eq}$ (δ 4.01; Table 1). There are examples of effective shielding of protons situated above a carbonyl group,[24] but the proton concerned is expected to be in close proximity to the carbonyl function (<2 Å).[17a] The O2–$H3_{eq}$ distance is 3.773 Å, and thus the anisotropic effect of the carbonyl group alone would be unable to account for the large observed shielding. The bond lengths of the C18–O2 (1.189 Å) and C20–O4 (1.191 Å) bonds are found to be very similar in the crytallographic structure of **3g**. Thus, the hydrogen bonding discussed above is believed to be a novel chemical property of **3g** in solution. This is also to our knowledge the first example of a hydrogen bonding involving such relatively "nonacidic" protons. A variable-temperature study in the range of 35–140 °C showed no appreciable change in chemical shift or broadening of peaks. This clearly suggests that **3g** is likely to adopt the indicated conformation in solution. The FTIR spectrum of **3g** in solution ($CHCl_3$) shows only one broad C=O absorption at 1695 cm^{-1} similar to values observed for **4g**, **5d**, and **5e**. Although a shift of the C=O absorption to a lower wavenumber has been observed in examples involving strong O–H···O=C hydrogen bonding,[25] there has been no reported evidence for such an observable shift in weaker C–H···O=C systems.

Dithiacyclophane **3g** was methylated to give the bissulfonium salt **8**. Stevens rearrangement of **8** in the presence of NaH[10] afforded the corresponding rearranged product **9** as a mixture of isomers. The general structure of **9** was supported by a molecular ion at *m/z* 419 and a set of singlets at δ 2.1–2.2 for SCH_3 protons in the mass and ^{1}H NMR spectra, respectively. Desulfurization[10,26] of **9** with Raney nickel[27] afforded [2$_2$]cyclophane **4g**.



8, R = CO_2CH_3 **9**, R = CO_2CH_3

The H8(H16) (δ 4.29)[28] of *anti* [2$_2$](1,3)cyclophane **10** and H15 (δ 4.63)[6] of *anti* thiophenophane **4a** were reported to be highly shielded. The H15 of **4g** (Figure 3a) is also significantly shifted upfield to δ 4.92 clearly indicating that **4g** exists as the *anti* isomer. The above results observed for **3g** and **4g** are comparable to reported examples which exhibit an abrupt change in conformational preference going from a rigid *syn* [3.3]phane to an *anti* [2.2]phane.[29] An X-ray crystallographic analysis of **4g** (Figure 3) confirmed that it adopts the *anti* conformation in the solid state. From the sectional view (Figure 3b), C15 and C12 are raised above the mean plane formed by C10, C11, C13, and C14 by 10.0° and 4.3°, respectively (Table 2) giving the benzene ring a boatlike conformation. The pyrrole ring is bent like an envelope with C7 tilted at 8.3°. These values are quite comparable to those (Table 2) observed for the related [2$_2$]metacyclophane

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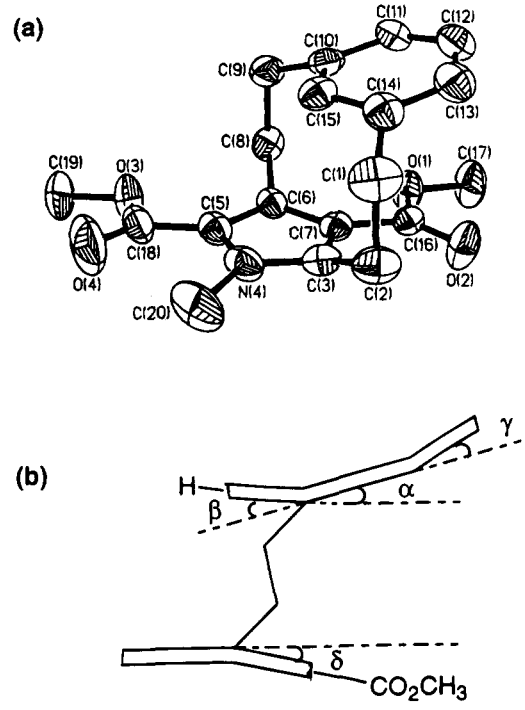


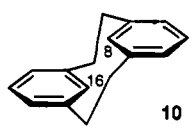
Figure 3. (a) Crystal structure (ORTEP) and (b) sectional view of cyclophane **4g**.

Table 2. Angles of Distortion in Selected [2$_2$](1,3)Cyclophanes

phane	α^a (deg)	β^a (deg)	γ^a (deg)	δ^a (deg)
4g	11.8	10.0	4.3	8.3
10[23]	0	11.8	3.4	
11[5]	2.7	13.0	2.6	9.7

[a] Refer to angles indicated in Figure 3b.

(**10**)[30] and [2]metacyclo[2]thiophenophane (**11**).[5] The ben-



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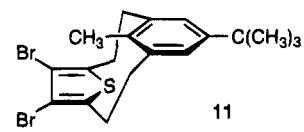

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zene and pyrrole rings in **4g** are, however, inclined at 11.8° with respect to each other—an angle much larger than the corresponding one observed for **11** (Table 2). It is believed that the steric demand of the ester group at C7 results in such significant deviation. The larger ring inclination angle in this case minimizes the steric interaction between the ester group at C7 and the opposite benzene ring.

Both the ester groups at C5 and C7 in **4g** are almost coplanar to the pyrrole ring in the crystallographic structure. The methoxy protons of the "internal" ester group at C7 are clearly still located in the shielding zone of the opposite *anti* benzene ring, being shielded to δ 3.35 compared to those (δ 3.91) of the "external" ester group at C5. An NOE experiment carried out with irradiation at the signal at δ 3.35 resulted in enhancement of all three aromatic signals of H11, H12, and H13, indicating that the ester group at C7 is likely to exhibit unrestricted free rotation in solution. The other protons of **4g** were readily assigned (see Experimental Section) by a series of NOE and decoupling experiments. The O2–H2$_{ax}$ (2.344 Å) and O2–H2$_{eq}$ (3.758 Å) distances in **4g** (Figure 3) are very similar to the corresponding O2–H3$_{ax}$ (2.344 Å) and O2–H3$_{eq}$ (3.758 Å) distances in **3g**. It was, however, noted that there is no unusually shielded or deshielded methylene proton. Methylene protons at C2 and C8 are relatively shifted downfield as expected from the anisotropic effects of the respective carbonyl groups. This is an indirect evidence to support the presence of a novel hydrogen bonding between O2 and H3$_{ax}$ in **3g**.

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Experimental Section

All melting points were determined with a GALEN III hot stage microscope and are uncorrected. ^{1}H NMR spectra were determined in $CDCl_3$ (unless otherwise stated) on a Bruker ACF300 (300 MHz) or AMX500 (500 MHz) spectrometer. All proton chemical shifts are reported in ppm downfield from TMS, which was used as an internal standard. EIMS was determined on a VG Micromass 7035 mass spectrometer at 70 eV. Relative intensities are given in parentheses. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore. All evaporations were carried out under reduced pressure on a rotary evaporator at about 40 °C, and all organic layers were washed with water (unless otherwise stated) and dried with anhydrous $MgSO_4$.

Dimethyl *N*-3,5-Trimethylpyrrole-2,4-dicarboxylate (5d). Powdered KOH (2.0 g, 30 mmol) and $(n\text{-Bu})_4NHSO_4$ (0.6 g, 1.8 mmol) were added to a stirred solution of compound **5c**[8] (4.0 g, 19 mmol) in CH_2Cl_2 (200 mL) at 0 °C. To the suspension was added dropwise a solution of CH_3I (3.5 g, 25 mmol) in CH_2Cl_2 (50 mL) in a period of 0.5 h. Stirring was continued for 4 h. The reaction mixture was poured into ice–water (300 mL). The organic layer was washed, dried, and evaporated. The residue was chromatographed on silica gel with CH_2Cl_2 as eluent to give 3.7 g (87%) of compound **5d**: mp 123–124 °C; IR (KBr) 1690, 1435,1390, 1270, 1255, 1115, 1095, 770 cm^{-1}; ^{1}H NMR δ 3.84, 3.81 (s, 6 H), 3.78 (s, 3 H), 2.52, 2.51 (s, 6 H); MS, *m/z* 225 (M^+, 90), 194 (100), 178 (20), 166 (22). Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.57; H, 6.74; N, 6.10.

Dimethyl *N*-Methyl-3,5-bis(bromomethyl)pyrrole-2,4-dicarboxylate (5e). A solution of compound **5d** (2.0 g, 8.9 mmol) in CCl_4 (150 mL) was kept at solvent refluxing temperature by using a 200 W light source. *N*-Bromosuccinimide (3.2 g, 18 mmol) and a catalytic amount of benzoyl peroxide were added, and the irradiation was continued for 2 h. The organic layer was washed with water, dried, and evaporated to give 3.3 g (95%) of compound **5e**: mp 157–158 °C; IR (KBr) 1700, 1500, 1470, 1440, 1286, 1256, 1220, 1195, 1120, 800 cm^{-1}; ^{1}H NMR δ 5.07, 4.91 (s, 4 H), 3.95 (s, 6 H), 3.93 (s, 3 H); MS *m/z* 381/383 (M^+, 6), 302/304 (100), 223 (70). Anal. Calcd for $C_{11}H_{13}Br_2NO_4$: C, 34.49; H, 3.42; N, 3.65. Found: C, 34.69; H, 3.43; N, 3.50.

Dimethyl *syn*-2,10-Dithia[3](1,3)cyclo[3](2,4)pyrrolophane-6,8-dicarboxylate (3g). To a solution of KOH (0.94 g, 16.8 mmol) in 95% EtOH (1 L) under N_2 was added dropwise a solution of compound **5e** (2.01 g, 5.25 mmol) and bis(mercaptomethyl)benzene[10] (0.89 g, 5.25 mmol) in benzene (200 mL) over a period of 6 h. After the addition, the solution was further stirred for 14 h. The solvent was evaporated under reduced pressure and the resulting residue was taken up in CH_2Cl_2 and chromatographed on silica gel using CH_2Cl_2 as eluent to afford 1.93 g (56%) of the dithiacyclophane **3g**. Recrystallization from EtOH/CH_2Cl_2 gave colorless crystals of **3g**: mp 147–148 °C; FTIR ($CHCl_3$) 3566, 3027, 3007, 2952, 1695, 1544, 1482, 1439, 1415, 1379, 1276, 1249, 1217, 1197, 1156, 1128, 1117, 1084, 975, 787, 763, 720, 665 cm^{-1}; ^{1}H NMR δ 7.14 (d, J = 7.5 Hz, 1 H), 7.06 (t, J = 7.5 Hz, 1 H), 6.94 (s, 1 H), 6.68 (d, J = 7.5 Hz, 1 H), 3.96, 3.81 (s, 6 H), 3.37 (s, 3 H); ^{13}C NMR δ 166.13, 160.99, 138.22, 137.85, 136.91, 131.42, 127.76, 127.56, 126.08, 125.09, 122.12, 115.40, 51.44, 50.92, 36.71, 35.52, 33.22, 27.96, 24.99; MS *m/z* 391 (M^+, 70), 359 (10), 286 (15), 254 (100), 224 (55). Anal. Calcd for $C_{19}H_{21}$-

NO_4S_2: C, 58.29; H, 5.41; N, 3.58; S, 16.38. Found: C, 58.43; H, 5.39; N, 3.84; S, 16.12.

Stevens Rearrangement of 3g. A solution of compound **3g** (1.30 g, 3.32 mmol) in CH_2Cl_2 (25 mL) was cooled to −40 °C under N_2. $(CH_3O)CHBF_4$[31] (1.72 g, 11.6 mmol) was added to the solution via a syringe. The mixture was stirred at −40 °C for 20 min followed by 14 h at room temperature. AcOEt (25 mL) was then added to the mixture, and stirring was continued for 2 h. The white precipitate was filtered, washed with AcOEt, and dried under vacuum to give 1.58 g (80%) of bis(sulfonium) salt **8** which was used directly without further purification.

The salt **8** was suspended in dry THF (40 mL). NaH (0.36 g, 15 mmol) was added and the mixture stirred at room temperature for 10 h. $NaHCO_3$ (3.0 g) was then added slowly to destroy excess NaH. CH_2Cl_2 was added to the mixture, and the organic layer was separated, washed, dried, and evaporated. The residual brown oil was chromatographed on silica gel using CH_2Cl_2 as eluent to give 0.81 g (58%) of a mixture of isomers of **9** as a yellow oil: IR (neat) 1695, 1520, 1480, 1440, 1250, 1110, 780 cm^{-1}; ^1H NMR δ 7.41 (d, J = 7.6 Hz, 1 H), 7.16 (dd, J = 7.6, 7.8 Hz, 1 H), 7.04 (d, J = 7.8 Hz, 1 H), 5.35 (dd, J = 10.5 Hz, 1 H), 5.18 (s, 1 H), 4.31, 3.95 (s, 6 H), 3.6–3.9 (m, 4 H), 3.40 (s, 3 H), 3.1–3.3 (m, 2 H), 2.17 (dd, J = 12.2 Hz, 1 H), 2.30, 2.16 (s, 6 H); MS m/z 419 (M^+, 100), 372, 324. M_r calcd for $C_{21}H_{25}NOS_2$ 419.1237, found (MS) 419.1225.

Dimethyl *anti*-[2](1,3)Cyclo[2](2,4)pyrrolophane-5,7-dicarboxylate (4g). A solution of compound **9** (0.30 g, 0.72 mmol) in absolute EtOH (30 mL) containing excess W-7 Raney nickel[32] was heated at solvent refluxing temperature for 2 h. After removal of the catalyst by filtration, the filtrate was concentrated. The resulting residue was chromatographed on silica gel using CH_2Cl_2 as eluent to give 0.20 g (85%) of cyclophane **4g**. Recrystallization from EtOH gave colorless crystals of **4g**: mp 151–152 °C; IR (KBr) 1685, 1520, 1450, 1250, 1110, 790 cm^{-1}; ^1H NMR δ 7.04 (t, J = 7.4 Hz, 1 H), 6.94–6.96 (m, 2 H), 4.92 (s, 1 H), 3.97 (s, 3 H), 3.91 (s, 3 H), 3.76–3.91 (m, 1 H), 3.54–3.58 (m, 1 H), 3.45–3.51 (m, 1 H), 3.35 (s, 3 H), 2.98–3.20 (m, 1 H), 2.87–2.92 (m, 2 H), 2.45–2.51 (m, 1 H), 2.36–2.42 (m, 1 H); MS m/z 327 (M^+, 55), 268 (100), 209 (70). Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.62; H, 6.35; N, 4.14.

Crystallograhic Section. 3g: $C_{19}H_{21}NO_4S_2$, M_w = 391.5; monoclinic; space group $C2/c$; a = 24.992(4) Å, b = 10.330(3) Å, and c = 17.389(5) Å; β = 122.71(2)°; V = 3777.4(17) Å^3; Z = 8; d_c = 1.377 g cm^{-3}, d_m = 1.34 g cm^{-3}; μ = 0.306 mm^{-1}; $F(000)$ = 1648; T = 295 K. **4g:** $C_{19}H_{21}NO_4$, M_w = 327.4; monoclinic; space group $P2_1/c$; a = 16.543(5) Å, b = 7.353(2) Å, and c = 13.473(3) Å; β = 96.14(2)°; V = 1629.5(7) Å^3; Z = 4; d_c = 1.334 g cm^{-3}, d_m = 1.32 g cm^{-3}; μ = 0.094 mm^{-1}; $F(000)$ = 696; T = 295 K. The author has deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Data collection: diffractometer, Siemens R3m/V; radiation, Mo Kα (0.710 73 Å), 30 mA, 50 kV; monochromator, graphite; data collecting mode, $\omega - 2\theta$ scan; data sets corrected for Lorentz and polarization effects, absorption correction not applied. **3g:** crystal size 0.20 × 0.25 × 0.35 mm; 2θ range 2.5 to 50.0°; index range $0 \le h \le 29$, $0 \le k \le 12$, $-10 \le l \le 17$; number of reflections, 3336 (independent), 2497 ($F > 3\sigma(F)$). **4g:** crystal size 0.23 × 0.20 × 0.32 mm; 2θ range 2.5 to 55.0°; index range $-21 \le h \le 21$, $-9 \le k \le 0$, $0 \le l \le 17$; number of reflections, 3755 (independent), 2359 ($F > 3\sigma(F)$).

Structure analysis: solution direct methods; method of refinement, full matrix least squares; software Siemens SHELX-TL PLUS (VMS); computer DEC MicroVax II; anisotropic thermal parameters for all non-H atoms and riding model for hydrogen atoms with fixed isotropic U. **3g:** number of parameters refined 236; R = 0.040, R_w = 0.053; final Fourier difference map 0.28 and −0.30 e Å^{-3}. **4g:** number of parameters refined 218; R = 0.060, R_w = 0.064; final Fourier difference map 0.25 and −0.22 e Å^{-3}.

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(32) See ref 27.