ENCOUNTER OF AN INFERIOR INTRAMOLECULAR CYCLIZATION IN AN APPROACH TOWARD THE SYNTHESIS OF 10-OXO-2-THIA[3.2]METACYCLOPHANE: PREPARATION OF TWO ISOMERIC DIOXO-2,19-DITHIA[3.2.3.2]METACYCLOPHANES

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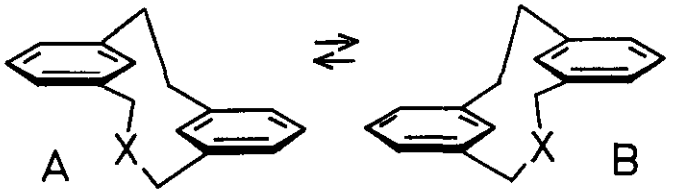
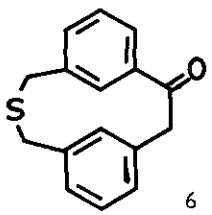
Abstract - *The sodium sulfide coupling of 1,2-bis(3-bromomethyl)phenylethanone, prepared in seven steps from m,α-dichlorotoluene, was attempted but failed to yield the desired 10-oxo-2-thia[3.2]metacyclophane. This is attributed to unfavorable geometry in the thiacyclophane due to introduction of the sp^2 carbonyl carbon. Two isomeric dioxo-dithia[3.2.3.2]metacyclophanes were however isolated from the coupling reaction. Both these cyclophanes were found to be conformationally highly mobile by variable-temperature NMR studies.*

Conformational behaviour of [3.2]metacyclophanes **1** - **5** have been studied[1-3] and interpreted in terms of the anti-anti interconversions **A** ⇄ **B**. Dynamic interconversions in the parent system **1** involve a conformational barrier of 73 kJ mol^{-1}.[1] Conformational studies[2] of the derivatives **2** showed that the energy barrier is dependent upon the steric nature of the substituent with energy barriers of 66-80 kJ mol^{-1}. The replacement of a $-CH_2-$ unit with a sulfur atom as in **3** makes the interconversions even easier compared to **1** and the barrier was estimated to be about 35 kJ mol^{-1}.[3] This lowering of the energy barrier is probably due to the increase in bond length of the C-S-C bridge. Formations of the corresponding sulfoxide **4** and sulfone **5** seem to progressively increase the conformational barrier[3] possibly due to a result of steric interactions and more rigid sulfur centers.

Our interest lies in the effect on the conformational barrier in the [3.2]meta-



	X
1	CH_2
2	CHR
3	S
4	S=O
5	SO_2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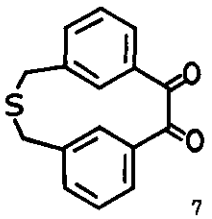
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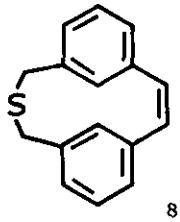
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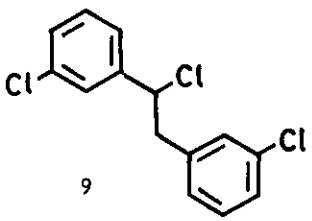
cyclophane system due to a change in the nature of the shorter bridge. The thia[3.2]metacyclophane 3 is chosen as the reference. Whether the cyclophane undergoes the anti-anti interconversions and/or dynamic motions of the longer bridge, the C-S-C bridge of 3 has an advantage over the C-C-C bridge of 1 in simplifying the ^{1}H-nmr conformational studies of these [3.2]metacyclophanes.[4] The $-CH_2S-$ protons in 3 appear as a singlet at high temperatures when the interconversions are rapid and an AB quartet when one conformer is 'frozen' at low temperatures. The oxo derivative 6 seems a good model to illustrate the effect on the geometry and conformational barrier due to a change from a sp^3 to a sp^2 center at the shorter bridge. It could also serve as a precursor to the dioxo derivative 7 and the cyclophan-ene 8, the conformational studies of which should provide more interesting results for comparison. As the coupling of dibromides with sodium sulfide has been successfully employed in the preparation of a large number of thiacyclophanes,[5] our aim was to study the coupling of 12 to form the desired 10-oxo-2-thia[3.2]metacyclophane 6.

Treatment[6] of m,α-dichlorotoluene with half an equiv of n-butyllithium in dry THF at -80°C yielded the trichloride 9 which was not isolated but allowed to undergo further elimination with t-BuOK to give 10. The hydroboration[7] of 10 proceeded readily with diborane generated in situ from $NaBH_4$ and $BF_3.Et_2O$. Oxidation of organoboranes with chromic acid is usually carried out at solvent refluxing temperatures. Such conditions, however, may be too vigorous for the oxidation of the organoborane derived from 10 to yield the ketone 11 as phenyl benzyl ketone and its derivatives are known to undergo oxidative cleavage in chromic acid under similar conditions.[8] Thus the organoborane derived from 10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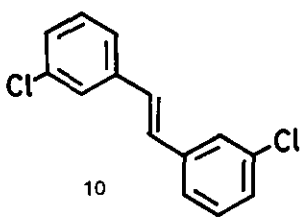
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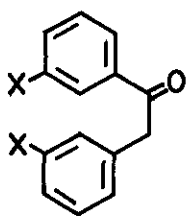
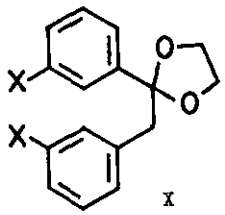


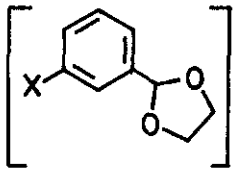
	X
11	Cl
12	CH_2Br

was treated with chromic acid at room temperature. The ir spectrum of the product mixture thus obtained showed a rather weak absorption at 1700 cm^{-1} and a strong absorption at 3400 cm^{-1}, clearly indicating incomplete oxidation. Further addition of chromic acid to a solution of the product mixture in acetone, however, afforded good yields (60-80%) of the desired ketone 11, mp 60-62°C. The mass spectrum of 11 recorded gave a very weak molecular ion at m/z 264 (3%) with a base peak at m/z 139 ($^{35}ClC_6H_4CO$) indicating a facile fragmentation at the $CO-CH_2$ bond.

As reducing agents DIBAL and $NaBH_4$ would be employed in the subsequent steps of our synthetic route, the carbonyl function of 11 was first protected. The ketal 13, obtained as a colorless oil, was readily formed by refluxing 11 with ethylene glycol in benzene in the presence of p-toluenesulfonic acid. The conversion of the dichloride 13 to the dinitrile 14 was achieved by the von Braun reaction using Cu(I)CN in refluxing N-methyl-2-pyrrolidinone. The desired product 14, mp 86-88°C, was however obtained only in low yields (20-35%) after chromatography. The characteristic strong absorption of C≡N at 2220 cm^{-1} was observed in the ir spectrum of 14. Reduction of the dinitrile 14 to the dialdehyde 15 was carried out with DIBAL in benzene. The dialdehyde 15, isolated as a colorless oil, showed the -CHO protons as two separate singlets at δ9.92 and 9.96 in its ^{1}H-nmr spectrum resulting from the unsymmetrical structure of 15. Further reduction of the dialdehyde 15 with $NaBH_4$ in THF led to the diol 16 in 70% yield. The two different $-CH_2OH$ protons were again clearly resolved at δ4.52 and 4.56 respectively in the ^{1}H-nmr spectrum. The ketals 13, 15 and 16 were all obtained as viscous oils which could not be crystallised. Attempted purification by repeated chromatography on silica gel seemed to cause partial hydrolysis of the ketal group. Thus no satisfactory micro-analytical data could be obtained. All IR and nmr spectral data obtained are however consistent with the respective structures. In the respective mass spectra of 13 - 16, no or very weak (<3%) molecular ion peaks were observed even when the mass spectra were determined at 10-15 eV with electron impact. Thus no accurate masses of the respective molecular ions could be determined by high resolution mass spectroscopy. All these molecules showed an easy cleavage of the bridging chain to give a base peak corresponding to the fragment of the general structure 17. We believe that this cleavage might have also occurred thermally in the conversion (refluxing N-methyl-2-pyrrolidinone, bp 202°C) of 13 to 14 which accounts for



	X
13	Cl
14	CN
15	CHO
16	CH_2OH



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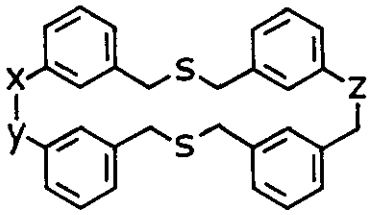
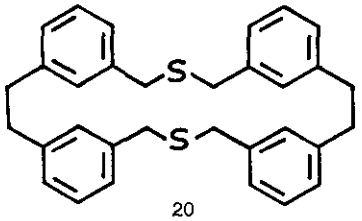


	X	Y	Z
18a	C=O	CH_2	C=O
18b	CH_2	C=O	C=O
19	CH_2	CH_2	CH_2



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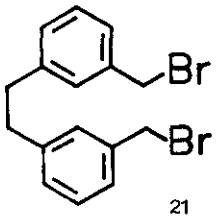

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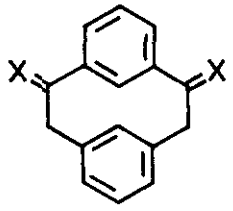

22 X = O

23 X = H_2

the low yields of 14 obtained in all our attempts. Similar thermal cleavage in a tetraphenylethane derivative under similar conditions has also been observed.[9]

Treatment of the diol 16 with PBr_3 in benzene yielded directly, although unexpectedly, the desired dibromide 12 in a 64% yield. The removal of the protecting ketal group, probably due to hydrolysis under the acidic condition during work-up (excess PBr_3 was used in our attempt), was apparent from the absence of the C-O-C stretch and the appearance of an intense C=O absorption at 1660 cm^{-1} in the IR spectrum. The $-CH_2Br$ protons appeared again as separate singlets at δ4.47 and 4.51 respectively in the ^1H-nmr spectrum. A weak molecular ion at m/z 380 ($C_{16}H_{14}{}^{79}Br_2O$) with a correct 1:2:1 pattern for two bromines was observed in the mass spectrum. An easy fragmentation at the CH_2-CO bond was indicated by the base peak at m/z 197 with a correct 1:1 isotope pattern for one bromine.

Having obtained the desired precursor 12, an attempt was made to obtain the thiametacyclophane 6 using sodium sulfide coupling under high dilution conditions.[5] Column chromatography of the product mixture obtained from the coupling reaction isolated a major fraction (ca. 26%) of colorless crystals (recrystallized from benzene), mp 208-215°C. The high and broad melting point range was rather unexpected although the IR spectrum showed the intense C=O stretching at 1680 cm^{-1}. However, a molecular ion at m/z 508 observed in the

mass spectrum was clearly consistent with a dimeric structure of 18. The broad melting point range recorded thus suggests the presence of both dimers 18a and 18b. This is further supported by the ^{1}H nmr spectrum (see below). T.l.c. studies however indicated identical R_f values for the mixture. Attempts to separate the two isomers by column chromatography also failed.

The ^{1}H nmr spectrum of the mixture 18a and 18b is of some special interests. Besides the aromatic multiplets, a rather broad singlet (half-height linewidth = 3.0 Hz; 4 protons) and four other singlet (total 8 protons) were observed at δ4.33, 3.61, 3.58, 3.53 and 3.50 respectively (Figure 1). The peak at δ4.33 could be readily assigned to the $-COC\underline{H}_2-$ protons; the four types of $-C\underline{H}_2S-$ protons, on the other hand, fully supports the presence of the two isomers 18a and 18b. The $-C\underline{H}O$, $-C\underline{H}_2OH$ and $-C\underline{H}_2Br$ protons of 15, 16 and 12 respectively all showed two separate singlets with Δδ = 0.04 ppm. By analogy, we have assigned the two singlets at δ3.61 and 3.58 (Δd = 0.03 ppm) and those at δ 3.53 and 3.50 (Δδ = 0.03 ppm) as the two separate pairs of $-C\underline{H}_2S-$ protons, although assignments of each of these pairs to isomer 18a or 18b would be rather impossible from the data in hand. The integration of these signals suggests that the population ratio of 18a to 18b would be close to 1. The broad peak at δ4.33, we believe, is due to almost identical chemical shifts of the respective $-COC\underline{H}_2-$ protons of the two isomers.

The [3.2.3.2]metacyclophanes 18a and 18b, having 22-membered macrorings, are expected to exist in various conformations. The fact that the $-COC\underline{H}_2-$ and $-C\underline{H}_2S-$ protons of these isomers, as mentioned earlier, appeared as singlets in the ^{1}H nmr spectrum at room temperature would indicate easy and rapid conformational interconversions. In principle, these protons are expected to appear as AB quartets if a single conformation for each isomer is frozen at low temperatures to enable estimation of the energy barriers.[10] An attempt was thus made to study the degree of conformational mobility of the mixture of 18a and 18b using variable ^{1}H nmr spectroscopy. Although peak broadening was clearly observed for the $-COC\underline{H}_2-$ and $-C\underline{H}_2-$ protons (Figure 1), complete coalescence of peaks was not observed even at -100^oC indicating a very high degree of conformational mobility. This is however not unexpected. Although 18a and 18b represent the first reported examples of dithia[3.2.3.2]metacyclophane with the parent 19 still unknown, conformational studies[11] of the related dithia[3.1.3.1]metacyclophane 20 have revealed that such a system is conformationally

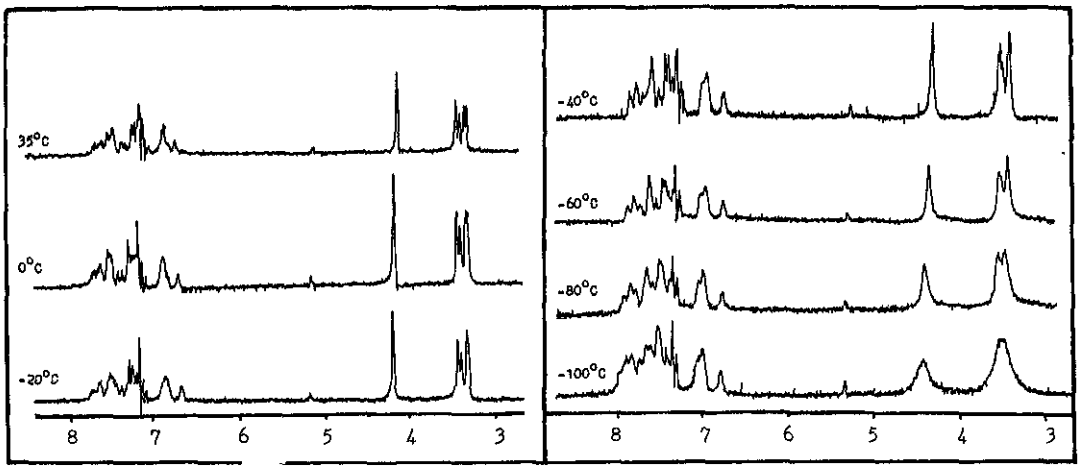

FIGURE 1. Variable temperature ^{1}H-nmr spectra [$CDCl_3/CD_2Cl_2$ (1:1); 90 MHz)] of the dioxo-dithia[3.2.3.2]metacyclophanes 18a and 18b.

too mobile to freeze the interconversion processes even at very low temperature. A similar coupling reaction of the dibromide 21 was reported[3] to successfully afford a 30% yield of the thiametacyclophane 1. However, altering the bridging centers of the [2.2]metacyclophane 22 to dioxo[2.2]metacyclophane 23 is known[12] to result in a less favorable (stable) geometry. Thus we believe that the failure in our attempt to obtain the monomer 6, coupled with a fair isolated yield of the dimers 18a and 18b, indicate that the oxo-thiametacyclophane 6 may also have an unfavorable geometry compared to the parent 1 due to the introduction of the carbonyl function. This would then discourage the intramolecular coupling of 12 to yield 6. Apparently, the much larger and flexible macrorings in the dimers 18a and 18b could however tolerate the increased geometric strain induced by changing the bridging carbons from sp^3 to sp^2 centers. This information, we believe, would be valuable in the future synthetic designs of new cyclophanes.

EXPERIMENTAL

All melting points were deterimined on a Sybron/Thermolyne MP12615 melting point apparatus and are uncorrected. The ^{1}H-nmr spectra were determined in $CDCl_3$ on a Perkin Elmer R32 (90 MHz) nmr spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane as internal standard. The IR spectra were recorded on a Perkin Elmer 1310 spectrophotometer. All strong and medium absorptions are coded. Mass spectra were determined on a VG Micromass 7035 mass spectrometer at 70 eV using electron impact. Only the molecular ion containing ^{35}Cl, or ^{79}Br is given for compounds containing these halogens. Correct isotope patterns were obtained in all cases. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore.

trans-1,2-Bis(3-chlorophenyl)ethene 10 — m, α -Dichlorotoluene (25.0 g, 155.3 mmol) in dry THF (400 ml) was cooled to -80°C under nitrogen. A solution of n-BuLi (1.5M; 82.1 mmol) in hexane was slowly added. After 5 h, the cooling bath was removed and the reaction mixture allowed to warm to room temperature. t-BuOK (11.39 g, 155 mmol) was added and the reaction mixture heated at reflux for 5 h. Sufficient water (200 ml) was added and the mixture was extracted with dichloromethane. All organic portions were combined, washed, dried and evaporated to give a pale yellow solid. It was chromatographed on silica gel using n-hexane as eluent to yield the stilbene 10, 15.5 g (80%). Recrystallization from n-hexane yielded colorless crystals, mp 94-95°C (lit.[13] 94-95°C). ^{1}H-Nmr 7.1-7.6 (m, 8H, ArH), 7.02 (s, 2H, -CH=CH-); Ir (KBr) 1600, 1565, 1475, 1430, 1320, 1240, 1225, 1080, 995, 970 (trans -CH=CH-), 890, 870, 770, 680 cm^{-1} ; ms m/z 248 (76), 213 (24), 212 (26), 178 (100), 177 (29), 176 (22), 107 (13), 106 (24). Anal. Calcd for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05. Found: C, 67.28; H, 3.84.

1,2-Bis(3-chlorophenyl)ethanone 11 — A solution of stilbene 10 (13.20 g, 53.0 mmol) in dry THF (250 ml) was added dropwise to sodium borohydride (3.01 g, 79.5 mmol) under nitrogen. The flask was cooled in a water bath and hydroboration was initiated by dropwise addition of borontrifluoride etherate (13.5 ml, 105.6 mmol) to the well-stirred suspension over a period of 5 h. Sufficient water was then added to dissolve the residual hydride. Chromic acid solution, prepared from sodium dichromate dihydrate (12.22 g) and 96% sulfuric acid (9.7 ml), and diluted with water to 50 ml, was slowly added to the stirred solution until a permanent orange color persisted. The mixture was extracted with dichloromethane. All organic portions were combined, washed with saturated sodium chloride solution and evaporated to give an oil. Incomplete oxidation was evident from the IR spectrum of the crude product. A solution of the mixture in acetone was further oxidised with chromic acid to yield, after usual work-up, a yellow solid Chromatography on silica gel using dichloromethane/hexane (1:3) as eluant gave the desired ketone **11**, 11.41 g (81%). Recrystallization from n-hexane gave colorless crystals of **11**, mp 60-62°C. ^{1}H Nmr δ 7.0-8.0 (m, 8H, ArH), 4 20 (s, 2H, -$COCH_2$-); Ir (KBr) 1690 (C=O), 1600, 1575, 1480, 1420, 1330, 1285, 1260, 1220, 1205, 1510, 1100, 1080, 1025, 1000, 900, 870, 830, 790, 740, 690 cm^{-1}; ms m/z 264 (3), 141 (89), 140 (22), 139 (100), 125 (11), 113 (23), 111 (66) Anal. Calcd for $C_{14}H_{10}OCl_2$: C, 63.42; H, 3.80. Found: C, 63.36; H, 3.72.

Ketal of 1,2-Bis(3-chlorophenyl)ethanone 13 — Ethylene glycol (27.96 g, 450.5 mmol) and traces of p-toluenesulfonic acid were added to a solution of the ketone **11** (23.90 g, 90.1 mmol) in benzene. The mixture was heated at reflux in a Dean-Stark apparatus for 5 h. After cooling to room temperature, the mixture was washed with water, dried and evaporated to give the ketal **13** as a colorless oil (23.82 g, 86%) ^{1}H Nmr δ 6.9-7.6 (m, 8H, ArH), 3.6-3.9 (m, 4H, -OCH_2-), 3.08 (s, 2H, $ArCH_2$-); Ir (neat) 1600, 1570, 1470, 1430, 1320, 1290, 1250, 1210, 1180, 1150, 1090, 1075, 1040, 1015, 950, 880, 850, 790, 735, 700, 680, 660 cm^{-1}; ms m/z 183 (100), 140 (23), 139 (66), 125 (12), 111 (25).

Ketal of 1,2-Bis(3-cyanophenyl)ethanone 14 — Copper(I) cyanide (14.20 g, 158.6 mmol) was added to a solution of **13** (9.16 g, 29.6 mmol) in N-methyl-2-pyrrolidinone (60 ml) and the reaction mixture heated at reflux. After 12 h, a further portion of CuCN (14.20 g) was added and the reflux continued for another 12 h. After cooling to ca. 100°C, the reaction mixture was poured into a mixture of ice (100 g) and ammonia (100 ml). After mixing thoroughly, the mixture was filtered and the residue extracted with dichloromethane thoroughly. The combined organic phase was washed, dried and evaporated. The resulting brown residue was chromatographed on silica gel using dichloromethane as eluant to yield **14**, 2.90 g (34%). Recrystallization from cyclohexane afforded colorless crystals of **14**, mp 86-88°C. ^{1}H Nmr δ 7.2-8.5 (m, 8H, ArH), 3.7-3.9 (m, 4H, -OCH_2-), 3.16 (s, 2H, $ArCH_2$-); Ir (KBr) 2220 (C=N), 1600, 1580, 1470, 1420, 1330, 1270, 1230, 1170, 1080, 1040, 1020, 980, 940, 900, 845, 820, 800, 755, 700, 670 cm^{-1}; ms m/z 174 (100), 130 (61), 102 (23). Anal. Calcd for $C_{18}H_{18}O_2N_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.76; H, 4.69; N, 9.82.

Ketal of 1,2-Bis(3-formylphenyl)ethanone 15 — Diisobutylaluminum hydride (14.5 ml, 14.5 mmol) was added dropwise under nitrogen to a solution of the dinitrile **14** (1.72 g, 5.9 mmol) in dry benzene (75 ml) at room temperature. After 12 h, the solution was decomposed slowly (ice-bath cooling) with methanol (5 ml), then by addition of methanol/water (1:1; 10 ml) and finally with conc. HCl/water (2:1) until the resultant solution was slightly acidic. The mixture was extracted with dichloromethane. The organic layer was washed, dried and evaporated to give **15** as a pale yellow oil, 1.46 g (84%). ^{1}H Nmr δ9.92, 9.96 (s,

total 2H, -CHO), 7.2-8.0 (m, 8H, ArH), 3.7-3.9 (m, 4H, $-OCH_2-$), 3.26 (s, 2H, $ArCH_2-$); Ir (neat) 1700 (C=O), 1605, 1590, 1480, 1440, 1390, 1320, 1300, 1290, 1280, 1245, 1200, 1180, 1160, 1140, 1090, 1040, 1010, 950, 920, 850, 800, 710, 690, 660, 630 cm^{-1}, ms m/z 177 (100), 174 (17), 138 (21), 134 (21), 119 (19), 105 (28).

Ketal of 1,2-Bis(3-hydroxymethyl)phenylethanone 16 — A solution of the dialdehyde **15** (1.48 g, 5 mmol) in dry THF (75 ml) was added dropwise to a stirred slurry of $NaBH_4$ (378 mg, 10 mmol) in THF (5 ml) at room temperature under nitrogen. After 12 h, the mixture was decomposed with conc. HCl/water (1:1) until it was slightly acidic. The aqueous layer was saturated with NaCl and extracted with dichloromethane. The organic layers were combined, dried and evaporated to give the dialcohol **16** as a colorless oil, 1.24 g (83%). ^1H Nmr 6.8-7.5 (m, 8H, ArH), 4.52, 4.56 (s, total 4H, $-CH_2OH$), 3.7-3.9 (m, 4H, $-OCH_2-$), 3.16 (s, 2H, $ArCH_2-$); Ir (neat) 3380 (O-H), 1600, 1480, 1360, 1310, 1260, 1170, 1040, 940, 890, 790, 760, 740 cm^{-1}; ms m/z 205 (14), 181 (20), 180 (26), 179 (100), 177 (11), 137 (12), 135 (63), 121 (11), 107 (13).

1,2-Bis(3-bromomethyl)phenylethanone 12 — A solution of PBr_3 (2 ml, 21.3 mmol) in dry benzene (20 ml) was added dropwise to a stirred solution of the dialcohol **16** (1.44 g, 5.6 mmol) in benzene (50 ml) at room temperature. After 12 h, the mixture was decomposed with ice water (25 ml). The organic layer was washed successively with water, $NaHCO_3$ solution and water, dried and evaporated. The resulting oil was chromatographed on silica gel using dichloromethane/hexane (1:1) as eluant to yield the dibromide **12**, 1.12 g (52%). ^1H Nmr δ 7.1-8.0 (m, 8H, ArH), 4.47, 4.51 (s, total 4H, $-CH_2Br$), 4.28 (s, 2H, $-COCH_2-$); Ir (neat) 1660 (C=O), 1600, 1585, 1475, 1440, 1330, 1310, 1280, 1240, 1155, 1080, 1030, 1005, 995, 960, 900, 860, 790, 770, 695 cm^{-1}; ms m/z 380 (3), 301 (16), 197 (100), 169 (19), 117 (57), 111 (70), 104 (25), 103 (12).

10,28-Dioxo-2,19-dithia[3.2.3.2]metacyclophane 18a and 10,27-dioxo-2,19-dithia-[3.2.3.2]metacyclophane 18b — A solution of the dibromide **12** (0.56 g, 1.5 mmol) in dry benzene (40 ml) was added dropwise through a syringe pump at the same rate as a solution prepared by dissolving powdered Na_2S (95%) (0.14 g, 1.8 mmol) in nitrogen-purged water (40 ml) to vigorously stirred 95% ethanol (1 l) under nitrogen over 7 h. The mixture was stirred for a further 12 h and the bulk of the solvent evaporated. Dichloromethane (100 ml) and water (100 ml) were added to the mixture and stirred until all solids dissolved. The organic layer was separated, dried and evaporated. The residue was chromatographed on silica gel using dichloro-methane/hexane (1:1) as eluant to yield a mixture of the isomers **18a** and **18b**, ca. 0.1 g (26 %), mp 208-215°C. ^1H Nmr δ 6.9-8.0 (m, 16H, ArH), 4.33 (s, 4H, $-COCH_2-$), 3.61, 3.58, 3.53, 3.50 (s, total 8H, $-CH_2S-$); Ir (KBr) 1680 (C=O), 1600, 1580, 1430, 1410, 1380, 1320, 1230, 1165, 1150, 1075, 1030, 1000, 990, 930, 895, 820, 795, 770, 720, 680, 660 cm^{-1}; ms at m/z 508 (57), 403 (18), 255 (14), 253 (13), 224 (14), 179 (14), 178 (14), 151 (28). Anal. Calcd for $C_{32}H_{28}O_2S_2$: C, 75.56; H, 5.55. Found, C, 75.31; H, 5.44.

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