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SYNTHESES AND PROPERTIES OF SOME POLYSULPHUR BRIDGED METACYCLOPHANES

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Abstract — 5,7,14,16-Tetrasubstituted hexathia[3.3]metacyclophanes **1**–**4** (R=H, Me, OMe, Cl) have been synthesized by coupling the appropriate dithioresorcinol derivatives with SCl_2 under high dilution conditions. Surprisingly, the reaction of mesitylene-2,4-dithiol with both SCl_2 and S_2Cl_2 gave the isomer hexathia[4.2]metacyclophane **5** and the higher homolog heptathia[4.3]metacyclophane **6**. The reaction of the latter dithiol with CH_2Br_2 afforded the expected 1,3,10,12-tetrathia[3.3]metacyclophane **7**. ^{1}H NMR and mass spectra of compounds **1**–**7** are discussed. ^{1}H NMR spectral properties suggest for these compounds either *syn* or *anti* conformations, depending on the nature of the bridges and the substitution pattern of the constituent aromatic rings.

Electron-releasing substituents confer high thermal stability to polysulphur bridged metacyclophanes, while electron-withdrawing substituents, such as Cl atoms in **4**, strongly promote sulphur extrusion from the bridging chains, affording the corresponding octathia[2.2.2.2]metacyclophane **9**

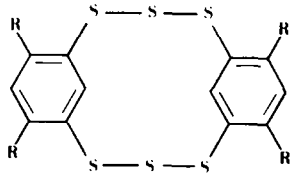
Interest in the synthesis of polysulphur bridged metacyclophanes[1–8] has promoted an insight into the stereochemistry of such compounds and a comparison of their structures and properties with those of corresponding metacyclophanes having hydrocarbon bridges.

In this paper we describe the synthesis and spectral properties of 1,2,3,10,11,12-hexathia[3.3]metacyclophanes **1**–**4**, and of 5,7,9,14,16,18-hexamethyl-1,3,10,12-tetrathia[3.3]metacyclophane **7**, and show the conformational preferences they can arise, due either to the nature of the bridges or to the substitution pattern of the constituent aromatic moieties. In this connexion, the anomalous behaviour of mesitylene-2,4-dithiol in the coupling reaction with sulphur chlorides (SCl_2 and S_2Cl_2) leading to the formation of the unsymmetrical polysulphur bridged metacyclophanes **5** and **6**,[6] has been interpreted in terms of a different stereochemistry of hexathia[3.3]metacyclophanes with respect to structurally related [3.3]metacyclophanes.[9,10]

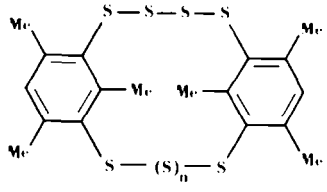
Furthermore, it has been found that electron-releasing substituents, such as Me or OMe groups, confer high thermal stability to polysulphur bridged metacyclophanes on heating in high boiling solvents, while electron-withdrawing substituents, such as Cl atoms in **4**, strongly promote sulphur extrusion from the bridging chains, affording the corresponding octathia[2.2.2.2]metacyclophane **9**.

RESULTS

Syntheses. Hexathia[3.3]metacyclophanes **1**–**4** were prepared according to Fehér's procedure[21] by



1: R = H
2: R = CH_3
3: R = OCH_3
4: R = Cl



5: n = 0
6: n = 1

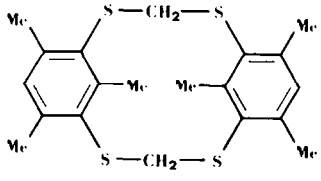


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Table 1. Analytical and physical properties, and ^{1}H NMR parameters (δ ppm) of hexathia[3.3]metacyclophanes 1–4

Compound	M.p. °C [cryst solvent]	Yield, %	Formula (MW)	Sulphur, % Calcd	Found	R	Ext-ArH	In-ArH	Solvent
1	115–116 (Et_2O)	15	$C_{12}H_8S_6$ (344.4)	55.83	55.72	-	7.16	8.37	CS_2
2	154–156 (benzene)	12	$C_{16}H_{16}S_6$ (400.6)	48.01	47.05	2.49	7.15	8.26	$CDCl_3$
3	208–210 (dioxane)	15	$C_{16}H_{16}O_4S_6$ (464.6)	41.28	41.40	3.93	6.74	8.40	DMSO-d_6
4	202–205 (CS_2)	41	$C_{12}H_4Cl_4S_6$ (482.3)	39.88	39.95	-	a	a	-

a) Not recorded because of solubility problems.

reacting the appropriate dithioresorcinol derivatives with SCl_2 in diethyl ether at room temperature, using the high dilution technique. The analytical and physical properties, and ^{1}H NMR parameters of compounds 1–4 are shown in Table 1. The yields of compounds 1–3 varied from 12 to 15%, while the yield of compound 4 was 41%.

As already observed in related 2,11-dithia[3.3]metacyclophanes,[22] it appears that electron-withdrawing substituents greatly increase the yield of the macrocycle formed, presumably due to charge-transfer stabilization of the transition state leading to ring closure.

Treatment of mesitylene-2,4-dithiol with SCl_2 under identical conditions produced the unsymmetrical isomer 6,8,10,14,16,18-hexamethyl-1,2,3,4,11,12-hexathia[4.2]metacyclophane 5 as major product, accompanied by minor amounts of the higher homolog 6,8,10,15,17,19-hexamethyl-1,2,3,4,11,12,13-heptathia[4.3]metacyclophane 6. Compounds 5 and 6 were formed in identical yield also using S_2Cl_2 instead of SCl_2. Other cyclic compounds were not detected in either reactions.

Coupling of the dipotassium mesitylene-2,4-dithiolate with methylene bromide in boiling tert-butyl alcohol afforded *anti*-5,7,9,14,16,18-hexamethyl-

Table 2. Analytical and physical properties, and ^{1}H NMR parameters in $CDCl_3$ (δ ppm) of intra-annularly methyl substituted polysulphur bridged metacyclophanes 5–7

Compound	M.p. °C [cryst solvent]	Yield, %	Formula (MW)	Sulphur, % Calcd	Found	Ar-H	Methylene	Ext-CH_3	In-CH_3	SCH$_3$	$\Delta\delta$ [b]
5	211–213 (dioxane)	50 [a]	$C_{15}H_{20}S_6$ (428.7)	44.86	44.66	7.21	-	2.71, 2.53	1.78	-	-1.12
6	170–171 (dioxane)	5 [a]	$C_{18}H_{20}S_7$ (460.7)	48.71	48.25	7.10	-	2.78, 2.63	2.08	-	-0.82
7	269–272 (benzene)	18	$C_{20}H_{24}S_4$ (392.6)	32.66	32.74	7.06	4.15	2.51	1.62	-	-1.28
8	-	-	-	-	-	7.04	-	2.54	1.90	2.20	-

a) By ^{1}H NMR analysis of the mixture; b) $\Delta\delta$ indicates the shielding experienced by intra-annular methyl groups, computed by difference of their absorption with that of corresponding methyl group in 2,4-bis(methylthiol)mesitylene 8.

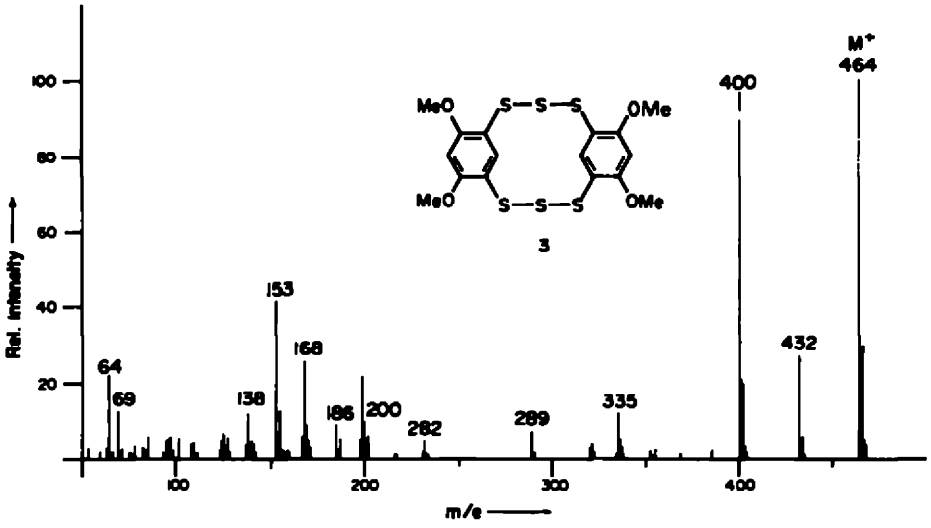


Fig. 1. Mass spectrum (70 eV) of compound 3.

1,3,10,12-tetrathia[3.3]metacyclophane 7. The analytical and physical properties of metacyclophanes 5–7, and their ^{1}H NMR parameters, compared with those of 2,4-bis(methylthio) mesitylene 8, are summarized in Table 2.

Mass spectra. The behaviour of hexathia[3.3]metacyclophanes to electron impact is shown by the spectrum relative to compound 3, reported in Fig. 1. It shows the molecular ion at *m/e* 464 (base peak) and two intense peaks at *m/e* 432 and 400, resulting from the molecular ion by loss of one and two S atoms, respectively. A strong metastable peak at about *m/e* 345 indicates that the fragment at *m/e* 400 is formed directly from the molecular ion. An intense peak at *m/e* 64 (S_2) is also present in the spectrum. Symmetrical splitting of the molecule leads to the fragment at *m/e* 232, which subsequently loses one and two S atoms to generate the fragments at *m/e* 200 and 168. The loss of a Me group from the fragment at *m/e* 168 accounts for the formation of the fragment at *m/e* 153.

The spectra of compounds 2 and 4–6, collected in Table 3, confirm this trend. In compound 1 instead the metastable peak corresponding to the transition $M^+ \rightarrow (M-S_2)^+$ is absent, suggesting for this compound a random loss of S atoms.

The isomer hexathia[4.2]metacyclophane 5 and the heptathia[4.3]metacyclophane 6 behave similarly to compounds 2–4, although the latter displays a lower molecular ion. Compound 7 shows a higher stability to electron impact with respect to polysulphur bridged metacyclophanes 1–6. The molecular ion at *m/e* 392 is the base peak (Table 3), and the intense peaks at *m/e* 209 and 195 are due to both unsymmetrical and symmetrical cleavage of the CH_2 S bonds, and subsequent rearrangement by loss of a H atom, respectively. The peaks at *m/e* 162 and 147 are generated from the fragment at *m/e* 195 by loss of SH (metastable peak at about *m/e* 134) and a Me group, respectively. The fragment at *m/e* 64 is absent.

In order to compare the electron-impact induced S extrusion from the bridging chains of polysulphur metacyclophanes with their thermal stability, compounds 1–6 were heated in high boiling solvents, such as *o*-dichlorobenzene and nitrobenzene. Compounds 2, 3, 5 and 6 were recovered unaltered even after prolongated ebollition, while compound 1 gave a gummy intractable material, which was not further characterized. On the contrary, compound 4 underwent immediately a thermal rearrangement in almost quantitative yield to a crystalline product 9 (Scheme 2), identical in all respects with an authentical sample of 4,6,12,14,20,22,28,30-octachloro-1,2,9,10,17,18,25,26-octathia[2.2.2.2]metacyclophane.[1,8]

These data indicate that electron-releasing substituents, such as Me or OMe groups, confer a high thermal stability to polysulphur bridged metacyclophanes, while electron-withdrawing substituents, such as Cl atom, strongly promote S extrusion, as it

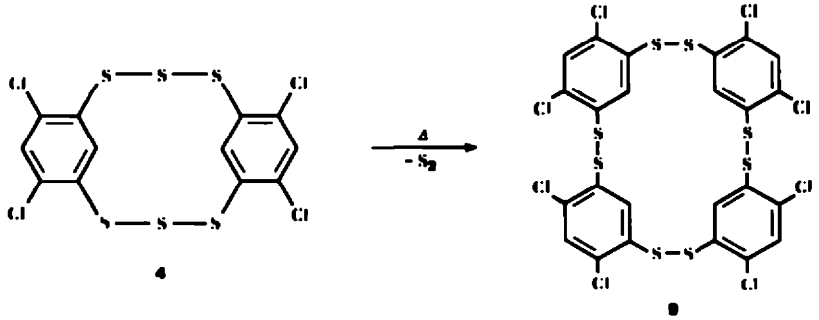


Table 3. Mass spectra (70 eV) of compounds 1 2 and 4 7

Compound	m/e (rel. intensity)
1	346(25), 345(19), 344(100), 314(6), 313(4), 312(27), 280(9), 250(4), 249(7), 248(40), 218(8), 217(11), 216(14), 184(8), 172(11), 171(5), 142(7), 140(16), 139(5), 108(24), 96(28), 95(8), 70(5), 69(16), 64(23).
2	404(5), 403(7), 402(31), 401(24), 400(100), 370(10), 369(9), 368(48), 338(7), 337(9), 336 (42), 304(12), 272(24), 271(18), 240(7), 239(10), 202(5), 201(10), 200(36), 199(46), 170(24), 169(35), 168(63), 167(96), 137(5), 136(20), 135(64), 134(42), 124(13), 123(22), 121(15), 91 (62), 77(22), 64(22).
4	486(18), 485(8), 484(53), 452(82), 481(9), 480(52), 454(7), 452(23), 451(5), 450(35), 448 (23), 422(5), 420(18), 418(32), 416(21), 354(9), 353(7), 352(31), 351(14), 350(68), 349(13), 348(63), 324(5), 322(9), 320(16), 319(6), 318(23), 317(7), 316(29), 242(10), 241(8), 240(15) 239(7), 212(7), 210(22), 209(9), 208(26), 207(28), 206(5), 205(45), 180(5), 178(23), 177(6), 176(37), 175(38), 174(10), 173(87), 166(7), 164(11), 163(8), 161(15), 143(7), 141(21), 140 (5), 139(5), 138(18), 137(9), 131(19), 129(47), 106(17), 105(15), 99(7), 97(26), 94(8), 93 (30), 76(23), 69(66), 66(7), 64(100).
5	432(5), 431(8), 430(30), 429(25), 428(100), 396(8), 366(9), 365(10), 364(37), 349(9), 332 (5), 331(17), 318(8), 317(7), 300(11), 299(8), 298(9), 285(5), 267(5), 266(7), 215(11), 214(26), 213(61), 212(28), 184(19), 183(20), 182(46), 181(61), 180(11), 167(9), 151(11), 150(8), 149(23), 148(13), 147(12), 135(9), 134(17), 119(9), 115(9), 105(14), 91(9), 77(9), 64(9).
6	462(8), 461(6), 460(22), 431(6), 430(25), 429(22), 428(100), 397(5), 396(18), 366(6), 365 (7), 364(28), 349(6), 331(13), 318(6), 317(8), 300(10), 299(7), 298(6), 266(5), 216(6), 215(12), 214(36), 213(74), 212(35), 184(23), 183(19), 182(58), 181(67), 167(10), 151(12), 150(9), 149(27), 148(14), 147(16), 135(10), 134(19), 119(10), 115(11), 105(16), 104(5), 91 (11), 77(10), 64(24).
7	395(5), 394(20), 393(25), 392(100), 211(11), 210(5), 209(24), 208(7), 198(6), 197(23), 196 (25), 195(31), 182(7), 181(13), 177(15), 165(9), 164(18), 163(36), 162(44), 161(12), 149(15) 148(17), 147(19), 135(6), 134(11), 119(7), 115(9), 105(6), 91(11).

could be expected by the presence in the mass spectrum of compound 4 of the fragment at *m/e* 64 (S_2) as the base peak.

^{1}H NMR *spectra.* The spectral parameters of hexathia [3.3]metacyclophanes 1–4 are listed in Table 1. Solubility problems did not allow us to record their spectra in the same solvent. They show in the aromatic region two signals, relative to intra-annular and external aryl protons. The assignment of these signals to the respective protons has been established by a comparison of their absorptions with those of pertinent protons in structurally related acyclic and cyclic compounds, previously investigated.[4,5,8]

It is interesting to note that the intra-annular aryl protons of compounds 1–3 resonate at very low field (δ 8.26–8.40) with respect to the corresponding protons in [3.3]metacyclophane (δ 6.58–7.0),[9] 2,11-dithia[3.3]metacyclophane (δ 6.63)[13] and 1,3,10,12-tetrathia[3.3]metacyclophane (δ 7.2).[20] These low field absorptions, although partly justified by the inductive effect of the trisulphide bridges,[23] strongly suggest for hexathia[3.3]metacyclophanes the *syn* conformation, shown in Fig. 2, in which the ring current shielding effect of the opposite aromatic ring is ineffective. *X*-ray analysis of compound 3 confirmed the syn geometry adopted by these compounds.[6] Furthermore, a temperature variable ^{1}H NMR study showed no change in their spectral patterns.

Table 2 shows the spectral parameters of intra-annularly methyl substituted polysulphur bridged metacyclophanes 5–7, and of 2,4-bis(methylthio-) mesitylene 8. A pattern of three signals for Me groups in compounds 5 and 6 is consistent with the unsymmetrical structures proposed. Considering that the deshielding effect of the neighbouring S atoms is additive,[23,24] the low field signals (δ 2.71 in 5 and 2.78 in 6) can be assigned to the Me groups adjacent the tetrasulphide bridge, and the intermediate signals (δ 2.53 in 5 and 2.63 in 6) to the Me groups adjacent the disulphide or trisulphide bridge, respectively. In spite of the deshielding effect of the surrounding S atoms, the intra-annular Me groups resonate at a higher field (δ 1.78 in 5 and 2.08 in 6) than the corresponding Me protons in 8 (δ 2.90). This suggests that these protons

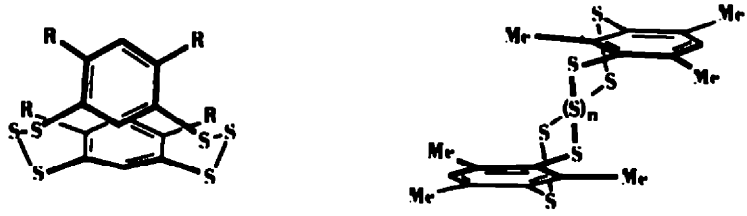


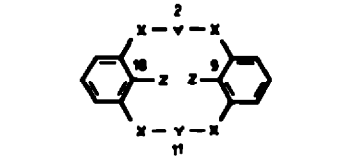
Fig. 2. Stereochemistry of polysulphur bridged metacyclophanes 1–6.

experience the ring current shielding effect of the opposite aromatic ring ($\Delta\delta$ + 1.12 in **5** and +0.82 in **6**), thus indicating for compounds **5** and **6** a stepped anti conformation, shown in Fig. 2. Moreover, a variable temperature study of their spectra showed no change in the spectral pattern between −88° (CS_2) and +186° (*o*-dichlorobenzene). X-ray analysis of compound **5** confirmed the anti geometry of this molecule.[6]

Accordingly with the above considerations, the high field signal (δ 1.62) of intra-annular Me groups in compound **7** ($\Delta\delta$ + 1.28) is again indicative for a stepped *anti* conformation. Moreover, this absorption is lower than that of corresponding Me groups in 5,7,9,14,16,18-hexamethyl-2,11-dithia[3.3]metacyclophane (δ 1.11),[17] due to the elongation of the bond length caused by replacing C atoms by S, which makes less effective the ring current shielding effect of the opposite aromatic ring. Therefore, the shielding experienced by intra-annular Me groups in these compounds serves not only for conformational assignments, but also as a measure of ring size.

DISCUSSION

It is well known that [3.3]metacyclophane **10**,[9] and its sulphur analogs 2,11-dithia[3.3]metacyclophane **11**[13] and 1,3,10,12-tetrathia[3.3]metacyclophane **12**,[10] are conformationally flexible molecules, and that the energy barrier required for the conformational change is quite low compared with the lower homologs;[17] nevertheless, with bulky substituents at the 9 and 18 positions, such a barrier is sufficiently large that the *syn* and *anti* conformers can be isolated and show no evidence for interconversion (Fig. 3).[11,12,14–19]



10: X = Y = CH_2; Z = H

11: X = CH_2; Y = S; Z = H

12: X = S; Y = CH_2; Z = H

Fig. 3. Stereochemistry of [3.3]metacyclophane ring systems containing hydrocarbon bridges.

In approaching the stereochemistry of hexathia-[3.3]metacyclophanes, it emerges that their conformational preferences are determined primarily by the nature of the trisulphide bridges. In fact, a literature survey[25,26] shows that polysulphur chains in polythionic compounds accommodate in such a conformation, that the dihedral angles of adjacent S atoms range from 74 to 110°. These values result from the repulsion of unshared electron pairs of adjacent S atoms, which reaches a minimum of energy for dihedral angles close to 90°.

X-ray analysis of compound **3** is in agreement with these considerations, since the C–S–S–S dihedral angles are found close to 90°. On the other hand, a hypothetic anti conformation for hexathia[3.3]metacyclophanes appears to be unlikely, as from the inspection of molecular models some different anti conformations become apparent by varying the C–C–S S dihedral angles, but none presents all C–S–S–S dihedral angles close to 90°.

This interpretation is further substantiated by the results of the coupling of mesitylene-2,4-dithiol with sulphur chlorides, which produced only the unsymmetrical metacyclophanes **5** and **6**, and neither *syn*- nor *anti*-hexathia[3.3]metacyclophane conformers were detected from this reaction.

These data demonstrate dramatically the stereochemical differences of hexathia[3.3]metacyclophanes compared with compounds **10**–**12**. Furthermore, besides confirming the unlikeliness of stable *anti*-hexathia [3.3]metacyclophanes, these findings show that the *syn*-hexathia[3.3]metacyclophane ring closure with bulky substituents at the 9 and 18 positions is prevented, owing to mutual sterical repulsions. Therefore one might predict that in these cases the reactions evolve towards the formation of sterically more favoured ring systems.

Finally, the interruption of the trisulphide bridges by replacement of the central S atoms with methylene bridges restores in [3.3]metacyclophane ring systems the expected stereochemistry, as shown by the formation of *anti*-5,7,9,14,16,18-hexamethyl-1,3,10,12-tetrathia[3.3]metacyclophane **7**.

EXPERIMENTAL

Materials and analytical procedures. All solvents and available organic materials were commercial products purified by standard procedures. Sulphur chlorides were used

without purification. Dithioresorcinol,[28] 4,6-dimethyldithioresorcinol,[38] 4,6-dimethoxy-dithioresorcinol,[28] 4,6-dichlorodithioresorcinol,[28] and mesitylene-2,4-dithiol[1] were prepared according to literature procedures. Elemental analyses were obtained commercially. Mass spectra were taken at 70 eV by direct insertion into the ion source of a LKB 9000S instrument. ^{1}H NMR spectra were recorded on a Varian EM 360 or a Varian A-60 D instrument equipped with a variable temperature controller. M.p. are uncorrected.

Typical procedure for the synthesis of hexathia-[3.3]metacyclophanes 1–4. Equimolar amounts of dithiol and SCl_2 (0.01 mole) in diethyl ether (250 ml) were dropped separately but syncronously from two dropping funnels into diethyl ether (1.5 l) during 3–5 hr, with vigorous stirring under N_2. When the evolution of HCl was judged complete, the mixture was filtered and the solvent removed under reduced pressure. Extraction and recrystallization from the opportune solvent (Table 1) afforded the desired hexathia[3.3]metacyclophane.

Reaction of mesitylene-2,4-dithiol with SCl_2 and S_2Cl_2. Mesitylene-2,4-dithiol (8.28 g, 0.045 mole) and SCl_2 (4.63 g, 0.045 mole) in diethyl ether (500 ml) were dropped under the above conditions into diethyl ether (6 l.) during 6 hr. The mixture was stirred overnight, then filtered and the solvent removed under reduced pressure. The oily residue was dissolved in benzene and chromatographed on neutral alumina, using benzene as an eluent, to give a mixture of 5 and 6 (ratio 5 to 6 *ca* 10:1 by ^{1}H NMR analysis) in a 55% overall yield. Twice recrystallization of the mixture from dioxane afforded 6, as yellow needles, m.p. 211–213°. Further crop of 6 was recovered by concentration of liquor mother. The resulting filtrate was concentrated *in vacuo*, and the residue twice recrystallized from dioxane to give yellow prisms of 6, m.p. 179–181°. Compounds 5 and 6 were formed in identical yield also using S_2Cl_2 instead of SCl_2.

anti-5,7,9,14,16,18-examethyl-1,3,10,12-tetrathia[3.3]metacyclophane 7. Mesitylene-2,4-dithiol (1.84 g, 0.01 mole) and KOH (1.12 g, 0.02 mole) in EtOH–BuOH 1:1 mixture (100 ml) and methylene bromide (1.74 g, 0.01 mole) in BuOH (100 ml) were dropped simultaneously into boiling BuOH (1 l.) during 3 hr. under vigorous stirring. When the addition was complete, the mixture was refluxed for additional 20 hr, then filtered. The filtrate was concentrated *in vacuo* and the residue recrystallized from benzene to yield colourless prisms of 7, m.p. 269–272°.

Thermal rearrangement of 3. Compound 3 (100 mg) was heated in *o*-dichlorobenzene (10 ml) under reflux for 5 min. After cooling, the ppt was filtered off and washed with CS_2. Recrystallization from *o*-dichlorobenzene afforded light yellow microcrystals of 9 (80 mg), m.p. 336–338°.

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