Condensation of 2,2'-Thiodiethanethiol with Benzaldehyde and Other Carbonyl Compounds (or Equivalents Thereof)

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The acid-catalysed condensation of 2,2'-thiodiethanethiol 1 with carbonyl compounds (or equivalents thereof) can, under properly chosen conditions, lead in good yield to thiocrown ethers containing thioacetal units. The reaction with benzaldehyde 2 has been examined in detail and the monomer (3), dimer (4), and polymer (5) products have all been characterized. The effects of solvent, concentration, and reaction time on the product distribution have been determined. In benzene all three products are in equilibrium in the presence of acid. At a concentration of 0.2 mol dm^{-3} in reactants in benzene at reflux, a mixture of products 3, 4 and 5 is obtained after several hours. By proper choice of conditions the reaction can be driven in good yield to any of these products. The structures of compounds 3 and 4 have been established by X-ray crystallography. The structure of compound 4 has a centre of symmetry and trans stereochemistry. The molecular-mass distribution of polymer 5 is M_w 21 394, M_n 11 246 and $D = 1.90$ as determined by gel permeation chromatography. The thermogravimetric analysis and differential scanning calorimetry analysis data for compounds 3, 4 and 5 show all these compounds to be thermally quite stable in the absence of acids. X-Ray structures have also been obtained for 2-(4-chlorophenyl)-1,3,6-trithiacyclooctane 7, 7,10,13,20,23,26-hexathiadispiro[5.7.5.7]hexacosane 14 and 2-(4-nitrophenyl)-1,3,6-trithiacyclooctane 19.

Thiocrown ethers and related ligands are known to form complexes with a variety of metal ions[1] and have been used, for example, as model systems for the blue copper proteins.[2] The potential is present that the coordination chemistry of thiocrown ethers could be used as the basis of industrially interesting applications in the areas of homogeneous catalysis[3] or receptors,[4] which might be used for removal of heavy metals in conjunction with protection of the environment.
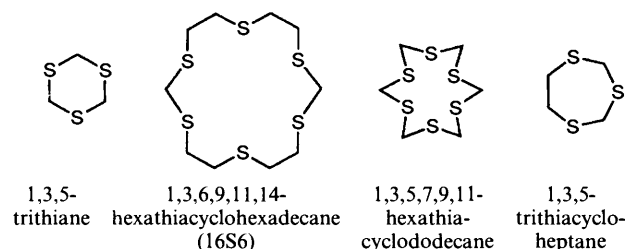
Syntheses of thiocrown ethers have often been achieved via caesium thiolates as illustrated in eqn. (1).[5]

X = Br, Cl, OSO₂R
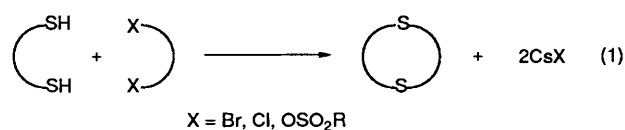
Reagents: Cs₂CO₃, DMF

There is, of course, interest in even simpler routes using inexpensive chemicals. This is particularly important when industrial and commercial aims are considered.[6]

Thiocrown ethers bearing thioacetal linkages represent particularly interesting cases. A range of examples is shown.

1,3,5-trithiane   1,3,6,9,11,14-hexathiacyclohexadecane (16S6)   1,3,5,7,9,11-hexathiacyclododecane   1,3,5-trithiacycloheptane

The 'mini' cycle, 1,3,5-trithiane, has, of course, been extensively studied.[7] The compounds 1,3,6,9,11,14-hexathiacyclohexa-

decane (16S6) and 1,3,5,7,9,11-hexathiacyclododecane are characteristic macrocyclic examples.[1a,8] We have described the synthesis of 1,3,5-trithiacycloheptane and analogous compounds using caesium thiolates wherein the thioacetal function was preformed into one of the chain components.[9] The presence of the thioacetal unit opens the way to further functionalization of the cycle by, for example, carbanion chemistry[10] as illustrated in eqn. (2).
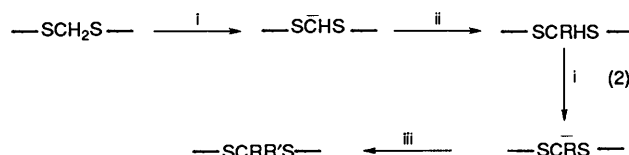
Reagents: i, BuLi; ii, RX; iii, R'X

Cyclization via condensation of a dithiol with a carbonyl group (or equivalent thereof) does not seem at first sight an attractive route to such macrocycles owing to the relatively low effective molarities to be expected for formation of many of the macrocyclic rings. There is, of course, extensive knowledge available on various aspects of the thiols with carbonyl groups or equivalents thereof.[11,12] We have examined in reasonable detail a prototype reaction, the condensation of 2,2'-thiodiethanethiol 1 with benzaldehyde 2 and have obtained unexpected results. These are described here together with a somewhat broader survey of the reactions of dithiol 1 with other carbonyl compounds or their equivalents. In addition, several crystal structures of macrocyclic products have been determined and are described here.

Results and Discussion

A. *Distribution of Products.*—The condensation approach is illustrated in eqn. (3). Some reaction conditions and results are given in Table 1. When substrates 1 (7.7 mmol) and 2 (7.7 mmol)

Table 1 Results of condensation of compound 1 with benzaldehyde 2 under various conditions

| Entry	Reactant (mmol)^a	Solvent (cm^3)	Catalyst (mg)	Reaction temperature ($T/^\circ$C)	Reaction time (t/h)	Proportions of products (%)[b]		
						3	4	5
1	7.7	C_6H_6 (5)	TsOH (5)	80	3	0	1	99
2	7.7	C_6H_6 (10)	TsOH (5)	80	3	2	8	90
3	7.7	C_6H_6 (20)	TsOH (5)	80	3	4	9	87
4	7.7	C_6H_6 (40)	TsOH (5)	80	3	15	8	76
5	7.7	C_6H_6 (80)	TsOH (5)	80	3	9	10	81
6	7.7	C_6H_6 (100)	TsOH (5)	80	3	34	17	49
7	7.7	C_6H_6 (150)	TsOH (5)	80	8	2	62	36
8	7.7	C_6H_6 (SAM)^c	TsOH (10)	50–55	50	23	44	34
9	7.7	C_6H_6 (SAM)	TsOH (10)	50–55	50	18	42	40
10	7.7	MeOH (SAM)	TsOH (10)	50–55	50	87	4	17
11	7.7	MeOH (SAM)	HCl	50–55	50	85	3	12

^a Ratio 1:2 = 1:1. *^b* Overall yields = 96–98%; the proportions of products 3, 4 and 5 were determined from 200 MHz NMR spectra. *^c* SAM = slow-addition method.

Table 2 Equilibration of compounds 3, 4 and 5 in benzene

Reactant^a	Solvent (cm^3)	Catalyst (mg)	Reaction temperature ($T/^\circ$C)	Reaction time (t/h)	Proportions of products (%)[b]		
					3	4	5
3	C_6H_6 (100)	TsOH (5)	80	12	9	40	51
3	C_6H_6 (10)	TsOH (5)	80	12	0	2	98
4	C_6H_6 (100)	TsOH (5)	80	12	7	45	48
4	C_6H_6 (10)	TsOH (5)	80	12	1	5	94
5	C_6H_6 (100)	TsOH (5)	80	12	6	47	47

^a Weight of reactants = 1 g [4.33 mmol (3) and 2.07 mmol (4)]. *^b* Overall yields = 100%; the proportions were measured from 200 MHz NMR spectra.
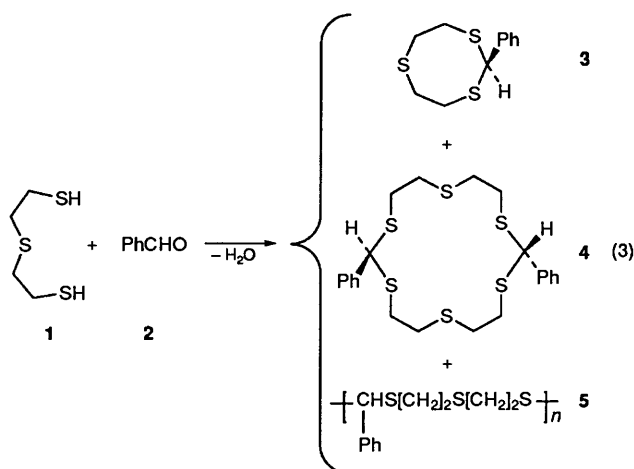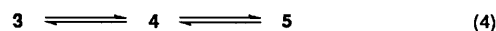

Reagents: H⁺, benzene

are refluxed in benzene (80 cm³) with TsOH (5 mg) for 3 h, there is obtained a 81% yield of polymer 5, a 9% yield of monomer 3 and a 10% yield of dimer 4 (entry 5). When the amount of solvent is increased to 150 cm³ and the reflux time is 8 h these three products 3, 4 and 5 are found in respective yields of 2, 62 and 36% (entry 7). The change of product composition as a function of concentration for constant reaction time can be followed in entries 1–8 (all of the cited numbers may vary by ~ 3% in absolute magnitude).

This observed variation in product distribution suggests reversible formation of products 3, 4 and 5 as illustrated in eqn. (4). All three products were isolated in pure form (see further for structural characterization). This permitted the development of a method for determination of the proportions of products: the –SCH(Ph)S– protons in compound 3 were found to resonate in $CDCl_3$ at δ 6.2, those of dimer 4 at δ 5.2 and those of

polymer 5 at δ 5.0–5.18. When the pure materials were subjected to the same reaction conditions (Table 2) a mixture of compounds 3, 4 and 5 was formed in all cases, which establishes that the postulated equilibrium of eqn. (4) is correct.

$$3 \rightleftharpoons 4 \rightleftharpoons 5 \tag{4}$$

Reagents and conditions: H⁺, benzene, reflux

An acid-catalysed equilibrium between thioacetals is in contrast with textbook expectation.[13] Thioacetals are normally deprotected not by using strong acids but rather by methods that either precipitate the thiol or oxidize it. At least in the case of benzaldehyde such reagents apparently prevent readdition of the thiol; proton acids in benzene are clearly capable of initiating reaction at the thioacetal centre (but not at the cost of irreversible destruction of thiol). In the present case reversible steps in formation of both hemithioacetal and thioacetal [eqn. (5)] must be operative.
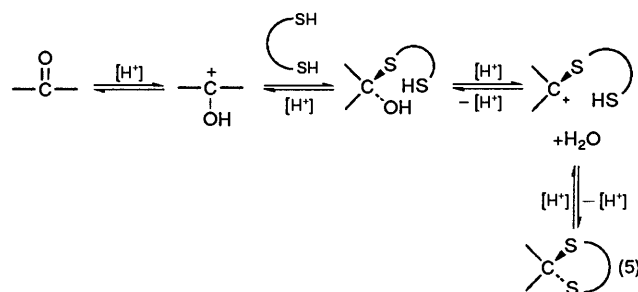

On the basis of the results given in Table 1 it would appear that dimer 4 is the thermodynamically more stable product, that the 8-membered ring 3 is the least stable and that polymer

5 is slightly less stable than the dimer (although judging from entries 1–5 it is formed faster than is dimer 4). It is not surprising that the medium ring 3 should have the greatest degree of strain and be least stable. Clearly, however, compound 3 can be a *kinetic* product, as indicated by the higher yields at shorter reaction times and under conditions of higher dilution (entry 6). The relative stability of dimer 4 relative to polymer 5 is unexpected and an obvious explanation does not present itself.

Change of solvent to methanol (entries 10 and 11, Table 1) using slow-addition techniques leads to a spectacular increase in the amount of monomer 3. The kinetic product is clearly being trapped very effectively under these conditions. Although the point has not been investigated in as much detail as in Table 2 (equilibration in benzene) we observed that, over a period of 8 h, compound 3 in methanol in the presence of acid under the reaction conditions of entries 10 and 11 in Table 1 undergoes no change. In contrast with benzene, the reaction in methanol clearly is not significantly reversible, allowing one to trap and maintain the kinetic product without complications of subsequent equilibration.

B. *Scope of the Reaction.*—A number of other condensations with dithiol 1 have been examined in order to obtain some idea of the scope of the reaction. These reactions have not been investigated in the same detail as that of benzaldehyde. The main effort has been to isolate and identify the monomeric and dimeric products. The polymer products have not been characterized. Reaction conditions have not been optimized and the effects of reversibility on the formation of product have not been investigated in a systematic manner. Conversions were generally monitored by the amount of water collected in a Dean–Stark trap. On this basis, conversions with aldehydes were nearly quantitative except for 2-chloro- and 2,4-dichloro-benzaldehyde for which conversions of ~40 and 35% were observed. These reactions were not investigated further. Not unsurprisingly, ketones are less reactive; cyclohexanone led to ~65% of the theoretical amount of water. In the reaction with cyclohexanone some oxidation of dithiol 1 took place to give a small amount of 1,2,5-trithiacycloheptane 6[14] [see eqn. (6)]. This likely reflects the lower reactivity of cyclohexanone whereby oxidation processes are able to compete with condensation. Small amounts of compound 6 were detected by chromatography in some other condensation reactions.
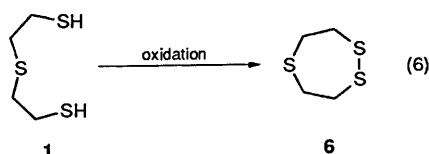
The results of those reactions for which monomeric and dimeric products were unambiguously characterized are summarized in eqn. (7). In several cases the reaction conditions were adjusted to favour formation of either monomer or dimer as desired. Both 4-chlorobenzaldehyde (products 7 and 8) and 4-nitrobenzaldehyde (products 19 and 20) react quite cleanly. There is a greater tendency to produce monomer (lesser tendency to form dimer) for the case of 4-nitrobenzaldehyde. This may reflect lack of reversibility in formation of the products.

Acetals can be used in place of aldehydes at least for several aliphatic examples. Dimethoxymethane (products 11 and 12) can be used with success and a vinyl ether serves as the precursor of products 15 and 16.[11a]
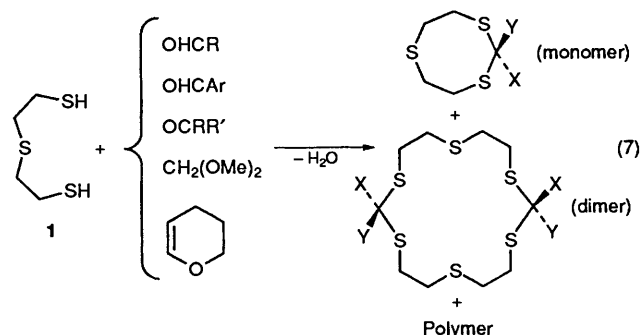
$$7 \ X = H, Y = 4\text{-ClC}_6\text{H}_4, \text{ monomer } (35\%)$$
$$8 \ X = H, Y = 4\text{-ClC}_6\text{H}_4, \text{ dimer } (57\%)$$
$$9 \ X = H, Y = \text{PhCH}_2\text{CH}_2, \text{ monomer } (90\%)$$
$$10 \ X = H, Y = \text{PhCH}_2\text{CH}_2, \text{ dimer } (12\%)$$
$$11 \ X = Y = H, \text{ monomer } (78\%)$$
$$12 \ X = Y = H, \text{ dimer } (68\%)$$
$$13 \ XY = -[\text{CH}_2]_5-, \text{ monomer } (22\%)$$
$$14 \ XY = -[\text{CH}_2]_5-, \text{ dimer } (16\%)$$
$$15 \ X = H, Y = \text{HOCH}_2\text{CH}_2\text{CH}_2, \text{ monomer } (35\%)$$
$$16 \ X = H, Y = \text{HOCH}_2\text{CH}_2\text{CH}_2, \text{ dimer } (12\%)$$
$$17 \ X = H, Y = \text{cyclohexyl, monomer } (89\%)$$
$$18 \ X = H, Y = \text{cyclohexyl, dimer } (42\%)$$
$$19 \ X = H, Y = 4\text{-NO}_2\text{C}_6\text{H}_4, \text{ monomer } (91\%)$$
$$20 \ X = H, Y = 4\text{-NO}_2\text{C}_6\text{H}_4, \text{ dimer } (17\%)$$
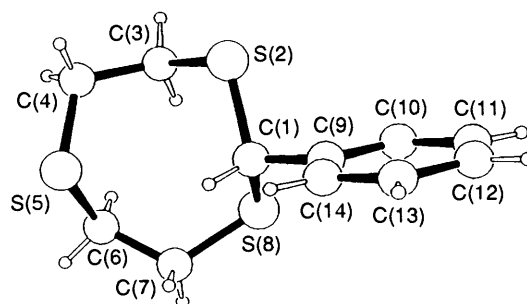
Reagents: H^{+}, solvent

Fig. 1 X-Ray molecular structure of compound 3

C. *Isolation and Identification of the Products.*—Products were generally isolated by chromatographic techniques as described in the Experimental section. The condensation of dithiol 1 with benzaldehyde 2 was studied first and isolation of the products entailed considerable effort owing to our failure to appreciate the reversibility of the reaction. Once pure products were in hand and their structural determination was secure it was possible to try to optimize conditions for the formation of each product.

All products were characterized by NMR spectra, mass spectra, and elemental analyses. For the case of monomer 3 and dimer 4 it was felt that mass spectra did not allow unambiguous distinction between the two and recourse was taken in X-ray crystallographic determination. In addition there was no obvious way that the stereochemistry of dimer 4 could be determined purely from NMR techniques.

The structure of compound 3 is illustrated in Fig. 1. Crystallographic data for monomer 3 as well as for other structures that have been determined are given in Table 3a. Characteristic bond lengths and bond angles are given in Table 3b.

Dimer 4 was readily isolated from reaction mixtures by crystallization. Comparison of the NMR spectra of pure material with crude reaction mixtures gave no indication of a second geometrical isomer. Within the capabilities of NMR detection we believe that a single geometrical isomer of dimer 4

Table 3a Crystal data for compounds 3, 4, 7, 14 and 19

Compounds	3	4	7	14	19
Formula	$C_{11}H_{14}S_3$	$C_{22}H_{28}S_6$	$C_{11}H_{13}ClS_3$	$C_{20}H_{36}S_6$	$C_{11}H_{13}NO_2S_3$
M_w	242.43	484.86	276.87	468.89	287.42
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$Pca2_1$	$P2_1$	$P2_1/c$	$P\text{-}1$	$P2_1/n$
Z	4	2	4	2	4
$a/\text{Å}$	19.472(2)	5.428(1)	7.360(1)	10.6710(6)	6.006(1)
$b/\text{Å}$	8.236(1)	8.192(1)	9.602(1)	11.0536(5)	10.723(1)
$c/\text{Å}$	7.495(1)	26.322(2)	18.569(1)	12.0371(4)	20.099(2)
α (deg)	90.0	90.0	90.0	82.026(4)	90.0
β (deg)	90.0	93.15(1)	97.25(1)	77.284(4)	93.24(1)
γ (deg)	90.0	90.00	90.0	62.093(4)	90.0
$V/\text{Å}^3$	1202.0(4)	1168.7(3)	1301.8(4)	1222.9(1)	1292.4(5)
Crystal size (mm)	0.30 × 0.25 × 0.20	0.50 × 0.40 × 0.10	0.40 × 0.25 × 0.20	0.45 × 0.35 × 0.35	0
D_{calc} (g cm^{-3})	1.34	1.38	1.41	1.273	.50 × 0.25 × 0.45
μ_{calc} (cm^{-1})	5.5	5.7	7.2	5.42	1.477
Radiation (Mo-Kα, Å)	0.710 73	0.710 73	0.710 73	0.710 73	5.393
$T/^{\circ}C$	24	24	24	24	0.710 73
R^a	0.044	0.075	0.057	0.060	24
R_w^b	0.051	0.089	0.072	0.074	0.060
					0.075

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|.$ $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{\frac{1}{2}}.$

**Table 3b** Selected bond distances (Å) and bond angles (°) for compound 3

Bond distances (Å)

S(8)–C(1)	1.820(6)	C(6)–C(7)	1.554(9)
S(8)–C(7)	1.798(6)	S(5)–C(4)	1.824(7)
S(5)–C(6)	1.803(7)	S(2)–C(1)	1.840(5)
S(2)–C(3)	1.786(6)	C(1)–C(9)	1.485(7)
C(3)–C(4)	1.493(9)		

Bond angles (°)

C(1)–S(8)–C(7)	102.5(3)	S(8)–C(7)–C(6)	117.9(5)
C(4)–S(5)–C(6)	102.1(3)	C(1)–C(9)–C(10)	121.6(5)
C(1)–S(2)–C(3)	105.5(3)	C(1)–C(9)–C(14)	118.5(5)
S(8)–C(1)–S(2)	114.4(3)	S(8)–C(1)–C(9)	113.0(4)
S(2)–C(1)–C(9)	106.2(4)	S(2)–C(3)–C(4)	118.4(5)
S(5)–C(4)–C(3)	116.4(5)	S(5)–C(6)–C(7)	114.7(4)

Table 3c Selected bond distances (Å) and bond angles (°) for compound 4

Bond distances (Å)

S(2)–C(1)	1.831(7)	C(6)–C(7)	1.52(1)
S(2)–C(3)	1.841(8)	S(5)–C(4)	1.820(8)
S(5)–C(6)	1.818(7)	S(8)–C(7)	1.811(7)
C(1)–C(9)	1.512(9)	C(3)–C(4)	1.48(1)

Bond angles (°)

C(1)–S(2)–C(3)	100.4(3)	C(1)–C(9)–C(14)	121.6(6)
C(4)–S(5)–C(6)	100.5(3)	S(2)–C(1)–C(9)	109.1(4)
S(2)–C(3)–C(4)	111.6(5)	S(5)–C(4)–C(3)	112.2(5)
S(5)–C(6)–C(7)	109.0(5)	S(8)–C(7)–C(6)	113.2(5)
C(1)–C(9)–C(10)	119.4(7)		

is formed. The stereochemistry is clearly *trans* as revealed from the X-ray structure shown in Fig. 2. Characteristic bond angles and lengths are given in Table 3c and the crystal properties are summarized in Table 3a. The seemingly exclusive formation of the *trans*-product is surprising and we have no convincing explanation why this should be so. It is possible, of course, that the *cis*-dimer is too unstable to accumulate under reversible conditions; there is, however, no obvious steric reason for instability of this isomer.

The structures of 2-(4-chlorophenyl)-1,3,6-trithiacyclooctane 7, 7,10,13,20,23,26-hexathiadispiro[5.7.5.7]hexacosane 14 and 2-(4-nitrophenyl)-1,3,6-trithiacyclooctane 19 have also been determined (see Figs. 3–5). Selected bond angles and bond lengths are given in Tables 3d–f.
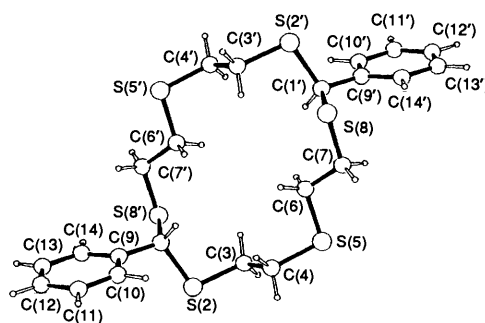
Fig. 2 X-Ray molecular structure of compound 4
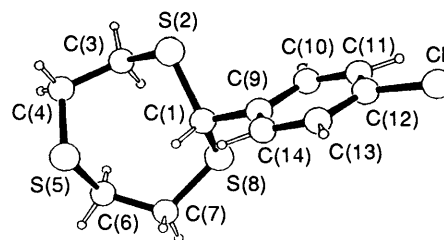
Fig. 3 X-Ray molecular structure of compound 7

A good number of X-ray structures of thiocrown ethers are now available.[15] Twelve-membered, fourteen-membered, fifteen-membered- and eighteen-membered-ring thiocrown ethers tend to have conformations in which all of the sulfur atoms are directed out of the cavity (exodentate). This reflects apparently a preference for *anti*-conformations of $-SCH_2CH_2S-$ units. On the other hand, 1,4,7-trithiacyclononane (nine-membered ring) has a sterically enforced endodentate conformation in which the sulfur atoms are directed toward the centre of the ring (C_3 symmetry).[1a,5b,15]

The structures of eight-membered rings 3, 7 and 19 are all based on the same repeated conformation. There are small differences in some bond lengths and bond angles, perhaps reflecting minor differences induced by the *para*-substituents on the aryl ring. However, by far the most striking structural aspect in the solid state is the remarkable similarity of conformations.

The dimer structures 4 and 14 are also relatively closely related although the differences in conformations are more pronounced than for the eight-membered rings 3, 7 and 19. Dimer 4 (sixteen-membered ring) has, in the crystal structure, four of the six sulfur atoms exodentate to the macrocyclic ring

Table 3d Selected bond distances (Å) and bond angles (°) for compound 7

Bond distances (Å)

S(2)–C(1)	1.843(6)	C(3)–C(4)	1.51(1)
S(2)–C(3)	1.778(7)	C(6)–C(7)	1.52(1)
S(5)–C(4)	1.797(7)	S(5)–C(6)	1.804(7)
S(8)–C(1)	1.823(6)	S(8)–C(7)	1.822(7)
Cl–C(12)	1.750(7)	C(1)–C(9)	1.495(8)

Bond angles (°)

C(1)–S(2)–C(3)	105.9(3)	C(4)–S(5)–C(6)	102.3(4)
C(1)–S(8)–C(7)	103.6(3)	S(2)–C(1)–S(8)	113.6(3)
S(2)–C(1)–C(9)	106.5(4)	S(8)–C(1)–C(9)	110.2(4)
Cl–C(12)–C(13)	118.5(6)	S(2)–C(3)–C(4)	118.8(5)
Cl–C(12)–C(11)	118.8(6)	S(5)–C(4)–C(3)	116.2(5)
S(5)–C(6)–C(7)	114.6(5)	S(8)–C(7)–C(6)	116.9(4)

**Table 3e** Selected bond distances (Å) and bond angles (°) for compound 14

Bond distances (Å)

S(2)–C(1)	1.819(6)	C(3)–C(4)	1.42(1)
S(2)–C(3)	1.806(9)	C(6)–C(7)	1.37(2)
S(5)–C(4)	1.75(1)	C(9)–C(22)	1.53(1)
S(5)–C(6)	1.78(2)	C(9)–C(26)	1.546(9)
S(8)–C(7)	1.83(1)	C(11)–C(12)	1.49(1)
S(8)–C(9)	1.828(5)	C(14)–C(15)	1.52(1)
S(10)–C(9)	1.816(7)	S(10)–C(11)	1.806(7)
S(13)–C(12)	1.808(7)	S(13)–C(14)	1.810(7)
S(16)–C(1)	1.837(8)	S(16)–C(15)	1.817(7)
C(1)–C(17)	1.524(9)	C(1)–C(21)	1.537(8)

Bond angles (°)

C(1)–S(2)–C(3)	103.3(3)	S(8)–C(9)–C(26)	112.8(4)
C(4)–S(5)–C(6)	104.8(6)	S(10)–C(9)–C(22)	111.8(4)
C(7)–S(8)–C(9)	102.3(4)	S(10)–C(9)–C(26)	104.6(4)
C(9)–S(10)–C(11)	104.4(3)	C(22)–C(9)–C(26)	109.7(6)
C(12)–S(13)–C(14)	102.7(3)	S(10)–C(11)–C(12)	108.6(5)
C(1)–S(16)–C(15)	102.9(3)	S(13)–C(12)–C(11)	114.7(6)
S(2)–C(1)–S(16)	112.1(4)	S(13)–C(14)–C(15)	112.9(5)
S(2)–C(1)–C(17)	105.1(4)	S(16)–C(15)–C(14)	108.1(4)
S(2)–C(1)–C(21)	111.0(4)	S(16)–C(1)–C(17)	112.4(5)
S(16)–C(1)–C(21)	105.8(5)	C(17)–C(1)–C(21)	110.6(6)
S(2)–C(3)–C(4)	114.1(6)	S(5)–C(4)–C(3)	118.4(7)
S(5)–C(6)–C(7)	118.0(1)	S(8)–C(7)–C(6)	114.0(1)
S(8)–C(9)–S(10)	112.1(4)	S(8)–C(9)–C(22)	106.1(4)

Table 3f Selected bond distances (Å) and bond angles (°) for compound 19

Bond distances (Å)

S(2)–C(1)	1.845(4)	C(1)–C(9)	1.500(5)
S(2)–C(3)	1.800(5)	C(3)–C(4)	1.509(6)
S(5)–C(4)	1.810(5)	C(6)–C(7)	1.517(7)
S(5)–C(6)	1.821(5)	S(8)–C(1)	1.817(4)
S(8)–C(7)	1.820(4)	O(16)–N(15)	1.214(6)
O(17)–N(15)	1.228(6)	N(15)–C(12)	1.468(5)

Bond angles (°)

C(1)–S(2)–C(3)	104.7(2)	S(8)–C(7)–C(6)	117.5(3)
C(4)–S(5)–C(6)	103.1(2)	C(1)–C(9)–C(10)	120.8(3)
C(1)–S(8)–C(7)	104.1(2)	C(1)–C(9)–C(14)	120.1(3)
O(16)–N(15)–O(17)	123.0(4)	O(16)–N(15)–C(12)	118.6(4)
O(17)–N(15)–C(12)	118.4(4)	S(2)–C(1)–S(8)	115.4(2)
S(2)–C(1)–C(9)	104.9(2)	S(8)–C(1)–C(9)	110.2(2)
S(2)–C(3)–C(4)	116.9(3)	S(5)–C(4)–C(3)	115.9(3)
S(5)–C(6)–C(7)	113.6(3)		

and the other two endodentate; compound 14 exhibits the same tendency to have *trans*-arrangements of the –SCH$_2$CH$_2$S– units.

The polymer 5 was characterized by NMR spectra as
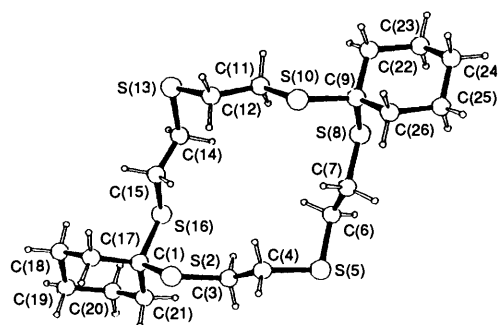
Fig. 4 X-Ray molecular structure of compound 14
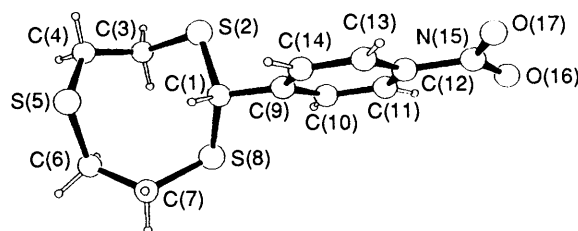
Fig. 5 X-Ray molecular structure of compound 19

described in the Experimental section. From gel permeation chromatography (GPC) analysis the molecular mass distribution of polymer 5 is M_w 21 394, M_n 11 246 and D 1.90. It deserves special mention that the viscous resin-like polymer can be converted into chiefly dimer 4 in the presence of acid (Table 2). By recycling, polymer could probably be converted quite efficiently into dimer.

D. *Thermal Analysis of Products 3, 4 and 5.*—A brief examination of the thermal behaviour of products 3–5 was made. By differential scanning calorimetry (DSC) the solid–liquid transition for compound 3 was found at 93.76 °C (ΔH 19.70 kJ mol^{-1}) and that for dimer 4 at 167.55 °C (ΔH 44.00 kJ mol^{-1}). By thermal gravimetric analysis (TGA) monomer 3 was found to decompose (95.6% weight loss) at 322–366 °C, as were dimer 4 (97.6% weight loss) at 300–324 °C and polymer 5 (98.0% weight loss) at 313–347 °C. Although the products of decomposition have not been identified further, it is not unlikely that depolymerization to afford thiirane and thiobenzaldehyde occurs in all cases. The essentially quantitative nature of this process for all three compounds—of widely differing structures—is very striking.

Experimental

Materials and Measurements.—All chemicals used in this work were commercially available; 2,2′-thiodiethanethiol was obtained from Janssen. Aluminium oxide 90 (activity 2–3) from Merck was used for column chromatography.

^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were determined on a Varian XR-200 instrument. CDCl$_3$ was used as a solvent and Me$_4$Si as internal reference. IR spectra were obtained in KBr pellets with a Perkin-Elmer 781 spectrometer. Mass spectra were recorded on an AEI-MS902 mass spectrometer at 70 eV. All m.p.s were determined on a Mettler FP1 melting apparatus and are uncorrected. TGA and DSC analytical data were determined on a Perkin-Elmer 7 Series Thermal Analysis System. The molecular-mass distribution of polymer 5 was determined on a Waters 150-C GPC apparatus.

General Procedures.—*Method A. Condensation of 2,2′-thio-diethanethiol with aldehydes and ketones.* A mixture of aldehyde

or ketone (7.7 mmol), compound **1** (7.7 mmol) and toluene-*p*-sulfonic acid (PTSA) (0.5 mg) dissolved in the desired amount of benzene was put in a 250 cm³ round-bottomed flask provided with a magnetic bar and attached to a reflux condenser. The reaction mixture was refluxed for a given period after which time the reaction was stopped and the small amount of water was removed. The reaction mixture was eluted over a small amount of aluminium oxide with dichloromethane as the elution solvent to remove the acid. The filtrate was concentrated on a rotary evaporator under reduced pressure. The residue was separated by column chromatography on aluminium oxide with toluene as eluent. Monomer and dimer were collected in that order. The polymer was eluted with dichloromethane. The solid materials were crystallized from dichloromethane or chloroform. The dimer **4** could be purified by dissolving the solid in a little dichloromethane to which hot absolute ethanol was added. The dimer precipitated as a white powder that was crystallized once again from chloroform.

Method B. Slow-addition method. A 500 cm³ three-necked, round-bottomed flask was fitted with a magnetic stirring bar, a reflux condenser, and a dropping funnel. The flask was charged with benzene or methanol (100 cm³) and PTSA (5 mg). The mixture was stirred and heated to 50–55 °C. A solution of aldehyde or ketone (7.7 mmol) (sometimes it is necessary to reflux the solution to dissolve solid reactants) and compound **1** (7.7 mmol) in the required solvent (200 cm³) was added to the well stirred methanol solution over a period of 8–10 h. After the addition was complete, the reaction mixture was stirred for a further 50 h. Work-up was carried out as described above.

Method C. Reaction of polymer **5** *in acidic medium.* A mixture of polymer **5** (2 g), PTSA (5 mg) and benzene (100 cm³) was heated under reflux and stirred overnight. Work-up was as described under Method A. The proportions of monomer **3**, dimer **4** and polymer **5** could be determined from the 200 MHz NMR spectra from the different chemical shifts of the –SC*H*PhS– protons.

Method D.[12,16] *Condensation of compound* **1** *with dimethoxymethane or 2,3-dihydropyran.* A vigorously stirred mixture of chloroform (30 cm³), acetic acid (18 cm³) and boron trifluoride–diethyl ether (8 cm³) was heated at reflux. A solution of compound **1** (7.7 mmol), dimethoxymethane (8 mmol) and chloroform (115 cm³) was added at a constant rate during 2 h and the mixture was refluxed for a further 2 h before being allowed to cool to room temperature, and was washed successively with water (2 × 20 cm³), 10% aq. potassium hydroxide (2 × 20 cm³) and water (2 × 20 cm³). The chloroform solution thus obtained was dried over potassium carbonate and was then concentrated under reduced pressure. The residue was separated on a column of aluminium oxide with ethyl acetate and/or ethanol as eluent to give compounds **15** and **16**.

2-Phenyl-1,3,6-trithiacyclooctane **3**. Yield: 87%. M.p. 90.5–92.5 °C; R_f 0.95 (Al₂O₃/toluene); δ_H(CDCl₃) 3.03 (8 H, m), 6.02 (1 H, s) and 7.39 (5 H, m); δ_C(CDCl₃) 34.05 (t), 35.70 (t), 58.76 (d), 127.12 (d), 127.86 (d), 128.65 (d) and 142.50 (s); ν_{max}(KBr)/cm⁻¹ 3015w, 3002w, 2946m, 2799m, 1593m, 1481m, 1445m, 1405s, 1283s, 1273s, 1259s, 1190m, 1141s, 1067m, 1023m and 696vs (Found: C, 54.5; H, 5.8; S, 39.8%; M⁺, 242.320. C₁₁H₁₄S₃ requires C, 54.50; H, 5.82; S, 39.68%; *M*, 242.320).

2,10-Diphenyl-1,3,6,9,11,14-hexathiacyclohexadecane **4**. Yield: 72%. M.p. 165–167 °C; R_f 0.85 (Al₂O₃/toluene); δ_H(CDCl₃) 2.97 (8 H, m), 5.21 (1 H, s) and 7.50 (5 H, m); δ_C(CDCl₃) 32.43 (t), 35.51 (t), 53.55 (d), 127.73 (d), 128.27 (d), 128.75 (d) and 139.80 (s); ν_{max}(KBr)/cm⁻¹ 3057m, 3026m, 2922s, 1597w, 1583w, 1490s, 1449s, 1419s, 1205s, 1071s, 1029m and 696vs (Found: C, 54.5; H, 5.8; S, 39.8%; M⁺, 484.642. C₂₂H₂₈S₆ requires C, 54.50; H, 5.82; S, 39.68%; *M*, 484.640).

Polymer **5**. The product was a viscous resin (99%). Analytical results from GPC [conditions: column, TSK GMH6 (60 cm) and PL gel 100 Å 10 μ (30 cm); CHCl₃ solvent, 10 cm³ min⁻¹]: M_w 21 394, M_n 11 246, *D* 1.90; δ_H(CDCl₃) 2.63 (8 H, m), 5.02 (1 H, s) and 7.34 (5 H, m); δ_C(CDCl₃) 31.93 (t), 32.27 (t), 53.68 (d), 127.71 (t), 128.30 (t), 128.77 (t) and 139.63 (s); ν_{max}(KBr)/cm⁻¹ 3057m, 3025m, 2912s, 1662w, 1597w, 1491m, 1450s, 1419s, 1262s, 1201s, 1073m, 1028m, 912w, 838w and 697vs [Found: C, 54.5; H, 5.8; S, 39.6% (C₁₁H₁₄S₃)ₙ requires C, 54.50; H, 5.82; S, 39.68%].

1,2,5-Trithiacycloheptane **6**. Method A was used. After 18 h of reflux, a viscous oily material (1.7 g) was obtained after work-up. The products were separated by column chromatography on aluminium oxide with cyclohexane as eluent. There was obtained, as first fraction, a liquid (0.3 g, 13%); R_f 0.4 (Al₂O₃/hexane); δ_H(CDCl₃) 3.06 (8 H, m); δ_C(CDCl₃) 35.55 (t) and 41.83 (t); ν_{max}(KBr)/cm⁻¹ 2899s, 1405s, 1276s and 833s (Found: C, 31.5; H, 5.3; S, 63.1%; M⁺, 152.266. Calc. for C₄H₈S₃: C, 31.55; H, 5.29; S, 63.16%; *M*, 152.265).

2-(4-Chlorophenyl)-1,3,6-trithiacyclooctane **7**. Method A was used with 4-chlorobenzaldehyde as reactant. After 15 h of reflux in C₆H₆ (200 cm³) and work-up, a viscous material (2.1 g) was obtained. The products were separated on aluminium oxide with toluene as eluent; a solid (0.74 g, 35%) was obtained from the first fraction; R_f 0.91 (Al₂O₃/toluene). The *product* was crystallized from CHCl₃; m.p. 111–113 °C; δ_H(CDCl₃) 3.01 (8 H, m), 6.19 (1 H, s) and 7.32 (4 H, m); δ_C(CDCl₃) 34.03 (t), 35.70 (t), 58.03 (d), 128.56 (d), 128.78 (d), 133.70 (s) and 141.20 (s); ν_{max}(KBr)/cm⁻¹ 3149w, 3041m, 2915m, 2896s, 1486s, 1455m, 1413s, 1399s, 1186m, 1145m, 1085s, 1010s, 891s, 829s, 744s and 684m (Found: C, 47.7; H, 4.7; Cl, 12.8; S, 34.7%; M⁺, 276.756. C₁₁H₁₃ClS₃ requires C, 47.72; H, 4.73; Cl, 12.80; S, 34.69%; *M*, 276.756).

2,10-Bis-(4-chlorophenyl)-1,3,6,9,11,14-hexathiacyclohexadecane **8**. Method A was used. After 5 h of reflux in C₆H₆ (100 cm³) a viscous oil (2.1 g) was obtained. Chromatography with toluene led to a solid (1.2 g, 57%); m.p. 174.5–176.5 °C; R_f(TLC) 0.85 (Al₂O₃/toluene); δ_H(CDCl₃) 2.90 (16 H, m), 5.15 (2 H, s) and 7.40 (8 H, m); δ_C(CDCl₃) 32.50 (t), 32.56 (t), 53.06 (d), 128.80 (d), 128.84 (d), 128.98 (d) and 133.94 (s); ν_{max}(KBr)/cm⁻¹ 2960m, 2919m, 1483s, 1410s, 1404s, 1189s, 1085s, 1010s, 832s, 752m and 679m (Found: C, 47.7; H, 4.7; Cl, 12.8; S, 34.7%; M⁺, 553.530. C₂₂H₂₆Cl₂S₆ requires C, 47.72; H, 4.73; Cl, 12.84; S, 34.74%; *M*, 553.531).

2-(2-Phenylethyl)-1,3,6-trithiacyclooctane **9**. Method A was used with 3-phenylpropionaldehyde as reactant. After 3 h of reflux in C₆H₆ (100 cm³) a viscous oil (2.08 g) was obtained. Chromatography with toluene led to an oil (1.15 g, 55%), R_f 0.94 (Al₂O₃/toluene). Method B led to a 90% yield; δ_H(CDCl₃) 2.10 (2 H, q), 2.94 (8 H, m), 3.27 (2 H, m), 4.95 (1 H, t) and 7.25 (5 H, m); δ_C(CDCl₃) 32.95 (t), 33.53 (t), 35.52 (t), 40.17 (t), 55.33 (d), 126.02 (d), 128.46 (d), 128.53 (d) and 141.26 (s); ν_{max}(KBr)/cm⁻¹ 3060m, 3025s, 2904s, 2854m, 1601s, 1582m, 1494s, 1452s, 1412s, 1277s, 1263s, 1029s, 749s and 701vs (Found: C, 57.7; H, 6.7; S, 35.7%; M⁺, 270.354. C₁₃H₁₈S₃ requires C, 57.73; H, 6.71; S, 35.56%; *M*, 270.354).

2,10-Bis-(2-phenylethyl)-1,3,6,9,11,14-hexathiacyclohexadecane **10**. Method A was used. After 3 h of reflux in C₆H₆ (100 cm³) a viscous oil (2.08 g) was obtained. Chromatography with toluene led to a solid (0.25 g, 12%), m.p. 104–107 °C; and R_f 0.78 (Al₂O₃/toluene); δ_H(CDCl₃) 2.13 (4 H, q), 2.79 (20 H, m), 3.85 (2 H, t) and 7.25 (10 H, m); δ_C(CDCl₃) 30.75 (t), 31.84 (t), 31.93 (t), 37.61 (t), 51.37 (d), 125.87 (d), 126.06 (d), 128.38 (d) and 140.56 (s); ν_{max}(KBr)/cm⁻¹ 3083m, 3060m, 2920s, 2853m, 1600m, 1494s, 1452s, 1419s, 1262s, 1196s, 750s and 700vs (Found: C, 57.7; H, 6.7; S, 35.55%; M⁺, 540.708. C₂₆H₃₆S₆ requires C, 57.73; H, 6.71; S, 35.56%; *M*, 540.707).

1,3,6-Trithiacyclooctane **11**. Method B was used with

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formaldehyde (37 wt. % aqueous solution) as reactant. After 60 h of reaction in methanol, followed by chromatography with ethyl acetate a solid (1.0 g, 78%) was obtained. Method D led to a 23% yield; m.p. 70–72.5 °C; δ_H(CDCl$_3$) 2.91 (8 H, m) and 4.78 (2 H, s); δ_C(CDCl$_3$) 31.50 (t), 32.68 (t) and 66.57 (t); v_{max}(KBr)/cm^{-1} 2903s, 2861m, 1494s, 1386s, 1178s, 1070m, 1006s, 848m, 702s and 670s (Found: C, 36.1; H, 6.1; S, 57.9%; M$^+$, 166.282. C$_5$H$_{10}$S$_3$ requires C, 36.11; H, 6.06; S, 57.83%; M, 166.281).

1,3,6,9,11,14-*Hexathiacyclohexadecane* 12. Method A was used. After 5 h of reflux in C$_6$H$_6$ (150 cm^3) and chromatography with ethyl acetate, a solid (0.87 g, 68%) was obtained, m.p. 92–94.5 °C; δ_H(CDCl$_3$) 2.91 (8 H, m) and 3.81 (2 H, s); δ_C(CDCl$_3$) 31.90 (t), 32.02 (t) and 36.55 (t); v_{max}(KBr)/cm^{-1} 2923s, 2871m, 1419s, 1374m, 1194s, 1180s, 1018s, 1037m, 812m, 730s and 676vs (Found: C, 36.1; H, 6.05; S, 57.9%; M$^+$, 332.565. C$_{10}$H$_{20}$S$_6$ requires C, 36.11; H, 6.06; S, 57.83%; M, 332.565).

7,10,13-*Trithiaspiro[5.7]tridecane* 13. Method A was used with cyclohexanone as reactant. After 18 h of reflux in C$_6$H$_6$ (100 cm^3) followed by work-up and chromatography with cyclohexane, an oil (0.4 g, 22%) was obtained, δ_H(CDCl$_3$) 1.58 (2 H, m), 1.71 (4 H, m), 1.84 (4 H, m) and 2.72 (8 H, m); δ_C(CDCl$_3$) 22.66 (t), 24.81 (t), 31.20 (t), 36.04 (t) and 60.45 (t); v_{max}(KBr)/cm^{-1} 2941vs, 2549s, 1450s, 1270s, 1206s, 1133m, 1011m, 748m and 686m (Found: C, 51.2; H, 7.7; S, 41.1%; M$^+$, 234.351. C$_{10}$H$_{18}$S$_3$ requires C, 51.23; H, 7.74; S, 41.03%; M, 234.353).

7,10,13,20,23,26-*Hexathiadispiro[5.7.5.7]hexacosane* 14. Method A was used. After 18 h of reflux in C$_6$H$_6$ (100 cm^3) followed by work-up and chromatography with toluene, a solid (0.29 g, 16%) was obtained, m.p. 147.5–149.5 °C; δ_H(CDCl$_3$) 1.45 (4 H, br), 1.62 (8 H, br), 1.74 (8 H, q) and 2.81 (16 H, m); δ_C(CDCl$_3$) 22.28 (t), 25.55 (t), 28.77 (t), 30.92 (t), 38.08 (t) and 62.77 (t); v_{max}(KBr)/cm^{-1} 2906m, 2848s, 2774s, 1435s, 1420s, 1347m, 1261m, 1189s, 1115m, 1006s, 865m, 821m, 746s and 668s (Found: C, 51.2; H, 7.7; S, 41.0%; M$^+$, 468.702. C$_{20}$H$_{36}$S$_6$ requires C, 51.23; H, 7.74; S, 41.03%; M, 468.702).

2-(3-*Hydroxypropyl*)-1,3,6-*trithiacyclooctane* 15. Method D was used with 2,3-dihydropyran as reactant. After 4 h of reaction in CHCl$_3$ followed by work-up and chromatography with ethyl acetate, a viscous oil (0.64 g, 35%) was obtained, δ_H(CDCl$_3$) 1.55 (4 H, br), 1.77 (2 H, br), 2.18 (1 H, s), 2.76 (8 H, m), 3.60 (2 H, t) and 4.88 (1 H, t); δ_C(CDCl$_3$) 25.51 (t), 32.16 (t), 35.83 (t), 52.77 (d) and 64.42 (t); v_{max}(KBr)/cm^{-1} 3414br s, 2926s, 2859s, 1405s, 1255s, 1189s, 1070s, 1030s, 1002s, 868m, 854m, 712s and 686m (Found: C, 45.3; H, 7.6; S, 40.4%; M$^+$, 238.349. C$_9$H$_{18}$OS$_3$ requires C, 45.34; H, 7.61; S, 40.34%; M, 238.349).

2,10-*Bis-(3-hydroxypropyl)*-1,3,6,9,11,14-*hexathiacyclohexadecane* 16. Method D was used. After 4 h of reaction in CHCl$_3$ followed by work-up and chromatography with ethanol, a solid (0.22 g, 12%) was obtained, m.p. 62–65.5 °C; δ_H(CDCl$_3$) 1.53 (8 H, br), 1.75 (4 H, br), 2.18 (2 H, s), 2.75 (16 H, m), 3.57 (4 H, t) and 3.86 (2 H, t); δ_C(CDCl$_3$) 23.88 (t), 30.06 (t), 32.01 (t), 52.39 (d) and 62.32 (t); v_{max}(KBr)/cm^{-1} 3415br s, 2934vs, 2860s, 1419s, 1260s, 1199s, 1073s, 1035s, 1006s, 878m, 866m, 718s and 686m (Found: C, 45.3; H, 7.6; S, 40.4%; M$^+$, 476.699. C$_{18}$H$_{36}$O$_2$S$_6$ requires C, 45.34; H, 7.61; S, 40.34%; M, 476.698).

2-*Cyclohexyl*-1,3,6-*trithiacyclooctane* 17. Method A was used with cyclohexanecarbaldehyde as reactant. After 3 h of reflux in C$_6$H$_6$ (150 cm^3) followed by work-up and chromatography with cyclohexane, a viscous oil (0.65 g, 34%) was obtained. Method B led to an 89% yield; δ_H(CDCl$_3$) 1.18–1.70 (11 H, m), 3.08 (8 H, m) and 5.02 (1 H, d); δ_C(CDCl$_3$) 26.18 (t), 29.74 (t), 32.97 (t), 35.87 (t), 39.99 (d) and 53.47 (d); v_{max}(KBr)/cm^{-1} 2924vs, 2852s, 1447s, 1412s, 1277m, 1263m, 1198m, 1077w, 1038w, 896w, 753w and 681w (Found: C, 53.1; H, 8.1; S, 38.8%;

M$^+$, 248.368. C$_{11}$H$_{20}$S$_3$ requires C, 53.17; H, 8.11; S, 38.71%; M, 248.368).

2,10-*Dicyclohexyl*-1,3,6,9,11,14-*hexathiacyclohexadecane* 18. Method A was used. After 10 h of reflux in C$_6$H$_6$ (150 cm^3) followed by work-up and chromatography with toluene, a solid (0.80 g, 42%) was obtained, m.p. 108–111 °C; δ_H(CDCl$_3$) 1.19–1.75 (22 H, m), 2.80 (16 H, m) and 3.82 (2 H, d); δ_C(CDCl$_3$) 26.24 (t), 30.62 (t), 31.73 (t), 32.21 (t), 43.67 (d) and 59.51 (d); v_{max}(KBr)/cm^{-1} 2922s, 2852m, 1412s, 1184s, 1128m, 735s and 669s (Found: C, 53.15; H, 8.1; S, 38.8%; M$^+$, 496.736. C$_{22}$H$_{40}$S$_6$ requires C, 53.17; H, 8.11; S, 38.71%; M, 496.735).

2-(4-*Nitrophenyl*)-1,3,6-*trithiacyclooctane* 19. Method A was used with 4-nitrobenzaldehyde as reactant. After 1 h of reflux in C$_6$H$_6$ (100 cm^3) followed by work-up and chromatography with toluene, a slightly yellow solid (1.0 g, 46%) was obtained. When the reaction was carried out in C$_6$H$_6$ (200 cm^3) at 70 °C a 91% yield was obtained. *Compound* 19 had m.p. 160–162 °C; R_f 0.44 (Al$_2$O$_3$/toluene); δ_H(CDCl$_3$) 3.05 (8 H, m), 6.31 (1 H, s) and 8.06 (4 H, q); δ_C(CDCl$_3$) 31.56 (t), 33.07 (t), 55.28 (d), 121.39 (d), 125.70 (d), 144.78 (s) and 147.10 (s); v_{max}(KBr)/cm^{-1} 3077m, 2921s, 2889m, 2346s, 1683m, 1579m, 1487s, 1390s, 1324s, 1176s, 1106s, 837s, 801s, 721m and 694s (Found: C, 46.0; H, 4.55; N, 4.8; S, 33.6%; M$^+$, 287.318. C$_{11}$H$_{13}$NO$_2$S$_3$ requires C, 45.97; H, 4.56; N, 4.87; S, 33.46%; M, 287.318).

2,10-*Bis-(4-nitrophenyl)*-1,3,6,9,11,14-*hexathiacyclodecane* 20. Method A was used. After 1 h of reflux in C$_6$H$_6$ (100 cm^3) a solid (2.2 g) was obtained. Chromatography with dichloromethane gave solid compound 20 (0.37 g, 17% recovery from the last fraction); m.p. 187.5–190 °C; δ_H(CDCl$_3$) 2.92 (16 H, m), 5.26 (2 H, s) and 7.86 (8 H, q); δ_C(CDCl$_3$) 32.40 (t), 32.57 (t), 53.10 (d), 123.91 (d), 128.67 (d), 147.02 (s) and 147.62 (s); v_{max}(KBr)/cm^{-1} 3104w, 3071w, 2921s, 2852m, 1594s, 1516s, 1417m, 1344s, 1263m, 1200m, 1109m, 861m, 825m and 722s (Found: C, 46.0; H, 4.6; N, 4.8; S, 33.55; M$^+$, 574.635. C$_{22}$H$_{26}$N$_2$O$_4$S$_6$ requires C, 46.0; H, 4.56; N, 4.87; S, 33.46%; M, 574.635).

X-Ray Data Collection and Refinement of Compound 3.— Crystals of compound 3 were grown by slow evaporation of a CHCl$_3$ solution of the compound. A crystal of the title compound, having approximate dimensions of 0.30 × 0.25 × 0.20 mm, was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo-Kα radiation (λ 0.710 73 Å) on a Nonius CAD4F computer-controlled kappa-axis diffractometer equipped with a graphite crystal, incident beam monochromator and interfaced to a VAX-730. Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $11.5° \leqslant \theta \leqslant 17.2°$.

The orthorhombic cell parameters and volume are: a = 19.472(2), b = 8.236(1), c = 7.495(1) Å and V = 1202.0(4) Å^3. For Z = 4 and F.W. = 242.43 the calculated density is 1.34 g cm^{-3}. From systematic absences the space group was determined to be $Pca2_1$. The data collection was performed at 293 K using the θ–2θ scan technique. The intensities of 3 standard reflections, which were measured every 3 h, were used to monitor drift in the primary beam and counting system and also the decrease in crystal quality.

From a total of 1885 reflections in the range $1° \leqslant \theta \leqslant 30°$, 1345 reflections had intensities 3.0 times their standard deviations and were used in the refinements. Scaling factors based on the fluctuations of the standard reflections, Lorentz and polarization corrections were applied to the data. No absorption corrections were made. The linear absorption coefficient was 5.5 cm^{-1}.

The structure was solved by direct methods.[17a] The remaining H-atoms could be revealed from succeeding Fourier

difference syntheses. Full-matrix least-squares of F converged to a final $R = 0.044$ and $R_w = 0.051$ ($w = 1$) respectively, including 127 variable parameters, using anisotropic temperature factors for the non-H-atoms and isotropic fixed temperature factors (B 4.0 Å^2) for the H-atoms. In the final refinements the H-atoms were riding on their corresponding atoms at a distance of 0.97 Å. Final residual electron density was 0.32 e Å^{-3} and final Δ/σ was 0.47. Scattering factors were taken from Cromer and Waber.[17b] All computations were performed on a VAX-730 system.

X-Ray Data Collection and Refinement of Compound 4.—

Crystals of compound 4 were grown by slow evaporation of a CHCl$_3$ solution of the compound. A crystal of the title compound, having approximate dimensions of 0.50 × 0.40 × 0.10 mm, was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo-Kα radiation (λ 0.710 73 Å) on a Nonius CAD4F computer-controlled kappa-axis diffractometer equipped with a graphite crystal, incident beam monochromator and interfaced to a VAX-730. Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $10.1° \leqslant \theta \leqslant 19.6°$.

The monoclinic cell parameters and volume are: $a = 5.428(1)$, $b = 8.192(1)$, $c = 26.322(2)$ Å, $\beta = 93.15(1)°$ and $V = 1168.7(3)$ Å^3. For $Z = 2$ and F.W. $= 484.86$ the calculated density is 1.378 g cm^{-3}. From systematic absences the space group was determined to be $P2_1$. The data collection was performed at 293 K using the θ–2θ scan technique. The intensities of 3 standard reflections, which were measured every 3 h, were used to monitor drift in the primary beam and counting system and also the decrease in crystal quality.

From a total of 2060 reflections in the range $1° \leqslant \theta \leqslant 25°$, 1716 reflections had intensities 3.0 times their standard deviations and were used in the refinements. Scaling factors based on the fluctuations of the standard reflections, Lorentz and polarization corrections and a numerical absorption correction were applied to the data. The relative coefficients ranged from 81.08 to 94.48 respectively. The linear absorption coefficient was 5.7 cm^{-1}.

The structure was solved by direct methods.[17a] The remaining H-atoms could be revealed from succeeding Fourier difference syntheses. Full-matrix least-squares of F converged to a final $R = 0.075$ and $wR = 0.089$ ($w = 1$) respectively, including 154 variable parameters, using anisotropic temperature factors for the non-H-atoms and isotropic fixed temperature factors (B 4.0 Å^2) for the H-atoms. In the final refinements the H-atoms were riding on their corresponding atoms at a distance of 0.97 Å. Final residual electron density was 0.68 e Å^{-3} and final Δ/σ was 0.12. Scattering factors were taken from Cromer and Waber.[17b] Anomalous dispersion effects were included in F_c:[17c] the values were those of Cromer.[17d] All computations were performed on a VAX-730 system. The structure has a centre of symmetry.

X-Ray Data Collection and Refinement of Compound 7.—

Crystals of compound 7 were grown by slow evaporation of a CHCl$_3$ solution of the compound. A crystal of the title compound, having approximate dimensions of 0.40 × 0.25 × 0.20 mm, was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo-Kα radiation (λ 0.710 73 Å) on a Nonius CAD4F computer-controlled kappa-axis diffractometer equipped with a graphite crystal, incident beam monochromator and interfaced to a VAX-730. Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement,

using the setting angles of 25 reflections in the range $10.1° \leqslant \theta \leqslant 20.9°$.

The monoclinic cell parameters and volume are: $a = 7.360(1)$, $b = 9.602(1)$, $c = 18.569(1)$ Å, $\beta = 97.25(1)°$ and $V = 1301.8(4)$ Å^3. For $Z = 4$ and F.W. $= 276.87$ the calculated density is 1.413 g cm^{-3}. From systematic absences the space group was determined to be $P2_1/c$. The data collection was performed at 293 K using the θ–2θ scan technique. The intensities of 3 standard reflections, which were measured every 3 h, were used to monitor drift in the primary beam and counting system and also the decrease in crystal quality.

From a total of 2291 reflections in the range $1° \leqslant \theta \leqslant 25°$, 1730 reflections had intensities 3.0 times their standard deviations and were used in the refinements. Scaling factors based on the fluctuations of the standard reflections, Lorentz and polarization corrections and an empirical absorption correction based on a series of psi-scans were applied to the data. The relative transmission coefficients ranged from 0.954 to 0.999. The linear absorption coefficient was 7.2 cm^{-1}.

The structure was solved by direct methods.[17a] The remaining H-atoms could be revealed from succeeding Fourier difference syntheses. Full-matrix least-squares of F converged to a final $R = 0.057$ and $wR = 0.072$ ($w = 1$) respectively, including 163 variable parameters, using anisotropic temperature factors for the non-H-atoms and isotropic fixed temperature factors (B 4.0 Å^2) for the H-atoms. In the final refinements the H-atoms were riding on their corresponding atoms at a distance of 0.97 Å. Final residual electron density was 0.39 e Å^{-3} and final Δ/σ was 0.12. Scattering factors were taken from Cromer and Waber.[17b] Anomalous dispersion effects were included in F_c:[17c] the values were those of Cromer.[17d] All computations were performed on a VAX-730 system.

X-Ray Data Collection and Refinement of Compound 14.—

Crystals of compound 14 were grown by slow evaporation of a CHCl$_3$ solution of the compound. A crystal of the title compound, having approximate dimensions of 0.45 × 0.35 × 0.35 mm, was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo-Kα radiation (λ 0.710 73 Å) on a Nonius CAD4F computer-controlled kappa-axis diffractometer equipped with a graphite crystal, incident beam monochromator and interfaced to a VAX-730. Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $10.5° \leqslant \theta \leqslant 23.2°$.

The triclinic cell parameters and volume are: $a = 10.6710(6)$, $b = 11.0536(5)$, $c = 12.0371(4)$ Å, $\alpha = 82.026(4)°$, $\beta = 77.284(4)°$, $\gamma = 62.093(4)°$ and $V = 1222.9(1)$ Å^3. For $Z = 2$ and F.W. $= 468.89$ the calculated density is 1.273 g cm^{-3}. From systematic absences the space group was determined to be P-1. The data collection was performed at 293 K using the θ–2θ scan technique. The intensities of 3 standard reflections, which were measured every 3 h, were used to monitor drift in the primary beam and counting system and also the decrease in crystal quality.

From a total of 3401 reflections in the range $1° \leqslant \theta \leqslant 23°$, 2769 reflections had intensities 3.0 times their standard deviations and were used in the refinements. Scaling factors based on the fluctuations of the standard reflections, Lorentz and polarization corrections and also an empirical absorption correction based on a series of psi-scans were applied to the data. The linear absorption coefficient was 5.4 cm^{-1}.

The structure was solved by direct methods.[17a] The remaining H-atoms could be revealed from succeeding Fourier difference syntheses. Full-matrix least-squares of F converged to a final $R = 0.060$ and $wR = 0.074$ ($w = 1$) respectively, including 296 variable parameters, using anisotropic temper-

ature factors for the non-H-atoms and isotropic fixed temperature factors (B 4.0 $Å^2$) for the H-atoms. In the final refinements the H-atoms were riding on their corresponding atoms at a distance of 0.97 Å. Final residual electron density was 0.52 e $Å^{-3}$ and final Δ/σ was 0.07. Scattering factors were taken from Cromer and Waber.[17b] Anomalous dispersion effects were included in F_c:[17c] the values were those of Cromer.[17d] All computations were performed on a VAX-730 system.

X-Ray Data Collection and Refinement of Compound 19.— Crystals of compound 19 were grown by slow evaporation of a $CHCl_3$ solution of the compound. A crystal of the title compound, having approximate dimensions of 0.50 × 0.25 × 0.45 mm, was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed with Mo-Kα radiation (λ 0.710 73 Å) on a Nonius CAD4F computer-controlled kappa-axis diffractometer equipped with a graphite crystal, incident beam monochromator and interfaced to a VAX-730. Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range 11.5° $\leqslant \theta \leqslant$ 28.2°.

The monoclinic cell parameters and volume are: a = 6.006(1), b = 10.723(1), c = 20.099(2) Å, β = 93.24(1)° and V = 1292.4(5) $Å^3$. For Z = 4 and F.W. = 287.42 the calculated density is 1.48 g cm^{-3}. From systematic absences the space group was determined to be $P2_1/n$. The data collection was performed at 293 K using the θ–2θ scan technique. The intensities of 3 standard reflections, which were measured every 3 h, were used to monitor drift in the primary beam and counting system and also the decrease in crystal quality.

From a total of 4445 reflections in the range 1° $\leqslant \theta \leqslant$ 32°, 3216 reflections had intensities 3.0 times their standard deviations and were used in the refinements. Scaling factors based on the fluctuations of the standard reflections, Lorentz and polarization corrections and also an empirical absorption correction based on a series of psi-scans was applied to the data. The linear absorption coefficient was 5.4 cm^{-1}.

The structure was solved by direct methods.[17a] The remaining H-atoms could be revealed from succeeding Fourier difference syntheses. Full-matrix least-squares of F converged to a final R = 0.060 and wR = 0.075 (w = 1) respectively, including 183 variable parameters, using anisotropic temperature factors for the non-H-atoms and isotropic fixed temperature factors (B 4.0 $Å^2$) for the H-atoms. In the final refinements the H-atoms were riding on their corresponding atoms at a distance of 0.97 Å. Final residual electron density was 0.41 e $Å^{-3}$ and final Δ/σ was 0.33. Scattering factors were taken from Cromer and Waber.[17b] Anomalous dispersion effects were included in F_c:[17c] the values were those of Cromer.[17d] All computations were performed on a VAX-730 system.

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