

# Synthesis of *trans*-(±)-1,2,3,3a,4a,5,6,7-Octaphenyl-3a*H*,4a*H*-dicyclopenta[*b,e*][1,4]dithiin by Dimerization and Further Rearrangement of the Transient 2,3,4,5-Tetraphenyl-2,4-cyclopentadiene-1-thione

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Thionation of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one and of 5-diazo-1,2,3,4-tetraphenyl-1,3-cyclopentadiene gives *trans*-(±)-1,2,3,3a,4a,5,6,7-octaphenyl-3a*H*,4a*H*-dicyclopenta[*b,e*]-[1,4]dithiin, most likely by dimerization of the primarily formed 2,3,4,5-tetraphenyl-2,4-cyclopentadiene-1-thione and subsequent phenyl migration. Characterization has been performed using X-ray crystallography. Calculations have been performed on derivatives of 2,4-cyclopentadien-1-one and -1-thione.

In a series of attempts to prepare derivatives of 2,4-cyclopentadiene-1-thione our interest has now focused on 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-thione **1** which we hoped to obtain by thionation of appropriate precursors.

Thus, following standard procedures for the conversion of ketones into thioketones with Lawesson's reagent<sup>1</sup> or with *in-situ* formed boron sulfide,<sup>2</sup> 2,3,4,5-tetraphenyl-2,4-cyclopentadiene-1-one **2** was thionated. In a supplementary experiment 5-diazo-1,2,3,4-tetraphenyl-1,3-cyclopentadiene **3** was thionated with elemental sulfur according to Raasch's method<sup>3</sup> (Scheme 1).

However, instead of the thioketone **1** the tricyclic compound *trans*-(±)-1,2,3,3a,4a,5,6,7-octaphenyl-3a*H*,4a*H*-dicyclopenta[*b,e*][1,4]dithiin **4**, characterized by a single crystal X-ray structure determination, was isolated. The novel compound **4** is a condensed derivative of the parent 1,4-dithiin; only more or less saturated derivatives of 3a*H*,4a*H*-dicyclopenta[*b,e*][1,3]dithiin **5** have been reported so far.<sup>4</sup> In order to account for the formation of **4**, some theoretical calculations were carried out.

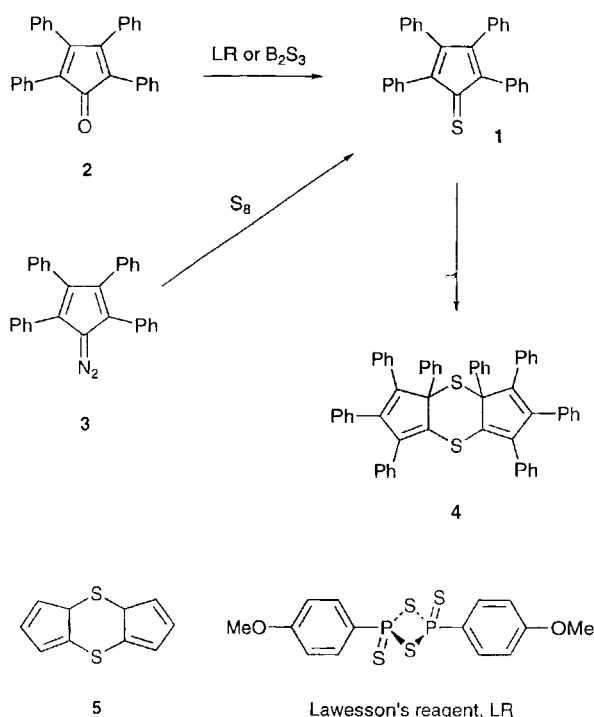
In earlier work<sup>5</sup> one of us attempted the preparation

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of 2,3,4,5-tetrachloro-2,4-cyclopentadiene-1-thione **6**. Here, as outlined in Scheme 2, **6** was formed by reaction of 5-diazo-1,2,3,4-tetrachloro-1,3-cyclopentadiene **7** with molten sulfur. However, the elusive **6** reacts with the starting compound **7** to give an ylide **8** which then rearranges to the tricyclic compound **9**.

In contrast with the 2,4-cyclopentadien-1-ones **10**, which are best represented by resonance form **10a** (Scheme 3), the analogous 2,4-cyclopentadiene-1-thiones **11** – by virtue of the more polarizable thiocarbonyl double bond and the less electronegative sulfur atom – could be expected to possess a structure with a larger contribution of resonance form **11b**. Thus, the stability of 2,4-cyclopentadiene-1-thiones must be expected to be governed by the balance between the amount of aromaticity in the five-membered ring on one hand and the amount of inverse polarizability and thereby reactivity of the thiocarbonyl group (as represented in resonance form **11b**) on the other.

The possible reactions of **1** are depicted in Scheme 4. In the absence of simpler or more plausible working hypotheses we assume that our starting ketone **2** (and diazo compound **3**) is thionated to the corresponding thioketone **1**. As a strong ambiphile **1** would be expected to be subject to facile head-to-tail dimerization, either in

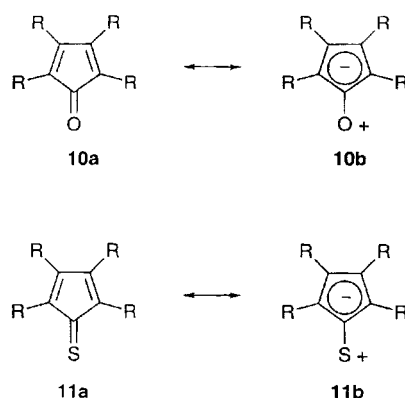


Scheme 1.

the photochemical [2+2] fashion typical of many thio-carbonyl compounds<sup>6</sup> leading to the 1,3-dithietane derivative **12** or in a thermochemically allowed [3+3] fashion leading to the 1,4-dithiane derivative **13** (Scheme 4). The hypothetical [4+4] dimerization is ruled out by the anti-Bredt features of the corresponding head-to-tail dimer **14**. We assume that the preference for the formation of **13** as the primary product is for predominantly steric reasons.

The actually isolated reaction product **4** is derived from **13** by a [1,5] phenyl migration. It remains to be seen whether the driving force for this rearrangement is primarily of steric or electronic nature.

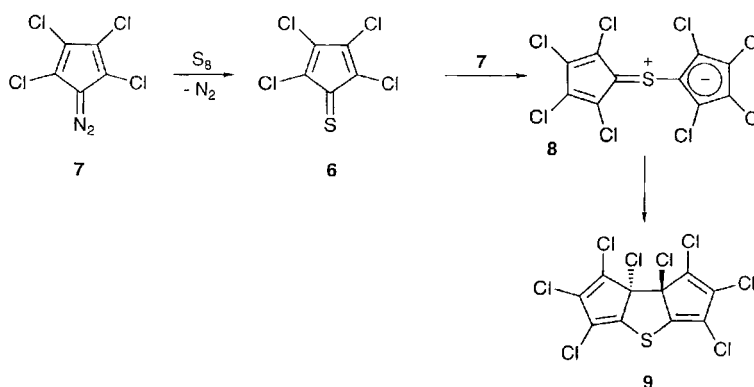
*Computational section.* *Ab initio* calculations were performed for analogous series of cyclopentadienone and



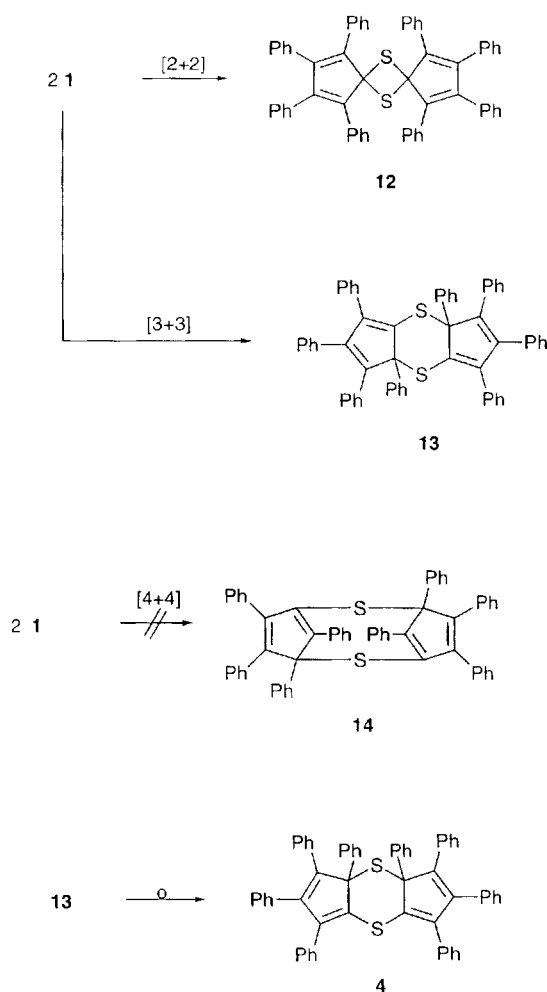
Scheme 3.

cyclopentadienethione derivatives in order to reveal electronic structure characteristics that could account for differences in reactivity between the former and the latter. Previous investigations have focused on the planar versus non-planar structures of the cyclopentadienone and cyclopentadienethione compounds.<sup>7-11</sup> All computations were performed using the GAUSSIAN 92 code.<sup>12</sup>

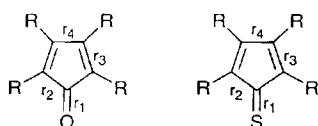
*Ab initio* geometry optimizations were performed for the two series of closed shell molecules (Fig. 1), at the restricted Hartree-Fock level of theory, applying the 6-13G\*\* Gaussian basis set.<sup>13</sup> In order to reduce the computational tasks symmetry constraints were applied during the geometry optimizations. In all cases, except for the tetraphenyl derivatives, the constraints correspond to a mirror plane along the carbonyl/thiocarbonyl bond, the plane being placed normal to the molecular plane. Additional requirements were made when R equaled CH<sub>3</sub> or CF<sub>3</sub>. In the case of CH<sub>3</sub> all three C-H bond lengths were forced to be equal and the angles between the hydrogens and the ring carbon atom (to which the methyl group is attached) were also forced to be equal. In the case of the tetraphenyl derivatives the above-mentioned symmetry constraints were relaxed such that the individual phenyl groups could rotate freely and bend out of the molecular plane. On the other hand the phenyl groups were assumed planar with a fixed hexa-



Scheme 2.



Scheme 4.

(R = H, Cl, Me, CF<sub>3</sub>, Ph)Fig. 1. Model molecules for *ab initio* geometry optimizations (R = H, Cl, Me, CF<sub>3</sub>, Ph).

gonal structure. Thus only two parameters allowed the different types of phenyl ring to expand or contract, in orthogonal directions. Furthermore, all C–H bonds in the phenyl groups are fixed at the same length. The geometry constraints involving the substituents are not expected to have a major influence on the bond lengths and angles of the five-membered rings.

**Molecular orbital analysis.** The molecular orbitals (MO) obtained from the 6-31G\*\* computations were inspected in order to identify characteristic electronic features, especially for those MOs close in energy to the HOMO and LUMO. In Fig. 2 we present results for cyclo-

pentadienone and cyclopentadienethione representing the general trend for the two series.

From Fig. 2a it is apparent that the HOMOs in both cases resemble  $\pi$ -orbitals of a butadiene fragment. The densities are generally quite similar for the two types of derivative. Focusing on the MOs right below the HOMO level, as shown in Fig. 2b, we observe, in both cases, no contribution to the  $\pi$ -system. Hence, these MOs are responsible for some of the  $\sigma$ -backbone and in-plane directed lone pair density on the chalcogen atoms. As seen from Fig. 2c the second MOs below the HOMOs lead to pure  $\pi$ -electron contributions and account for  $\pi$ -electron density distributed over the entire ring and carbonyl/thiocarbonyl group. Proceeding to the MOs one step further below shows (not shown in the figures) contributions to the  $\sigma$ -backbone and lone pair structure of the chalcogen atoms. The final set of occupied MOs, which constitute the  $\pi$ -system, are depicted in Fig. 2d and they constitute the 'bonding' counterpart of the MOs shown in Fig. 2c. All other lower lying MOs have no reference to the  $\pi$ -system at all.

The LUMOs, sketched in Fig. 2e, refer only to the  $\pi$ -system and are generally quite similar going from cyclopentadienone to cyclopentadienethione. The MOs right above the LUMOs (Fig. 2f) describe solely  $\pi$ -electron density, but in this case we note that generally the cyclopentadienone structures have negligible density on the carbonyl group. In some cases it happens that an MO with reference to the underlying  $\sigma$ -bond structure gets squeezed in between the LUMOs and the MOs shown in Fig. 2f, thereby only affecting the relative position of the MOs.

From the magnitude of the individual MO densities assigned to the above-mentioned MOs we make the following observations. (a) The  $\pi$ -electron density for the carbonyl group generally favors the oxygen whereas for the thiocarbonyl compound most density is found on the carbon atom. (b) For cyclopentadienone the  $\pi$ -electron density at the butadiene fragment is generally dominated by the density at the carbonyl group. This is reversed for the cyclopentadienethione derivatives.

In Tables 1 and 2 we have listed energy differences between some of those MOs that we believe would be most susceptible to reaction. From Table 1 we observe that: (c) the energy difference between the LUMO and the highest occupied MO having pronounced density at the chalcogen atom generally decreases by 0.1 au (and at most 0.16 au) on going from cyclopentadienone to cyclopentadienethione. The same observations are seen for the HOMO–LUMO gap, where energy separations are generally in the interval 0.024–0.06 au.

**Geometry optimized bond lengths.** In Table 3 important bond lengths are listed for the entire series of structures. Inspection immediately reveals the following points. (d) The  $r_2$  and  $r_4$  values for the carbonyl series are close to the values found for the corresponding bonds in cyclopentadiene, while for the thiocarbonyl case these

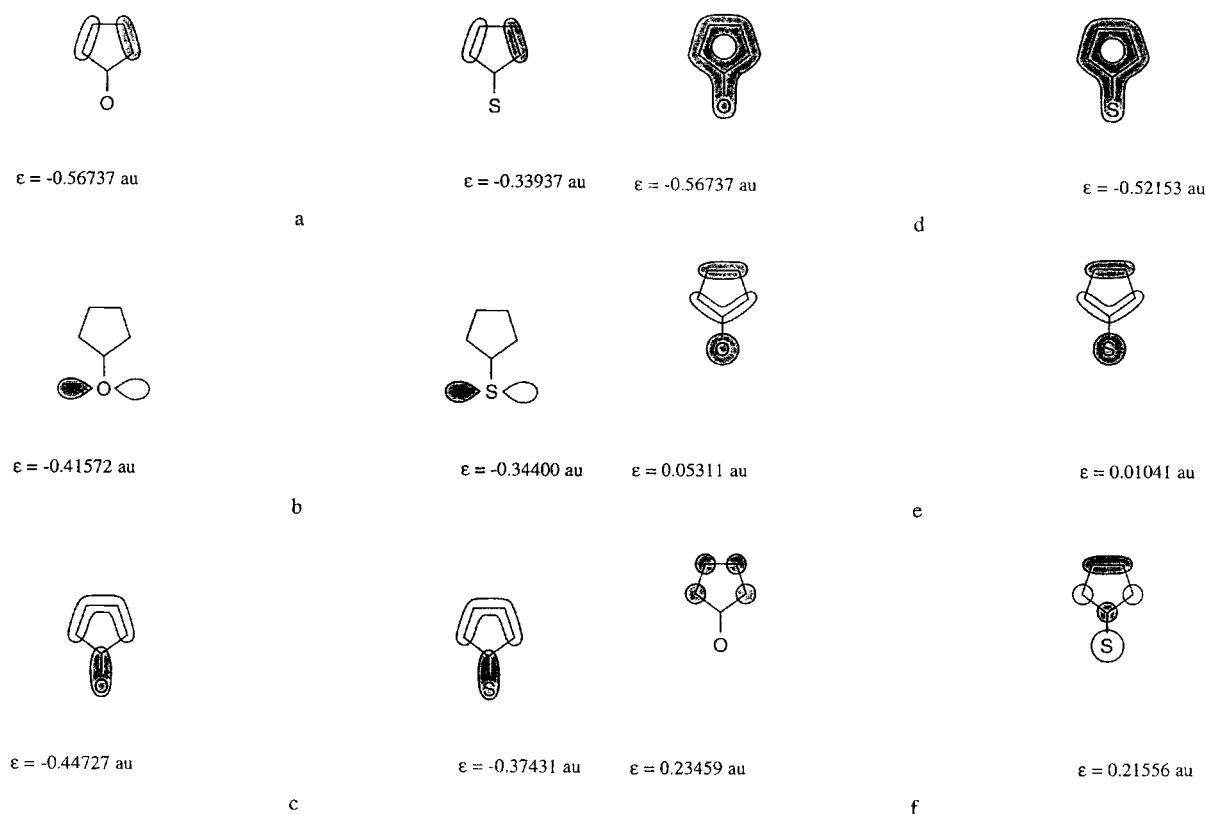


Fig. 2. Various occupied molecular orbitals: (2a) p-electron density contribution from the HOMOs; (2b) the pronounced lone pair contribution to the MO directly below the HOMO level; (2c) p-electron densities for the second level below the HOMOs; (2d) the bonding 'aromatic' part of the p-system, various unoccupied molecular orbitals; (2e) p-electron density contribution from the LUMOs; (2f) molecular orbitals directly above the LUMO level.

Table 1. Orbital spacing between the LUMOs and MOs right below describing chalcogenic lone pair character.

R	S: $ E_{\text{LUMO}} - E_{\text{MO}} $ au.	O: $ E_{\text{LUMO}} - E_{\text{MO}} $ au.
H	0.3544 # = 24	0.4688 # = 20
Cl	0.3526 # = 56	0.4579 # = 51
Me	0.3591 # = 40	0.4704 # = 30
CF <sub>3</sub>	0.3436 # = 89	0.4594 # = 84
Ph	0.3367 # = 103	0.4572 # = 92

Table 2. The respective HOMO–LUMO gaps.

R	S: $ E_{\text{LUMO}} - E_{\text{HOMO}} $ au.	O: $ E_{\text{LUMO}} - E_{\text{HOMO}} $ au.
H	0.3498	0.3954
Cl	0.3193	0.3619
Me	0.3340	0.3819
CF <sub>3</sub>	0.3436	0.4038
Ph	0.3042	0.3281

values are smaller than in cyclopentadiene. (e) The bond lengths,  $r_3$ , are generally larger compared with the corresponding bond length found in cyclopentadiene. Accordingly we note that on going from the cyclopentadienones to the cyclopentadienethiones these values expand. Finally, (f) the bond lengths in the carbonyl/thiocarbonyl groups,  $r_1$ , change substantially

Table 3. Geometry optimized theoretical bond lengths with reference to Fig. 1.

(Å)		H	Cl	CH <sub>3</sub>	Ph	CF <sub>3</sub>
$r_1$	O	1.1877	1.1777	1.1915	1.1888	1.1772
	S	1.6104	1.5973	1.6165	1.6123	1.6015
$r_2$	O	1.506	1.5066	1.5029	1.50744	1.5134
	S	1.4851	1.4895	1.4908	1.4928	1.4935
$r_3$	O	1.3218	1.3205	1.327	1.333	1.3233
	S	1.3273	1.3254	1.3316	1.337	1.3314
$r_4$	O	1.5029	1.5075	1.5229	1.5259	1.5205
	S	1.4949	1.4946	1.5136	1.5154	1.5042

compared with the values of the corresponding bond lengths determined for the cyclopentane derivatives.<sup>14</sup>

*Theoretical total atomic charges.* When the atomic charges were analyzed it immediately became clear that these calculations also suffered from the inability of the Mulliken scheme to render meaningful results. Only the charges on the carbonyl/thiocarbonyl group showed consistent trends, and in Table 4 we can observe the following. (g) The polarity of the carbonyl/thiocarbonyl bond changes when oxygen is replaced by sulfur, the polarity of the carbonyl bond being such that oxygen appears as

**Table 4.** Theoretical total atomic charges at the carbonyl and thiocarbonyl groups.

R	Carbon	Oxygen	Carbon	Sulfur
H	0.209	-0.205	-0.098	0.125
Cl	0.243	-0.154	-0.099	0.247
Me	0.197	-0.222	-0.099	0.086
CF <sub>3</sub>	0.224	-0.168	-0.106	0.213
Ph	0.203	-0.213	-0.100	0.117

the negative site. (h) The  $\alpha$ -carbon atom carries a negative charge in all cyclopentadienethione structures while the opposite applies for the case of the cyclopentadienone structures.

## Discussion

Upon replacement of oxygen by sulfur part of the electronic density moves into the cyclopentadiene ring, as seen from the above points (a), (b), (g) and (h). This partial donation of an electron results in increased aromaticity of the sulfur derivatives as confirmed by observations (d), (e) and (f). Along with the fact that the sulfur derivatives have never been isolated either as monomers or dimers (the Diels–Alder dimerization product) and that compound **4** has recently been isolated, one might expect that this aromatization may lead to a more reactive thiocarbonyl group.

In order to examine the actual reaction scheme we have, in view of the above discussions, undertaken computational investigations utilizing semiempirical studies on the relevant compounds in the reaction mechanism. We have examined the experimentally obtained structure **4** and the proposed intermediate **13** through semiempirical calculations, utilizing the MOPAC program<sup>15</sup> at the MNDO level of theory.<sup>16</sup> The compounds were fully geometrically optimized in the gas phase. According to these calculations, the proposed intermediate **13** is located 82.9 kJ mol<sup>-1</sup> above the isolated product **4**. Thus, in terms of relative energies, the proposed mechanism involving **13** as an intermediate for the formation of **4** is in good agreement with our calculations.

## Experimental

*trans-(±)-1,2,3,3a,4a,5,6,7-Octaphenyl-3aH,4aH-dicyclopenta[b,e][1,4]dithiin 4 from 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one 2 and Lawesson's reagent.* In a typical experiment, **2** (5.00 g, 12.48 mmol) and Lawesson's reagent (3.03 g, 7.49 mmol) were placed in a 250 ml three-necked reaction flask fitted with a rubber septum, a condenser with a bubbler and a nitrogen inlet. The system was flushed with nitrogen, and 100 ml sodium-dried toluene were added with a syringe. The mixture was refluxed with stirring for 2–3 d until it was golden brown and TLC showed the absence of the starting ketone. The reaction was cooled to room temperature after which some polymeric material was filtered

off. The filtrate was adsorbed on the minimum amount of silica gel and the solvent removed with a rotary evaporator. Immediately thereafter the adsorbate was column chromatographed (silica gel, 30% CH<sub>2</sub>Cl<sub>2</sub> in pet. ether). A small amount of a colorless compound, identified as 1,2,3,4-tetraphenyl-1,3-cyclopentadiene, was isolated as the first fraction. The second yellow fraction, which was evaporated to a yellow powder, was identified as **4**. The yield was 650 mg, 13%, m.p. 249.6–252.2 °C. IR (KBr):  $\nu$  3060, 3020, 1600, 1490, 1440, 1080, 1035, 915, 770, 720, 700, 580 cm<sup>-1</sup>. MS (FAB):  $m/z$  800, 402, 401, 400, 323, 321, 307, 289, 154, 136. MS (70 eV):  $m/z$  401, 400, 370, 323, 321, 308, 289, 165, 161, 91, 77. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.28 (s), 7.20 (m). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  67.45, 127.45, 127.59, 127.71, 128.05, 128.16, 128.23, 128.58, 128.99, 129.65, 130.09, 130.42, 134.12, 134.73, 135.69, 139.19, 142.34, 143.21, 144.16, 148.34. Found: C 86.43, H 5.20, S 8.07; calc. for C<sub>58</sub>H<sub>40</sub>S<sub>2</sub> (801.093): C 86.96, H 5.03, S 8.01%. The following column fractions could be evaporated to greasy substances. Although very small fractions were collected, TLC showed the presence of a very large number of compounds in each fraction. None of these compounds was identified.

*trans-(±)-1,2,3,3a,4a,5,6,7-Octaphenyl-3aH,4aH-dicyclopenta[b,e][1,4]dithiin 4 from 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one 2 and in situ formed B<sub>2</sub>S<sub>3</sub>.* In a typical experiment, **2** (2.37 g, 6.15 mmol) and bis[tris(cyclohexyl)tin] sulfide (5.20 g, 6.77 mmol) were placed in a 250 ml three-necked flask fitted with a rubber septum and a condenser. The system was gently flushed with argon and 50 ml sodium dried toluene were added. A 1.0 M solution of BCl<sub>3</sub> in hexane (4.10 ml, 4.10 mmol) was added with a syringe. The mixture was heated to reflux and kept at this temperature for 2–3 d. Column chromatography was performed (silica gel, 30% CH<sub>2</sub>Cl<sub>2</sub> in pet. ether). The first fraction collected was tris(cyclohexyl)tin chloride, followed by a yellow fraction, which could be identified as **4**. Typical yields: 250–370 mg, 10–15%.

*trans-(±)-1,2,3,3a,4a,5,6,7-Octaphenyl-3aH,4aH-dicyclopenta[b,e][1,4]dithiin 4 from 5-diazo-1,2,3,4-tetraphenyl-1,3-cyclopentadiene 3 and elemental sulfur.* Compound **3**<sup>17</sup> (500 mg, 1.26 mmol), dissolved in 20 ml DMF, was slowly added to DMF (4 ml) containing sulfur (40 mg, 1.26 mmol) kept at 120 °C. An argon atmosphere was maintained in the system. With every portion added gas evolution was seen, the color changing from orange in the beginning to dark red at the end. When the gas evolution had ceased the mixture was cooled to room temperature and the solvent removed on a rotary evaporator. Column chromatography (silica gel, 25% CH<sub>2</sub>Cl<sub>2</sub> in pet. ether) yielded **4** as a yellow fraction, yield: 60.5 mg, 12%.

*Crystallography.* Crystal data for *trans-(±)-1,2,3,3a,4a,5,6,7-Octaphenyl-3aH,4aH-dicyclopenta[b,e][1,4]dithiin 4*, C<sub>58</sub>H<sub>40</sub>S<sub>2</sub>,  $M = 801.08$ , triclinic, space group  $P\bar{1}$ ,

Table 5. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\times 10^3$ ),  $U_{eq} = (1/3)$ .

Atom	$x/a$	$y/b$	$z/c$	$U_{eq}$
S1	11334(7)	3548(6)	1012(4)	53(2)
S2	8736(7)	2932(6)	3050(4)	56(2)
C1	9182(19)	1885(13)	2489(11)	52(2)
C2	9147(14)	1446(16)	3258(10)	59(2)
C3	10400(20)	1985(17)	3175(12)	64(2)
C4	11339(15)	2799(17)	2370(12)	63(2)
C5	10586(24)	2718(22)	2003(14)	53(2)
C1'	9518(16)	4048(12)	2126(10)	50(2)
C2'	8270(17)	3645(16)	2033(11)	55(2)
C3'	8237(15)	3097(17)	1180(12)	53(2)
C4'	9276(18)	3036(16)	718(9)	47(2)
C5'	10034(24)	3507(20)	1215(14)	46(2)
C6	8323(13)	691(12)	2005(7)	57(2)
C7	7038(14)	195(14)	2170(9)	65(2)
C8	6248(14)	-904(14)	1725(11)	80(2)
C9	6717(18)	-1542(13)	1101(10)	87(3)
C10	7993(19)	-1059(14)	931(9)	78(4)
C11	8783(15)	40(14)	1377(8)	64(3)
C12	7853(13)	489(12)	3943(8)	67(2)
C13	7201(15)	883(13)	4690(9)	77(3)
C14	6011(15)	3(18)	5320(9)	94(3)
C15	5436(15)	-1299(16)	5222(10)	99(3)
C16	6073(16)	-1704(13)	4482(11)	88(3)
C17	7264(15)	-823(13)	3853(9)	73(3)
C18	10831(13)	1849(10)	3762(9)	76(3)
C19	10236(15)	1821(14)	4690(9)	93(6)
C20	10632(19)	1696(14)	5231(9)	109(7)
C21	11636(18)	1595(13)	4860(12)	109(6)
C22	12237(16)	1621(14)	3939(13)	95(6)
C23	11840(14)	1746(12)	3398(9)	79(5)
C24	12832(16)	3712(13)	2042(8)	78(2)
C25	13572(16)	3578(15)	1184(9)	89(3)
C26	14947(16)	4419(19)	882(11)	115(3)
C27	15624(16)	5419(17)	1428(13)	131(2)
C28	14902(17)	5564(15)	2281(13)	120(2)
C29	13527(17)	4723(14)	2583(10)	94(2)
C6'	10550(13)	5442(13)	2324(6)	58(2)
C7'	11455(14)	5794(13)	2667(8)	68(2)
C8'	12405(14)	7077(15)	2849(10)	86(3)
C9'	12480(16)	8047(14)	2695(9)	94(3)
C10'	11587(17)	7710(12)	2355(9)	81(3)
C11'	10637(14)	6427(13)	2172(8)	64(3)
C12'	7532(13)	4119(10)	2726(9)	71(3)
C13'	6681(15)	4122(13)	2556(10)	85(3)
C14'	6002(16)	4558(16)	3194(12)	111(4)
C15'	6152(18)	5005(15)	4023(11)	124(5)
C16'	6994(19)	5007(15)	4201(9)	109(5)
C17'	7673(16)	4570(14)	3562(9)	83(3)
C18'	7173(13)	2587(11)	849(8)	65(3)
C19'	5860(13)	1509(14)	1231(10)	94(2)
C20'	4881(14)	1040(16)	927(13)	117(3)
C21'	5184(16)	1634(16)	231(12)	107(5)
C22'	6485(17)	2706(16)	-156(10)	74(5)
C23'	7464(14)	3176(13)	149(9)	55(4)
C24'	9496(12)	2397(11)	-180(8)	54(3)
C25'	10690(13)	3082(12)	-890(9)	58(3)
C26'	10892(16)	2494(17)	-1717(8)	75(4)
C27'	9906(18)	1203(16)	-1860(10)	89(5)
C28'	8715(17)	511(13)	-1160(11)	84(4)
C29'	8513(14)	1099(12)	-334(9)	67(3)
Sol1-O	960(35)	5026(33)	4783(18)	167(15)
Sol2-C	2177(25)	5870(22)	4598(13)	32(8)
Sol3-C	140(27)	4488(22)	4954(14)	15(9)

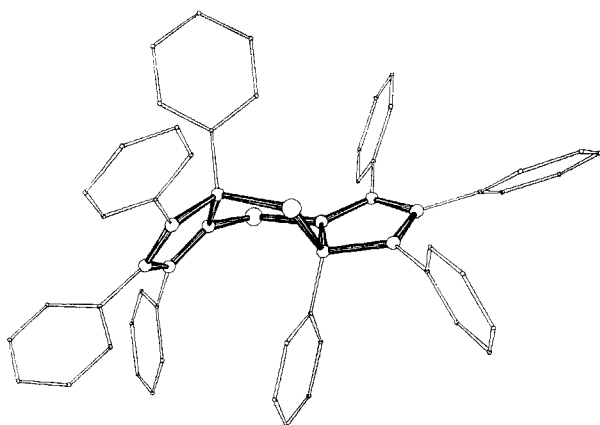


Fig. 3. The molecular structure of **4**, *trans*-(±)-1,2,3,3a,4a,5,6,7-octaphenyl-3aH,4aH-dicyclopenta[*b,e*][1,4]dithiin, C<sub>58</sub>H<sub>40</sub>S<sub>2</sub> in a perspective drawing showing the relative positions of the phenyl groups attached to the central buckled dicyclopentadithiin part of the molecule, which is seen side on.

$Z=2$ ,  $a=14.419(9)$ ,  $b=13.874(8)$ ,  $c=16.723(9)$  Å,  $\alpha=108.80(3)$ ,  $\beta=62.58(3)$ ,  $\gamma=132.38(3)^\circ$ ,  $V=2193.2$  Å<sup>3</sup>,  $D_c=1.21$  g cm<sup>-3</sup>,  $\mu=2.2$  cm<sup>-1</sup>. Data were measured on a HUBER four-circle diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda=0.7107$  Å) in the  $\omega$ - $2\theta$  scan mode. Crystal dimensions  $0.12 \times 0.12 \times 0.08$  mm. Crystals of **4** for the X-ray structure determination were difficult to obtain. Slow evaporation of a saturated solution of **4** in a chloroform-ethanol mixture gave the best results, although just tiny crystals. Outside  $2\theta=30^\circ$  very few significant reflections could be observed. The structure was solved by direct methods using the SHELX-86 program package.<sup>18</sup> 1009 reflections with  $F > 4\sigma(F)$  were used in a constrained refinement using the Aarhus KRYSTAL program package.<sup>19</sup>  $R(F)=0.0953$ . The structure was described by 102 parameters, with the eight phenyl groups as rigid moieties of *mm* symmetry undergoing identical rigid body motion. Fig. 3 shows the

molecular structure of **4** and Fig. 4 depicts a 'perpendicular' view of the central dicyclopentadithiin part of the molecule. The atomic thermal displacements of this part of the molecule are described as rigid body motion of a separate moiety. Three peaks in the Fourier synthesis near a center of symmetry are interpreted as solvent of crystallization. Atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms are given in Table 5. Supplementary material, including lists of structure factors, bond lengths and angles, and thermal parameters, has been deposited at the Cambridge Crystallographic Data Centre.

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## References

1. For a contemporary review of thionation reactions, including reactions of carbonyl compounds with Lawesson's reagent, see Brillon, D. *Sulfur Rep.* **12** (1992) 297.
2. Steliou, K. and Mrani, M. *J. Am. Chem. Soc.* **104** (1982) 3104.
3. Raasch, M. S. *J. Org. Chem.* **44** (1979) 632.
4. (a) Asinger, F., Thiel, M., Usbeck, H., Gröbe, K.-H., Grundmann, H. and Tränkner, S. *Liebigs Ann. Chem.* **634** (1960) 144; (b) Krespan, C. G. (E. I. du Pont de Nemours & Co.) *U.S. 3,096,342* (1963); *Chem. Abstr.* **59** (1963) 12825; (c) Krespan, C. G. and England, D. C. *J. Org. Chem.* **33** (1968) 1850; (d) Russell, G. A., Tanikaga, R. and Talaty, E. R. *J. Am. Chem. Soc.* **94** (1972) 6125; (e) Moriarty, R. M., Chien, C. C. and Jefford, C. W. *Tetrahedron Lett.* (1973) 4429; (f) Gollnick, K. and Hartmann, H. *Tetrahedron Lett.* (1982) 2651.
5. Senning, A., Christensen, T. B., Belsky, V. K. and Zavodnik, E. *Sulfur Lett.* **17** (1994) 217.
6. Duus, F. In: Jones, N. D., Ed., *Comprehensive Organic Chemistry*, Pergamon Press, Oxford 1979, Vol. 3, p. 373.
7. Hutter, W., Bodenseh, H.-K. and Dakkour, M. *J. Mol. Struct.* **321** (1994) 255.

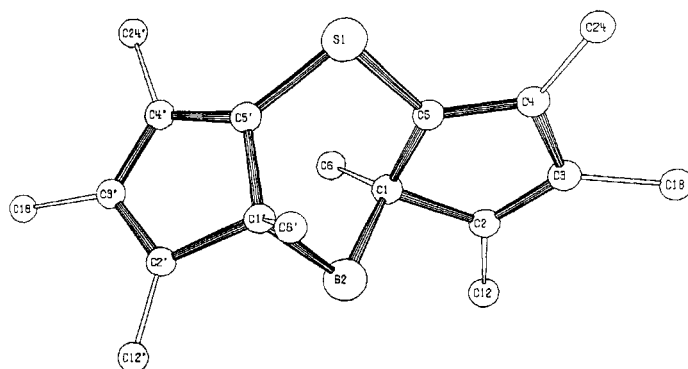


Fig. 4. A 'perpendicular' view of the central dicyclopentadithiin part of the molecule **4**. Only the attaching bonds of phenyl groups are retained in the figure. Bond lengths (Å): S1-C5 1.77(2), S1-C5' 1.71(3), S2-C1 1.80(2), S2-C1' 1.91(2), C1-C5 1.43(3), C1-C2 1.56(2), C2-C3 1.36(2), C3-C4 1.47(2), C4-C5 1.40(3), C1'-C5' 1.55(3), C1'-C2' 1.56(2), C2'-C3' 1.39(2), C3'-C4' 1.38(2), C4'-C5' 1.35(2). Selected bond angles ( $^\circ$ ): C5-S1-C5' 95.5(12), C1-S2-C1' 104.2(8), S1-C5-C1 124(2), S1-C5-C1' 119(2), S2-C1-C5 106(1), S2-C1-C5' 108(1), C5-C1-C2 100(2), C1-C2-C3 112(1), C2-C3-C4 107(1), C3-C4-C5 108(1), C4-C5-C1 114(2), C5'-C1'-C2' 100(1), C1'-C2'-C3' 109(1), C2'-C3'-C4' 110(1), C3'-C4'-C5' 112(2), C4'-C5'-C1' 109(2).

8. Maier, Q., Schmidt, C., Reisenauer H. P., Endlein, E., Becker, D., Eckwert, J., Hess, B. A. Jr. and Schaad, L. *J. Chem. Ber.* 126 (1993) 2337.
9. Glukhovtsev, M. N., Schleyer, P. v. R., van E. Hommes, N. J. R. and Minkin, V. I. *Chem. Phys. Lett.* 205 (1993) 529.
10. Tielemans, M., Areschka, V., Colomer J., Promel, R., Langenaeker, W. and Geerlings, P. *Tetrahedron* 48 (1992) 10575.
11. Tielemans, M., Promel, R. and Geerlings, P. *Tetrahedron Lett.* 29 (1988) 1687.
12. GAUSSIAN 92, Frisch, M. J., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P. and Pople, J. A., Gaussian Inc., Pittsburgh, PA 1992.
13. Hehre, W. J., Ditchfield, R. and Pople, J. A. *J. Chem. Phys.* 56 (1972) 2257; Hariharan, P. C. and Pople, J. A. *Theor. Chim. Acta* 28 (1973) 213.
14. The calculated molecular structures can be obtained upon request. The molecules are: 2,4-cyclopentadien-1-one, 2,4-cyclopentadiene-1-thione, 2,3,4,5-tetramethyl-2,4-cyclopentadien-1-one, 2,3,4,5-tetramethyl-2,4-cyclopentadiene-1-thione, 2,3,4,5-tetrachloro-2,4-cyclopentadien-1-one, 2,3,4,5-tetrachloro-2,4-cyclopentadiene-1-thione, 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadien-1-one, 2,3,4,5-tetrakis(trifluoromethyl)-2,4-cyclopentadiene-1-thione, 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one and 2,3,4,5-tetraphenyl-2,4-cyclopentadiene-1-thione.
15. Dewar Research Group and Stewart, J. J. P. *Quantum Chemistry Program Exchange*, Indiana University, Bloomington, IN.
16. Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.* 99 (1977) 4899.
17. Regitz, M. and Liedhegener, A. *Tetrahedron* 23 (1967) 2701.
18. Sheldrick, G. M. (1994) SHELX-86. Institut für Anorganische Chemie der Universität Göttingen, Tammannstraße 4, D-37077 Göttingen, Germany.
19. Hazell, A. (1995) KRYSTAL. An Integrated System of Crystallographic Programs. Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.

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