

The pyridine moiety is essentially planar (within 0.01 Å), while in the cyclohexene moiety C(7) is 0.67 (1) Å away from the plane formed by C(5), C(6), C(8), C(9) and C(10). The dihedral angle between the mean planes of the two rings is 9.7 (5)°. The presence of *gem*-dichloro substituents at C(5), C(7) and C(8) induces a considerable amount of strain in the molecule. This strain is mainly distributed in the vicinity of the bulky Cl substituents. The distances between Cl atoms attached to the same C atom are 2.906 (1), 2.880 (2) and 2.892 (2) Å for Cl(1)···Cl(2), Cl(3)···Cl(4) and Cl(5)···Cl(6), respectively, similar to the value in hexachlorocyclohexa-2,5-dienone of 2.897 (1) Å (Gali, Miravittles & Font-Altava, 1975). The distances Cl(3)···Cl(5), Cl(3)···Cl(6) and Cl(4)···Cl(5) are 3.191 (2), 3.248 (2) and 3.273 (1) Å, which minimize van der Waals repulsive interactions between neighbouring Cl atoms. This effect also results in a considerable shortening of the bonds C(7)–Cl(3) = 1.754 (5) Å and C(8)–Cl(5) = 1.751 (5) Å as compared to the standard C(sp<sup>3</sup>)–Cl distance of 1.781 (1) Å (Lide, 1962), and a lengthening of the C(8)–Cl(6) distance to 1.812 (4) Å as in perchlorocyclopentadiene (Chang & Bauer, 1971) and *trans*-2,2,3,4,5,6-hexachloro-6-methylcyclohex-3-enone (Hartshorn, Martyn & Vaughan, 1984). Due to the presence of the highly negative Cl substituents at vicinal

C atoms, the C=O distance [1.178 (6) Å] is slightly shortened (Hartshorn *et al.*, 1984).

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## Structure and Disorder in Two Isomeric Racemic Cyclooctatriene Compounds

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**Abstract.** The crystal structures of *trans*-5a,11a-dihydro-2,3-dimethylcycloocta[*b*][1,4]benzodithiin (I) and 8,9-dihydro-2,3-dimethylcycloocta[*b*][1,4]benzodithiin (II) are reported. {These IUPAC names show the relationship between (I) and (II); (I) was called 10,11-(4,5-dimethylbenzo)-9,12-dithia-*trans*-

bicyclo[6.4.0]dodeca-2,4,6,10-tetraene in a previous structure determination [Kaiser, Richter, Moegel & Schroth (1979). *Tetrahedron*, **35**, 505–509].} (I) C<sub>16</sub>H<sub>16</sub>S<sub>2</sub>, *M<sub>r</sub>* = 272.4, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.724 (2), *b* = 6.542 (4), *c* = 20.435 (3) Å, β = 101.28 (1)°, *V* = 1405.95 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.29 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 3.09 cm<sup>-1</sup>, *F*(000) = 576, *T* = 293 K, *R* = 0.048 for 2779 unique

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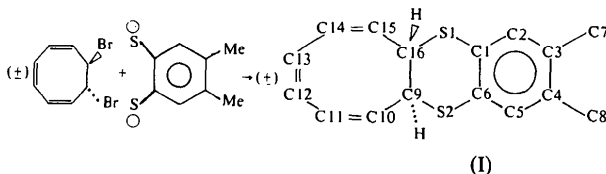
observed reflexions. (II)  $C_{16}H_{16}S_2$ ,  $M_r = 272.4$ , triclinic,  $P\bar{1}$ ,  $a = 9.56$  (2),  $b = 9.88$  (2),  $c = 8.87$  (2) Å,  $\alpha = 103.25$  (9),  $\beta = 99.5$  (1),  $\gamma = 61.4$  (1)°,  $V = 714$  Å<sup>3</sup>,  $D_x = 1.27$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54186$  Å,  $\mu = 30.55$  cm<sup>-1</sup>,  $F(000) = 288$ ,  $T = 293$  K,  $R = 0.063$  for 1264 unique reflexions. The abnormal features in the previously reported structure of (I) have been shown to be due to disordering of the optical isomers between sites in the racemic crystal rather than the formation of mixed crystals with (II) or the corresponding tetraene. Packing-energy calculations suggest that the stability of the crystal is increased by 0.67 kJ mol<sup>-1</sup> by this disorder. (II) has a highly ordered structure with the optical isomers exclusively in the correct sites. Mis-siting in (II) would be expected to reduce the stability of the crystal by 3.85 kJ mol<sup>-1</sup>.

**Introduction.** In a recent paper (Barnes, Paton, Schroth & Moegel, 1982) attention was drawn to some unsatisfactory features in the structure of (I) (Kaiser, Richter, Moegel & Schroth, 1979). The thermal ellipsoids reported for C(9) and C(16) are twice the volume of those of the other ring atoms and have their principal axes roughly normal to the plane S(1),-C(16),C(9),S(2). The bond length (C9)—C(16) (a formal single bond) was reported as 1.38 Å, and this was explained as a consequence of the *trans*-annelated configuration.

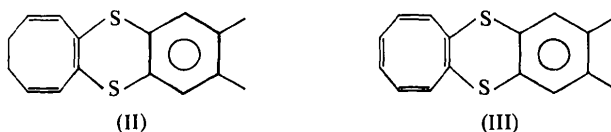
Racemic mixtures usually crystallize with the isomers segregated onto centrosymmetrically related sites. In a crystal-structure determination in the correct space group the final model for a racemate would have one isomer (usually chosen fortuitously) as the asymmetric unit with bridgehead atoms such as C(9) and C(16) showing rather small thermal parameters because of bonding constraints.

It seemed possible that the crystal of (I) used for the original data collection was a solid solution containing (II) or, more probably, (III) which could replace (I) very closely except for C(9) and C(16).

(I) is prepared by the reaction



(I) is known to rearrange thermally into the isomeric triene (II) with facile oxidation to the tetraene (III) (Moegel, Schroth & Werner, 1978).



(I) has been used as an intermediate in further syntheses so that uncertainty about its structure raised doubts about the mechanisms leading to the derived products. Fresh samples of (I) and (II) have been prepared and their structures are reported below along with a re-examination of the original data set.

**Experimental. Data collection.** Compound (I). Data set A. A copy of the original  $F_o$ ,  $F_c$  listing was made available by the authors (Kaiser *et al.*, 1979). This data set was derived from densitometer measurements on Weissenberg photographs of levels  $h0-4l$  and  $0kl$  obtained from the same crystal. There were 1732 unique reflexions of which 900 with  $F > 3.0$  were used in the current refinement.

Data set B. A crystal  $0.3 \times 0.4 \times 0.2$  mm was selected from a new preparation of (I) and mounted in a Lindemann-glass capillary. Weissenberg photographs showed strong Bragg reflexions to the limit of the Cu sphere and no sign of thermal diffuse scattering. Data collected on an Enraf-Nonius CAD-4F diffractometer (SERC Service at Edinburgh University), Mo  $K\alpha$  radiation, with unit-cell dimensions refined from 25 reflexions with  $\theta \sim 15^\circ$ . One quadrant of data collected for  $\theta \leq 30^\circ$ . Intensity and orientation checks showed no significant drift. Data corrected for absorption using a  $\psi$ -scan technique on the diffractometer (transmission range 0.92–1.10). Lorentz and polarization corrections applied. 4292 measured reflexions gave 4092 unique reflexions (internal consistency 0.016) of which 2779 with  $F_o > 2\sigma(F_o)$  used in the final refinement, index range  $h-15/14$ ,  $k 0/9$ ,  $l 0/28$ .

Compound (II). A new sample of very pale-yellow crystals was prepared as described previously (Moegel *et al.*, 1978). Intensities obtained from multi-film Weissenberg photographs scanned by the SERC Microdensitometer Service (Daresbury Laboratory), crystal size  $0.4 \times 0.4 \times 0.3$  mm. Unit-cell dimensions refined as part of the intensity measurement. Data collected for layers  $0-7kl$ ,  $h0-2l$  and  $hk0-1$  of a triclinic cell  $a = 8.87$  (1),  $b = 9.93$  (1),  $c = 9.56$  (1) Å,  $\alpha = 119.1$  (2),  $\beta = 99.5$  (1),  $\gamma = 93.97$  (9)°. After Lorentz and polarization corrections 2306 reflexions were merged to give 1264 unique reflexions (internal consistency 0.069) and then re-indexed to the reduced cell given above, index range  $h-11/10$ ,  $k-11/10$ ,  $l 0/10$ .

**Structure analysis.** All calculations performed on the Dundee University DEC 10 computer using *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975), *TRACER* (Lawton & Jacobson, 1965) and *PLUTO* (Motherwell & Clegg, 1978). Molecular packing-energy calculations carried out with *OPEC* (Gavezzotti, 1983). Atomic scattering parameters from *International Tables for X-ray Crystallography* (1974).

Compound (I). After preliminary refinement attempts with data set A, data set B was used to refine

the original ordered model, and a disordered model allowing for a solid solution of (I) and (III). The ordered model gave  $R = 0.080$  for an otherwise excellent cyclooctatetraene with unacceptable thermal parameters for C(9) and C(16); the (I, III) disordered model gave  $R = 0.058$  with an equally unacceptable (III) molecule.

Next, a model was introduced corresponding to the molecular site being occupied by a mixture of  $R,R$  and  $S,S$  isomers of (I). Atoms C(9) and C(16) were replaced by C(91), C(92) and C(161), C(162), respectively, and their site-occupancy factors included in the refinement. This model refined successfully, removing the abnormality in the thermal parameters. After removal of geometrical constraints, atoms H(91), H(92), H(161) and H(162) were introduced in calculated positions but then allowed to refine isotropically. H atoms of the methyl groups were located and refined with a single isotropic thermal parameter. All other H atoms were placed in calculated positions and assigned grouped thermal parameters which were refined.

Final blocked full-matrix least-squares refinement (minimizing  $\sum w|F_o - |F_c||^2$ ): 232 refined parameters,  $R = 0.048$ ,  $wR = 0.056$ ,  $w = 1.5702/[\sigma^2(F) + 0.000402F^2]$ , mean shift/e.s.d. = 0.15, max. shift/e.s.d. = 0.63 (H atoms), max. difference peak 0.40 e Å<sup>-3</sup> [close to S(1)], max. negative electron density -0.22 e Å<sup>-3</sup>.

The final model from data set *B* was tested on data set *A*, giving  $R = 0.08$  with satisfactory thermal parameters and bond lengths for the [I( $R,R$ ) + I( $S,S$ )] model, with a site-occupancy factor of 70 (3)% for the major component compared with 60.7 (1.9)% for data set *B*.

Compound (II). Structure solved by direct methods. All non-H atoms located on 8th-ranked *E* map. Conventional least-squares refinement, anisotropic thermal parameters for non-H atoms; H atoms treated as in compound (I); refinement showed no anomalous features.

Final refinement (minimizing  $\sum w|F_o - |F_c||^2$ ): 192 refined parameters,  $R = 0.064$ ,  $wR = 0.085$ ,  $w = 1.000/[\sigma(F)^2 + 0.007127F^2]$ , mean shift/e.s.d. = 0.13, max. shift/e.s.d. = 0.67 (excluding H), 0.78 (for H), max. difference peak 0.58 e Å<sup>-3</sup> [close to S(1)], max. negative electron density -0.36 e Å<sup>-3</sup>.

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1 [compound (I)] and Table 2\* [compound (II)]. Bond

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and further details pertaining to the structure determination of compound (I) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42494 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lengths and angles for both compounds are in Table 3. The molecules and packing diagrams are shown in Figs. 1 and 2 (I) and 3 and 4 (II). The development of the models for the disorder in (I) is shown by contrasting the anisotropic thermal parameters of C(9), C(91) and C(92) with those of the adjacent atom C(10) for the single-molecule model, the (I + III) model and the [I( $R,R$ ) + I( $S,S$ )] model.\* Only the last model gives the expected result that the bridgehead atoms C(91),

\* A table of selected anisotropic thermal parameters for different models of structure (I) has been deposited.

Table 1. *Coordinates* ( $\times 10^4$ ) and *equivalent isotropic temperature factors* ( $\text{\AA}^2 \times 10^3$ ) for non-H atoms with *e.s.d.'s* in parentheses for compound (I)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
S(1)	-1156 (1)	5998 (1)	3097 (1)	51 (1)
S(2)	-2002 (1)	1556 (1)	3608 (1)	56 (1)
C(1)	-2333 (2)	4476 (3)	2607 (1)	41 (1)
C(2)	-2967 (2)	5222 (3)	1997 (1)	48 (1)
C(3)	-3950 (2)	4158 (4)	1605 (1)	51 (1)
C(4)	-4301 (2)	2260 (4)	1822 (1)	51 (1)
C(5)	-3648 (2)	1484 (3)	2420 (1)	49 (1)
C(6)	-2678 (2)	2575 (3)	2822 (1)	41 (1)
C(7)	-4605 (3)	5053 (6)	943 (2)	77 (1)
C(8)	-5356 (3)	1021 (7)	1412 (2)	80 (1)
C(91)*	-397 (3)	2613 (7)	3875 (3)	39 (1)
C(92)†	-309 (6)	2086 (12)	3542 (6)	46 (2)
C(10)	495 (2)	763 (3)	4034 (1)	52 (1)
C(11)	1334 (2)	855 (4)	4599 (1)	63 (1)
C(12)	1682 (2)	2614 (4)	5034 (1)	66 (1)
C(13)	1979 (2)	4462 (4)	4856 (1)	59 (1)
C(14)	2055 (2)	5194 (3)	4189 (1)	55 (1)
C(15)	1267 (2)	4993 (3)	3610 (1)	50 (1)
C(161)*	27 (4)	3952 (7)	3352 (4)	41 (1)
C(162)†	-85 (6)	4316 (11)	3668 (6)	42 (2)

\* Major component, occupancy 60.7 (1.9)%.

† Minor component, occupancy 39.3 (1.9)%.

Table 2. *Coordinates* ( $\times 10^4$ ) and *U<sub>eq</sub> values* ( $\text{\AA}^2 \times 10^3$ ) for non-H atoms with *e.s.d.'s* in parentheses for compound (II)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
S(1)	7955 (2)	6335 (2)	1083 (2)	51 (1)
S(2)	5141 (2)	7004 (2)	3123 (2)	49 (1)
C(1)	8300 (6)	5111 (6)	2427 (6)	38 (1)
C(2)	9798 (6)	3868 (7)	2631 (6)	42 (1)
C(3)	10153 (7)	2945 (7)	3753 (6)	42 (1)
C(4)	8933 (7)	3248 (7)	4655 (6)	41 (1)
C(5)	7412 (7)	4459 (6)	4403 (6)	40 (1)
C(6)	7076 (6)	5409 (6)	3312 (6)	38 (1)
C(7)	11810 (8)	1614 (8)	3948 (8)	61 (2)
C(8)	9237 (8)	2320 (8)	5908 (7)	59 (2)
C(9)	4810 (6)	7025 (6)	1076 (6)	39 (1)
C(10)	3130 (6)	7388 (6)	464 (6)	43 (1)
C(11)	2184 (8)	8573 (8)	-318 (7)	56 (2)
C(12)	2718 (9)	9722 (8)	-617 (9)	74 (2)
C(13)	3433 (10)	9223 (9)	-2130 (10)	79 (2)
C(14)	4826 (8)	7701 (8)	-2399 (7)	56 (2)
C(15)	5856 (7)	6696 (7)	-1488 (6)	49 (1)
C(16)	5971 (6)	6767 (6)	234 (6)	38 (1)

*etc.* have smaller thermal ellipsoids than their neighbours. Comparison of the thermal ellipsoids of C(10) and C(15) with those of C(11) and C(14) gives no evidence of disorder for the former, showing the excellent match which is obtained by substituting the I(*S,S*) isomer onto the I(*R,R*) site.

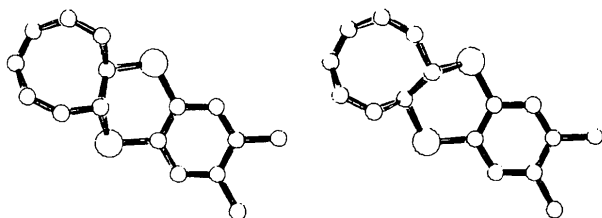


Fig. 1. Compound (I), viewed perpendicular to the plane of the benzene ring. Left, major component; right, minor component. [This figure can be viewed as a stereo pair to show the disorder at C(9) and C(16).]

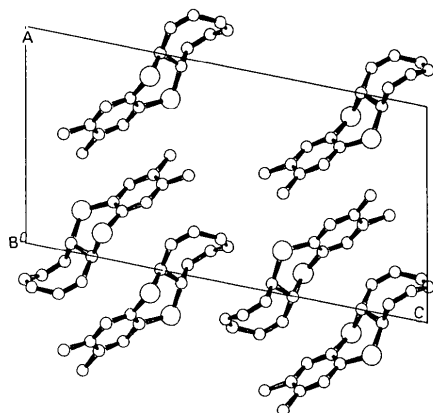


Fig. 2. Packing diagram for compound (I), viewed along *b*.

The observed muddle with *R,R* and *S,S* isomers sometimes occupying the wrong sites in (I) could have three possible explanations.

(i) That the synthesis is not symmetric and gives only one isomer. In which case the true space group is not  $P2_1/c$  but  $P2_1$  for a half-sized cell with  $Z = 2$  and the ratio of site occupancy seen in  $P2_1/c$  must be 50:50. This can be rejected because data set *A* gives a site occupancy of 70 (3)% for the major component and data set *B* gives 60.7 (1.9)%.

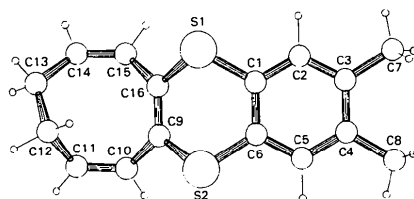


Fig. 3. Compound (II), viewed perpendicular to the plane of the benzene ring.

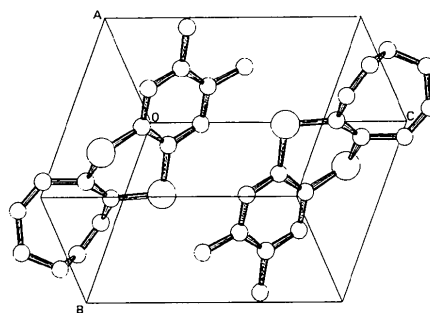


Fig. 4. Packing diagram for compound (II).

Table 3. Bond lengths (Å) and selected bond angles (°)

	(I)	(II)		(I)	(II)		(I)	(II)
S(1)—C(1)	1.758 (2)	1.773 (7)	C(2)—C(3)	1.381 (3)	1.395 (9)	C(11)—C(12)	1.458 (4)	1.535 (14)
S(1)—C(16)		1.802 (5)	C(3)—C(4)	1.394 (3)	1.397 (9)	C(12)—C(13)	1.319 (4)	1.480 (12)
S(1)—C(161)	1.848 (4)		C(3)—C(7)	1.514 (4)	1.512 (7)	C(13)—C(14)	1.463 (3)	1.454 (9)
S(1)—C(162)	1.836 (8)		C(4)—C(5)	1.382 (3)	1.395 (7)	C(14)—C(15)	1.318 (3)	1.334 (8)
S(2)—C(6)	1.757 (2)	1.778 (5)	C(4)—C(8)	1.506 (4)	1.505 (10)	C(15)—C(16)		1.501 (8)
S(2)—C(9)		1.794 (5)	C(5)—C(6)	1.389 (3)	1.389 (9)	C(15)—C(161)	1.495 (5)	
S(2)—C(91)	1.836 (4)		C(9)—C(10)		1.501 (8)	C(15)—C(162)	1.542 (8)	
S(2)—C(92)	1.879 (7)		C(91)—C(10)	1.537 (5)		C(16)—C(9)		1.330 (9)
C(1)—C(2)	1.387 (3)	1.387 (6)	C(92)—C(10)	1.471 (9)		C(161)—C(91)	1.518 (9)	
C(1)—C(6)	1.394 (3)	1.393 (9)	C(10)—C(11)	1.318 (3)	1.350 (8)	C(162)—C(92)	1.492 (10)	
S(1)—C(1)—C(6)	122.1 (1)	120.2 (4)	S(1)—C(161)—C(91)	109.5 (3)		C(14)—C(15)—C(16)		131.5 (5)
C(1)—C(6)—S(2)	122.6 (1)	121.4 (4)	S(1)—C(162)—C(92)	114.6 (6)		C(14)—C(15)—C(161)	137.0 (3)	
C(6)—S(2)—C(9)		103.8 (2)	C(9)—C(10)—C(11)		123.9 (7)	C(14)—C(15)—C(162)	114.0 (5)	
C(6)—S(2)—C(91)	108.9 (2)		C(91)—C(10)—C(11)	116.1 (3)		C(15)—C(16)—C(9)		126.1 (5)
C(6)—S(2)—C(92)	95.6 (3)		C(92)—C(10)—C(11)	141.2 (4)		C(15)—C(161)—C(91)	112.5 (5)	
S(2)—C(9)—C(16)		121.3 (4)	C(10)—C(11)—C(12)	128.3 (2)	122.6 (6)	C(15)—C(162)—C(92)	112.9 (6)	
S(2)—C(91)—C(161)	113.6 (4)		C(11)—C(12)—C(13)	127.1 (2)	112.2 (6)	C(16)—C(9)—C(10)		125.2 (5)
S(2)—C(92)—C(162)	107.1 (5)		C(12)—C(13)—C(14)	128.1 (2)	117.6 (7)	C(161)—C(91)—C(10)	110.1 (4)	
S(1)—C(16)—C(9)		121.7 (4)	C(13)—C(14)—C(15)	131.4 (2)	134.3 (8)	C(162)—C(92)—C(10)	113.8 (7)	

Table 4. *Geometry of 1,3,5-cyclooctatriene rings*

	(I) (major component)	(I) (minor component)	(II)
Height of atoms above mean plane of <i>ABEF</i> (Å)			
<i>C</i>	0.651 (2)	0.676 (3)	0.749 (8)
<i>D</i>	0.676 (2)	0.651 (3)	0.820 (7)
<i>G</i>	0.480 (3)	0.495 (4)	0.480 (8)
<i>H</i>	1.100 (3)	1.044 (4)	1.067 (6)
Selected bond lengths (Å) and bond angles (°)			
<i>A-H</i>	1.537 (5)	1.542 (8)	1.535 (14)
<i>H-G</i>	1.518 (9)	1.492 (10)	1.480 (12)
<i>G-F</i>	1.495 (5)	1.471 (9)	1.454 (9)
<i>D-E-F</i>	131.4 (2)	128.3 (2)	131.5 (5)
<i>E-F-G</i>	137.0 (3)	141.2 (4)	134.4 (6)
<i>H-A-B</i>	116.1 (3)	114.0 (5)	122.6 (6)
Torsion angles (°)			
<i>A-B-C-D</i>	48.9 (5)	47.6 (6)	54.8 (7)
<i>B-C-D-E</i>	1.2 (5)	1.2 (5)	3.8 (6)
<i>C-D-E-F</i>	-47.6 (6)	-48.9 (6)	-53.5 (7)
<i>D-E-F-G</i>	2.6 (5)	9.9 (6)	0.0 (6)
<i>E-F-G-H</i>	6.9 (5)	5.5 (5)	15.2 (5)
<i>F-G-H-A</i>	68.0 (6)	64.4 (5)	58.8 (6)
<i>G-H-A-B</i>	-102.9 (5)	-100.4 (5)	-93.2 (5)
<i>H-A-B-C</i>	11.9 (5)	16.0 (6)	2.2 (5)

(ii) That the synthesis is not totally symmetric and yields a bad racemic mixture so that the excess of, say, *S,S* molecules have to adopt *R,R* sites.

(iii) That the synthesis does give a genuine racemic mixture but that the extreme similarity of the molecules allows errors of site-choice during crystallization.

The correct model has been shown to be (iii), as follows. Coordinates were generated for the molecule related by a centre of symmetry to the parent. Both sets of coordinates were used together in a refinement using the existing unit cell in space group  $P2_1$ , with  $Z = 4$ , allowing the two molecules to refine independently. The occupancy of the major component was the same in both molecules within  $1\sigma$ , 57.5 (2.8)% for *C(91R)* and 59.6 (3.5)% for *C(92S)*. That is, the cell contains equal amounts of the two isomers. The variation in site occupancy between data set *A* and data set *B* indicates that slight variations in the conditions of crystal growth can alter the degree of disorder.

As an alternative to the random mis-siting of molecules throughout the crystal, the data could be explained by a microdomain structure. Each microdomain would be ordered but the molecules on a particular site in the unit cell would be *R,R* in one type of domain and *S,S* in the other. Similar behaviour has been suggested in dibenzoyl peroxide (Sax & McMullan, 1967). However, dibenzoyl peroxide crystals show extensive diffuse scattering both at 173 and 298 K whereas (I) shows no diffuse scattering.

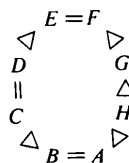
The packing potential-energy program *OPEC* has been used to estimate the cost of placing an *S,S* molecule on an *R,R* site. The packing energy for the ideal ordered crystal is  $-231.56 \text{ kJ mol}^{-1}$ . Introduction of one *S,S* molecule onto an *R,R* site in an otherwise perfect and unperturbed lattice gives the surprising

result that the stability increases slightly to  $-232.23 \text{ kJ mol}^{-1}$ .

In (II) there is the possibility of a similar misplacing of conformational isomers. In this case the atoms affected would be *C(12)* and *C(13)*. The ellipsoid for *C(12)* is appreciably larger than that for *C(11)* but not sufficiently anisotropic to suggest a disordered model. Coordinates for the 'wrong' isomer on the site in (II) have been calculated and used in an *OPEC* calculation. The ordered crystal has a packing energy of  $-233.94 \text{ kJ mol}^{-1}$  and the introduction of one wrong molecule per unit cell reduces this to  $-230.09 \text{ kJ mol}^{-1}$ .

Racemic mixtures in solution will crystallize with the ideal separation of *R* and *S* isomers onto centrosymmetrically related sites as long as the lattice energy of the crystal is minimized by so doing. In (II) the packing potential-energy difference in favour of the ideal structure is only  $3.85 \text{ kJ mol}^{-1}$  but this suffices. However, in (I) the energy balance is  $0.67 \text{ kJ mol}^{-1}$  in favour of disorder, and disorder is observed. These differences in energy are very small so that the agreement with the observed structures could well be fortuitous.

Both (I) and (II) can be visualized as *ortho*-substituted octa-1,3,5-trienes. (I) is substituted at the 7,8-positions and (II) at the 3,4-positions by the dimethyldithiobenzene group, where the only feature of interest is that both *S* atoms lie above the plane of the benzene ring, one at *ca*  $0.07 \text{ \AA}$  and the other at *ca*  $0.11 \text{ \AA}$  in each case. The difference between these distances represents  $18\sigma$  for (I) and  $4\sigma$  for (II). In both molecules the cyclooctatriene ring adopts a distorted tub conformation with the base of the tub below and closely parallel to the plane of the benzene ring. The geometries are summarized in Table 4 where the atoms are referred to by a common lettering scheme to aid comparison.



The base of the tub consists of atoms *A*, *B*, *E* and *F*. The single bond *G-H* is tilted so that *H* is more remote (*ca*  $1.0 \text{ \AA}$ ) from the *ABEF* plane than is *G* (*ca*  $0.48 \text{ \AA}$ ). *H* corresponds to *C(91)* and *C(162)* respectively for the major and minor components in (I) and to *C(12)* in (II). The rest of the numbering increases clockwise for the major component and anticlockwise for the minor component, and for (II). In each case the portion *ABCDEF* is very similar to part of a cyclooctatetraene ring with typical bond lengths, bond angles and torsion angles (Barnes *et al.*, 1982) except that, in (II), *F* is  $0.222 (9) \text{ \AA}$  out of the plane of *ABE* whereas in (I) *A*, *B*, *E* and *F* are within

0.022 (4) Å of their mean plane. Also angle *DEF* is always at the large end of the experimental range for angles in a cyclooctatetraene ring. However, the angle *EFG* has values between 134.4 (6) and 141.2 (4)° compared with the experimental average in cyclooctatetraene of 126.1° whereas angle *HAB* lies in the range 114.0 (5) to 122.6 (6)°. In each case the bond lengths decrease in the order *AH* > *HG* > *GF* with differences of 3–4σ. Since the substitution pattern is quite different in (I) and (II), these observations appear to be features of octa-1,3,5-trienes in general. The dithiaocta-1,3,6-triene ring in the closely related 8,9-dimethyl-1,6-benzodithiocin (Barnes, Schroth & Moegel, 1978) has a twisted ring which does not resemble a cyclooctatetraene tub.

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## Structures of the *s-cis* and *s-trans* Conformers of (*E*)-5-Methylthio-1,5-diphenyl-1-penten-3-one

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**Abstract.** (I) (*E*)-5-Methylthio-1,5-diphenyl-1-penten-*s-cis*-3-one, C<sub>18</sub>H<sub>18</sub>OS, *M<sub>r</sub>* = 282.4, monoclinic, *Pc*, *a* = 10.270 (1), *b* = 9.931 (1), *c* = 7.633 (1) Å, β = 98.31 (1)°, *V* = 770.3 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.22 Mg m<sup>-3</sup>, Cu *Kα*, λ = 1.5418 Å, μ = 1.74 mm<sup>-1</sup>, *F*(000) = 300, *T* = 293 K, *R* = 0.031 for 1229 reflections. (II) (*E*)-5-Methylthio-1,5-diphenyl-1-penten-*s-trans*-3-one, C<sub>18</sub>H<sub>18</sub>OS, *M<sub>r</sub>* = 282.4, monoclinic, *C2/c*, *a* = 16.361 (3), *b* = 5.680 (1), *c* = 35.705 (8) Å, β = 112.81 (1)°, *V* = 3058.7 (9) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.23 Mg m<sup>-3</sup>, Cu *Kα*, λ = 1.5418 Å, μ = 1.76 mm<sup>-1</sup>, *F*(000) = 1200, *T* = 293 K, *R* = 0.058 for 1968 reflections. Molecules (I) and (II) have been found to have somewhat twisted *s-cis* and almost planar *s-trans* conformations, respectively (torsion angles –11.0 and 178.8°, respectively), for the α,β-unsaturated ketone

system. The carbonyl and phenyl groups are in the *trans* configuration with respect to the C=C bond in the two conformers.

**Introduction.** A number of papers have been published on the conformations of α,β-unsaturated ketone derivatives. Some of the ketone derivatives are obtained either as the *s-cis* or as the *s-trans* form, mainly because of the steric and/or packing effect (Noack & Jones, 1961; Jungk & Schmidt, 1970; Ohkura, Kashino & Haisa, 1973; Rabinovich & Shakked, 1974), and others exist as equilibrium mixtures of different conformers at least in solution (Fuson, Josien & Shelton, 1954; Kronenberg & Havinga, 1965; Hayes & Timmons, 1968; Dimmock, Carter & Ralph, 1968; Silver & Boykin, 1970; Winecoff & Boykin, 1972).