The Crystal and Molecular Structure of 2,5-Diphenyl-3,4-dimethylene-1,6,6a-trithiapentalene

BJØRN BIRKNES, ASBJØRN HORDVIK and LEIF J. SÆTHRE

Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, Box 953, N-9001 Tromsø, Norway

Crystals of the title compound are orthorhombic, space group *Pnma*, with four molecules in a unit cell of dimensions $a = 7.165(1)$ Å, $b = 29.704(4)$ Å, and $c = 7.372(3)$ Å.

The structure was refined by full-matrix least-squares calculations on 1754 reflections (MoKα) measured within $\theta = 27°$.

The molecule lies across the crystallographic mirror plane m, the central ring system is almost planar, and the phenyl groups are twisted 30° about their respective connecting bonds.

The S−S bond distances are 2.351(1) Å, and the S(1)−S(6a)−S(6) angle is 173.43(6)°. Other bond lengths in the 1,6,6a-trithiapentalene system are: S(1)−C(2) = 1.725(4) Å, S(6a)−C(3a) = 1.716(5) Å, C(2)−C(3) = 1.374(5) Å, and C(3)−C(3a) = 1.407(4) Å.

Bond lengths in the dimethylene bridge are C(3)−C(7) = 1.529(5) Å and C(7)−C(8) = 1.566(5) Å, and the lengths of the bonds connecting the phenyl groups to the central ring system are 1.489(5) Å. The bond lengths have been corrected for libration.

A relationship between the C(3)−C(3a)−C(4) bond angles (114.1, 122.3, and 126.0°) and the S(6a)−C(3a) bond lengths (1.716, 1.753, and 1.779 Å) in 2,5-diphenyl-3,4-dimethylene-, 2,5-diphenyl-, and 2,5-diphenyl-3,4-dimethyl-1,6,6a-trithiapentalene, respectively, is shown to be consistent with the results from CNDO/2 calculations.
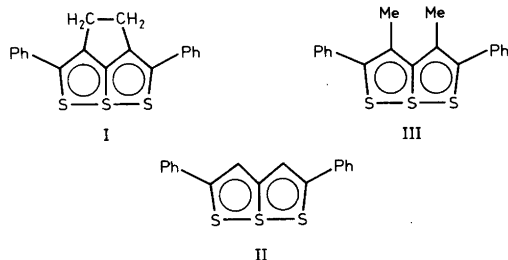
The title compound (I) possesses intramolecular strain caused by the presence of the dimethylene bridge. A structure study of I has been carried out in order to find to which extent this intramolecular strain affects the bonding in the 1,6,6a-trithiapentalene system of I as compared to the bonding in the 1,6,6a-trithiapentalene system of compounds II and III;[1,2] compound II is regarded as a strainless molecule, and in compound III there is a repulsion between the methyl groups.

STRUCTURE ANALYSIS

Crystal data.[3,4]

$C_{19}H_{14}S_3$ F.W. = 338.50

Space group *Pnma*

$a = 7.165(1)$ Å, $b = 29.704(4)$ Å, $c = 7.372(3)$ Å

$V = 1569.0$ Å^3

$D_x = 1.433$ g/cm^3, D_m (flotation) = 1.427 g/cm^3

$Z = 4$

$\mu = 4.5$ cm^{-1} (MoKα)

Crystal size, 0.2 × 0.1 × 0.4 mm in axial directions.

The unit cell dimensions were determined from the 2θ values of 19 high order reflections measured at room temperature, $t = 22$ °C. A least squares procedure gave the values quoted above.

The intensities of the reflections were measured by means of the five-value scan technique.[5] Reflections for which the net count was greater than two times the respective standard deviation in the net count, were accepted as observed. With this criterion 934 out of 1754 observable independent reflections within $\theta = 27°$ were regarded as observed.

The scattering factors for sulfur and carbon were taken from the *International Tables*.[6] For hydrogen,

Table 1. Fractional atomic coordinates, and temperature parameters U_{ij}(Å^2) for sulfur and carbon, and U(Å^2) for hydrogen. The expressions used are $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots 2hka^*b^*U_{12} + \cdots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$, respectively. Standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	0.22633(14)	0.17014(3)	0.03756(15)	.0271(5)	.0452(6)	.0555(7)	.0067(5)	−.0012(6)	−.0051(6)
S(6a)	0.24468(18)	0.25000	0.03357(21)	.0198(7)	.0516(9)	.0450(9)	.0000	.0000	−.0027(8)
C(2)	−0.01204(47)	0.16928(13)	0.01112(49)	.0282(17)	.0467(23)	.0301(25)	.0020(19)	.0015(22)	−.0011(17)
C(3)	−0.09816(45)	0.21029(13)	−0.00687(47)	.0256(16)	.0361(18)	.0293(23)	.0016(18)	.0019(23)	−.0009(17)
C(3a)	0.00810(65)	0.25000	0.00243(74)	.0221(24)	.0358(30)	.0351(37)	.0000	.0000	−.0029(27)
C(7)	−0.30269(44)	0.22366(12)	−0.02591(61)	.0256(18)	.0399(23)	.0435(24)	−.0015(15)	−.0044(21)	−.0008(19)
C(9)	−0.10433(53)	0.12452(11)	0.01239(55)	.0365(21)	.0315(21)	.0323(24)	.0034(18)	−.0032(19)	−.0066(23)
C(10)	−0.26621(64)	0.11585(13)	−0.08533(54)	.0470(25)	.0398(26)	.0504(27)	.0029(25)	.0022(21)	−.0109(26)
C(11)	−0.34525(64)	0.07311(16)	−0.08911(69)	.0517(28)	.0525(30)	.0631(36)	−.0089(24)	.0002(25)	−.0101(25)
C(12)	−0.26354(68)	0.03863(13)	0.00500(59)	.0578(27)	.0376(23)	.0616(32)	−.0035(27)	−.0030(20)	.0077(31)
C(13)	−0.10571(70)	0.04651(15)	0.10617(66)	.0615(31)	.0398(28)	.0607(31)	.0100(25)	.0064(25)	.0008(29)
C(14)	−0.02605(60)	0.08908(14)	0.10858(59)	.0427(25)	.0413(26)	.0525(30)	.0050(22)	−.0006(24)	−.0060(24)

Atom	x	y	z	U		Atom	x	y	z	U
H(10)	−0.3206(49)	0.1394(11)	−0.1537(46)	.043(13)		H(14)	0.0822(51)	0.0954(11)	0.1776(44)	.049(12)
H(11)	−0.4527(60)	0.0686(13)	−0.1635(57)	.080(16)		H(71)	−0.3573(52)	0.2108(13)	−0.1334(46)	.055(13)
H(12)	−0.3193(40)	0.0044(13)	−0.0007(48)	.050(10)		H(72)	−0.3695(47)	0.2109(12)	0.0888(43)	.043(10)
H(13)	−0.0472(53)	0.0233(12)	0.1738(45)	.057(14)						

Table 2. Rigid body libration tensors for the entire molecule (L), the three central rings plus C(9) and C(15), (L$_1$), and the 2-phenyl group plus C(2) (L$_2$).

	Eigenvalues	Eigenvectors	a	
	14.50 (°)^2	0	−10000	0
L	3.23	3767	0	−9263
	2.33	9264	0	3766
	15.54	0	−10000	0
L$_1$	3.87	4434	0	−8963
	0.12	8963	0	4434
	53.56	−3523	−9353	−334
L$_2$	9.17	−3598	1024	9274
	6.48	−8640	3387	3726

^{a} Direction cosines × 10^4 relative to a, b and c, respectively.

the scattering factor curve given by Stewart *et al.*[7] was used.

The refinement procedure is given in Ref. 8. Hydrogen positions were found from a difference map. Corrections for secondary extinction were carried out according to the method of Zachariasen,[9] and the final agreement factors are $R = 0.037$ and $R_w = 0.030$.

Final atomic coordinates and temperature parameters are listed in Table 1. The final structure factor list is available on request.

Rigid body analyses for the entire molecule as well as for certain parts of the molecule have been carried out according to the method of Schomaker and Trueblood.[10] The parts of the molecule treated in this way are the three central rings plus C(9) and

Table 3. Bond lengths *l(ij)*, bond angles ∠ *(ijk)*, and deviations Δ$_j$ from least squares plane. Bond lengths *l'(ij)* have been corrected according to the librational tensor **L**, and bond lengths *l''(ij)* have been corrected according to the librational tensors **L$_1$** and **L$_2$**.

| Atom			Bond lengths (Å)			Bond angles (°) ∠ *(ijk)*	Plane deviations (Å) Δj
i	*j*	*k*	*l''(ij)*	*l'(ij)*	*l(ij)*		
C(2)	S(1)	S(6a)	1.725	1.624	1.720(4)	94.8(1)	.015
S(1)	S(6a)	S(6)	2.351	2.351	2.349(1)	173.43(6)	−.031
C(3a)	S(6a)	S(1)	1.716	1.715	1.711(5)	86.92(4)	
S(1)	C(2)	C(3)				115.5(2)	.038
S(1)	C(2)	C(9)				117.9(2)	
C(3)	C(2)	C(9)	1.374	1.374	1.372(5)	126.5(3)	
C(3a)	C(3)	C(2)	1.407	1.408	1.406(4)	119.8(3)	−.015
C(7)	C(3)	C(2)	1.529	1.529	1.525(5)	132.2(3)	
C(3a)	C(3)	C(7)				107.8(3)	
C(3)	C(3a)	C(4)				114.1(3)	−.044
C(3)	C(3a)	C(6a)				122.9(2)	
C(8)	C(7)	C(3)	1.566	1.566	1.565(5)	105.1(3)	.031
C(2)	C(9)	C(10)	1.489	1.487	1.485(5)	122.3(3)	.131
C(14)	C(9)	C(2)	1.398	1.390	1.388(6)	120.2(3)	
C(14)	C(9)	C(10)				117.5(3)	
C(9)	C(10)	C(11)	1.400	1.393	1.390(6)	121.3(3)	−.437
C(10)	C(11)	C(12)	1.394	1.392	1.390(6)	120.0(4)	−.392
C(11)	C(12)	C(13)	1.379	1.371	1.369(6)	120.0(4)	.221
C(12)	C(13)	C(14)	1.386	1.378	1.375(7)	120.0(4)	.818
C(13)	C(14)	C(9)	1.391	1.389	1.387(6)	121.2(4)	.763
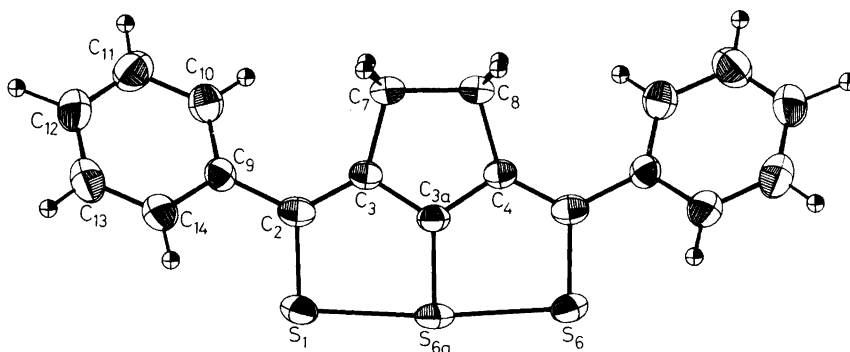
Fig. 1. ORTEP[11] drawing of the molecular structure of the title compound with numbering of atoms.

its symmetry equivalent and the 2-phenyl group plus C(2). The corresponding librational tensors are given in Table 2.

The calculations mentioned above were carried out on an IBM 360/50H computer. The programs, with some exeptions, originate from the Weizmann Institute of Science, Rehovoth, Israel, and have been modified for the 360 by D. Rabinovich, L. M. Milje, K. Maartmann-Moe and K. Åse.

DISCUSSION

Molecular shape and dimensions. The molecular structure of compound I as found in the present study is shown in Fig. 1. Bond lengths and angles are given in Table 3. The molecule lies across the crystallographic mirror plane *m*.

The bond lengths between nonhydrogen atoms have been corrected[12] for rigid-body libration according to the libration tensors given in Table 2. The corrections which give the *l'*-values are based on the libration tensor L and the corrections leading to the *l″* values are based on L_1 and L_2. The axis of maximum libration for L_2 runs close to the direction C(2) − C(9) − C(12), and this shows that the phenyl groups librate about the respective connecting bonds. In accordance with this, one notes from Table 3 that the *l″* values for the C − C bonds of the phenyl ring are more realistic than the *l'* values.

Deviations from the least squares plane of the atoms of the 1,6,6a-trithiapentalene system are given in Table 3.

One notes that the two central rings are almost planar, and the phenyl groups point slightly out of this plane. The phenyl groups are twisted 30° about

the respective connecting bonds.

A comparison with related molecules is given in Fig. 2. The 3,4-dimethylene bridge in I as well as the 3,4-dimethyl substituents in III introduces strain in the respective molecules, and this strain has caused changes in molecular dimensions. One notes for example for I, when compared with II, that the C(3) − C(3a) − C(4) and the S(1) − S(6a) − S(6) angles as
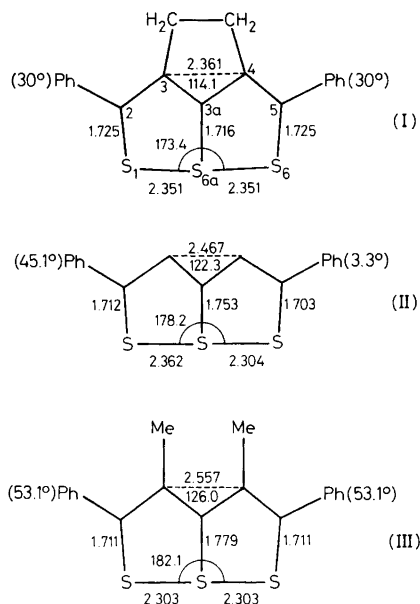

Fig. 2. A comparison of the structure of the present compound (I) with the structures of compounds II and III. Bond lengths are given in Å units and bond angles in degrees.
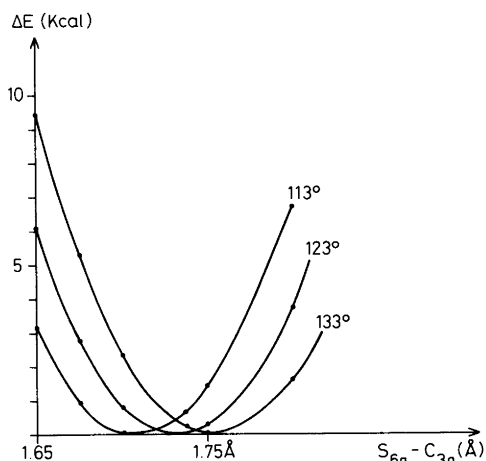
Fig. 3. The change in total energy, ΔE, relative to the minimum energy value, as a function of the S(6a)–C(3a) bond distance for three different molecular models. See the text for further explanation.

Fig. 4. Some bond distances (Å) and angles (°) from X-ray studies of three naphthalenes.

well as the C(3)···C(4) and S(6a)–C(3a) distances have decreased, while the sum of the S–S bond lengths have increased; for III the corresponding changes are seen to be the opposite.

It is tempting to point out that the mentioned changes in molecular dimensions are in accordance with what might be expected from "elastic" molecular models, *cf.* Fig. 2. Thus the external sulfur atoms have been pulled out in I and pushed in in III, and the C(3)–C(3a)–C(4) and S(1)–S(6a)–S(6) angles have changed their values accordingly.
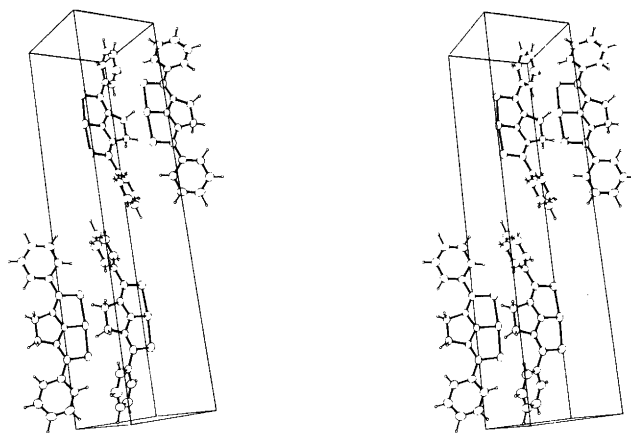
The most apparent changes have taken place around C(3a). One notes that the difference between the C(3)–C(3a)–C(4) bond angles in I and III and the difference between the S(6a)–C(3a) bond lengths in these compounds are 11.9° and 0.063 Å, respectively. Furthermore, the S(6a)–C(3a) bond in I, 1.716(5) Å, is shorter, and the S(6a)–C(3a) bond in III, 1.779(4) Å, is longer than that of 1.75 Å usually found in 1,6,6a-trithiapentalenes.[8]

There seems to be a relationship between the magnitude of the C(3)–C(3a)–C(4) bond angle and the length of the S(6a)–C(3a) bond, and this relationship is consistent with the results from CNDO/2 calculations as discussed below.

Fig. 5. A stereo view of the crystal structure.

The structure of the mother compound 1,6,6a-trithiapentalene as found by X-ray studies[8] was used as the basic model for the CNDO/2 calculations. Two other model structures were derived from this by changing the $C(3) - C(3a) - C(4)$ angle symmetrically from $123°$ to 113 and $133°$, respectively, keeping the other molecular dimensions, except those involving $S-S$ bonds, constant.

The CNDO/2 total energy[13] has been calculated as a function of the $S(6a) - C(3a)$ bond length for the three model structures. Sulfur d-orbitals were included in the calculations, which were carried out using the program CNINDO distributed by the QCPE organization.[14] The change in total energy relative to the minimum energy value as a function of the $S(6a) - C(3a)$ bond distance is given in Fig. 3. One notes that the $S(6a) - C(3a)$ bond distance corresponding to minimum total energy, increases from $1.70 - 1.75$ Å when the $C(3) - C(3a) - C(4)$ bond angle increases from $113 - 133°$. This trend agrees with the experimental results.

The analogy with naphthalenes is illustrated in Fig. 4. Naphthalene and 1,6,6a-trithiapentalene are both aromatic 10π-electron systems. The values given in the figure are taken from the X-ray studies of IV,[15] V,[16] and VI,[17] respectively.

One notes that the 1,8-dimethylene bridge in IV has caused a decrease in the $C(1) - C(9) - C(8)$ angle and the $C(9) - C(10)$ bond distance, and the 1,8-dimethyl groups in VI have caused an increase in these molecular dimensions relative to those in V.

A stereo view of the crystal structure is given in Fig. 5. There are no intermolecular contacts shorter than corresponding van der Waals distances.

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