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The Crystal and Molecular Structure of 3,4-Dimethyl-1,6-diphenyl-1,2,5,6-tetra-aza-6a-thiapentalene

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Crystals of the title compound $C_{17}H_{16}N_4S$ are orthorhombic, space group *Pbca*, with unit cell dimensions $a=12.393(4)$ Å, $b=8.560(3)$ Å, $c=29.024(5)$ Å, and $Z=8$. The structure was solved by direct methods and refined by full-matrix least-squares.

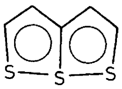
The central ring system is almost planar with bond distances, N(1)–S(6a) = 1.895(4), N(6)–S(6a) = 1.873(4), N(1)–N(2) = 1.340(6), N(2)–C(3) = 1.330 (6), C(3)–C(3a) = 1.398(6), C(3a)–S(6a) = 1.738(4), C(3a)–C(4) = 1.411(6), C(4)–N(5) = 1.351(6), and N(5)–N(6) = 1.329(5) Å; the N(1)–S(6a)–N(6) angle is 167.4(2)°.

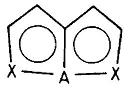
The 1- and 6-phenyl groups are twisted 18 and 15° about the respective connecting bonds, and the N(1)–C(15)–C(18) and the N(6)–C(9)–C(12) sequences point slightly out to opposite sides of the central ring plane. The methyl carbons C(7) and and C(8) lie 0.09 and −0.13 Å off this plane.

The 1,6,6a-trithiapentalene system (Ia) has now been known for more than twenty years,[1] and its interesting structure has been thoroughly studied, *e.g.* by X-ray crystallography, electron diffraction, ESR, and ESCA, as well as by theoretical methods.[2–4]

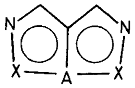
Since the beginning of 1958 several new compounds, *e.g.* Ib–Id, analogous to Ia, have been synthesized,[5–10] and for a series of these the structures have been determined.[2]

The molecular structure of a compound which contains the ring system Ic, with A = S and X = N · Ar, has not been reported so far, and the present study of II was therefore carried out.

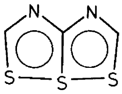

(Ia)

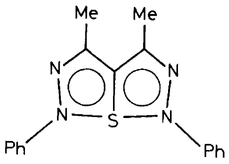

(Ib)

A	X
Se	Se, S
Se, S	O
Se, S	N·R


(Ic)

A	X
Se, S	N·Ar
Te, Se, S	O


(Id)



(II)

STRUCTURE ANALYSIS

Crystals of II were generously supplied by D.H. Reid.[10] The crystals are dark red.

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(6a)	0.23214(8)	0.17578(13)	0.12454(3)	.0509(6)	.0619(6)	.0587(6)	.0033(5)	−.0015(5)	−.0012(6)
N(1)	0.1179(3)	0.2534(4)	0.08778(12)	.0605(22)	.0636(24)	.0660(24)	.0037(19)	−.0032(19)	−.0010(20)
N(2)	0.1479(3)	0.3426(4)	0.05217(12)	.0704(24)	.0637(25)	.0608(22)	−.0020(20)	−.0032(19)	.0000(20)
N(5)	0.4523(3)	0.1590(4)	0.12770(13)	.0507(19)	.0645(24)	.0738(24)	−.0020(18)	.0048(18)	−.0054(21)
N(6)	0.3643(2)	0.1195(4)	0.15098(12)	.0461(19)	.0659(24)	.0624(21)	.0034(17)	.0000(17)	−.0050(18)
C(3)	0.2548(4)	0.3440(5)	0.04899(14)	.696(28)	.0587(27)	.0583(23)	.0003(23)	.0012(23)	−.0031(22)
C(3a)	0.3122(3)	0.2631(5)	0.08285(14)	.0636(26)	.0460(24)	.0599(26)	−.0016(21)	.0057(21)	−.0057(21)
C(4)	0.4237(3)	0.2414(5)	0.08998(16)	.0630(27)	.0557(28)	.0654(29)	−.0022(23)	.0031(23)	−.0055(23)
C(7)	0.3031(4)	0.4382(6)	0.01032(16)	.0950(35)	.0798(36)	.0735(30)	.0000(29)	.0095(27)	.0101(29)
C(8)	0.5136(4)	0.2933(6)	0.05872(17)	.0649(29)	.1006(41)	.0819(33)	−.0060(28)	.0108(26)	−.0017(30)
C(9)	0.3764(3)	0.0187(5)	0.19019(14)	.0496(22)	.0578(27)	.0586(25)	.0029(20)	−.0042(20)	−.0077(22)
C(10)	0.4729(3)	−0.0520(5)	0.20006(15)	.0508(24)	.0725(31)	.0709(28)	.0054(22)	.0021(22)	−.0013(26)
C(11)	0.4797(3)	−0.1522(6)	0.23767(17)	.0587(27)	.0910(37)	.0862(36)	.0134(27)	−.0026(26)	.0076(30)
C(12)	0.3909(4)	−0.1788(6)	0.26528(16)	.0700(29)	.0868(36)	.0717(30)	.0074(28)	.0001(25)	.0114(28)
C(13)	0.2953(3)	−0.1073(6)	0.25492(16)	.0566(26)	.0924(35)	.0705(29)	.0028(25)	.0048(23)	.0067(28)
C(14)	0.2873(3)	−0.0062(6)	0.21780(15)	.0472(24)	.0896(34)	.0661(27)	.0104(23)	−.0006(20)	.0025(26)
C(15)	0.0066(3)	0.2445(5)	0.09882(15)	.0595(26)	.0607(27)	.0573(26)	.0025(23)	−.0083(22)	−.0075(23)
C(16)	−0.0261(4)	0.1330(5)	0.12999(16)	.0665(29)	.0700(32)	.0818(33)	−.0025(24)	−.0120(25)	.0115(27)
C(17)	−0.1333(4)	0.1267(6)	0.14255(18)	.0685(32)	.0942(40)	.0799(32)	−.0081(29)	−.0091(26)	.0103(30)
C(18)	−0.2085(4)	0.2261(6)	0.12492(17)	.0616(29)	.0996(42)	.0781(32)	−.0029(27)	−.0002(27)	.0027(32)
C(19)	−0.1755(4)	0.3361(6)	0.09367(17)	.0610(29)	.0956(40)	.0782(32)	.0131(28)	−.0108(25)	−.0105(31)
C(20)	−0.0674(4)	0.3468(6)	0.08025(14)	.0675(28)	.0751(33)	.0582(27)	.0049(26)	−.0090(22)	−.0037(24)

Atom	x	y	z	U	Atom	x	y	z	U
H(10)	0.534(3)	−0.024(5)	0.1831(15)	.080(15)	H(19)	−0.230(4)	0.413(6)	0.0804(16)	.100(18)
H(11)	0.553(4)	−0.209(6)	0.2460(18)	.113(19)	H(20)	−0.040(3)	0.429(5)	0.0583(15)	.073(15)
H(12)	0.393(4)	−0.258(6)	0.2898(18)	.105(20)	H(71)	0.339(4)	0.358(7)	−0.0083(18)	.097(19)
H(13)	0.228(3)	−0.125(5)	0.2736(14)	.076(14)	H(72)	0.245(5)	0.484(7)	−0.0001(19)	.123(25)
H(14)	0.220(3)	0.043(4)	0.2106(12)	.055(11)	H(73)	0.356(4)	0.532(7)	0.0211(18)	.117(21)
H(16)	0.027(4)	0.061(6)	0.1422(18)	.105(19)	H(81)	0.513(3)	0.244(5)	0.0336(17)	.072(16)
H(17)	−0.153(4)	0.044(7)	0.1639(20)	.112(24)	H(82)	0.514(4)	0.418(7)	0.0561(19)	.123(24)
H(18)	−0.291(4)	0.223(5)	0.1338(16)	.093(17)	H(83)	0.585(4)	0.249(6)	0.0694(16)	.089(18)

CRYSTAL DATA

$C_{17}H_{16}N_4S$; F.W. = 308.40
Space group *Pbca*
$a = 12.393(4)$ Å, $b = 8.560(3)$ Å, $c = 29.024(5)$ Å
$V = 3079.0$ Å^3
$D_c = 1.330$ g/cm^3, D_m(flotation) = 1.34 g/cm^3
$Z = 8$
$\mu = 18.22$ cm^{-1} (Cu$K\alpha$)

All the X-ray measurements were carried out on a paper-tape controlled Siemens AED diffractometer using Cu$K\alpha$ radiation. The unit cell dimensions were determined from the 2θ values of high order reflections measured at room temperature, $t = 22$ °C, $\lambda\alpha_1 = 1.5404$ Å. A least-squares procedure gave the values quoted above.

The intensities were measured by means of the five-value scan technique.[11] Reflections for which the net count was greater than two times the respective standard deviations in the net count, were accepted as observed. With this criterion 2270 independent reflections within $\theta = 71°$ were accepted as observed. The data set comprises in addition the 696 unobserved reflections.

Lp corrections and absorption corrections[12] were applied. The dimensions of the crystal were $0.3 \times 0.5 \times 0.3$ mm in the three axial directions; a grid of $8 \times 16 \times 8$ points was used.

The scattering factors for sulfur, nitrogen and carbon were taken from *International Tables.*[13] For hydrogen, the scattering factor curve given by Stewart *et al.*[14] was used.

The structure was solved by a symbolic addition procedure programmed by Long.[15] Only parts of the molecule showed up in the *E*-map, but a subsequent *F*-map with signs calculated on the basis of these parts, showed all the nonhydrogen atoms. The positions of the phenyl hydrogens were calculated, and the positions of the methyl hydrogens were found from a difference map. The atomic parameters were refined by full-matrix least-squares (see for example Ref. 16) to an R of 0.070.

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

Rigid body analysis has been carried out according to the method of Schomaker and Trueblood.[17] In this analysis the central ring system plus C(7), C(8), C(9) and C(15), *cf.* Fig. 1, were regarded as a rigid body. The corrections in bond lengths due to libration are small, less than the corresponding standard deviations, *cf.* Table 2. The corrections have been carried out according to the method of Cruickshank.[18]

The calculations mentioned above were carried out on an IBM 360/50H computer. The programs,

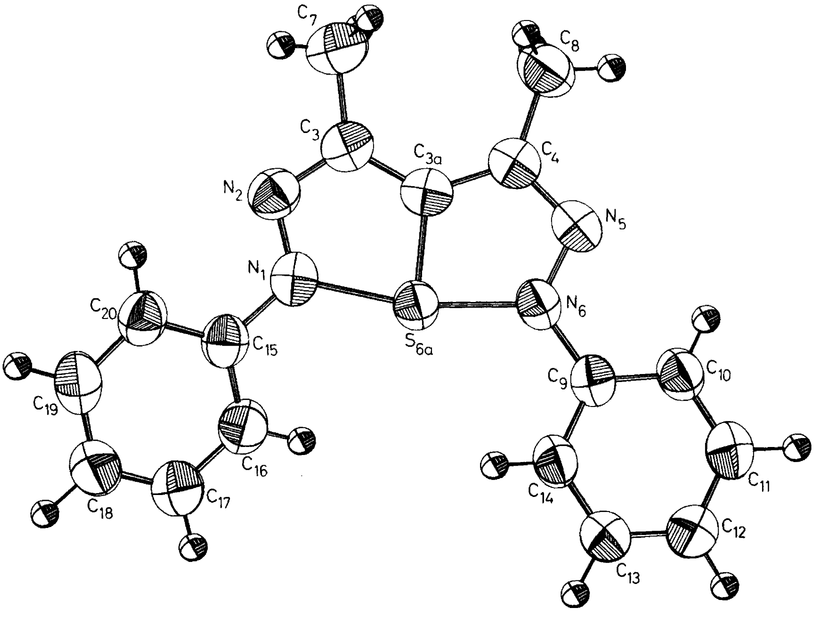


Fig. 1. The molecular structure of compound II with numbering of atoms. ORTEP[20] drawing.

Table 2. Bond lengths $l(jk)$ and $l'(jk)$, bond angles $\angle(ijk)$, and deviations Δ from least-squares plane for compound II. Standard deviations in parentheses. The bond lengths $l'(jk)$ have been corrected for libration. The deviations for atoms which are included in the least-squares plane calculations are printed in italics.

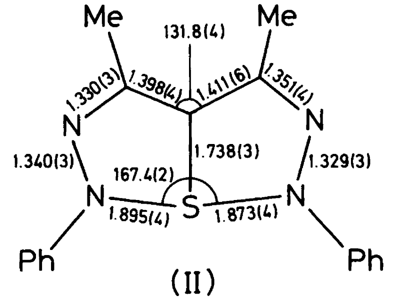
Atoms			Bond lengths (Å)		Bond angles (°)	Plane deviations (Å)	
i	*j*	*k*	$l(jk)$	$l'(jk)$	$\angle(ijk)$	Δ*j*	Δ*k*
N(1)	S(6a)	N(6)			167.4(2)	*−.001*	
C(3a)	S(6a)	N(1)	1.893(4)	1.895	83.3(2)		
C(3a)	S(6a)	N(6)	1.872(4)	1.873	84.0(2)		
S(6a)	N(1)	N(2)	1.338(6)	1.340	115.3(3)	*−.050*	
N(2)	N(1)	C(15)	1.418(6)	1.421	118.5(3)		
S(6a)	N(1)	C(15)			125.5(3)		
N(1)	N(2)	C(3)	1.328(6)	1.330	109.6(3)	*.037*	
N(2)	C(3)	C(3a)	1.397(6)	1.398	117.1(4)	*.023*	
N(2)	C(3)	C(7)	1.506(9)	1.510	117.2(4)		
C(3a)	C(3)	C(7)			125.7(5)		.088
C(3)	C(3a)	C(4)	1.410(6)	1.411	131.8(4)	*−.011*	
C(3)	C(3a)	S(6a)	1.734(4)	1.738	114.4(3)		
S(6a)	C(3a)	C(4)			113.8(3)		
C(3a)	C(4)	N(5)	1.350(6)	1.351	116.3(4)	*−.028*	
C(3a)	C(4)	C(8)	1.504(9)	1.508	126.9(4)		−.132
C(8)	C(4)	N(5)			116.8(4)		
C(4)	N(5)	N(6)	1.327(5)	1.329	109.4(3)	*−.016*	
N(5)	N(6)	S(6a)			116.3(3)	*.044*	
N(5)	N(6)	C(9)	1.436(6)	1.438	118.2(3)		
S(6a)	N(6)	C(9)			124.8(2)		
N(6)	C(9)	C(10)			121.6(4)		
N(6)	C(9)	C(14)			118.1(3)		
C(14)	C(9)	C(10)			120.3(4)	−.060	
C(9)	C(10)	C(11)	1.388(8)		119.6(4)	−.394	
C(10)	C(11)	C(12)	1.379(8)		120.5(5)	−.511	
C(11)	C(12)	C(13)	1.370(8)		119.3(5)	−.287	
C(12)	C(13)	C(14)	1.385(8)		120.8(4)	.038	
C(13)	C(14)	C(9)	1.380(6)		119.5(4)	.174	
C(16)	C(15)	N(1)			118.3(4)		
N(1)	C(15)	C(20)			121.6(4)		
C(20)	C(15)	C(16)	1.375(7)		120.1(4)	.034	
C(15)	C(16)	C(17)	1.379(8)		119.0(5)	−.284	
C(16)	C(17)	C(18)	1.358(8)		122.7(5)	−.156	
C(17)	C(18)	C(19)	1.374(9)		118.0(5)	.261	
C(18)	C(19)	C(20)	1.398(7)		121.1(5)	.567	
C(19)	C(20)	C(15)	1.379(7)		119.1(4)	.457	

with some exceptions, 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

The molecular structure of compound II as found in the present study is shown in Fig. 1. Bond lengths and angles with standard deviations, calculated from the values in Table 1, are listed in Table 2. A more realistic estimate of the standard deviations might probably be obtained by multiplying those given by a factor of two.[19]

Deviations of atoms from a least-squares plane through the atoms of the central rings are given in Table 2. Weights equal to atomic weights were used in this calculation. One notes from Table 2 that the central ring system is nearly planar and that the N(1)−C(15)−C(18) and the N(6)−C(9)−C(12) sequences point slightly out to opposite sides of this



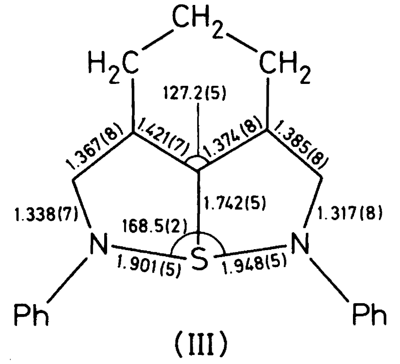


Fig. 2. Bond lengths (Å) and angles (°) in the central ring system of the present compound (II) and it the central ring system of 1,6-diphenyl-3,4-trimethylene-1,6-diaza-6a-thiapentalene (III).

plane. The methyl carbons C(7) and C(8) lie 0.09 and −0.13 Å, respectively, off the plane of the central rings.

The 1- and 6-phenyl groups are twisted 18 and 15° about the respective connection bonds, *cf.* Fig. 3. The twist angle about N(1)−C(15) was taken as the angle between the normal to the least-squares plane through C(15), N(1), N(2) and S(6a) and the normal to the least-squares plane through C(20, C(16), C(15) and N(1); the twist about N(6)−C(9) was calculated similarly.

Calculations show that the environments of N(1) and N(6) are slightly pyramidal. Thus, N(1) lies −0.051 Å out from the plane through C(15), N(2), and S(6a), and N(6) lies 0.072 Å off the plane through C(9), N(5) and S(6a).

A comparison of bond lengths and angles in the central ring system of the present compound with bond lengths and angles in the central ring system of 1,6-diphenyl-3,4-trimethylene-1,6-diaza-6a-thiapentalene (III)[21] is given in Fig. 2. One notes that the sum of the N−S distances is 3.768 Å in II and 3.849 Å in III; the difference of 0.081 Å is significant. It should be mentioned in this connection that the difference between the sum of S−S bond lengths in 2,5-diphenyl-1,6,6a-trithiapentalene,[22] 4.666 Å, and the sum of S−S bond lengths in 2,5-diphenyl-3,4-dimethyl-1,6,6a-trithiapentalene,[23] 4.606 Å, is 0.060 Å, and this difference as well as that mentioned above should be seen in relation to the repulsion

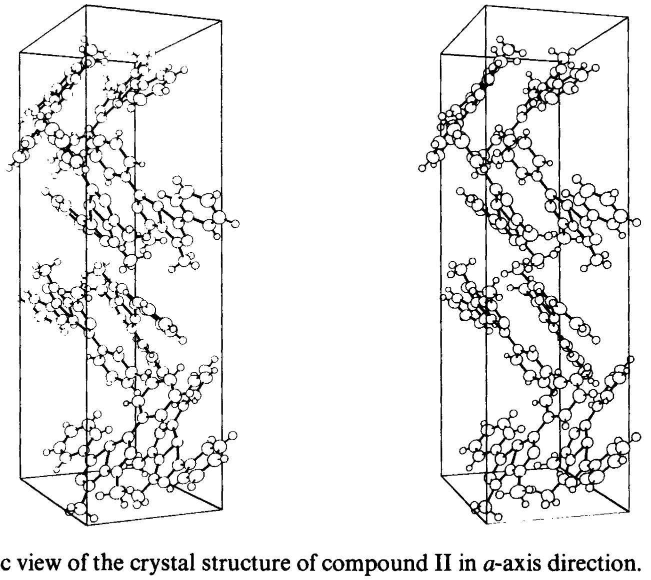


Fig. 3. A stereoscopic view of the crystal structure of compound II in *a*-axis direction.

between the methyl groups in 3- and 4-positions. A discussion of this effect has recently been reported.[24]

The lengths of other bonds in II are normal. Apart from the N – S bonds one notes that the double bond characters of equivalent bonds in the central ring systems of molecules II and III agree within the experimental error.

A stereoscopic view of the molecular packing in the unit cell is given in Fig. 3. There are no intermolecular contacts shorter than corresponding van der Waals distances.

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