The Crystal and Molecular Structure of 2-Diisopropyl-amino-4-methyl-3,4-diaza-1,6,6a-trithiapentalenylium-5-thiolate, $C_{10}H_{17}N_3S_4$

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The crystal and molecular structure of the title compound has been determined by X-ray methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions, $a = 5.946(2)$, $b = 9.021(2)$, $c = 13.900(3)$ Å, $\alpha = 91.06(2)$, $\beta = 99.81(2)$, and $\gamma = 98.02(2)°$. There are two molecules in the unit cell. The structure was solved by the heavy-atom method and refined full matrix least squares to an R-value of 0.040 for 1948 observed reflections.

The two five-membered rings of the central ring system deviate a little from planarity, and the angle between the least squares planes of the rings is 9.9°. Bond lengths in the central part of the molecule are: $S(1) - S(6a) = 2.554(2)$ and $S(6a) - S(6) = 2.190(2)$ Å with the angle $S(1) - S(6a) - S(6) = 172.99(6)°$, $S(1) - C(2) = 1.693(3)$, $S(6a) - C(3a) = 1.755(3)$, $S(6) - C(5) = 1.706(4)$, $C(2) - N(3) = 1.378(5)$, $N(3) - C(3a) = 1.297(5)$, $C(3a) - N(4) = 1.389(4)$, and $N(4) - C(5) = 1.378(5)$ Å. The bond lengths have been corrected for libration. In the crystal structure there is a short intermolecular $S \cdots S$ contact of 3.48(2) Å.

It has been shown in two earlier papers[1,2] that the $= N - Ph$ (Ia) as well as the $= N - Me$ group (Ib) in 6-position of 1,6a-dithiapentalene derivatives (I) perturbs the bonding in the linear $S - S - N$ sequences of these molecules, although to slightly different degrees. Thus, in Ia the $S - S$ and $S - N$ bonds are 2.447(1) and 1.863(2) Å, respectively, while they are 2.494(1) and 1.814(2) Å in Ib. It has further been shown that different heteroatoms such as S, Se, O and $N - Ph$ (IIa-d) in 6-position of 1,6a-dithiapentalene analogues (II) have different effects on the $S(1) - S(6a)$ bonding.[3−6] The $S(1) - S(6a)$ bond length is found to vary from 2.106(3) Å

in IIc $(X = O)$[5] to 2.499(3) Å in IIa $(X = S)$.[3] For IId $(X = N-Ph)$[6] and IIb $(X = Se)$[4] the values are 2.396(12) and 2.492(3) Å, respectively. The present structure analysis has been carried out in order to find the length of the $S(1) - S(6a)$ bond in Ic where the 6-position in I is occupied by a sulfur atom. The results may then be compared with the $S(1) - S(6a)$ bond lengths as found in Ia and Ib.

$X_6 = N-Ph$ (Ia)
$X_6 = N-Me$ (Ib)
$X_6 = S$ (Ic)

$X_6 = S$ (IIa)
$X_6 = Se$ (IIb)
$X_6 = O$ (IIc)
$X_6 = N-Ph$ (IId)
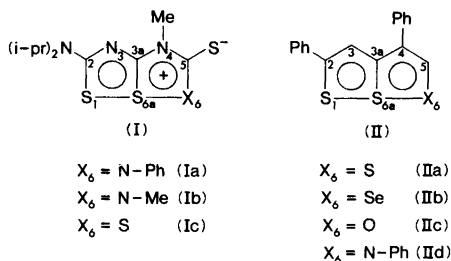
STRUCTURE ANALYSIS

The title compound was synthesized by Dr. J. Goerdeler, University of Bonn.[7] The crystals were bright yellow prisms and a crystal of dimensions $0.40 \times 0.25 \times 0.20$ mm was used for all X-ray measurements.

Crystal data

$C_{10}H_{17}N_3S_4$; M.W. = 307.52
Space group $P\bar{1}$ with $Z = 2$
$a = 5.946(2)$ Å, $b = 9.021(2)$ Å, $c = 13.900(3)$ Å

$\alpha = 91.06(2)°$, $\beta = 99.81(2)°$, $\gamma = 98.02(2)°$
$V = 726.8(9)$ Å^3
$D_x = 1.405$ g/cm^3, $D_m = 1.39$ g/cm^3
$\mu(MoK\alpha) = 6.14$ cm^{-1}, $F_{000} = 324$

The X-ray measurements were made on an Enraf-Nonius CAD4 diffractometer using graphite mono-chromator and MoKα radiation ($\lambda = 0.71069$ Å). The unit cell dimensions were calculated from the setting angles of 24 reflections with $2\theta > 32°$.

Three dimensional intensity data for 3484 independent reflections within $2\theta < 56°$ were measured at 20 °C by the $\omega - 2\theta$ scan technique and a scan width of $\Delta\omega = 0.75° + 0.35° \tan\theta$. After data reduction including Lp-correction but no absorption correction 1948 reflections with net intensity I greater than $2\sigma(I)$ were regarded as observed; $\sigma(I)$ was based on counting statistics.

The structure was solved by the heavy atom (S) method from a sharpened Patterson map. The four

Table 1. Atomic coordinates and temperature parameters U_{ij} (Å)^2 for the sulfur, nitrogen and carbon atoms. The temperature factor is $\exp(-2\pi^2(h^2a^{*2}U_{11} + ...2hka^*b^*U_{12} + ...))$. The U_{ij}'s are multiplied by 10^4.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	.69730(20)	.26995(11)	.06155(7)	823(9)	541(6)	314(5)	359(6)	64(5)	42(4)
S(6a)	.43435(19)	.44592(11)	.11281(7)	652(7)	449(6)	334(5)	261(5)	35(5)	56(4)
S(6)	.22548(21)	.59090(12)	.17518(7)	688(8)	565(7)	517(6)	363(6)	52(6)	38(5)
S(7)	.32449(21)	.71946(11)	.37535(8)	779(9)	499(6)	551(6)	255(6)	256(6)	-3(5)
C(2)	.78379(62	.24219(37)	.18117(23)	426(23)	391(20)	345(19)	109(17)	43(16	29(15)
N(3)	.74475(49)	.33900(29)	.25206(19)	441(19)	358(16)	321(15)	120(14)	55(14)	29(13)
C(3a)	.59811(60)	.43138(34)	.22852(23)	441(24)	315(19)	335(18)	76(17)	94(17)	45(15)
N(4)	.56535(51)	.52660(30)	.30274(20)	463(20)	349(16)	359(16)	106(14)	110(14)	24(13)
C(5)	.38605(65)	.60968(37)	.28945(26)	507(26)	330(19)	486(22)	95(18)	177(19)	72(16)
C(8)	.71939(102)	.52995(71)	.39739(34)	752(39)	711(35)	357(23)	258(30)	40(24)	-82(25)
N(9)	.89417(53)	.12882(30)	.21428(20)	572(21)	382(17)	374(16)	216(16)	28(15)	8(13)
C(10)	.97454(66)	.10539(41)	.31970(25)	422(24)	415(21)	392(20)	119(19)	-12(18)	68(16)
C(11)	1.16651(84)	.22615(53)	.36499(35)	521(30)	594(29)	528(27)	104(24)	-52(23)	-11(22)
C(12)	.77963(92)	.07819(62)	.37781(38)	580(34)	699(34)	584(30)	118(28)	139(26)	235(26)
C(13)	.93776(86)	.01344(46)	.14353(29)	904(37)	539(27)	418(23)	415(26)	-26(23)	-67(20)
C(14)	1.19240(102)	.00935(59	.15120(41)	910(44)	591(32)	714(36)	282(30)	379(33)	17(27)
C(15)	.80357(97)	-.13813(60)	.15779(55)	526(35)	630(34)	1355(58)	138(28)	-118(36)	-456(37)

Table 2. Atomic coordinates and isotropic thermal parameters U (Å)^2 for the hydrogen atoms. The temperature factor is $\exp\{-8\pi^2 U(\sin^2\theta/\lambda^2)\}$. The U's are multiplied by 10^3.

Atom	x	y	z	U	Atom	x	y	z	U
H(81)	.6813(96)	.4690(56)	.4268(36)	103(25)	H(123)	.6595(78)	.0154(48)	.3446(31)	89(18)
H(82)	.6828(87)	.6106(54)	.4306(36)	119(20)	H(13)	.8939(62)	.0530(38)	.0784(25)	63(12)
H(83)	.9016(103)	.5638(59)	.3733(38)	172(25)	H(141)	1.2938(78)	.1107(50)	.1410(32)	101(18)
H(10)	1.0507(58)	.0195(36)	.3192(23)	49(10)	H(142)	1.2670(75)	-.0245(46)	.2106(30)	82(16)
H(111)	1.2264(73)	.1953(44)	.4290(29)	81(15)	H(143)	1.2129(66)	-.0639(41)	.1042(27)	67(13)
H(112)	1.1066(77)	.3209(48)	.3682(31)	99(17)	H(151)	.8266(78)	-.1928(49)	.1053(31)	87(17)
H(113)	1.3120(85)	.2290(48)	.3270(32)	118(19)	H(152)	.8759(90)	-.1773(52)	.2256(35)	117(21)
H(121)	.7171(84)	.1820(52)	.3918(32)	115(18)	H(153)	.6318(79)	-.1293(47)	.1427(31)	93(16)
H(122)	.8528(77)	.0495(48)	.4448(32)	105(17)					

sulfur atoms were located, and a subsequent Fourier map revealed the remaining non-hydrogen atoms. The hydrogen atoms were found from difference maps and the atomic parameters were refined by full matrix least squares to an R factor of 0.040. The weighted R_w was 0.029. The average shift was less than 0.05σ and the shifts in all parameters were less than 0.2σ.

The atomic scattering factors used for sulfur, nitrogen and carbon were those of Doyle and Turner,[8] and for hydrogen those of Stewart et al.[9] Final atomic coordinates and temperature parameters for the non-hydrogen atoms are listed in Table 1; those of the hydrogen atoms are listed in Table 2. The final structure factor list is available from the author on request.

Rigid body analysis (RBM) has been carried out according to the method of Schomaker and Trueblood.[10] The system treated as a rigid body was the central ring system plus the atoms S(7), C(8), N(9), C(10) and C(13).

All calculations were carried out on the UNIVAC 1110 computer at the University of Bergen. The programs used were mainly those of the X-RAY 76 program system except for the data reduction and RBM-analysis programs which were adopted for the UNIVAC 1110 computer by L.K. Hansen and L. J. Sæthre, this University.

DISCUSSION

An ORTEP[12] drawing showing the structure of the title compound and the numbering of atoms is given in Fig. 1. The rings A and B deviate both slightly from planarity. The equations for the least squares planes through rings A and B are:

Plane A:

$$3.92969\ x + 5.80658\ y - 3.43527\ z = 3.99363$$

Plane B:

$$3.37000\ x + 6.31804\ y - 5.13653\ z = 3.64117$$

with x, y and z as fractional coordinates.

The largest deviations from the planes are -0.13 Å for atom C(2) in plane A and -0.07 Å for atom

Table 3. Bond lengths (l) in 2-diisopropylamino-4-methyl-3,4-diaza-1,6,6a-trithiapentalenylium-5-thiolate. Standard deviations in parentheses. The l^l values have been corrected for libration.

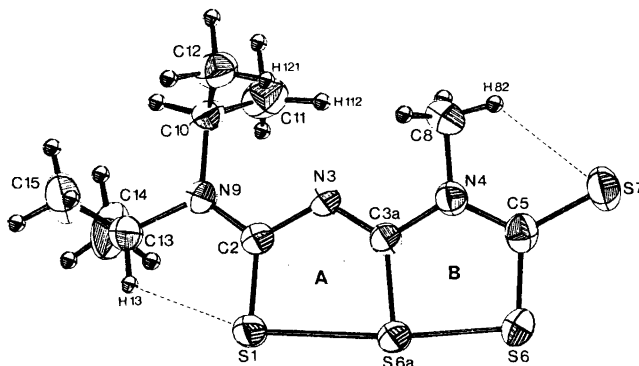| Bond	$l(Å)$	$l^l(Å)$
S(1) – S(6a)	2.550(2)	2.554
S(6a) – S(6)	2.187(2)	2.190
S(1) – C(2)	1.689(3)	1.693
S(6a) – C(3a)	1.750(3)	1.755
S(6) – C(5)	1.701(4)	1.706
C(2) – N(3)	1.375(5)	1.378
N(3) – C(3a)	1.295(5)	1.297
C(3a) – N(4)	1.387(4)	1.389
N(4) – C(5)	1.376(5)	1.378
C(5) – S(7)	1.657(4)	1.661
N(4) – C(8)	1.467(5)	1.471
C(2) – N(9)	1.338(5)	1.340
N(9) – C(10)	1.491(4)	1.495
N(9) – C(13)	1.497(5)	1.500
C(10) – C(11)	1.506(6)	
C(10) – C(12)	1.517(7)	
C(13) – C(14)	1.505(8)	
C(13) – C(15)	1.518(7)	

Fig. 1. ORTEP[12] drawing of the title compound with numbering of atoms. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Table 4. Bond angles $\angle (ijk)$ in 2-diisopropyl-amino-4-methyl-3,4-diaza-1,6,6a-triapentalenylium-5-thiolate. The standard deviations in parentheses.

i	j	k	$\angle (ijk)°$
C(2)	S(1)	S(6a)	88.0(1)
S(1)	S(6a)	S(6)	172.99(6)
S(1)	S(6a)	C(3a)	82.7(1)
C(3a)	S(6a)	S(6)	90.4(1)
S(6a)	S(6)	C(5)	96.5(1)
S(6)	C(5)	S(7)	121.3(2)
S(6)	C(5)	N(4)	114.3(3)
S(7)	C(5)	N(4)	124.4(3)
C(5)	N(4)	C(8)	121.0(4)
C(5)	N(4)	C(3a)	120.9(3)
C(8)	N(4)	C(3a)	118.1(4)
N(4)	C(3a)	S(6a)	116.9(3)
N(4)	C(3a)	N(3)	116.7(3)
S(6a)	C(3a)	N(3)	126.4(3)
C(3a)	N(3)	C(2)	119.0(3)
N(3)	C(2)	N(9)	115.3(3)
C(1)	C(2)	N(3)	120.7(3)
S(1)	C(2)	N(9)	124.0(3)
C(2)	N(9)	C(10)	124.2(3)
C(2)	N(9)	C(13)	119.8(3)
N(9)	C(10)	C(11)	111.9(3)
N(9)	C(10)	C(12)	113.4(3)
N(9)	C(13)	C(14)	110.7(3)
N(9)	C(13)	C(15)	110.4(4)
C(11)	C(10)	C(12)	113.5(4)
C(10)	N(9)	C(13)	116.1(3)
C(14)	C(13)	C(15)	112.8(4)

C(3a) in plane *B*. The angle between the planes is 9.9°. The atoms of the diisopropylamino group, N(9), C(10) and C(13) lie out of plane *A*, by −0.47, −0.65 and −0.72 Å, respectively, while the substituent atoms S(7) and C(8) lie 0.07 and 0.09 Å, respectively, out of plane *B*.

Bond lengths and angles for the non-hydrogen atoms are listed in Tables 3 and 4. The bond lengths between non-hydrogen atoms, with the exceptions of the C−C bonds in the isopropyl-groups, have been corrected for libration, *cf.* Table 3. The l^i values are corrected according to Cruickshank's[13] method. The maximum angle of libration is 3.7°, and the corrections range from 0.002 to 0.005 Å.

The S(1)−S(6a) bond length of the present structure is 2.554(2) Å and the S(6a)−S(6) bond length 2.190(2) Å; the S(1)−S(6a)−S(6) angle is 173.0(1)°. A comparison with the S(1)−S(6a) bond lengths in Ia and Ib, respectively, shows that those are 0.107 and 0.060 Å shorter than those of the present structure. Thus, by replacing the N−R group in I with sulfur the S(1)−S(6a) bond becomes significantly longer. This observation is in good agreement with results from structural studies on trithiapentalene derivatives.[3,6] Thus, in IId[6] the S(1)−S(6a) bond length is 2.396(12) Å while that in IIa[3] is 2.499(3) Å. The increase in the S(1)−S(6a) bond length is 0.103 Å as compared with the difference of 0.107 Å between the S(1)−S(6a) bond lengths in Ic and Ia. A comparison of the lengths of other bonds in Ic with those of equivalent bonds in Ia and Ib shows insignificant differences.
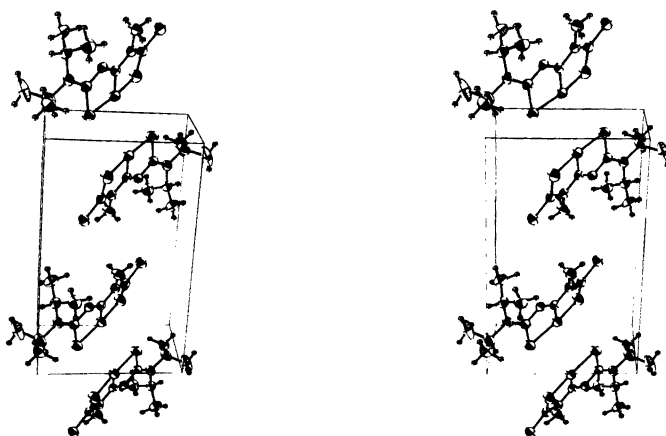
Fig. 2. A stereoscopic view of the arrangement of molecules in the unit cell.

The C−H bond lengths have a mean value of 0.98(10) Å. The bond angles involving hydrogen atoms have a mean value of 109(6)°.

As in Ia and Ib there are also a few short intra-molecular S⋯H and N⋯H contacts in Ic. These are, S(1)⋯H(13)=2.41(4) Å, S(7)⋯H(82)=2.48(5) Å, N(3)⋯H(121)=2.44(4) Å and N(3)⋯H(112)= 2.49(4) Å, *cf.* Fig. 1. Especially the S⋯H distances are rather short compared to the corresponding van der Waals distance of 3.05 Å.[14] There is also a short intermolecular distance S(6a)⋯S(6a)=3.48(2) Å across a symmetry center. A stereoscopic view of the arrangements of molecules in the unit cell is given in Fig. 2.[12]

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