

The Crystal and Molecular Structure of 2-Diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-olate, $C_{11}H_{20}N_4OS_2$

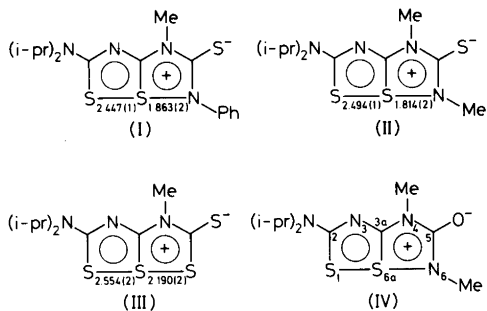
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The structure of $C_{11}H_{20}N_4OS_2$ has been determined by X-ray crystallographic methods. 4091 independent reflections were measured on a diffractometer using the $\omega-2\theta$ scan technique and $MoK\alpha$ radiation. The compound crystallizes in an orthorhombic space group $P2cb$ with unit cell dimensions, $a = 7.000(1)$, $b = 20.321(2)$ and $c = 22.027(2)$ Å. There are two independent molecules per asymmetric unit, giving a total of 8 molecules in the unit cell. The structure was solved by Patterson synthesis and refined by full matrix least squares to an R of 0.040 for 2607 observed reflections. The central ring system is planar in both molecules with the planes normal to the a -axis. The two independent molecules are related by a rotation of approximately 90° about $[100]$ and the thiazazole parts of the two molecules overlap. Differences in the bond lengths for corresponding bonds in the two molecules are insignificant except for the $S(1)-S(6a)$ bond distances which are found to be $2.522(1)$ Å in one of the molecules and $2.561(1)$ Å in the other. Other sulfur-containing bond lengths in the central part of molecule 1 are, $S(6a1)-N(61) = 1.791(2)$ Å, $S(11)-C(21) = 1.711(3)$ Å and $S(6a1)-C(3a1) = 1.758(3)$ Å. Corresponding bond lengths in molecule 2 are, $S(6a2)-N(62) = 1.780(2)$ Å, $S(12)-C(22) = 1.719(3)$ Å and $S(6a2)-C(3a2) = 1.758(3)$ Å. The lengths of the C–O bonds are $1.235(4)$ and $1.228(3)$ Å, respectively, in 1 and 2. The angles $S(1)-S(6a)-N(6)$ are $169.3(1)$ and $169.0(1)^\circ$, respectively, in molecules 1 and 2. The bond lengths have been corrected for libration.

The results from CNDO/2 calculations show that the electron charge density distribution is different in the S–S–N sequences of the respective molecules. This difference, caused by the crystal packing, may explain why the S–S bond lengths are found to be different in the two molecules.

Recent studies on three 1,6a-dithiapentalenylium-5-thiolates (I–III)^{1–3} have shown that different substituents in the 6-position have a considerable influence on the $S(1)-S(6a)$ bond length.



The value of the $S(1)-S(6a)$ bond distances varies from $2.447(1)$ Å in I to $2.554(2)$ Å in III. Furthermore, since it is possible to exchange the sulfur substituent in 5-position of *e.g.* II with the more electronegative element oxygen (IV),⁴ it was thought of interest to carry out an X-ray structure determination of IV in order to find out whether this change of 5-substituent causes a change in the $S(1)-S(6a)-N(6)$ bonding.

STRUCTURE ANALYSIS

The crystals were supplied by Dr. J. Goerdeler, University of Bonn.⁴ Recrystallization from acetone gave crystals suitable for single crystal X-ray work. The crystals are colourless prisms, and a crystal of dimensions $0.50 \times 0.30 \times 0.30$ mm was used for all X-ray measurements.

CRYSTAL DATA

 $C_{11}H_{20}N_4OS_2$; M.W. = 288.44
Space group $P2cb$ (No. 32) with $Z=8$
 $a=7.0001(12)$ Å, $b=20.3207(23)$ Å, $c=22.0274(21)$ Å
 $V=3133(1)$ Å³
 $D_x=1.223$ g/cm³, $D_m(\text{floatation})=1.21$ g/cm³
 $\mu(\text{MoK}\alpha)=5.19$ cm⁻¹, $F_{000}=1232$

Unit cell dimensions and intensity data were collected on a CAD4 diffractometer using graphite monochromator and MoK α radiation ($\lambda=0.71069$ Å). The unit cell dimensions were determined from 25 reflections with $2\theta > 40^\circ$. Three-dimensional intensity data for 4091 independent reflections within $2\theta < 56^\circ$ were collected at room temperature (20°C) by the $\omega-2\theta$ scan technique and with scan width $\Delta\omega=0.75^\circ+0.35^\circ \tan \theta$. Lp-corrections were carried out but absorption corrections were considered unnecessary. 2607 reflections with net intensity I greater than $2\sigma(I)$ were regarded as observed; $\sigma(I)$ based on counting statistics.

Precession photographs indicated that the $h00$ reflections are systematically absent for $h=2n+1$ thus indicating a 2-fold screw axis. But this observation leads to a space group that could not be derived from International Tables.⁵ A more careful examination of the profile of each reflection along the a -axis taken from the diffractometer output showed no systematic absences. The observed structure factors together with their standard deviations are listed in Table 1 for the $h00$ reflections. One notes that the reflections with odd h indices are very weak, although observed, as compared to the even h indices. It can therefore be concluded that the a -axis is not a 2-fold screw axis.

Program NORMSF⁶ was used to try to establish whether the space group is centrosymmetric or not, e.g. $Pmcb$ or $P2cb$. The statistics indicated a non-centrosymmetric space group. The space group $P2cb$

was therefore chosen and further work confirmed this assumption. This means that there are two independent molecules in the asymmetric unit.

As mentioned above, the other possible space group was the centrosymmetric $Pmcb$. Refinement in this space group with the molecules in the mirror planes at $x=0$ and $\frac{1}{2}$ leads to unrealistic bond lengths and temperature parameters, and it was concluded that the non-centrosymmetric space group was the correct one in agreement with the statistics.

The structure was solved by Patterson synthesis and from this map 4 sulfur atoms were located. Subsequent Fourier maps revealed the remaining non-hydrogen atoms and the hydrogen atoms were eventually found from difference maps. The hydrogen atoms were included in the further refinement with isotropic thermal parameters, and all of them refined to reasonable positions. The atomic parameters were refined by full matrix least squares to an R factor of 0.040. The weighted R_w was 0.031. The function minimized in the refinement was $\sum w(|F_o| - |(1/k)F_c|)^2$, where $w=1/\sigma F^2$. Due to the large number of parameters, 483, only one of the molecules was refined at a time, but the final refinement was done on all atoms simultaneously, refining the parameters in 5 blocks. At the end of this refinement the average shift/error ratio was 0.18.

The scattering factors used in the structure factor calculations were those of Stewart *et al.*⁷ for hydrogen and of Cromer and Mann⁸ for the other atoms. Final atomic coordinates and temperature parameters for the non-hydrogen atoms are listed in Table 2; those of the hydrogen atoms are listed in Table 3. The final structure factor list is available from the author on request.

Rigid body analyses have been carried out on the central parts of the two independent molecules according to the method of Schomaker and Trueblood.⁹ The corresponding librational tensors are given in Table 4.

All calculations were carried out on the CYBER 171 MP computer at the University of Tromsø. The programs used were mainly those of the X-RAY 76 program system.⁶ The data reduction programs and the RBM-analysis program used were adopted for the CYBER 171 MP computer by the author.

Table 1. Observed structure factors (F_o) and standard deviations (σF_o) for the $h00$ reflections.

h	F_o	σF_o	Status
1	10.24	0.05	Obs.
2	294.19	0.71	Obs.
3	2.19	0.44	Obs.
4	159.48	0.79	Obs.
5	3.91	0.14	Obs.
6	64.72	0.21	Obs.
7	1.60	0.48	Weak
8	23.04	0.12	Obs.
9	1.91	0.57	Weak

DISCUSSION

ORTEP¹⁰ drawings of the two independent molecules of the title compound are shown in Fig. 1 with the numbering of atoms. Least squares planes show that both molecules are planar within the error. The estimated errors are 0.03 and 0.04 Å, respectively, for molecules 1 and 2. The plane

Table 2. Atomic coordinates and temperature parameters $U_{ij}(\text{\AA}^2 \times 10^3)$ for the sulfur, oxygen, nitrogen and carbon atoms. The temperature factor is $\exp\{-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)\}$.

MOLECULE 1									
ATOM	\bar{x}	\bar{y}	\bar{z}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(11)	.0016(6)	.42282(4)	.43478(3)	104(1)	51(1)	44(1)	-5(3)	8(2)	-1(1)
S(6A1)	0.0000	.36845(3)	.33223(3)	73(1)	63(1)	38(1)	-3(1)	2(1)	2(1)
C(21)	.0029(19)	.34794(13)	.46908(11)	51(2)	58(2)	39(1)	9(7)	1(7)	-4(1)
N(31)	-.0068(15)	.29208(10)	.43547(9)	56(2)	53(1)	36(1)	9(6)	-4(6)	-3(1)
C(3A1)	.0022(18)	.29725(12)	.37634(11)	41(2)	58(2)	43(1)	-7(8)	-1(7)	-3(1)
N(41)	.0025(17)	.24224(10)	.34131(9)	57(1)	56(1)	44(1)	2(7)	6(6)	-8(1)
C(51)	.0090(20)	.25216(17)	.27798(13)	50(3)	86(2)	42(2)	-6(8)	-10(5)	-15(2)
N(61)	-.0002(17)	.31616(12)	.26730(8)	85(2)	76(2)	35(1)	8(8)	-0(7)	-3(1)
C(71)	.0095(22)	.34522(17)	.20635(12)	143(5)	104(3)	39(2)	21(9)	-34(6)	-2(2)
O(81)	.0007(13)	.20631(10)	.24169(8)	101(2)	91(2)	53(1)	9(8)	-3(7)	-26(1)
C(91)	.0029(19)	.17598(14)	.36695(12)	84(3)	60(2)	61(2)	-24(7)	-13(7)	-10(2)
N(101)	-.0021(16)	.34089(10)	.52966(8)	81(2)	53(1)	37(1)	3(8)	6(8)	-1(1)
C(111)	-.0068(25)	.27529(15)	.55993(12)	109(3)	56(2)	36(1)	13(10)	-2(10)	-0(1)
C(121)	.1828(18)	.2369(5)	.5474(6)	122(9)	80(10)	56(7)	40(7)	-15(7)	2(6)
C(131)	-.1793(23)	.2379(6)	.5485(6)	169(12)	101(13)	70(9)	-47(10)	-14(9)	20(8)
C(141)	-.0109(29)	.39923(16)	.56888(15)	169(5)	59(2)	41(2)	-15(11)	-12(10)	-7(1)
C(151)	.1507(28)	.3987(6)	.6136(6)	316(14)	79(5)	92(5)	-59(7)	-94(7)	1(4)
C(161)	-.1979(29)	.4053(8)	.6004(7)	355(20)	125(8)	174(13)	70(11)	171(14)	21(7)

MOLECULE 2									
ATOM	\bar{x}	\bar{y}	\bar{z}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(12)	.4961(5)	.14164(3)	.43899(3)	83(1)	52(1)	40(1)	-1(2)	-5(2)	-1(1)
S(6A2)	.4983(5)	.25698(3)	.39284(3)	55(1)	47(1)	53(1)	4(2)	-0(2)	-4(1)
C(22)	.4914(17)	.10836(12)	.36779(11)	51(2)	49(1)	45(1)	9(6)	-3(6)	3(1)
N(32)	.4983(14)	.14790(9)	.31809(8)	67(2)	43(1)	42(1)	-3(7)	-11(6)	2(1)
C(3A2)	.4943(16)	.21143(12)	.32556(11)	45(2)	52(2)	47(1)	18(6)	-2(6)	2(1)
N(42)	.5012(14)	.25170(10)	.27626(9)	70(2)	48(1)	47(1)	-8(7)	-3(7)	7(1)
C(52)	.5030(18)	.31997(13)	.28759(13)	60(2)	49(2)	76(2)	14(7)	-11(8)	11(2)
N(62)	.4987(15)	.32897(9)	.34726(10)	74(2)	42(1)	70(2)	6(7)	-0(8)	-0(1)
C(72)	.4879(19)	.39381(14)	.37589(15)	82(3)	49(2)	97(2)	-12(6)	-18(7)	-5(2)
O(82)	.4965(13)	.36116(9)	.24710(9)	107(2)	57(1)	88(1)	6(6)	0(8)	26(1)
C(92)	.5041(20)	.22629(14)	.21440(12)	104(3)	64(2)	52(2)	11(8)	-11(8)	13(1)
N(102)	.5060(15)	.04396(10)	.35739(9)	81(2)	42(1)	41(1)	-0(6)	2(5)	2(1)
C(112)	.4815(21)	.01570(15)	.29472(14)	129(5)	41(2)	48(2)	-14(6)	22(6)	-3(1)
C(122)	.3122(15)	.0324(5)	.2619(5)	139(8)	67(7)	62(6)	-20(6)	-49(7)	7(5)
C(132)	.6743(17)	.0294(6)	.2597(5)	207(13)	79(8)	86(9)	-0(8)	47(9)	-27(6)
C(142)	.4926(20)	-.00351(14)	.40826(12)	112(3)	49(2)	47(2)	30(7)	6(8)	5(1)
C(152)	.3157(13)	-.0423(4)	.4122(4)	122(7)	94(5)	86(6)	-53(6)	-27(5)	47(5)
C(162)	.6854(22)	-.0422(7)	.4077(5)	339(17)	253(12)	99(9)	194(13)	5(9)	35(8)

Table 3. Atomic coordinates and isotropic temperature parameters $U(\text{\AA}^2 \times 10^3)$ for the hydrogen atoms. The temperature factor is $\exp\{-8\pi^2U(\sin^2\theta/\lambda^2)\}$.

MOLECULE 1					MOLECULE 2				
ATOM	\bar{x}	\bar{y}	\bar{z}	U	ATOM	\bar{x}	\bar{y}	\bar{z}	U
H(711)	-.058(6)	.3150(16)	.1818(14)	82(13)	H(721)	.552(4)	.4308(12)	.3472(11)	53(9)
H(712)	-.057(9)	.3912(27)	.2053(24)	182(29)	H(722)	.561(3)	.3890(11)	.4152(9)	64(8)
H(713)	.155(5)	.3503(15)	.1913(14)	84(12)	H(723)	.341(6)	.4071(18)	.3849(17)	107(15)
H(911)	-.038(6)	.1483(11)	.3356(10)	58(9)	H(921)	.438(4)	.2624(12)	.1883(11)	56(9)
H(912)	-.095(4)	.1733(14)	.4048(13)	77(9)	H(922)	.641(6)	.2131(20)	.2091(18)	99(15)
H(913)	.145(7)	.1628(25)	.3813(18)	133(20)	H(923)	.422(5)	.1899(13)	.2109(15)	76(15)
H(111)	.027(7)	.2890(11)	.6025(10)	66(9)	H(112)	.541(4)	-.0305(9)	.2992(9)	37(7)
H(1211)	.228(5)	.2069(15)	.5770(15)	47(10)	H(1221)	.358(5)	.0071(17)	.2184(15)	73(12)
H(1212)	.307(6)	.2647(20)	.5535(20)	70(13)	H(1222)	.182(6)	.0153(18)	.2883(17)	86(14)
H(1213)	.170(4)	.2121(14)	.5061(13)	52(9)	H(1223)	.302(4)	.0756(15)	.2506(14)	79(8)
H(1311)	-.283(11)	.2810(25)	.5712(28)	215(29)	H(1321)	.741(4)	.0007(14)	.2354(13)	45(9)
H(1312)	-.252(5)	.2439(18)	.5139(16)	71(11)	H(1322)	.644(10)	.0714(28)	.2311(28)	242(28)
H(1313)	-.138(5)	.1914(16)	.5693(14)	59(11)	H(1323)	.775(7)	.0439(24)	.2947(21)	116(18)
H(141)	-.042(5)	.4371(10)	.5397(9)	42(8)	H(142)	.463(5)	.0229(9)	.4452(8)	40(8)
H(1511)	.244(5)	.3667(16)	.6185(14)	78(11)	H(1521)	.338(4)	-.0716(14)	.4485(12)	42(8)
H(1512)	.241(3)	.4154(10)	.5865(8)	78(5)	H(1522)	.323(7)	-.0734(20)	.3736(18)	112(16)
H(1513)	.161(5)	.4439(14)	.6296(12)	66(9)	H(1523)	.198(7)	-.0075(24)	.4277(22)	162(20)
H(1611)	-.228(11)	.3571(16)	.6185(18)	176(21)	H(1621)	.763(11)	-.0227(26)	.4460(29)	218(29)
H(1612)	-.175(5)	.4396(16)	.6370(13)	79(11)	H(1622)	.643(4)	-.0922(14)	.4172(13)	40(8)
H(1613)	-.308(9)	.4185(24)	.5812(20)	219(24)	H(1623)	.766(5)	-.0457(17)	.3812(16)	67(10)

calculations comprise all atoms except the methyl groups.

Bond lengths and angles for the non-hydrogen atoms as calculated from the atomic coordinates in

Table 2, are listed in Tables 5 and 6. It is realized that the temperature factors for carbon atoms in the isopropyl groups show unusually high values, e.g. atoms C(151), C(161) and C(162). However,

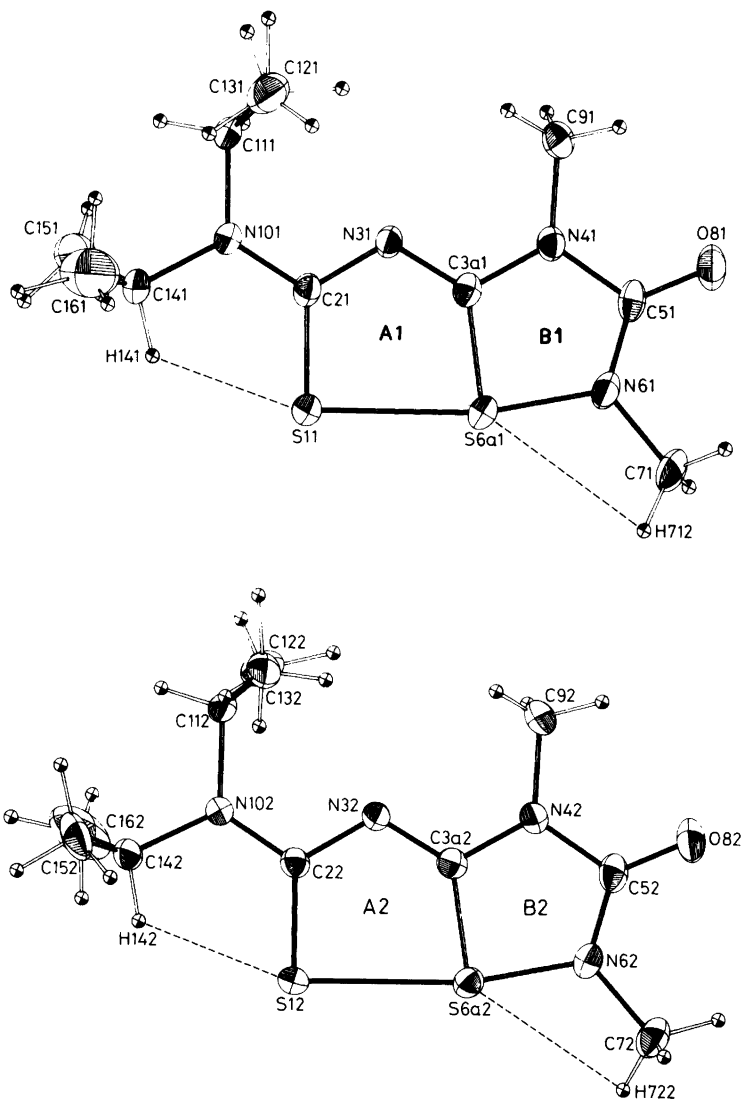


Fig. 1. ORTEP¹⁰ drawings of the two molecules in the title compound with the numbering of the atoms in the molecules. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 20 % probability level.

values of such magnitude are often found for carbon atoms in isopropyl substituent groups, see *e.g.* Ref. 11. The bond lengths between the atoms that were included in the least squares plane calculation have been corrected for libration, *cf.* Table 5. The l' values are corrected according to the librational tensors L_1 and L_2 given in Table 4 using Cruickshank's¹² method. The corrections range from 0.004 to 0.012 Å. The r.m.s. differences between

observed U_{ij} 's and those calculated from the derived T,L,S molecular tensors are 0.0100 and 0.0096 Å², respectively, for molecules 1 and 2.

The bonds in the 'linear' S—S—N sequences are S(11)—S(6a1)=2.522(1) Å and S(6a1)—N(61)=1.791(2) Å for molecule 1, and S(12)—S(6a2)=2.561(1) Å and S(6a2)—N(62)=1.780(2) Å for molecule 2. The S(1)—S(6a)—N(6) angles are 169.3(1) and 169.0(1)°, respectively, for molecules

Table 4. Rigid body libration tensors L_1 and L_2 of the 2-diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-olate molecules.

Eigenvalues	Eigenvectors Direction cosines $\times 10^4$ relative to a , b , and c , respectively.			
L_1	$41.6(^{\circ})^2$	- 534	2658	9626
	15.7	- 1182	9555	- 2704
	6.0	- 9916	- 1281	- 197
L_2	$35.5(^{\circ})^2$	- 526	- 9600	2751
	10.5	- 4348	2700	8591
	5.8	- 8990	- 744	- 4316

1 and 2. Except for the S-S bonds, the other non-hydrogen bond lengths in the two molecules are equal within the error (3σ). According to Hamilton and Abrahams¹³ a more realistic estimate of the deviations would probably be obtained by multiplying those by a factor of 2. This means that the C(111)-C(131), C(112)-C(122) and C(142)-C(152) bond lengths, cf. Table 5, are not significantly different from the accepted value for a $C(sp^3)$ - $C(sp^3)$ bond length of 1.536 Å.¹⁴ A comparison with the analogous compound II shows that the S-S and S-N bonds in IV are significantly different from the corresponding values in II. In II S(1)-S(6a)=2.492(1) Å and S(6a)-N(6)=1.814(2) Å. The differences can be explained by the fact that when the sulfur substituent in 5-position in II is replaced by the more electronegative oxygen substituent in IV, there will be a redistribution of charge on the neighbouring atoms. The nitrogen atom in 6-position in IV will have a more positive charge relative to the same atom in II. It has been shown^{15,16} that the more positive the charge on the 6-position atom is, the shorter becomes the 6a-6 bond length. A comparison of other equivalent bonds in II and IV shows only minor or insignificant differences.

A projection on the yz -plane of the two molecules in the asymmetric unit is given in Fig. 2 and a stereoscopic view of the arrangements of molecules is shown in Fig. 3.¹⁰ The molecules are stacked upon each other almost perpendicular to the a -axis, and the spacing between two molecules are about $a/2$, i.e. 3.50 Å. It can further be seen from Fig. 2 that the two molecules overlap each other partly; the overlapping parts being rings B1 and B2, cf. Fig. 1.

Table 5. Bond lengths l in 2-diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-olate. Standard deviations in parentheses. The l' values have been corrected for libration according to the librational tensors L_1 and L_2 .

Bond	$l(\text{Å})$	$l'(\text{Å})$
Molecule 1		
S(11)-S(6a1)	2.513(1)	2.522
S(11)-C(21)	1.699(3)	1.711
S(6a1)-C(3a1)	1.746(3)	1.758
S(6a1)-N(61)	1.784(2)	1.791
C(21)-N(31)	1.357(3)	1.364
C(21)-N(101)	1.343(3)	1.348
N(31)-C(3a1))	1.308(3)	1.313
C(3a1)-N(41)	1.358(3)	1.365
N(41)-C(51)	1.410(4)	1.416
N(41)-C(91)	1.460(3)	1.470
C(51)-N(61)	1.323(4)	1.333
C(51)-O(81)	1.229(4)	1.236
N(61)-C(71)	1.468(3)	1.475
N(101)-C(111)	1.491(4)	1.501
N(101)-C(141)	1.468(4)	1.475
C(111)-C(121)	1.563(19)	
C(111)-C(131)	1.450(21)	
C(141)-C(151)	1.500(24)	
C(141)-C(161)	1.486(27)	
Molecule 2		
S(12)-S(6a2)	2.555(1)	2.561
S(12)-C(22)	1.708(3)	1.719
S(6a2)-C(3a2)	1.748(3)	1.758
S(6a2)-N(62)	1.774(2)	1.780
C(22)-N(32)	1.359(3)	1.365
C(22)-N(102)	1.332(3)	1.337
N(32)-C(3a2)	1.302(3)	1.306
C(3a2)-N(42)	1.361(3)	1.366
N(42)-C(52)	1.410(3)	1.415
N(42)-C(92)	1.457(3)	1.467
C(52)-N(62)	1.327(4)	1.336
C(52)-O(82)	1.224(3)	1.228
N(62)-C(72)	1.463(4)	1.470
N(102)-C(112)	1.505(4)	1.515
N(102)-C(142)	1.482(4)	1.487
C(112)-C(122)	1.429(16)	
C(112)-C(132)	1.580(17)	
C(142)-C(152)	1.470(15)	
C(142)-C(162)	1.562(19)	

The overlap is such that the most electronegative atoms, oxygen and nitrogen, come close to the more electropositive atoms, carbon and sulfur. Furthermore, the methyl group C(91) is positioned below

Table 6. Bond angles in 2-diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-olate. Standard deviations in parentheses.

Bond angle	(°)
Molecule 1	
S(6a1)–S(11)–C(21)	90.4(1)
S(11)–S(6a1)–C(3a1)	82.2(1)
S(11)–S(6a1)–N(61)	169.3(1)
S(11)–C(21)–N(31)	120.4(2)
S(11)–C(21)–N(101)	122.5(2)
C(3a1)–S(6a1)–N(61)	87.1(2)
S(6a1)–C(3a1)–N(31)	128.3(3)
S(6a1)–C(3a1)–N(41)	111.6(2)
S(6a1)–N(61)–C(51)	116.4(2)
S(6a1)–N(61)–C(71)	119.5(3)
N(31)–C(21)–N(101)	116.9(3)
C(21)–N(31)–C(3a1)	118.3(3)
C(21)–N(101)–C(111)	122.7(3)
C(21)–N(101)–C(141)	120.0(3)
N(31)–C(3a1)–N(41)	120.0(3)
C(3a1)–N(41)–C(51)	116.4(3)
C(3a1)–N(41)–C(91)	122.6(3)
C(51)–N(41)–C(91)	121.0(3)
N(41)–C(51)–N(61)	108.3(3)
N(41)–C(51)–O(81)	122.2(4)
N(61)–C(51)–O(81)	128.8(4)
C(51)–N(61)–C(71)	123.8(3)
C(111)–N(101)–C(141)	117.3(3)
N(101)–C(111)–C(121)	110.5(11)
N(101)–C(111)–C(131)	114.1(11)
N(101)–C(141)–C(151)	110.5(12)
N(101)–C(141)–C(161)	112.3(13)
C(121)–C(111)–C(131)	114.5(8)
C(151)–C(141)–C(161)	111.0(10)
Molecule 2	
S(6a2)–S(12)–C(22)	89.9(1)
S(12)–S(6a2)–C(3a2)	81.5(1)
S(12)–S(6a2)–N(62)	169.0(1)
S(12)–C(22)–N(32)	120.3(2)
S(12)–C(22)–N(102)	123.0(3)
C(3a2)–S(6a2)–N(62)	87.5(2)
S(6a2)–C(3a2)–N(32)	129.2(2)
S(6a2)–C(3a2)–N(42)	111.0(2)
S(6a2)–N(62)–C(52)	116.5(2)
S(6a2)–N(62)–C(72)	119.9(2)
N(32)–C(22)–N(102)	116.1(3)
C(22)–N(32)–C(3a2)	118.9(3)
C(22)–N(102)–C(112)	121.6(3)
C(22)–N(102)–C(142)	120.3(3)
N(32)–C(3a2)–N(42)	119.7(3)
C(3a2)–N(42)–C(52)	116.8(3)
C(3a2)–N(42)–C(92)	122.3(3)
C(52)–N(42)–C(92)	120.9(3)

Table 6. Continued.

N(42)–C(52)–N(62)	108.1(3)
N(42)–C(52)–O(82)	122.9(3)
N(62)–C(52)–O(82)	128.8(3)
C(52)–N(62)–C(72)	123.5(3)
C(112)–N(102)–C(142)	116.0(3)
N(102)–C(112)–C(122)	117.9(9)
N(102)–C(112)–C(132)	106.5(10)
N(102)–C(142)–C(152)	116.6(9)
N(102)–C(142)–C(162)	105.5(9)
C(122)–C(112)–C(132)	114.8(7)
C(152)–C(142)–C(162)	117.3(7)

the center of A2 and methyl group C(72) above the S(11)–S(6a1) bond. A *ca.* 90° rotation of one of the molecules in the *yz*-plane makes the two molecules overlap almost exactly. Thus, it can be concluded that the molecules are packed in the *a*-axis direction by stacking-forces consisting of both electrostatic and van der Waals' interactions.

The stacking of the molecules also explains the variation in intensity of the *h*00 reflections (see Table 1).

The only significant differences in the two molecules are between the S–S bonds. An explanation for this may be that the two S–S–N sequences have different surroundings. N(61) of molecule 1 may exchange π -electron charge with atom C(52) of molecule 2, and N(62) may interact with the central sulfur atom S(6a1) of molecule 1. The methyl group C(91) has a distance of 3.45 Å to the least squares plane of molecule 2. There may, therefore, be a transfer of π -electron charge from S(12) to the methyl group, thus increasing the σ -electron density on S(12), which implies a longer S(12)–S(6a2) bond relative to the same bond in an isolated molecule.¹⁶

The methyl group C(72) is situated so that π -electron charge may be transferred from both sulfur atoms S(11) and S(6a1), thus giving rise to a redistribution of charge on the two sulfur atoms.

There are a few more intermolecular contacts shorter than the corresponding van der Waals' distances^{17–19} between symmetry related molecules, S(11)[*x, y, z*]...H(141)[*x, \bar{y}, \bar{z}*] = 2.92(2) Å and O(82)[*x, y, z*]...H(112)[*x, $\frac{1}{2} + y, \frac{1}{2} - z$*] = 2.45(2) Å.

A few intramolecular contacts in the two molecules are indicated in Fig. 1. These interactions seem to fix the conformation of both the methyl groups

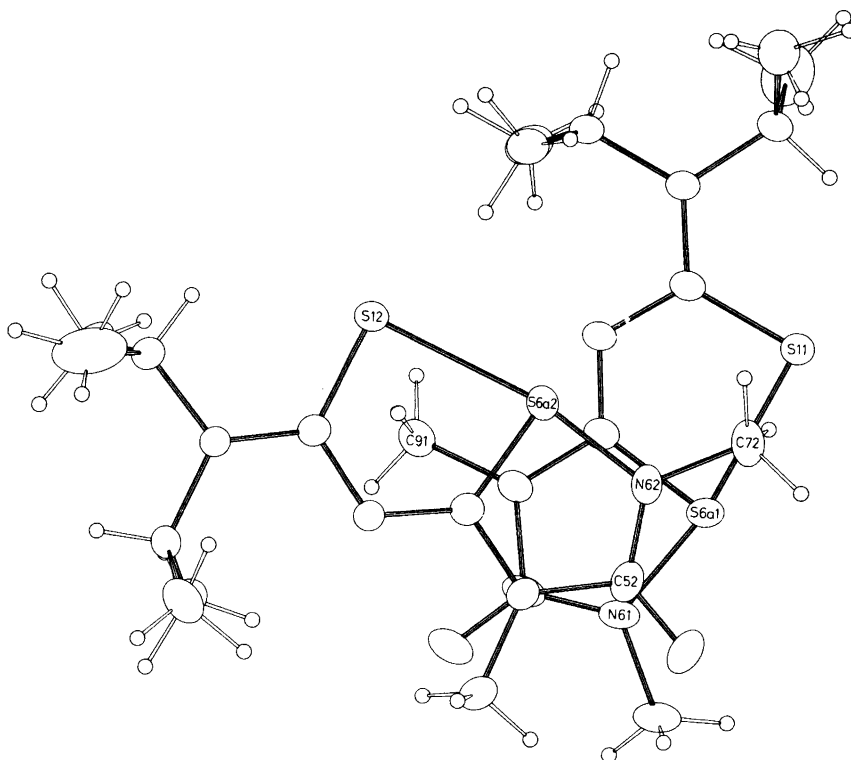


Fig. 2. A projection on the yz -plane of the stacking of the molecules in the unit cell.

and the isopropyl groups relative to the central ring systems, thus making the orientation of the substituent groups almost identical in the two independent molecules. In molecule 1 we have S(11)

$\cdots\text{H}(141)=2.35(2)\text{ \AA}$ and $\text{S}(6a1)\cdots\text{H}(712)=2.86(2)\text{ \AA}$. In molecule 2 we have contacts between the same atoms $\text{S}(12)\cdots\text{H}(142)=2.43(2)$ and $\text{S}(6a2)\cdots\text{H}(722)=2.76(2)\text{ \AA}$.

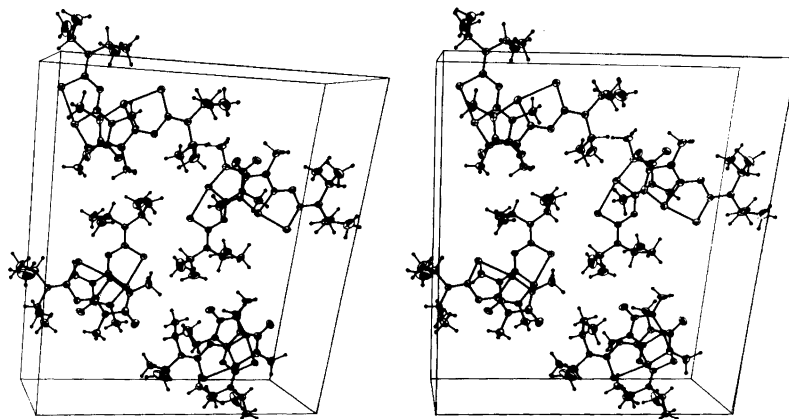


Fig. 3. A stereoscopic view of the arrangement of the molecules in the unit cell.

Table 7. Net charges (q) on the atoms in the S–S–N sequence from the CNDO/2 calculations on the two models of IV. The values given are for the σ -, π - and $(\sigma + \pi)$ - net charges.^a Models (i) and (ii) comprise a non-interacting molecule and two interacting molecules, respectively.

Atom	q_σ (e)	q_π (e)	$q_{(\sigma + \pi)}$ (e)	S–S–N bond lengths (Å)
Model (i)				
S(1)	–0.408	0.147	–0.261	
S(6a)	–0.049	–0.011	–0.060	
N(6)	–0.545	0.333	–0.212	
Model (ii)				
S(11)	–0.401	0.148	–0.253	
S(6a1)	–0.056	–0.004	–0.060	
N(61)	–0.550	0.338	–0.212	
S(12)	–0.422	0.141	–0.281	
S(6a2)	–0.048	–0.019	–0.067	
N(62)	–0.540	0.330	–0.210	

^a 2 π -electrons assumed in the valence shell for sulfur and nitrogen.

CNDO/2 calculations. The only significant difference in bond length between the two molecules is found for the S–S bonds of the respective S–S–N sequences. Since the surroundings of the sequences are different, it was thought worthwhile to calculate the charge distribution by semiempirical CNDO/2 calculations.²⁰ The calculations were performed with two different models: (i) a non-interacting molecule with bond lengths and angles being the average values of molecules 1 and 2; (ii) the two molecules together with values as found in the present X-ray work. In both models the molecules were assumed exactly planar and the two isopropyl groups were replaced by H-atoms. The N–H and C–H bond lengths were chosen to be 1.04 Å and 1.09 Å, respectively.²¹

It has been shown earlier through CNDO/2 calculations on 1,6,6a-trithiapentalenes¹⁶ that changes in the S–S bond lengths are related to variations in the net charges on the sulfur atoms. If the S–S bond length in the 1,6,6a-trithiapentalene molecule is varied from 2.35 to 2.60 Å the difference in net charge between atom S(1) and S(6a) varies from –0.082 to –0.189 in total $(\sigma + \pi)$ net charge $\Delta q_{\sigma + \pi}$; from –0.049 to –0.357 in σ net charge Δq_σ and from –0.033 to +0.168 in π net charge Δq_π . This means that a change in bond length of 0.25 Å gives a variation in $(\sigma + \pi)$, σ and π net charge differences of –0.107, –0.308 and +0.201 electrons, respectively, and it shows that the variation in the σ and π net charge differences are 3 and 2 times, respectively, more sensitive to changes in the

Table 8. Net charge differences Δq between S(1)–S(6a) and N(6)–S(6a) in the two models. Differences are given for σ , π and $(\sigma + \pi)$.

Bond	l (Å)	Net charge difference			
		Δq_σ (e)	Δq_π (e)	$\Delta q_{(\sigma + \pi)}$ (e)	
S(1)–S(6a)	2.542	–0.359	0.158	–0.201	Model (i)
S(11)–S(6a1)	2.522	–0.345	0.152	–0.193	Model (ii)
S(12)–S(6a2)	2.561	–0.374	0.160	–0.214	
N(6)–S(6a)	1.786	–0.496	0.344	–0.152	Model (i)
N(61)–S(6a1)	1.791	–0.494	0.342	–0.152	Model (ii)
N(62)–S(6a2)	1.780	–0.492	0.349	–0.143	

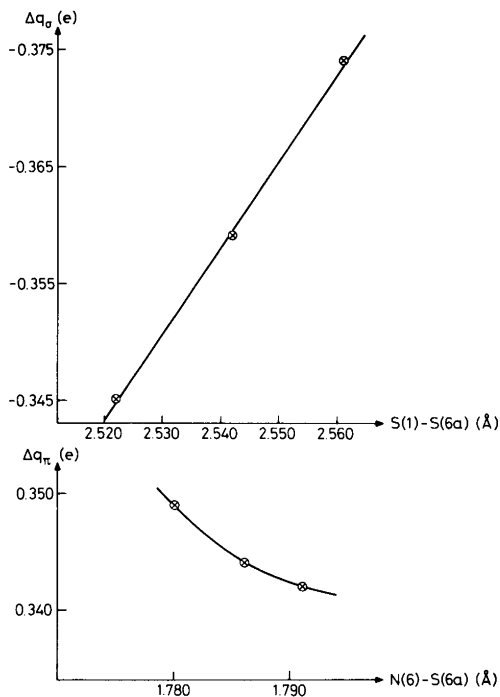


Fig. 4. Net charge differences Δq_σ and Δq_π in models (i) and (ii) as functions of the S(1)–S(6a) and N(6)–S(6a) bond lengths.

S–S bond lengths than the ($\sigma + \pi$) net charge differences.

The results from the CNDO/2 calculations on the atoms in the S–S–N sequence in the present work are given in Table 7. It shows that atom N(61) has an increase in σ -electron charges and N(62) a decrease in σ -electron charges relative to a non-interacting molecule. Atom S(12) has also increased its σ -electron charge while atoms S(11) and S(6a1) have had a decrease and an increase, respectively, in the σ -electron charge density. The net charge differences between the terminal atoms S(1) and N(6) and the central atom S(6a) are given in Table 8. The results for the variations in the σ net charge difference with the S(1)–S(6a) bond length and the π net charge difference with the N(6)–S(6a) bond length are plotted on Fig. 4. The plots show that for the Δq_σ charge difference the relationship with bond length is almost linear and that the largest difference implies the longest S(1)–S(6a) bond length. For the Δq_π charge difference the relationship is non-linear and the smallest difference gives the largest S(6a)–N(6) bond length.

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These observations are in accordance with what has been found earlier for the 1.6,6a-trithiapentalene molecule.¹⁶

Acknowledgement. The author wishes to thank Dr. J. Goerdeler, University of Bonn, for supplying a crystalline sample of the title compound.

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Received April 20, 1982.