The Crystal and Molecular Structure of 2-Diisopropylamino-4-methyl-6-phenyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate, $C_{16}H_{22}N_4S_3$

LARS KR. HANSEN

Department of Chemistry, Institute of Mathematical and Physical Sciences, University of Tromsø, Box 790, N-9001 Tromsø, Norway

The title compound crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$ and unit cell dimensions, $a=9.675(2)$, $b=15.054(3)$, $c=12.788(3)$ Å, and $\beta=92.37(2)^\circ$. The structure was solved by direct methods and refined by full matrix least squares to a final R of 0.041.

Each of the two five-membered rings in the central ring system is planar with an angle of 3.7° between the normals of the two planes. The 6-phenyl group is twisted 45° about the connecting bond $N(6)-C(7)$.

The bond lengths in the central ring system are: $S(1)-S(6a)=2.447(1)$ and $S(6a)-N(6)=1.863(2)$ Å with the angle $S(1)-S(6a)-N(6)=168.99(8)^\circ$, $S(1)-C(2)=1.715(3)$, $S(6a)-C(3a)=1.746(3)$, $N(6)-C(5)=1.338(3)$, $C(2)-N(3)=1.363(3)$, $N(3)-C(3a)=1.302(3)$, $C(3a)-N(4)=1.368$, and $N(4)-C(5)=1.398(3)$ Å. Corrections for rigid body libration have been applied. The X-ray investigation shows that the molecule is a 6-aza-1,6a-dithiapentalene derivative.

It is known that 5-(dialkylamino)-3-(alkyl- or arylimino)-1,2,4-dithiazoles (I) forms adducts with 1,3-dipolarophiles (isocyanates, isothiocyanates or carbon disulfide), but there has been some controversy about the structural formula of these adducts. With isothiocyanate (II) for example the two isomers (IIIa) and (IIIb) may be formed.^{2,3}

On the basis of 1H NMR spectra Goerdeler first assigned formula (IIIb) to the adduct with $R'=CH(CH_3)_2$, $R''=CH_3$ and $R=C_6H_5$.^{1,2} Then later, on the basis of UV and ^{13}C NMR data formula (IIIa) was assigned.³ In the meantime Oliver *et al.* published the syntheses of some similar compounds for which formula (IIIa) was proposed ($R'=CH_3$, $R''=CH_3$, C_6H_5 , $R=CH_3$, C_6H_5).⁴ The structures of two adducts with $R=(CH_3)_2NCS-$ have been studied by X-ray methods and are shown to be of the (IIIa) type.^{5,6}

The present X-ray study has been carried out in order to establish which of the forms (IIIa) or (IIIb) is the correct one for an adduct formed with a "simple" isothiocyanate like $C_6H_5N=C=S$. Further, information about the bonding in the possible linear sequences $S\cdots S-S$ or $S\cdots S-N$ was of interest.

STRUCTURE ANALYSIS

A sample of the title compound, consisting of colourless, prismatic crystals was provided by Dr. J. Goerdeler, University of Bonn.² The crystal used for all X-ray measurements was mounted parallel to the crystallographic a -axis. The dimensions of the crystal were $0.65\text{ mm} \times 0.33\text{ mm} \times 0.28\text{ mm}$ along $[100]$, $[011]$, and $[0\bar{1}\bar{1}]$, respectively.

Crystal data

$C_{16}H_{22}N_4S_3$; M.W. = 366.57

Monoclinic, space group $P2_1/c$ with $Z=4$

$a = 9.675(2)$ Å, $b = 15.054(3)$ Å, $c = 12.788(3)$ Å
 $\beta = 92.37(2)^\circ$
 $V = 1860.9(8)$ Å³
 $D_x = 1.308$ g/cm³, $D_m = 1.30$ g/cm³
 $\mu(\text{MoK}\alpha) = 3.92$ cm⁻¹, $F_{000} = 776$

The cell dimensions were calculated from diffractometer measurements of the setting angles for 12 reflections with $2\theta > 39^\circ$.

The intensities of 4528 independent reflections within $2\theta = 55^\circ$ were recorded on a Picker FACS-1 automatic diffractometer using $\theta - 2\theta$ scan and niobium filtered MoK α radiation. All measurements were made at 20°C. Scan ranges were calculated according to the relationship $\Delta\theta = 1.2 + 0.692 \tan \theta$,⁷ where 0.692 is a dispersion correction for molybdenum radiation. A scan speed of 2° min⁻¹ in 2θ was used with the background recorded 20 s at each side of the reflections.

3314 reflections with net intensity I greater than $2\sigma(I)$ were regarded as observed, $\sigma(I)$ being defined as $\{\sigma_N^2 + (0.01N_{\text{net}})^2\}^{1/2}$ where the last term accounts for a 1% instrumental

instability. σ_N is the statistical counting error and N_{net} the net peak count. 1214 reflections had net counts less than $2\sigma(I)$. These reflections were given a threshold value of $2\sigma(I)$ and were later included in the refinement only if $|F_{\text{calc}}| > F_{\text{threshold}}$.

Corrections for Lorentz and polarization effects were carried out in the usual way. Absorption corrections were considered unnecessary.

The structure was solved by direct methods. This process was carried out with the X-RAY 72 programs NORMSF, SINGEN and PHASE.⁸ 262 phases with $E > 1.80$ were generated, and these phases were used to calculate an E map. All the non-hydrogen atoms except C(18) and C(21) were found from this E map, and structure factors calculated from the coordinates of these 21 atoms resulted in an R factor of 0.23 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). A subsequent Fourier map revealed the two remaining carbon atoms, and the hydrogen positions were found from a difference map. The atomic parameters were refined by full matrix least squares

Table 1. Atomic coordinates and temperature parameters U_{ij} (Å)² for the sulfur, nitrogen and carbon atoms. The temperature factor is $\exp \{-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{13} + \dots)\}$. The U_{ij} 's are multiplied by 10⁴.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.11757(11)	0.41860(5)	0.23233(6)	971(7)	393(4)	535(4)	161(4)	-312(4)	-82(3)
S(6a)	0.26094(8)	0.36953(4)	0.38296(5)	602(4)	321(3)	404(3)	39(3)	-104(3)	-17(2)
N(6)	0.37007(24)	0.35508(14)	0.50468(15)	537(13)	382(11)	355(10)	23(10)	-75(10)	33(9)
C(2)	0.10413(29)	0.52268(17)	0.28452(20)	514(16)	304(13)	433(13)	39(12)	-46(12)	9(11)
N(3)	0.15735(24)	0.53871(13)	0.38255(16)	544(13)	332(10)	402(11)	39(10)	-34(10)	11(8)
C(2a)	0.22957(28)	0.47621(16)	0.42901(18)	493(15)	331(12)	363(12)	-35(11)	2(11)	-1(9)
H(4)	0.29096(25)	0.49167(14)	0.52508(15)	588(14)	345(11)	354(11)	-1(10)	-49(10)	-4(8)
C(5)	0.37656(29)	0.42528(17)	0.56018(19)	493(15)	425(13)	368(12)	-36(12)	-9(11)	28(10)
C(7)	0.43295(28)	0.27085(17)	0.52300(20)	458(14)	367(13)	465(14)	6(11)	-101(12)	27(11)
C(8)	0.49457(31)	0.22867(19)	0.44093(21)	557(17)	465(15)	484(15)	-1(13)	-71(13)	-27(12)
C(9)	0.55084(35)	0.14479(21)	0.45608(26)	630(20)	548(10)	710(20)	104(16)	-76(16)	-170(15)
C(10)	0.54757(37)	0.10442(20)	0.55259(29)	700(22)	410(15)	869(24)	93(15)	-275(19)	22(15)
C(11)	0.48421(37)	0.14569(21)	0.63330(26)	706(22)	519(17)	679(20)	33(16)	-124(17)	176(15)
C(12)	0.42505(32)	0.22840(19)	0.61902(22)	584(18)	502(16)	496(15)	59(14)	-27(13)	108(12)
S(13)	0.46988(9)	0.43850(6)	0.67930(6)	653(5)	631(5)	429(4)	-17(4)	-152(3)	-34(3)
C(14)	0.27097(39)	0.57730(19)	0.57654(23)	935(25)	417(15)	517(16)	54(16)	-131(17)	-121(13)
H(15)	0.04437(25)	0.59030(14)	0.23335(17)	569(14)	372(11)	456(12)	51(10)	-66(11)	35(9)
C(16)	0.03440(31)	0.68092(17)	0.28017(22)	526(16)	363(13)	558(16)	29(12)	-10(13)	60(12)
C(17)	-0.05696(37)	0.68048(21)	0.37264(27)	717(22)	513(17)	768(21)	95(16)	227(18)	-43(16)
C(18)	0.17415(36)	0.72430(21)	0.30009(27)	656(21)	483(17)	789(22)	-06(16)	22(17)	10(15)
C(19)	-0.01451(36)	0.57885(20)	0.12522(23)	729(21)	491(16)	509(16)	97(15)	-177(15)	45(13)
C(20)	-0.16774(42)	0.59680(34)	0.11721(33)	639(24)	1397(41)	871(28)	-74(26)	-248(21)	-73(27)
C(21)	0.06111(73)	0.63533(56)	0.05002(35)	1132(44)	1675(62)	475(21)	-355(42)	-115(24)	194(29)

Table 2. Atomic coordinates and isotropic thermal parameters U ($\text{\AA}^2$) 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(8)	0.4953(29)	0.2563(18)	0.3773(20)	53(8)	H(173)	-0.1463(42)	0.6358(27)	0.3615(29)	114(14)
H(9)	0.5951(31)	0.1209(19)	0.4000(22)	67(9)	H(181)	0.2265(38)	0.6966(25)	0.3593(28)	101(12)
H(10)	0.5871(35)	0.0490(22)	0.5640(25)	87(11)	H(182)	0.2339(36)	0.7172(23)	0.2427(27)	86(11)
H(11)	0.4721(33)	0.1165(21)	0.7029(23)	77(10)	H(183)	0.1627(36)	0.7828(23)	0.3187(26)	87(11)
H(12)	0.3818(33)	0.2571(21)	0.6717(24)	80(10)	H(19)	-0.0004(36)	0.5188(22)	0.1084(25)	89(11)
H(141)	0.3081(38)	0.5746(23)	0.6410(27)	91(11)	H(201)	-0.2002(37)	0.5866(24)	0.0474(28)	96(12)
H(142)	0.1607(45)	0.5792(27)	0.5917(30)	125(15)	H(202)	-0.2081(45)	0.5602(30)	0.1723(33)	140(15)
H(143)	0.3032(40)	0.6226(25)	0.5356(28)	111(13)	H(203)	-0.1978(56)	0.6541(37)	0.1473(40)	203(21)
H(16)	-0.0145(26)	0.7141(16)	0.2259(18)	40(7)	H(211)	0.0616(60)	0.7006(36)	0.0676(40)	153(24)
H(171)	-0.0821(35)	0.7318(22)	0.3941(24)	81(11)	H(212)	0.0344(43)	0.6234(27)	-0.0189(33)	100(14)
H(172)	-0.0182(37)	0.6476(23)	0.4371(25)	87(11)	H(213)	0.1554(65)	0.6282(44)	0.0608(46)	183(28)

Fig. 1. ORTEP²⁰ drawing of the title compound with the numbering of the atoms in the molecule. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50 % probability level. Note that carbon atom C(19) is concealed by C(20).

Table 3. Rigid body libration tensors L_1 and L_2 for various parts of the molecule.

Eigenvalues ($^\circ$) ²	Eigenvectors ^a			
L_1	26.9	-5574	7729	-3031
	5.2	-6700	-6344	-3856
	1.6	-4903	-118	8715
L_2	46.7	4734	-5840	6594
	7.1	1346	-6918	-7094
	2.8	8705	4245	-2490

^a Direction cosinus $\times 10$ relative to a , b , and c^* , respectively.

Acta Chem. Scand. A 31 (1977) No. 10

(X-RAY 72 program CRYLSQ).⁶ With anisotropic temperature factor coefficients for all atoms except hydrogen, the final R factor is 0.041. The weighted R is 0.041. The function minimized in the refinement was $\sum w(|F_o| - \frac{1}{h}|F_c|)^2$, where $w = 1/\sigma_F^2$. At the end of the refinement the average shift/error ratio was 0.17. No indication of secondary extinction was observed. The scattering factors used for sulfur, nitrogen and carbon were those of Doyle and Turner⁹ and for hydrogen the scattering factor curve of Stewart *et al.*¹⁰ was used. Final atomic coordinates and temperature parameters are listed in Tables 1 and 2. The final structure

factor list is available from the author on request.

Rigid body analyses for various parts of the molecule have been carried out according to the method of Schomaker and Trueblood.¹¹ The parts of the molecule treated in this way are, the central ring system plus C(7), S(13), C(14), N(15), C(16) and C(19), and the phenyl group plus N(6). The corresponding librational tensors L_1 and L_2 respectively, are given in Table 3.

All the calculations were carried out on the UNIVAC 1110 computer at the University of Bergen.

DISCUSSION

Fig. 1 shows the structure of the title compound and the numbering of the atoms in the molecule. It is verified that the molecule is a 6-aza-1,6a-dithiapentalene derivative (IIIb) and not a 1,6,6a-trithiapentalene derivative (IIIa).

Table 4. Bond lengths (*l*) in 2-diisopropylamino-4-methyl-6-phenyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate. The μ^I and μ^{II} values have been corrected for libration according to the librational tensors L_1 and L_2 , respectively.

Bond	<i>l</i> (Å)	μ^I (Å)	μ^{II} (Å)
S(1)–S(6a)	2.441(1)	2.447	
S(6a)–N(6)	1.857(2)	1.863	
S(1)–C(2)	1.710(3)	1.715	
S(6a)–C(3a)	1.742(3)	1.746	
N(6)–C(5)	1.333(3)	1.338	
C(2)–N(3)	1.357(3)	1.363	
N(3)–C(3a)	1.301(3)	1.302	
C(3a)–N(4)	1.362(3)	1.368	
N(4)–C(5)	1.397(3)	1.398	
C(5)–S(13)	1.664(3)	1.670	
N(6)–C(7)	1.422(3)	1.423	1.426
C(7)–C(8)	1.383(4)		1.393
C(8)–C(9)	1.386(4)		1.391
C(9)–C(10)	1.377(5)		1.382
C(10)–C(11)	1.371(5)		1.381
C(11)–C(12)	1.379(4)		1.384
C(12)–C(7)	1.389(4)		1.394
N(4)–C(14)	1.464(4)	1.468	
C(2)–N(15)	1.329(3)	1.331	
N(15)–C(16)	1.495(3)	1.499	
N(15)–C(19)	1.484(4)	1.490	
C(16)–C(17)	1.505(5)		
C(16)–C(18)	1.514(5)		
C(19)–C(20)	1.506(5)		
C(19)–C(21)	1.497(7)		

Calculations of least squares planes through the rings A, B and C, cf. Fig. 1, show that these rings are planar within the error. The angle between the normals of the planes of A and B is 3.7°. The substituents C(7), S(13) and C(14) lie slightly out of plane B, –0.08, 0.11 and –0.05 Å, respectively; and N(15), C(16) and C(19) are 0.18, 0.25 and 0.28 Å, respectively, out of plane A. The phenyl group C is twisted 45° about the connecting bond N(6)–C(7), with the atoms N(6), C(7) and C(10) –0.00, –0.08 and –0.26 Å, respectively, out of plane B.

Table 5. Bond angles $\angle(ijk)$ in 2-diisopropylamino-4-methyl-6-phenyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate.

<i>i</i>	<i>j</i>	<i>k</i>	$\angle(ijk)^\circ$
C(2)	S(1)	S(6a)	91.10(9)
S(1)	S(6a)	N(6)	168.99(8)
S(1)	S(6a)	C(3a)	83.48(8)
C(3a)	S(6a)	N(6)	85.73(11)
S(6a)	N(6)	C(7)	117.9(2)
S(6a)	N(6)	C(5)	115.4(2)
C(5)	N(6)	C(7)	126.7(2)
N(6)	C(5)	S(13)	128.7(2)
N(6)	C(5)	N(4)	108.3(2)
S(13)	C(5)	N(4)	122.9(2)
C(5)	N(4)	C(14)	122.7(2)
C(5)	N(4)	C(3a)	117.6(2)
C(14)	N(4)	C(3a)	119.7(2)
N(4)	C(3a)	S(6a)	112.8(2)
N(4)	C(3a)	N(3)	119.6(2)
S(6a)	C(3a)	N(3)	127.6(2)
C(3a)	N(3)	C(2)	118.0(2)
N(3)	C(2)	N(15)	117.3(2)
S(1)	C(2)	N(3)	119.4(2)
S(1)	C(2)	N(15)	123.2(2)
C(2)	N(15)	C(16)	122.4(2)
C(2)	N(15)	C(19)	120.8(2)
N(15)	C(16)	C(17)	111.2(2)
N(15)	C(16)	C(18)	112.9(2)
N(15)	C(19)	C(20)	112.4(3)
N(15)	C(19)	C(21)	110.7(3)
C(17)	C(16)	C(18)	114.8(3)
C(16)	N(15)	C(19)	116.8(2)
C(20)	C(19)	C(21)	111.1(4)
N(6)	C(7)	C(8)	118.7(2)
N(6)	C(7)	C(12)	121.1(2)
C(8)	C(7)	C(12)	120.1(2)
C(7)	C(8)	C(9)	119.4(3)
C(8)	C(9)	C(10)	120.3(3)
C(9)	C(10)	C(11)	120.2(3)
C(10)	C(11)	C(12)	120.4(3)
C(11)	C(12)	C(7)	119.6(3)

Fig. 2. A stereoscopic view of the arrangement of the molecules in the unit cell.

Bond lengths and angles for non-hydrogen atoms in the present structure as calculated from the positional parameters in Table 1, are listed in Tables 4 and 5. The standard deviations given for the bond lengths and angles are based on the standard deviations in positional parameters from the least squares refinement. According to Hamilton and Abrahams¹⁸ a more realistic estimate of the standard deviations would probably be obtained by multiplying those given by a factor of two.

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 4. The U and U^{II} values are corrected according to the librational tensors L_1 and L_2 , respectively. The U values are chosen to represent the central ring system as well as the lengths of the C(5)—S(13), N(4)—C(14), C(2)—N(15), N(15)—C(16) and N(15)—C(19) bonds. For the dimensions of the phenyl group the U^{II} values have been used.

The S(1)—S(6a) bond in the present structure is 2.447(1) Å and the S(6a)—N(6) bond is 1.863(2) Å. These lengths are compatible with those found in two other 6-phenyl-6-aza-1,6a-dithiapentalenes.^{13,14} In 2-*t*-butyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene¹³ the bond distances are S(1)—S(6a)=2.426(1) and S(6a)—N(6)=1.841(2) Å, and in 3,4-dimethyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene¹⁴ the corresponding bonds are 2.487(1) and 1.774(1) Å, respectively.

The S—S bond in the present structure is 0.34 Å longer than the accepted single bond distance of 2.10 Å,¹⁵ but appreciable shorter than the van der Waals contact of 3.40 Å.^{16,17}

The S—N bond is 0.11 Å longer than the S—N single bond of 1.75 Å.¹⁸

The sum of the S(1)—S(6a) and the S(6a)—N(6) bond length is 4.30 Å. This value is 11.7 % longer than the sum of the two single bond distances (3.85 Å) and in good agreement with what has been found for analogous compounds.¹⁹ The S—C(sp^3) and N—C(sp^3) bond distances are all in the region between single bonds and double bonds, indicating π -conjugation throughout the system.

The C—H bond lengths all lie in the region 0.86 to 1.10 Å with a mean value of 0.96 Å. The mean value for the C(sp^3)—H and the C(sp^2)—H bonds is 0.94 and 0.96 Å, respectively. Standard deviations in the individual C—H distances range from 0.02 to 0.06 Å. The standard deviation of the mean value is 0.06 Å.

The bond angles involving hydrogen atoms in the phenyl group range from 116 to 124°, with a mean value of 120°. The standard deviation in the individual C—C—H angles is 2° and that of the mean value is 3°. The bond angles involving hydrogen atoms in the methyl group and the isopropyl groups range from 94 to 117° with standard deviations ranging from 1 to 5°. The mean value is 109° with a standard deviation of 6°.

There are a few short intramolecular S $\cdots$ H and N $\cdots$ H distances in the molecule. S(1) $\cdots$ H(19)=2.44(3) Å, S(13) $\cdots$ H(14)=2.61(4) Å, N(3) $\cdots$ H(181)=2.49(4) Å and N(3) $\cdots$ H(172)=2.48(4) Å, respectively, *cf.* Fig. 1. Atom H(19) lies only 0.03 Å out of the plane through S(1), C(2), N(15) and C(19),

while H(141) lies -0.10 Å out of the plane through S(13), C(5), N(4) and C(14). These two short contacts as well as the two contacts N(3)···H(181) and N(3)···H(172) seem to contribute to the conformation of the methyl group and the two isopropyl groups in the solid state.

There are no intermolecular contacts shorter than van der Waals distances. A stereoscopic view of the arrangement of molecules in the unit cell is given in Fig. 2.²⁰

Acknowledgement. The author wishes to thank Dr. J. Goerdeler, University of Bonn, for supplying a sample of the title compound. He also wishes to thank Tech. lic. J. Hjortås, Institutt for Røntgenteknikk, The University of Trondheim, for assistance with the data collection, and Prof. A. Hordvik, this University, for helpful comments and advice.

REFERENCES

1. Goerdeler, J. and Ulmen, J. *Chem. Ber.* 105 (1972) 1568.
2. Goerdeler, J. Lecture held at The 4th. Int. Congress of Heterocyclic Chemistry, Salt Lake City 1973.
3. Goerdeler, J. *Private communication*.
4. Oliver, J. E. and Brown, R. T. *J. Org. Chem.* 39 (1974) 2228.
5. Oliver, J. E., Flippen, J. L. and Karle, J. *Chem. Commun.* (1972) 1153.
6. Flippen, J. L. *J. Am. Chem. Soc.* 95 (1973) 6073.
7. Alexander, L. E. and Smith, G. S. *Acta Crystallogr.* 17 (1964) 1195.
8. *X-RAY Program System* (1972). Version of June 1972, Technical Report Tr-192 of the Computer Science Center, Univ. of Maryland, College Park.
9. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
10. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
11. Schomaker, V. and Trueblood, K. N. *Acta Crystallogr. B* 24 (1968) 63.
12. Hamilton, W. C. and Abrahams, S. C. *Acta Crystallogr. A* 26 (1970) 18.
13. Hansen, L. K. and Tomren, K. *Acta Chem. Scand. A* 31 (1977) 292.
14. Darro, L. P. and Hansen, L. K. *Acta Chem. Scand. A* 31 (1977) 412.
15. Hordvik, A. *Quart. Rep. Sulfur Chem.* 5 (1970) 21.
16. Sletten, J. *Acta Chem. Scand.* 25 (1971) 3577.
17. Sletten, J. *Doctoral thesis*, Univ. of Bergen 1976, p. 19.
18. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
19. Hordvik, A. and Sæthre, L. *J. Israel J. Chem.* 10 (1972) 239.
20. Johnson, C. K. *ORTEP-II: A Fortran Thermal-Ellipsoid Plot Program For Crystal Structure Illustrations*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1971.

Received June 22, 1977.