The Crystal and Molecular Structure of 2-*t*-Butyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene, a New Thiathiophthene Analogue

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The title compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions, $a = 12.483(3)$, $b = 6.134(2)$, $c = 19.388(8)$ Å, and $\beta = 107.35(3)°$.

X-Ray data were collected on a Siemens AED diffractometer using MoKα radiation and the five-value scan technique. The structure was solved by Patterson methods and refined by full matrix least squares.

The title compound may be described as a 5,6-diaza analogue of 6a-thiathiophthene. The central ring system is planar and the 2-*t*-butyl group and the 6-phenyl group point slightly out of this plane, the phenyl group is twisted 2.5° about the connecting bond N(6) − C(11).

Bond lengths in the central part of the molecule: S(1) − S(6a) = 2.435(1) and S(6a) − N(6) = 1.849(3) Å with the angle S(1) − S(6a) − N(6) = 171.66(9)°, S(1) − C(2) = 1.711(3), S(6a) − C(3a) = 1.735(3), N(6) − N(5) = 1.330(4), C(2) − C(3) = 1.376(5), C(3) − C(3a) = 1.400(4), C(3a) − C(4) = 1.405(5) and C(4) − N(5) = 1.320(4) Å. The connecting bonds C(2) − C(7) and N(6) − C(11) are 1.525(4) and 1.414(4) Å, respectively. The bond lengths have been corrected for libration.

Christie *et al*,[1,2] have shown that the reaction of 2-*t*-butyl-3-methyl-1,2-dithiolium perchlorate with benzene diazonium fluoroborate yields a compound, which, on the basis of spectral data, may be formulated either as an azo-coupling product of a 1,2-dithole (Ia) or as a diaza analogue of a 6a-thiathiophene (Ib). An X-ray structure study has been carried out in order to find which formulation would be the correct one.
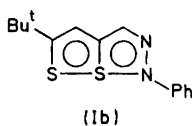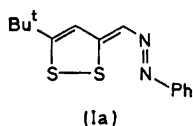
STRUCTURE ANALYSIS

A sample of the title compound was generously supplied by Reid.[1,2] The crystals are dark red prisms.

Crystal data.
$C_{14}H_{16}N_2S_2$ M.W. = 276.41
Monoclinic, space group $P2_1/c$ with $Z = 4$
$a = 12.483(3)$ Å, $b = 6.134(2)$ Å, $c = 19.388(8)$ Å,
$\beta = 107.35(3)°$
$V = 1417.0$ Å³
$D_x = 1.296$ g/cm³, $D_m = 1.30$ g/cm³
$\mu_{MoK\alpha} = 3.51$ cm⁻¹

Unit cell dimensions and intensity data were measured on a paper-tape controlled Siemens AED diffractometer using MoKα radiation.

A least squares procedure on the 2θ values of 11 high order reflections, measured at 20 °C, gave the cell dimensions quoted above. The crystal used for all X-ray measurements had the dimensions 0.2 mm × 0.4 mm × 0.2 mm in the axial directions.

The intensities of 3092 independent reflections within $\theta = 27°$ were measured by means of the five-value scan technique.[3] 1322 of these were regarded as unobserved because their intensities were smaller than the chosen threshold value $2\sigma(I)$.

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

Scattering factors from the *International Tables*[4] were used for sulfur, nitrogen and carbon, and a scattering factor curve given by Stewart *et al*.[5] was used for hydrogen.

(Ia)   (Ib)

Table 1. Atomic coordinates in fractions of corresponding cell edges. The standard deviations in parentheses refer to the last digits of the respective values.

Atom	x	y	z
S(1)	0.22744(7)	0.25388(14)	0.23276(5)
S(6a)	0.05608(7)	0.12632(13)	0.14571(5)
N(6)	−0.06847(20)	−0.00975(42)	0.08569(14)
C(2)	0.24815(25)	0.01698(51)	0.28011(17)
C(3)	0.16809(27)	−0.14019(56)	0.25636(18)
C(3a)	0.07596(25)	−0.11151(47)	0.19509(17)
C(4)	−0.00861(30)	−0.26229(61)	0.16462(21)
N(5)	−0.08659(23)	−0.20947(44)	0.10452(16)
C(7)	0.35402(26)	−0.01867(55)	0.34289(18)
C(8)	0.40080(51)	0.19870(90)	0.37830(31)
C(9)	0.44080(41)	−0.12446(120)	0.31111(32)
C(10)	0.32947(58)	−0.16938(142)	0.39855(34)
C(11)	−0.13912(25)	0.07984(51)	0.02122(17)
C(12)	−0.23220(30)	−0.03041(69)	−0.02076(22)
C(13)	−0.29910(34)	0.06334(77)	−0.08271(23)
C(14)	−0.27482(32)	0.26629(79)	−0.10432(22)
C(15)	−0.18324(32)	0.37615(72)	−0.06334(20)
C(16)	−0.11518(31)	0.28391(63)	−0.00049(20)
H(3)	0.171(2)	−0.282(5)	0.279(2)
H(4)	−0.011(2)	−0.399(5)	0.184(2)
H(81)	0.467(3)	0.168(6)	0.418(2)
H(82)	0.343(4)	0.245(9)	0.403(3)
H(83)	0.432(4)	0.293(9)	0.334(3)
H(91)	0.459(4)	−0.012(8)	0.280(3)
H(92)	0.393(5)	−0.301(11)	0.298(3)
H(93)	0.506(4)	−0.138(7)	0.350(2)
H(101)	0.394(4)	−0.189(7)	0.434(2)
H(102)	0.279(7)	−0.071(15)	0.414(4)
H(103)	0.314(5)	−0.334(11)	0.376(3)
H(12)	−0.249(3)	−0.164(5)	−0.005(2)
H(13)	−0.366(3)	−0.009(7)	−0.111(2)
H(14)	−0.322(3)	0.336(6)	−0.146(2)
H(15)	−0.160(3)	0.522(6)	−0.077(2)
H(16)	−0.055(3)	0.359(6)	0.028(2)

The sulfur positions were found from a three-dimensional Patterson map, the nitrogen and carbon atoms revealed themselves during subsequent Fouriers, and the hydrogen positions were found from difference maps. The atomic parameters were refined by full matrix least squares (*cf.* Ref. 6) to an R of 0.04.

Final atomic coordinates and temperature parameters are listed in Tables 1 and 2, respectively. 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.[7] The parts of the molecule treated in this way are the central

ring system and the phenyl group plus N(6). The corresponding librational tensors are given in Table 3. One notes from the values there that the libration is rather anisotropic in each case.

All the calculations mentioned above were carried out on the UNIVAC 1110 computer at the University of Bergen. The programs, with a few exceptions, originate from the Weizmann Institute of Science, Rehovoth, Israel.

DISCUSSION

The molecular structure of the title compound with numbering of atoms is shown in Fig. 1.

The central ring system is almost planar. Deviations from a least squares plane through

Table 2. Temperature parameters U_{ij} ($Å^2$) for sulfur, nitrogen and carbon, and U($Å^2$) for hydrogen. The expressions used are exp $\{-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)\}$ and exp $\{-8\pi^2U(\sin^2\theta/\lambda^2)\}$ The U_{ij}'s and the U's are multiplied by 10^4 and 10^3, respectively. Standard deviations in parentheses refer to the last digits of the respective values.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	685(6)	467(5)	738(6)	$-97(5)$	104(5)	56(4)
S(6a)	585(5)	389(4)	641(5)	$-24(4)$	24(4)	166(3)
N(6)	527(15)	461(15)	625(17)	$-52(13)$	$-11(14)$	192(13)
C(2)	548(19)	471(18)	580(19)	59(16)	47(16)	227(15)
C(3)	598(20)	402(18)	668(22)	24(17)	72(19)	275(18)
C(3a)	520(18)	381(16)	656(20)	1(15)	15(16)	252(15)
C(4)	666(23)	436(20)	779(26)	$-76(19)$	60(20)	260(20)
N(5)	649(18)	509(17)	747(20)	$-140(14)$	2(15)	229(16)
C(7)	562(20)	587(21)	616(21)	7(17)	64(19)	179(17)
C(8)	939(37)	1025(39)	951(38)	$-18(32)$	$-110(36)$	$-108(34)$
C(9)	642(29)	1406(53)	1104(40)	370(35)	121(42)	200(30)
C(10)	1088(43)	1490(62)	882(37)	$-228(43)$	600(42)	$-55(33)$
C(11)	477(18)	532(20)	578(20)	$-12(16)$	$-75(16)$	221(16)
C(12)	609(24)	647(25)	745(26)	$-56(21)$	$-37(23)$	198(20)
C(13)	606(25)	908(34)	784(29)	$-69(23)$	$-110(25)$	77(22)
C(14)	614(24)	898(31)	663(25)	109(25)	22(26)	112(20)
C(15)	720(25)	711(26)	721(26)	$-3(23)$	63(24)	193(21)
C(16)	598(22)	668(25)	658(24)	$-82(20)$	19(21)	104(19)

Atom	U	Atom	U	Atom	U
H(3)	58(9)	H(92)	202(27)	H(12)	59(10)
H(4)	53(9)	H(93)	101(14)	H(13)	105(13)
H(81)	103(14)	H(101)	104(15)	H(14)	93(13)
H(82)	149(23)	H(102)	309(56)	H(15)	93(13)
H(83)	170(22)	H(103)	180(27)	H(16)	80(11)
H(91)	129(20)				

the atoms of this part of the molecule, with triple weight on sulfur, are, S(1) -0.002, S(6a) 0.014, N(6) -0.026, C(2) -0.030, C(3) 0.007, C(3a) 0.022, C(4) 0.016, and N(5) -0.028 Å. The t-butyl and phenyl groups point slightly out of this plane. Thus, C(7) lies -0.166 Å off the plane, and the deviations for C(11) and C(14) are -0.117 and -0.289 Å, respectively. The phenyl group is twisted 2.5° about the N(6)−C(11) bond. This twist angle was taken as the angle between the normal to the plane through N(6), C(11), C(12), and C(16), and the normal to the plane through N(6), C(11), N(5), and S(6a).

Bond lengths and angles with standard deviations, calculated from the values in Table 1, are listed in Tables 4 and 5, respectively. We realize that a more realistic estimate of the standard deviations might probably be obtained by multiplying those given by a factor of two.[8]

The bond lengths between non-hydrogen atoms have been corrected for rigid body

libration,[9] and the values l', l'' and l''' in Table 4 include corrections according to L_1, L_2, and L_3, respectively, *cf.* Table 3.

Table 3. Rigid body libration tensors for the entire molecule (L_1), the central ring system (L_2), and the phenyl group plus N(6) (L_3).

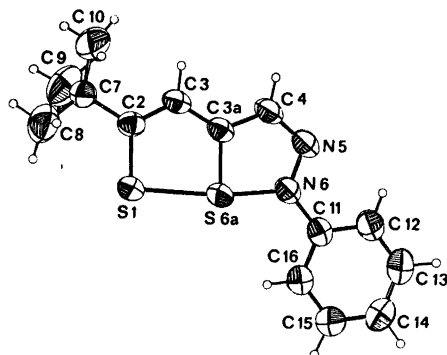| Eigenvalues(°)^2		Eigenvectors (direction cosinus $\times 10^4$ relative to a, b, and c^*, respectively)		
L_1	54.72	-5845	1024	-8049
	8.74	-6538	-6469	3925
	6.53	-4805	7557	4450
L_2	43.77	-5914	-50	-8064
	6.68	-7653	-3117	5632
	2.94	-2541	9502	1804
L_3	67.22	-2128	5179	-8286
	11.98	-1969	-8533	-4828
	9.68	-9571	603	2835

Fig. 1. The 2-*t*-butyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene molecule with numbering of sulfur, nitrogen and carbon atoms. Thermal ellipsoids are shown. The thermal ellipsoids enclose 50 % probability.

One notes that there are only minor differences between the l' and the l'' values, and we have chosen the former to represent the dimensions of the central ring system and the *t*-butyl group. A comparison of the l' and the l''' values show pronounced differences for two of the bonds, namely C(11) – C(12) and C(14) – C(15), the differences are 0.008 and 0.007 Å, respec-

tively, as compared with the corresponding standard deviations of 0.005 and 0.006 Å. Such differences may be expected when the phenyl group has some additional libration relative to the other part of the molecule.[10] The l''' values were therefore taken to represent the lengths of the C – C bonds of the phenyl group.

The S(1) – S(6a) bond of 2.435(1) Å, *cf.* Table 4, and the S(6a) – N(6) bond of 1.849(3) Å are partial bonds weaker than corresponding single bonds. The former is 16 % longer than the proposed length of 2.10 Å for the S – S single bond in a *cis* planar disulfide group,[11] and the latter is 5.7 % longer than the sum of the covalent radii for sulfur and nitrogen, 1.75 Å.[12] Furthermore, in 3,4-diphenyl-6a-thiathiopthene [13] where the S(1) – S(6a) bond of 2.43 Å is almost equal to that of the present structure, the S(6a) – S(6) bond is 2.24 Å, and thus 6.7 % longer than the corresponding single bond. The

Table 4. Bond lengths l in 2-*t*-butyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene. Standard deviations are given in parentheses. The l', l'', and l''' values have been corrected for libration according to the librational tensors L_1, L_2, and L_3, respectively.

Bond	l(Å)	l'(Å)	l''(Å)	l'''(Å)
S(1) – S(6a)	2.426(1)	2.435	2.431	
S(6a) – N(6)	1.841(3)	1.849	1.846	
S(1) – C(2)	1.697(3)	1.711	1.709	
S(6a) – C(3a)	1.722(3)	1.735	1.733	
N(6) – N(5)	1.317(4)	1.330	1.327	
C(2) – C(3)	1.366(5)	1.376	1.373	
C(3) – C(3a)	1.396(4)	1.400	1.399	
C(3a) – C(4)	1.395(5)	1.405	1.402	
C(4) – N(5)	1.317(4)	1.320	1.319	
C(2) – C(7)	1.522(4)	1.525		
C(7) – C(8)	1.533(6)	1.547		
C(7) – C(9)	1.540(8)	1.555		
C(7) – C(10)	1.520(9)	1.534		
N(6) – C(11)	1.409(4)	1.414		1.414
C(11) – C(12)	1.380(5)	1.387		1.395
C(12) – C(13)	1.369(6)	1.373		1.373
C(13) – C(14)	1.376(7)	1.389		1.388
C(14) – C(15)	1.360(6)	1.367		1.374
C(15) – C(16)	1.382(5)	1.387		1.387
C(16) – C(11)	1.381(5)	1.395		1.394

Table 5. Bond angles $\angle$ (ijk) in 2-*t*-butyl-6-phenyl-5,6-diaza-1,6a-dithiapentalene. Standard deviations are given in parentheses.

|	j	k	$\angle$(ijk)°
C(2)	S(1)	S(6a)	93.48(10)
S(1)	S(6a)	N(6)	171.66(9)
S(1)	S(6a)	C(3a)	86.30(10)
C(3a)	S(6a)	N(6)	85.52(12)
S(6a)	N(6)	C(11)	124.8(2)
S(6a)	N(6)	N(5)	115.4(2)
N(5)	N(6)	C(11)	119.7(2)
N(6)	N(5)	C(4)	109.4(3)
N(5)	C(4)	C(3a)	118.6(3)
C(4)	C(3a)	S(6a)	111.1(2)
C(4)	C(3a)	C(3)	127.2(3)
S(6a)	C(3a)	C(3)	121.7(2)
C(3a)	C(3)	C(2)	122.1(2)
C(3)	C(2)	S(1)	116.4(2)
C(3)	C(2)	C(7)	122.8(3)
S(1)	C(2)	C(7)	120.8(2)
C(2)	C(7)	C(8)	110.9(3)
C(2)	C(7)	C(9)	106.7(3)
C(2)	C(7)	C(10)	110.1(3)
C(8)	C(7)	C(9)	109.0(4)
C(8)	C(7)	C(10)	110.0(4)
C(9)	C(7)	C(10)	110.0(5)
N(6)	C(11)	C(12)	121.7(3)
N(6)	C(11)	C(16)	119.3(3)
C(12)	C(11)	C(16)	119.0(3)
C(11)	C(12)	C(13)	119.8(3)
C(12)	C(13)	C(14)	121.0(3)
C(13)	C(14)	C(15)	119.6(4)
C(14)	C(15)	C(16)	120.1(4)
C(15)	C(16)	C(11)	120.5(3)
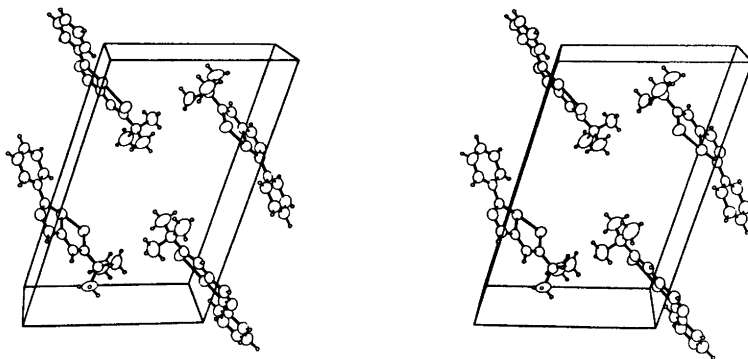
Fig. 2. Stereoview of the molecular packing.

present molecule may therefore be described as a 5,6-diaza analogue of 6a-thiathiophthene.

Another characteristic feature for thiathiophthenes is the difference in length between the central C(3) − C(3a) and C(3a) − C(4) bonds and the terminal C(2) − C(3) and C(4) − C(5) bonds,[14] the former being somewhat longer and the latter somewhat shorter than the aromatic C − C bond in benzene, 1.397 Å. The same structural feature is found in the present molecule. Thus, the lengths of the central C − C bonds are 1.400(4) and 1.405(5) Å, respectively, and the length of the C(2) − C(3) bond is 1.376(5) Å. The C(4) − N(5) bond is found to be 1.320(4) Å as compared with the length of the aromatic C − N bond of 1.340 Å in pyridine.[15]

Finally it should be mentioned that the S(6a) − C(3a) bond length of 1.735(3) Å and the S(1) − C(2) bond lengths of 1.711(3) Å agree with the lengths usually found for such bonds in thiathiophthenes,[14] and the N(5) − N(6) bond of 1.330(4) Å fits nicely into this picture.

The connecting bond N(6) − C(11) = 1.414(4) Å has some double bond character, and the phenyl group shows slight quinoid features. Thus, the average length of C(12) − C(13) and C(15) − C(16) is 1.380 Å, while the average length of the other C − C bonds of the phenyl group is 1.388 Å.

A stereoscopic view [16] of the molecular packing in the unit cell is given in Fig. 2. There are no intermolecular contacts shorter than corresponding van der Waals distance.

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