September, 1984] © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *57, 2581—2583 (1984)* 2581

The Crystal and Molecular Structure of 3,4-Dimethyl-2,5-diphenyl-3,4-dihydro-3a-thia-1,3,4,6-tetraazapentalene

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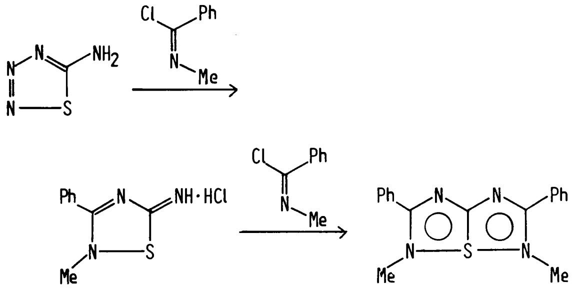
(Received March 5, 1984)

The crystal structure of 3,4-dimethyl-2,5-diphenyl-3,4-dihydro-3a-thia-1,3,4,6-tetraazapentalene has been determined by the X-ray method. The crystals are orthorhombic, space group Pbcn, a=14.533(4), b=9.285(3), c=11.305(2) Å, V=1525.4(6) Å^3, Z=4, D_x=1.343 Mg m^{-3}. The final R value is 0.060 for 1107 reflections. The molecule has an exact C_2 symmetry, with the central S–C bond coincident with the 2-fold axis of the crystal symmetry. The length of 1.904 Å of the two equivalent S–N bonds indicates that the molecule is a tetraaza analogue of the thiathiophthenes. The length of this S–N bond is 9% longer than the N–S single bond and significantly less than the sum of the van der Waals radii.

In the course of the 1,3-dipolar addition to 4,5-dihydro-1,2,4-thiadiazole a bond switch has taken place at the π-hypervalent sulfur atom,[1,2] An intermediate state of the reaction should be of a thiathiophthene type; in fact, a molecule of such a type has been found in the crystalline state.[3] An addition of *N*-methylbenzimidoyl chloride to 5-amino-1,2,3,4-thiatriazole gave 2-methyl-3-phenyl-5-imino-2,5-dihydro-1,2,4-thiadiazole hydrochloride. Further addition gave the molecule **I**.[4] For such symmetric substituents it is interesting to investigate whether the molecule of **I** has a symmetric or unsymmetric structure. An X-ray structure analysis was undertaken to elucidate the structure of **I**.



(I)

Scheme 1.

Experimental

Crystal Data: $C_{17}H_{16}N_4S$, Mw=308.40, Orthorhombic, Pbcn, a=14.533(4), b=9.285(3), c=11.305(2) Å, V=1525.4(6) Å^3, Z=4, D_x=1.343 Mgm^{-3}.

Colorless crystals were grown from benzene-hexane solution. Intensities were collected on a Rigaku automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation, using the crystal with approximate dimensions 0.15X0.25X0.35 mm. Reflections in the range $2\theta \leq 55°$ were measured by the $\omega-2\theta$ scan technique with a scan width of $1.2° + 0.5° \tan\theta$ and a scanning rate of 4° min^{-1} in 2θ. At both ends of the scan range 10 s background counts were taken for each reflection. 1107 Reflections had $|F_o| \geq 3\sigma(F_o)$ and were considered observed. No absorption corrections were applied.

The structure was solved by the direct method with the program MULTAN 78.[5] Non-hydrogen atoms were refined by the block-diagonal least-squares with anisotropic temperature factors to an R value of 0.09. A difference map showed the all hydrogen atoms. A possibility of a disordered structure was clearly eliminated by the examination of the D-map and anisotropic temperature factors. Further refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for H gave the final R value of 0.060. The quantity minimized was $\sum w(|F_o| - k^{-1}|F_c|)^2$. w=0.3 if $|F_o| < 4.0$, w=1.0 if $4.0 \leq |F_o| \leq 16.0$ and $w = (16.0/|F_o|)^2$ if $|F_o| > 16.0$. Atomic scattering factors were taken from "International Tables for X-ray Crystallography".[6] All computations were performed on a HITAC M180 Computer of the Data Processing Center of the University of Electro-Communications with the programs UNICS III,[7] MULTAN 78,[5] and ORTEP II.[8] The final atomic parameters are given in Table 1.[9]

Discussion

Figure 1 shows the atomic numbering of the crystal-chemical unit. Bond lengths and angles are listed in Table 2. The molecule has an exact C_2 symmetry, with

TABLE 1. ATOMIC COORDINATES ($\times 10^4$, FOR H $\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS

For non-H atoms $B = B_{eq} = 4/3\sum_i\sum_j\beta_{ij}a_i \cdot a_j$.

Atom	x	y	z	B_{eq}/Å^2
S (6)	5000	4845(1)	2500	2.8
C (3)	5000	2945(6)	2500	2.5
N (1)	5787(2)	4586(4)	3830(3)	2.9
C (2)	5854(3)	3216(4)	4117(3)	2.7
N (3)	5433(2)	2270(3)	3383(3)	2.7
C (11)	6157(3)	5834(5)	4454(4)	3.4
C (21)	6288(3)	2623(5)	5200(3)	2.9
C (22)	5859(3)	1479(5)	5760(4)	3.4
C (23)	6215(4)	899(5)	6787(4)	4.0
C (24)	7014(4)	1435(6)	7247(4)	4.4
C (25)	7454(4)	2561(6)	6695(4)	4.3
C (26)	7099(3)	3159(5)	5674(4)	3.5
H (11)	676(3)	601(5)	420(4)	3.2(9)
H (12)	609(3)	575(5)	518(4)	2.8(9)
H (13)	580(3)	669(6)	420(4)	4.2(11)
H (22)	534(4)	95(7)	548(5)	4.6(12)
H (23)	589(3)	22(6)	718(4)	3.8(10)
H (24)	728(4)	111(6)	796(5)	4.8(12)
H (25)	796(3)	293(5)	694(4)	3.1(10)
H (26)	744(4)	390(7)	533(5)	5.8(14)

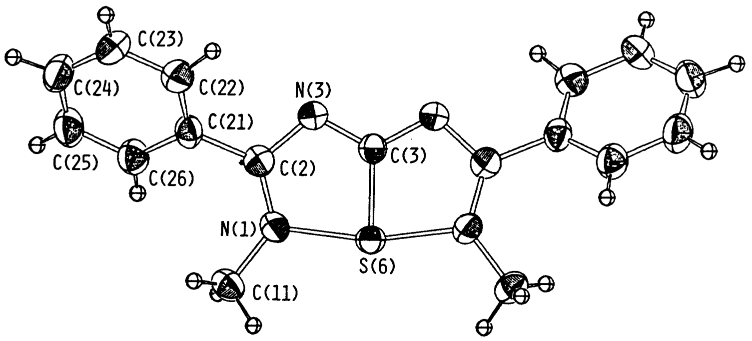
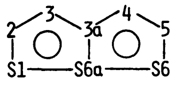


Fig. 1. Molecular structure with atomic numbering of the crystal-chemical unit. Twofold axis lies on the C(3)-S(6) bond. Each non-H atom is represented as a thermal ellipsoid with a 50% probability.

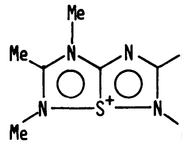
Table 2. Bond length and angle with their estimated standard deviations

Distance	l/Å	Distance	l/Å
S(6)-C(3)	1.764(5)	C(24)-C(25)	1.375(8)
S(6)-N(1)	1.904(4)	C(25)-C(26)	1.380(8)
N(1)-C(2)	1.316(5)	C(11)-H(11)	0.94(5)
C(2)-N(3)	1.354(5)	C(11)-H(12)	0.83(4)
C(3)-N(3)	1.336(6)	C(11)-H(13)	0.99(5)
N(1)-C(11)	1.460(6)	C(22)-H(22)	0.96(6)
C(2)-C(21)	1.483(6)	C(23)-H(23)	0.91(5)
C(21)-C(22)	1.385(6)	C(24)-H(24)	0.94(6)
C(21)-C(26)	1.388(6)	C(25)-H(25)	0.86(5)
C(22)-C(23)	1.380(7)	C(26)-H(26)	0.94(6)
C(23)-C(24)	1.367(8)		
Angle	ϕ/°	Angle	ϕ/°
C(3)S(6)N(1)	82.7(2)	C(21)C(26)C(25)	119.8(5)
N(1)S(6)N(1$^{\text{i}}$)	165.5(2)	N(1)C(11)H(11)	110(3)
S(6)N(1)C(2)	111.2(3)	N(1)C(11)H(12)	111(3)
S(6)N(1)C(11)	120.2(3)	N(1)C(11)H(13)	108(3)
C(2)N(1)C(11)	128.4(4)	H(11)C(11)H(12)	115(4)
N(1)C(2)N(3)	116.3(4)	H(11)C(11)H(13)	105(4)
N(1)C(2)C(21)	126.4(4)	H(12)C(11)H(13)	108(4)
N(3)C(2)C(21)	117.2(4)	C(21)C(22)H(22)	127(4)
C(3)N(3)C(2)	111.5(4)	C(23)C(22)H(22)	112(4)
S(6)C(3)N(3)	117.9(4)	C(22)C(23)H(23)	119(3)
N(3)C(3)N(3$^{\text{i}}$)	124.1(5)	C(24)C(23)H(23)	121(3)
C(2)C(21)C(22)	118.1(4)	C(23)C(24)H(24)	124(3)
C(2)C(21)C(26)	123.2(4)	C(25)C(24)H(24)	116(3)
C(22)C(21)C(26)	118.7(4)	C(24)C(25)H(25)	124(3)
C(21)C(22)C(23)	121.1(4)	C(26)C(25)H(25)	116(3)
C(22)C(23)C(24)	119.8(5)	C(21)C(26)H(26)	124(4)
C(23)C(24)C(25)	119.9(5)	C(25)C(26)H(26)	117(4)
C(24)C(25)C(26)	120.8(5)		

Superscript (i) $1-x$, y, $1/2-z$



(II)



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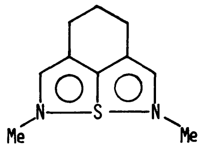

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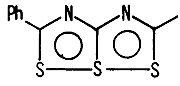

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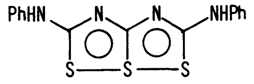
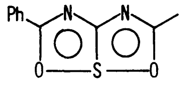
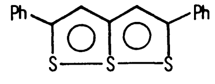


(VI)



(VII)



(VIII)

the S(6)-C(3) bond coincident with the crystallographic 2-fold axis along the b axis. The S(6)-N(1) distance is 1.904 Å, 9% longer than the normal S-N single bond (1.74 Å).[10] Thus the molecule is found to be 3a-thia-1,3,4,6-tetraazapentalene, the tetraaza analogue of thiathiophthene (1,6,6a-trithiapentalene, **II**).[11] The corresponding lengths in **III**[3] are 1.983 and 1.833 Å, and in **IV**[12] 1.901 and 1.948 Å respectively. The average lengthening of the S-S bonds in the thiathiophthenes is 12%. The S-X (X=S, N, and O) bonds in the thiathiophthenes and in the related substances are weaker than other bonds in the molecule, and therefore are more affected by the substituents and/or by the crystalline field. The present molecule is the first example with the exactly equal S-N bonds among the N-S-N analogues of 1,6,6a-trithiapentalene. The CNDO/2 calculation based on the determined structure shows the net charges on the S and N atoms being +0.208 and −0.258 respectively. This suggests that there is an electrostatically attractive interaction between S and N. The existence of the molecule with the symmetrical N-S-N bond in the stable state is very interesting from the point of view of the 1,3-dipolar addition, where the bond-switch takes place at the π-hypervalent sulfur. Bürgi[13] pointed out that the correlation between the non-bonded and bonded S-S interactions of the thiathiophthenes corresponds to the reaction path of the linear exchange reac-

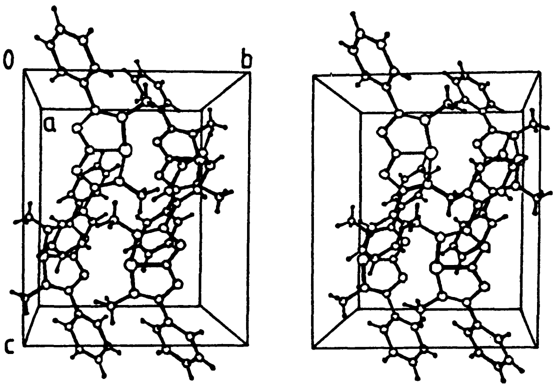


Fig. 2. Stereoscopic view of the crystal structure.

tion. The molecule of the symmetrical type should correspond to the intermediate model of the reaction such as 1,3-dipole additions.

Although the C(3)–S(6) length is longer than the corresponding ones in **III** (1.717 Å) and **IV** (1.742 Å), the longer values are also found in **V** (1.784 Å)[14] and in **VI** (1.789 Å).[15] The S(6a)–C(3a) lengths in the 1,6,6a-trithiapentalenes are remarkably constant within the range of 1.74—1.76 Å. The difference between the lengths of the S(6a)–C(3a) bonds in **I**, **V**, **VI**, and those of 1,6,6a-trithiapentalenes seems due to the presence of the two divalent N atoms in the rings of **I**, **V**, and **VI**. But for the dioxa derivative (**VII**) the short S–C bond (1.719 Å) was reported.[16] The length of the cyclic C(2)–N(3) bond is slightly longer than those in **V** (1.325 Å) and the length of the aromatic C–N bond in pyridine (1.340 Å), while the N(3)–C(3) distance is shorter than that of **V** (1.344 Å). In the 1,6,6a-trithiapentalenes the sum of the outer C(2)–C(3) and C(4)–C(5) lengths is always found to be smaller than the sum of the inner C(3a)–C(3) and C(3a)–C(4) lengths. This is the typical feature showing the resemblance between 1,6,6a-trithiapentalenes and naphthalene.[11] But in the case of 3,4-diaza derivatives such as **I**, **V**, **IV**, and **VII** no significant difference between the outer and inner N–C bonds is observed. The N(1)–C(2) bond is shorter than that of **IV** (1.388 Å) and the aromatic C–N bond. The C(2)–C(21) length is close to the average value of the corresponding C–C lengths in **V**. The N(1)–C(11) length is slightly shorter than the C–N single bond (1.47 Å). Such short C–N bonds are also found in **IV** (1.441 and 1.454 Å).

The equation for the least squares plane through the five membered ring is

$$-0.8152X+0.0375Y+0.5780Z=-4.163 \text{ (Å)}$$

where X, Y, and Z in Å unit referred to the a, b, and c axes respectively. The deviations of S(6), N(1), C(2), N(3), C(3), C(11) and C(21) are 0.033, −0.039, 0.024, 0.012, −0.030, −0.028 and 0.198 Å respectively. The phenyl ring is planar with deviations within 0.007 Å. The dihedral angle between the planes of the central ring and the phenyl ring is 40.0°. The corresponding angles are 2.0 and 7.0° in **V**, 45.1 and 3.3° in **VIII**,[17] and nearly 0° in **VII**.

Figure 2 shows the stereoscopic view of the molecular packing. There are no significant intermolecular contacts shorter than the sum of the van der Waals radii.

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