

# The Crystal and Molecular Structure of 2,5-Dianilino-3,4-diaza-1,6,6a-trithiapentalene

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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  $a=17.915(3)$  Å,  $b=4.004(1)$  Å,  $c=20.958(3)$  Å, and  $\beta=98.25(2)^\circ$ . The structure was solved by means of Patterson maps, and refined by full matrix least squares methods.

The  $S(1)-S(6a)$  and  $S(6a)-S(6)$  bond lengths are 2.227(2) and 2.477(2) Å, respectively, with the angle  $S(1)-S(6a)-S(6)=174.3(1)^\circ$ . Other bond lengths in the central ring system are,  $S(1)-C(2)=1.738(5)$  Å,  $S(6a)-C(3a)=1.796(5)$  Å,  $S(6)-C(5)=1.697(6)$  Å,  $C(2)-N(3)=1.338(7)$  Å,  $N(3)-C(3a)=1.335(7)$  Å,  $C(3a)-N(4)=1.327(7)$  Å, and  $N(4)-C(5)=1.346(7)$  Å. The exocyclic C–N bonds are,  $C(5)-N(7)=1.358(7)$  Å,  $N(7)-C(8)=1.405(8)$  Å,  $C(2)-N(14)=1.334(7)$  Å, and  $N(14)-C(15)=1.425(7)$  Å. The bond lengths have been corrected for libration.

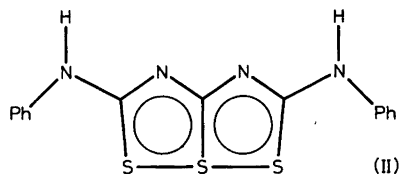
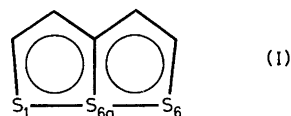
The central ring system is almost planar, the anilino groups are twisted  $5^\circ$  (clockwise) and  $7^\circ$  (anticlockwise) about the  $C(2)-N(14)$  and  $C(5)-N(7)$  directions, respectively, and the twist angles of the phenyl groups about the  $N(14)-C(15)$  and the  $N(7)-C(8)$  directions are  $51^\circ$  (clockwise) and  $11^\circ$  (anticlockwise), respectively.

In the crystal the molecules are held together in pairs over centres of symmetry through  $N-H\cdots N$  hydrogen bonds of length 3.028(7) Å.

Substituent effects on the sulfur–sulfur bonding in 1,6,6a-trithiapentalenes (I) and related compounds have been shown through a series of structure studies.<sup>1</sup> Different substituents perturb the S–S bonding to different extents, and the effect of phenyl and methyl substituents on the S–S bonding is consistent with the results from CNDO/2 calculations.<sup>2</sup>

The degree to which interaction between molecules in a crystal lattice may perturb the S–S

bonding is much less known. A structural study of compound II, where intermolecular  $N-H\cdots N$  hydrogen bonding might occur in the crystal structure, was therefore thought to be of interest.



## STRUCTURE ANALYSIS

The title compound was prepared according to a method of Behringer and Weber.<sup>3</sup> Crystallization from pyridin gave light yellow needles and plates elongated along  $b$ . It was rather difficult to grow crystals which could be used for single crystal work.

A brief account of the structure determination has been reported earlier,<sup>4</sup> and a more detailed description is given here.

## Crystal data.

$C_{15}H_{12}N_4S_3$  F.W. = 344.47  
 Space group  $P2_1/c$   
 $a = 17.915(3)$  Å,  $b = 4.004(1)$  Å,  $c = 20.958(3)$  Å,  
 $\beta = 98.25(2)^\circ$   
 $V = 1487.79$  Å<sup>3</sup>  
 $D_c = 1.538$  g/cm<sup>3</sup>,  $D_m$  (flotation) = 1.53 g/cm<sup>3</sup>  
 $Z = 4$   
 $\mu = 43.8$  cm<sup>-1</sup> (CuK $\alpha$ )  
 Crystal size 0.04 × 0.06 × 0.3 mm.

The structure analysis is based on photographic data and comprises 2691 independent  $h0l-h3l$  reflections including 484 unobserved.

The unit cell dimensions were determined from high-order reflections on  $h0l$  and  $hk0$  Weissenberg photographs, where Pb(NO<sub>3</sub>)<sub>2</sub> powder lines had

been superimposed for reference;  $a_{Pb(NO_3)_2} = 7.8566$  Å,  $t = 23$  °C.<sup>5a</sup> A least squares procedure on 90 measured  $2\theta$  values gave the cell dimensions quoted above.

The intensities were estimated visually from photographs taken with Ni-filtered CuK $\alpha$  radiation,  $hk0$  reflections from the zero layer about  $c$  were used for scaling only.

Lp corrections and absorption corrections<sup>6</sup> were applied. Scattering factors for sulfur, nitrogen and carbon were taken from *International Tables*.<sup>5b</sup> For hydrogen, the scattering factor curve given by Stewart *et al.*<sup>7</sup> was used.

The structure was solved by the heavy atom method, and the positions of the hydrogen atoms were found from difference maps. The atomic

Table 1. Fractional atomic coordinates for 2,5-dianilino-3,4-diaza-1,6,6a-trithiapentalene with temperature parameters  $U_{ij}$  (Å<sup>2</sup>) for sulfur, nitrogen and carbon, and  $U$  (Å<sup>2</sup>) for hydrogen. The expressions used are  $\exp[-2\pi^2(h^2a^*U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$  and  $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$ , respectively. Standard deviations in parentheses.

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S(1)	-0.06489(8)	0.3910(4)	0.33027(6)	.0404(6)	.0422(10)	.0322(6)	.0059(6)	.0008(5)	.0059(6)
S(6a)	0.05424(8)	0.3779(4)	0.31163(6)	.0432(6)	.0329(10)	.0292(6)	.0006(6)	.0012(5)	.0035(5)
S(6)	0.18918(8)	0.3227(5)	0.29979(7)	.0449(7)	.0496(11)	.0402(7)	.0002(7)	.0047(5)	.0080(7)
N(3)	0.0287(3)	0.120(2)	0.4263(2)	.036(2)	.050(4)	.031(2)	.001(2)	.005(2)	-.002(2)
N(4)	0.1502(3)	0.077(2)	0.4085(2)	.035(2)	.046(3)	.032(2)	-.001(2)	.001(2)	.001(2)
N(7)	0.2726(3)	0.008(2)	0.4001(2)	.037(2)	.059(4)	.039(2)	-.002(2)	.003(2)	.006(2)
N(14)	-0.0951(3)	0.153(2)	0.4431(2)	.038(2)	.054(4)	.035(2)	.001(2)	.004(2)	.004(2)
C(2)	-0.0427(3)	0.205(2)	0.4052(3)	.038(2)	.039(4)	.033(2)	-.005(2)	.001(2)	.000(2)
C(3a)	0.0805(3)	0.177(2)	0.3878(2)	.039(2)	.036(4)	.029(2)	-.001(2)	-.004(2)	.003(2)
C(5)	0.2048(3)	0.123(2)	0.3716(3)	.038(2)	.044(4)	.036(2)	-.004(2)	-.004(2)	-.004(2)
C(8)	0.3429(3)	-0.022(2)	0.3787(3)	.034(2)	.046(4)	.055(3)	.001(3)	.002(2)	-.004(3)
C(9)	0.3553(4)	0.009(3)	0.3157(3)	.055(4)	.083(6)	.057(4)	.018(4)	.009(3)	.016(4)
C(10)	0.4278(5)	-0.031(3)	0.3006(5)	.064(4)	.080(7)	.073(5)	.006(4)	.022(4)	.008(5)
C(11)	0.4867(4)	-0.108(3)	0.3452(4)	.050(4)	.077(6)	.076(5)	.000(4)	.012(3)	-.008(4)
C(12)	0.4742(5)	-0.143(3)	0.4080(5)	.045(3)	.115(9)	.088(6)	.011(5)	-.004(4)	-.020(6)
C(13)	0.4037(4)	-0.101(3)	0.4251(4)	.045(3)	.096(7)	.059(4)	.015(4)	-.004(3)	-.003(4)
C(15)	-0.1733(3)	0.216(2)	0.4254(3)	.041(2)	.036(4)	.034(2)	-.001(2)	.003(2)	.004(2)
C(16)	-0.2113(4)	0.401(2)	0.4669(3)	.049(3)	.040(4)	.044(3)	.004(3)	.007(2)	.004(3)
C(17)	-0.2874(4)	0.456(2)	0.4513(4)	.054(3)	.041(5)	.065(4)	.010(3)	.017(3)	.001(3)
C(18)	-0.3267(4)	0.333(2)	0.3944(4)	.049(3)	.056(5)	.071(4)	.012(4)	.000(3)	.016(4)
C(19)	-0.2891(4)	0.155(2)	0.3529(4)	.053(3)	.057(5)	.052(3)	-.001(3)	-.007(3)	.006(3)
C(20)	-0.2127(3)	0.089(2)	0.3686(3)	.046(3)	.044(4)	.041(3)	.001(3)	.003(2)	.002(3)

Atom	x	y	z	U	Atom	x	y	z	U
H(7)	0.270(4)	-0.06(2)	0.440(3)	.05(2)	H(14)	-0.071(4)	0.08(2)	0.487(3)	.06(2)
H(9)	0.311(4)	0.08(2)	0.279(4)	.06(2)	H(16)	-0.175(4)	0.49(3)	0.511(4)	.07(2)
H(10)	0.434(5)	0.01(3)	0.255(4)	.08(3)	H(17)	-0.317(4)	0.57(2)	0.478(3)	.04(2)
H(11)	0.543(5)	-0.10(2)	0.336(4)	.08(3)	H(18)	-0.380(4)	0.39(2)	0.384(3)	.05(2)
H(12)	0.520(6)	-0.19(3)	0.440(4)	.12(3)	H(19)	-0.318(5)	0.03(3)	0.318(4)	.07(3)
H(13)	0.401(6)	-0.15(3)	0.468(4)	.11(4)	H(20)	-0.184(3)	-0.07(2)	0.338(3)	.03(2)

Table 2. Librational tensors from the rigid-body analyses of certain parts of the title compound molecule.  $L_1$  refer to the central ring system plus N(7) and N(14),  $L_2$  refer to ring A plus N(7), and  $L_3$  refer to ring B plus N(14).

Eigenvalues ( $^{\circ}$ ) <sup>2</sup>	Eigenvectors Direction cosines relative to $a$ , $b$ and $c^*$ , respectively.			
$L_1$	22.0	-.9857	.1296	.1080
	3.7	-.0382	.4416	-.8964
	1.9	-.1642	-.8876	-.4304
$L_2$	103.2	-.8924	.2501	.3755
	12.6	-.4109	-.1068	-.9054
	4.1	-.1864	-.9623	.1981
$L_3$	24.6	.9230	.2660	-.2780
	12.5	.2398	.1669	.9564
	9.7	.3008	-.9494	.0903

parameters were refined by full matrix least squares methods (see for example Ref. 8) to an  $R$  of 0.08.

Atomic coordinates and temperature parameters are listed in Table 1. The structure factor list is available on request.

The intensities of 89 low order reflections were difficult to estimate due to spot shape effects. These reflections have been excluded from the refinement.

Separate rigid body (RBM) analyses<sup>9</sup> have been carried out for those parts of the molecule which may be regarded as being rigid. Those parts are the central ring system plus N(7) and N(14), the phenyl group A plus N(7), and the phenyl group B plus N(14), *cf.* Figs. 1 and 2, and the corresponding librational tensors  $L_1$ ,  $L_2$ , and  $L_3$  are given in Table 2. The relevance of such a procedure has been discussed (see for example Ref. 10), and it is

supported by the results from the present analyses. One finds namely, *cf.* Table 2 and Fig. 1, that the maximum libration ( $4.7^{\circ}$ ) in  $L_1$  occurs about an axis parallel to the C(2)–C(5) direction, the maximum libration ( $10.2^{\circ}$ ) in  $L_2$  occurs about an axis close to the N(7)–C(8) bond and the maximum libration ( $5.0^{\circ}$ ) in  $L_3$  occurs about an axis close to the N(14)–C(15) bond. Furthermore, the RBM analysis of the mentioned parts of the molecule gave a better fit between observed and calculated  $U_{ij}$ 's than did the RBM analysis of the entire molecule. While the r.m.s. difference of  $U_{ij}$ 's is  $0.0059 \text{ \AA}^2$  for the latter, it is  $0.0023 \text{ \AA}^2$  for the central ring system plus N(7) and N(14),  $0.0041 \text{ \AA}^2$  for ring A plus N(7), and  $0.0018 \text{ \AA}^2$  for ring B plus N(14).

All calculations were carried out on an IBM 360/50H computer. The programs, with a few exceptions, originate from the Weizmann Institute of Science, Rehovoth, Israel, and have been modified by D. Rabinovich, L. M. Milje and K. Åse.

## DISCUSSION

The molecular structure of II is shown in Fig. 1. Bond lengths and angles are listed in Table 3. We are aware of Hamilton and Abrahams' critical view on the standard deviations.<sup>11</sup> The bond lengths in the three rigid parts of the molecule have been corrected for libration according to the librational tensors  $L_1$ ,  $L_2$  and  $L_3$ , respectively.

The central ring system of II is almost planar, and the equation of the least squares plane for this part of the molecule, calculated with weights equal to the respective atomic weights, is

$$2.1277x + 3.5760y + 8.6429z = 4.1397$$

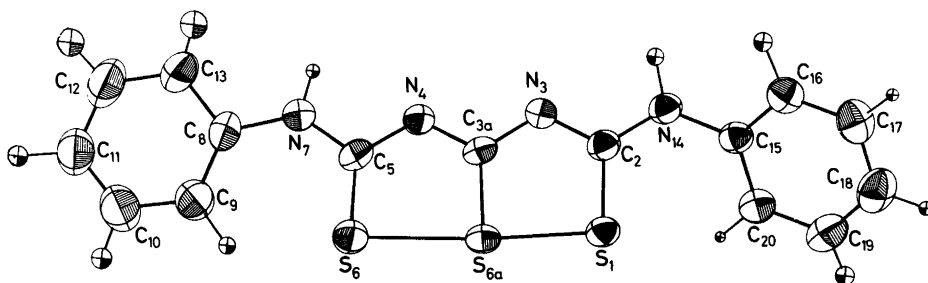


Fig. 1. The molecular structure of 2,5-dianilino-3,4-diaza-1,6,6a-trithiapentalene with numbering of atoms.

Table 3. Bond lengths  $l(ij)$ , bond angles  $\angle(ijk)$  and deviations  $\Delta_i$  from least squares plane. The deviations for atoms which are included in the least squares plane calculations are printed in italics. Bond lengths  $l(ij)$  have been corrected for libration. Standard deviations in parentheses.

Atoms <i>i</i>	<i>j</i>	<i>k</i>	Bonds $l(ij)$ Å	$l(ij)$ Å	Angles $\angle(ijk)^\circ$	Deviations from plane $\Delta_i$ Å
S(1)	S(6a)	S(6)	2.225(2)	2.227	174.3(1)	-.025
S(1)	S(6a)	C(3a)			89.4(2)	
S(1)	C(2)	N(3)	1.731(5)	1.738	119.6(4)	
S(1)	C(2)	N(14)			121.3(4)	
S(6a)	S(1)	C(2)			92.7(2)	.021
S(6a)	S(6)	C(5)	2.475(2)	2.477	89.6(2)	
S(6a)	C(3a)	N(3)	1.789(5)	1.796	120.0(3)	
S(6a)	C(3a)	N(4)			122.9(3)	
S(6)	C(5)	N(4)	1.691(6)	1.697	122.5(4)	.008
S(6)	C(5)	N(7)			125.2(4)	
S(6)	S(6a)	C(3a)			85.1(2)	
N(3)	C(2)	N(14)	1.336(7)	1.338	119.1(4)	.034
N(3)	C(3a)	N(4)	1.333(7)	1.335	117.1(4)	
N(4)	C(5)	N(7)	1.344(7)	1.346	112.3(4)	-.014
N(7)	C(8)	C(9)	1.401(8)	1.405	125.1(5)	
N(7)	C(8)	C(13)			116.5(5)	-.073
N(14)	C(15)	C(16)	1.419(7)	1.425	118.9(4)	
N(14)	C(15)	C(20)			121.3(5)	.033
C(2)	N(3)	C(3a)			118.2(4)	
C(2)	N(14)	C(15)	1.332(7)	1.334	124.7(4)	.006
C(3a)	N(4)	C(5)	1.325(7)	1.327	119.9(4)	.015
C(5)	N(7)	C(8)	1.356(7)	1.358	132.7(5)	-.053
C(8)	C(9)	C(10)	1.375(10)	1.391	119.4(6)	-.216
C(9)	C(10)	C(11)	1.390(11)	1.395	122.4(7)	-.625
C(10)	C(11)	C(12)	1.340(11)	1.359	118.1(7)	-.742
C(11)	C(12)	C(13)	1.374(14)	1.390	121.3(7)	-.506
C(12)	C(13)	C(8)	1.373(11)	1.378	120.3(7)	-.117
C(13)	C(8)	C(9)	1.387(9)	1.407	118.4(6)	.033
C(15)	C(16)	C(17)	1.393(9)	1.400	119.6(5)	-.061
C(16)	C(17)	C(18)	1.374(9)	1.379	120.8(6)	.880
C(17)	C(18)	C(19)	1.386(10)	1.394	119.7(6)	.779
C(18)	C(19)	C(20)	1.371(11)	1.378	120.4(6)	-.237
C(19)	C(20)	C(15)	1.387(9)	1.393	119.8(5)	-1.150
C(20)	C(15)	C(16)	1.389(8)	1.397	119.7(5)	-1.087

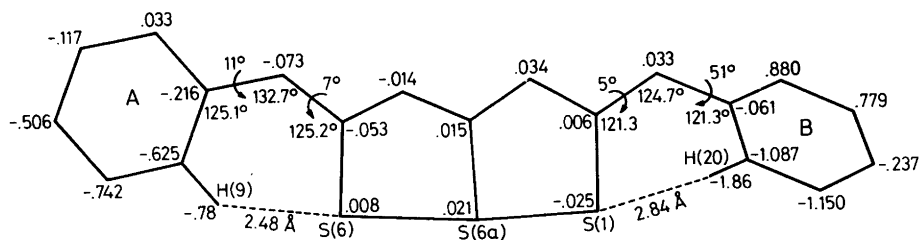


Fig. 2. A projection of the molecular structure of the title compound in the plane of the central ring system, showing deviations (Å) from plane, twist angles, some exocyclic bond angles and intra-molecular H...S distances.

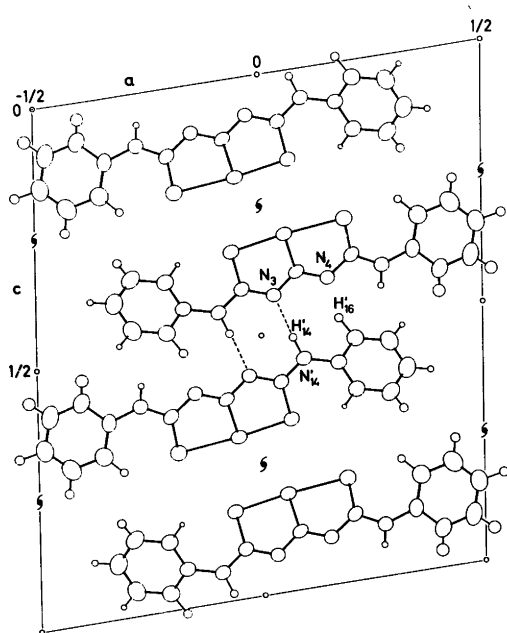


Fig. 3. The crystal structure of the title compound in *b*-axis projection.

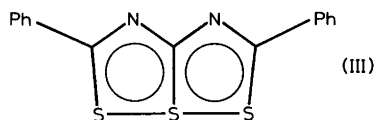
where *x*, *y* and *z* are fractional coordinates.

Deviations of atoms from this plane are given in Table 3 and shown on Fig. 2. One notes that the anilino groups are twisted 5° (clockwise) and 7° (anticlockwise) about the C(2)–N(14) and the C(5)–N(7) bond directions, respectively. Furthermore, phenyl groups *B* and *A* are twisted 51° (clockwise) and 11° (anticlockwise) about the N(14)–C(15) and the N(7)–C(8) bond directions, respectively.

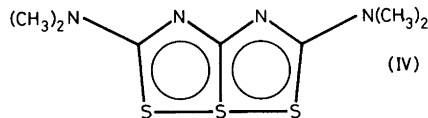
A comparison of bond lengths in the central ring system of the present compound with those in the central ring system of compounds III<sup>12</sup> and IV<sup>13</sup> are given in Table 4. It shows that although the three molecules are symmetrically substituted the S–S bonds are found to be of equal lengths (in III and IV) as well as of different lengths (in II).

In crystals of IV the molecules lie on twofold axes coinciding with the S(6a)–C(3a) bond, and therefore the two equivalent halves of the molecule have equal environments.<sup>13</sup>

In crystals of III there are no intermolecular contacts shorter than corresponding van der Waals contacts. Furthermore, the molecule is nearly planar, and corresponding angles and bond lengths



2,5-Diphenyl-3,4-diaza-1,6,6a-trithiapentalene



2,5-Dimethylamino-3,4-diaza-1,6,6a-trithiapentalene

in the two equivalent halves of the molecule agree within the experimental error.<sup>12</sup>

In crystals of the present compound, *cf.* Fig. 3, the molecules are held in pairs over centres of symmetry through N–H···N hydrogen bonding; the N(14)···N(3) distance is 3.028(7) Å with the hydrogen atom H(14') close to the connecting line. There is in addition another weaker contact of 2.42(8) Å between N(4) and H(16') of a neighbouring molecule.

As a consequence of this the spatial orientations of the anilino groups become unsymmetrical relative to the central ring system. Furthermore there is an intramolecular close contact of 2.48(8) Å, between H(9) and S(6), *cf.* Fig. 2, which seems to have caused differences in exocyclic bond angles.

This shows that molecule II is unsymmetrically perturbed, mainly through intermolecular interaction, and therefore the S–S bond lengths become different; the bond lengths are, S(1)–S(6a) = 2.227(2) Å and S(6a)–S(6) = 2.477(2) Å with the angle S(1)–S(6a)–S(6) = 174.3(1)°.

The bond lengths in Table 4 may be compared with those in the 1,6,6a-trithiapentalene molecule (Ia).<sup>14</sup>

The S(6a)–C(3a) bond length in Ia is 1.748(3) Å, and a length close to this value is usually found for the S(6a)–C(3a) bond in 1,6,6a-trithiapentalenes.<sup>14</sup>

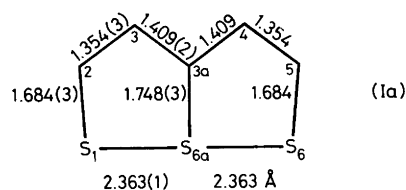


Table 4. A comparison of bond lengths in the 3,4-diaza-1,6,6a-trithiapentalen system of compounds II, III and IV.

Bonds	Bond lengths (Å)		
	II	III	IV
S(1)–S(6a)	2.227(2)	2.319(3)	2.346(1)
S(6a)–S(6)	2.477(2)	2.328(3)	2.346(1)
S(1)–C(2)	1.738(5)	1.692(9)	1.705(4)
S(6a)–C(3a)	1.796(5)	1.786(8)	1.856(7)
S(6)–C(5)	1.697(6)	1.698(8)	1.705(4)
C(2)–N(3)	1.338(7)	1.325(10)	1.347(5)
N(3)–C(3a)	1.335(7)	1.330(9)	1.309(5)
C(3a)–N(4)	1.327(7)	1.344(10)	1.309(5)
N(4)–C(5)	1.346(7)	1.336(10)	1.347(5)

In the 3,4-diaza-1,6,6a-trithiapentalenes, however, the S(6a)–C(3a) bond is longer, *cf.* Table 4. Thus, in II and III it is 1.796(5) and 1.786(8) Å, respectively, and in IV it is found to be 1.856(7) Å, which is even longer than the accepted value 1.82 Å for the C–S single bond length.<sup>15</sup>

The terminal C–C bonds in Ia are seen to be 0.055 Å shorter than the central ones, and this is a typical feature in 1,6,6a-trithiapentalenes.<sup>14</sup> A smaller difference, 0.006 Å, in the same direction occurs between the average values of central and terminal C–N bond lengths in III. In II and IV, however, the difference is in the opposite direction, and this may be due to the fact that C(2) and C(5) in these compounds are strongly engaged in  $\pi$ -bonding with external atoms, while this is not so in II. The mentioned  $\pi$ -bonding may also explain why the outer C–S bonds in II and IV, average length 1.711(4) Å, are found to be somewhat longer than those in III, average length 1.695(6) Å.

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