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The Crystal and Molecular Structure of 2-Diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate, $C_{11}H_{20}N_4S_3$

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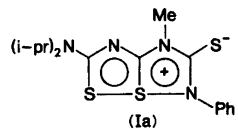
The crystal and molecular structure of the title compound has been determined by X-ray methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions, $a = 6.114(1)$, $b = 10.601(1)$, $c = 12.034(2)$ Å, $\alpha = 78.19(1)$, $\beta = 81.59(1)$, and $\gamma = 82.13(2)°$. There are two molecules in the unit cell. The structure was determined by direct methods and refined by full matrix least squares to an R-value of 0.033 for 3021 observed reflections.

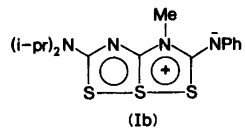
Each of the two five-membered rings in the central ring system is planar with an angle of 4.9° between the two planes. Bond lengths in the central part of the molecule are: S(1)–S(6a) = 2.4942(9) and S(6a)–N(6) = 1.814(2) Å with the angle S(1)–S(6a)–N(6) = 168.89(6)°, S(1)–C(2) = 1.703(2), S(6a)–C(3a) = 1.743(2), N(6)–C(5) = 1.315(2), C(2)–N(3) = 1.369(2), N(3)–C(3a) = 1.311(3), C(3a)–N(4) = 1.370(2), and N(4)–C(5) = 1.403(3) Å. The bond lengths have been corrected for libration.

CNDO/2 calculations have been performed on the present molecule and on a phenyl derivative. The theoretical results show, when compared with the experimental data from X-ray crystallographic structure determinations, that the CNDO/2 calculations predict the differences in the two structures reasonably well.

It has been shown that the adduct of 5-diisopropylamino-3-methylimino-1,2,4-dithiazole (DTA) and phenylisothiocyanate gives a compound which may be formulated as (Ia) rather than (Ib).[1] The X-ray study on (Ia) showed further that the molecule could be considered as a 6-aza-1,6a-dithiapentalene derivative with bond lengths compatible with those of the 1,6,6a-trithiapentalene molecular system.[2] The present X-ray structure determination of the adduct (II) of DTA and methylisothiocyanate is carried out in order to study the influence of a methyl group on the bonding in the linear S–S–N sequence as compared to that of a phenyl group.



(Ia)



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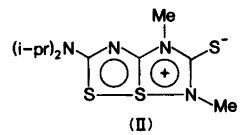

(II)

STRUCTURE ANALYSIS

A sample of the title compound was generously supplied by Goerdeler.[3–5] The crystals are elongated, colourless prisms. The dimensions of the crystal used for all measurements were 0.55 × 0.28 × 0.25 mm.

Crystal data.

$C_{11}H_{20}N_4S_3$ M.W. = 304.50
Triclinic, space group $P\bar{1}$ with $Z = 2$
$a = 6.114(1)$ Å, $b = 10.601(1)$ Å, $c = 12.034(2)$ Å,
$\alpha = 78.19(1)°$, $\beta = 81.59(1)°$, $\gamma = 82.13(2)°$
$V = 750.6(4)$ Å^3
$D_x = 1.347$ g/cm^3, $D_m = 1.34$ g/cm^3
$\mu_{MoK\alpha} = 5.19$ cm^{-1}, $F_{000} = 324$

0302-4377/81/010061-06$02.50

Unit cell dimensions and intensity data were measured on an automatic Enraf-Nonius CAD4 diffractometer using graphite monochromator and Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The unit cell dimensions were determined from 25 reflections with $2\theta > 36°$.

Three-dimensional intensity data for 3717 independent reflections within $2\theta < 55°$ were collected at 20 °C by the $\omega - 2\theta$ scan technique and with $\Delta\omega = 0.75° + 0.35°\text{tg}\theta$. After data reduction including L*p*-correction but no absorption correction, 3021 reflections with net intensity I greater than $2\sigma(I)$, where $\sigma(I)$ was based on counting statistics, were regarded as observed.

The statistics from NORMSF [6] did not show clearly whether the space group was centric or noncentric. But from the fact that the density measurements indicated two molecules in the unit cell, space group $P\bar{1}$ was chosen and further work confirmed this assumption.

The structure was solved by direct methods using the program PHASE of X-RAY 76.[6] The signs of 3 reflections $5\,0\,\bar{1}$, $1\,1\,0\,6$ and $5\,1\,1\,2$ were systematically changed until the most probable solution was found, and this solution gave the signs of 229 reflections with $E > 1.80$. Twelve out of eighteen non-hydrogen atoms were located in the corresponding E-map, and a structure factor calculation based on these atoms resulted in an R factor of 0.42. A subsequent Fourier map revealed the remaining 6 non-hydrogen atoms and the hydrogen atoms were thereafter found from difference maps. The atomic parameters were refined by full matrix least squares to an R of 0.033. The weighted R is 0.030. At the end of the refinement the average shift/error ratio was 0.19.

The form factors used in the structure factor calculations were those of Stewart *et al.*[7] for hydrogen and of Cromer and Mann [8] for the other atoms. Final atomic coordinates and temperature parameters for the non-hydrogen atoms are listed in Table 1; those of the hydrogen atoms are listed in Table 2. The final structure factor list is available from the author on request.

Rigid body analysis have been carried out for the central ring system plus C(7), S(8), C(9), N(10), C(11) and C(14), according to the method of Schomaker and Trueblood.[9] The corresponding librational tensors are given in Table 3.

All calculations mentioned above were carried out on the UNIVAC 1110 computer at the University of Bergen. The programs used were mainly those of the X-RAY 76 program system.[6] The data reduction

Table 1. Atomic coordinates and temperature parameters U_{ij} (Å)^2 for the sulfur, nitrogen and carbon atoms. The temperature factor is $\exp\{-2\pi^2(h^2a^{*2}U_{11} + \cdots 2hka^*b^*U_{12} + \cdots)\}$. The U_{ij}'s are multiplied by 10^4.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S (1)	.25551 (9)	.57330 (5)	.92110 (4)	526 (3)	411 (3)	333 (3)	-203 (2)	- 78 (2)	178 (2)
S(6a)	.49890 (8)	.73678 (5)	.93809 (4)	474 (2)	380 (3)	322 (2)	-144 (2)	-123 (2)	-184 (2)
C (2)	.20744(27)	.65561(17)	.78902(14)	284 (9)	342 (9)	327 (9)	- 60 (7)	- 20 (7)	- 88 (7)
N (3)	.27794(24)	.77526(13)	.74925(12)	391 (8)	294 (8)	338 (8)	- 94 (6)	- 98 (6)	- 49 (6)
C(3a)	.40460(28)	.81613(16)	.81006(14)	342 (9)	290 (9)	301 (9)	- 65 (7)	- 42 (7)	- 63 (7)
N (4)	.48394(24)	.93374(13)	.77156(12)	435 (9)	288 (8)	362 (8)	-107 (7)	-104 (7)	- 40 (6)
C (5)	.63928(30)	.96354(18)	.83415(16)	388(10)	358(10)	433(11)	-100 (8)	- 57 (8)	-130 (8)
N (6)	.66322(26)	.87031(15)	.92293(13)	473(10)	436 (9)	439 (9)	-173 (8)	-163 (8)	- 75 (8)
C (7)	.81351(48)	.86525(29)	1.00765(23)	565(16)	677(17)	567(15)	-174(13)	-257(12)	-145(13)
S (8)	.76887(10)	1.09784 (5)	.79703 (5)	654 (4)	447 (3)	679 (4)	-301 (3)	-115 (3)	-105 (3)
C (9)	.41499(48)	1.01865(23)	.66864(22)	757(18)	329(11)	487(13)	-152(11)	-235(12)	53(10)
N(10)	.10381(24)	.60923(14)	.71776(12)	360 (8)	333 (8)	348 (8)	-115 (6)	- 48 (6)	- 84 (6)
C(11)	.02117(32)	.48005(18)	.75340(17)	433(11)	372(10)	434(11)	-179 (9)	- 13 (9)	- 99 (9)
C(12)	-.21883(39)	.48474(28)	.73231(31)	370(13)	584(16)	1078(24)	-194(12)	42(14)	-313(17)
C(13)	.17224(42)	.37925(23)	.69679(25)	501(14)	371(12)	795(19)	- 62(10)	- 50(13)	-141(12)
C(14)	.08965(32)	.67457(19)	.59731(16)	450(11)	389(11)	379(10)	- 84 (9)	-142 (9)	- 91 (9)
C(15)	.31657(43)	.68973(27)	.52719(20)	616(15)	571(15)	369(12)	-171(13)	- 8(10)	- 74(11)
C(16)	-.06641(49)	.80003(26)	.58656(27)	625(17)	527(15)	738(19)	63(13)	329(15)	-116(14)

Table 2. Atomic coordinates and isotropic thermal parameters U (Å)^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 (71)	.9554(48)	.8481(28)	.9778(24)	105(11)	H(131)	.1839(35)	.4007(21)	.6125(19)	64 (7)
H (72)	.7630(48)	.8001(30)	1.0785(26)	128(12)	H(132)	.3230(41)	.3694(23)	.7159(20)	86 (9)
H (73)	.7892(46)	.9423(28)	1.0335(24)	114(11)	H(133)	.1280(38)	.2978(23)	.7252(20)	78 (8)
H (91)	.4531(47)	.9851(28)	.6096(23)	107(11)	H (14)	.0263(28)	.6147(17)	.5626(14)	37 (5)
H (92)	.2386(59)	1.0309(31)	.6788(27)	153(14)	H(151)	.3845(36)	.7550(22)	.5460(18)	64 (7)
H (93)	.4609(47)	1.0999(28)	.6643(23)	112(11)	H(152)	.2990(33)	.7162(20)	.4469(19)	65 (7)
H (11)	.0281(31)	.4573(18)	.8358(16)	52 (6)	H(153)	.4154(46)	.6127(27)	.5424(23)	105(11)
H(121)	-.2323(40)	.5014(24)	.6438(23)	94(10)	H(161)	-.2102(44)	.7863(25)	.6224(22)	91(10)
H(122)	-.2745(41)	.4102(25)	.7699(21)	87 (9)	H(162)	-.0242(39)	.8623(23)	.6239(20)	87 (9)
H(123)	-.3132(39)	.5509(24)	.7669(20)	81 (8)	H(163)	-.0808(37)	.8319(22)	.5076(21)	75 (8)

programs and RBM-analyses programs used were adopted for the UNIVAC 1110 computer by L. K. Hansen and L. J. Sæthre, this University.

DISCUSSION

The structure of the title compound as found in the present study is shown in Fig. 1; the numbering of atoms is given in Fig. 1. The rings *A* and *B* are both planar within the error limits, and the angle between the planes is 4.9°. The substituent atoms C(7), S(8) and C(9) lie out of plane *B*, by −0.07, −0.04 and 0.07 Å, respectively, while the atoms of the diisopropylamino group, N(10), C(11) and C(14) lie −0.26, −0.37 and −0.54 Å, respectively, out of plane *A*.

Bond lengths and angles for non-hydrogen atoms as calculated from the atomic coordinates in Table 1, are listed in Tables 4 and 5. 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 l^I values are corrected according to the librational tensor L given in Table 3 using Cruickshank's [10] method.

Table 3. Rigid body libration tensor **L** of the 2-diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate molecule.

Eigenvalues	Eigenvectors Direction cosinus × 10^4 relative to *a*, *b*, and *c**, respectively.		
L { 24.9(°)^2	−5135	−8034	−3016
L { 5.9	−8548	4483	2615
L { 3.5	−745	3914	−9172

The results of the rigid body motion analysis show that the maximum angle of libration is 5.0°, and the corresponding principal axis of libration is roughly parallel to the S(1)−S(6a) direction. The r.m.s. difference between observed and calculated U_{ij} values was 0.0036 Å. The lengthenings range from 0.003 Å to 0.008 Å, with the largest corrections on the bonds "perpendicular" to the S(1)−S(6a) direction.

Table 4. Bond lengths (l) in 2-diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate. Standard deviations in parentheses refer to the last digits of the respective values. The l^I values have been corrected for libration according to the librational tensor **L**.

Bond	l(Å)	l^I(Å)
S(1)−S(6a)	2.4900(9)	2.4942
S(6a)−N(6)	1.810(2)	1.814
S(1)−C(2)	1.695(2)	1.703
S(6a)−C(3a)	1.735(2)	1.743
N(6)−C(5)	1.309(2)	1.315
C(2)−N(3)	1.366(2)	1.369
N(3)−C(3a)	1.308(3)	1.311
C(3a)−N(4)	1.367(2)	1.370
N(4)−C(5)	1.399(3)	1.403
C(5)−S(8)	1.673(2)	1.677
N(6)−C(7)	1.458(4)	1.462
N(4)−C(9)	1.454(3)	1.461
C(2)−N(10)	1.340(3)	1.343
N(10)−C(11)	1.483(3)	1.487
N(10)−C(14)	1.483(2)	1.489
C(11)−C(12)	1.518(3)	
C(11)−C(13)	1.517(3)	
C(14)−C(15)	1.525(3)	
C(14)−C(16)	1.521(3)	

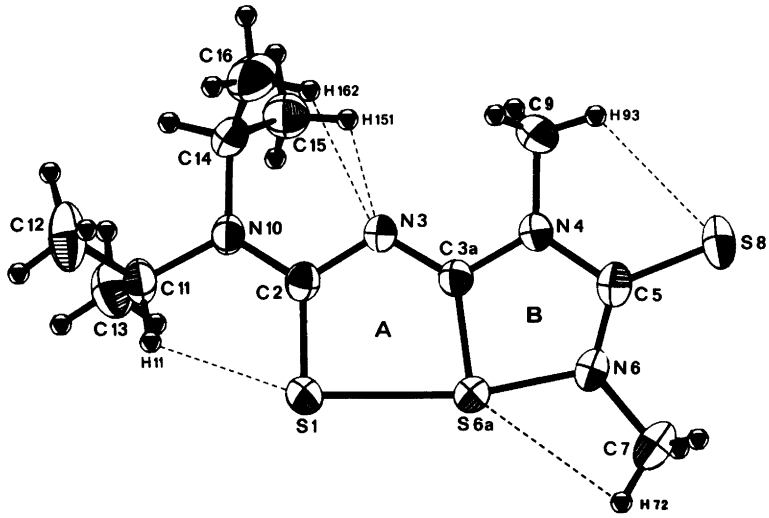

Fig. 1. ORTEP[10] drawing of the title compound with the numbering of the atoms in the molecule. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Table 5. Bond angles <(ijk) in 2-diisopropylamino-4,6-dimethyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate. The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	k	∠(ijk)°
C(2)	S(1)	S(6a)	90.33(7)
S(1)	S(6a)	N(6)	168.89(6)
S(1)	S(6a)	C(3a)	82.76(7)
C(3a)	S(6a)	N(6)	86.20(8)
S(6a)	N(6)	C(7)	118.4(1)
S(6a)	N(6)	C(5)	116.4(1)
C(5)	N(6)	C(7)	125.2(2)
N(6)	C(5)	S(8)	127.4(2)
N(6)	C(5)	N(4)	108.8(2)
S(8)	C(5)	N(4)	123.8(1)
C(5)	N(4)	C(9)	123.1(1)
C(5)	N(4)	C(3a)	116.1(1)
C(9)	N(4)	C(3a)	120.8(2)
N(4)	C(3a)	S(6a)	112.2(1)
N(4)	C(3a)	N(3)	119.6(1)
S(6a)	C(3a)	N(3)	128.1(1)
C(3a)	N(3)	C(2)	117.8(1)
N(3)	C(2)	N(10)	116.3(1)
S(1)	C(2)	N(3)	120.2(1)
S(1)	C(2)	N(10)	123.6(1)
C(2)	N(10)	C(11)	120.2(1)
C(2)	N(10)	C(14)	122.7(1)
N(10)	C(11)	C(12)	111.9(2)
N(10)	C(11)	C(13)	111.1(2)
N(10)	C(14)	C(15)	113.3(2)
N(10)	C(14)	C(16)	112.9(2)
C(12)	C(11)	C(13)	111.8(2)
C(11)	N(10)	C(14)	116.7(2)
C(15)	C(14)	C(16)	113.1(2)

The S(1)–S(6a) bond in the present structure is 2.494(1) Å and the S(6a)–N(6) bond is 1.814(2) Å. The sum of the S(1)–S(6a) and the S(6a)–N(6) bond length is 4.31 Å, with an angle S(1)–S(6a)–N(6) = 168.9(1)°. In the analogue compound 2-diisopropylamino-4-methyl-6-phenyl-3,4,6-triaza-1,6a-dithiapentalenylium-5-thiolate[1] (Ia) the S(1)–S(6a) bond is 2.447(1) Å and the S(6a)–N(6) bond is 1.863(2) Å. The sum of the two bond lengths is 4.31 Å as in the present compound and the angle S(1)–S(6a)–N(6) = 169.0(1)°. By replacing a phenyl group with a methyl group the S(1)–S(6a) bond in (II) has become 0.047 Å longer and the S(6a)–N(6) bond 0.049 Å shorter. A comparison of the other equivalent bonds in the two structures show only minor or insignificant differences.

The C–H bond lengths lie in the region 0.85 to 1.06 Å with a mean value of 0.96 Å. The standard deviation of the mean value is 0.05 Å.

The bond angles involving hydrogen atoms range from 103 to 116° with a mean value of 109° and a standard deviation in the mean value of 3°.

There are a few short intramolecular S···H and N···H distances. S(1)···H(1) = 2.43(2) Å, S(8)···H(93) = 2.64(3) Å, S(6a)···H(72) = 2.74(3) Å, N(3)···H(151) = 2.48(2) Å and N(3)···H(162) = 2.51(2) Å, respectively, *cf.* Fig. 1. Especially, the S(1)···H(11) bond distance of 2.43 Å is rather short compared to the corresponding van der Waals distance of 3.05 Å.[11] It is, in fact, almost

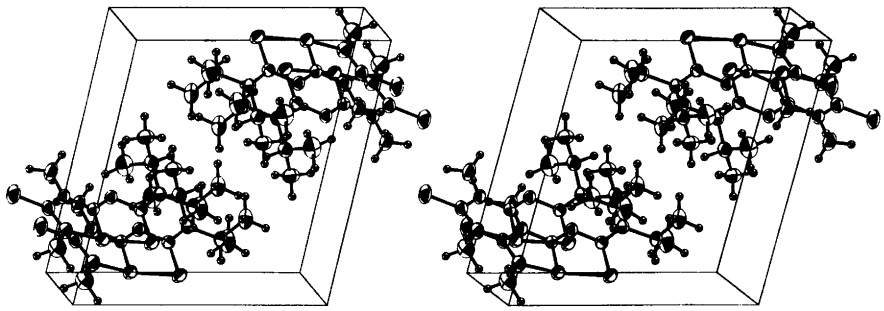

Fig. 2. A stereoscopic view of the arrangement of the molecules in the unit cell.

as short as that found in *N,N'*-diisopropylthiooxalamide [12] in an intramolecular N···H···S hydrogen bond. Also the three S···H contacts in the present molecule seem to take part in the formation of three rings systems and least squares planes calculations show that the rings are "planar". For the two 5-membered rings involving atoms S(1), C(2), N(10), C(11), H(11) and S(8), C(5), N(4), C(9), H(93), respectively, the atoms lie, −0.05, 0.04, 0.01, −0.09, 0.09 Å and −0.05, 0.05, 0.00, −0.10, 0.10 Å out of the respective planes. For the 4-membered ring comprising atoms S(6a), N(6), C(7) and H(72) the deviations are −0.04, 0.07, −0.10 and 0.06 Å from the least squares plane. These intramolecular S···H contacts seem to stabilize the observed conformation for both the two methyl groups and the two isopropyl groups in the solid state of the molecule.

There are no intermolecular contacts shorter than van der Waals distances. A stereoscopic view of the arrangements of molecules in the unit cell is given in Fig. 2.[13]

CNDO/2 calculations. It is well known from structural data on trithiapentalenes [2,14] that different substituent groups on the carbon skeleton perturb the bonding in the three-sulfur sequence to different extents. This has also been shown through CNDO/2 calculations on the trithiapentalene molecule and on its 2- and 3-methyl and 2- and 3-phenyl derivatives.[15] The results from the present study and those from the study of (Ia) [1] show that different substituents in the 6-position of 1,6a-dithia-6-azapentalenes also perturb the bonding in the "linear" S−S−N sequences to different extents. It was, therefore, thought of interest to carry out CNDO/2 calculations on this system as well.

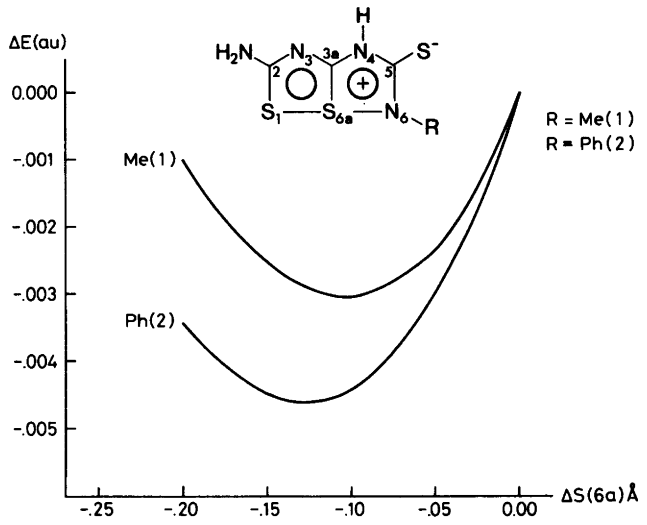

Fig. 3. The change in CNDO/2 total energy for compounds (Ia) and (II) as a function of the displacement of S(6a).

The calculations have been performed according to a modified CNDO/2 program [16] using the following molecular model: A planar molecule with bond lengths and angles taken as the averaged values of (Ia) and (II),[1,17] and with the two isopropyl groups and the methyl group attached to N(4) replaced by H-atoms. The N–H bond length was chosen to be 1.04 Å.[18]

The calculations have been carried out with the inclusion of 3*d*-orbitals on the sulfur atoms. Recent CNDO/2 and *ab initio* calculations on disulfides and thiapentalenes [19–23] discuss the role of including 3*d*-orbitals on the sulfur atoms. It has been observed that CNDO/2 calculations based on standard parameters and without 3*d*-orbitals predict too long S–S bonds *e.g.* in dithioles [20,24] while calculations with 3*d*-orbitals on sulfur yield too short S–S bonds.[20] Thus, when comparing experimental bond lengths with those predicted theoretically, the relative changes rather than the absolute values are relevant for a discussion.

The relative change in the CNDO/2 total energy for a methyl group (1) and for a phenyl group (2) in the model structure, *cf.* Fig. 3, has been calculated as a function of the displacement ΔS(6a) of sulfur atom S(6a), keeping the geometry of the remainder of the model molecule constant. The S(6a)–N(6) distance corresponding to minimum energy was derived by interpolation according to a second order polynomial fit.

One sees from Fig. 3 that the minimum for the phenyl derivative (2) corresponds to an S(6a)–N(6) bond length that is 0.03 Å longer than that of the methyl derivative (1). Exclusion of 3*d*-orbitals on the sulfur atoms give the same qualitative results. The X-ray results gave S(6a)–N(6) = 1.86 Å in (2) and 1.81 Å in (1). This gives a difference of 0.05 Å and leads to the conclusion that the relative change in the S(6a)–N(6) bond distance is described fairly well by the semi-empirical calculations.

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REFERENCES

1. Hansen, L. K. *Acta Chem. Scand. A 31* (1977) 855.
2. Hansen, L. K., Hordvik, A. and Sæthre, L. J. In Sterling, C. I. M., Ed., *Organic Sulphur Chemistry*, Butterworths, London 1975, pp. 1–17.
3. Goerdeler, J. and Ulmen, J. *Chem. Ber. 105* (1972) 1568.
4. Goerdeler, J. *Lecture held at the 4th. Int. Congress of Heterocyclic Chemistry*, Salt Lake City 1973.
5. Goerdeler, J. *Private communication.*
6. Stewart, J. M., Ed., *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
7. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
8. Cromer, D. and Mann, J. *Acta Crystallogr. A 24* (1968) 321.
9. Schomaker, V. and Trueblood, K. N. *Acta Crystallogr. B 24* (1968) 63.
10. Cruickshank, D. W. J. *Acta Crystallogr. 9* (1956) 757.
11. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
12. Klaska, K. H., Jarchow, O., Schäm, W., Widjaja, H., Voss, J. and Schmalle, H. W. *J. Chem. Research S* (1980) 104.
13. 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.
14. Hordvik, A. and Sæthre, L. J. *Israel J. Chem. 10* (1972) 239.
15. Hansen, L. K., Hordvik, A. and Sæthre, L.J. *Chem. Commun.* (1972) 222.
16. Fægri, K., Jr. and Manne, R. *CNDO/2 Programs*, Department of Chemistry, University of Bergen, N-5014 Bergen.
17. This work.
18. *CRC Handbook of Chemistry and Physics*, 52nd Ed., (1971–1972) F-175.
19. Palmer, M. H. and Findlay, R. H. *J. Chem. Soc. Perkin Trans. 2 (1974)* 1885.
20. Sæthre, L. J. *Acta Chem. Scand. A 29* (1975) 558.
21. Gleiter, R. and Cygax, R. *Topics in Current Chemistry, Vol. 63*, Springer, Berlin 1976, p. 49.
22. Nyburg, S. C., Theodorakopoulos, G. and Csizmadia, I. G. *Theor. Chim. Acta 45* (1977) 21.
23. Fægri, K., Jr. and Støgård, Å. *J. Mol. Struct. 41* (1977) 271.
24. Kiers, C. T. and Vos, A. *Recl. Trav. Chim. Pays-Bas 91* (1972) 126.

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