

The Crystal and Molecular Structures of 2,5-Dimethyl-1,6-dioxa-6a-thiapentalene and 2,5-Diphenyl-3,4-diaza-1,6-dioxa-6a-thiapentalene

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The crystal and molecular structures of the title compounds have been determined by X-ray crystallographic methods.

2,5-Dimethyl-1,6-dioxa-6a-thiapentalene (I) crystallizes in the orthorhombic space group $Pnma$ with $Z=4$ and cell dimensions, $a=7.089(2)$ Å, $b=11.180(2)$ Å, and $c=9.696(2)$ Å. The molecule is planar and lies across the mirror plane m . The dimensions of the molecule are, $S(6a)-O(1)=1.873(2)$ Å, $S(6a)-C(3a)=1.732(4)$ Å, $O(1)-C(2)=1.326(4)$ Å, $C(2)-C(3)=1.371(4)$ Å, $C(3)-C(3a)=1.390(3)$ Å, $C(2)-C(20)=1.492(5)$ Å, and $O(1)-S(6a)-O(6)=173.9(1)^\circ$.

2,5-Diphenyl-3,4-diaza-1,6-dioxa-6a-thiapentalene (II) crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$ and cell dimensions, $a=11.732(3)$ Å, $b=21.853(6)$ Å, $c=5.028(2)$ Å, and $\beta=97.19(3)^\circ$. The molecule is planar and the dimensions of the central ring system are, $O(1)-S(6a)=1.852(2)$ Å, $O(6)-S(6a)=1.917(2)$ Å, $C(3a)-S(6a)=1.729(3)$ Å, $O(1)-C(2)=1.297(3)$ Å, $C(2)-N(3)=1.334(4)$ Å, $N(3)-C(3a)=1.334(4)$ Å, $C(3a)-N(4)=1.338(4)$ Å, $N(4)-C(5)=1.328(3)$ Å, $C(5)-O(6)=1.297(3)$ Å, and $O(1)-S(6a)-O(6)=168.2(1)^\circ$. The lengths of the bonds connecting the phenyl groups to the central ring system are, $C(2)-C(13)=1.461(4)$ Å, and $C(5)-C(7)=1.474(4)$ Å.

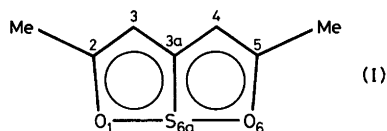
The structure of I was solved by direct methods (MULTAN) and the structure of II by Patterson methods. Refinements were carried out according to least squares procedures. Final R factors: 0.045 for I (591 reflections) and 0.055 for II (2197 reflections).

Rigid body analyses have been carried out, and the bond lengths have been corrected for libration.

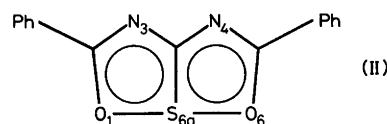
In the crystal structures of I and II there are no

intermolecular contacts shorter than the corresponding van der Waals distances.

In connection with systematic structure studies on 1,6,6a-trithiapentalenes and related compounds¹ we became interested in the molecular structures of compounds I and II. The structure of the 3,4-diaza-1,6-dioxa-6a-thiapentalene ring system (in II) has not been studied so far, and results for only one molecular structure containing the 1,6-dioxa-6a-thiapentalene ring system (in I) have been reported.² More information, especially on the O–S–O bonding in such compounds, was desirable, and the structures of compounds I and II have therefore been determined.



2,5-Dimethyl-1,6-dioxa-6a-thiapentalene



2,5-Diphenyl-3,4-diaza-1,6-dioxa-6a-thiapentalene

STRUCTURE ANALYSES

Colourless prismatic crystals of compound I were kindly supplied by Reid.³ They had to be kept in capillaries during data collection in order to prevent sublimation. The dimensions of the crystal used for cell parameter determination as well as for data collection were $0.3 \times 0.3 \times 0.3$ mm.

Crystals of compound II were kindly supplied by Beer;⁴ they are also colourless prisms. The dimension of the crystal used for all diffractometer measurements were $0.15 \times 0.3 \times 0.6$ mm.

Crystal data.

$C_7H_8O_2S$ (I) F.W. = 156.20
Space group $Pnma$
 $a = 7.089(2)$ Å, $b = 11.180(2)$ Å, $c = 9.696(2)$ Å
 $V = 768.4$ Å³
 $D_c = 1.350$ g/cm³, D_m (flotation) = 1.36 g/cm³
 $Z = 4$
 $\mu = 3.5$ cm⁻¹ (MoK α)

$C_{15}H_{10}N_2O_2S$ (II) F.W. = 282.32
Space group $P2_1/n$
 $a = 11.732(3)$ Å, $b = 21.853(6)$ Å, $c = 5.028(2)$ Å,
 $\beta = 97.19(3)^\circ$
 $V = 1278.9$ Å³
 $D_c = 1.466$ g/cm³, D_m (flotation) = 1.48 g/cm³
 $Z = 4$
 $\mu = 2.6$ cm⁻¹ (MoK α).

The X-ray measurements were carried out on a computer-controlled Enraf-Nonius CAD4 diffractometer using graphite monochromatized MoK α radiation ($\lambda = 0.71069$ Å). The unit cell dimensions were determined from the 2θ values of 25 high order reflections measured at 20 °C. A least squares procedure gave the values quoted above.

Intensity data were collected at 20 °C by means of the $\omega - 2\theta$ scan technique and a scan width ($^\circ$) $\Delta\omega = 0.80 + 0.35 \tan \theta$ for compound I and $\Delta\omega = 0.75 + 0.35 \tan \theta$ for compound II.

The intensities of 973 reflections in the θ -range $1 - 28^\circ$ were measured for I, and the intensities of 4070 reflections in the θ -range $1 - 30^\circ$ were measured for II. In either case two intensity control reflections were measured at regular X-ray time intervals and showed weak deterioration of the crystals. This was accounted for during data reduction.

Lp corrections were applied but absorption corrections were considered unnecessary. Reflections for which $I > 2\sigma(I)$, where $\sigma(I)$ is based on counting statistics, were in the case of I accepted as observed. For compound II this threshold value was set to $3\sigma(I)$.

By these criteria 591 reflections for I and 2197 reflections for II were accepted as observed. The unobserved reflections were excluded from the structure refinements.

The structure of I was solved by direct methods (MULTAN),⁵ and the structure of II was solved by means of Patterson methods. Structure refinements were carried out by means of CRYLSQ of X-RAY-76.⁶ The hydrogen positions were found from difference maps. Final R factors for I and II are 0.045 and 0.055, respectively.

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

Final coordinates and temperature parameters for I and II are listed in Tables 1 and 2, respectively. The final structure factor lists are available on request.

Table 1. Fractional atomic coordinates, and temperature parameters (Å²) for compound I. The expression used for sulfur, oxygen and carbon is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$, and the expression used for hydrogen is $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$. Standard deviations in parentheses.

| Atom | x | y | z | U_{11} | U_{22} | U_{33} | U_{12} | U_{23} | U_{13} |
|-------|------------|------------|------------|-----------|-----------|-----------|------------|------------|-----------|
| S(6a) | .70356(17) | .75000 | .48009(10) | .1014(9) | .0844(7) | .0671(7) | .0 | -.0197(7) | .0 |
| O(1) | .71020(29) | .58338(15) | .48906(18) | .1060(16) | .0832(12) | .0791(12) | -.0058(12) | -.0135(12) | .0056(11) |
| C(2) | .7811(4) | .54792(26) | .6063(3) | .0546(17) | .1065(21) | .0754(17) | .0063(17) | .0135(16) | .0224(18) |
| C(3) | .8326(4) | .63705(28) | .6934(3) | .0595(17) | .1157(24) | .0647(16) | .0000(17) | -.0025(15) | .0035(18) |
| C(3a) | .8015(5) | .7500 | .6404(3) | .0517(22) | .0897(25) | .0582(21) | .0 | .0001(20) | .0 |
| C(20) | .7973(7) | .4159(3) | .6259(5) | .1005(26) | .0889(21) | .1141(28) | .0055(25) | .0118(25) | .0321(24) |
| H(3) | .883(4) | .6298(19) | .7856(26) | .098(9) | | | | | |
| H(21) | .673(5) | .364(3) | .622(4) | .188(18) | | | | | |
| H(22) | .880(5) | .3614(25) | .559(4) | .172(15) | | | | | |
| H(23) | .833(6) | .3838(27) | .707(4) | .161(17) | | | | | |

Table 2. Fractional atomic coordinates, and temperature parameters (\AA^2) for compound II. The expressions used are given in the caption of Table 1. Standard deviations in parentheses.

| Atom | x | y | z | U_{11} | U_{22} | U_{33} | U_{12} | U_{23} | U_{13} |
|-------|------------|-------------|-------------|-----------|-----------|-----------|------------|-----------|------------|
| S(6a) | .11663(6) | .08784(4) | -.06594(15) | .0392(4) | .0625(5) | .0437(4) | .0029(4) | .0100(3) | .0013(4) |
| O(1) | .11824(15) | .02972(9) | .2024(4) | .0425(11) | .0649(14) | .0456(11) | .0005(10) | .0138(9) | .0049(10) |
| O(6) | .14851(14) | .14625(9) | -.3311(4) | .0418(11) | .0627(14) | .0424(11) | .0052(10) | .0075(8) | .0060(10) |
| N(3) | .30787(17) | .04366(10) | .1840(5) | .0425(13) | .0498(16) | .0411(14) | -.0024(11) | .0095(10) | .0029(12) |
| N(4) | .32668(17) | .11678(11) | -.1524(4) | .0408(12) | .0487(15) | .0375(13) | -.0002(11) | .0080(10) | .0032(12) |
| C(2) | .22318(22) | .01596(13) | .2899(5) | .0415(16) | .0475(19) | .0399(15) | -.0030(14) | .0110(13) | -.0093(14) |
| C(3a) | .26380(20) | .08222(13) | -.0070(5) | .0395(14) | .0430(17) | .0315(13) | .0006(13) | .0072(11) | -.0061(14) |
| C(5) | .25839(22) | .15026(13) | -.3247(5) | .0430(15) | .0462(19) | .0298(14) | .0028(14) | .0036(12) | -.0055(13) |
| C(7) | .30606(22) | .19267(12) | -.5099(5) | .0441(15) | .0428(17) | .0304(14) | .0015(13) | .0043(12) | -.0067(13) |
| C(8) | .23487(25) | .22851(14) | -.6854(6) | .0424(17) | .0517(20) | .0424(17) | .0039(15) | .0051(13) | .0023(15) |
| C(9) | .28014(27) | .26856(15) | -.8562(6) | .0581(20) | .0527(21) | .0376(17) | .0065(16) | .0025(14) | .0039(16) |
| C(10) | .39682(28) | .27249(16) | -.8529(6) | .0605(22) | .0589(22) | .0389(17) | -.0083(18) | .0080(15) | .0027(16) |
| C(11) | .46782(28) | .23677(17) | -.6810(7) | .0444(18) | .0821(27) | .0585(20) | -.0061(18) | .0053(16) | .0157(19) |
| C(12) | .42316(25) | .19677(16) | -.5116(6) | .0478(18) | .0679(23) | .0429(17) | .0039(17) | .0035(14) | .0123(17) |
| C(13) | .24846(23) | -.02904(13) | .5038(5) | .0458(16) | .0439(17) | .0386(15) | -.0032(14) | .0139(12) | -.0052(14) |
| C(14) | .16065(26) | -.05781(15) | .6209(6) | .0476(17) | .0560(20) | .0432(17) | -.0041(15) | .0144(14) | -.0043(16) |
| C(15) | .18751(29) | -.09893(15) | .8253(6) | .0649(22) | .0567(23) | .0523(19) | -.0096(19) | .0248(16) | .0012(17) |
| C(16) | .29885(30) | -.11194(15) | .9158(6) | .0735(23) | .0530(21) | .0422(17) | .0001(18) | .0134(16) | .0037(16) |
| C(17) | .38642(29) | -.08465(16) | .8038(7) | .0548(20) | .0645(24) | .0642(21) | .0013(19) | .0074(17) | .0133(20) |
| C(18) | .36000(28) | -.04365(16) | .5975(7) | .0484(19) | .0639(24) | .0636(22) | -.0060(17) | .0160(16) | .0129(19) |

| Atom | x | y | z | U | Atom | x | y | z | U |
|-------|-----------|-----------|----------|----------|-------|-----------|------------|----------|----------|
| H(8) | .1545(21) | .2244(11) | -.706(5) | .042(7) | H(14) | .0833(21) | -.0488(11) | .562(5) | .043(8) |
| H(9) | .2275(20) | .2960(12) | .042(5) | .049(8) | H(15) | .1254(23) | -.1212(14) | .878(6) | .070(10) |
| H(10) | .4301(22) | .3017(14) | -.939(6) | .054(9) | H(16) | .3133(23) | -.1439(15) | 1.064(6) | .081(11) |
| H(11) | .5526(25) | .2423(13) | -.660(6) | .074(10) | H(17) | .4624(24) | -.0925(13) | .880(6) | .067(10) |
| H(12) | .4751(21) | .1685(12) | -.403(5) | .053(8) | H(18) | .4106(25) | -.0234(15) | .529(6) | .073(11) |

Scattering factors given by Cromer and Mann were used for sulfur, oxygen, nitrogen and carbon.⁷ For hydrogen, the scattering factor curve given by Stewart *et al.*⁸ was used.

DISCUSSION

Compound I. The molecular structure of I as found by the present study is shown in Fig. 1. Bond

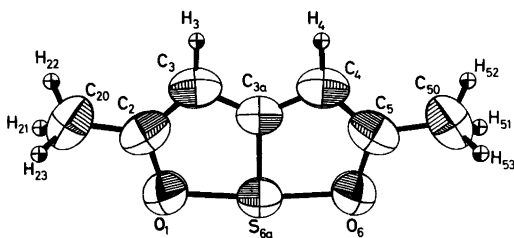


Fig. 1. The molecular structure of compound I with numbering of atoms.

lengths and angles are given in Table 3. The standard deviations given in Table 3 are based on the standard deviations in positional parameters from the least squares refinement as given in Table 1. A more realistic estimate of the standard deviations would, according to Hamilton and Abrahams, probably be obtained by multiplying those given by a factor of two.⁹

Rigid body analysis has been carried out according to the method of Schomaker and Trueblood,¹⁰ and the bond lengths have been corrected for libration, *cf.* Table 3. The libration is rather anisotropic with the axis of maximum libration (10.3°) close to the C(2)–C(5) direction, *cf.* Fig. 1.

The molecule is planar within the experimental error and lies across the crystallographic mirror plane *m*. The equation for the least squares plane of the molecule, calculated with equal weights and hydrogens neglected, is

$$6.47829x - 3.93726z = 2.67640$$

Table 3. Bond lengths $l(ij)$ and $l'(ij)$, bond angles $\angle(ijk)$, and deviations Δ_i from least squares plane for compound I. Standard deviations in parentheses. The bond lengths $l'(ij)$ have been corrected for libration.

| Atoms <i>i</i> | <i>j</i> | <i>k</i> | Bonds $l(ij)$ Å | $l'(ij)$ Å | Angles $\angle(ijk)^\circ$ | Deviations from plane Δ_i Å |
|-------------------|----------|----------|--------------------|------------|-------------------------------|--|
| S(6a) | C(3a) | C(3) | 1.702(4) | 1.732 | 113.9(2) | -.009 |
| O(1) | S(6a) | O(6) | 1.865(2) | 1.873 | 173.9(1) | -.001 |
| O(1) | S(6a) | C(3a) | | | 87.0(1) | |
| C(2) | O(1) | S(6a) | 1.305(4) | 1.326 | 110.7(2) | -.004 |
| C(20) | C(2) | O(1) | 1.492(5) | 1.500 | 116.2(3) | .024 |
| C(20) | C(2) | C(3) | | | 128.8(3) | |
| C(3) | C(2) | O(1) | 1.356(4) | 1.371 | 115.0(3) | -.013 |
| C(3) | C(3a) | C(4) | 1.381(3) | 1.390 | 132.2(3) | |
| C(3a) | C(3) | C(2) | | | 113.4(3) | -.005 |

with x and z as fractional coordinates. Deviations of atoms from the least squares plane are given in Table 3.

Due to the symmetry of compound I the two S–O bonds must be equal; their lengths of 1.873(2) Å are 9.5 % greater than the sum of the covalent radii for sulfur¹¹ and oxygen,¹² 1.71 Å. A lengthening of 12.3 % relative to the S–S single bond of 2.10 Å in a *cis* planar disulphide group¹¹ is found for the S–S bonds of 2.358(1) Å in the analogous sulfur compound 2,5-dimethyl-1,6,6a-trithiapentalene.^{13,14}

The terminal C(2)–C(3) and C(4)–C(5) bonds in I, 1.371(4) Å, are seen to be somewhat shorter than the central C(3)–C(3a) and C(4)–C(3a) bonds, 1.390(3) Å, *cf.* Fig. 1 and Table 3. Such a difference is, in fact, a typical feature of the 1,6,6a-trithiapentalenes.¹⁵

The C(2)–O(1) and C(5)–O(6) bonds, 1.326(4) Å, are seen to possess double bond character when compared with the proposed Csp^2 –O single bond length of 1.38 Å and the double bond length of 1.22 Å.^{12,16} The same applies to the S(6a)–C(3a) bond of 1.732(4) Å when compared with the C–S single and double bond lengths of 1.82 and 1.61 Å, respectively.¹⁷

The S(6a)–C(3a) bond length agrees with those found in 1,6,6a-trithiapentalenes where, as a rule, the C(2)–S(1) and the C(5)–S(6) bonds are somewhat shorter than the central C(3a)–S(6a) bond.¹⁵ For the present compound, however, it is difficult to conclude whether the C–O bonds or the C(3a)–S(6a) bond has the more pronounced double bond character.

A comparison of bond angles in I with those in 2,5-dimethyl-1,6,6a-trithiapentalene is given in Fig.

2. It is interesting to note the degree to which the bond angles in I have changed relative to those in the trithiapentalene in order to obtain a linear O–S–O sequence; the O(1)–S(6a)–O(6) angle is 173.9(1)°.

The C(2)–C(20) and the C(5)–C(50) bonds of 1.499(5) Å are normal Csp^2 – Csp^3 bonds.

The dimensions given above for the 1,6-dioxo-6a-thiapentalene system in compound I agree with those found for this system in 2,3-(5'-methoxybenzo)-4,5-(4'-methoxybenzo)-1,6-dioxo-6a-thiapentalene.²

An ORTEP¹⁸ stereoscopic view of the crystal structure of I is given in Fig. 3. There are no intermolecular contacts shorter than corresponding van der Waals distances.

Compound II. The molecular structure of II (as found by the present study) is shown in Fig. 4. Bond lengths and angles are given in Table 4. The standard deviations given in Table 4 are based on

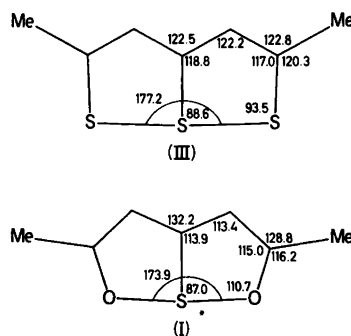


Fig. 2. A comparison of bond angles in compound I with those in 2,5-dimethyl-1,6,6a-trithiapentalene (III).

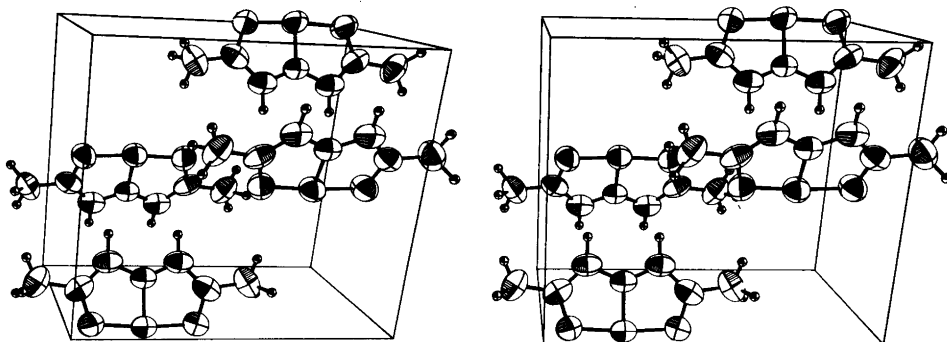


Fig. 3. A stereoscopic view of the crystal structure of compound I.

the standard deviations in positional parameters as given in Table 2. The bond lengths have been corrected for libration. In the thermal analysis the entire molecule was regarded as a rigid body. The libration is rather anisotropic with the axis of maximum libration (5.9°) in the C(7)–C(13) direction.

The molecule is planar within the experimental error, and the equation for the least squares plane of the molecule, calculated with equal weights and hydrogen atoms neglected, is

$$-0.77711x + 15.96076y + 3.43325z = 1.09053$$

with x , y and z as fractional coordinates. Deviations of atoms from this plane are given in Table 4.

O(1)–S(6a) = 1.852(2) Å is significantly shorter than O(6)–S(6a) = 1.917(2) Å, but apart from that the dimensions of the two equivalent halves of molecule II are very nearly equal, *cf.* Fig. 4 and Table 4.

The average O–S bond length in II, 1.885 Å, is 10.2 % longer than the sum of the covalent radii for sulfur and oxygen.^{11,12}

In the analogous sulfur compound 2,5-diphenyl-3,4-diaza-6a-trithiapentalene¹⁹ the average S–S bond length, 2.324(3) Å, is 10.7 % longer than the appropriate value for the S–S single bond length, 2.10 Å, in such compounds.¹¹ The individual S–S bonds of the latter compound, 2.319(3) and 2.328(3) Å, are not significantly different.

The mentioned O–S and S–S bonds are, judging from their lengths, weaker than other bonds in the respective molecules, and therefore more liable to changes in bond lengths if the molecules are perturbed. It has been shown for 1,6,6a-trithiapentalenes, through a series of structure studies,¹ that intramolecular as well as intermolecular perturbation affect the S–S bonding there, and similar effects might therefore be expected for the O–S bonds in 1,6-dioxa-6a-thiapentalenes.

It is difficult to find a specific reason for the O–S bonds in II to be of different lengths. Intramolecular perturbation seems unlikely since the molecule is planar and symmetric, and intermolecular perturbation seems doubtful as there are no intermolecular contacts in the crystal structure shorter than corresponding van der Waals contacts.

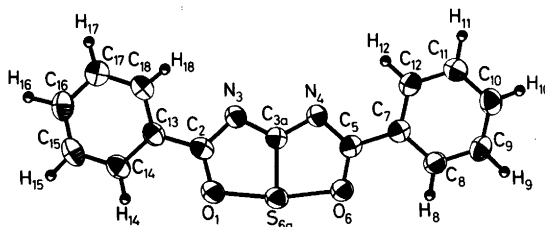


Fig. 4. The molecular structure of compound II with numbering of atoms.

Table 4. Bond lengths $l(ij)$ and $l'(ij)$, bond angles $\angle(ijk)$, and deviations Δ_i from least squares plane for compound II. Standard deviations in parentheses. The bond lengths $l'(ij)$ have been corrected for libration.

| Atoms <i>i</i> | <i>j</i> | <i>k</i> | Bonds $l(ij)$ Å | $l'(ij)$ Å | Angles $\angle(ijk)^\circ$ | Deviations from plane Δ_i Å |
|-------------------|----------|----------|--------------------|------------|-------------------------------|--|
| S(6a) | O(1) | C(2) | 1.852(2) | 1.852 | 109.3(2) | -.006 |
| S(6a) | O(6) | C(5) | 1.916(2) | 1.917 | 108.1(2) | |
| S(6a) | C(3a) | N(3) | 1.719(3) | 1.729 | 117.4(2) | |
| S(6a) | C(3a) | N(4) | | | 118.5(2) | |
| O(1) | S(6a) | O(6) | | | 168.2(1) | -.013 |
| O(1) | S(6a) | C(3a) | | | 84.7(1) | |
| O(1) | C(2) | N(3) | 1.290(3) | 1.297 | 119.1(2) | |
| O(1) | C(2) | C(13) | | | 120.4(2) | |
| O(6) | C(5) | N(4) | 1.288(3) | 1.296 | 120.0(2) | .000 |
| O(6) | C(5) | C(7) | | | 119.0(2) | |
| O(6) | S(6a) | C(3a) | | | 83.6(1) | |
| N(3) | C(2) | C(13) | 1.330(4) | 1.334 | 120.6(2) | -.002 |
| N(3) | C(3a) | N(4) | 1.333(3) | 1.334 | 124.1(2) | |
| N(4) | C(5) | C(7) | 1.324(3) | 1.328 | 121.0(2) | -.004 |
| C(2) | C(13) | C(14) | 1.460(4) | 1.461 | 121.4(2) | -.014 |
| C(2) | C(13) | C(18) | | | 120.5(3) | |
| C(2) | N(3) | C(3a) | | | 109.5(2) | |
| C(3a) | N(4) | C(5) | 1.336(4) | 1.338 | 109.9(2) | -.007 |
| C(5) | C(7) | C(8) | 1.473(4) | 1.474 | 120.9(2) | -.008 |
| C(5) | C(7) | C(12) | | | 120.2(2) | |
| C(7) | C(8) | C(9) | 1.380(4) | 1.384 | 120.6(3) | -.004 |
| C(8) | C(9) | C(10) | 1.378(4) | 1.380 | 119.7(3) | .003 |
| C(9) | C(10) | C(11) | 1.370(5) | 1.377 | 120.1(3) | .039 |
| C(10) | C(11) | C(12) | 1.367(5) | 1.371 | 120.5(3) | .022 |
| C(11) | C(12) | C(7) | 1.370(5) | 1.371 | 120.3(3) | -.013 |
| C(12) | C(7) | C(8) | 1.378(4) | 1.385 | 118.9(3) | -.035 |
| C(13) | C(14) | C(15) | 1.398(4) | 1.402 | 119.9(3) | -.017 |
| C(14) | C(15) | C(16) | 1.372(4) | 1.373 | 120.6(3) | -.006 |
| C(15) | C(16) | C(17) | 1.359(5) | 1.366 | 120.7(3) | .018 |
| C(16) | C(17) | C(18) | 1.369(5) | 1.373 | 118.9(3) | .035 |
| C(17) | C(18) | C(13) | 1.376(5) | 1.378 | 121.7(3) | .018 |
| C(18) | C(13) | C(14) | 1.372(4) | 1.379 | 118.2(3) | -.016 |

One notes, however, *cf.* Fig. 5, that the O(1) and O(6) atoms have different environments in the crystal structure.

The average lengths for external and central C-N bonds in II are 1.331(4) and 1.336(4) Å, respectively, and the corresponding values for 2,5-

diphenyl-3,4-diaza-1,6,6a-trithiapentalene are 1.331(9) and 1.337(9) Å.¹⁹ Thus, the structural feature, typical for 1,6,6a-trithiapentalenes,¹ with short (2)-(3) and (4)-(5) bonds and longer (3)-(3a) and (4)-(3a) bonds, is less predominant for 3,4-diaza-1,6-dioxa-6a-thiapentalenes and 3,4-

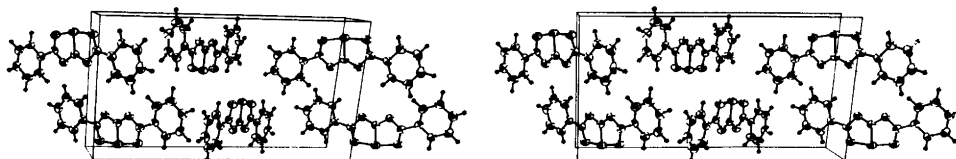


Fig. 5. A stereoscopic view of the crystal structure of compound II.

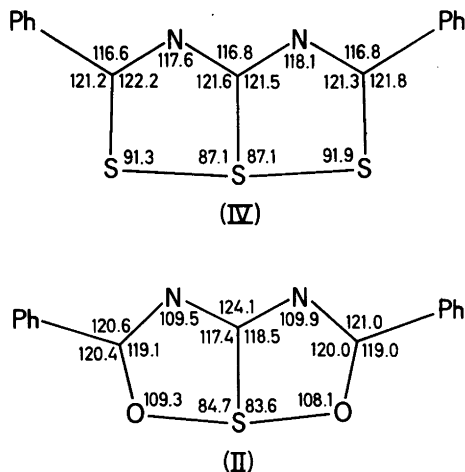


Fig. 6. A comparison of bond angles in compound II with those in 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene(IV).

diaza-1,6,6a-trithiapentalenes. The mentioned C–N bond lengths agree with the length of the aromatic C–N bond, 1.340 Å, found in pyridine.²⁰

The C(3a)–S(6a) bond length in II, 1.729(2) Å agrees with that in I, 1.732(4) Å, but is somewhat shorter than that in 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene, 1.786(8) Å.¹⁹

The difference between the C–O bond lengths in II, 1.297(3) and 1.296(3) Å, and those in I, 1.326(4) Å, may be significant and due to the presence of the nitrogen atoms in the central ring system of II. Indication of a similar difference is namely given by the lengths of the outer S–C bonds as found in 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene,¹⁹ 1.692(9) and 1.698(10) Å, and as found in 2,5-diphenyl-1,6,6a-trithiapentalene, 1.703(6) and 1.712(6) Å.²¹

A comparison of bond angles in II with those in 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene is given in Fig. 6. One notes again how the angles adjust themselves in order to obtain efficient O–S–O bonding.

REFERENCES

- Hansen, L. K., Hordvik, A. and Sæthre, L. J. In Stirling, C. J. M., Ed., *Organic Sulphur Chemistry*, Butterworth, London 1975, p. 1.
- Gilardi, R. D. and Karle, I. L. *Acta Crystallogr. B* 27 (1971) 1073.
- Reid, D. H. and Webster, R. G. *Chem. Commun.* (1972) 1283.
- Beer, R. J. S. and Hart, I. *Chem. Commun.* (1977) 143.
- Main, P., Woolfson, M. M. and Germain, G. *MULTAN: A Computer Program for the Automatic Solution of Crystal Structures*, Department of Physics, Univ. York, York 1976.
- Stewart, J. M., Ed., *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science, University of Maryland, College Park 1976.
- Cromer, D. and Mann, J. *Acta Crystallogr. A* 24 (1968) 321.
- Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
- Hamilton, W. C. and Abrahams, S. C. *Acta Crystallogr. A* 26 (1970) 18.
- Schomaker, V. and Trueblood, K. N. *Acta Crystallogr. B* 24 (1968) 63.
- Hordvik, A. *Acta Chem. Scand.* 20 (1966) 1885.
- Pauling, L. *The Nature of the Chemical Bond*, 3rd. Ed., Cornell University Press, New York 1960.
- Bezzi, S., Mammi, M. and Garbaglio, C. *Nature* 182 (1958) 247.
- Leung, F. and Nyburg, S. C. *Chem. Commun.* 4 (1969) 137.
- Hansen, L. K. and Hordvik, A. *Acta Chem. Scand.* 27 (1973) 411.
- Baird, N. C., Dewar, M. J. S. and Sustman, R. J. *J. Chem. Phys.* 50 (1969) 1275.
- Hordvik, A. *Q. Rep. Sulphur Chem.* 5 (1970) 21.
- 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.
- Hordvik, A. and Milje, L. M. *Acta Chem. Scand.* 24 (1973) 510.
- Bak, B., Hansen-Nygaard, L. and Rastrup-Andersen, J. *Mol. Spectrosc.* 2 (1958) 361.
- Hordvik, A. *Acta Chem. Scand.* 25 (1977) 1583.

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