The Crystal and Molecular Structure of 1,6-Dimethyl-3,4-
trimethylene-6a-thia-azophthene

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Crystals of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene belong to the orthorhombic space group P̅2ca, with unit cell dimensions, a = 16.115(5) Å, b = 21.670(8) Å, and c = 5.825(14) Å. There are eight molecules per unit cell.

The structure was solved by three-dimensional Patterson synthesis, and refined by full-matrix least squares methods. The refinement comprises 167I hkl−hkl4 reflections including 582 unobserved.

The atoms of the two fused five-membered rings lie in the same plane, and the methyl carbons C(7) and C(8) lie −0.069 and −0.077 Å, respectively, out of this plane. Furthermore, the distances from the plane for the methylene carbons C(9), C(10), and C(11) are 0.076, −0.566, and −0.024 Å, respectively.

Bond lengths: N(1)−S(6a) = 1.901(5) Å, N(6)−S(6a) = 1.948(5) Å, N(1)−C(2) = 1.338(7) Å, N(1)−C(7) = 1.441(9) Å, N(6)−C(5) = 1.317(8) Å, N(6)−C(8) = 1.454(9) Å, C(2)−C(3) = 1.367(8) Å, C(3)−C(3a) = 1.421(7) Å, C(3)−C(9) = 1.517(8) Å, C(4)−C(3a) = 1.374(8) Å, C(4)−C(5) = 1.358(9) Å, C(4)−C(11) = 1.523(9) Å, C(9)−C(10) = 1.527(13) Å, C(10)−C(11) = 1.512(13) Å, and S(6a)−C(3a) = 1.742(5) Å. The N(1)−S(6)a−N(6) angle is 168.5(2)°.

The S−N, S−C, C−N, and C−C bond lengths have been corrected for libration.

Structure studies of the analogous compounds 6a-thiathiophthene (I), 6a-selenathiophthene (II), and 6a-selenaselenophthene (III), have been carried out.

Crystals of I are isomorphous with crystals of II, and the molecules lie in both cases across a crystallographic mirror plane passing through the 3a and 6a positions perpendicular to the molecular plane. Hence the sulphur-sulphur bonds in I, and also the selenium-sulphur bonds in II, are of equal length; they are 2.363(1) and 2.446(5) Å, respectively. The selenium-selenium bonds in III are 2.586(3) and 2.579(3) Å, and thus equal within three standard deviations.

Accepted values for the lengths of the S−S, the Se−S, and the Se−Se single bonds are 2.10, 2.22, and 2.34 Å, respectively. Thus the S−S, the

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Se – S, and the Se – Se bonds in compounds I – III are 0.26, 0.23, and 0.24 Å, or 12.4, 10.4, and 10.3 % longer than the corresponding single bonds.

The preparation of compounds containing ring system IV, analogous to the 6a-thiathiophene system, has recently been described by Reid and Symon. We thought it might be of interest to obtain molecular dimensions for IV and compare them with those of compounds I – III. The present structure study of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene has therefore been carried out.

STRUCTURE DETERMINATION

Crystals of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene (V) were generously supplied by Reid. The crystals are yellow and belong to the orthorhombic space group $Pbca$.

The structure study is based on photographic data, taken with Weissenberg camera and CuKα radiation. The data comprise 1671 independent $hk0$ – $hk4$ reflections including 582 unobserved.

The sulphur position was found from a three-dimensional Patterson map, and the nitrogen and carbon atoms revealed themselves during a subsequent Fourier synthesis. The hydrogen positions were found from difference Fouriers.

The structure was refined by a full-matrix least squares procedure (see for example Ref. 8). The constants $a_1$ and $a_2$ in the weighting scheme were in the present case set equal to 1.0.

Anisotropic temperature factors were applied to sulphur, nitrogen, and carbon, and isotropic to hydrogen.

Six low-order reflections, supposed to be affected by secondary extinction, were excluded from the least squares refinement. The final R factor is 7.3 % when unobserved reflections are included, and 7.2 % when they are omitted.

A rigid-body analysis of the thermal parameters has been carried out according to the method of Schomaker and Trueblood, and the S–N, S–C, N–C, and C–C bond lengths have been corrected for rigid-body libration according to Cruickshank’s formula. For further details with respect to the structure determination, see Experimental.

DISCUSSION

Molecular shape and dimensions. Bond lengths and angles in the 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene molecule, together with their standard deviations, are listed in Tables 1 and 2, and shown in Fig. 1, a and b.

*We name the ring system IV “6a-thia-azophthene” in order to bring out the structure analogy with 6a-thiathiophene.

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THIA-AZOPHTHENE COMPOUNDS

Fig. 1. (a) Bond lengths (Å) and (b) bond angles (°) in the 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene molecule.

Table 1. Bond lengths (l) and standard deviations in bond lengths σ(l). Bond lengths (l') include correction for rigid-body libration.

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<th>l(Å)</th>
<th>σ(l)(Å)</th>
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**Table 2.** Bond angles $\angle(ijk)$. The standard deviations given in parentheses refer to the last digits of the respective values.

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The molecule is presented in Fig. 1, a and b in a projection on to the least squares plane of the atoms of the 6a-thia-azophthene system. The equation for this plane, with weights inversely proportional to standard deviations in atomic coordinates, is

$$0.21716 \times + 0.77553 \times - 0.59278 \times Z = 4.97249$$

with $X$, $Y$, and $Z$ in Å units. The 6a-thia-azophthene system is planar within the limits of error. The methyl carbons, C(7) and C(8), lie −0.069 and −0.077 Å off the plane, and the methylene carbons, C(9), C(10), and C(11), lie 0.075, −0.566, and −0.024 Å off.

One notes from Fig. 1, a and b that the molecule is almost symmetric about a plane through S (6a) and C(10) perpendicular to the molecular plane. The greatest differences in length between corresponding bonds in the two halves occur between C(3)−C(3a) = 1.421(7) Å and C(3a)−C(4) = 1.374(8) Å, and between N(1)−S(6a) = 1.901(5) Å and N(6)−S(6a) = 1.948(5) Å. These differences are greater than three times the respective standard deviations, and they are therefore significant.

**Comparison with related molecules.** The nitrogen-sulphur bonds in the present structure (Fig. 1) are longer than a nitrogen-sulphur single bond, 1.75 Å, the average length of the N(1)−S(6a) and the N(6)−S(6a) bonds, 1.925 Å, is 10% longer than the N−S single bond. This agrees with the lengthening.
of the S–S bonds in I, 12.4 %, the Se–S bonds in II, 10.4 %, and the Se–Se bonds in III, 10.3 %, relative to the respective single bonds.

The structures of the 6a-thiathiophthene isomers VI and VII have been determined by Leung and Nyburg,\textsuperscript{11} it is the iodide of VII which has been studied.

![Chemical Structure](image)

The S(6a)–N(6) bond in VI, 1.887(2) Å, is slightly shorter than the S–N bonds in V (Fig. 1a); it is, however, 0.13 Å or 7 % longer than an S–N single bond. The S(6a)–N(6) bond in VII, 1.717(7) Å, is found to be somewhat shorter than a single bond. According to Leung and Nyburg,\textsuperscript{11} the “S-methylation weakens the S⋯S interaction and forms a normal S–N single bond”.

The present authors look at the S–N bond in VII in a slightly different way. We believe that this S–N bond is not a normal single bond, as discussed below.

The S(6a)–C(3a)–C(4)–C(5)–N(6) ring system in VII possesses a sextet of $p–\pi$ electrons available for bonding and is isoelectronic with the $\pi$-system of the 1,2-dithiolium ion (VIII). Structure investigations of 1,2-dithiolium salts\textsuperscript{12} have shown that the S–S bond in the 1,2-dithiolium ion is shortened through $\pi$-bonding. The S–S bond in VIII, from these studies, is 2.00 Å, as compared with the S–S single bond length of 2.10 Å in a cis planar disulphide group. In analogy with the bonding in the 1,2-dithiolium ion, one may expect that the S–N bond in an isothiazolium ion (IX) is shortened through $\pi$-bonding by about 0.10 Å. Hence a reasonable guess at the S–N bond length in IX is 1.65 Å.

![Chemical Structure](image)

1,2-Dithiolium ion.

Isothiazolium ion.

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Fig. 2. The crystal structure of 1,6-dimethyl-3,4-trimethylene-6a-thiaazophthene as seen along the c-axis.

Table 3. Atomic coordinates in fractions of corresponding cell edges. The standard deviations given in parentheses refer to the last digits of the respective values.

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The S–N bond in VII, therefore, is affected by the S···S interaction, and the lengthening of the bond relative to the S–N bond in the isothiazolium ion is about 0.07 Å.

From Fig. 1a the bonds between nitrogen and methyl carbon, N(1)–C(7) = 1.441(9) Å and N(6)–C(8) = 1.454(9) Å, are slightly shorter than the accepted length, 1.47 Å, for a C–N single bond. The lengths of the cyclic C–N bonds, N(1)–C(2) = 1.338(7) Å and N(6)–C(5) = 1.317(8) Å, agree with the length of the aromatic C–N bond, 1.340 Å, found in pyridine. The cyclic C–N bonds in compounds VI and VII are reported to be 1.321* and 1.324 Å, respectively.

The average length of the C(2)–C(3) and C(4)–C(5) bonds (Fig. 1a), and that of the C(3)–C(3a) and C(3a)–C(4) bonds, are 1.363 and 1.398 Å.

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Table 4. Temperature parameters $U_{ij}$ (Å²) for sulphur, nitrogen, and carbon, and $U$ (Å²) for hydrogen. The expressions used are $\exp[-2\pi^2(h\alpha^*U_{11}+\cdots+2h\alpha^*b^*U_{13}+\cdots)]$ and $\exp[-8\pi^2U(\sin^2\theta/\lambda)^2]$, respectively. All values are multiplied by $10^4$. Standard deviations in parentheses refer to the last digits of the respective values.

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Table 5. Libration tensor $L$ from the rigid-body analysis.

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* The standard deviations for these bond lengths are not given in Ref. 11.
| H | K | L | F(1G) | F(1C) | H | K | L | F(1G) | F(1C) | H | K | L | F(1G) | F(1C) | H | K | L | F(1G) | F(1C) |
| 4 0 | 6 | 440 | 447 | 5 26 | 0 | 74 | 76 | 16 | 4 | 0 | 88 | 31 | 10 | 237 | 234 | 7 | 9 | 1 | 59 | 20 |
| 8 0 | 0 | 793 | 106 | 0 | 154 | 156 | 16 | 3 | 0 | 58 | 3 | 11 | 156 | 156 | 7 | 10 | 294 | 294 |
| 12 0 | 0 | 1260 | 1260 | 0 | 220 | 3 | 14 | 0 | 50 | 50 | 3 | 12 | 325 | 325 | 11 | 1 | 56 | 88 |
| 16 0 | 0 | 837 | 837 | 0 | 228 | 6 | 22 | 0 | 68 | 68 | 3 | 14 | 306 | 306 | 11 | 2 | 57 | 68 |
| 20 0 | 0 | 401 | 401 | 0 | 196 | 198 | 14 | 0 | 0 | 38 | 38 | 3 | 22 | 52 | 52 | 11 | 3 | 68 | 73 |
| 24 0 | 0 | 150 | 150 | 0 | 196 | 196 | 14 | 0 | 0 | 38 | 38 | 3 | 22 | 52 | 52 | 11 | 3 | 68 | 73 |
| 28 0 | 0 | 498 | 498 | 0 | 226 | 66 | 26 | 0 | 68 | 68 | 3 | 14 | 306 | 306 | 11 | 2 | 57 | 68 |
| 32 0 | 0 | 1051 | 1051 | 0 | 228 | 228 | 14 | 0 | 0 | 38 | 38 | 3 | 22 | 52 | 52 | 11 | 3 | 68 | 73 |
| 36 0 | 0 | 401 | 401 | 0 | 196 | 196 | 14 | 0 | 0 | 38 | 38 | 3 | 22 | 52 | 52 | 11 | 3 | 68 | 73 |
| 40 0 | 0 | 401 | 401 | 0 | 196 | 196 | 14 | 0 | 0 | 38 | 38 | 3 | 22 | 52 | 52 | 11 | 3 | 68 | 73 |
| 44 0 | 0 | 401 | 401 | 0 | 196 | 196 | 14 | 0 | 0 | 38 | 38 | 3 | 22 | 52 | 52 | 11 | 3 | 68 | 73 |

Table 6. Observed and calculated structure factors for 1,6-dimethyl-3,4-trimethylen-6a-thia-azophenine. The values are ten times the absolute values. Unoberved reflections are marked with a minus sign in front of $F_o$. 

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*Acta Chem. Scand.* 26 (1972) No. 1
| H | K | L | FQ2 | FQ1 | H | K | L | FQ2 | FQ1 | H | K | L | FQ2 | FQ1 | H | K | L | FQ2 | FQ1 | H | K | L | FQ2 | FQ1 | H | K | L | FQ2 | FQ1 |
| 18 | 1 | 34 | 1 | 42 | 2 | 166 | 178 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -3 | 5 | 23 | 1 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -3 | 5 | 23 | 1 | 4 |
| 19 | 1 | 35 | 2 | 45 | 3 | 355 | 366 | 6 | 22 | 3 | -29 | 6 | 14 | 10 | -3 | 5 | 23 | 1 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -3 | 5 | 23 | 1 | 4 |
| 20 | 1 | 34 | 1 | 46 | 2 | 156 | 165 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -4 | 5 | 23 | 1 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -4 | 5 | 23 | 1 | 4 |
| 21 | 1 | 36 | 3 | 45 | 3 | 335 | 346 | 6 | 22 | 3 | -28 | 6 | 14 | 10 | -4 | 5 | 23 | 1 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -4 | 5 | 23 | 1 | 4 |
| 22 | 1 | 34 | 1 | 44 | 2 | 117 | 129 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -5 | 5 | 23 | 1 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -5 | 5 | 23 | 1 | 4 |
| 23 | 1 | 37 | 3 | 44 | 3 | 318 | 329 | 6 | 22 | 3 | -28 | 6 | 14 | 10 | -5 | 5 | 23 | 1 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -5 | 5 | 23 | 1 | 4 |
| 24 | 1 | 35 | 1 | 42 | 2 | 165 | 176 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -6 | 5 | 23 | 1 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -6 | 5 | 23 | 1 | 4 |
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| 26 | 1 | 35 | 1 | 41 | 2 | 135 | 146 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -7 | 5 | 23 | 1 | 4 | 22 | 3 | -29 | 6 | 14 | 10 | -7 | 5 | 23 | 1 | 4 |
| 27 | 1 | 36 | 3 | 40 | 3 | 309 | 321 | 6 | 22 | 3 | -28 | 6 | 14 | 10 | -7 | 5 | 23 | 1 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -7 | 5 | 23 | 1 | 4 |
| 28 | 1 | 35 | 1 | 40 | 2 | 129 | 142 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -8 | 5 | 23 | 1 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -8 | 5 | 23 | 1 | 4 |
| 29 | 1 | 34 | 1 | 40 | 2 | 129 | 142 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -9 | 5 | 23 | 1 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -9 | 5 | 23 | 1 | 4 |
| 30 | 1 | 34 | 1 | 40 | 2 | 129 | 142 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -10 | 5 | 23 | 1 | 4 | 22 | 3 | -28 | 6 | 14 | 10 | -10 | 5 | 23 | 1 | 4 |

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respectively. These bond lengths agree with the lengths of the terminal and central C–C bonds, 1.354(3) and 1.409(3) Å, in 6a-thiophene (I). The average lengths for the equivalent bonds in VI are 1.376 and 1.406 Å, respectively.

The S(6a)–C(3a) bond length in the present structure, 1.742(5) Å, agrees closely with that of 1.748(3) Å in I and also with that of 1.744 Å in VI.

The lengths of the exocyclic C–C bonds (Fig. 1a), ranging from 1.512 to 1.527 Å, are quite normal for such single bonds.

The crystal structure of 1,6-dimethyl-3,4-trimethylene-6a-thiophene as seen along the c-axis is shown in Fig. 2. There are no intermolecular atomic distances shorter than corresponding van der Waals distance.

**EXPERIMENTAL**

The unit cell dimensions for crystals of 1,6-dimethyl-3,4-trimethylene-6a-thiophene were determined from high-order reflections on hk0 and 0kl Weissenberg photographs where sodium chloride powder lines had been superimposed for reference (c(NaCl) = 5.6396 Å). A least squares procedure on 56 measured 20-values gave a = 46.115(6) Å, b = 21.676(8) Å, and c = 5.825(14) Å.

Eight molecules per unit cell give a calculated density of 1.269 g/cm³ as compared with the density 1.28 – 1.30 g/cm³ found by flotation.

The intensities of the hk0 – hkl reflections were estimated visually from Weissenberg photographs taken with Ni-filtered CuKα radiation (μ = 23.7 cm⁻¹). 0kl reflections from the zero layer about a were used for scaling only.

A crystal with dimensions about 0.08 × 0.04 × 0.4 mm in the three axial directions was used for the intensity data collection. Lp corrections, and corrections for extended spots on upper layer Weissenberg films, were applied, but absorption corrections were not applied.

The scattering factors used for sulphur, nitrogen, carbon, and hydrogen in the structure factor calculations were those given in the *International Tables*. Final atomic coordinates from the least squares refinement are listed in Table 3, and the temperature parameters in Table 4.

An analysis of the thermal parameters of the S, N, and C atoms, assuming the whole molecule except the methyl groups a rigid body, was carried out according to the method of Schomaker and Trueblood. The libration tensor, L, arrived at is given in Table 5. Bond lengths, which have been corrected according to the libration tensor L, are listed in the first column of Table 1. The final list of structure factors is given in Table 6.
Acknowledgements. The authors are indebted to Dr. D. H. Reid, Department of Chemistry, The University, St. Andrews, Scotland, for providing a sample of 1,6-dimethyl-3,4-trimethylene-6a-thia-azophthene.

REFERENCES


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