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The Crystal and Molecular Structure of 2,5-Bis-(dicyanomethylene)-2,5-dihydrothiophene ($C_{10}H_2N_4S$)

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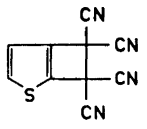
The main purpose of the present investigation has been to determine the molecular structure of a solid compound of the composition $C_{10}H_2N_4S$. The X-ray analysis has shown that the compound might be described as 2,5-bis-(dicyanomethylene)-2,5-dihydrothiophene. The symmetry is orthorhombic, space group *Pbnm* (No. 62). The unit cell contains four $C_{10}H_2N_4S$ units and has the dimensions $a = 10.969$ Å, $b = 14.074$ Å, $c = 6.473$ Å. The single crystal film data have been refined to a final R-factor of 6.5 %.

In the course of an investigation of the reactions of aromatic heterocyclic compounds with tetracyanoethylene oxide, Gronowitz and Uppström [1] discovered that the reaction with 2,3,5-tribromothiophene took an unexpected route. A yellow solid of composition $C_{10}HN_4BrS$ resulted. A solution of this compound in dioxane was treated with hydrogen in the presence of a Pd-catalyst and by means of this reaction the present compound $C_{10}H_2N_4S$ was obtained. Possible structural formulae for this compound are:



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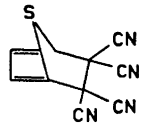

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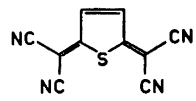

III

The present X-ray investigation was started to decide which of the above possibilities was correct.

STRUCTURE DETERMINATION

Cell dimensions and density. X-Ray powder diffraction photographs were recorded in a Guinier-Hägg focusing camera with Cu$K\alpha$ radiation. Potassium chloride was added as an internal standard. The following lattice parameters

Table 1. The first few lines of the X-ray powder photograph of 2,5-bis-(dicyanomethylene)-2,5-dihydrothiophene. Cu$K\alpha_1$ radiation was used and potassium chloride was added as an internal standard.

I_{obs}	$h\,k\,l$	$10^5 \sin^2\theta_{calc}$	$10^5 \sin^2\theta_{obs}$
m	110	790	793
vw	111	2 208	2 209
m	021	2 611	2 614
vw	140	5 288	5 286
m	301	5 854	5 854
vvw	231	6 082	6 084
m	311	6 145	6 153
w	112	6 461	6 457
w	141	6 697	6 702
vvw	321	7 045	7 052
vvw	410	8 197	8 189
m	340	9 246	9 230
vw	151	9 399	9 398
vw	411	9 612	9 605
vw	450	15 370	15 378

were obtained with the aid of least-squares calculations: $a = 10.969 \pm 0.003$ Å; $b = 14.074 \pm 0.004$ Å; $c = 6.473 \pm 0.003$ Å; $V = 999.3 \pm 0.6$ Å^3.

The observed and calculated $\sin^2\theta$-values of the first few lines in the powder photograph are given in Table 1. The density of the crystals was determined by flotation to be 1.32 g/cm^3; the calculated density, assuming 4 $C_{10}H_2N_4S$ molecules per unit cell, is 1.40 g/cm^3.

Single crystal work. Single crystals of $C_{10}H_2N_4S$ were kindly supplied by Dr. Uppström, Division of Organic Chemistry 1, University of Lund. The crystals form needles and a small single crystal was mounted in a Weissenberg camera with its needle axis as rotation axis. The layers $hk0 - hk5$ were registered using Ni-filtered CuK radiation and an integrating Weissenberg camera. The multiple film technique was used and the intensities were measured with the aid of a Nonius Mark II micro densitometer. The following conditions limiting possible reflections were found: hkl no conditions; $h0l$ $h + l = 2n$; $0kl$ $k = 2n$.

These conditions are characteristic of the space groups *Pbnm* (No. 62)* and $Pbn2_1$ (No. 33).* As seen from the following a plausible structure could be obtained assuming space group *Pbnm*.

The point positions of space group *Pbnm* are:

8(*d*): $\pm(x,y,z;\ x,y,\frac{1}{2}+z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z;\ \frac{1}{2}-x,\frac{1}{2}+y,z)$
4(*c*): $\pm(x,y,\frac{1}{4};\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{4})$
4(*b*): $0,\frac{1}{2},0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},0,0$
4(*a*): $0,0,0;\ 0,0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0$

Positions of the non-hydrogen atoms. The positions of the sulphur atoms were determined from three-dimensional Patterson functions, and as expected

* Orientation different from that given in the International Tables.

Table 2. Analysis of the weighting scheme used in the last cycle of least-squares refinement. The weighting factor $w=(4+|F_o|+0.03|F_o|^2)^{-1}$. The averages $w(|F_o|^2-|F_c|^2)^2=\overline{w\Delta^2}$ are normalized.

Interval $\|F_o\|$	$\overline{w\Delta^2}$	No. of reflections	Interval sin θ	$\overline{w\Delta^2}$	No. of reflections
0.0 – 10.5	0.95	34	0.00 – 0.43	0.81	95
10.5 – 12.0	1.03	35	0.43 – 0.54	0.61	60
12.0 – 13.5	1.08	35	0.54 – 0.62	0.84	60
13.5 – 15.6	1.06	35	0.62 – 0.69	0.80	50
15.6 – 17.7	0.77	35	0.69 – 0.74	0.62	30
17.7 – 20.1	0.81	35	0.74 – 0.78	0.44	17
20.1 – 22.2	0.96	35	0.78 – 0.83	0.63	15
22.2 – 25.9	0.79	36	0.83 – 0.86	0.83	9
25.9 – 32.4	0.90	35	0.86 – 0.90	1.04	12
32.4 – 104.8	1.66	36	0.90 – 0.93	3.39	3

the four sulphur atoms were found to occupy the point position 4(*c*). Signs for a sufficient number of reflections could be obtained from the positions of these atoms to determine the positions of all non-hydrogen atoms from a three-dimensional Fourier difference synthesis. All atoms were found to occupy

Table 3. Final positional and thermal parameters for 2,5-bis-(dicyanomethylene)-2,5-dihydrothiophene. The estimated standard deviations are given within brackets and refer to the last decimal places of the respective values. The thermal parameters of the sulphur and nitrogen atoms are given separately. The temperature factor expression used for these atoms is exp $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$. In the present case $\beta_{13}=\beta_{23}=0$ as all atoms are situated in the special point position 4(*c*).

Atom	*x*	*y*	*z*	*B* (Å²)
S	0.4520 (3)	0.5622 (2)	0.25	For β_{ij}, see below
N_1	0.7221(12)	0.3993 (8)	0.25	»
N_2	0.9005(13)	0.6755(11)	0.25	»
N_3	0.1323(12)	0.5110(10)	0.25	»
N_4	0.1361(11)	0.8308 (8)	0.25	»
C_1	0.3675(14)	0.6690 (7)	0.25	2.47(21)
C_2	0.4493(11)	0.7487 (9)	0.25	3.15(22)
C_3	0.5691(15)	0.7279 (8)	0.25	2.77(23)
C_4	0.5902(12)	0.6237 (7)	0.25	2.76(22)
C_5	0.2449(11)	0.6692 (9)	0.25	2.73(21)
C_6	0.1815(11)	0.7588 (8)	0.25	3.23(24)
C_7	0.1763(15)	0.5822(10)	0.25	4.40(30)
C_8	0.7002(12)	0.5814 (8)	0.25	3.33(23)
C_9	0.8082(16)	0.6309(10)	0.25	4.59(28)
C_{10}	0.7101(14)	0.4776 (8)	0.25	3.11(23)
H_1	0.419 (12)	0.820 (9)	0.25	2 (3)
H_2	0.643 (13)	0.374 (9)	0.25	4 (4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}
S	0.00628(29)	0.00263(13)	0.0161 (7)	0.00004(27)
N_1	0.0143 (20)	0.0061 (7)	0.0179(23)	0.0006 (10)
N_2	0.0101 (17)	0.0077 (9)	0.0573 (9)	−0.0020 (11)
N_3	0.0119 (17)	0.0058 (8)	0.0583 (8)	−0.0016 (9)
N_4	0.0114 (14)	0.0055 (7)	0.0269(32)	0.0013 (9)

the point position 4(*c*) and the molecule is thus planar by symmetry. A least-squares refinement was made, using at first isotropic temperature factors. At this stage the *R*-factor was 7.9 % for 351 reflections and 8.4 % for all observed 355 reflections. Anisotropic temperature factors were then introduced for the sulphur and nitrogen atoms. Simultaneously an overall scale factor was refined, obtained by fixing the interlayer scale factors to the values found in the last isotropic refinement. The *R*-factor changed to 6.8 % for 351 and to 7.3 % for 355 reflections.

Positions of the hydrogen atoms. The hydrogen atoms were assumed also to occupy the point position 4(*c*). A difference Fourier map was therefore made at $z = \frac{1}{4}$ and the geometrically expected positions for the two hydrogen atoms of the asymmetric part of the unit cell were compared to the positions of the highest peaks in the map. In this way trial positions were obtained for the hydrogen atoms. A new least-squares refinement was made and the final *R*-factor was 6.5 % for 351 and 6.8 % for 355 reflections. Individual weighting factors were applied to the $|F_o|$-values according to Cruickshank.

No effort was made to investigate if the real symmetry is $Pbn2_1$ instead of *Pbnm*, but it should be noted that the deviation from the centrosymmetric case, if any, must be very small. The final weight analysis is given in Table 2 and the final positional and thermal parameters are given in Table 3. Lists of observed and calculated structure factors are available on request from the Division of Inorganic Chemistry 2, Box 740, S-220 07 Lund 7, Sweden.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The numbering of the atoms of $C_{10}H_2N_4S$ used for the crystallographic description is given in Fig. 1a. Bond lengths and angles within a molecule are given in Figs. 1b and 1c. A survey of intramolecular distances and their e.s.d.'s is given in Table 4a.

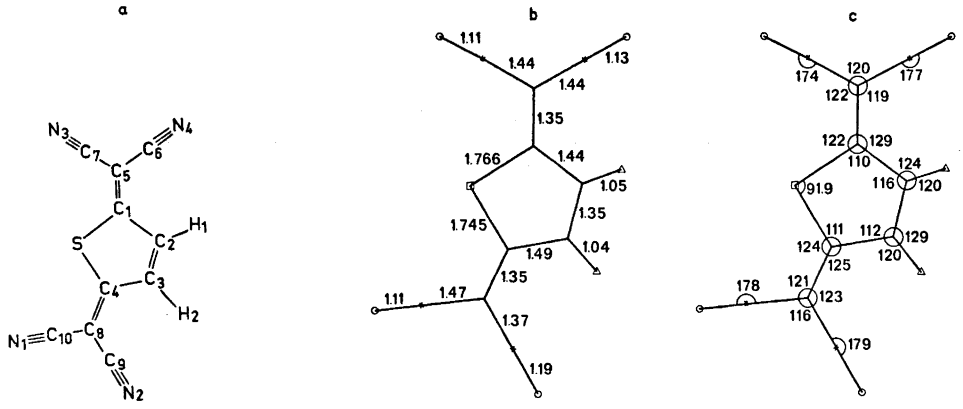

Fig. 1. a. Numbering of the atoms in the molecule of $C_{10}H_2N_4S$ used for the crystallographic description. b. Bond distances (Å) in the molecule of $C_{10}H_2N_4S$. E.s.d.'s for the distances given have values of 0.01 – 0.02 Å (*cf.* Table 4a). c. Angles within the molecule of $C_{10}H_2N_4S$. E.s.d.'s of the angles are about 1°.

Table 4a. Pertinent *intramolecular* distances for $C_{10}H_2N_4S$. E.s.d.'s are given within brackets.

Atoms	Distance (Å)	Atoms	Distance (Å)
$S-C_1$	1.766(12)	C_5-C_6	1.439(17)
$S-C_4$	1.745(13)	C_5-C_7	1.438(19)
C_1-C_2	1.436(18)	C_6-N_4	1.130(17)
C_1-C_5	1.345(17)	C_7-N_3	1.112(20)
C_2-H_1	1.05 (12)	C_8-C_9	1.374(21)
C_2-C_3	1.347(21)	C_8-C_{10}	1.466(16)
C_3-H_2	1.04 (14)	C_9-N_2	1.192(23)
C_3-C_4	1.485(16)	$C_{10}-N_1$	1.110(16)
C_4-C_8	1.345(18)		

As seen from Fig. 1a the molecules in the crystal structure of $C_{10}H_2N_4S$ correspond to structural formula III and the substance may therefore be described as 2,5-bis-(dicyanomethylene)-2,5-dihydrothiophene. The e.s.d.'s in the distances and angles are of the order of 0.01 – 0.02 Å and 1°, respectively, and a detailed discussion of the bonding system can therefore not be made. However, the bond distances and angles agree fairly well with the values that could be expected from structural formula III. If the assumed space group *Pbnm* is the correct one, the molecule is, as mentioned before, planar by symmetry. It is seen from Figs. 1a and 1b that the molecule has a pseudo-mirror plane running through the sulphur atom and through the midpoint of the line C_2-C_3.

The packing of the molecules in the crystal structure is indicated in Fig. 2, which shows the projection of the cell content on the *ab* plane. Molecules at $z=\frac{1}{4}$ are indicated by full-drawn and molecules at $z=\frac{3}{4}$ by dashed lines. Intermolecular distances less than 3.50 Å are summarized in Table 4b.

Table 4b. Intermolecular distances less than 3.50 Å in the crystal structure of $C_{10}H_2N_4S$. Carbon atoms in a molecule which are also bonded to hydrogen atoms are indicated by C(H). E.s.d.'s are given within brackets.

Atoms	Distance (Å)	Atoms	Distance (Å)
$S-N_4$	3.40 (1)	N_2-N_4	3.39 (2)
N_1-H_2	2.30(14)	N_2-N_3	3.44 (2)
$N_1-C_3(H)$	3.33 (2)	$N_2-2C_2(H)$	3.45 (1)
N_1-2C_5	3.40 (1)	N_3-H_1	2.75(12)
N_1-N_2	3.42 (2)	N_4-2C_4	3.34 (1)
N_1-2C_7	3.43 (1)	$N_4-2C_3(H)$	3.42 (1)
N_2-2H_1	3.24 (1)	$C_3(H)-2C_6$	3.47 (1)
N_2-C_6	3.30 (2)	C_6-2H_2	3.30 (3)
N_2-C_7	3.30 (2)	$C_{10}-H_2$	3.28(14)

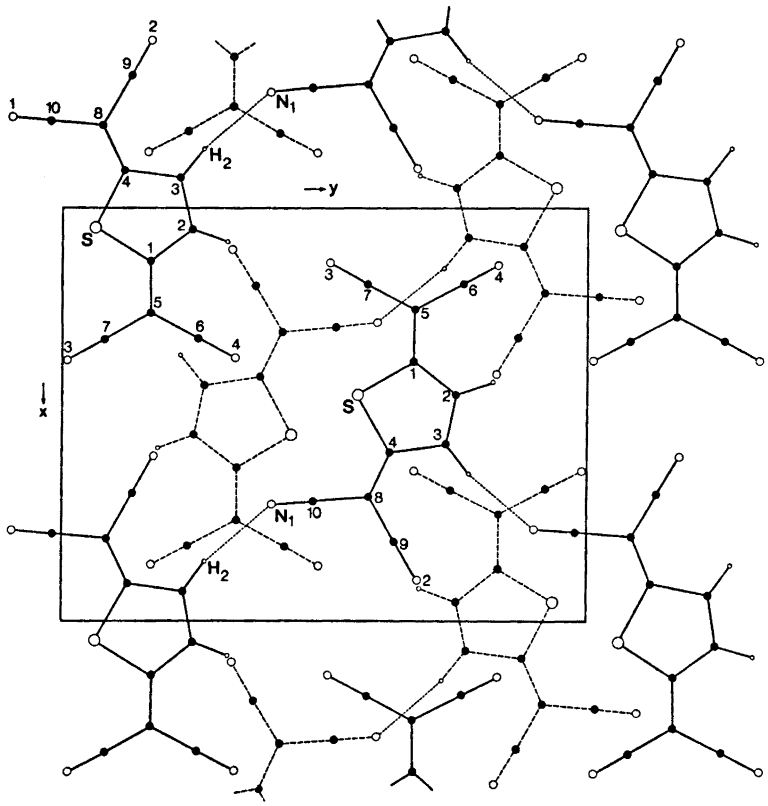

Fig. 2. Projection of the cell content of one unit cell of $C_{10}H_2N_4S$ on the *ab* plane. Large, medium, and small unfilled circles denote S, N, and H atoms, respectively. Filled circles denote C atoms. Molecules at $z = \frac{1}{4}$ are denoted by full-drawn lines, molecules at $z = \frac{3}{4}$ by dashed. Short (C)H···N distances are indicated. Numbering of the atoms, *cf.* Fig. 1a.

All contacts seem to be of the van der Waals type, though a few of them are somewhat short. Witt [2] states that the C···N distance of a van der Waals contact is 3.40 Å, whereas similar contacts in the present compound are slightly shorter (3.30 Å, *cf.* Table 4b). The $N_1 - C_3(H)$ distance (*cf.* Table 4b) of 3.33 Å is shorter than expected, but $N - C(H_2)$ distances of similar lengths have been observed in other cyano compounds, *e.g.* 3.31 and 3.35 Å in methylene dithiocyanate.[3] One of the two N – H distances given in Table 4b is quite short, *viz.* the $H_2 - N_1$ distance of 2.30 Å. These distances are indicated in Fig. 2. (C) – H···O distances as short as 2.20 Å are, however, regarded as van der Waals contacts [4] and by analogy there accordingly seems to be no reason to postulate a (C) – H···N hydrogen bond in the present compound.

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