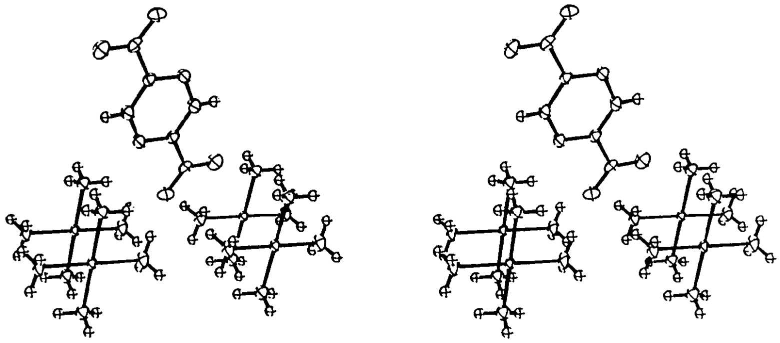

Fig. 2. Partial packing diagram.

Fig. 1 also shows (dashed lines) some of the interionic distances between possible hydrogen-donor atoms, N(1) and N(2), and hydrogen-acceptor atoms, O(1), O(2) and N(3); the dashed lines represent all distances less than 3·3 Å. In addition Fig. 2, a partial packing diagram, shows the relative orientation of the hydrogen atoms attached to N(1) and N(2) and gives a clearer indication of possible hydrogen bonds.

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References

Brown, S. B. & Dewar, M. J. S. (1973). Private communication.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1974). B**30**, 1372

The Crystal Structure of Tetra-(2-thienyl)silane

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Abstract. $(C_4H_3S)_4Si$, tetragonal, $P\bar{4}2_1c$, $a=11\cdot368$ (9), $c=6\cdot535$ (5) Å, $Z=2$, $D_c=1\cdot42$, $D_o=1\cdot42$ (1) g cm^{-3} (by flotation in aqueous KI solution). The structure is orientationally disordered. Each thienyl ring has two conformations rotated 179° with respect to the Si–C(1) bond. The structure was refined by rigid-body least-squares methods to $R=9\cdot1$ %.

Introduction. Colorless, elongated needle crystals of tetra-(2-thienyl)silane were grown by slow evaporation of a benzene solution from a sample kindly provided by Dr L. Spialter of the Air Force Materials Laboratory, Wright–Patterson Air Force Base, Ohio. A single crystal of approximate dimensions $0\cdot12\times0\cdot12\times0\cdot25$ mm was used. From indexed Weissenberg photographs the systematic absences $h00$ for h odd and hhl for l odd uniquely determined the space group to be $P\bar{4}2_1c$.

Three-dimensional intensity data were collected on a Picker FACS-1 diffractometer equipped with a scintillation counter and pulse-height analyzer; zirconium-filtered Mo $K\alpha$ ($\lambda=0\cdot71069$ Å) radiation was used. In total, 1159 reflections out to 55° in 2θ were measured using the θ–2θ scan mode. In $P\bar{4}2_1c$ the hkl and khl reflections are equivalent by symmetry for $h\neq k$. Averaging of the corresponding equivalent hkl and khl pairs yielded 540 reflections. There were an additional 79 hhl type reflections to give a total of 619 independent reflections. Of these, 497 had $I>\sigma(I)$ and were used in subsequent calculations.

The space group $P\bar{4}2_1c$ has eight general positions which requires that the two silicon atoms per unit cell be constrained at special positions of $\bar{4}$ symmetry. There is only one thienyl ring in the asymmetric unit. An electron-density map phased by the silicon atom revealed the essential features of the independent thienyl ring. However, attempts to improve the positions of the ring atoms with a series of difference Fourier syntheses proved unsuccessful. Each successive map gave consistently unrealistic bond distances within the thienyl ring which suggested the presence of disorder. An isotropic full-matrix least-squares calculation at this juncture verified the existence of disorder in the structure. In particular the C(1)–S and C(1)–C(2) distances both refined to 1·64 Å while the temperature factors for C(2) and sulfur became negative and unreasonably large, respectively. This result is what may be expected for a disordered structure. A further refinement allowing the atom occupancy factors for the ring atoms to vary also led to occupancy factors near 0·5 for C(2) and S although the C(1)–S and C(1)–C(2) distances remained essentially the same. The conventional R value, $R=\sum||F_o|-|F_c||/\sum|F_o|$, could not be reduced below 30%. These results indicated an orientational disorder wherein the thienyl ring has two equivalent conformations rotated 180° with respect to the Si–C(1) bond.

At this point a rigid-body refinement procedure following the method given by Scheringer (1963) was initiated. The asymmetric unit in our disordered model was taken to consist of a silicon atom and two thienyl rings (rings A and B) rotated by 180°. To insure the correct number of atoms in the unit cell, the occupancy factors for all ring atoms were fixed at 0·5. In this approach rings A and B were treated as rigid groups. The geometry of each thienyl ring was fixed to be that found in free thiophene (Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen, 1961). In the rigid-group refinement the orientation and origin of each thienyl ring were allowed to vary and were defined by six parameters: x_c, y_c, z_c, the origin of the rigid group which was taken at the corresponding C(1) position in each ring and χ_1, χ_2, χ_3, the three orientational angles which bring about alignment of the internal rigid-group coordinate system with an external-coordinate system (Scheringer, 1963). The three independent hydrogen atoms in each ring were placed in theoretical positions calculated assuming a C–H length of 1·08 Å. The silicon atom was allowed to refine anisotropically, but only an over-all isotropic temperature factor was refined for each ring. All the atoms in each ring were assigned the corresponding ring over-all temperature factor. The structure was refined by full-matrix least-squares methods; the quantity minimized was $\sum w(|F_o|-|F_c|)^2$ where the weight, w, applied to each observation was taken to be $1/\sigma^2(F)$. The $\sigma(F)$ were obtained from counting statistics (Stout & Jensen, 1968). The final refinement results in a conventional R value of 9·1% and a weighted R value, $\sum w(|F_o|-|F_c|)^2/w\sum|F_o|^2$, of 8·9%. The standard deviation in an observation of unit weight was 2·41.

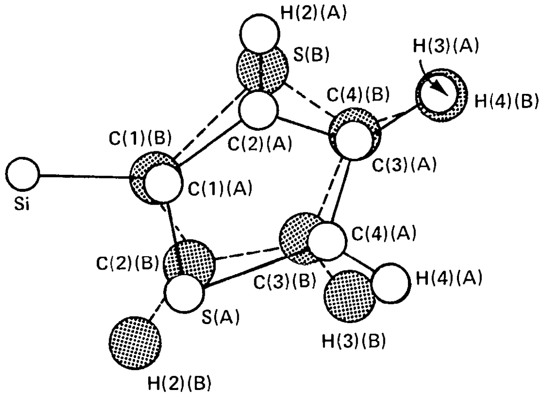

Fig. 1. The disordered model for tetra-(2-thienyl)silane. Only the asymmetric unit is shown.

There were no significantly large positive or negative electron-density peaks in a final difference Fourier synthesis, which indicates that the disordered model is a reasonable approximation to the structure.

The atomic scattering factors of silicon, carbon and sulfur were taken from Cromer & Waber (1965) and for hydrogen from *International Tables for X-ray Crystallography* (1968). In addition to local programs for the IBM 370/165 computer, the programs used in this determination were *FORDAP* (Zalkin, 1974), *ORFLS* (Busing, Martin & Levy, 1962), *ORTEP* (Johnson, 1965), and *PLANET* (Smith, 1964).

The results from the rigid-group refinement are presented in Tables 1 and 2 and a listing of observed and calculated structure-factor amplitudes is available.*

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30349 (4pp.). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final parameters from the rigid-group refinement*

For silicon the anisotropic temperature factor is in the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.
For rings A and B the overall group isotropic temperature factors, B, are given. The angles χ_1, χ_2, χ_3 are given in radians.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	0	0	0	0·0039 (3)	0·0039 (3)	0·0164 (8)	0	0	0

	x_c	y_c	z_c	B	χ_1	χ_2	χ_3
Ring A	0·1317 (9)	0·0212 (11)	0·1714 (24)	4·95 (11)	−0·014 (8)	0·015 (7)	0·035 (10)
Ring B	0·1389 (9)	0·0099 (10)	0·1583 (19)	3·21 (8)	0·021 (6)	0·003 (8)	0·026 (8)

Thiophene parameters used in the rigid-group refinement (for both A and B rings)

C(1)–S, C(4)–S	1·714 Å	C(2)–C(1)–S, C(3)–C(4)–S	111°28′
C(1)–C(2), C(3)–C(4)	1·370	C(1)–C(2)–C(3), C(2)–C(3)–C(4)	112°27′
C(2)–C(3)	1·423	C(1)–S–C(4)	92°10′

Table 2. *Derived thienyl ring atom parameters from the rigid-group refinement* (× 10^4)

	x	*y*	*z*
C(1) (*A*)	1317	212	1714
C(2) (*A*)	1503	1065	3158
C(3) (*A*)	2619	957	4127
C(4) (*A*)	3255	24	3395
S(*A*)	2500	−722	1533
H(2) (*A*)	873	1745	3522
H(3) (*A*)	2930	1545	5307
H(4) (*A*)	4123	−212	3926
C(1) (*B*)	1378	99	1583
C(2) (*B*)	2360	−616	1468
C(3) (*B*)	3262	−270	2854
C(4) (*B*)	2955	696	3987
S(*B*)	1574	1186	3372
H(2) (*B*)	2432	−1357	441
H(3) (*B*)	4095	−719	2962
H(4) (*B*)	3514	1099	5125

Discussion. Although the disorder precluded determination of individual atomic coordinates, the rigid-group analysis gave conclusively the molecular orientation in the unit cell and the conformation of the thienyl ring. The results from the refinement are in excellent agreement with the chosen disordered model. Ring *A* is very nearly coplanar with ring *B*: the angle between them is 179·1°. The disordered model and the molecular configuration are shown in Figs. 1 and 2. The Si–C(1) (*A*) and Si–C(1) (*B*) distances are 1·885 (3) and 1·890 (3) Å, which compare with the Si–C distance of 1·872 (7) Å found in $(C_6H_5)_4Si$ (Glidewell & Sheldrick, 1971).

Comparison with tetraphenylsilane is facilitated by expressing the tetra-(2-thienyl)silane structure in terms of three angular parameters which concisely fix the orientation and conformation in the unit cell. These parameters are: φ, the angle between the projection of the M–C(1) bond on the *ab* plane and the *a* axis; this angle defines the rotation of the molecule about the *c* axis; α, the angle between the thienyl ring plane and the C(1)($\bar{x}\bar{y}z$)–Si–C(1) plane; this angle defines the rotation of the thienyl ring about the Si–C(1) bond (a clockwise rotation is taken as positive looking from the thienyl ring to the silicon atom); θ, the C(1) ($\bar{x}\bar{y}z$)–Si–C(1) valency angle. In tetra-(2-thienyl)silane $\varphi=9{\cdot}1°$, $\alpha=58{\cdot}8°$, $\theta=107{\cdot}1°$ for ring *A* and $\varphi=4{\cdot}1°$, $\alpha=55{\cdot}4°$, $\theta=113{\cdot}6°$ for ring *B*. The mean values $\varphi=6{\cdot}6°$, $\alpha=57{\cdot}1°$, $\theta=110{\cdot}3°$ compare well with 7·1°, 52·4° and 107·3°, respectively, found in tetraphenylsilane (Glidewell & Sheldrick, 1971). The similarity in the two structures indicates that the thienyl ring provides intra- and intermolecular contacts essentially comparable with the phenyl ring (Karipides & Haller, 1972; Karipides, Forman, Thomas & Reed, 1974). This is a further example of the apparent ease with which thiophene derivatives crystallize in the same way as the benzene analogs. The situation with disordered thiophenchromium tricarbonyl as compared with benzenechromium tricarbonyl as well as crystalline thiophene and benzene have been discussed by Bailey & Dahl (1965).

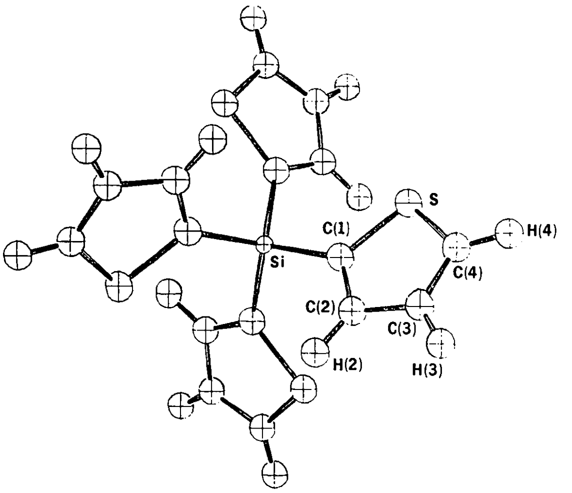

Fig. 2. Molecular configuration of tetra-(2-thienyl)silane. For clarity only ring *A* is shown.

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References

Bailey, M. F. & Dahl, L. F. (1965). *Inorg. Chem.* **4**, 1306–1314.

Bak, B., Christensen, D., Hansen-Nygaard, L. & Rastrup-Andersen, J. (1961). *J. Mol. Spectrosc.* **7**, 58–63.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Glidewell, C. & Sheldrick, G. M. (1971). *J. Chem. Soc.* (*A*), pp. 3127–3129.

International Tables for X-ray Crystallography (1968). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794 (revised 1970), Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Karipides, A., Forman, C., Thomas, R. H. P. & Reed, A. T. (1974). *Inorg. Chem.* In the press.

Karipides, A. & Haller, D. A. (1972). *Acta Cryst.* B**28**, 2889–2892.

Scheringer, C. (1963). *Acta Cryst.* **16**, 546–550.

Smith, D. L. (1964). *PLANET*, Ph.D. Thesis, Univ. of Wisconsin, Madison, Wisconsin.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Crystal Structure Determination*, pp. 454–458. London: Collier-Macmillan.

Zalkin, A. (1974). Unpublished.