Mackenzie, G. A., Arthur, J. W. & Pawley, G. S. (1977). *J. Phys. C*, **10**, 1133–1149.
Mackenzie, G. A., Pawley, G. S. & Dietrich, O. W. (1975). *Acta Cryst.* A**31**, 851–852.
Pawley, G. S. (1972). *Advances in Structure Research by Diffraction Methods*. Vol. 4, edited by W. Hoppe & R. Mason. Oxford: Pergamon Press.
Pawley, G. S. & Dietrich, O. W. (1975). *J. Phys. C*, **8**, 2549–2558.
Pawley, G. S., Mackenzie, G. A. & Dietrich, O. W. (1977). *Acta Cryst.* A**33**, 142–145.
Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
Zallen, R., Griffiths, C. H., Slade, M. L., Hayek, M. & Brafman, O. (1976). *Chem. Phys. Lett.* **39** (1), 85–89.

Acta Cryst. (1978). B**34**, 1923–1927

The Crystal Structures of Some Oligomeric Conjugated Dithienylalkapolyenes

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(*Received* 11 *August* 1977; *accepted* 6 *December* 1977)

Crystals of *trans*-1,4-di(2-thienyl)-1,3-butadiene, $C_{12}H_{10}S_2$, monoclinic, space group $P2_1$, and *trans*-1,6-di(2-thienyl)-1,3,5-hexatriene, $C_{14}H_{12}S_2$, triclinic, space group $P\bar{1}$, have the lattice parameters: a = 11·683 (6), b = 7·559 (4), c = 6·333 (3) Å, β = 104·52 (2)°; and a = 9·736 (2), b = 10·312 (4), c = 6·338 (3) Å, α = 92·40 (2), β = 96·27 (2), γ = 100·11 (2)°. The number of formulae per unit cell is two in both cases. The structures were determined by direct methods and refined by the full-matrix least-squares method using three-dimensional X-ray data. In both cases the final residual R was 0·039. Bond lengths and angles in the thiophene rings are compared with those in unsubstituted thiophene. The crystal structures are two-layered and controlled by intermolecular electrostatic attraction between protons and delocalized π electrons.

Introduction

The crystal structures of two oligomeric conjugated dithienylalkapolyenes, *trans*-1,4-di(2-thienyl)-1,3-butadiene (A) and *trans*-1,6-di(2-thienyl)-1,3,5-hexatriene (B), are reported here; that of *trans*-1,2-di(2-thienyl)ethylene has already been published (Ruban & Zobel, 1975). Besides the general crystallographic interest which these structures have (they can be compared to those of stilbene and related compounds) there is special interest in them since they have semiconducting properties and, because of their chemical simplicity, may serve for basic investigations in the field of organic semiconductors. Both compounds were synthesized by Bohn (1975). Crystals are transparent and colorless (A) or yellow (B).

Experimental

Platelet-shaped crystals were grown by solvent evaporation from methanol solutions (A) or by sublimation at a temperature of 185 °C under N_2 gas (B). The space groups determined from Weissenberg photographs were $P2_1$ for A and $P1$ or $P\bar{1}$ for B. Densities were measured by the neutral buoyancy method. Additional crystal data are given in Table 1. Crystal A was elongated in the [010], crystal B in the [100] direction. The crystal volumes were 0·016 (A) and 0·0024 mm³ (B), and the platelet thicknesses 0·07 (A) and 0·02 mm (B).

The intensity data were collected at room temperature with Cu $K\alpha$ radiation on an automatic four-circle single-crystal X-ray diffractometer, applying the

Table 1. *Crystal data not given elsewhere*

	A	*B*
Formula	$C_{12}H_{10}S_2$	$C_{14}H_{12}S_2$
M_r	218·4	244·38
Unit-cell volume, V	541·4 (8) Å³	621·5 (7) Å³
Number of formula units per asymmetric volume	1	2/2
Density calculated [measured], ρ	1·340 (2) [1·3] g cm⁻³	1·306 (2) [1·3] g cm⁻³
Number of electrons per unit cell, $F(000)$	228	256
Linear absorption coefficient for Cu $K\alpha$ radiation, μ	38·2 cm⁻¹	34·65 cm⁻¹

θ–2θ scan technique. Integrated intensities of reflections belonging to a unique set with $0 < (\sin\theta)/\lambda < 0{\cdot}61$ Å^{-1} were obtained. 1197 (*A*) and 2010 (*B*) reflections were recorded of which 35 (*A*) and 297 (*B*) were regarded as unobserved ($I < 2\sigma$). Data reduction was carried out, as were most of the computations mentioned below, by means of the XRAY system 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on CDC Cyber 72 and 175 computers.

Determination and refinement of the structures

Both structures were solved by direct methods and Fourier syntheses. The scattering factors applied for H were those of Stewart, Davidson & Simpson (1965) and for C and S those of Cromer & Mann (1968).

For the structure of *A*, the statistics and distribution of the normalized structure amplitudes strongly favored noncentrosymmetry. The successful three-dimensional *E* map showed all C and S atoms. The *y* coordinate of S(1) was used to fix the cell origin on the monoclinic axis, while all other atomic parameters and one *F* scale factor were refined by full-matrix least-squares calculations and used to compute a difference Fourier synthesis map which revealed seven of the ten H atoms. Successive least-squares-refinement runs, including constant anomalous-dispersion corrections to the scattering factors of S and C atoms taken from *International Tables for X-ray Crystallography* (1974), and difference Fourier syntheses gave indications for positioning the remaining three H atoms at somewhat displaced sites. The conventional *R* was 0·054 at this stage. An absorption correction of the reflection intensities was carried out (maximum correcting factor: 3·91) which together with the weighting scheme $1/\sigma^2(I)$ resulted in least-squares refinement cycles converging at an *R* of 0·039 with final parameter shifts less than one tenth of the parameter standard deviations and improved H atom positions. In order to check the absolute configuration the *y* coordinate of all atomic positions was inverted. Least-squares refinement now ended at a higher *R* value and the Hamilton test gave a clear preference for the first choice. Fig. 1 represents a line diagram of the molecule, giving the atom numbering and bond lengths and angles. The final positional parameters of the 24 atoms are listed in Table 2.*

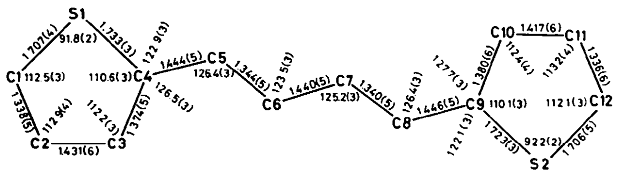

Fig. 1. Bond lengths (Å) and angles (°) of *trans*-1,4-di(2-thienyl)-1,3-butadiene with the H atoms omitted, molecule *A*.

Structure *B* was solved by the multisolution method with the fully automatic program *MULTAN* (Germain, Main & Woolfson, 1971). Here the statistics and distribution of the *E*'s were definitely in favor of an inversion center as part of the space-group symmetry. The 300 strongest *E* values ($E > 1{\cdot}44$) were used to produce eight sets of phased amplitudes, of which one had a highest figure of merit of 1·084. The corresponding *E* map clearly represented the actual structure, revealing all 16 independent non-hydrogen atoms. It showed that there are two symmetrically independent molecules in the unit cell, referred to as molecules *B*1 and *B*2, occupying two nonequivalent inversion centers of the crystal structure so that two unique, nonattached half molecules are in the asymmetric unit. This structural specialty often occurs in crystals of similar flat molecules, *i.e.* stilbene (Hoekstra, Meertens & Vos, 1975), diphenyldiacetylene (Wyckoff, 1971), and 2,5-distyrylpyrazine (Sasada, Shimanouchi, Nakanishi & Hasegawa, 1971). The intensity data were corrected for

Table 2. *Final positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *with standard deviations derived from the least-squares refinement for trans*-1,4-*di*(2-*thienyl*)-1,3-*butadiene*

	x	*y*	*z*
S(1)	−1803 (1)	1100 (–)	2098 (1)
S(2)	4401 (1)	3126 (2)	70 (1)
C(1)	−2591 (3)	1278 (6)	4023 (6)
C(2)	−1979 (3)	2077 (6)	5842 (6)
C(3)	−825 (3)	2623 (5)	5715 (6)
C(4)	−594 (3)	2161 (4)	3765 (5)
C(5)	498 (3)	2447 (5)	3138 (6)
C(6)	800 (3)	1728 (4)	1413 (5)
C(7)	1907 (3)	2075 (5)	880 (5)
C(8)	2236 (3)	1396 (5)	−833 (5)
C(9)	3305 (3)	1811 (4)	−1489 (5)
C(10)	3596 (4)	1324 (6)	−3390 (7)
C(11)	4688 (3)	2052 (7)	−3549 (7)
C(12)	5209 (3)	3042 (6)	−1830 (7)
H(1)	−340 (5)	78 (6)	369 (8)
H(2)	−221 (5)	241 (9)	684 (9)
H(3)	−41 (5)	306 (9)	656 (9)
H(5)	101 (4)	344 (6)	402 (7)
H(6)	27 (4)	90 (7)	50 (6)
H(7)	247 (4)	281 (7)	195 (8)
H(8)	177 (4)	77 (7)	−162 (8)
H(10)	322 (4)	82 (6)	−418 (7)
H(11)	510 (7)	180 (10)	−470 (10)
H(12)	581 (4)	357 (6)	−165 (7)

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* Lists of structure factors and thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33313 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

absorption by a program according to Burnham (1966) (maximum correcting factor: 2·03) and the final convergent least-squares refinement with nine scale factors, dispersion corrections and unit weights reached an R of 0·039. Fig. 2 gives the atom numbering and bond lengths and angles of the two molecules. Table 3 lists the final positional parameters of the 28 unique atoms.*

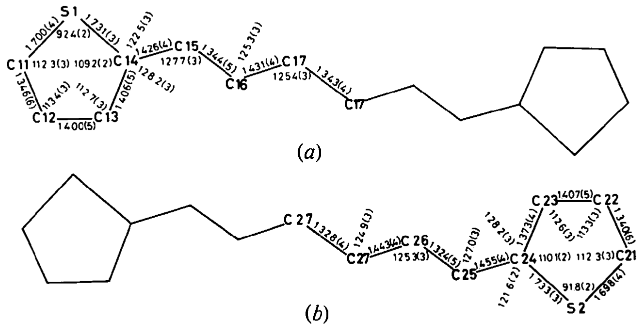

Fig. 2. Bond lengths (Å) and angles (°) of *trans*-1,6-di(2-thienyl)-1,3,5-hexatriene with the H atoms omitted. (*a*) Molecule *B*1, (*b*) molecule *B*2.

Table 3. *Final positional parameters* (×10⁴, *for* H ×10³) *with standard deviations derived from the least-squares refinement for trans-*1,6-*di*(2-*thienyl*)-1,3,5-*hexatriene*

	x	*y*	*z*
S(1)	6162 (1)	2147 (1)	5065 (1)
C(11)	5553 (4)	1386 (3)	2627 (6)
C(12)	6569 (4)	1434 (3)	1337 (6)
C(13)	7883 (4)	2099 (3)	2290 (6)
C(14)	7850 (3)	2576 (3)	4390 (5)
C(15)	8966 (4)	3343 (3)	5802 (5)
C(16)	8890 (3)	3910 (3)	7724 (5)
C(17)	10040 (3)	4705 (3)	9050 (5)
H(11)	458 (4)	98 (3)	228 (5)
H(12)	637 (4)	120 (4)	−21 (7)
H(13)	847 (4)	223 (3)	178 (5)
H(15)	972 (4)	347 (3)	531 (5)
H(16)	800 (3)	385 (3)	825 (4)
H(17)	1092 (3)	481 (3)	862 (5)
S(2)	7764 (1)	8868 (1)	4557 (1)
C(21)	8486 (4)	9565 (4)	6992 (6)
C(22)	8487 (4)	8675 (4)	8473 (6)
C(23)	7899 (3)	7380 (4)	7667 (5)
C(24)	7442 (3)	7313 (3)	5531 (5)
C(25)	6721 (3)	6164 (3)	4183 (5)
C(26)	6094 (3)	6155 (3)	2219 (5)
C(27)	5344 (3)	4996 (3)	964 (5)
H(21)	888 (4)	1039 (4)	706 (6)
H(22)	882 (4)	883 (3)	992 (6)
H(23)	787 (3)	676 (3)	836 (5)
H(25)	668 (4)	539 (3)	490 (6)
H(26)	612 (3)	697 (3)	155 (5)
H(27)	535 (3)	413 (3)	168 (5)

Results and discussion

The four independent thiophene rings of the two structures are in good agreement with each other. They are all monosubstituted in the same manner and their dimensions deviate systematically and significantly from those of unsubstituted thiophene (Table 4). The results of Ruban & Zobel (1975) and Zobel (1976) relating to thiophene rings in equivalent molecular positions do not fit in so well, obviously because of their lower accuracy. Domenicano, Vaciago & Coulson (1975) and Domenicano & Vaciago (1976) discussed the conjugative effects of some benzene-ring substituents on the ring geometry. The thiophene-ring distortions are analogous to the benzene-ring distortions induced by a substituent with a neighboring C atom. In solution the molecules *A* and *B* are planar to maximize the overlap of atomic π orbitals and thereby the delocalization energy of the π electrons. This was shown by Kossmehl, Bohn & Broser (1976) with spectroscopic data and MO calculations. In the crystals the molecules are still approximately planar. The bond lengths show that the conjugation is strongest in crystal molecule *B*1. The acute angles between the ring planes

Table 4. *Average bond-parameter shifts Δ in the monosubstituted thiophene rings*

Thiophene bond	Bond length of unsubstituted thiophene*	Δ
S–C(4)	1·718 Å	+0·012 (4) Å
S–C(1)	1·718	−0·015 (4)
C(4)–C(3)	1·352	+0·031 (13)
C(1)–C(2)	1·352	−0·012 (4)
C(2)–C(3)	1·455	−0·041 (12)

Internal angle at	Bond angle of unsubstituted thiophene*	Δ
S	91·3°	+0·8 (3)°
C(4)	112·6	−2·6 (5)
C(1)	112·6	−0·3 (1)
C(2)	111·8	+1·4 (2)
C(3)	111·8	+0·7 (2)

* From Bak, Christensen, Rastrup-Andersen & Tannenbaum (1956).

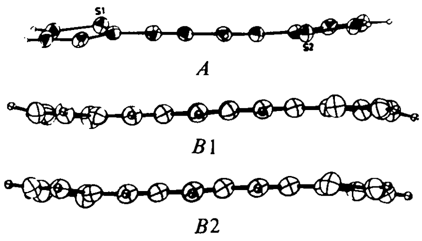

Fig. 3. The three molecules viewed 'from the side' to show their crystal-field twistings.

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* See footnote on p. 1924.

and the hexatriene plane are 9·5° in molecule *B*2, but only 6·2° in molecule *B*1. The corresponding angles in molecule *A* are 11·8 and 8·4°. Fig. 3 shows these crystal-field torsions of the thiophenes from the polyene groups, which destroy the symmetry of the whole molecule (*A*) or a part of it (*B*). The ring-atom distances from the ring planes are less than 0·008 Å for *A*, 0·004 Å for *B*1 and 0·002 Å for *B*2. The four butadiene C atoms of molecule *A* all lie about 0·0026 Å away from their common plane. Molecule *B*1 is apparently least disturbed by crystal-field effects; therefore, the results obtained here fit best the conditions of the free molecule. The conjugation between the hexatriene and the ring parts of the molecule shortens the distance between the ring C and the substituent C atom. The *s* character of the hybrid orbital of the ring C, pointing in the outward bond direction, is thereby strengthened and consequently the *p* character of the two other hybrid orbitals in peripheral directions is also strengthened. As a result the endocyclic angle at C(4) is closed up and the peripheral bond distances of the atom are increased. A number of different molecules can be cited where crystallographic investigation has brought similar results: stilbene (Hoekstra *et al.*, 1975), 2,5-distyrylpyrazine (Sasada *et al.*, 1971), bis(2-thienyl)methane (Towns & Simonsen, 1975), and 2,5-distyrylthiophene and 2,5-bis(2-thienylvinyl)thiophene (Zobel & Ruban, 1978; partly in disagreement).

The packing of the molecules in the two structures is apparently governed by a special kind of electrostatic intermolecular attraction, which results from the presence of protons in one outer area of the molecule and delocalized π electrons in another. Figs. 4 and 5 present stereodrawings of the structure packings.

The structures are two-layered. Each layer is formed by identical molecules. From Fig. 4 it can be derived that the protons, which are arranged fringe-like around the long, flat molecule, on either side of a molecule *A* are near π orbital areas of neighboring molecules in the next crystal layers. The same observation is made for structure *B* (Fig. 5). Here it looks as if this attraction is also effective between neighboring molecules of the same layer, giving the specific overlap. It can now be understood that the structures are two-layered and that the molecules in both lattices have a unique general direction. The molecule planes in the two layers approach a vertical orientation with respect to each other. The same features are shown by the crystal structures of 1,4-bis(2-thienylvinyl)benzene (Zobel, 1976), 2,5-distyrylthiophene and 2,5-bis(2-thienylvinyl)thiophene (Zobel & Ruban, 1978), and 2,5-distyrylpyrazine (Sasada *et al.*, 1971). This seems to support the significance of intermolecular attraction, described above, in the formation of crystal structures. The structure of *trans*-1,2-di(2-thienyl)ethylene (Ruban & Zobel, 1975) also has this particular two-layer packing, though with somewhat differing main molecule directions for steric reasons; Fig. 6 shows this in a stereodrawing. Stilbene follows the same packing principle (Hoekstra *et al.*, 1975); here the inclination between the molecule directions in the two layers is

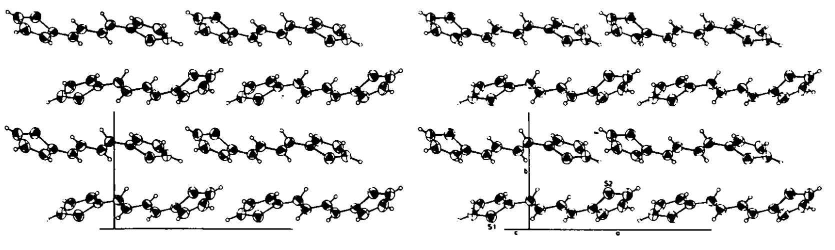

Fig. 4. Stereodrawing of the packing (in two directions) of crystal *A*.

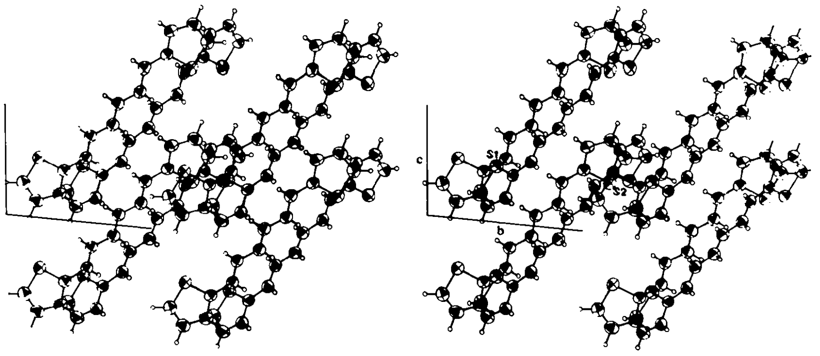

Fig. 5. Stereodrawing of the packing (in two directions) of crystal *B*.

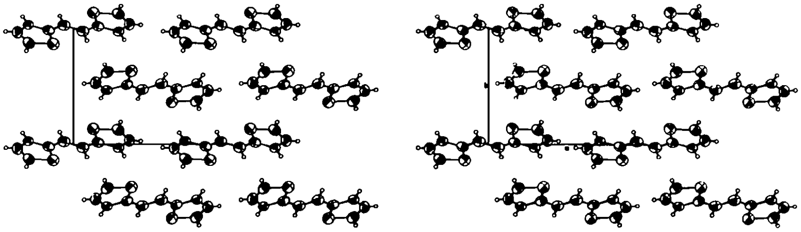

Fig. 6. Stereodrawing of the packing (in two directions) of the *trans*-1,2-di(2-thienyl)ethylene crystal.

greater and the special intermolecular attraction is apparently effective in three nearly perpendicular directions, possibly because of weaker conjugation. Tolane (Samarskaya, Myasnikova & Kitaigorodskii, 1969) and diphenyldiacetylene (Wyckoff, 1971) have the same structure. Even when looking at the packing of orthorhombic solid benzene (Wyckoff, 1969), which has four molecules with different orientations, it is easy to recognize the presence of intermolecular attraction between outer protons and delocalized π electrons.

In most cases the space group belongs to the monoclinic system, the monoclinic axis comprising a twofold screw axis. This axis is the normal to the layer planes. In crystal *A* the unique molecule direction is within the layer planes but not in the axis direction. The angle between the molecule planes in the two layers is 65·2°, giving a value of 32·6° for the angles of these planes with the *ac* plane to which the layers are parallel. In crystal *B* the unique molecule direction forms an angle of 33·2° with the layer planes which are parallel to the *ac* plane. The planes through the two independent molecules form an angle of 67·8°; this value is close to the corresponding one for *A*.

As far as the intermolecular distances are concerned, there is not a single one in either structure that is shorter than the relevant van der Waals distance, although of course many come close to it. The shortest S—S distance may be of interest; in crystal *A* it is 3·750 (1) Å and in crystal *B* 3·818 (1) Å, the van der Waals S^{2-}—S^{2-} distance being 3·70 Å.

References

Bak, B., Christensen, D., Rastrup-Andersen, J. & Tannenbaum, E. (1956). *J. Chem. Phys.* **25**, 892.

Bohn, B. (1975). Dissertation, Freie Univ. Berlin.

Burnham, C. W. (1966). *Am. Mineral.* **51**, 159–165.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Domenicano, A. & Vaciago, A. (1976). Collected Abstracts. Third European Crystallographic Meeting, Zurich, pp. 274–276.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 221–234.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hoekstra, A., Meertens, P. & Vos, A. (1975). *Acta Cryst.* B**31**, 2813–2817.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 148–150. Birmingham: Kynoch Press.

Kossmehl, G., Bohn, B. & Broser, W. (1976). *Makromol. Chem.* **177**, 2369–2395.

Ruban, G. & Zobel, D. (1975). *Acta Cryst.* B**31**, 2632–2634.

Samarskaya, V. D., Myasnikova, R. M. & Kitaigorodskii, A. I. (1969). *Sov. Phys. Crystallogr.* **13**, 525–529.

Sasada, Y., Shimanouchi, H., Nakanishi, H. & Hasegawa, M. (1971). *Bull. Chem. Soc. Jpn*, **44**, 1262–1270.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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

Towns, R. L. R. & Simonsen, S. H. (1975). *Cryst. Struct. Commun.* **4**, 473–475.

Wyckoff, R. W. G. (1969). *Crystal Structures*. Vol. 6, part 1, pp. 1–2. New York: John Wiley.

Wyckoff, R. W. G. (1971). *Crystal Structures*. Vol. 6, part 2, pp. 151–153. New York: John Wiley.

Zobel, D. (1976). *Acta Cryst.* B**32**, 2838–2841.

Zobel, D. & Ruban, G. (1978). *Acta Cryst.* B**34**, 1652–1657.