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The Crystal Structure of 4*H*-Cyclopenta[2,1-*b*: 3,4-*b*′]dithiophene at –160 °C

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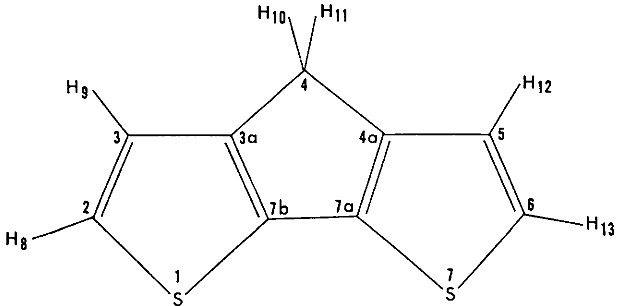
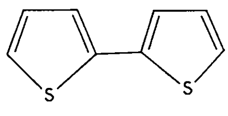
The crystal structure of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene, $C_9H_6S_2$, has been determined from three-dimensional diffractometer data taken at −160 °C to detect possible hyperconjugation effects. The crystals are monoclinic, space group $P2_1/c$, $a=12{\cdot}500$, $b=11{\cdot}154$, $c=11{\cdot}284$ Å, $\beta=98{\cdot}00°$, $Z=8$. The positional and anisotropic thermal parameters were refined by the method of least squares, $R=0{\cdot}032$ for 8146 reflexions. The observed bond lengths do not indicate the presence of hyperconjugation effects. The molecule is approximately planar, the largest deviation from the least-squares plane being 0·035 Å for C and S. There is much strain in the molecule; the angles S–C–C and C–C–C range from 102 to 139°. As to the values of the bond lengths and angles the molecule has the symmetry *mm*. Estimated standard deviations are 0·002 Å for C–C and C–S, 0·02 Å for C–H and 0·1° for C–S–C, C–C–C and C–C–S.

Introduction

The synthesis of the six isomeric cyclopentadithiophenes, $C_9H_6S_2$ (Wynberg & Kraak, 1964) has encouraged studies of the properties of these thiophene analogues of fluorene. Charge transfer properties (Kraak & Wynberg, 1968), spectra of ions (Janssen & de Jong, 1967) and aromatic character (Kraak, Wiersema, Jordens & Wynberg, 1968) have been or are being studied in the Laboratory of Organic Chemistry of this University. Preliminary results of these studies indicate interesting differences between the properties of the isomeric cyclopentadithiophenes and the corresponding dithienyls. For instance, the ultraviolet absorption bands of the cyclopentadithiophenes in solution generally lie at longer wavelengths than those of the corresponding dithienyls. A suitable explanation for the observed shifts could not be given by qualitative discussion of the following effects: (*a*) The increase in coplanarity of the thiophene rings because of the presence of the CH_2 bridge (see Fig. 1), (*b*) possible hyperconjugation *via* the CH_2 group, or (*c*) the strain in the molecule. We thought it, therefore, worth while to do an accurate determination of the bond lengths and angles for one of the isomers $C_9H_6S_2$ by means of X-ray diffraction at low temperature (−160 °C). The isomer chosen is 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (I). For this compound the U.V. shifts are +0 and +10 for the 2,2′-di-



(I)



(II)

Fig. 1. 4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (I) and the corresponding 2,2′-dithienyl (II).

thienyl (II) bands at 247 and 302 nm respectively (Kraak & Wynberg, 1968).

Crystal structure determinations of the three isomeric dithienyls were carried out in this laboratory some years ago, but were strongly hampered by the occurrence of disorder in the crystals (Visser, Heeres, Wolters & Vos, 1968).

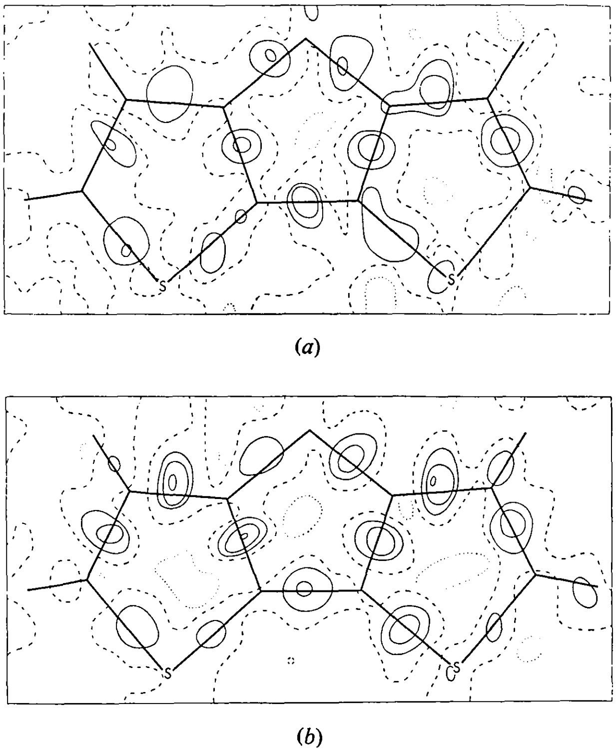


Fig. 2. Residual density in the planes of the two independent molecules. Contours are at intervals of 0·150 e.Å^{-3}; thick lines indicate positive regions, dotted lines negative ones, the zero line is dashed.

Experimental

The compound 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene was kindly given to us by Dr A. Kraak of the Laboratory of Organic Chemistry. For the preparation of the compound, see Kraak, Wiersema, Jordens & Wynberg (1968). Suitable crystals for X-ray diffraction were obtained by slow evaporation of a solution of the compound in petroleum spirit (40–60°C). The cell parameters were calculated from the 2θ values of six reflexions $h00$, five reflexions $0k0$ and five reflexions $00l$.The angles 2θ were measured with an accuracy of 0·01° with Mo $K\alpha$ radiation on a three circle Nonius diffractometer at -160°C, the 2θ values used range from 19·82 to 60·26°. The density was measured by flotation methods. The crystallographic data are:

4*H*-cyclopenta[2,1-*b*: 3,4-*b*′]dithiophene, $C_9H_6S_2$, M.W. 172·28,
Monoclinic, space group $P2_1/c$, from systematic extinctions: $0k0$ absent for $k=2n+1$ and $h0l$ absent for $l=2n+1$, $a=12·500$ ($\pm0·003$), $b=11·154$ ($\pm0·002$), $c=11·284$ ($\pm0·001$) Å, and $\beta=98·00$ ($\pm0·01$)°.
$D_m=1·4$ g.cm^{-3}, $D_x=1·39$ g.cm^{-3}, $Z=8$,
μ(Mo $K\alpha$)$=5·8$ cm^{-1}.

The intensities were collected on a three circle automated Nonius diffractometer. Two crystals with approximate dimensions of 0·5 × 0·6 × 0·7 mm^3 were used. The crystals were cooled down to -160°C by a stream of cold nitrogen gas, surrounded by a jacket of room temperature nitrogen gas (for principle of apparatus, see Verschoor & Keulen, 1970). The $\theta/2\theta$ scan technique was applied with Zr filtered Mo radiation, attenuation filters were used to keep errors due to non-linearity smaller than 1%. All 9750 reflexions with $2\theta<80$° were measured; for 8146 reflexions the intensity appeared to be significantly higher than zero. The data of the two crystals were put on the same relative

Table 1. *Final coordinates and estimated standard deviations*

For numbering of atoms see Fig. 1. *A* and *B* refer to the two independent molecules.

	x(*A*)	*y*(*A*)	*z*(*A*)	*x*(*B*)	*y*(*B*)	*z*(*B*)
S(1)	0·43077 (2)	0·41158 (2)	0·20999 (2)	0·18191 (2)	0·02136 (2)	0·03677 (2)
C(2)	0·31333 (8)	0·38913 (9)	0·11067 (9)	0·28553 (9)	−0·02671 (9)	0·14462 (10)
C(3)	0·23422 (7)	0·47101 (9)	0·12511 (8)	0·29247 (7)	0·03988 (9)	0·24832 (9)
C(3*a*)	0·26935 (7)	0·55465 (8)	0·21727 (8)	0·21218 (7)	0·13054 (8)	0·24025 (8)
C(4)	0·22346 (8)	0·66353 (9)	0·27228 (9)	0·17821 (8)	0·22818 (9)	0·32022 (8)
C(4*a*)	0·31633 (8)	0·69877 (8)	0·36711 (8)	0·08269 (7)	0·28302 (8)	0·24111 (8)
C(5)	0·33737 (9)	0·78739 (9)	0·45788 (9)	0·01123 (8)	0·38055 (9)	0·24776 (9)
C(6)	0·43867 (9)	0·77479 (9)	0·52143 (9)	−0·05659 (8)	0·39620 (9)	0·14223 (9)
S(7)	0·50967 (2)	0·65579 (2)	0·47169 (2)	−0·03457 (2)	0·29204 (2)	0·03405 (2)
C(7*a*)	0·40278 (7)	0·62168 (8)	0·36403 (8)	0·06644 (7)	0·22559 (8)	0·13119 (8)
C(7*b*)	0·37399 (7)	0·53292 (8)	0·27162 (8)	0·14618 (7)	0·13102 (8)	0·13074 (8)
H(8)	0·310 (1)	0·321 (2)	0·062 (2)	0·328 (2)	−0·090 (2)	0·127 (2)
H(9)	0·165 (1)	0·472 (1)	0·082 (2)	0·343 (1)	0·023 (2)	0·316 (2)
H(10)	0·159 (1)	0·645 (2)	0·308 (1)	0·158 (1)	0·195 (2)	0·394 (2)
H(11)	0·209 (1)	0·731 (2)	0·213 (2)	0·238 (1)	0·288 (2)	0·340 (2)
H(12)	0·291 (1)	0·846 (1)	0·476 (1)	0·007 (1)	0·432 (2)	0·312 (2)
H(13)	0·471 (2)	0·821 (2)	0·582 (2)	−0·107 (1)	0·451 (2)	0·126 (1)

scale by comparison of the 255 reflexions *hk*0 which had been measured for both crystals. After this scaling $\sum|\Delta F|/\sum|F|$, ΔF being the difference in amplitude for the two crystals, appeared to be 0·028 for the 255 reflexions. Corrections for absorption were calculated with a program written according to the Busing & Levy (1957) scheme.

Structure determination and refinement

In space group $P2_1/c$ the general position is fourfold. With $Z=8$ this means that there are two independent molecules in the unit cell, which will be indicated as molecule *A* and molecule *B*. The unit cell thus contains four independent sulphur atoms and 18 independent carbon atoms.

The positions of the four sulphur atoms could easily be found from a three-dimensional Patterson synthesis. After refinement of the positions and the isotropic thermal parameters of these atoms with least-squares techniques, a three-dimensional Fourier synthesis was calculated for the reflexions with reliable sign. This map clearly showed the positions of the 18 carbon atoms.

The parameters of the sulphur and carbon atoms were refined by anisotropic least-squares techniques on a TR4 computer; the temperature factor was defined as:

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2lhc^*a^*U_{31})\right].$$

When *R* had decreased to 0·043 a difference map (hydrogen not included in F_c) of the reflexions with $\sin\theta/\lambda < 0{\cdot}45$ Å^{-1} was calculated to locate the hydrogen atoms. All hydrogen atoms were easily found in this map. In the final stages of the refinement the hydrogen atoms were taken into account with isotropic thermal parameters in addition to the 'heavy' atoms for which the thermal motion was assumed to be anisotropic. Throughout the refinement all 8146 observed reflexions were taken into account with uniform weight. A least-squares program in block-diagonal approximation was used (Cruickshank, 1961). For the scattering factors the following values were taken: for H, Stewart, Davidson & Simpson's (1965) *f*-curve, for C, Moore's (1963) analytical constants for the low order reflexions ($\sin\theta/\lambda < 0{\cdot}7$ Å^{-1}) and Cromer & Waber's (1965) analytical constants for the high order reflexions, for S, Moore's val-

Table 2. *Thermal parameters*

The U_{ij} values for C and S are given in 10^{-4} Å^2 in the order U_{11}, U_{22}, U_{33}, $2U_{12}$, $2U_{23}$, $2U_{31}$. For the hydrogen atoms *B* values from the isotropic temperature factor $\exp(-B\sin^2\theta/\lambda^2)$ in *F* are given. The standard deviations in parentheses are the values obtained by the least-squares structure refinement program. The U_{obs} values are compared with the U_c values based on the rigid body model of Table 3.

	$U_{obs}(A)$	$U_c(A)$	$\Delta U(A)$	$U_{obs}(B)$	$U_c(B)$	$\Delta U(B)$
S(1)	1465 (8)	1653	188	2321 (10)	2152	−169
	1678 (9)	1640	−38	1424 (9)	1457	33
	1799 (9)	1841	42	1866 (9)	1698	−168
	370 (14)	199	−171	419 (16)	464	45
	−1095 (15)	−971	24	−484 (15)	−486	−2
	−27 (14)	−160	−133	1161 (16)	950	−211
C(2)	1750 (35)	1912	162	2236 (41)	2020	−216
	1749 (35)	1582	−167	1613 (36)	1691	78
	1590 (33)	1677	87	2595 (44)	2276	−319
	−222 (56)	−92	130	1096 (63)	1091	−5
	−609 (55)	−797	−188	468 (65)	386	−82
	−63 (54)	−43	20	1696 (69)	238	−1458
C(3)	1497 (32)	1696	199	1813 (36)	1666	−147
	1699 (34)	1528	−171	1799 (96)	1921	122
	1447 (31)	1639	192	2130 (39)	1987	−143
	−318 (53)	−227	91	924 (59)	740	−184
	175 (53)	−506	−681	1013 (60)	580	−433
	3 (50)	−249	−252	946 (60)	337	−609
C(3*a*)	1452 (31)	1430	−22	1652 (33)	1518	−134
	1443 (31)	1462	19	1421 (30)	1543	122
	1390 (31)	1606	218	1535 (32)	1443	−92
	67 (50)	−113	−180	401 (51)	190	−211
	144 (50)	−460	−604	444 (51)	−12	−456
	357 (49)	13	344	672 (52)	162	−510
C(4)	1664 (34)	1446	−218	1889 (36)	2004	115
	1624 (34)	1665	41	1833 (36)	1779	−54
	1827 (35)	2008	181	1325 (31)	1341	−16
	645 (56)	208	−437	640 (58)	56	−584
	39 (57)	−811	−850	19 (55)	−507	−526
	234 (55)	−101	−335	326 (53)	−11	−337

Table 2 (*cont.*)

	$U_{obs}(A)$	$U_c(A)$	$\Delta U(A)$	$U_{obs}(B)$	$U_c(B)$	$\Delta U(B)$
C(4*a*)	1860 (35)	1480	−380	1569 (32)	1819	250
	1324 (3)	1533	209	1502 (31)	1387	−115
	1595 (32)	1750	155	1440 (31)	1425	−5
	318 (53)	93	−225	369 (52)	200	−169
	−82 (52)	−738	−656	102 (52)	−431	−533
	570 (54)	−251	−821	600 (50)	565	−35
C(5)	2418 (42)	1813	−605	1862 (36)	2389	527
	1358 (33)	1707	349	1621 (34)	1535	−86
	1916 (37)	192	−1724	1791 (34)	1948	157
	192 (59)	257	65	676 (56)	839	63
	−528 (57)	−1126	−598	−340 (56)	−440	−100
	1017 (63)	128	−889	959 (57)	1293	344
C(6)	2489 (42)	1917	−572	1701 (35)	2046	345
	1468 (33)	1591	123	1745 (36)	1669	−76
	1867 (37)	1190	−677	2138 (39)	2263	125
	−614 (62)	−83	531	966 (58)	1084	118
	−657 (58)	−815	−158	238 (60)	353	115
	640 (63)	−270	−910	726 (58)	1256	530
S(7)	1711 (9)	1568	143	1518 (8)	1594	49
	1494 (9)	1497	3	1794 (9)	1757	−37
	1753 (9)	1643	−110	1565 (8)	1718	153
	−366 (14)	−177	189	436 (14)	480	44
	−634 (14)	−472	162	113 (15)	322	209
	−119 (14)	143	262	−6 (13)	−216	−210
C(7*a*)	1624 (32)	1377	−247	1434 (30)	1423	−11
	1412 (32)	1395	−17	1288 (29)	1273	−16
	1422 (31)	1473	46	1441 (30)	1328	−113
	−144 (52)	−114	30	204 (48)	96	−107
	−244 (51)	−429	−190	106 (49)	−174	−280
	195 (50)	−199	74	523 (49)	368	155
C(7*b*)	1455 (31)	1381	−74	1639 (32)	1449	190
	1386 (31)	1401	15	1201 (29)	1256	55
	1393 (30)	1480	98	1481 (31)	1326	155
	13 (50)	−99	−112	194 (50)	96	−98
	−287 (50)	−448	−161	102 (49)	−207	−309
	291 (49)	239	−52	639 (51)	397	−242
H(8)	2·315 (0·378)			2·811 (0·442)		
H(9)	1·252 (0·256)			2·515 (0·346)		
H(10)	1·478 (0·315)			1·671 (0·337)		
H(11)	1·991 (0·340)			2·161 (0·357)		
H(12)	1·554 (0·262)			1·857 (0·315)		
H(13)	2·431 (0·363)			2·152 (0·301)		

ues for Cu and Mo radiation for the low and high order reflexions respectively.

At the end of the refinement $(\Delta F)^2$ did not vary systematically with F. The residual $R=0·032$ for the 8146 reflexions. A list of F_o, F_c and ΔF is available on request. The final coordinates and their standard deviations as calculated by the least-squares program are listed in Table 1; the thermal parameters are given in Table 2. After the refinement the residual density was calculated in the planes of the two independent molecules, the sections are given in Fig. 2. The standard deviation in the residual density is 0·076 e.Å^{-3} (Cruickshank, 1949). It may be noted that there are maxima on the middle of all C–C, C–S, and most of the C–H bonds. The heights of the maxima on the C–C bonds vary from 0·291 to 0·513 e.Å^{-3} and for C–S from 0·094 to 0·372 e.Å^{-3}. Possible differences between the residual densities on chemically non-equivalent C–C or C–S bonds are obscured by the rather large errors in the residual density, the maxima on C–S tend to be lower than those on C–C. A more quantitative discussion of the bonding effects is not possible on the basis of the present experimental data.

To get an idea of the thermal motions of the molecules, a rigid body analysis was made according to Cruickshank's (1956) method. The molecules were assumed to librate about their centres of gravity. The **T** and **ω** tensors obtained are listed in Table 3; the U_c values based on the rigid body model of Table 3 are given in Table 2. Comparison with the U_o values shows that the molecules cannot be considered as rigid bodies librating about their centres of gravity, because a large number of the ΔU values are larger than ten times the standard deviations estimated for the corresponding

U_0 values. Nevertheless the **T** and **ω** tensors in Table 3 give a rough impression of the translations and librations of the molecules. It appears that both the translations and librations are approximately isotropic. The terms E_{ii} in Table 3 are equal to the corresponding average values within the standard deviations given in the Table. In general the terms E_{ij} with $i \neq j$ are equal to zero within two times their standard deviations. Exceptions are $\omega_{31}(A)$ and $\omega_{23}(B)$ which are equal to three and four times their standard deviations respectively.

Because of the low temperature used, the errors in the bond lengths and angles due to libration effects are small. Approximate values for the libration corrections were calculated from the rigid body analysis described above, and are 0·001 Å for both C–S and C–C. No corrections for libration were applied to the coordinates in Table 2 and to the bond lengths and angles in Fig. 4 and Table 4.

Description of the structure

Fig. 3 shows the arrangement of the molecules in [010] projection. The coordinates of the two independent molecules in the top right hand corner are listed in Table 1;

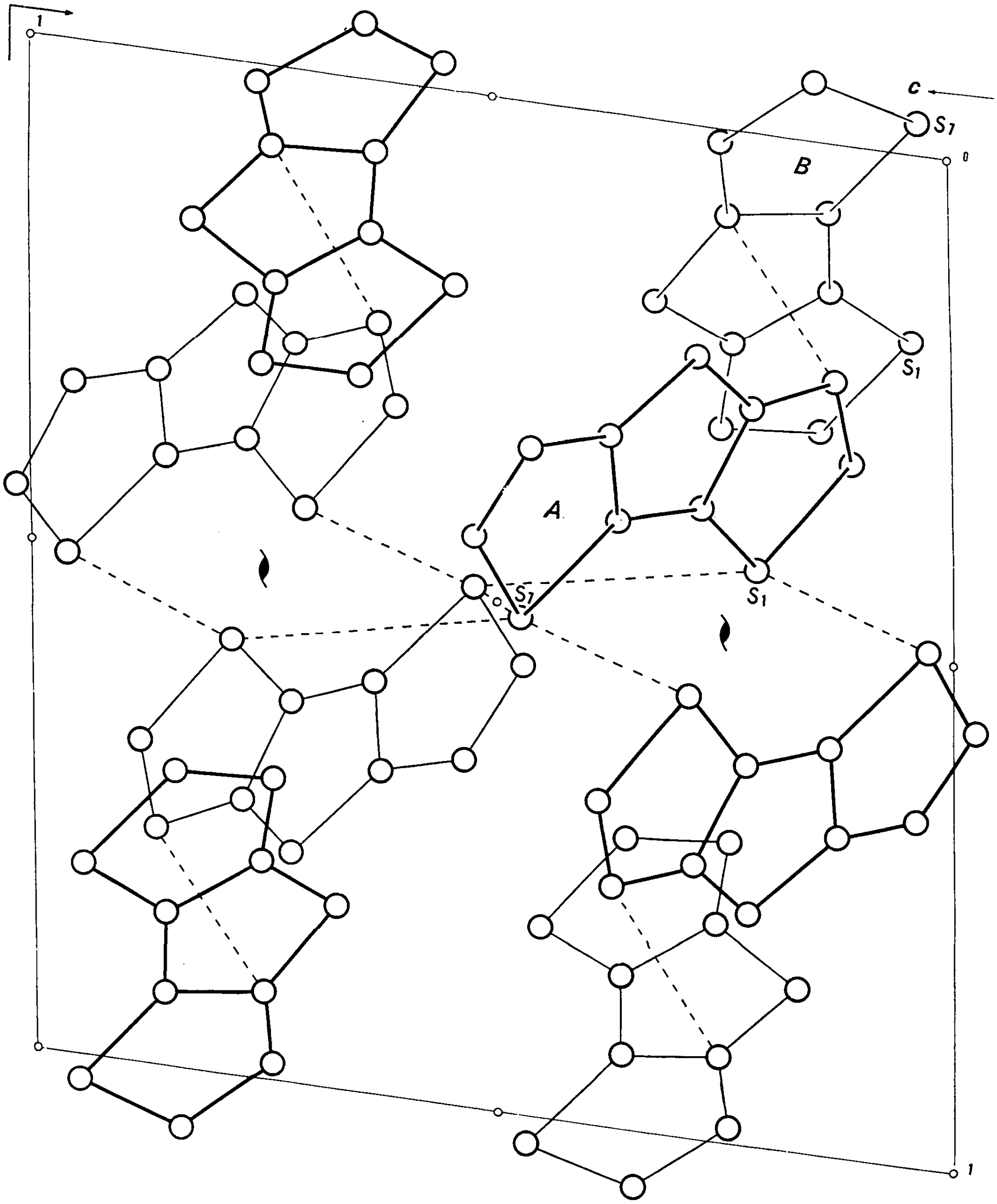


Fig. 3. The arrangement of the molecules in [010] projection. The coordinates of the two independent molecules in the top right-hand corner are listed in Table 1. The intermolecular distances which are approximately equal to the sum of the van der Waals radii are indicated by dotted lines.

the remaining molecules are related to this set by the symmetry elements given in the figure. Dashed lines indicate intermolecular distances which are shorter than 0·1 Å plus the sum of the corresponding van der Waals radii, *i.e.* 1·85 Å for S and 1·60 Å for C (Pauling, 1967).

None of the distances appeared to be shorter than the sum of the van der Waals radii.

The intramolecular bond lengths and angles are shown in Fig. 4 and Table 4 respectively. The best planes through the atoms of the respective molecules and the atomic distances to these planes are given in Table 5. None of the molecules is completely planar. For most of the atoms the deviations from the best planes are small but significant, and unequal for chemically equivalent atoms of the two thiophene rings in a molecule. This means that, strictly speaking, the molecules are asymmetric. With regard to the bond lengths and angles, however, the molecules obey the symmetry *mm*, as may be seen from Fig. 4 and Table 4. Moreover comparison of the molecules *A* and *B* shows that corresponding bond lengths and angles in the two molecules are equal within experimental error. Average values are given in Fig. 5(*a*).

It may be noticed that the thiophene rings in the molecules are asymmetric. The bond b_1 is 0·012 Å shorter than b_2, whereas s_1 is 0·016 Å longer than s_2 [Fig. 5(*b*)].

Table 3. **T** *and* **ω** *tensors relative to the orthogonal axes a^*, b, c*

The centres of libration were taken to coincide with the centres of gravity of the molecules. The tensor elements are given as E_{ij}. T_{ij} in 10^{-4} Å^2, ω_{ij} in 10^{-4} rad^2. The standard deviations in parentheses are estimated from the ΔU values in Table 2.

	E_{11}	E_{22}	E_{33}	E_{12}	E_{23}	E_{31}	$\overline{E_{ii}}$
T(*A*)	135 (8)	139 (9)	149 (11)	−5 (6)	−20 (9)	−8 (7)	141
ω(*A*)	7 (3)	11 (4)	9 (4)	4 (2)	4 (4)	6 (2)	9
T(*B*)	140 (8)	124 (8)	128 (7)	2 (7)	11 (6)	3 (6)	131
ω(*B*)	11 (3)	14 (4)	10 (2)	−4 (3)	−4 (1)	−2 (1)	12

Table 4. *Bond angles*

For numbering of atoms, see Fig. 1. The e.s.d. are 0·1° for C–S–S, C–C–C and C–C–S, 1·3° for S–C–H and C–C–H, and 1·5° for H–C–H. For symmetry *mm* of the molecules the angles in columns 2 and 3 should be equal to those in columns 5 and 6 respectively.

Angle	Mol. *A*	Mol. *B*	Angle	Mol. *A*	Mol. *B*
C(7*b*)–S(1)—C(2)	90·9°	91·1°	C(7*a*)–S(7)—C(6)	90·9°	90·8°
S(1) —C(2)—C(3)	112·7	112·4	S(7) —C(6)—C(5)	112·7	112·7
C(2)—C(3)—C(3*a*)	111·7	111·7	C(6)—C(5)—C(4*a*)	111·7	111·7
C(3)—C(3*a*)–C(7*b*)	112·7	112·8	C(5)—C(4*a*)–C(7*a*)	112·5	112·8
C(3)—C(3*a*)–C(4)	137·0	136·9	C(5)—C(4*a*)–C(4)	137·3	136·8
C(4)—C(3*a*)–C(7*b*)	110·3	110·3	C(4)—C(4*a*)–C(7*a*)	110·2	110·2
C(3*a*)–C(7*b*)–S(1)	112·1	111·9	C(4*a*)–C(7*a*)–S(7)	112·2	112·0
C(3*a*)–C(7*b*)–C(7*a*)	108·9	108·9	C(4*a*)–C(7*a*)–C(7*b*)	109·0	108·9
S(1) —C(7*b*)–C(7*a*)	139·0	139·2	S(7) —C(7*a*)–C(7*b*)	139·0	139·2
C(3*a*)–C(4)—C(4*a*)	101·6	101·7			
S(1) —C(2)—H(8)	117·7	118·8	S(7) —C(6)—H(13)	118·9	119·7
C(3)—C(2)—H(8)	129·3	128·8	C(5)—C(6)—H(13)	128·4	127·6
C(2)—C(3)—H(9)	125·2	122·7	C(6)—C(5)—H(12)	121·7	120·2
C(3*a*)–C(3)—H(9)	123·1	125·6	C(4*a*)–C(5)—H(12)	126·6	128·1
H(10)–C(4)—H(11)	109·9	109·7			
H(10)–C(4)—C(3*a*)	112·6	111·7	H(10)–C(4)—C(4*a*)	111·3	111·9
H(11)–C(4)—C(3*a*)	112·1	110·5	H(11)–C(4)—C(4*a*)	109·0	111·2

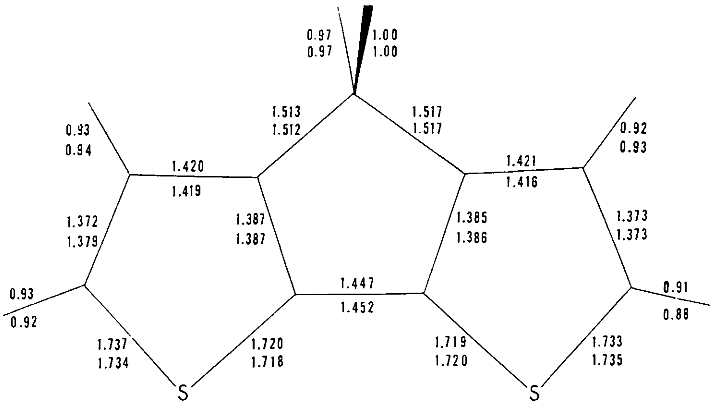


Fig. 4. The 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene molecule. The upper values for the bond lengths are for molecule *A*, the lower ones for *B*. The e.s.d. are 0·002 Å for C–S and C–C and 0·02 Å for C–H.

Table 5. *Atomic distances* (Å) *to the best molecular planes*

In calculating the planes weights of 3,1 and 0 were used for S, C and H respectively. The equations of the planes for the molecules *A* and *B* are respectively:

$$0{\cdot}6415X+0{\cdot}6303Y-0{\cdot}4372Z=\ \ 1{\cdot}5646$$
$$-0{\cdot}3605X+0{\cdot}6013Y+0{\cdot}7131Z=-3{\cdot}5174$$

with $X=x\sin\beta$, $Y=y$ and $Z=z+x\cos\beta$ (Å).

	Mol. *A*	Mol. *B*		Mol. *A*	Mol. *B*		Mol. *A*	Mol. *B*		Mol. *A*	Mol. *B*
S(1)	−0·010	−0·013	S(7)	0·008	0·019						
C(2)	0·011	0·019	C(6)	0·016	0·026	H(8)	0·10	0·03	H(13)	0·01	−0·01
C(3)	0·029	0·036	C(5)	−0·002	−0·014	H(9)	0·07	0·03	H(12)	0·01	0·06
C(3*a*)	0·010	0·014	C(4*a*)	−0·019	−0·045	H(10)	0·76	0·76			
C(7*b*)	−0·004	−0·017	C(7*a*)	−0·020	−0·048	H(11)	−0·86	−0·85			
C(4)	−0·016	0·010									

Although these differences are small, they may be considered significant, as may be seen from a discussion of the estimated standard deviations. From the variation in the lengths of the bonds equivalent for symmetry *mm* (Fig. 4) it may be concluded that the least-squares estimate of 0·002 Å for the standard deviation in both C–C and C–S is realistic for the present structure. The largest difference between the extreme values for a set of bonds equivalent for symmetry mm is 0·007 Å. This is just more than twice the standard deviation of 0·003 Å calculated for the difference between two C–C (C–S) bond lengths. For the differences b_1–b_2 and s_1–s_2, obtained from four independent sets of bond lengths, standard deviations of 0·003/(4)$^{1/2}$=0·0015 Å are calculated. It cannot be excluded, however, that systematic errors occur which are of the same order of this standard deviation. Also the bond angles in Fig. 5(*a*) indicate that the thiophene rings are asymmetric.

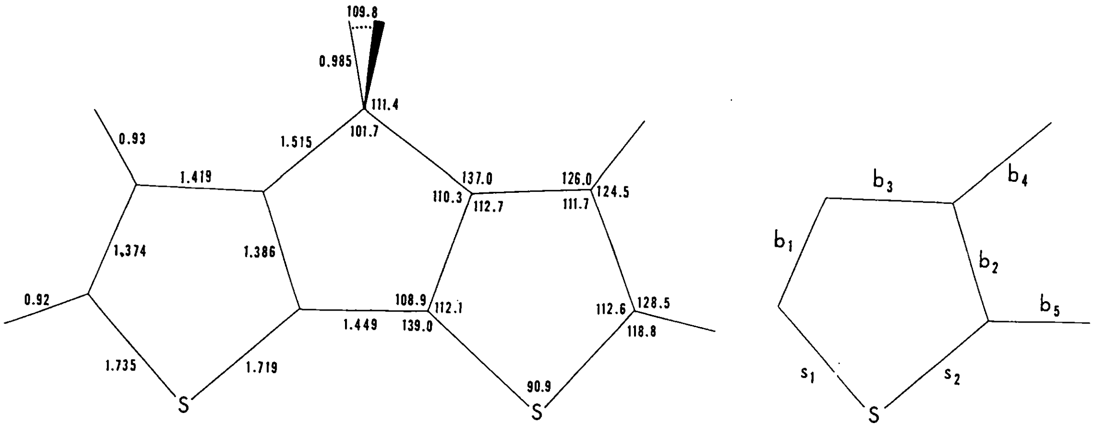
Discussion of the bond lengths and angles

It would be interesting to compare the bond lengths and angles in the bridged compound (I) with those in 2,2′-dithienyl (II) (Fig. 1). An accurate comparison is not possible, however, as the bond lengths and angles in 2,2′-dithienyl are not known accurately, although it has been studied both in the gaseous and in the solid state. In the electron diffraction study by Almenningen, Bastiansen & Svendsås (1958) the thienyl rings in the 2,2′-dithienyl molecule were assumed to have mirror

Table 6. *Comparison of the experimental bond lengths l*(*exp*) *with the results of two PPP calculations* (*Pople*, 1953; *Pariser & Parr*, 1953).

For numbering of the bonds see Fig. 5(*b*). The bond length (*l*) – bond order (*P*) curve used for C–C is $l=1{\cdot}517-0{\cdot}18P$, for C–S the experimental bond lengths are compared with the theoretical bond orders. The parameters of the PPP calculations are in eV: For *l*(*a*): α(C)=−11·22, α(S)=−20·0, β(C–C)=−2·318, β(C–S)=−1·623 (Fabian, Mehlhorn & Zahradnik, 1968), γ(CC)=10·53, γ(SS)=10·84, $\gamma_{\mu\nu}$ according to Nishimoto & Mataga (1957). For *l*(*b*): α(C)=O in general, α(C)=−0·5 for carbons adjacent to S, α(S)=−18·0, β(C–C)=β(C–S)=−2·4, γ(SS)=11·90, γ(CC)=11·13, $\gamma_{\mu\nu}$ according to the uniformly charged sphere approximation (Wachters & Davies, 1964).

Bond	*l*(exp)	*l*(*a*)	*l*(*b*)
s_1	1·735 Å	0·436	0·291
s_2	1·719	0·411	0·282
b_1	1·374	1·374	1·364
b_2	1·386	1·383	1·374
b_3	1·419	1·419	1·428
b_4	1·515	1·517	1·517
b_5	1·449	1·449	1·451



(*a*) (*b*)

Fig. 5. (*a*) Average values for the bond lengths and angles. (*b*) Numbering of the bonds for the theoretical discussion.

symmetry so that possible deviations from this symmetry, as occur in the cyclopentadithiophene compound, may be obscured. The investigation in the solid state was strongly hampered by decomposition of the crystals (Visser *et al.*, 1968).

To get more insight in the bonding in 4*H*-cyclopenta-[2,1-*b*: 3,4-*b*′]dithiophene theoretical PPP calculations were done on the π-electrons in the molecule. First a possible influence of the CH_2 group was neglected. The PPP parameters and the results of two calculations are given in Table 6. It may be noticed that the calculated lengths of the C–C bonds show a considerable variation by changing the parameters. As far as the C–C bonds are concerned the calculated values $l(a)$ are in excellent agreement with the observed values. The bond orders calculated for C–S are in the wrong sense, however, for both sets of parameters. Attempts to improve the bond orders for C–S considering hyperconjugation of the CH_2 group failed. Both an inductive model (by changing the Coulomb integrals of the carbon atoms adjacent to the CH_2 group) and a conjugative model (Cumper, 1966) were considered. In neither case were the C–S bond orders calculated in the right sense by giving the CH_2 group, as usual, an electron repulsive character. This makes clear that inclusion of hyperconjugation does not improve the theoretical model for the molecule.

From the above discussion, it may be concluded that, in contradistinction to the C–C bond lengths, the C–S bond lengths are not adequately explained by considering π-electron delocalization only. Moreover it is not clear yet why the average value of the C–S bond lengths, 1·727 Å, in the present compound is larger than the length, 1·714 Å, of the C–S bonds in thiophene (Bak, Christensen, Hansen-Nygaard& Rastrup-Andersen, 1961).

It is remarkable that an asymmetry in C–S bond lengths analogous to the asymmetry observed in the cyclopentadithiophene appears to be a general phenomenon for molecules containing the grouping $-(CH_2)-X-(C'H)-Y$ with $X=O$ or S and $Y=Cl$ or Br (Romers, Altona, Buys & Havinga, 1969). In *trans*-2,3-dichlorothioxane, for instance $X-C' = 1{\cdot}795$ and $X-C = 1{\cdot}820$ Å. Romers *et al.* have tentatively ascribed the asymmetry in the C–X bond lengths to the occurrence of resonance structures of type $-(CH_2)-X^+=(C'H)\ Y^-$. Owing to the relatively large electronegativity of Y this structure may be expected to contribute more than the analogous form in which C–X rather than C′–X is double. Without performing extensive calculations in which the σ electrons are considered in addition to the π electrons, it is not possible to decide whether resonance structures of the kind mentioned above contribute significantly to the structure of the cyclopentadithiophene studied in the present paper. It is worth mentioning that unequal C–S bonds have also been observed in α-chloro- and in α-bromo-thiophene in an electron diffraction study in the gas phase by Harshbarger & Bauer (1970). The electron diffraction work did not show clearly, however, which of the two C–S bonds is the shorter one. In analogy to the compounds mentioned above one would expect this to be the case for the C–S bond adjacent to the halogen atom.

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