binding interactions of 'toxic-coplanar' PCB's in biological systems. Likely binding sites in proteins for stacking interactions are the rigid side chains of aromatic amino acids as well as the heme prosthetic group in hemoproteins as represented by the PCB–porphine interaction model (McKinney *et al.*, 1985).

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References

Akhmad, N. A., Farag, M. S. & Amin, A. (1971). *Zh. Strukt. Khim.* **12**, 738–739.

Almenningen, A. & Bastiansen, O. (1958). *K. Nor. Vidensk. Selsk. Skr.* **4**, 1–16.

Bandiera, S., Safe, S. & Okey, A. B. (1982). *Chem.-Biol. Interact.* **39**, 259–277.

Brock, C. P. (1979). *Mol. Cryst. Liq. Cryst.* **52**, 157–162.

Brock, C. P. (1980). *Acta Cryst.* B**36**, 968–971.

Brock, C. P. & Haller, K. L. (1984). *J. Phys. Chem.* **88**, 3570–3574.

Burkert, U. & Allinger, A. L. (1982). *Molecular Mechanics*. ACS Monogr. No. 177, ch. 9, and references therein.

Busing, W. R. (1983). *Acta Cryst.* A**39**, 340–347.

Cailleau, H., Baudour, J. L., Meinnel, J., Dworkin, A., Moussa, F. & Zeyen, C. M. E. (1980). *Faraday Discuss. Chem. Soc.* pp. 7–18.

Casalone, G., Mariani, C., Mugnoli, A. & Simonetta, M. (1968). *Mol. Phys.* **15**(4), 339–348.

Charbonneau, G. & Delugeard, Y. (1976). *Acta Cryst.* B**32**, 1420–1423.

Czikkely, V., Forsterling, H. D. & Kuhn, H. (1970). *Chem. Phys. Lett.* **6**, 207–210.

Darden, T., McKinney, J. D., Gottschalk, K. E., Maynard, A. T. & Pedersen, L. G. (1986). *J. Am. Chem. Soc.* **108**, 207–211.

Goldstein, J. A. (1980). *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Compounds*, edited by R. D. Kimbrough, pp. 151–190. New York: Elsevier/North-Holland.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98, 149–150. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Korolkovas, A. (1970). *Essentials of Molecular Pharmacology*, p. 182. New York: Wiley–Interscience.

Long, G., McKinney, J. & Pedersen, L. (1987). *Quant. Struct.-Act. Relat.* **6**, 1–7.

McKinney, J. D., Darden, T., Lyerly, M. A. & Pedersen, L. G. (1985). *Quant. Struct.-Act. Relat.* **4**, 166–172.

McKinney, J. D., Fannin, R., Jordan, S., Chae, K., Rickenbacher, U. & Pedersen, L. (1987). *J. Med. Chem.* **30**(1), 79–86.

McKinney, J. D., Gottschalk, K. E. & Pedersen, L. G. (1983*a*). *J. Mol. Struct.* **104**, 445–450.

McKinney, J. D., Gottschalk, K. E. & Pedersen, L. G. (1983*b*). *J. Mol. Struct.* **105**, 427–438.

McKinney, J. D. & Pedersen, L. G. (1986). *Biochem. J.* **240**, 621–623, and references therein.

McKinney, J. D. & Singh, P. (1981). *Chem.-Biol. Interact.* **33**, 271–283.

McKinney, J. D., Singh, P., Levy, L. A. & Walker, M. P. (1980). *Safe Handling of Chemical Carcinogens, Mutagens, Teratogens and Highly Toxic Substances*, Vol. II, edited by D. B. Walters, pp. 421–438. MI: Ann Arbor Science.

Pauling, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.

Safe, S., Bandiera, S., Sawyer, T., Zmudzka, B., Mason, G., Romkes, M., Denomme, M. A., Sparling, J., Okey, A. B. & Fujita, T. (1985). *Environ. Health Perspect.* **61**, 21–33.

Sheldrick, G. M. (1983). *SHELXTL Users' Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Singh, P., Posner, H. & McKinney, J. D. (1987). *Acta Cryst.* C**43**, 106–109.

Acta Cryst. (1988). C**44**, 562–564

Structure of 5,5′-Dibromo-2,2′-bithiophene

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Abstract. $C_8H_4Br_2S_2$, $M_r = 324{\cdot}06$, orthorhombic, *Pccn*, $a = 7{\cdot}525\,(1)$, $b = 22{\cdot}333\,(3)$, $c = 5{\cdot}828\,(1)$ Å, $V = 979{\cdot}4\,(2)$ Å^3, $Z = 4$, $D_m = 2{\cdot}21\,(1)$, $D_x = 2{\cdot}198$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 8{\cdot}55$ mm^{-1}, $F(000) = 616$, $T = 296$ K, $R = 0{\cdot}048$ for 538 independent reflections. The bithiophene molecule is completely planar. The C—Br bond length is 1·869 (8) Å and the C—S bond length is 1·728 (9) Å. The C—S—C bond angle is 91·0 (4)°. The major deviations from $2mm$ (C_{2v}) symmetry involve the bond angles at C(3) and C(4) which are 114·1 (7) and 111·6 (8)° respectively.

Introduction. Substituted 2,2′-bithiophenes and polythienyls have nematocidal activity strongly dependent on the number and type of substituents present in the

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thiophene-ring system (Uhlenbroeck & Bijloo, 1960). No structural features directly related to nematocidal activity, however, have yet been identified in these molecules. 5,5′-Dibromo-2,2′-bithiophene was first synthesized by direct bromination of 2,2′-bithiophene (Auwers & Bredt, 1894), and has been subsequently prepared by a Grignard coupling of bromothiophene (Steinkopf & Roch, 1930) and by bromination of bithiophene by *N*-bromosuccinimide (Kellogg, Schaap & Wynberg, 1969). Copper(II) bromide which has been shown to brominate aromatic hydrocarbons is used here to prepare the dibromo derivative of 2,2′-bithiophene.

Ultraviolet photoelectron (Meunier, Coustale, Guimon & Pfister-Guillouzo, 1977) and absorption spectroscopy (Meunier, Coustale & Arriau, 1978) studies indicate that the dibromobithiophene molecule is nonplanar and the angle between the two thiophene planes is 35° in the gas phase and in slightly polar solvents. ^{1}H NMR studies in liquid crystals, however (Veracini, Macciantelli & Lunazzi, 1973), indicate that the molecule is planar and exists predominantly in the *anti* conformation. In the solid state, X-ray crystal structures of unsubstituted bithiophene (Visser, Heeres, Wolters & Vos, 1968) and 5,5′-bis[dimethyl(2-thienyl)-silyl]-2,2′-bithiophene (Lipka & von Schnering, 1977) reveal coplanar thiophene rings, although there is evidence for a small deviation from coplanarity: 3·3° in the dinitro compound (Panfilova, Antipin, Struchkov, Churkin & Lipkin, 1980). Substituents in the bithiophene molecule may not only cause the two thiophene rings to be noncoplanar, but may also result in distortion. For example, the bond lengths and bond angles obtained from electron diffraction studies of 2-bromothiophene (Harshbarger & Bauer, 1970; Karl & Bauer, 1972) show that the thiophene ring no longer has $2mm$ (C_{2v}) symmetry. The structure of 5,5′-dibromo-2,2′-bithiophene was expected, therefore, to exhibit the combined influence of the bromine and thienyl substituents on the thiophene ring.

Experimental. Single crystals of 5,5′-dibromo-2,2′-bithiophene were obtained from the reaction of copper(II) bromide with 2,2′-bithiophene in acetonitrile after separation of the reaction product and crystallization from *n*-hexane. The density was measured by flotation in aqueous bromide. A pale yellow prism with approximate dimensions 0·53 × 0·27 × 0·22 mm was mounted on a Nicolet/Syntex $P2_1$ diffractometer. The cell constants were determined from 25 reflections in the range $25 < 2\theta < 35°$. The space group was determined to be *Pccn* from the systematic absences ($0kl$, $l = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$). The $2\theta/\theta$ scan method with a variable scan rate from 2 to 8° min^{-1} (2θ) ($h = 0$ to 8; $k = 0$ to 31; $l = 0$ to 7) was used to collect the data. Three standard reflections which were collected after every 46 reflections had a standard deviation of 0·91%. The relative transmission coefficients ranged from 6·4 to 20·8. The data were corrected for Lorentz, polarization factors and absorption effects. 2270 reflections with $2\theta < 63°$ [$(\sin\theta)/\lambda \leq 0{\cdot}7293$ Å^{-1}] were measured, of which 1935 were unique and not systematically absent. No equivalent reflections were collected. The structure was solved by Patterson and Fourier methods. The positions of the H atoms were calculated assuming the C—H bond bisects the C—C—C angle and a C—H bond length of 0·95 Å. The H-atom coordinates were not refined. 538 reflections with intensities greater than 3σ were used in a full-matrix least-squares refinement of 55 parameters where $\sum w(|F_o| - |F_c|)$ was minimized; w was calculated from $w = 4F/\sigma^2(F^2)$. The refinement converged with $R = 0{\cdot}048$ and $wR = 0{\cdot}050$. The ratio of $\Delta_{\max}/\sigma$ was 0·03 and the largest peak in the Fourier difference map was 0·75 (16) e Å^{-3}. The scattering factors used were from Cromer & Waber (1974) and anomalous-dispersion effects were included in the values of F_c; the values of f' and f'' were from Cromer (1974). The absorption correction was that of Coppens, Leiserowitz & Rabinovich (1965). All calculations were performed on a PDP-11 computer with the software package *SDP-plus*, Version 1.1 (Frenz, 1983).

Discussion. Table 1 contains the final positional and isotropic thermal parameters.* The bond lengths and angles with standard deviations are in Table 2. The structure of 5,5′-dibromo-2,2′-bithiophene is shown in Fig. 1 in an *ORTEP* (Johnson, 1965) drawing with 50% thermal ellipsoids and the stereoview of the unit cell is shown in Fig. 2. The molecule consists of two planar thiophene rings with the largest deviation from the least-squares plane being 0·010 Å for C(4). The rings in the bithiophene molecule are constrained to be coplanar by symmetry and the molecule possesses a center of inversion at the midpoint of the C(2)—C(2′) bond.

In the thiophene ring, the S—C(2) and S—C(5) bond lengths are the same within experimental error, the average bond length being 1·728 Å. The substitution of a thienyl group on a thiophene ring has no effect on the C—S bond length (Visser, Heeres, Wolters & Vos, 1968); the C(2)—C(3) and C(4)—C(5) distances, however, are different. These differences are small and cannot be considered to be significant because the standard deviations of the positional parameters are relatively large (approximately a factor of 1·5 larger than for the dibromobithiophene structure). In contrast, the substitution of a bromine on the thiophene ring results in the S—C(2) bond being longer than the

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* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44546 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic thermal parameters*

	x	y	z	B^*(Å^2)
Br	0·0580 (2)	0·19378 (4)	0·0878 (2)	4·81 (2)
S	−0·0815 (3)	−0·05968 (9)	0·7788 (3)	3·48 (5)
C(2)	0·007 (1)	−0·0317 (4)	0·524 (1)	2·3 (2)
C(3)	−0·086 (1)	0·0766 (3)	0·597 (1)	3·1 (2)
C(4)	0·073 (1)	−0·1335 (4)	0·508 (1)	3·8 (2)
C(5)	0·014 (1)	0·1306 (4)	0·290 (1)	3·1 (2)
H(3)	−0·145	0·070	0·739	5·0
H(4)	−0·119	0·169	0·556	5·0

* For anisotropically refined atoms the form of the isotropic equivalent thermal parameter is defined as $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

Table 2. *Bond lengths* (Å) *and angles* (°)

Br	C(5)	1·869 (8)	Br	C(5)	S	119·8 (5)
S	C(2)	1·744 (8)	Br	C(5)	C(4)	127·0 (7)
S	C(5)	1·713 (9)	S	C(2)	C(3)	110·1 (6)
C(2)	C(3)	1·363 (11)	S	C(5)	C(4)	113·2 (6)
C(3)	C(4)	1·413 (11)	C(2)	S	C(5)	91·0 (4)
C(4)	C(5)	1·350 (12)	S	C(2)	C(2′)	119·1 (6)
C(2)	C(2′)	1·447 (11)	C(2)	C(3)	C(4)	114·1 (7)
			C(3)	C(4)	C(5)	111·6 (8)
			C(3)	C(2)	C(2′)	130·7 (7)

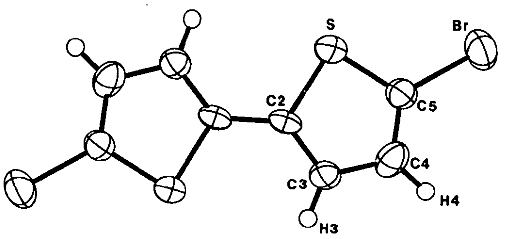

Fig. 1. Molecular geometry of 5,5′-dibromo-2,2′-bithiophene.

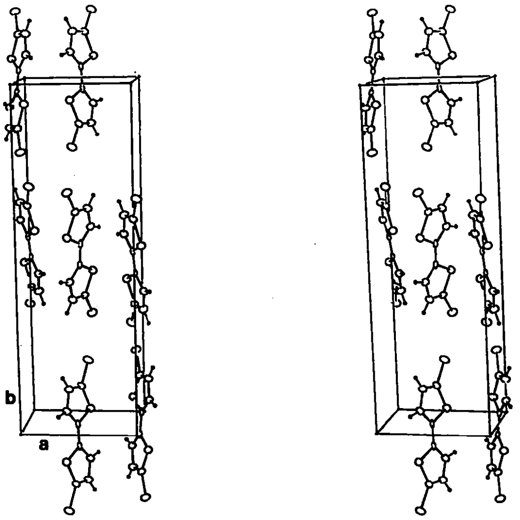

Fig. 2. Packing diagram in the unit cell.

S—C(5) bond, with the C—C bonds remaining unaffected (Harshbarger & Bauer, 1970; Karl & Bauer, 1972).

The C—S—C angles in 2-bromothiophene and dibromobithiophene are equal, as are the S—C(2)—C(3) and S—C(5)—C(4) angles. The major deviations from $2mm$ (C_{2v}) symmetry occur in the C(2)—C(3)—C(4) and C(3)—C(4)—C(5) angles, which are 112·4° in thiophene. While the sum of these two angles remains constant for the three molecules, the difference between the two angles is substantial for both 2-bromothiophene and bithiophene (5·1 and 9·0° respectively). In both cases the smaller of the two angles is centered on the substituted C atoms. The difference in the two angles is 2·5° for dibromobithiophene with the smaller angle being closest to the Br atom. The combination of the electron-donating ability of the thienyl group and the electron-withdrawing capacity of the Br atom would be expected to cancel for 5,5′-dibromo-2,2′-bithiophene which has both substituents.

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References

Auwers, K. & Bredt, T. V. (1894). *Chem. Ber.* **27**, 1741–1747.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2*B*. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Frenz, B. A. (1983). *Enraf–Nonius Structure Determination Package; SDP Users Guide*, version 1.1. Enraf–Nonius, Delft, The Netherlands.

Harshbarger, W. R. & Bauer, S. H. (1970). *Acta Cryst.* B**26**, 1010–1020.

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

Karl, R. R. & Bauer, S. H. (1972). *Acta Cryst.* B**28**, 2619–2621.

Kellogg, R. M., Schaap, A. P. & Wynberg, H. (1969). *J. Org. Chem.* **34**, 343–346.

Lipka, A. & von Schnering, H. G. (1977). *Chem. Ber.* **110**, 1377–1381.

Meunier, P., Coustale, M. & Arriau, J. (1978). *Bull. Soc. Chim. Belg.* **87**, 27–39.

Meunier, P., Coustale, M., Guimon, C. & Pfister-Guillouzo, G. (1977). *J. Mol. Struct.* **36**, 233–242.

Panfilova, L. V., Antipin, M. Yu., Struchkov, Yu. T., Churkin, Yu. D. & Lipkin, A. E. (1980). *Strukt. Khim.* **21**, 190–192.

Steinkopf, W. & Roch, J. (1930). *Ann. Chem.* **482**, 251–264.

Uhlenbroek, J. H. & Bijloo, J. D. (1960). *Recl Trav. Chim.* **79**, 1181–1196.

Veracini, C. A., Macciantelli, D. & Lunazzi, L. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 751–754.

Visser, G. J., Heeres, G. J., Wolters, J. & Vos, A. (1968). *Acta Cryst.* B**24**, 467–473.