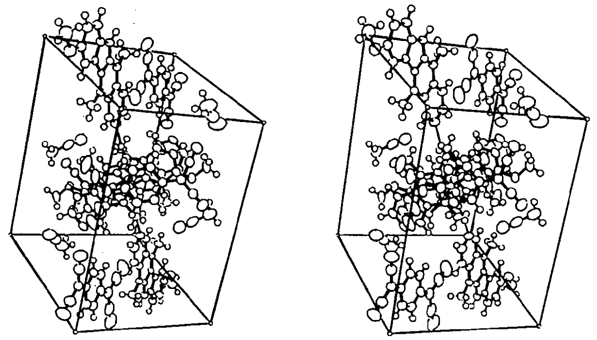

Fig. 2. Vue stéréoscopique de l'empilement moléculaire avec représentation des liaisons hydrogène.

prises en sandwich entre deux molécules de TCNQ suivant la séquence d'empilement de type alterné [TCNQ – 'ellipticine' – 'ellipticine' – TCNQ]$_n$.

Le recouvrement entre les molécules d''ellipticine' homologues par le centre de symétrie est assez faible, la distance entre plans moyens correspondants est de 3,503 Å. En revanche, le recouvrement entre les molécules de TCNQ et d''ellipticine' est plus important, essentiellement au niveau du noyau carbazole; la distance entre les plans moyens y est plus courte et vaut 3,237 Å. Cette dernière valeur, relativement faible, laisse supposer une interaction de transfert de charge non négligeable, par comparaison avec la valeur de 3,34 Å entre les plans moyens homologues calculée par Kobayashi (1973) dans le complexe carbazole–TCNQ. Les couches doubles TCNQ–'ellipticine', homologues par le plan de glissement c, sont approximativement parallèles au plan (120) et ($1\bar{2}0$). Elles sont liées entre elles, au niveau des molécules d''ellipticine' par la liaison hydrogène N(6)—H(6)···N(2^{i}) [2,833 (4) Å et 168 (3)°; code de symétrie: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$]. La cohésion cristalline est en outre assurée par des liaisons intermoléculaires mettant en jeu non seulement les molécules de TCNQ et d''ellipticine', mais encore la molécule d'acétonitrile solvate, dont la plus courte distance C(32)—O(20^{iv}) vaut 3,206 (8) Å [code de symétrie: (iv) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$].

En conclusion, l'adjonction du cycle pyridinique au noyau carbazole conduit, lors de la complexation avec le TCNQ à un transfert de charge plus important que dans le cas de l'adjonction du cycle pyrimidinique. Cependant, ce transfert reste très limité par suite de la disposition alternée des molécules de donneur et d'accepteur d'électrons.

Nous exprimons nos remerciements à la Société SANOFI qui a mis gracieusement à notre disposition la méthoxy-9 ellipticine.

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Structure of 3,3,5′-Tribromo-2,2′-bithiophene

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Abstract. $C_8H_3Br_3S_2$, $M_r = 402{\cdot}99$, monoclinic, $P2_1$, $a = 3{\cdot}995$ (1), $b = 12{\cdot}254$ (2), $c = 10{\cdot}951$ (1) Å, $\beta = 97{\cdot}47°$, $V = 531{\cdot}5$ (1) Å^3, $Z = 2$, $D_x = 2{\cdot}519$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 11{\cdot}60$ mm^{-1}, $F(000) = 376$, $T = 296$ K, $R = 0{\cdot}031$ for 960 independent reflections. The dihedral angle between the two rings is

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4·6°. The mean C—Br bond distance is 1·874 (8) Å and the mean C—S bond distance is 1·734 (8) Å. The mean C—S—C bond angle is 91·0 (4)°.

Introduction. The nematocidal activity of substituted 2,2′-bithiophenes and polythienyls has been shown to depend strongly on the number and type of substituents (Uhlenbroeck & Bijloo, 1960). Of the disubstituted bithiophenes, the 5,5′-dichloro and 5,5′-dimethyl derivatives exhibit strong activity while 5,5′-dibromo-2,2′-bithiophene has no activity. No trisubstituted derivative has as yet been investigated for this property. 3,5,5′-Trichloro-2,2′-bithiophene was synthesized directly using an excess of sulfuryl chloride (Eberhardt, 1895) and was identified by Steinkopf & von Petersdorf (1940). The 3,5,5′-trinitro derivative has been prepared by a direct multistep nitration of bithiophene using nitric acid (Carpanelli & Leandrii, 1961). 5,5′-Dibromo- and 3,3′,5,5′-tetrabromo-2,2′-bithiophene were originally synthesized by direct bromination (Auwers & Bredt, 1894). The tribromo derivative is probably an intermediate in this reaction, but has not been previously isolated. Molecular-orbital calculations on bithiophene indicate that the 5 position is the most reactive and that the next most reactive is the 3 position (Kellogg, Schaap & Wynberg, 1969). In this work copper(II) bromide has been shown to be a sufficiently strong brominating agent to halogenate bithiophene to the 3,5,5′-tribromo derivative.

Several halogenated bithiophenes have been shown to exist in two conformations. An equilibrium of planar conformations is observed in the solid state and in liquid crystals for the 5,5′-dichloro, 5,5′-dibromo and 5,5-dinitro derivatives (Veracini, Macciantelli & Lunazzi, 1973). A twisted configuration with a dihedral angle of 35° is observed for 3,3′-dibromo- and 5,5′-dibromo-2,2′-bithiophene in the gas phase and in solution (Meunier, Coustale, Guimon & Pfister-Guillouzo, 1977; Meunier, Coustale & Arriau, 1978). The solid-state conformation is sensitive to the nature of the substituents. 5,5′-Dibromo-2,2′-bithiophene is planar and shows the combined effect of thienyl and bromo substitution (Pyrka, Fernando, Inoue, Inoue & Velazquez, 1988), whereas 5,5′-dinitro-2,2′-bithiophene exhibits a small dihedral angle of 3·3° (Panfilova, Antipin, Struchkov, Churkin & Lipkin, 1980). The substitution of a third electron-withdrawing Br atom is expected to alter the π system and cause asymmetric distortions in the two rings.

Experimental. Single crystals of 3,5,5′-tribromo-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. A pale-yellow prism with approximate dimensions 0·23 × 0·36 × 0·02 mm was mounted on a Nicolet/Syntex $P2_1$ diffractometer. The cell constants were determined from 25 reflections in the range $25 < 2\theta < 34°$. The space group was determined to be $P2_1$ on the basis of the systematic absences ($0k0$, $k = 2n + 1$) and the interpretation of the Patterson function. The $2\theta/\theta$ scan method with a variable scan rate from 2 to 8° min^{-1} (2θ) ($h = 0$ to 5; $k = 0$ to 15; $l = -14$ to 14) 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 factors ranged from 12·8 to 74·0. The data were corrected for Lorentz, polarization factors and absorption effects. 1476 reflections with $2\theta < 55°$ were measured of which 1291 were unique. Intensities of equivalent reflections were averaged. 10 reflections were rejected from the averaging process. $R_{\rm merge}$ for the 293 multiply observed reflections was 2·1% based on intensity and 1·6% based on F_o. 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. 960 reflections with $I > 3\sigma(I)$ were used in a full-matrix least-squares refinement of 117 parameters where $\sum w(|F_o| - |F_c|)$ was minimized; w was calculated from $w = 4F/\sigma^2(F^2)$. The individual refinements for the two enantiomorphs of the molecule converged with $R = 0·031$, $wR = 0·036$ and $R = 0·036$, $wR = 0·042$. The solution for the enantiomorph with the lower R factor is reported on the basis of the Hamilton (1965) R-factor test at the 0·005 level. The ratio $\Delta_{\rm max}/\sigma$ was 0·06 and the largest peak in the Fourier difference map was 0·50 (13) e Å^{-3}. The scattering factors used were from Cromer & Waber (1974) and anomalous-dispersion effects were included in the calculation 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 e.s.d.'s are in Table 2. The structure of 3,5,5′-tribromo-2,2′-bithiophene is shown in Fig. 1 in an *ORTEP* (Johnson, 1965) drawing with 50% thermal ellipsoids, and a stereoview of the unit cell is shown in Fig. 2. The molecule consists of two planar substituted thiophene rings with the largest deviation from the least-squares plane being 0·027 (16) Å for C4*A* in the dibrominated ring and 0·022 (16) Å for C5*B* in the

* Lists of structure factors, anisotropic thermal parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51063 (14 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)
Br3*A*	0·3591 (4)	0·4221 (2)	0·2942 (1)	3·32 (3)
Br5*A*	0·6060 (4)	0·7845 (2)	−0·0140 (1)	3·67 (3)
S*A*	0·776 (1)	0·7511 (3)	0·2697 (3)	2·84 (7)
C2*A*	0·677 (3)	0·631 (1)	0·342 (1)	2·4 (3)
C3*A*	0·517 (3)	0·562 (1)	0·258 (1)	2·5 (3)
C4*A*	0·464 (4)	0·601 (1)	0·134 (1)	3·2 (3)
C5*A*	0·603 (4)	0·701 (1)	0·129 (1)	2·7 (3)
H4*A*	0·349	0·562	0·066	5·0
Br5*B*	0·8331 (4)	0·500	0·8440 (1)	3·53 (3)
S*B*	0·6614 (9)	0·5135 (3)	0·5624 (3)	2·74 (7)
C2*B*	0·772 (3)	0·624 (1)	0·474 (1)	2·0 (2)
C3*B*	0·955 (4)	0·699 (1)	0·550 (1)	2·9 (3)
C4*B*	0·991 (3)	0·669 (1)	0·677 (1)	2·7 (3)
C5*B*	0·857 (3)	0·573 (1)	0·696 (1)	2·5 (3)
H3*B*	1·045	0·765	0·521	5·0
H4*B*	1·102	0·713	0·741	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 bond angles* (°)

S*A*	C2*A*		1·740 (8)	S*B*	C2*B*		1·750 (8)
S*A*	C5*A*		1·718 (8)	S*B*	C5*B*		1·728 (7)
C2*A*	C3*A*		1·345 (11)	C2*B*	C3*B*		1·389 (11)
C3*A*	C4*A*		1·427 (11)	C3*B*	C4*B*		1·428 (10)
C4*A*	C5*A*		1·354 (13)	C4*B*	C5*B*		1·314 (11)
Br3*A*	C3*A*		1·882 (8)	C3*B*	H3*B*		0·950 (9)
Br5*A*	C5*A*		1·874 (8)	Br5*B*	C5*B*		1·866 (7)
C4*A*	H4*A*		0·950 (9)	C4*B*	H4*B*		0·950 (8)
C2*A*	C2*B*		1·455 (10)				
C2*A*	S*A*	C5*A*	90·8 (4)	C2*B*	S*B*	C5*B*	91·3 (4)
S*A*	C2*A*	C2*B*	117·2 (6)	C2*A*	C2*B*	S*B*	123·1 (6)
S*A*	C2*A*	C3*A*	110·0 (5)	S*B*	C2*B*	C3*B*	109·6 (6)
C3*A*	C2*A*	C2*B*	132·8 (7)	C2*A*	C2*B*	C3*B*	127·3 (7)
C2*A*	C3*A*	C4*A*	115·7 (8)	C2*B*	C3*B*	C4*B*	112·6 (8)
Br3*A*	C3*A*	C2*A*	124·9 (6)	Br3*A*	C3*A*	C4*A*	119·3 (6)
C3*A*	C4*A*	C5*A*	109·4 (8)	C3*B*	C4*B*	C5*B*	113·4 (8)
Br5*A*	C5*A*	S*A*	120·6 (5)	Br5*B*	C5*B*	S*B*	117·6 (4)
Br5*A*	C5*A*	C4*A*	125·4 (7)	Br5*B*	C5*B*	C4*B*	129·2 (6)
S*A*	C5*A*	C4*A*	114·0 (7)	S*B*	C5*B*	C4*B*	113·0 (6)

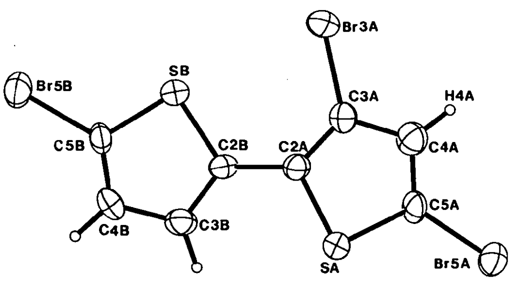

Fig. 1. Molecular geometry of 3,5,5′-tribromo-2,2′-bithiophene.

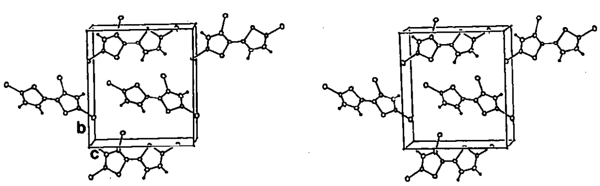

Fig. 2. Packing diagram in the unit cell.

monobrominated ring. Unlike 5,5′-dibromo-2,2′-bithiophene, the two rings are not coplanar and have a dihedral angle of 4·6° between the planes of the rings.

The S—C2 and S—C5 bond lengths for the monobromo- and dibromo-substituted rings are identical within experimental error, 1·734 (8) Å. These values are the same as found for 5,5′-dibromo-2,2′-bithiophene. The C—Br bond distances also remain unaffected. The C2—C3 bond distance is significantly longer than the C4—C5 bond length in the monosubstituted ring, 1·39 (1) *vs* 1·31 (1) Å. This differs from the 5,5′-dibromo derivative, where the two corresponding bond lengths are similar. The C2—C3 and C4—C5 bond lengths are identical in the dibromo-substituted ring.

The C—S—C bond angles in both rings are the same as those found for other bithiophenes. The C2—C3—C4 and C3—C4—C5 bond angles are essentially identical in the monobromo-substituted ring. In the disubstituted ring, however, the difference between the corresponding angles is 6·3°. The smaller of the two angles is centered on C4 which is bonded to an H atom.

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endo,endo,exo-2,6,10-Tribromo-*exo*-5-methoxy-13-oxa-*trans*-bicyclo[7.3.1]tridecane

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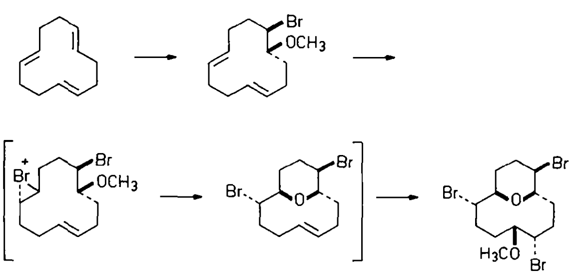
Abstract. $C_{13}H_{21}Br_3O_2$, $M_r = 449{\cdot}04$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}739$ (1), $b = 12{\cdot}270$ (3), $c = 19{\cdot}231$ (2) Å, $V = 1590{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}88$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 7{\cdot}53$ mm^{-1}, $F(000) = 880$, $T = 296$ K, final $R = 0{\cdot}028$ for 1085 unique observed reflections. The title compound was obtained, *via* transannular *O*-heterocyclization, in the methoxybromination of (*E,E,E*)-cyclododeca-1,5,9-triene. The pyran ring has a chair and the oxacyclodecane ring a distorted boat–chair–boat conformation.

Introduction. Two types of transannular cyclizations have been observed in the methoxybromination of cycloalkadienes and cycloalkatrienes with medium- and large-sized rings. Transannular π-cyclizations with formation of bicyclo[*n*.4.0]alkanes have been found for nine-, ten- and eleven-membered cycloalka-1,5-dienes (Haufe & Mühlstädt, 1979), whereas under similar conditions, transannular *O*-heterocyclizations with formation of oxabicyclic compounds have been found for eight-, twelve- and thirteen-membered 1,5-dienes and 1,5,9-trienes (Graefe, Haufe & Mühlstädt, 1976; Haufe, 1984; Haufe & Mühlstädt, 1984; Rissanen, Valkonen & Haufe, 1987). The reaction pathway is determined by the ring size, the configuration of the double bonds and the conformation of the unsaturated carbocycle.

The reaction of (*E,E,E*)-cyclododeca-1,5,9-triene with *N*-bromosuccinimide and methanol yields a mixture of simple *anti*-1,2-addition products, two oxatricyclic compounds and one oxabicyclic compound. The structure of the latter compound, a tribromomethoxy-13-oxabicyclo[7.3.1]tridecane, could not be determined completely from spectroscopic data (Haufe, 1987).

To establish the exact composition, configuration and conformation of the compound, we determined its crystal and molecular structure. The title compound is presumably formed by the following mechanism.



The first step, a typical methoxybromination, yields the *cis*-1,2-addition product. Repeated attack of the electrophilic bromonium species leads to a cation from which, through transannular *O*-participation of the methoxy group and subsequent demethylation, *endo,exo*-2,10-dibromo-13-oxabicyclo[7.3.1]tridec-(*E*)-5-ene is formed. This compound could not be isolated. The *E* double bond of the oxacyclodecene system, which contains a medium-sized ring, is likely more strained and hence more reactive than the *E* double bonds in the starting triene. Thus another attack of a brominium species from the *endo* side and nucleophilic attack of methanol on carbon C(5) can be presumed to take place, leading to the final product, *endo,endo,exo*-2,6,10-tribromo-*exo*-5-methoxy-13-oxa-*trans*-bicyclo-[7.3.1]tridecane.

Experimental. Colourless crystals, synthesized according to Haufe (1987), 0·15 × 0·12 × 0·25 mm, mounted on a glass fibre, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, ω–2θ method, lattice parameters from 25 reflections with $6 < \theta < 12°$, two standard reflections measured every hour, linear 15% loss of intensity; corrected, 2675 independent reflections (h: 0→9, k: 0→17, l: 0→26) with $\theta < 30°$,

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