Data collection

Siemens *P*3/PC diffractometer
$2\theta/\theta$ scans
Absorption correction: none
2429 measured reflections
2173 independent reflections
1072 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 100 reflections
intensity decay: <3%

Refinement

Refinement on *F*
$R = 0.061$
$wR = 0.068$
$S = 1.11$
1072 reflections
210 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.001481F^2]$

$(\Delta/\sigma)_{\rm max} = 0.069$
$\Delta\rho_{\rm max} = 0.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S(1)	0.3012 (4)	0.8984 (2)	0.5726 (2)	0.052 (1)
O(1)	0.8712 (10)	0.9989 (5)	0.8839 (5)	0.072 (2)
O(2)	0.7038 (9)	1.0157 (5)	0.7169 (4)	0.068 (2)
N(1)	0.3120 (10)	0.7212 (5)	0.8686 (5)	0.040 (2)
N(2)	0.7037 (11)	0.9672 (5)	0.7970 (5)	0.049 (3)
N(3)	0.1334 (10)	0.7424 (5)	0.6822 (4)	0.042 (2)
N(4)	0.6675 (10)	0.8399 (5)	0.9783 (5)	0.046 (2)
C(2)	0.1416 (11)	0.6904 (6)	0.7719 (6)	0.037 (3)
C(4)	0.3136 (12)	0.8340 (6)	0.6909 (6)	0.039 (3)
C(5)	0.5085 (12)	0.8732 (6)	0.7903 (6)	0.040 (3)
C(6)	0.4960 (11)	0.8126 (6)	0.8806 (6)	0.037 (3)
C(7)	−0.0534 (12)	0.5836 (6)	0.7564 (6)	0.041 (3)
C(8)	−0.0352 (13)	0.5062 (7)	0.8307 (6)	0.049 (3)
C(9)	−0.2156 (14)	0.4068 (8)	0.8157 (7)	0.059 (3)
C(10)	−0.4204 (14)	0.3835 (8)	0.7281 (6)	0.057 (3)
C(11)	−0.4390 (13)	0.4595 (8)	0.6545 (6)	0.053 (3)
C(12)	−0.2630 (13)	0.5587 (7)	0.6670 (6)	0.047 (3)
C(13)	0.0232 (14)	0.8108 (9)	0.4806 (7)	0.057 (3)
C(14)	0.6569 (16)	0.7707 (10)	1.0641 (8)	0.061 (4)

Table 2. *Selected geometric parameters* (Å, °)

S(1)—C(4)	1.751 (8)	S(1)—C(13)	1.788 (7)
O(1)—N(2)	1.238 (7)	O(2)—N(2)	1.224 (9)
N(1)—C(2)	1.328 (8)	N(1)—C(6)	1.336 (8)
N(2)—C(5)	1.412 (9)	N(3)—C(2)	1.35 (1)
N(3)—C(4)	1.332 (8)	N(4)—C(6)	1.342 (8)
N(4)—C(14)	1.45 (1)	C(2)—C(7)	1.483 (9)
C(4)—C(5)	1.428 (8)	C(5)—C(6)	1.43 (1)
C(7)—C(8)	1.39 (1)	C(7)—C(12)	1.410 (9)
C(8)—C(9)	1.37 (1)	C(9)—C(10)	1.38 (1)
C(10)—C(11)	1.37 (1)	C(11)—C(12)	1.36 (1)
C(4)—S(1)—C(13)	100.7 (4)	C(2)—N(1)—C(6)	118.1 (6)
O(1)—N(2)—O(2)	121.3 (6)	O(1)—N(2)—C(5)	119.4 (7)
O(2)—N(2)—C(5)	119.3 (5)	C(2)—N(3)—C(4)	117.1 (5)
C(6)—N(4)—C(14)	121.5 (6)	N(1)—C(2)—N(3)	126.6 (6)
N(1)—C(2)—C(7)	117.5 (6)	N(3)—C(2)—C(7)	115.8 (5)
S(1)—C(4)—N(3)	116.3 (4)	S(1)—C(4)—C(5)	122.7 (5)
N(3)—C(4)—C(5)	121.0 (6)	N(2)—C(5)—C(4)	120.7 (7)
N(2)—C(5)—C(6)	122.4 (5)	C(4)—C(5)—C(6)	116.9 (6)
N(1)—C(6)—N(4)	116.6 (7)	N(1)—C(6)—C(5)	120.2 (5)
N(4)—C(6)—C(5)	123.1 (6)	C(2)—C(7)—C(8)	120.6 (6)
C(2)—C(7)—C(12)	121.1 (7)	C(8)—C(7)—C(12)	118.3 (6)
C(7)—C(8)—C(9)	120.5 (6)	C(8)—C(9)—C(10)	120.8 (8)
C(9)—C(10)—C(11)	118.9 (7)	C(10)—C(11)—C(12)	121.7 (7)
C(7)—C(12)—C(11)	119.8 (8)		

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *SHELXTL-Plus* (Sheldrick, 1990). Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,3′-Bis(octyloxy)-2,2′-bithiophene at 195 K

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Abstract

In the solid state, the title molecule, $C_{24}H_{38}O_2S_2$, possesses a crystallographic centre of symmetry. The bithiophene ring system is planar and the central C2—C2′ bond length is 1.445 (2) Å. The O atom is within the thiophene mean plane and the torsion angles in the octyloxy chains are all *trans*, except for the angle around the first C—C bond which is *gauche*. The octyloxy chains are all parallel to one another and are aligned along the bisector of the *ac* face of the unit cell.

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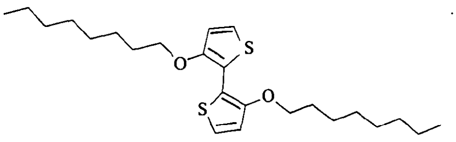
Comment

There is a growing interest in conducting polymers, especially those based on substituted thiophenes, since polythiophene itself decomposes upon heating and is not soluble in most organic solvents and is thus not easily amenable to the formation of polymeric films or fibres. However, it has been shown that the presence of side chains lowers the melting point and makes the substituted polythiophenes soluble in most organic solvents, such as chloroform, tetrahydrofuran or toluene (Jen, Miller & Elsenbaumer, 1986; Sato, Tanaka & Kaeriyama, 1986). It seems that the presence of side chains does not greatly affect the conducting properties. It is therefore of interest to establish the structure of the poly(alkoxythiophenes). In order to arrive at the structure of the parent polymer, a number of related model compounds were synthesized and their crystal structures established. The structure reported here is that of 3,3′-bis(octyloxy)-2,2′-bithiophene, (I), a model for poly(3-octyloxythiophene), and will be referred to as DOBT. The bond distances and angles are compared in Table 2 with those of bithiophene (Pelletier & Brisse, 1994).



(I)

A perspective representation of the title compound with the atomic numbering is shown in Fig. 1. It is of interest to note that this structure is completely ordered, *i.e.* no disorder in either the bithiophene system or the side chains. The molecule, which is centrosymmetric, consists of a planar bithiophene ring system to which side chains are attached at atoms C3 and C3($1 - x$, $-y$, $1 - z$). The distance between the rings is 1.445 (2) Å. Atom O3 is practically in the thiophene least-squares plane [deviation 0.026 (1) Å]. The first torsion angle in the octyloxy chain of DOBT, τ(C4—C3—O3—C31), is −4.7 (2)°. A similar observation was noted in other substituted bithiophene systems, such as 3,3′-dibutoxy-2,2′-bithiophene (τ = 2.4°; Pelletier, Brisse, Cloutier & Leclerc, 1995) and 3,3′-dimethoxy-2,2′-bithiophene (τ = 4.7°; Paulus, Daniel, Kämpf, Wegener, Siam, Wolinski & Schäfer, 1988). In this orientation, sulfur interactions with the lateral chain are minimized. The next torsion angle in the chain, around the C31—C32 bond, is *gauche*, while the other torsion angles all have a *trans* conformation. Although not completely planar, since some torsion angles deviate by up to 5° from 180°, the plane formed by the group of aliphatic C atoms from C31 to C38 is tilted by 67 (1.5)° from the bithiophene plane (Fig. 2), but is nearly parallel to the bithiophene plane of its nearest neighbour. The packing of the DOBT molecules in the unit cell is shown in Fig. 3. All the molecules are parallel to one another and are aligned in the direction of the bisector of the *ac* face of the unit cell.

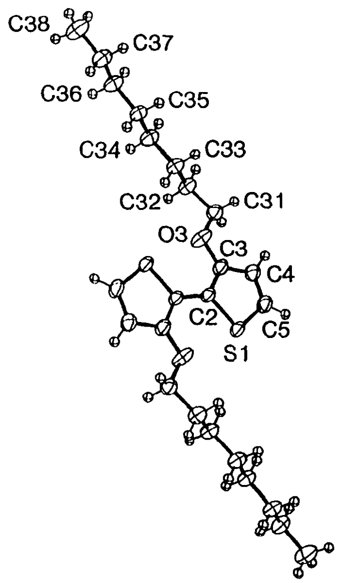


Fig. 1. Perspective drawing of the title compound showing the atomic numbering. Displacement ellipsoids are drawn at the 40% probability level and H atoms are represented by spheres of arbitrary radii.

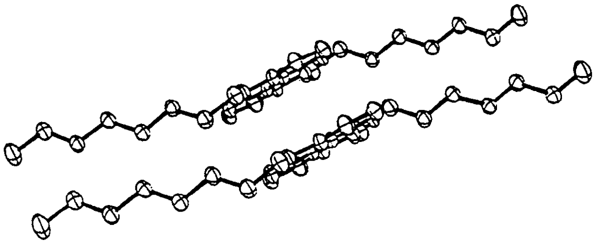


Fig. 2. Two molecules shown to reveal the relative orientations of the bithiophene ring system and the alkoxy chains.

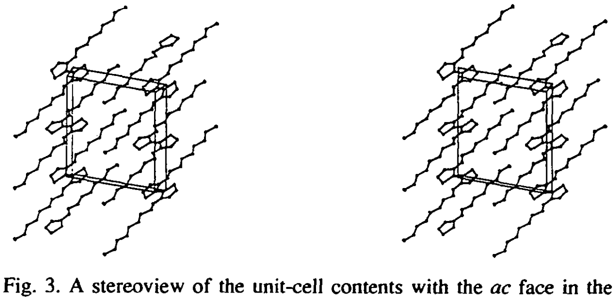


Fig. 3. A stereoview of the unit-cell contents with the *ac* face in the plane of the page and the *c* axis vertical.

Experimental

The title compound was obtained by the alkylation of 3-bromothiophene with sodium alcoholate using CuO and KI as catalysts. Suitable single crystals were grown by slow evaporation of a hexane solution. D_m was measured by flotation in $ZnCl_2$ solution.

Crystal data

$C_{24}H_{38}O_2S_2$
$M_r = 422.69$
Monoclinic
$P2_1/c$
$a = 11.968\ (2)$ Å
$b = 7.340\ (1)$ Å
$c = 13.539\ (2)$ Å
$\beta = 99.77\ (1)°$
$V = 1172.1\ (3)$ Å^3
$Z = 2$
$D_x = 1.192$ Mg m^{-3}
$D_m = 1.19$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 20–25°$
$\mu = 2.12$ mm^{-1}
$T = 195$ K
Platelet
0.25 × 0.23 × 0.09 mm
Dark blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8842 measured reflections
2211 independent reflections
1910 observed reflections $[I > 1.96\sigma(I)]$

$R_{\text{int}} = 0.079$
$\theta_{\text{max}} = 70°$
$h = -14 \rightarrow 14$
$k = -8 \rightarrow 8$
$l = -16 \rightarrow 16$
5 standard reflections monitored every 400 reflections intensity decay: $\leq 1.6\%$

Refinement

Refinement on F
$R = 0.036$
$wR = 0.046$
$S = 1.749$
1910 reflections
127 parameters
All H-atoms fixed
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\text{max}} = 0.10$
$\Delta\rho_{\text{max}} = 0.42$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.25$ e Å^{-3}
Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.66466 (3)	0.07073 (6)	0.59276 (3)	0.0289 (1)
C2	0.5421 (1)	0.0712 (2)	0.5030 (1)	0.0246 (4)
C3	0.5419 (1)	0.2225 (2)	0.4426 (1)	0.0278 (4)
C4	0.6395 (1)	0.3349 (3)	0.4669 (1)	0.0319 (5)
C5	0.7122 (1)	0.2678 (3)	0.5467 (1)	0.0320 (5)
O3	0.4520 (1)	0.2525 (2)	0.3673 (1)	0.0360 (4)
C31	0.4534 (2)	0.4204 (3)	0.3125 (1)	0.0321 (5)
C32	0.3379 (2)	0.4455 (3)	0.2487 (1)	0.0327 (5)
C33	0.3053 (2)	0.3012 (3)	0.1677 (1)	0.0308 (5)
C34	0.1913 (2)	0.3431 (3)	0.1023 (1)	0.0330 (5)
C35	0.1605 (2)	0.2126 (3)	0.0146 (1)	0.0305 (5)
C36	0.0493 (2)	0.2600 (3)	−0.0540 (1)	0.0335 (5)
C37	0.0211 (2)	0.1293 (3)	−0.1419 (1)	0.0385 (5)
C38	−0.0894 (2)	0.1740 (3)	−0.2110 (2)	0.0497 (6)

Table 2. *Comparison of the bond distances* (Å) *and angles* (°) *in the bithiophene moiety of* DOBT *and bithiophene itself*

	DOBT at 195 K (This work)	Bithiophene at 133 K (Pelletier & Brisse, 1994)
S1—C2	1.739 (2)	1.713 (3)
C2—C3	1.379 (2)	1.432 (4)
C3—C4	1.422 (3)	1.444 (5)
C4—C5	1.362 (3)	1.357 (5)
C5—S1	1.710 (2)	1.698 (4)
C2—C2$^{\text{i}}$	1.445 (2)	1.448 (4)
S1—C2—C3	109.4 (1)	112.5 (2)
C2—C3—C4	114.3 (2)	108.8 (3)
C3—C4—C5	111.3 (2)	114.9 (3)
C4—C5—S1	112.9 (1)	112.1 (3)
C5—S1—C2	92.1 (1)	92.5 (2)
S1—C2—C2$^{\text{i}}$	122.4 (1)	121.1 (2)
C3—C2—C2$^{\text{i}}$	128.2 (2)	126.4 (3)

Symmetry code: (i) $1 - x, -y, 1 - z$.

Table 3. *Selected geometric parameters* (Å, °) *in the aliphatic segment of* DOBT

C3—O3	1.369 (2)	C34—C35	1.521 (3)
O3—C31	1.440 (2)	C35—C36	1.528 (3)
C31—C32	1.512 (3)	C36—C37	1.521 (3)
C32—C33	1.527 (3)	C37—C38	1.521 (3)
C33—C34	1.527 (3)		
C2—C3—O3	119.6 (2)	C32—C33—C34	111.8 (2)
C4—C3—O3	126.2 (2)	C33—C34—C35	113.6 (2)
C3—O3—C31	116.4 (1)	C34—C35—C36	113.7 (2)
O3—C31—C32	108.0 (1)	C35—C36—C37	112.7 (2)
C31—C32—C33	115.0 (2)	C36—C37—C38	113.6 (2)
C4—C3—O3—C31	−4.7 (2)	C32—C33—C34—C35	174.6 (2)
C2—C3—O3—C31	175.2 (2)	C33—C34—C35—C36	−177.1 (2)
C3—O3—C31—C32	−168.5 (1)	C34—C35—C36—C37	179.2 (2)
O3—C31—C32—C33	−64.0 (2)	C35—C36—C37—C38	179.9 (9)
C31—C32—C33—C34	−176.2 (2)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

The structure was solved by direct methods using *SHELX*76 (Sheldrick, 1976) and refined by block-diagonal least squares using *SHELXS*86 (Sheldrick, 1985). H atoms were allowed for but were not refined (C—H 0.94–1.00 Å).

The financial support of the Natural Sciences and Engineering Research Council of Canada is hereby acknowledged. We are also thankful to Dr M. Simard for the X-ray collection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: FG1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimethyl 4-*exo*,9-*endo*-Dibromobicyclo[3.3.1]non-2-ene-2,3-dicarboxylate

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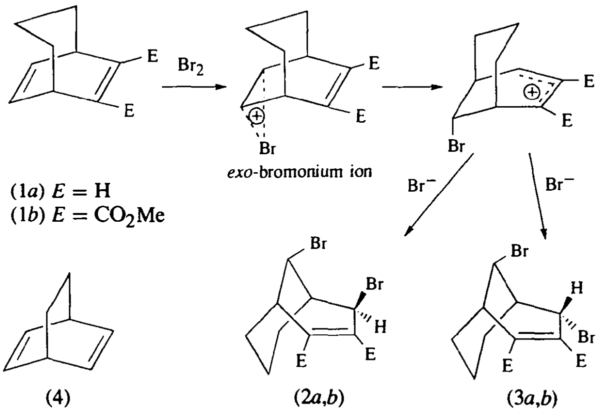
Abstract

The bromination reaction of dimethyl bicyclo[3.2.2]nona-6,8-diene-6,7-dicarboxylate, (1*b*), gave the title compound (2*b*), $C_{13}H_{16}Br_2O_4$, and dimethyl 4-*exo*,9-*exo*-dibromobicyclo[3.3.1]non-2-ene-2,3-dicarboxylate, (3*b*). The saturated six-membered ring of (2*b*) adopts a chair conformation with the Br atom in an equatorial position.

Comment

The electrophilic bromination reaction of norbornadiene, which gave the skeleton-rearranged dibromide, is of interest in connection with the intramolecular mutual interaction of the two double bonds (Winstein & Shatavsky, 1956; Schmerling, Luvisi & Welch, 1956). On the other hand, in the case of the norbornadiene homologues, bicyclodienes (1*a*) and (4), 1,5- and 1,2-addition, under similar conditions, of the bromine to the common cyclohexa-1,4-diene part in the molecule occurred to give dibromides without any skeleton-rearrangement products (Fickes & Metzs, 1978; Gagneux & Grob, 1959; Grob & Hostynek, 1963). Regarding the synthetic work for the norbornadiene homologues bicyclo[4.2.2]deca-7,9-diene and bicyclo[5.2.2]undeca-8,10-diene (Satake, Usumoto, Hikasa, Kimura, Kishima & Morosawa, 1992), a reinvestigation of the bromination reaction of the bicyclodiene (1*a*) and its dimethoxycarbonyl derivative (1*b*) was undertaken in order to investigate a systematic change in features of the mutual intramolecular interactions of the 1,4-cyclohexadiene part of the structure.



When equimolar bromine was added to a dichloromethane solution of bicyclodiene (1*a*) or (1*b*) at 273 K, a hitherto unknown skeletal rearrangement occurred in both cases to give mixtures of dibromides presumably *via* an *exo*-bromonium ion of the starting bicyclodiene. The mixtures were chromatographed independently on silica gel and gave 9-*endo*- and 9-*exo*-dibromides (2*a*) and (3*a*), and (2*b*) and (3*b*), respectively. On the basis of ^1H and ^{13}C NMR spectra, these dibromides were shown to have the same carbon skeleton. We report here the structure of (2*b*) (Fig. 1).

The structure reported here is the first example of an X-ray structural analysis of the bicyclo[3.3.1]non-2-ene system. The features of the bicyclic ring are summarized as a chair-form cyclohexane ring [C(1)—C(9)—C(5)—C(6)—C(7)—C(8)] and a bending cyclohexene ring [C(1)—C(2)—C(3)—C(4)—C(5)—C(9)] whose five C

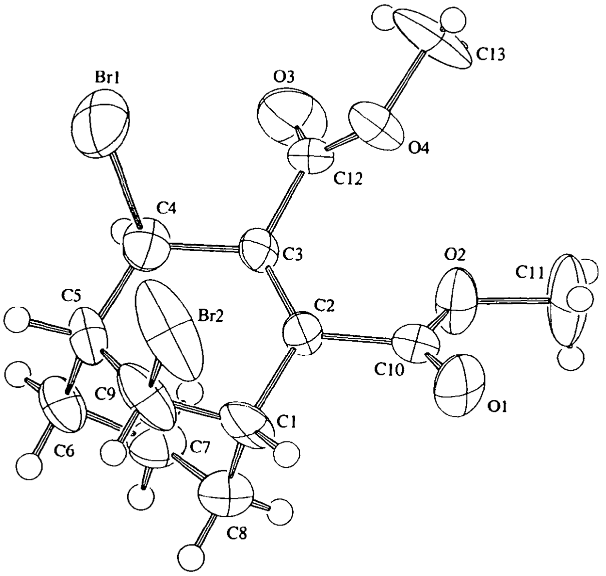


Fig. 1. *ORTEP*II diagram (Johnson, 1976) of the title compound with displacement ellipsoids of 50% probability drawn for non-H atoms. H atoms are represented as spheres equivalent to $B = 1.0$ Å^2.

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