*inter*molecular bond of the NH_2—N (sp^2) type, N3···H27*A* 2·07 (4), N3···N27 2·830 (4) Å and N3···H27*A*—N27 127 (3)° for the title compound, and N···H 2·19 (5), N···NH_2 3·030 (4) Å, N···H—N 171 (2)° for the compound referenced. The intramolecular hydrogen bond completes a six-membered ring adopting a sofa conformation. The packing arrangement in the crystal shows no contacts less than the sum of the van der Waals radii.

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Acta Cryst. (1988). C**44**, 545–547

Structure of Dithieno[3,4-*b*:3′,4′-*d*]thiophene

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(*Received* 13 *July* 1987; *accepted* 10 *November* 1987)

Abstract. $C_8H_4S_3$, M_r = 196·31, monoclinic, $P2_1/n$, a = 15·137 (6), b = 5·943 (3), c = 9·022 (4) Å, β = 97·1 (2)°, V = 805 (1) Å^3, $F(000)$ = 400, μ = 8·07 cm^{-1}, D_x = 1·62 g cm^{-3}, Z = 4, Mo $K\alpha$ radiation, λ = 0·71073 Å, T = 293 K, R = 3·8% based on 1112 independent reflections. The structure consists of the packing of planar discrete molecules. The geometric features as compared with thiophene analogues and a dithienothiophene isomer evidence a variation in 'aromaticity', according to a previously discussed trend. No short contacts are observed in the crystal packing.

Introduction. In the field of electroconducting polymers, polyheterocyclic systems have recently achieved major consideration because of their stability in air and processability and also in view of their relatively easy preparation by electrosynthesis, thus providing directly doped highly conducting materials. With the double purpose of elucidating conduction models suitable for these polymers and envisaging potential aplications, we have prepared polydithieno[3,4-*b*:3′,4′-*d*]thiophene (Bolognesi, Catellani, Destri, Zamboni & Taliani, 1987), a polymer exhibiting interesting optical and electronic properties. The understanding of these properties and their relation to the conduction process cannot disregard the structural evidence of the polymer. Moreover, *ab initio* calculations for determining electronic parameters, namely band gap, ionization potential, band width and electronic affinity, require the accurate knowledge of the system geometry. Therefore we report on the structure of the monomer dithieno[3,4-*b*:3′,4′-*d*]thiophene (DTT1) with particular reference to the analogue dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT).

Experimental. The synthesis of the title compound was carried out according to the literature (De Jong & Janssen, 1971) and the product was crystallized from a solution of 50% aqueous ethanol. In Table 1 the experimental details and the crystal data are summarized. Intensity data were collected on a Nonius CAD-4 computer-controlled diffractometer with a randomly-oriented crystal; they were subsequently corrected for Lorentz and polarization effects and an experimental absorption correction was applied (North, Phillips & Mathews, 1968). The absorption correction values range from 0·91 to 1·00. A linear correction for decay (*ca* 10% during the collection) was also applied. Unit-cell parameters and their e.s.d.'s were determined by an accurate centring of 25 strong reflections (θ range 5–12°) and then refined by least squares. The structure was solved by direct methods (*MULTAN*; Main, Lessinger, Woolfson, Germain & Declercq, 1977), using the solution with the highest figure of merit from 64 different sets (2500 relationships, $E_{\min}$ = 1·4). A subsequent Fourier map revealed the positions of all

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Table 1. *Experimental data*

Scan mode	θ–2θ
Scan speed (° min^{-1})	2·8
Scan width (°)	1·3 + 0·35 tanθ
θ range (°); $d_{\min}$ (Å)	3–25; 0·84
Measured reflections	h −18/18, k 0/7, l 0/11
Number of collected reflections	1589
Number of observed reflections (with $I > 2{\cdot}0\sigma$)*	1112
Standard reflections (measured every 130 reflections)	$\bar{3}1\bar{4}$, 413, 430†
Wavelength (Å) (Mo $K\alpha$ graphite-monochromated radiation)	0·7107
μ(Mo $K\alpha$) (cm^{-1})‡	8·07
Temperature (K)	293
Approximate crystal size (mm)	0·50 × 0·40 × 0·30

* $\sigma^2(I)$ = peak counts + total background counts.

† The intensity variation of the standard reflections during the collection was about 10%: a linear correction for decay was therefore applied (see text).

‡ The variation in transmittance was estimated at +10% and an absorption correction was applied (see text).

non-hydrogen atoms. The positional and thermal parameters were refined, using full-matrix least squares, minimizing $\sum w(F_o - KF_o)^2$, with weight factors equal to the inverse of σ^2. After a difference Fourier map, which allowed the localization of all H atoms ($\rho_{\max}$ and $\rho_{\min}$ $\pm 0{\cdot}3$ e Å^{-3}), six anisotropic least-squares cycles were carried out refining also the positional and thermal (isotropic) parameters of H atoms, to a conventional unweighted R value equal to 0·038 and a weighted wR of 0·040 (final shift-to-e.s.d. ratio and goodness of fit were $<0{\cdot}15\sigma$ and 1·60 respectively). Both real and imaginary components of the anomalous dispersion were included in the atomic scattering factor calculations (*International Tables for X-ray Crystallography,* 1974). All the computer programs used are part of the Nonius package (B. A. Frenz & Associates Inc., 1982). The atomic fractional coordinates and the thermal parameters are given in Table 2.*

Discussion. In Fig. 1 an *ORTEP* drawing (Johnson, 1976) of the molecule (DTT1) is shown, while interatomic distances and angles are reported in Table 3. The condensed rings lie roughly in a plane; in particular, each thiophene residue is planar, the maximum displacement observed being 0·006 Å. The whole molecule is slightly bent; the dihedral angles between the central ring (S1) and terminal rings are 1·2 (1) (S2) and 2·4 (1)° (S3). The geometric features of this molecule can be compared with the corresponding ones observed for dithieno[3,2-*b*:2′,3′-*d*]thiophene (Bertinelli, Palmieri, Stremmenos, Pelizzi & Taliani, 1983) (DTT). In fact the C—S distances in DTT1 are longer in the inner thiophene ring [1·756 (1) Å average] than in the outer rings [1·704 (1) Å average] as observed, to a lesser extent, in the case of DTT. The π delocalization of the C—S bond is decreased in the

Table 2. *Atomic fractional coordinates* (*with e.s.d.'s in parentheses*) *and thermal parameters* (Å^2)

	x	y	z	B/B_{eq}
S1	0·35896 (5)	0·3884 (1)	0·51209 (8)	4·05 (1)
S2	0·48019 (5)	−0·0316 (2)	0·21066 (9)	4·90 (2)
S3	0·13791 (5)	−0·0262 (2)	0·58283 (9)	4·74 (2)
C1	0·2731 (2)	0·1981 (5)	0·5356 (3)	3·12 (5)
C2	0·2769 (2)	−0·0045 (4)	0·4523 (3)	2·71 (5)
C3	0·3533 (2)	−0·0061 (4)	0·3687 (3)	2·76 (5)
C4	0·4026 (2)	0·1975 (5)	0·3915 (3)	3·18 (5)
C5	0·4740 (2)	0·2063 (5)	0·3133 (3)	4·35 (6)
C6	0·3883 (2)	−0·1467 (5)	0·2714 (3)	3·55 (6)
C7	0·2069 (2)	−0·1432 (5)	0·4680 (3)	3·52 (6)
C8	0·2019 (2)	0·2097 (5)	0·6135 (3)	4·09 (6)
H5	0·507 (1)	0·317 (4)	0·312 (3)	4·3 (6)*
H6	0·366 (1)	−0·289 (4)	0·240 (3)	3·8 (6)*
H7	0·193 (2)	−0·277 (4)	0·431 (3)	3·7 (6)*
H8	0·183 (2)	0·327 (5)	0·669 (3)	4·6 (6)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *in the molecule, with e.s.d.'s in parentheses*

S1—C1	1·755 (2)	C1—C2	1·424 (3)
S1—C4	1·756 (2)	C2—C3	1·457 (3)
S2—C5	1·699 (2)	C3—C4	1·423 (3)
S2—C6	1·700 (1)	C1—C8	1·359 (3)
S3—C7	1·707 (1)	C2—C7	1·364 (3)
S3—C8	1·707 (1)	C3—C6	1·365 (3)
C—H$_{ave}$	0·96 (3)*	C4—C5	1·363 (3)
C1—S1—C4	90·0 (1)	S3—C8—C1	110·2 (2)
C5—S2—C6	93·2 (1)	C1—C2—C3	111·4 (2)
C7—S3—C8	93·2 (1)	C2—C3—C4	110·8 (2)
S1—C1—C2	113·7 (2)	C1—C2—C7	111·9 (2)
S1—C4—C3	114·1 (2)	C2—C1—C8	113·7 (2)
S2—C5—C4	110·5 (2)	C3—C4—C5	113·2 (2)
S2—C6—C3	111·1 (2)	C4—C3—C6	112·0 (2)
S3—C7—C2	111·0 (2)		

* A correction for thermal libration in the independent-motion approximation was applied (Johnson, 1970).

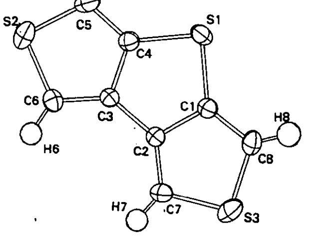

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the molecule, viewed normal to the plane of the rings, at 50% of the probability level of the thermal ellipsoids.

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* Lists of structure factors, anisotropic thermal parameters and equations of molecular best planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44523 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

central ring. It is worth considering the C—C distances. In the inner ring the difference between 'short' and 'long' bonds is only 0·033 (3) Å; for the outer rings the corresponding difference is 0·061 (3) Å. The comparable differences in DTT are 0·043 (3) and 0·070 (3) Å respectively. Hence one can infer that the inner ring exhibits a quite different bond order compared with the outer rings, thus exhibiting an enhanced degree of 'aromaticity'. We have actually discussed a trend for thiophene and analogues towards variation in 'aromaticity', passing from thiophene to fused-ring molecules (Bolognesi, Catellani, Destri & Porzio, 1987). However, this evidence cannot be stressed in view of the variation of the electronic charge distribution and geometric requirements induced by steric hindrance during ring formation. The corresponding bond angles of both DTT and DTT1 are quite similar, as expected. The intermolecular packing is governed by S···C and C···C contacts which are quite comparable to the sum of the van der Waals radii (S···C_{min} 3·60 and C···C_{min} 3·57 Å).

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Acta Cryst. (1988). C**44**, 547–550

Niflumate de Morpholinoéthyle (DCI: Morniflumate)

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(*Reçu le* 6 *juillet* 1987, *accepté le* 4 *novembre* 1987)

Abstract. Morpholinoethyl 2-{[3-(trifluoromethyl)-phenyl]amino}-3-pyridinecarboxylate, $C_{19}H_{20}F_3N_3O_3$, $M_r = 395\cdot4$, triclinic, $P\bar{1}$, $a = 10\cdot123\,(2)$, $b = 9\cdot157\,(2)$, $c = 11\cdot707\,(2)$ Å, $\alpha = 114\cdot04\,(2)$, $\beta = 100\cdot55\,(1)$, $\gamma = 102\cdot01\,(2)$°, $V = 924\cdot7\,(9)$ Å^3, $Z = 2$, $D_x = 1\cdot420$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 0\cdot97$ mm^{-1}, $F(000) = 412$, $T = 295\,(1)$ K, $R = 0\cdot040$ for 2328 independent reflections. The plane of the pyridine ring makes an angle of 22·65 (7)° with that of the phenyl ring. The carboxylate group and the pyridine ring bearing it are almost coplanar, the angle between the two planes being 9·37 (7)°. As in niflumic acid and other fenamates, a strong internal N—H···O hydrogen bond [2·696 (2) Å, 143 (2)°] forms a pseudo-ring, the plane of which is near to the pyridine ring plane. The morpholine ring exhibits a chair conformation. Each F atom shows high thermal motion and occupies three positions. The cohesion of the structure is due to van der Waals interactions.

Introduction. Les acides fénamique [acides (phénylamino-2)benzoïque] et niflumique sont des anti-inflammatoires non stéroïdiens. Plusieurs ont déjà fait l'objet d'une étude structurale. C'est le cas de l'acide méfénamique (McConnell & Company, 1976), de l'acide niflumique (Krishna Murthy & Vijayan, 1979), de l'acide méclofénamique (Krishna Murthy & Vijayan, 1981) et de deux formes de l'acide flufénamique

0108-2701/88/030547-04$03.00