

Data collection

Stoe Stadi-4 diffractometer $\theta_{\max} = 25.02^\circ$
 ω/θ scans $h = -12 \rightarrow 12$
 Absorption correction: none $k = 0 \rightarrow 13$
 5868 measured reflections $l = -16 \rightarrow 16$
 5562 independent reflections 3 standard reflections
 4215 reflections with frequency: 60 min
 $I > 2\sigma(I)$ intensity decay: none
 $R_{\text{int}} = 0.0181$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.0397$ $\Delta\rho_{\max} = 0.233 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.1072$ $\Delta\rho_{\min} = -0.218 \text{ e } \text{\AA}^{-3}$
 $S = 1.053$ Extinction correction: none
 5562 reflections Scattering factors from
 397 parameters *International Tables for*
 H atoms riding *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.9331P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

C1—C20	1.512 (3)	C1'—C20'	1.511 (3)
C1—S2	1.820 (3)	C1'—S2'	1.814 (3)
S2—C3	1.809 (2)	S2'—C3'	1.804 (3)
C3—C4	1.517 (3)	C3'—C4'	1.512 (3)
C4—C11	1.426 (3)	C4'—C11'	1.429 (3)
C11—C12	1.513 (3)	C11'—C12'	1.512 (3)
C12—S13	1.818 (3)	C12'—S13'	1.809 (3)
S13—C14	1.807 (2)	S13'—C14'	1.805 (3)
C14—C15	1.516 (3)	C14'—C15'	1.512 (3)
C15—C20	1.402 (3)	C15'—C20'	1.401 (3)
C3—S2—C1	101.63 (11)	C3'—S2'—C1'	101.59 (12)
C14—S13—C12	102.37 (11)	C14'—S13'—C12'	102.00 (12)
C20—C1—S2—C3	59.09 (19)		
C1—S2—C3—C4	78.4 (2)		
C11—C12—S13—C14	−58.92 (19)		
C12—S13—C14—C15	−78.2 (2)		
C20'—C1'—S2'—C3'	−60.69 (19)		
C1'—S2'—C3'—C4'	−74.4 (2)		
C11'—C12'—S13'—C14'	60.7 (2)		
C12'—S13'—C14'—C15'	74.5 (2)		

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of atomic coordinates, displacement parameters, least-squares-planes data, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Thieno[2,3-c]pyridine, the First Structure of a Thienopyridine

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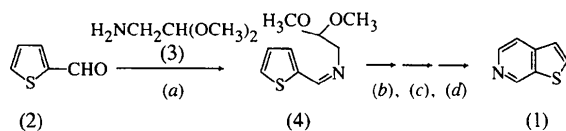
Abstract

The title molecule, $\text{C}_7\text{H}_5\text{NS}$, is planar to within 0.009 $\text{\AA}$. Bond lengths at the heteroatoms are S1—C2 1.7276 (14), S1—C7a 1.7308 (13), N6—C5 1.354 and N6—C7 1.332 (2) $\text{\AA}$; the C—S—C angle is 90.76 (6)°. A libration analysis indicated corrections of 0.003–0.004 $\text{\AA}$. Short intermolecular contacts [S1...N6 3.229 (1) $\text{\AA}$] link the molecules into chains parallel to the y axis.

Comment

Thieno[2,3-c]pyridine, (1), is of pharmacological interest because it is an isostere of isoquinoline (Friedrichsen, 1984). It represents a fused 10 π -ring system containing the π -rich thiophene and the π -deficient pyridine [for a review see Friedrichsen (1984)]. Recently, the *ab initio* geometries of all six isomers were discussed with regard to the mutual influence of the two heteroaromatics, but the absence of known structures necessarily prevented any correlation with structural data (Webber & Woolley, 1995). As a heteronaphthalene, (1) is an inherently polarized push–pull system with a ground-state dipole moment of 2.85 D (Klemm & Jacquot, 1975). The

polarization of (1) can be improved by introduction of donors to the thiophene and/or acceptors to the pyridine ring. The resonance stabilization of (1) is expected to be lower than that of naphthalene since the resonance energies per electron and also the aromatic energies of the parent heterocycles are smaller than for benzene (Gilchrist, 1992). Charge transfer between the donor and acceptor groups should therefore occur more easily in (1) than in naphthalene itself. As a result of these properties, we have used (1) as a π -bridge in the development of non-linear optical chromophores for blue transparent frequency doublers and also for electro-optical materials (Blenkle *et al.*, 1996; Nerenz, 1996). Polymers from compound (1) and its isomers should possess promising non-linear $\chi^{(3)}$ properties (Yamamoto *et al.*, 1996).



In order to calculate the non-linear optical properties (first hyperpolarizabilities β) by semi-empirical *PM3* methods (Clark & Wiedel, 1992) on the basis of the experimental geometry, we were interested in the crystal structure and electron density distribution of (1), which we prepared by modification of known procedures in 55% overall yield [full details are given by Nerenz (1996)]. We report here the crystal structure, which is the first of any of the six possible isomeric thienopyridines.

The planar molecule (mean deviation from least-squares plane of 0.009 Å) crystallizes in the centrosymmetric space group *Pbca* with no imposed symmetry (Fig. 1). The C—S bonds [S1—C2 1.7276 (14) and S1—C7a 1.7308 (13) Å] (unless otherwise stated, non-corrected values are used in this discussion) are slightly longer than in the electron diffraction structure of free thiophene (1.714 Å; Bonham & Momany, 1963); the

corresponding values in the non-fused system 2-(2'-thienyl)pyridine are 1.712 (3) and 1.723 (3) Å, to the substituted and non-substituted C atoms, respectively (Ghosh & Simonsen, 1993). The S—C—S angle of 90.76 (6)° in (1) is slightly narrower than in free thiophene [92.2 (2)°]. The C2—C3 bond [1.351 (2) Å] is essentially a double bond, whereas C3—C3a is the longest C—C bond at 1.433 (2) Å.

The N—C bond lengths [N6—C5 1.354 and N6—C7 1.332 (2) Å] are similar to the average of 1.336 Å (libration corrected 1.347 Å) for eight chemically equivalent bonds in the structure of solid pyridine (Mootz & Wussow, 1981). Indeed, the general pattern of bond lengths and angles in the six-membered ring of (1) is closely similar to that of free pyridine, except for a slight lengthening of the C3a—C7a bond [1.414 (2) Å], which is common to both rings.

The calculated *ab initio* geometry (Webber & Woolley, 1995) and our own *PM3* geometry are in good agreement with the experimental data (maximum deviation 0.015 Å/2.1° for *ab initio* and 0.013 Å/3.2° for *PM3*).

The packing diagram (Fig. 2; supplementary material) shows that the molecules are arranged in chains parallel to the *y* axis, with a short S1...N6($\frac{3}{2} - x, -\frac{1}{2} + y, z$) intermolecular contact of 3.229 (1) Å. This may be compared with the intramolecular S...N contact of 2.933 Å in 2-(2'-thienyl)pyridine (Ghosh & Simonsen, 1993).

Experimental

The title compound was synthesized in a four-step Pomeranz–Fritsch reaction using modifications of known methods (Birch, Jackson & Shannon, 1974; Maffrand & Eloy, 1976; Wikel, Denney & Vasileff, 1993): (a) equimolar amounts of thiophene-2-carbaldehyde, (2), and aminoacetaldehyde-dimethyl-acetal, (3), gave the imine (4) (100% yield); (b) the corresponding amine was obtained by reduction with sodium borohydride in 97% yield; (c) transformation to the *N*-tosyl derivative was effected with 4-toluenesulfonyl chloride (98% yield); (d) treatment with concentrated hydrogen chloride in dioxane then gave the title compound, (1), which was finally purified by sublimation (323 K, 20 Pa; 58% yield). Single crystals were obtained by sublimation at 293 K and atmospheric pressure over a period of several weeks.

Crystal data

C₇H₅NS

M_r = 135.18

Orthorhombic

Pbca

a = 5.7618 (6) Å

b = 14.4939 (18) Å

c = 14.5031 (18) Å

V = 1211.2 (2) Å³

Z = 8

D_x = 1.483 Mg m^{−3}

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 63 reflections

θ = 4.0–12.5°

μ = 0.420 mm^{−1}

T = 173 (2) K

Tablet

0.80 × 0.35 × 0.15 mm

Colourless

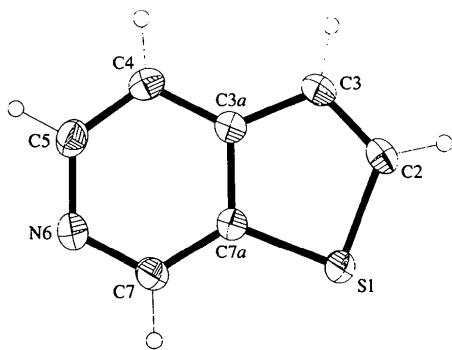


Fig. 1. The molecule of the title compound in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.

Data collection

Siemens P4 diffractometer $\theta_{\max} = 27.50^\circ$
 ω scans $h = -7 \rightarrow 0$
 Absorption correction: none $k = -18 \rightarrow 13$
 2569 measured reflections $l = 0 \rightarrow 18$
 1391 independent reflections 3 standard reflections
 1158 reflections with every 247 reflections
 $I > 2\sigma(I)$ intensity decay: none
 $R_{\text{int}} = 0.0202$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.0263$ $\Delta\rho_{\max} = 0.275 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.0776$ $\Delta\rho_{\min} = -0.230 \text{ e } \text{\AA}^{-3}$
 $S = 1.060$ Extinction correction: none
 1391 reflections Scattering factors from
 82 parameters *International Tables for*
 H atoms riding *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0457P)^2$
 $+ 0.123P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

S1—C2	1.7276 (14)	C3a—C7a	1.414 (2)
S1—C7a	1.7308 (13)	C4—C5	1.373 (2)
C2—C3	1.351 (2)	C5—N6	1.354 (2)
C3—C3a	1.433 (2)	N6—C7	1.332 (2)
C3a—C4	1.402 (2)	C7—C7a	1.397 (2)
C2—S1—C7a	90.76 (6)	N6—C5—C4	124.83 (13)
C3—C2—S1	114.04 (11)	C7—N6—C5	117.57 (13)
C2—C3—C3a	112.08 (12)	N6—C7—C7a	122.08 (13)
C4—C3a—C7a	117.29 (12)	C7—C7a—C3a	119.98 (12)
C4—C3a—C3	131.10 (12)	C7—C7a—S1	128.51 (10)
C7a—C3a—C3	111.60 (12)	C3a—C7a—S1	111.51 (9)
C5—C4—C3a	118.25 (13)		

A rigid-body libration analysis (Schomaker & Trueblood, 1968) gave corrections of $+0.004 \text{ \AA}$ for the bonds C2—S1 and C7a—S1, and $+0.003 \text{ \AA}$ for all other bonds. The RG value of 0.039 confirms that the rigid-body approximation is a reasonable one.

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994). Software used to prepare material for publication: SHELXL93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1264). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methylhexamethylenetetramine Fluoride Tetrahydrate, MeHMTAF.4H₂O

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Abstract

The novel title fluoride source, $\text{C}_7\text{H}_{15}\text{N}_4^+\cdot\text{F}^-\cdot 4\text{H}_2\text{O}$, was crystallized from methanol. The cations adopt an alternating up–down arrangement and are separated into layers by an extended hydrogen-bonded fluoride–water sheet network.

Comment

In the course of our work producing novel fluoride sources for the fluorodenitration of aromatic compounds,