Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
5868 measured reflections
5562 independent reflections
4215 reflections with
$I > 2\sigma(I)$
$R_{\rm int} = 0.0181$

$\theta_{\rm max} = 25.02°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0397$
$wR(F^2) = 0.1072$
$S = 1.053$
5562 reflections
397 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.9331P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.233$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.218$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

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: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Fonds der Chemischen Industrie for financial support and Mr. A. Weinkauf for technical assistance.

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.

References

Bodwell, G., Ernst, L., Hopf, H. & Jones, P. G. (1989). *Tetrahedron Lett.* **30**, 6005–6008.
Jones, P. G., Hopf, H. & Kuś, P. (1996). *Z. Kristallogr.* **211**, 839–840.
Kuś, P. (1987). *Pol. J. Chem.* **61**, 95–98.
Okajima, T., Wang, Z.-H. & Fukazawa, Y. (1989). *Tetrahedron Lett.* **30**, 1551–1554.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stoe & Cie (1992*a*). *DIF*4. *Diffractometer Control Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU*4. *Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). C**53**, 787–789

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

HEIKO NERENZ,[a] WALTER GRAHN[a] AND PETER G. JONES[b]*

[a]*Institut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and* [b]*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de*

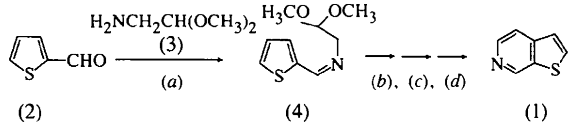
(*Received 28 November 1996; accepted 3 February 1997*)

Abstract

The title molecule, C_7H_5NS, is planar to within 0.009 Å. 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) Å; the C—S—C angle is 90.76 (6)°. A libration analysis indicated corrections of 0.003–0.004 Å. Short intermolecular contacts [S1···N6 3.229 (1) Å] 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 10π-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 *PM*3 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.

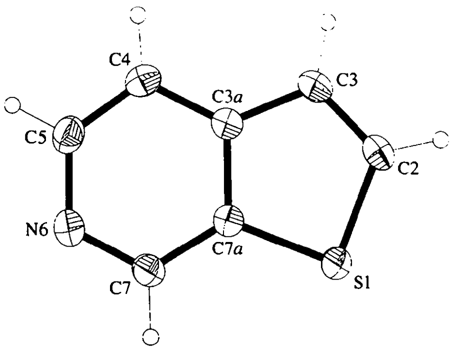


Fig. 1. The molecule of the title compound in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.

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 *PM*3 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 *PM*3).

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–dimethylacetal, (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

C_7H_5NS
$M_r = 135.18$
Orthorhombic
Pbca
$a = 5.7618\,(6)$ Å
$b = 14.4939\,(18)$ Å
$c = 14.5031\,(18)$ Å
$V = 1211.2\,(2)$ Å^3
$Z = 8$
$D_x = 1.483$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 63 reflections
$\theta = 4.0$–$12.5°$
$\mu = 0.420$ mm^{-1}
$T = 173\,(2)$ K
Tablet
0.80 × 0.35 × 0.15 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2569 measured reflections
1391 independent reflections
1158 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.0202$
$\theta_{\max} = 27.50°$
$h = -7 \rightarrow 0$
$k = -18 \rightarrow 13$
$l = 0 \rightarrow 18$
3 standard reflections every 247 reflections intensity decay: none

Refinement

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

Table 1. *Selected geometric parameters (Å, °)*

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 Å for the bonds C2—S1 and C7a—S1, and +0.003 Å 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: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Volkswagen–Stiftung, the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

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.

References

Birch, A. J., Jackson, A. H. & Shannon, P. V. R. (1974). *J. Chem. Soc. Perkin Trans.* 1, pp. 2185–2190.

Blenkle, M., Boldt, P., Bräuchle, C., Grahn, W., Ledoux, I., Nerenz, H., Stadler, S., Wichern, J. & Zyss, J. (1996). *J. Chem. Soc. Perkin Trans.* 2, pp. 1377–1384.

Bonham, R. A. & Momany, F. A. (1963). *J. Phys. Chem.* **67**, 2474–2477.

Clark, T. & Wiedel, B. (1992). *VAMPC*4.45 *Program Package.* University of Erlangen, Germany.

Fait, J. (1991). *XSCANS Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Friedrichsen, W. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 4, edited by A. R. Katritzky & C. W. Rees, pp. 973–1036. Oxford: Pergamon Press.

Ghosh, R. & Simonsen, S. H. (1993). *Acta Cryst.* C**49**, 1031–1032.

Gilchrist, T. L. (1992). In *Heterocyclic Chemistry.* Harlow: Longman Scientific & Technical.

Klemm, L. H. & Jacquot, R. D. (1975). *J. Heterocycl. Chem.* **12**, 615–618.

Maffrand, J. P. & Eloy, F. (1976). *J. Heterocycl. Chem.* **13**, 1347–1349.

Mootz, D. & Wussow, H.-G. (1981). *J. Chem. Phys.* **75**, 1517–1522.

Nerenz, H. (1996). PhD thesis, Technical University of Braunschweig, Germany. [ISBN 3-932243-02-1]

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XP. Interactive Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Webber, J. S. & Woolley, R. G. (1995). *J. Mol. Struct. (Theochem.)*, **341**, 181–200.

Wikel, J. H., Denney, M. L. & Vasileff, R. T. (1993). *J. Heterocycl. Chem.* **30**, 289–290.

Yamamoto, T., Zhou, Z.-H., Kanbara, T., Shimura, M., Kizu, K., Maruyama, T., Nakamura, Y., Fukuda, T., Lee, B.-L., Ooba, N., Tomaru, S., Kurihara, T., Kaino, T., Kubota, K. & Sasaki, S. (1996). *J. Am. Chem. Soc.* **118**, 10389–10399.

Acta Cryst. (1997). C**53**, 789–791

Methylhexamethylenetetramine Fluoride Tetrahydrate, MeHMTAF.4H$_2$O

DAVID J. NIGHTINGALE, LEROY CRONIN AND JAMES H. CLARK

Department of Chemistry, University of York, Heslington, York YO1 5DD, England. E-mail: jhc1@york.ac.uk

(Received 19 November 1996; accepted 14 January 1997)

Abstract

The novel title fluoride source, $C_7H_{15}N_4^+.F^-.4H_2O$, 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,

Acta Crystallographica Section C
ISSN 0108-2701 © 1997