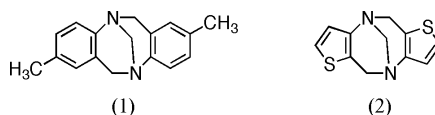


4,5,9,10-Tetrahydro-4,9-methanodithieno-
[3,2-*b*:3',2'-*f*][1,5]diazocineTomoshige Kobayashi,^{a*} Takashi
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Key indicators

Single-crystal X-ray study
T = 93 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.043
wR factor = 0.101
Data-to-parameter ratio = 21.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.In the title compound, $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2$, which is the first thiophene
analogue of Tröger's base, the dihedral angle between the two
thiophene rings is $100.73 (7)^\circ$.Received 11 April 2003
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Comment

Tröger's base, (1), and its analogues have recently received
much attention as a basic skeleton to construct molecular
receptors, due to the rigid structure and concave shape
(Demeunynck & Tatibouët, 1999). However, Tröger's base
and its analogues exhibit various values of the dihedral (hinge)
angle between the two aromatic rings, depending on the
nature of the fused aromatic rings and their substituents, in
spite of the rigid bicyclic skeleton (Demeunynck & Tatibouët,
1999). For example, the dihedral angle of (1) was reported as
being $92.9 (2)$ and $97.4 (2)^\circ$ (Wilcox, 1985; Sucholeiki *et al.*,
1988). The angles vary from $88.6 (1)$ to $104.01 (6)^\circ$, depending
on the substituents of the benzene ring. The dihedral angles of
heteroaromatic analogues, such as pyrazole [$96.4 (4)^\circ$; Cudero
et al., 1997] and porphyrin (81.0 and 89.7° ; Crossley *et al.*, 1995)
have also been reported.We recently reported the synthesis of the title compound,
(2) (Kobayashi *et al.*, 2002), which is the first example of a
thiophene analogue of Tröger's base. An X-ray crystal struc-
ture determination of (2) was undertaken in order to estimate
the concave space as well as the dihedral angle between the
two thiophene rings.No significant differences of bond lengths and angles for the
thiophene rings of (2) were observed, compared with those
previously reported for thiophene (Nygaard *et al.*, 1969) and a
thiophene fused with a norbornadiene skeleton (Kobayashi *et al.*,
1993). The dihedral angle between the two thiophene rings
was found to be $100.73 (7)^\circ$, which is slightly larger than that in
Tröger's base. Therefore, compound (2) seems to have a
longer concave space than that of (1), and it is of interest to
synthesize molecular receptors based on (2), as well as to
investigate the effect of the concave space for selective
binding. The synthetic approach toward new molecular
receptors will be reported elsewhere in due course.

Experimental

The title compound, (2), was prepared according to the procedure of
Kobayashi *et al.* (2002), and recrystallized from methanol to give
colorless blocks.

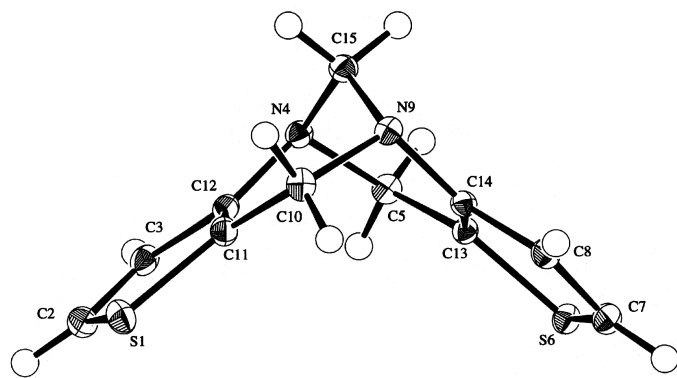


Figure 1
A view of the title compound, (2), showing the atom-labelling scheme and 50% displacement ellipsoids for non-H atoms.

Crystal data

$C_{11}H_{10}N_2S_2$
 $M_r = 234.33$
 Monoclinic, $P2_1/c$
 $a = 7.700$ (2) Å
 $b = 19.601$ (5) Å
 $c = 7.332$ (2) Å
 $\beta = 112.58$ (2)°
 $V = 1021.8$ (5) Å³
 $Z = 4$

$D_x = 1.523$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 10963 reflections
 $\theta = 3.0$ – 30.0°
 $\mu = 0.48$ mm⁻¹
 $T = 93.2$ K
 Block, colorless
 $0.15 \times 0.10 \times 0.05$ mm

Data collection

Rigaku R-AXIS RAPID Imaging
 Plate diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.879$, $T_{\max} = 0.976$
 12265 measured reflections

2979 independent reflections
 2255 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -27 \rightarrow 26$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.101$
 $S = 1.02$
 2969 reflections
 136 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.69$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Selected geometric parameters (Å).

S1—C2	1.728 (2)	N9—C15	1.477 (2)
S1—C11	1.729 (2)	C2—C3	1.362 (3)
S6—C7	1.726 (2)	C3—C12	1.430 (3)
S6—C13	1.724 (2)	C5—C13	1.511 (3)
N4—C5	1.486 (2)	C7—C8	1.368 (3)
N4—C12	1.433 (2)	C8—C14	1.434 (3)
N4—C15	1.478 (2)	C10—C11	1.512 (3)
N9—C10	1.483 (3)	C11—C12	1.370 (3)
N9—C14	1.437 (2)	C13—C14	1.371 (3)

H-atom positional parameters were calculated geometrically ($C-H = 0.95$ Å) and these atoms were constrained to ride on their parent atoms, with $U_{\text{iso}}(H) = U_{\text{eq}}(\text{parent atom})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 1999); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Crossley, M. J., Hambley, T. W., Mackay, L. G., Try, A. C. & Walton, R. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1077–1079.
- Cudero, J., Pardo, C., Ramos, M., Gutierrez-Puebla, E., Monge, A. & Elguero, J. (1997). *Tetrahedron*, **53**, 2233–2240.
- Demeunynck, M. & Tatibouët, A. (1999). *Prog. Heterocycl. Chem.* **11**, 1–11.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kobayashi, T., Moriwaki, T., Tsubakiyama, M. & Yoshida, S. (2002). *J. Chem. Soc. Perkin Trans. 1*, pp. 1963–1967.
- Kobayashi, T., Ono, K., Suda, H., Yamashita, Y. & Kato, H. (1993). *Bull. Chem. Soc. Jpn.* **66**, 2707–2713.
- Molecular Structure Corporation & Rigaku (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan.
- Nygaard, L., Nielsen, J. T., Kirchner, J., Maltesen, G., Rastruo-Andersen, J. & Sørensen, G. O. (1969). *J. Mol. Struct.* **3**, 491–506.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sucholeiki, I., Lynch, V., Phan, L. & Wilcox, C. S. (1988). *J. Org. Chem.* **53**, 98–104.
- Wilcox, C. S. (1985). *Tetrahedron Lett.* **26**, 5749–5752.