

(1Z,2Z)-1,2-Bis(3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidene)hydrazineTaku Nakano,^{a*} Hiroko Kakuda,^a Yoshihiro Mori^a and Motoo Shiro^b^aDepartment of Pharmaceutical Sciences, University of Toyama, 2630 Sugitani, Toyama-shi, Toyama 930-0194, Japan, and ^bRigaku Corporation, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo 196-8666, Japan

Correspondence e-mail: tnakano@pha.u-toyama.ac.jp

Received 14 March 2006

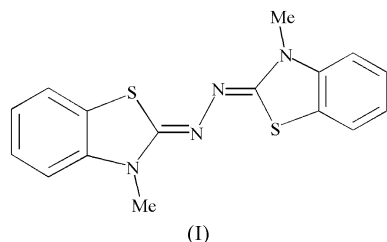
Accepted 19 April 2006

Online 24 May 2006

The title compound, C₁₆H₁₄N₄S₂, crystallizes in symmetry group C₂. The molecule is planar with C_{2h} symmetry, with the inversion centre at the mid-point of the hydrazine N–N bond, and it has an N–N *s-trans* conformation and a *Z,Z* configuration. The particular crystal examined was a racemic twin, as suggested by the Flack parameter of 0.41 (2) [Flack (1983). *Acta Cryst.* **A39**, 876–881].

Comment

The molecular structure of the title compound, (I), examined at 93 K is shown in Fig. 1. Selected bond distances and angles and the torsion angles relating to the >C=N–N=C< chain are listed in Table 1. The packing of the molecules is indicated in Fig. 2. The particular crystal studied here proved to be a racemic twin, as suggested by the Flack parameter (Flack, 1983) of 0.41 (2). During the refinement, the structure was treated as a racemic twin.



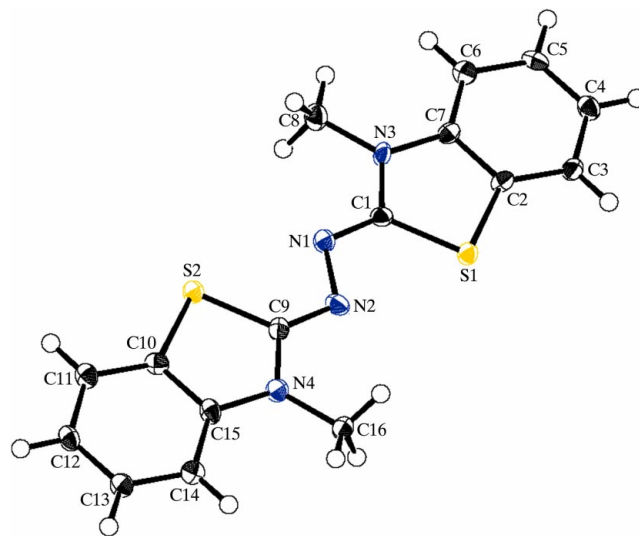
Compound (I) was oxidized by air to a cation radical in acetonitrile or on silica gel. The cation radical is blue and stable for weeks. Its visible spectrum shows a broad band with three peaks at 659, 733 and 818 nm (Nakano & Mori, 2005; Sawicki *et al.*, 1963). The spectrum is very similar to that of the cation radical of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) [ABTS; systematic name: 2,2'-(hydrazine-1,2-diylidene)bis(3-ethyl-2,3-dihydrobenzo[*d*]thiazole-6-sulfonate)] which is a water-soluble analogue of the present compound (Henriquez & Lissi, 2002). Compound (I) was previously described in reaction with oxidants such as nitrite (Sawicki *et*

al., 1963) and potassium ferricyanide (Bartsch *et al.*, 1970). This electron-donating character to form the stable cation radical suggests that compound (I) would be useful for forming charge-transfer complexes with electron acceptors such as TCNQ (Guerin *et al.*, 2002).

A recent point of concern regarding compounds with azine groups has appeared in the term 'conjugate stopper' for heteroatoms in 1,3-diene systems including N atoms (Glaser *et al.*, 1993; Zuman & Ludvik, 2000; Choitun *et al.*, 2004). It was thought that the conjugation effect through the azine group was determined by the bond distances of =N1–N2= and –C1=N1– (–C9=N2–) and the torsion angle about the N–N bond of the >C=N–N=C< chain; the single-bond character of N–N and the double-bond character of C=N indicate a lack of delocalization of π electrons, while the planar structure of C=N–N=C indicates π conjugation.

The molecular geometry of compound (I) including >C=N–N=C< is completely planar (torsion angle of less than 1°; Table 1). It has a *Z,Z* configuration, with angles of 111.0 and 110.2° for C1–N1–N2 and N1–N2–C9, respectively (Fig. 1). On the other hand, the bond distances of N1–N2 and C1=N1 (C9=N2) are 1.409 and 1.287 Å (1.294 Å), respectively (Table 1). The former indicates almost a single bond if compared with the value of 1.45 Å in NH₂NH₂ (Liminga & Olovsson, 1964), and the latter almost a double bond if compared with the value of 1.28 Å in imines (Allen *et al.*, 1987). Additionally, these data are very similar to those of formaldehyde azine, where the distances for N–N and C=N are 1.418 and 1.277 Å, respectively, and the angles for C–N–N and H–C–N are 111.4 and 120.7°, respectively (Lide, 1993). These bond distances suggests less delocalization of π electrons, while the molecule is completely flat, permitting interaction between π bonds of the C=N groups.

The packing of the molecules of (I) in the solid state indicates the lack of intra- and intermolecular hydrogen bonds,

**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

suggesting no hydrogen-bonding effect on the lone-pair electrons of the azine group.

The concept of the 'conjugation stopper' of the azine group relating to distances and geometry has not been convincing to date and the present structural results add to the knowledge in the field. The fact that the cation radical of compound (I) is stable gives additional information about the electronic structure of azine groups.

Experimental

Compound (I) was prepared by the oxidation of 3-methyl-2-benzothiazolinone hydrazone (MBTH; alternative name: 2-hydrazino-3-methyl-2,3-dihydrobenzo[d]thiazole), (II), in air, catalyzed by a water-soluble iron porphyrin, FeTMPyPCl₅ {[5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphine]iron(III) pentachloride}, in a phosphate buffer solution (0.1 M; pH 7.0) (Nakano *et al.*, 2005). Through the redox reaction of the iron porphyrin, the superoxide anion radical is released and the porphyrin peripheral eventually decomposes after 30 min. Reagent (II) acts not only as a reducing one-electron donor, but is also oxidized to form compound (I), and dinitrogen is released from the system. In the present study, the reaction was performed under conditions of 7.0×10^{-4} M MBTH hydrochloride and a catalytic concentration of hemin (1×10^{-5} M). The product, (I), was extracted from the reaction mixture into dichloromethane, purified by column chromatography (silica gel, dichloromethane) and then crystallized from a solution in dichloromethane–petroleum ether (1:1) by free evaporation of the solvents overnight. Crystals were collected on filter paper, washed with petroleum ether and dried. A single crystal was selected and used for the data collection. Analysis: $m/z = 326.0661$; ¹H NMR (300 MHz, acetonitrile-*d*₃): δ 7.44 (2H), 7.27 (2H), 7.20 (4H), 3.48 (6H); sublimation at 500–503 K (literature m.p. 534–535 K; Hünig & Quast, 1968).

Crystal data

C₁₆H₁₄N₄S₂
 $M_r = 326.43$
 Monoclinic, C2
 $a = 16.0038$ (17) Å
 $b = 5.8679$ (7) Å
 $c = 15.9529$ (18) Å
 $\beta = 104.235$ (8)°
 $V = 1452.1$ (3) Å³

$Z = 4$
 $D_x = 1.493$ Mg m⁻³
 Cu $K\alpha$ radiation
 $\mu = 3.33$ mm⁻¹
 $T = 93$ (1) K
 Block, pale yellow
 $0.15 \times 0.15 \times 0.10$ mm

Data collection

Rigaku R-AXIS RAPID
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.597$, $T_{\max} = 0.717$

7214 measured reflections
 2506 independent reflections
 2352 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 68.2^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.094$
 $S = 1.10$
 2506 reflections
 203 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 2.2491P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³
 Absolute structure: Flack (1983),
 with 1044 Friedel pairs
 Flack parameter: 0.41 (2)

Table 1

Selected geometric parameters (Å, °).

S1—C1	1.765 (3)	N2—C9	1.294 (3)
S2—C9	1.762 (3)	N3—C1	1.384 (4)
N1—N2	1.409 (3)	N4—C9	1.375 (4)
N1—C1	1.287 (3)		
N2—N1—C1	111.0 (2)	S1—C1—N1	127.7 (2)
N1—N2—C9	110.2 (2)	S1—C1—N3	110.7 (2)
C1—N3—C8	119.8 (2)	N1—C1—N3	121.6 (3)
C9—N4—C16	120.2 (2)	S2—C9—N2	127.3 (2)
C1—N1—N2—C9	−178.9 (3)	N2—N1—C1—N3	−179.2 (3)
N1—N2—C9—N4	−179.5 (3)	N2—N1—C1—S1	0.3 (4)
N1—N2—C9—S2	0.6 (4)		

H atoms were refined using a riding model, with C—H distances in the range 0.95–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CrystalStructure*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3007). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bartsch, R. A., Hünig, S. & Quast, H. (1970). *J. Am. Chem. Soc.* **92**, 6007–6011.
- Choytun, D. D., Langlois, L. D., Johannsson, T. P., Macdonald, C. L. B., Leach, G. W., Weinberg, N. & Clyburne, J. A. C. (2004). *Chem. Commun.* pp. 1842–1843.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Glaser, R., Chen, G. S. & Barnes, C. L. (1993). *J. Org. Chem.* **58**, 7446–7455.
- Guerin, D., Lorcy, D., Carlier, R., Los, S. & Piekara-Sady, L. (2002). *J. Solid State Chem.* **168**, 590–596.
- Henriquez, C. & Lissi, E. (2002). *Bol. Soc. Chil. Quim.* **47**, 563–566.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Hünig, S. & Quast, H. (1968). *Liebigs Ann. Chem.* **711**, 139–156.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lide, D. R. (1993). Editor. *CRC Handbook of Chemistry and Physics*, 74th ed., pp. P9–P32. Boca Raton: CRC Press.
- Liminga, R. & Olovsson, I. (1964). *Acta Cryst.* **17**, 1523–1528.
- Nakano, T. & Mori, Y. (2005). Unpublished results.
- Nakano, T., Ohto, K., Okafuji, F., Mori, Y., Kakuda, H., Hatanaka, Y. & Masuoka, N. (2005). *Bull. Chem. Soc. Jpn.* **78**, 703–709.
- Rigaku (1998). *PROCESS-AUTO*. Version 1.06. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2005). *CrystalStructure*. Version 3.7. Rigaku Americas Corporation, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Sawicki, E., Stanley, T. W., Praff, J. & Johnson, H. (1963). *Anal. Chem.* **35**, 2183–2191.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Zuman, P. & Ludvik, J. (2000). *Tetrahedron Lett.* **41**, 7851–7853.