Partial support of this research from Southern Illinois University through doctoral fellowship (YH), distinguished professorship (CYM) and NCRR Minority Initiative (DS) funding and from the University Research Foundation (URF, La Jolla, CA) is graciously acknowledged.

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S-Methyl β-N-[4-(Dimethylamino)benzylidene]dithiocarbazate

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Abstract

The title compound, $C_{11}H_{15}N_3S_2$, a Schiff base, forms a centrosymmetric dimeric structure linked by N—H···S hydrogen bonds. The dithiocarbazate moiety shows an

E configuration about both the C2—N2 and C1—N1 bonds.

Comment

Recently, there has been considerable interest in the chemistry of Schiff base compounds containing N and S donors and their metal complexes. This is due to their biological properties, chelating ability with transition metal ions (Ali & Tarafdar, 1977; Ali & Bose, 1984; Davies, El-Sayed, El-Toukhy & Henary, 1990; Tian, Duan, Lu, You, Fun & Kandasamy, 1996) and non-linear optical properties (Tian, Duan, Lu, You & Mak, 1996). As part of our studies on the synthesis and characterization, as well as the potential non-linear optical properties, of new Schiff base derivatives, we report here the crystal structure of the title compound, (1).
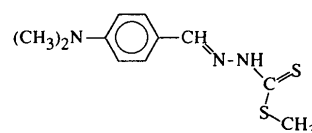
(1)

The dithiocarbazate moiety shows an E configuration about both the C2—N2 and C1—N1 bonds as found in most dithiocarbazates (Fun *et al.*, 1995) and thiosemicarbazones (Mathew & Palenik, 1971). Though non-planar as a whole, the molecule contains two planar fragments, namely the dithiocarbazate moiety, (I), and the aminophenyl moiety, (II). The dihedral angle between them is *ca* 7.2° [mean deviations of (I) and (II) are 0.007 and 0.011 Å, respectively]. The value for the C1—S1 bond, 1.663 Å, agrees well with those of related compounds, being intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond (Sutton, 1965). The corresponding bond distance for C1—N1, 1.333 Å, is indicative of some double-bond character.

The H atom attached to the amino N atom has the potential to act as a hydrogen-bond donor. The intermolecular hydrogen bonds which link molecules to-
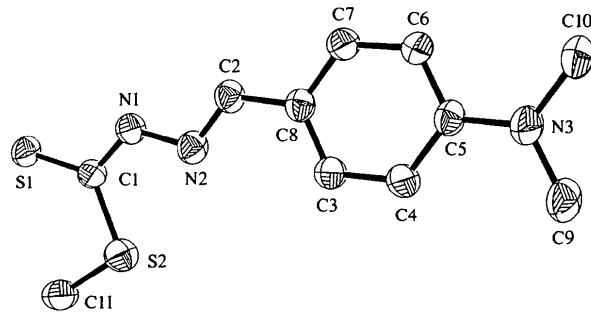

Fig. 1. A view (*ORTEP*; Johnson, 1965) of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.
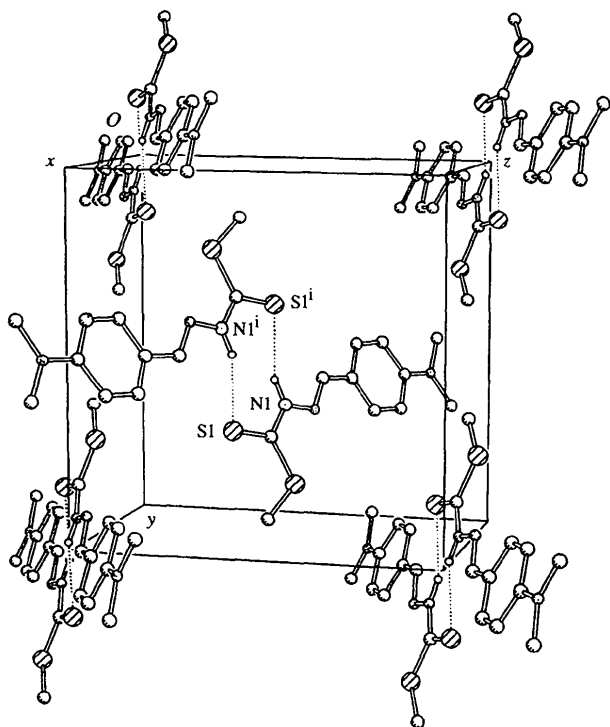
Fig. 2. Packing viewed down the a axis.

gether in the solid state are shown in Fig. 2, which features a centrosymmetric dimeric structure consolidated by hydrogen bonds of the type N1—H···S1^i [symmetry code: (i) $-x$, $1-y$, $1-z$], which are weak because the N···S separation, 3.389 (6) Å, is at the upper end of the range summarized by Srinivasan & Chacke (1967). The bond angle around the H atoms, N1—H1···S1^i, is 159.0 (5)°.

Experimental

The title compound was obtained by the reaction of S-methyldithiocarbazate and p-dimethylaminobenzaldehyde (molar ratio 1:1) in absolute ethanol. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a benzene solution in air.

Crystal data

$C_{11}H_{15}N_3S_2$	Mo $K\alpha$ radiation
$M_r = 253.40$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 8.364$ (2) Å	$\theta = 11–18°$
$b = 12.684$ (3) Å	$\mu = 0.389$ mm^{-1}
$c = 12.224$ (2) Å	$T = 294$ K
$\beta = 92.36$ (3)°	Prism
$V = 1295.7$ (7) Å^3	$0.41 \times 0.36 \times 0.28$ mm
$Z = 4$	Yellow
$D_x = 1.299$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7R four-circle-diffractometer	$R_{int} = 0.056$
	$\theta_{max} = 27.50°$
Profile-fitted ω scans	$h = 0 \rightarrow 10$
Absorption correction: none	$k = 0 \rightarrow 16$
3165 measured reflections	$l = -15 \rightarrow 15$
2970 independent reflections	3 standard reflections
1982 reflections with	frequency: 97 min
$F > 6\sigma(F)$	intensity decay: 0.965%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.280$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.079$	$\Delta\rho_{min} = -0.360$ e Å^{-3}
$wR(F^2) = 0.080$	Extinction correction:
$S = 1.080$	SHELXL93 (Sheldrick,
1982 reflections	1993)
146 parameters	Extinction coefficient:
H atoms refined as riding	0.0010 (4)
model, with U_{iso} fixed	Scattering factors from
$w = 1/\sigma^2(F_o^2)$	International Tables for
$(\Delta/\sigma)_{max} = 0.083$	Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C1	1.663 (4)	N3—C10	1.450 (6)
S2—C1	1.744 (4)	C2—C8	1.452 (5)
S2—C11	1.788 (5)	C3—C4	1.380 (5)
N1—N2	1.381 (4)	C3—C8	1.399 (5)
N1—C1	1.333 (5)	C4—C5	1.410 (5)
N2—C2	1.281 (5)	C5—C6	1.397 (5)
N3—C5	1.371 (5)	C6—C7	1.387 (5)
N3—C9	1.438 (6)	C7—C8	1.389 (5)
C1—S2—C11	100.5 (2)	C4—C3—C8	120.7 (3)
N2—N1—C1	121.2 (3)	C3—C4—C5	121.3 (3)
N1—N2—C2	114.6 (3)	N3—C5—C4	120.7 (3)
C5—N3—C9	121.5 (3)	N3—C5—C6	121.6 (3)
C5—N3—C10	121.0 (4)	C4—C5—C6	117.7 (3)
C9—N3—C10	117.4 (4)	C5—C6—C7	120.5 (3)
S1—C1—S2	125.0 (2)	C6—C7—C8	121.7 (3)
S1—C1—N1	121.0 (3)	C2—C8—C3	122.9 (3)
S2—C2—N1	114.0 (3)	C2—C8—C7	119.0 (3)
N2—C2—C8	122.6 (3)	C3—C8—C7	118.7 (3)

The H-atom positions were generated geometrically (C—H bond lengths fixed at 0.96 Å), assigned appropriate isotropic displacement parameters and allowed to ride on their parent C atoms.

Data collection: SHELXTL-Plus (Sheldrick, 1987). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXS86. Molecular graphics: ORTEP (Johnson, 1965).

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Redetermination of 1,3-Dimethylimidazole-2-thione

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Abstract

The title compound, 1,3-dimethylimidazole-2(3H)-thione, $C_5H_8N_2S$, has molecular symmetry $mm2$ (C_{2v}) in the crystal.

Comment

The present study is part of a program investigating the structure/property relationships among nonlinear optical (NLO) materials. A solution of the title compound, DMIT, exhibits optical nonlinearities, including nonlinear refraction and two-photon absorption. DMIT was initially chosen for our investigations because the structure was known and it represents the basic template for a series of substituted compounds in which we also have interest. In earlier work, DMIT (Ansell, Forkey &

Moore, 1970) was reported to have crystallized in the orthorhombic space group *Bmmb*. A redetermination of the structure was undertaken since the previous authors reported no atomic coordinates.

(I)   (II)

(III)
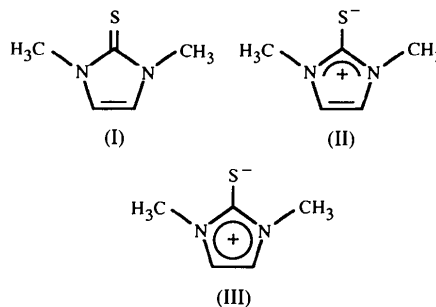
The C1—S bond length corresponds to a partial double bond. Based on bond distances within the ring, Ansell, Forkey & Moore (1970) concluded that the electronic structure of DMIT would best be represented by a resonance hybrid of structures (I) and (II). The bond distances found in this study correspond to the more delocalized resonance structure (III).
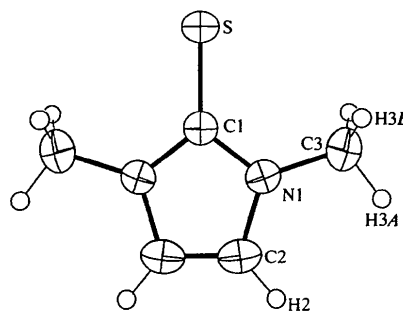

Fig. 1. The molecular structure of DMIT. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was synthesized from *N*-methylimidazole by alkylation with methyl iodide to give the 1,3-dimethylimidazolium halide. Subsequent treatment with sulfur in methanolic carbonate (Ansell, Forkey & Moore, 1970) yields DMIT (m.p. 454 K).

Crystal data

$C_5H_8N_2S$	Mo $K\alpha$ radiation
$M_r = 128.19$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
Cmcm	reflections
$a = 8.4680\,(14)$ Å	$\theta = 4–13°$
$b = 11.1997\,(7)$ Å	$\mu = 0.39$ mm^{-1}
$c = 6.8220\,(9)$ Å	$T = 296$ K
$V = 646.99\,(14)$ Å^3	Parallelepiped
$Z = 4$	$0.40 \times 0.15 \times 0.10$ mm
$D_x = 1.316$ Mg m^{-3}	Colorless
$D_m = 1.286$ Mg m^{-3}	
D_m measured by flotation in	
CCl$_4$/hexane	

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