Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

S-Methyl 3-[4-(diethylamino)benzylidene]-dithiocarbazate

Jian Hua Yu,[a] Xiao Lu Zhao,[a] Sheng Li Li,[a]* Hoong-Kun Fun[b] and Jeannie Bee-Jan Teh[b]

[a]Deparment of Chemistry Anhui University, Hefei 230039, People's Republic of China, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: ancea@163.com

Received 12 April 2006
Accepted 11 May 2006

Key indicators

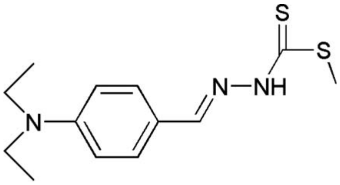
Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.005 Å
R factor = 0.067
wR factor = 0.159
Data-to-parameter ratio = 21.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{13}H_{19}N_3S_2$, is a Schiff base prepared by the reaction of *S*-methylendithiocarbazate and and 4-(diethylamino)benzaldehyde. Weak intermolecular N—H···S hydrogen bonds link the molecules into dimers.

Comment

Organic materials with delocalized π-electron systems have aroused considerable interest as potential materials for non-linear optical (NLO) studies. It has been found (Long, 1995) that the delocalized conjugated electrons contribute to enhancing the NLO response through their capability for hyperpolarization. Schiff base compounds having extensively conjugated π-electron systems have been reported to display second harmonic generation (Messier *et al.*, 1991; Zyss & Ledoux, 1994). We have synthesized the title compound, (I), to explore its potential as a prospective NLO material.



(I)

In (I) (Fig. 1), the dithiocarbazate group adopts an *E* configuration about the C7═N2 bond as found in most dithiocarbazates (Fun *et al.*, 1995) and thiosemicarbazones (Mathew & Palenik, 1971). The C—S bond lengths (Table 1) lie in the range 1.669 (3)–1.797 (4) Å and agree well with those observed in related compounds, being intermediate between the 1.56 and 1.82 Å for C—S double and single bonds, respectively (Sutton, 1965). The C9—N3 and C3—N1 bond lengths are indicative of double-bond character. Therefore, there is high electron delocalization in the π-system of the whole molecule. However, since the title compound crystallizes in a centrosymmetric space group, it does not exhibit second-order NLO properties.

In the crystal structure, weak intermolecular N—H···S hydrogen bonds (Table 2) link the molecules into centrosymmetric dimers (Fig. 2).

Experimental

4-(Diethylamino)benzaldehyde (50 mmol) and *S*-methylenedithiocarbazate (50 mmol) were mixed in EtOH (25 ml) and heated to reflux for 2 h. Pale-yellow microcrystals were collected and dried *in vacuo*. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a benzene solution.

Crystal data

$C_{13}H_{19}N_3S_2$
$M_r = 281.43$
Triclinic, $P\overline{1}$
$a = 6.9340\ (6)$ Å
$b = 8.3979\ (8)$ Å
$c = 13.8832\ (13)$ Å
$\alpha = 89.343\ (2)^\circ$
$\beta = 84.071\ (2)^\circ$
$\gamma = 70.321\ (2)^\circ$
$V = 756.91\ (12)$ Å^3
$Z = 2$
$D_x = 1.235$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.34$ mm^{-1}
$T = 297\ (2)$ K
Block, yellow
0.56 × 0.24 × 0.16 mm

Data collection

Siemens SMART CCD area detector diffractometer
ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 1996)
$T_{\min} = 0.833$, $T_{\max} = 0.948$
4816 measured reflections
3557 independent reflections
2394 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 28.3^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.159$
$S = 1.07$
3557 reflections
166 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.5524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C9	1.669 (3)	N1—C11	1.489 (5)
S2—C9	1.739 (3)	N3—C9	1.323 (4)
S2—C10	1.797 (4)	N3—N2	1.388 (3)
N1—C3	1.368 (3)	C7—N2	1.278 (4)
N1—C13	1.455 (4)		
C9—S2—C10	102.26 (16)	C3—N1—C11	121.7 (3)
C3—N1—C13	122.3 (3)	C13—N1—C11	115.0 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···S1$^{\rm i}$	0.86	2.56	3.371 (3)	157

Symmetry code: (i) $-x+1, -y+1, -z$.

The H atoms were positioned geometrically and allowed to ride on their parent atoms with N—H = 0.86 Å, C—H = 0.93–0.97 Å, and $U_{\rm iso}$(H)= 1.2 or 1.5 times $U_{\rm eq}$(parent atom).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

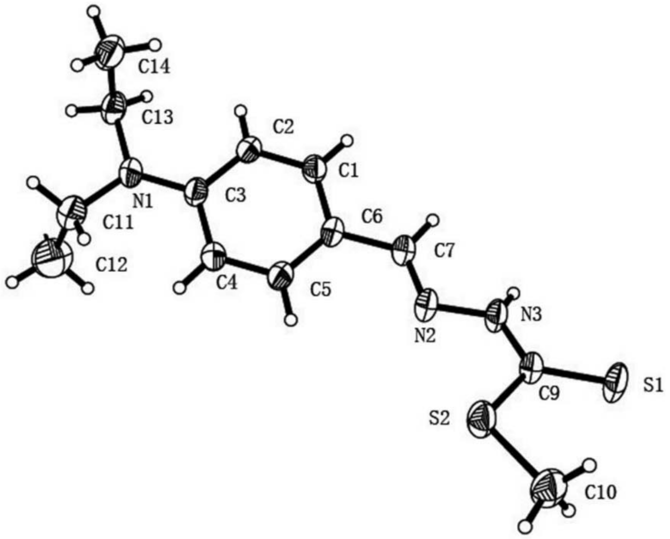


Figure 1
View of (I) with the atomic numbering and displacement ellipsoids drawn at the 30% probability level.

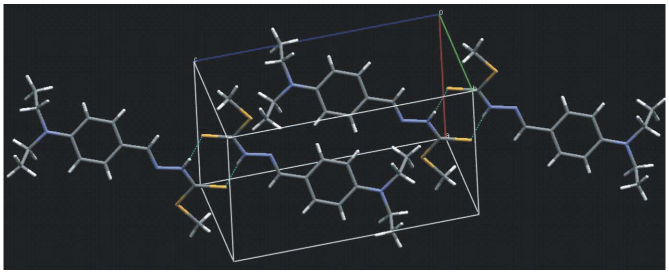


Figure 2
View of the crystal packing, showing the hydrogen-bonded (dashed lines) dimers.

This work was supported by grants from the National Natural Science Foundation of China (No. 50335050), the Education Office Foundation of Anhui Province (2005 KJ101) and the Malaysian Government and Universiti Sains Malaysia (research grant R&D No. 305/PFIZIK/610961).

References

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Fun, H.-K., Sivakumar, K., Yip, B.-C., Tian, Y.-P., Duan, C.-Y., Lu, Z.-L. & You, X.-Z. (1995). *Acta Cryst.* C**51**, 2080–2083.
Long, N. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 21–38.
Mathew, M. & Palenik, G. J. (1971). *Acta Cryst.* B**27**, 59–66.
Messier, J., Kajzar, F. & Prasad, P. (1991). *Organic Molecules for Nonlinear Optics and Photonics.* Dordrecht: Kluwer Academic Publishers.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1996). *SADABS*. Universuty of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS, Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Special Publication No. 18. London: The Chemical Society.
Zyss, J. & Ledoux, L. (1994). *Chem. Rev.* **94**, 77–106.

o2388 Yu *et al.* • $C_{13}H_{19}N_3S_2$ *Acta Cryst.* (2006). E**62**, o2387–o2388