Crystal structure of *S*-methyl β-*N*-(methylacetyl)methylene-dithiocarbazate, $C_6H_{10}N_2OS_2$

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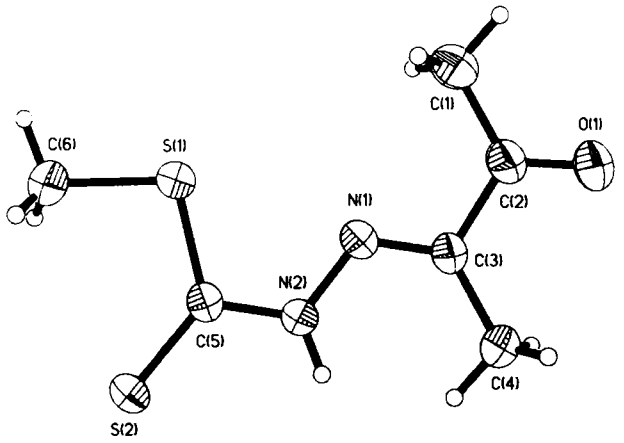

Abstract

$C_6H_{10}N_2OS_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 4.2699(1)$ Å, $b = 13.7544(2)$ Å, $c = 15.8280(4)$ Å, $\beta = 97.263(1)°$, $V = 922.1$ Å^3, $Z = 4$, $R(F) = 0.063$, $wR_{ref}(F^2) = 0.173$, $T = 293$ K.

Source of material

S-methyldithiocarbazate (SMDTC, 0.0125 mole) which was prepared as previously described [1] was dissolved in absolute ethanol (35 ml). To this solution 2,3-butanedione (0.0125 mole) was added and the mixture was stirred for 15 minutes while it is still hot. Light yellow crystals formed when the mixture was cooled to room temperature. The crystals were collected and dried in vacuum over P_2O_5. The results of the elemental analysis (%C = 37.41, %H = 5.15, %N = 15.94) are in good agreement with the values calculated on the basis of crystal structure investigation (37.89, 5.26, 14.74). Yield = 87%, mp = 427 K.

Discussion

The title compound is in *keto* tautomeric form, where the C1, C2, O2, C3, N1, N2 atoms are essentially planar but the C6S1C5S2 plane is slightly deviated with torsion angle of N1N2C5S1 and C6S1C5S2 of 3.3(4)° and 1.5(3)°, respectively. The effect of conjugation in the O1C2C3N1 plane is shown by the slight shortening of the bond lengths of N1—N2 and C5–S2 of 1.372(4) Å and 1.651(4) Å, respectively, compared with 1.396(8) Å and 1.681(5) Å, respectively, for *S*-methyldithiocarbazate [2]. On the other hand no significant shortening of the N—N bond was observed in a conjugation system by aromatic group such as in *p*-methoxybenzyldehyde isonicotinoylhydrazone monohydrate where the N—N bond length is 1.391(1) Å [3]. However, the N2—C5 of 1.360(5) Å is longer than in *S*-methyldithiocarbazate of 1.324(6) Å. In the crystal, the molecules are alligned parallel to one another along both *a* and *b* axes as dimers. The centrosymmetric dimers are formed by means of N–H···S (2.77 Å) and C–H···S (2.591 Å) hydrogen bonds involving the imino-nitrogen, C4-methyl and thiono-sulfur atoms between both molecules.

Table 1. Data collection and handling.

Crystal:	yellowish rectangular block, size 0.14 × 0.18 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.25 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	58.68°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6526, 2303
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1157
$N(param)_{refined}$:	100
Programs:	PARST [4], SADABS [5], SHELXTL [6], PLATON [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	4*e*	0.2308	0.9663	0.5954	0.048
H(1A)	4*e*	1.0245	0.8073	0.8685	0.090
H(1B)	4*e*	0.9458	0.7835	0.7713	0.090
H(1C)	4*e*	0.6729	0.7923	0.8285	0.090
H(4A)	4*e*	0.4470	1.0715	0.6540	0.081
H(4B)	4*e*	0.7975	1.0876	0.6945	0.081
H(4C)	4*e*	0.5233	1.0950	0.7514	0.081
H(6A)	4*e*	0.0515	0.5703	0.5564	0.089
H(6B)	4*e*	0.0802	0.6434	0.4818	0.089
H(6C)	4*e*	–0.2087	0.6497	0.5336	0.089

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.2298(2)	0.71857(7)	0.61082(6)	0.0605(7)	0.0322(5)	0.0421(6)	0.0020(4)	–0.0164(5)	0.0021(4)
S(2)	4*e*	–0.1137(3)	0.85126(8)	0.47709(7)	0.0640(8)	0.0393(6)	0.0437(6)	–0.0005(5)	–0.0242(5)	0.0035(4)
O(1)	4*e*	1.0091(9)	0.9836(2)	0.8403(2)	0.102(3)	0.048(2)	0.072(2)	–0.010(2)	–0.049(2)	–0.007(2)
N(1)	4*e*	0.4799(7)	0.8866(2)	0.6816(2)	0.043(2)	0.034(2)	0.035(2)	0.002(1)	–0.009(1)	–0.001(1)
N(2)	4*e*	0.2712(7)	0.9071(2)	0.6107(2)	0.044(2)	0.029(2)	0.042(2)	–0.000(1)	–0.014(1)	0.002(1)
C(1)	4*e*	0.875(1)	0.8171(3)	0.8186(3)	0.081(3)	0.050(3)	0.042(3)	–0.001(2)	–0.018(2)	0.007(2)
C(2)	4*e*	0.8482(9)	0.9238(3)	0.7990(2)	0.050(2)	0.042(2)	0.040(2)	0.002(2)	–0.010(2)	–0.006(2)
C(3)	4*e*	0.6266(9)	0.9568(3)	0.7230(2)	0.045(2)	0.032(2)	0.037(2)	–0.001(2)	–0.009(2)	–0.004(2)
C(4)	4*e*	0.596(1)	1.0620(3)	0.7040(3)	0.068(3)	0.031(2)	0.055(3)	–0.004(2)	–0.019(2)	–0.000(2)
C(5)	4*e*	0.1297(9)	0.8318(3)	0.5651(2)	0.043(2)	0.033(2)	0.035(2)	0.001(2)	–0.007(2)	–0.003(2)
C(6)	4*e*	0.013(1)	0.6358(3)	0.5371(3)	0.077(3)	0.033(2)	0.060(3)	–0.003(2)	–0.022(2)	–0.005(2)

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