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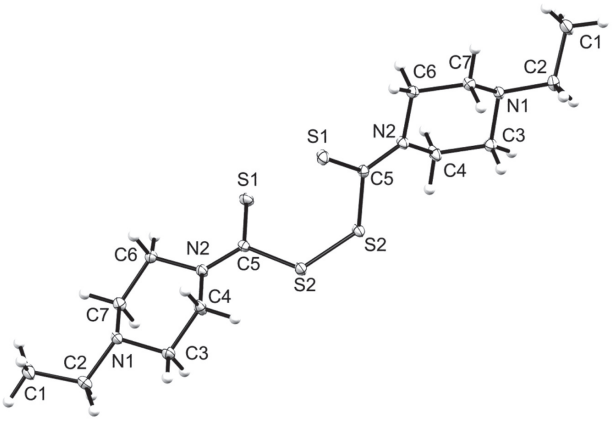
Crystal structure of 4-ethylpiperazine-1-carbothioic dithioperoxyanhydride, $C_{14}H_{26}N_4S_4$



https://doi.org/10.1515/ncrs-2019-0246
Received April 5, 2019; accepted June 25, 2019; available online July 24, 2019

Abstract

$C_{14}H_{26}N_4S_4$, monoclinic, $C2/c$ (no. 15), $a = 16.9951(10)$ Å, $b = 11.4397(7)$ Å, $c = 9.7678(6)$ Å, $\beta = 103.913(1)°$, $V = 1843.33(19)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0200$, $wR_{ref}(F^2) = 0.0553$, $T = 100(2)$ K.

CCDC no.: 1936339

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a stirred solution of 1-ethylpiperazine (3.8 mmol) in 10 mL ethanol was added aqueous (5 mL) potassium hydroxide (3.8 mmol), which was left to stir for 5 min. To this stirred mixture was slowly added carbon disulfide (3.8 mmol) which yields a pale yellow solid and iodine (3.8 mmol) resulting in a brighter yellow solid. The mixture was further stirred for 8 h, filtered and washed with ethanol (20 mL) and isolated as a bright yellow solid.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.37 × 0.22 × 0.15 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.52 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10800, 2308, 0.013
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2209
$N(param)_{refined}$:	101
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
S1	0.89363(2)	0.71200(2)	0.10142(2)	0.01718(7)
S2	0.96140(2)	0.51976(2)	0.31315(2)	0.01490(7)
N1	0.68171(4)	0.61248(6)	0.40719(8)	0.01417(15)
N2	0.82653(4)	0.63573(6)	0.30597(8)	0.01385(15)
C1	0.54521(6)	0.65707(10)	0.44411(11)	0.0240(2)
H1A	0.567736	0.687977	0.539026	0.036*
H1B	0.492018	0.622163	0.439901	0.036*
H1C	0.539340	0.720723	0.375251	0.036*
C2	0.60184(5)	0.56457(8)	0.41026(10)	0.01887(18)
H2A	0.609009	0.501810	0.481982	0.023*
H2B	0.576840	0.529416	0.317370	0.023*
C3	0.74288(6)	0.52018(8)	0.42839(10)	0.01782(18)
H3A	0.729263	0.463850	0.349261	0.021*
H3B	0.743254	0.477517	0.516721	0.021*
C4	0.82614(5)	0.57178(9)	0.43667(9)	0.01782(18)
H4A	0.840784	0.625611	0.518206	0.021*
H4B	0.866962	0.508388	0.450809	0.021*
C5	0.88593(5)	0.63073(7)	0.23756(9)	0.01258(16)
C6	0.76170(5)	0.72410(7)	0.27127(10)	0.01531(17)
H6A	0.759532	0.757006	0.176696	0.018*
H6B	0.773814	0.788662	0.340654	0.018*
C7	0.68001(5)	0.67053(8)	0.27288(9)	0.01506(17)
H7A	0.638227	0.732642	0.256393	0.018*
H7B	0.664852	0.613013	0.195272	0.018*

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Experimental details

The structure was solved by the direct method using the SHELXS [2] program and refined. The visual crystal structure information was performed using ORTEP-3 [4] system software.

All hydrogen atoms were placed in idealized positions and refined in riding models with U_{iso} assigned the values of 1.2 times those of their parent atoms and the distances of C—H were constrained to 0.95 Å.

Comment

Sulfur-rich compounds have been explored in various ways as ligands in coordination chemistry. One of such class of compounds are the dithiocarbanates which have been reported to have diverse applications in medicine [5, 6] and agriculture [7]. Our group has explored these compounds as single source molecular precursors in preparation of nanomaterials [8–11]. These nanomaterials have potentials in application for solar energy [12]. The title compound is a side product of our study on dithio-carbamates. Wieczorek and coworkers [13] have studied the structure and dynamics of bis (organothiophosphoryl) disulfides in solid state which can be applied to the title compound. The three possible geometries classified in that study were, anti-anti where both sulfur atoms (P=S) point away from the disulfide bridge; *syn-syn* where both point toward the disulfide bridge; and *anti-syn* which is a hybrid of the other two geometries.

The asymmetric unit contains half of the title compound with the complete molecule generated by a 2-fold rotation along the crystallographic *b* axis between the S—S bond. The S2—S1—$S1^i$—$S2^i$ (symmetry code: (i) = 2 − *x*, *y*, 2 − *z*) torsion angle was found to be 84.6° which coincides with that of the closely related compounds in literature [14]. The S2 = C5—S1—S1—C5 = S2 backbone possesses a *syn-syn* conformation with a S1—S1—C5 = S2 torsion angle of −4.05° which is similar to that observed in bis(organothiophosphoryl) disulfides [15, 16].

Acknowledgements: NR thanks the National Research Foundation (NRF), South Africa through the South African Research Chair Initiative (SARChI) program for financial support.

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