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The crystal structure of a matrine derivative, 13-(methylamine-1-yl) carbodithioate matrine, $C_{17}H_{27}N_3OS_2$

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Abstract

$C_{17}H_{27}N_3OS_2$, monoclinic, $P2_1$ (no. 4), $a = 8.8052(10)$ Å, $b = 10.8860(10)$ Å, $c = 18.6705(2)$ Å, $\beta = 99.2730(10)^\circ$, $V = 1766.24(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0298$, $wR_{ref}(F^2) = 0.0802$, $T = 100.00(10)$ K.

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The asymmetric unit of 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.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.20 \times 0.20 \times 0.20$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	2.79 mm^{-1}
Diffractometer, scan mode:	XtaLAB AFC12, ω
$\theta_{\max}$, completeness:	73.9° , 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16370, 6521, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6505
$N(\text{param})_{\text{refined}}$:	418
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3]

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Source of material

Carbon disulfide (2.0 mL) was added to a mixture of water (2.0 mL) and methylamine (2.0 mL). After vigorously stirring at 60 °C for 1 hour, sophoroline (0.31 g) and water (0.2 mL) were added. The reaction mixture was heated for 12 h. After steaming and concentrating, methanol (10.0 mL) was added while stirring. The insoluble impurities were removed by filtration and the filtrate was concentrated to give a yellow oil. The residue was purified with column chromatography on silica gel using ethyl acetate/ethanol ($V/V = 10/1$) as eluent. Crystallization was carried out by adding ethanol/petroleum

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
N1	1.9628(2)	0.39803(19)	1.12643(10)	0.0168(4)
C2	2.1160(3)	0.4028(3)	1.17039(12)	0.0222(5)
H2A	2.1146	0.3581	1.2152	0.027*
H2B	2.1419	0.4876	1.1828	0.027*
C3	2.2384(3)	0.3483(3)	1.13118(13)	0.0240(5)
H3A	2.2168	0.2620	1.1215	0.029*
H3B	2.3383	0.3548	1.1616	0.029*
C4	2.2409(3)	0.4166(3)	1.05961(13)	0.0225(5)
H4A	2.3107	0.3752	1.0323	0.027*
H4B	2.2787	0.4995	1.0698	0.027*
C5	2.0797(2)	0.4216(2)	1.01401(12)	0.0161(4)
H5	2.0837	0.4805	0.9746	0.019*
C6	1.9600(2)	0.4690(2)	1.05852(11)	0.0141(4)
H6	1.9839	0.5549	1.0714	0.017*
C7	1.7978(2)	0.4638(2)	1.01310(11)	0.0144(4)
H7	1.7976	0.5152	0.9700	0.017*
C8	1.6809(3)	0.5175(2)	1.05698(13)	0.0183(5)
H8A	1.7027	0.6039	1.0664	0.022*
H8B	1.5781	0.5106	1.0294	0.022*
C9	1.6890(3)	0.4489(3)	1.12877(12)	0.0213(5)
H9A	1.6210	0.4878	1.1580	0.026*
H9B	1.6549	0.3648	1.1195	0.026*
C10	1.8524(3)	0.4496(2)	1.16966(12)	0.0214(5)
H10A	1.8819	0.5333	1.1831	0.026*
H10B	1.8564	0.4022	1.2139	0.026*
C11	1.7637(2)	0.3300(2)	0.98755(11)	0.0135(4)
H11	1.7835	0.2775	1.0307	0.016*
C12	1.5999(2)	0.3045(2)	0.95060(12)	0.0162(4)
H12A	1.5280	0.3434	0.9778	0.019*
H12B	1.5809	0.2167	0.9500	0.019*
C13	1.5741(2)	0.3534(2)	0.87327(12)	0.0159(4)
H13	1.6018	0.4406	0.8744	0.019*
C14	1.6801(3)	0.2840(2)	0.83034(12)	0.0168(4)
H14A	1.6443	0.1999	0.8233	0.020*
H14B	1.6741	0.3215	0.7828	0.020*
C15	1.8469(3)	0.2832(2)	0.86740(12)	0.0144(4)
N16	1.8773(2)	0.29631(18)	0.94019(10)	0.0143(4)
C17	2.0354(2)	0.2968(2)	0.97905(12)	0.0167(5)
H17A	2.1052	0.2769	0.9455	0.020*
H17B	2.0463	0.2341	1.0164	0.020*
O18	1.94890(18)	0.26599(16)	0.82991(9)	0.0192(4)
S19	1.37632(6)	0.33770(5)	0.82914(3)	0.01834(14)
C20	1.2936(3)	0.4801(2)	0.84908(11)	0.0161(4)
S21	1.39293(7)	0.60406(5)	0.88123(3)	0.02273(14)
N22	1.1412(2)	0.47562(19)	0.83279(10)	0.0175(4)
H22	1.0987	0.4056	0.8217	0.021*
C23	1.0425(3)	0.5824(2)	0.83271(12)	0.0208(5)
H23A	1.0510	0.6327	0.7913	0.031*
H23B	1.0734	0.6289	0.8763	0.031*
H23C	0.9377	0.5562	0.8305	0.031*
N24	0.5130(2)	0.53400(18)	0.36795(10)	0.0170(4)
C25	0.3537(3)	0.5460(3)	0.33135(14)	0.0254(5)
H25A	0.3422	0.5029	0.2853	0.030*
H25B	0.3313	0.6321	0.3213	0.030*
C26	0.2384(3)	0.4951(3)	0.37592(15)	0.0292(6)
H26A	0.2547	0.4075	0.3832	0.035*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H26B	0.1347	0.5076	0.3503	0.035*
C27	0.2581(3)	0.5604(3)	0.44934(14)	0.0246(5)
H27A	0.1916	0.5224	0.4796	0.029*
H27B	0.2277	0.6457	0.4422	0.029*
C28	0.4255(3)	0.5537(2)	0.48776(13)	0.0166(4)
H28	0.4353	0.6087	0.5298	0.020*
C29	0.5368(2)	0.5995(2)	0.43843(11)	0.0141(4)
H29	0.5175	0.6871	0.4290	0.017*
C30	0.7046(2)	0.5841(2)	0.47575(11)	0.0138(4)
H30	0.7181	0.6333	0.5203	0.017*
C31	0.8131(3)	0.6357(2)	0.42696(13)	0.0201(5)
H31A	0.7983	0.7238	0.4219	0.024*
H31B	0.9188	0.6209	0.4492	0.024*
C32	0.7831(3)	0.5757(3)	0.35202(13)	0.0244(5)
H32A	0.8447	0.6158	0.3202	0.029*
H32B	0.8125	0.4898	0.3560	0.029*
C33	0.6132(3)	0.5866(3)	0.32020(12)	0.0233(5)
H33A	0.5875	0.6726	0.3118	0.028*
H33B	0.5945	0.5447	0.2738	0.028*
C34	0.7341(2)	0.4484(2)	0.49811(11)	0.0139(4)
H34	0.7049	0.3979	0.4546	0.017*
C35	0.8988(2)	0.4159(2)	0.53018(11)	0.0148(4)
H35A	0.9680	0.4442	0.4982	0.018*
H35B	0.9092	0.3274	0.5350	0.018*
C36	0.9408(2)	0.4762(2)	0.60437(12)	0.0170(4)
H36	0.9212	0.5645	0.5988	0.020*
C37	0.8364(3)	0.4244(3)	0.65472(12)	0.0219(5)
H37A	0.8704	0.3418	0.6688	0.026*
H37B	0.8482	0.4740	0.6984	0.026*
C38	0.6676(3)	0.4199(2)	0.62242(12)	0.0174(5)
N39	0.6279(2)	0.41769(18)	0.54955(10)	0.0151(4)
C40	0.4660(2)	0.4242(2)	0.51616(12)	0.0171(4)
H40A	0.4015	0.4022	0.5517	0.021*
H40B	0.4465	0.3660	0.4764	0.021*
O41	0.5709(2)	0.41293(18)	0.66373(9)	0.0249(4)
S42	1.14168(6)	0.45448(5)	0.64259(3)	0.01768(13)
C43	1.2118(3)	0.6073(2)	0.65654(11)	0.0177(5)
S44	1.10382(7)	0.73384(5)	0.64499(4)	0.02557(15)
N45	1.3627(2)	0.6074(2)	0.67861(11)	0.0209(4)
H45	1.4105	0.5383	0.6810	0.025*
C46	1.4517(3)	0.7179(3)	0.69895(16)	0.0305(6)
H46A	1.4353	0.7756	0.6595	0.046*
H46B	1.5590	0.6975	0.7097	0.046*
H46C	1.4195	0.7538	0.7410	0.046*

ether (1:4), and finally colourless block crystals suitable for X-ray diffraction were obtained in a yield of about 85%.

Experimental details

Hydrogen atoms were placed in calculated positions and were refined in the riding model approximation.

Comment

Matrine is an alkaloid-based broad-spectrum pesticide with insecticidal, bactericidal and acaricidal activities. It's also the main bioactive component of traditional Chinese herb *Sophora flavescens*, *Sophora alopecuroides*, and *Sophora subprostrata* [4–6]. Although matrine is a widely used botanical pesticide, it still has a significant gap in activity compared with chemical pesticides. Currently, the main application of matrine in agriculture is synergistic with other active compounds [7–9]. Structural modification is a commonly used technique for improving the activity of natural products [10, 11]. It is reported that chloroquinoline-modified matrine has a good insecticidal and acaricidal activity [12]. Furthermore, matrine ester exhibits better agricultural activity [13]. Carbon disulfide, amines and methyl compounds are the raw materials and intermediates of common pesticides. Therefore, introducing these active groups to the skeleton of matrine is a potential way to increase its pesticidal activity.

As shown in the figure, carbon disulfide and methylamine were introduced at the C-13 position of matrine forming the bonds C13–S19 [1.810(2) Å] and N22–C23 [1.452(3) Å] with the angle of C20–S19–C13 [102.63(11)°] and C20–N22–C23 [123.6(2)°]. All bond lengths and angles of this $Z' = 2$ structure are within the norm and in good agreement with those of a closely related structure [14]. The crystal packing is sustained by N–H...O, C–H...S and C–H...O hydrogen bonds. A series of assays to investigate the agricultural activities of this new matrine derivative is planned as part of future studies.

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