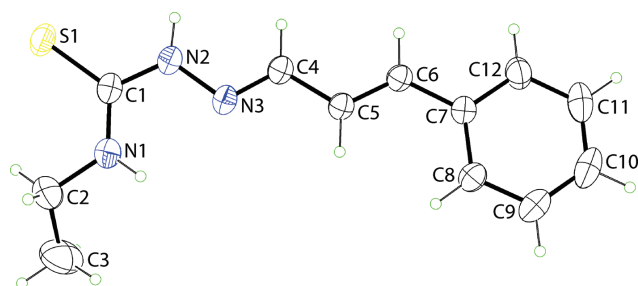


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Crystal structure of 3-ethyl-1-[(*E*)-[(2*E*)-3-phenylprop-2-en-1-ylidene]amino]thiourea, $C_{12}H_{15}N_3S$



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Abstract

$C_{12}H_{15}N_3S$, orthorhombic, *Pbca* (no. 61), $a = 11.9612(5)$ Å, $b = 8.1215(3)$ Å, $c = 27.5865(12)$ Å, $V = 2679.83(19)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0520$, $wR_{ref}(F^2) = 0.1514$, $T = 293(2)$ K.

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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

4-Ethyl-3-thiosemicarbazide (1.192 g, 0.01 mol) was dissolved in heated ethanol (50 mL). Cinnamaldehyde (1.50 mL, 0.01 mol) was added into heated ethanolic 4-ethyl-3-thiosemicarbazide while stirring and heating for around 30 mins. The yellow precipitate was filtered, washed with cold ethanol and dried *in vacuo*. Single crystals were grown

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Table 1: Data collection and handling.

Crystal:	Colourless slab
Size:	0.50 × 0.50 × 0.20 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	1.96 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	74.2°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	5668, 2612, 0.024
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2077
$N(param)_{refined}$:	153
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	x	y	z	U_{iso}^*/U_{eq}
S1	0.40769(5)	1.07994(8)	0.56349(2)	0.0808(3)
N1	0.20400(17)	0.9676(3)	0.54422(8)	0.0840(6)
H1N	0.161(2)	0.895(3)	0.5314(10)	0.101*
N2	0.33773(15)	0.9067(2)	0.48914(6)	0.0625(4)
H2N	0.4060(10)	0.908(3)	0.4787(8)	0.075*
N3	0.25787(14)	0.82382(19)	0.46276(6)	0.0607(4)
C1	0.30945(17)	0.9790(2)	0.53135(7)	0.0626(5)
C2	0.1582(3)	1.0259(5)	0.58985(11)	0.1101(10)
H2A	0.197919	1.124233	0.599923	0.132*
H2B	0.168847	0.942470	0.614581	0.132*
C3	0.0386(3)	1.0632(5)	0.58535(17)	0.1391(14)
H3A	0.028524	1.153114	0.563184	0.209*
H3B	0.009184	1.092909	0.616522	0.209*
H3C	-0.000141	0.967978	0.573391	0.209*
C4	0.28904(16)	0.7701(2)	0.42132(6)	0.0570(4)
H4	0.362028	0.787942	0.410951	0.068*
C5	0.21236(16)	0.6825(2)	0.39066(6)	0.0551(4)
H5	0.141266	0.659052	0.402428	0.066*
C6	0.23898(15)	0.6335(2)	0.34599(6)	0.0557(4)
H6	0.310561	0.659404	0.335262	0.067*
C7	0.16775(15)	0.5435(2)	0.31210(6)	0.0541(4)
C8	0.06033(17)	0.4929(2)	0.32368(7)	0.0636(5)
H8	0.030544	0.519669	0.353807	0.076*
C9	-0.0029(2)	0.4039(3)	0.29140(10)	0.0829(7)
H9	-0.074344	0.369578	0.300014	0.099*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C10	0.0386(3)	0.3657(4)	0.24700(12)	0.1029(9)
H10	-0.004487	0.305024	0.225343	0.123*
C11	0.1430(3)	0.4160(4)	0.23407(10)	0.1037(9)
H11	0.170577	0.391110	0.203416	0.124*
C12	0.2087(2)	0.5047(3)	0.26659(8)	0.0773(6)
H12	0.280185	0.537972	0.257693	0.093*

at room temperature from the slow evaporation of a mixture of ethanol and acetonitrile (1:2 *v/v*). Yield: 74%; **M. Pt.**: 446 K. **FT-IR** (ATR (solid) cm⁻¹): 3317 *v*(N–H), 3133 *v*(Ar C–H), 3000 *v*(C–H), 2971, 2873 *v*(C–H), 1625 *v*(C=N), 1545, 1523 *v*(Ar C=C), 1084 *v*(C=S). **¹H NMR** (500 MHz, CDCl₃): δ 10.00 (s, 1H, N–NH), 7.71 (d, 1H, 4CH), 7.45 (d, 2H, 8CH and 12CH), 7.37–7.30 (m, 4H, C–NH, 9CH, 10CH and 11CH), 6.90 (d, 1H, 6CH), 6.81 (dd, 1H, 5CH), 3.77–3.70 (m, 2H, 2CH₂), 1.30 (t, 3H, CH₃). **¹³C{¹H} NMR** (500 MHz, CDCl₃): δ 176.71 (C1), 144.57 (C4), 140.24 (C7), 135.89 (C6), 129.21 (C10), 128.96 (C9 and C11), 127.13 (C8 and C12), 124.39 (C5), 39.40 (CH₂), 14.60 (CH₃).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C). The N-bound H atoms were refined with N–H = 0.86 ± 0.01 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(N). An extinction correction was applied with the coefficient refining to 0.0055(5).

Comment

Cinnamaldehyde is major component of cinnamon essential oil extracted from a number of cinnamon bark species and along with derivatives is known to exhibit potential biological activities [5], for example, anti-diabetic [6], anti-fungal [7] and anti-microbial activity against various foodborne pathogenic bacteria such as *Escherichia coli* and *Staphylococcus aureus* [8]. However, the application of cinnamaldehyde as an anti-microbial agent remains challenging owing to its strong odour and high volatility [9]. The presence of the conjugated double bond in cinnamaldehyde allows for the formation of stable Schiff base compounds after reaction with an amine, chemistry motivated by the desire to decrease the drawbacks associated with cinnamaldehyde's odour and volatility [10]. In the present report, the synthesis and crystal structure determination of a cinnamaldehyde-based Schiff base compound EtN(H)C(=S)N(H)N=C(H)C(H)=C(H)Ph, (I), is described.

The molecular structure of (I) is shown in the figure (25% displacement ellipsoids) and adopts an extended [all trans] conformation. This is seen in the sequence of C1–N2–N3–C4 [174.56(17)°], N2–N3–C4–C5 [–179.71(15)°], N3–C4–C5–C6

[175.63(17)°] and C4–C5–C6–C7 [179.69(17) Å] torsion angles with the major twist in this part of the molecule observed about the N2–N3 bond. The greatest deviation from planarity in the molecule is observed for the terminal methyl group with the C1–N1–C2–C3 torsion angle being 154.8(3)°. The conformation about each of the C4=N3 [1.279(2) Å] and C5=C6 [1.333(2) Å] double bonds is E. The amide-H atoms lie to either side of the molecule which enables the formation of an intramolecular amide-N–H···N(imine) hydrogen bond [N1–H1n···N3: H1n···N3 = 2.29(3) Å, N1···N3 = 2.613(3) Å with angle at H1n = 102(2)°] to close a S(6) loop.

In the crystal of (I), centrosymmetric dimers are formed via amide-N–H···S(thione) hydrogen bonds [N2–H2n···S1ⁱ: H2n···S1ⁱ = 2.516(15) Å, N2···S1ⁱ = 3.3752(19) Å with angle at H2n = 171.7(19)° for symmetry operation (i) 1–*x*, 2–*y*, 1–*z*] which lead to the formation of an eight-membered {···HNCS}₂ synthon. The connections between the aggregates thus formed to form a supramolecular layer in the *ab*-plane are of the type amide-N–H···S(thione) [N1–H1n···S1ⁱⁱ: H1n···S1ⁱⁱ = 2.83(2) Å, N1···S1ⁱⁱ = 3.461(2) Å with the angle at H1n = 132(2)° for (ii) 1–*x*, 2–*y*, 1–*z*] involving the same amide-N–H atom that participates in the intramolecular N–H···N hydrogen bond which, therefore, may be considered bifurcated. Additional stability to the layers are provided by a phenyl-C–H···S(thione) [C8–H8···S1ⁱⁱⁱ: H8···S1ⁱⁱⁱ = 2.83 Å, C8···S1ⁱⁱⁱ = 3.657(2) Å with angle at H8 = 148° for (iii) –1/2 + *x*, 3/2 – *y*, 1 – *z*] interaction. Despite the phenyl rings projecting to either side of the layers, which stack along the *c*-axis, no specific interactions between molecules are noted along the *c*-axis. In order to investigate the nature of the supramolecular association further, the Hirshfeld surfaces were calculated along with the full and delineated two-dimensional fingerprint plots using Crystal Explorer 17 [11] following published procedures [12].

The fingerprint plot delineated into H···S/S···H contacts show sharp spikes corresponding to the N–H···S hydrogen bonds and overall, contribute 14.7% of all contacts to the surface. Reflecting the overall molecular packing, including the nature of the inter-layer region, H···H [55.9%] and H···C/C···H [19.6%] contacts make greater contributions to the surface. The remaining contributions are all small, for example, 3.5% for H···N/N···H and 2.5% for C···C contacts.

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