

Synthesis, crystal structure and Hirshfeld surface analysis of 4-[(1*E*)-1-[(carbamothioylamino)-imino]ethyl]phenyl propanoate

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The title compound, C₁₂H₁₅N₃O₂S, adopts an *E* configuration with respect to the C=N bond. The propionate group adopts an antiperiplanar (*ap*) conformation. There are short intramolecular N—H···N and C—H···O contacts, forming *S*(5) and *S*(6) ring motifs, respectively. In the crystal, molecules are connected into ribbons extending parallel to [010] by pairs of N—H···S interactions, forming rings with *R*₂²(8) graph-set motifs, and by pairs of C—H···S interactions, where rings with the graph-set motif *R*₂¹(7) are observed. The O atom of the carbonyl group is disordered over two positions, with a refined occupancy ratio of 0.27 (2):0.73 (2). The studied crystal consisted of two domains.

1. Chemical context

Thiosemicarbazone derivatives have found applications in drug development for the treatment of central nervous system disorders and bacterial infection, as well as analgesic and anti-allergic agents. They are inhibitors of DNA replication and are effective against proteases. This inhibitory activity explains the level of attention given to them in the fight against microbial and parasitic diseases (Mani *et al.*, 2015). Moreover, thiosemicarbazones have many biological activities, such as anti-parasital (Du *et al.*, 2002), antibacterial, antitumour (Papageorgiou *et al.*, 1997), anti-African trypanosome (Fatondji *et al.*, 2013), antimicrobial, sodium channel blocker, antimalarial, antitubercular (Khanye *et al.*, 2011), antiviral (Venkatesh *et al.*, 2016), antifungal and locomotor activity (Singh *et al.*, 2011), and they are used as a cure for leprosy, rheumatism and trypanosomiasis (Parul *et al.*, 2012). They are also important intermediates in organic synthesis, mainly for obtaining heterocyclic rings, such as thiazolidones, oxadiazoles, pyrazolidones and thiadiazoles (Greenbaum *et al.*, 2004). Thiosemicarbazones have also received considerable attention in view of their simplicity of preparation and various complexing abilities that can be used in analytical applications (Garg & Jain, 1988; Casas *et al.*, 2000). They are well known as *N,S*-donors, with a wide range of coordination modes (Lobana *et al.*, 2009).

In view of such important applications, we herein report the crystal structure determination and Hirshfeld surface analysis of the title thiosemicarbazone derivative, namely, 4-[(1*E*)-1-[(carbamothioylamino)imino]ethyl]phenyl propanoate, (I).

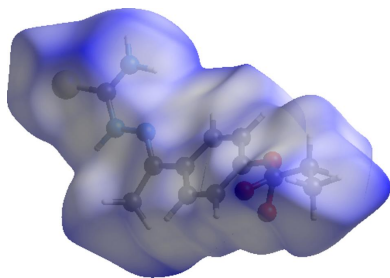


Table 1

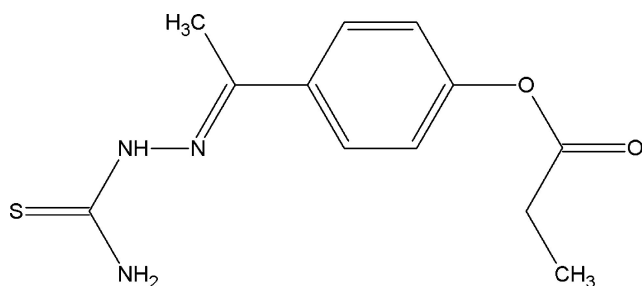
Hydrogen-bond geometry (Å, °).

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| N3—H3B···N1 | 0.80 (3) | 2.27 (5) | 2.588 (6) | 104 (4) |
| C5—H5···O1B | 0.93 | 2.32 | 2.812 (7) | 113 |
| N2—H2···S1 ⁱ | 0.84 (3) | 2.69 (3) | 3.525 (4) | 173 (4) |
| N3—H3A···S1 ⁱⁱ | 0.85 (3) | 2.55 (3) | 3.402 (5) | 177 (5) |
| C11—H11B···S1 ⁱ | 0.96 | 2.77 | 3.452 (5) | 128 |

Symmetry codes: (i) $-x - 1, -y + 1, -z$; (ii) $-x - 1, -y + 2, -z$.

2. Structural commentary

The molecular structure of compound (I) is shown in Fig. 1. It adopts an *E* configuration with respect to the C10=N1 bond (Fig. 1), showing a C10—N1—N2—C12 torsion angle of 175.4 (2)°. The N1—N2—C12—S1 torsion angle of -171.5 (1)° suggests that the thionyl S1 atom is located *trans* to the azomethine N1 atom. The C10=N1 bond length [1.285 (6) Å] is close to that of a formal C=N double bond [1.284 (3) Å; Seena *et al.*, 2006]. Similarly, the C12=S1 bond length [1.679 (4) Å] is close to that of formal C=S bond [1.685 (3) Å; Jacob & Kurup, 2012], and the N1—N2 bond length of 1.369 (5) Å is similar to those found in the Cambridge Structural Database (Allen, 2002) for thiosemicarbazone systems (371 hits, mean N—N distance is 1.374 Å). All other bond lengths and angles are normal and correspond well to those observed in the crystal structures of related semicarbazone and thiosemicarbazone derivatives (Carballo *et al.*, 2014).



The propionate group adopts an antiperiplanar (*ap*) conformation, as can be seen from the C1—C2—C3—O2 torsion angle of -176.3 (2)°. The semicarbazone unit is nearly planar, showing an N3—C12—N2—N1 torsion angle of 7.4 (2)°. The maximum deviation from the mean plane of the

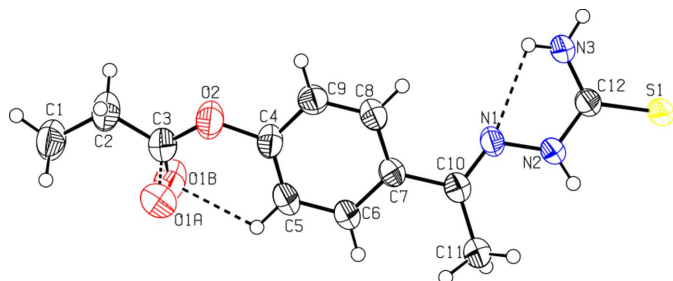


Figure 1

The molecular structure of compound (I), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Intra-molecular contacts are shown as dashed lines.

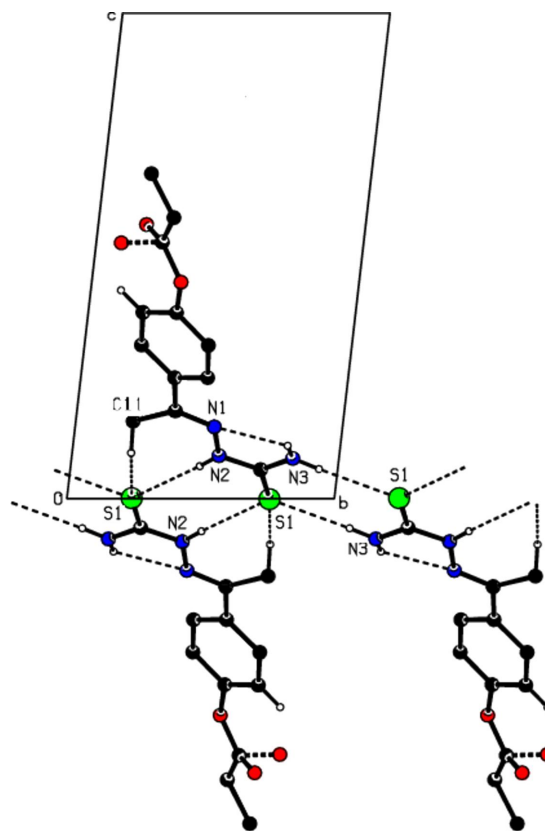


Figure 2

A view along the *a* axis of the crystal structure of (I). Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted.

non-H atoms of the C10/C11/C12/N1/N2/N3 fragment is -0.037 (5) Å for the N2 atom. The dihedral angle between this mean plane and the plane of the aromatic ring is 25.3 (1)°. Intramolecular N—H···N and C—H···O contacts, forming *S*(5) and *S*(6) ring motifs (Bernstein *et al.* 1995), respectively, lead to the stabilization of the molecular conformation (Fig. 1 and Table 1).

3. Supramolecular features

Several supramolecular hydrogen-bonding interactions are observed in (I). In the crystal, individual molecules are connected by pairs of N—H···S interactions, forming ribbons

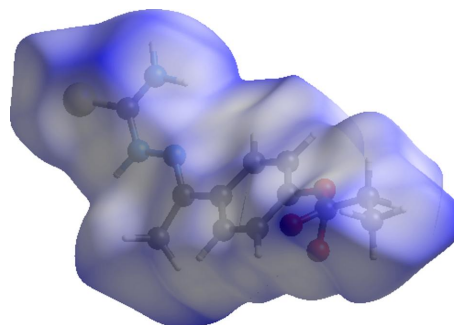


Figure 3

The Hirshfeld surface of (I), mapped over d_{norm} .

extending parallel to [010], where rings with $R_2^2(8)$ graph-set motifs (Bernstein *et al.*, 1995) are formed (N2–H2···S1 and N3–H3A···S1), and by pairs of C11–H11B···S1 interactions, where rings with the graph-set motif $R_2^1(7)$ are observed (Fig. 2). C–H··· π and π – π intermolecular interactions are not present in the crystal.

4. Hirshfeld surface analysis

A recent review by Tiekink and collaborators (Tan *et al.*, 2019) describes the use and utility of Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) for analysis of intermolecular contacts in crystals. Corresponding calculations were performed with *CrystalExplorer* (Spackman *et al.*, 2021).

The Hirshfeld surface of compound (I) mapped over d_{norm} is given in Fig. 3, and the intermolecular contacts are illu-

strated in Fig. 4(a). They are colour mapped with the normalized contact distance, d_{norm} , from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The d_{norm} surface was mapped over a fixed colour scale of -0.469 (red) to 1.632 (blue) for (I), where the red spots indicate the intermolecular contacts involved in hydrogen-bonding interactions. The electrostatic potential was also mapped on the Hirshfeld surface using a STO-3G basis set and the Hartree–Fock level of theory (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005). The presence of interactions is indicated by a red and blue colour on the shape-index surface [Fig. 4(b)]. Areas on the Hirshfeld surface with high curvedness tend to divide the surface into contact patches with each neighbouring molecule. The number of interacting molecules around a central molecule in the crystal correlates with the curvedness of the Hirshfeld surface [Fig. 4(c)]. The nearest-neighbour coordination environment of a molecule is identified from the colour

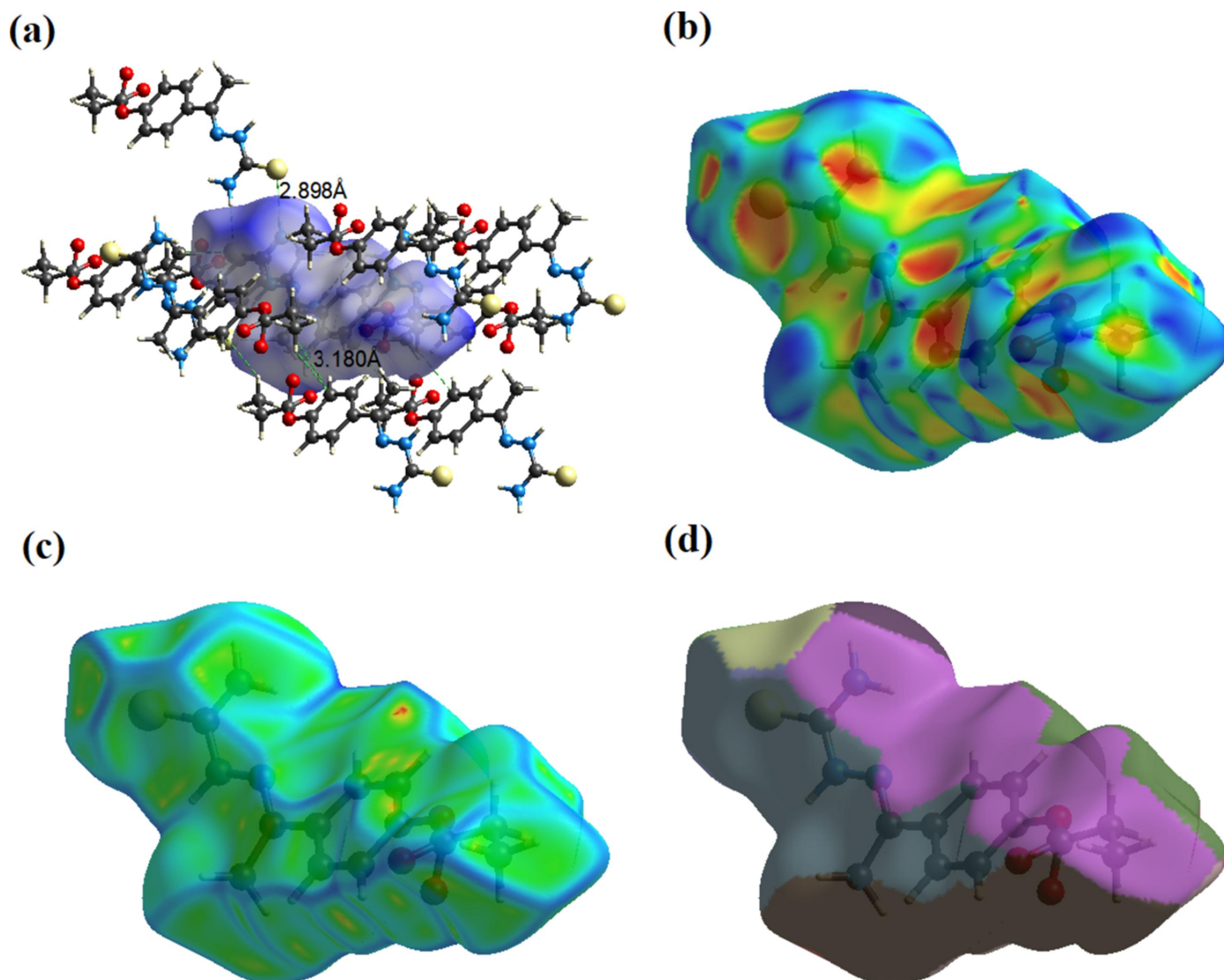


Figure 4

The Hirshfeld surfaces for visualizing the intermolecular contacts of compound (I): (a) d_{norm} with various intermolecular contacts in the crystal, (b) shape index, (c) curvedness and (d) fragment patches.

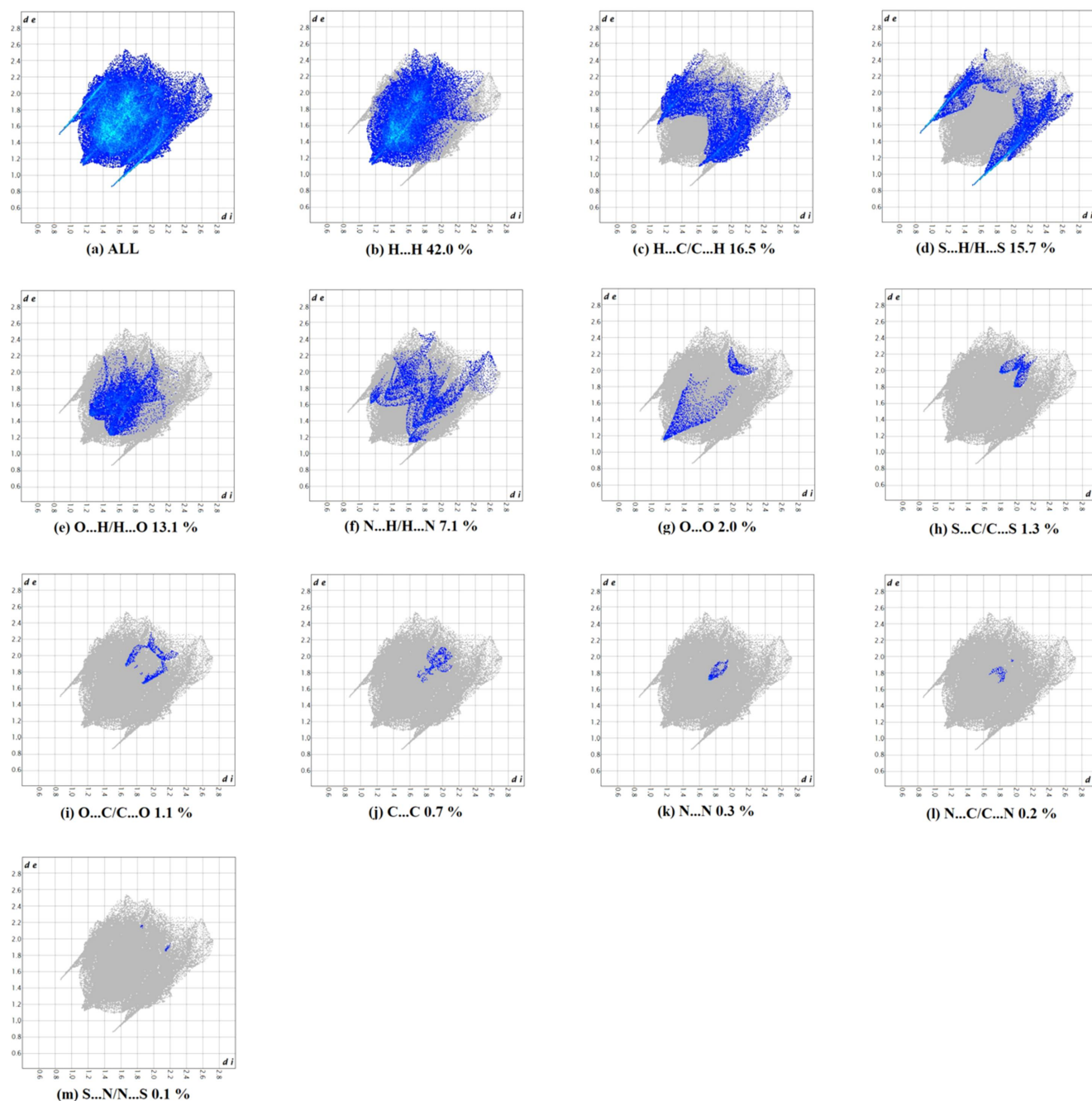


Figure 5

(a) The full two-dimensional fingerprint plot for title compound and those delineated into (b) H···H, (c) C···H/H···C, (d) S···H/H···S, (e) O···H/H···O, (f) N···H/H···N, (g) O···O, (h) S···C/C···S, (i) O···C/C···O, (j) C···C, (k) N···N, (l) N···C/C···N and (m) S···N/N···S contacts.

patches on the Hirshfeld surface depending on their closeness to adjacent molecules [Fig. 4(d)].

The fingerprint plots of (I) are given in Fig. 5. They reveal that the principal intermolecular contacts are H···H contacts with a 42.0% contribution [Fig. 5(b)], followed by H···C/C···H contacts with a 16.5% contribution (Fig. 5c), S···H/H···S with 15.7% [Fig. 5(d)], O···H/H···O with 13.1% [Fig. 5(e)] and N···H/H···N with 7.1% [Fig. 5(f)]. O···O contacts with a contribution of 2.0% [Fig. 5(g)], S···C/C···S with 1.3% [Fig. 5(h)], O···C/C···O with 1.1% [Fig. 5(i)],

C···C with 0.7% [Fig. 5(j)], N···N with 0.3% [Fig. 5(k)], N···C/C···N with 0.2% [Fig. 5(l)] and S···N/N···S with 0.1% [Fig. 5(m)] contribute less to the packing.

5. Database survey

Given the interest in semithiocarbazones owing to their biological potential, it is not surprising that a search of the Cambridge Structural Database (CSD, Version 5.37, last update May 2016; Groom *et al.*, 2016) revealed almost 100 hits

for the $\text{CC(H)=NN(H)C(=S)N(H)}_2$ fragment. The only restriction in the search was that the heaviest atom was sulfur. In the absence of this restriction, there were nearly 400 hits. All bond lengths and angles are normal and correspond well to those observed in the crystal structures of related semicarbazone and thiosemicarbazone derivatives (Naik & Palenik, 1974; Wang *et al.*, 2004; Pelosi *et al.*, 2005; Yathirajan *et al.*, 2006; Sarojini *et al.*, 2007; Reddy *et al.*, 2014; Carballo *et al.*, 2014).

6. Synthesis and crystallization

To 4-hydroxyacetophenone (0.5 mol) were added 200 ml of chloroform under continuous stirring and cooling to 288–293 K. Propanoyl chloride (0.5 mol) was added dropwise to the reaction mixture and stirring continued for another 15 min, when 0.5 mol of potassium carbonate were added slowly. The reaction was continued for another 4 h and was monitored using thin-layer chromatography (TLC). The reaction mass was then washed twice with water (2×250 ml). The chloroform layer was separated and washed with 10 wt% NaOH solution (2×250 ml). The aqueous phase was separated, dried with anhydrous sodium sulfate, followed by concentration under reduced pressure using a rotary vacuum system, and cooled before hexane was added.

Thiosemicarbazide (0.91 g, 0.01 mole) was added to 50 ml of an ethanolic solution of 4-acetylphenyl propionate (0.01 mol) with continuous stirring for 4–5 h. The resulting mixture was refluxed at 333 K and the purity of the products, as well as the composition of the reaction mixture, was monitored by TLC using ethyl acetate–hexane (3:7 *v:v*). The reaction mixture was cooled to room temperature and the separated product was filtered, dried and finally recrystallized from chloroform solution, yielding colourless crystals of (I).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Carbon-bound H atoms were placed in calculated positions ($\text{C–H} = 0.95\text{--}0.96 \text{ \AA}$) and included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms. The N-bound H atoms were located in a difference Fourier map and freely refined. The O1 atom of the carbonyl group was found to be disordered over two positions, with a refined occupancy ratio of 0.73 (2):0.27 (2). The C=O bond length and ADPs were subjected to restraints to yield sensible geometrical parameters. The crystal under investigation consists of two domains. The crystal structure was refined using HKLF5-type data with all reflections of component 1 (including the overlapping ones) resulting in a BASF value of 0.3587 (2).

Acknowledgements

The authors thank the SAIF, IIT, Madras, India, for the data collection.

Table 2

Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2\text{S}$ |
| M_r | 265.33 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 296 |
| a, b, c (Å) | 5.7700 (1), 8.3069 (2), 14.6243 (5) |
| α, β, γ (°) | 82.891 (2), 87.004 (4), 74.172 (2) |
| V (Å ³) | 669.07 (3) |
| Z | 2 |
| Radiation type | Mo $K\alpha$ |
| μ (mm ⁻¹) | 0.24 |
| Crystal size (mm) | 0.29 × 0.24 × 0.20 |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE diffractometer with PHOTON II detector |
| Absorption correction | Multi-scan (SADABS; Krause <i>et al.</i> , 2015) |
| $T_{\text{min}}, T_{\text{max}}$ | 0.723, 0.863 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 8530, 8530, 6376 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹) | 0.595 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.065, 0.219, 1.09 |
| No. of reflections | 8530 |
| No. of parameters | 188 |
| No. of restraints | 197 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.26, -0.26 |

Computer programs: APEX3 (Bruker, 2016), SAINT (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012), Mercury (Macrae *et al.*, 2020), WinGX (Farrugia, 2012), publCIF (Westrip, 2010) and PLATON (Spek, 2020).

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Computing details

4-[(1*E*)-1-[(Carbamothioylamino)imino]ethyl]phenyl propanoate

Crystal data

$C_{12}H_{15}N_3O_2S$

$M_r = 265.33$

Triclinic, $P\bar{1}$

$a = 5.7700$ (1) Å

$b = 8.3069$ (2) Å

$c = 14.6243$ (5) Å

$\alpha = 82.891$ (2)°

$\beta = 87.004$ (4)°

$\gamma = 74.172$ (2)°

$V = 669.07$ (3) Å³

$Z = 2$

$F(000) = 280$

$D_x = 1.317$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8530 reflections

$\theta = 1.4$ – 25.0 °

$\mu = 0.24$ mm⁻¹

$T = 296$ K

Block, colourless

$0.29 \times 0.24 \times 0.20$ mm

Data collection

Bruker D8 VENTURE

diffractometer with PHOTON II detector

ω and φ scans

Absorption correction: multi-scan

(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.723$, $T_{\max} = 0.863$

8530 measured reflections

8530 independent reflections

6376 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 1.4$ °

$h = -6$ → 6

$k = -9$ → 9

$l = -17$ → 17

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.219$

$S = 1.09$

8530 reflections

188 parameters

197 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1179P)^2 + 0.1922P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.26$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|-------------|--------------|---------------|----------------------------------|-----------|
| C1 | 1.0534 (11) | 0.1766 (9) | 0.6695 (4) | 0.0748 (18) | |
| H1A | 1.177682 | 0.206605 | 0.699122 | 0.112* | |
| H1B | 1.105508 | 0.059493 | 0.660560 | 0.112* | |
| H1C | 0.909702 | 0.196951 | 0.707362 | 0.112* | |
| C2 | 1.0027 (10) | 0.2796 (8) | 0.5790 (3) | 0.0627 (16) | |
| H2A | 0.959090 | 0.397789 | 0.588404 | 0.075* | |
| H2B | 1.148613 | 0.257722 | 0.541123 | 0.075* | |
| C3 | 0.8076 (11) | 0.2464 (8) | 0.5289 (4) | 0.0605 (15) | |
| C4 | 0.6029 (8) | 0.3302 (7) | 0.3831 (3) | 0.0460 (12) | |
| C5 | 0.4929 (9) | 0.2042 (7) | 0.3839 (3) | 0.0553 (14) | |
| H5 | 0.527970 | 0.112943 | 0.429410 | 0.066* | |
| C6 | 0.3285 (9) | 0.2129 (7) | 0.3165 (3) | 0.0518 (13) | |
| H6 | 0.257115 | 0.125208 | 0.316087 | 0.062* | |
| C7 | 0.2684 (8) | 0.3510 (6) | 0.2492 (3) | 0.0392 (11) | |
| C8 | 0.3902 (8) | 0.4745 (7) | 0.2493 (3) | 0.0443 (12) | |
| H8 | 0.359427 | 0.565770 | 0.203699 | 0.053* | |
| C9 | 0.5552 (8) | 0.4633 (7) | 0.3159 (3) | 0.0463 (12) | |
| H9 | 0.634613 | 0.546995 | 0.315112 | 0.056* | |
| C10 | 0.0799 (8) | 0.3681 (6) | 0.1809 (3) | 0.0402 (11) | |
| C11 | 0.0131 (9) | 0.2144 (7) | 0.1596 (3) | 0.0538 (14) | |
| H11A | 0.138562 | 0.115539 | 0.179483 | 0.081* | |
| H11B | -0.007165 | 0.220584 | 0.094384 | 0.081* | |
| H11C | -0.134948 | 0.208693 | 0.191289 | 0.081* | |
| C12 | -0.3239 (8) | 0.7118 (6) | 0.0597 (3) | 0.0414 (11) | |
| N1 | -0.0217 (6) | 0.5204 (5) | 0.1479 (2) | 0.0407 (10) | |
| N2 | -0.2082 (7) | 0.5502 (5) | 0.0885 (3) | 0.0420 (10) | |
| N3 | -0.2309 (9) | 0.8273 (6) | 0.0830 (4) | 0.0623 (13) | |
| O2 | 0.7779 (6) | 0.3338 (5) | 0.4461 (2) | 0.0654 (12) | |
| S1 | -0.5771 (2) | 0.75787 (17) | -0.00106 (11) | 0.0586 (5) | |
| O1A | 0.829 (7) | 0.0938 (10) | 0.527 (2) | 0.114 (13) | 0.27 (2) |
| O1B | 0.6526 (17) | 0.1802 (15) | 0.5647 (4) | 0.084 (4) | 0.73 (2) |
| H2 | -0.271 (7) | 0.483 (5) | 0.067 (3) | 0.035 (13)* | |
| H3A | -0.280 (9) | 0.930 (5) | 0.061 (3) | 0.071 (18)* | |
| H3B | -0.105 (6) | 0.803 (6) | 0.109 (3) | 0.051 (15)* | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|-------------|--------------|--------------|-------------|
| C1 | 0.085 (4) | 0.079 (5) | 0.060 (3) | -0.012 (4) | -0.028 (3) | -0.013 (3) |
| C2 | 0.058 (3) | 0.080 (5) | 0.052 (3) | -0.020 (3) | -0.016 (3) | -0.001 (3) |
| C3 | 0.071 (4) | 0.059 (4) | 0.053 (3) | -0.020 (3) | -0.021 (3) | 0.003 (3) |
| C4 | 0.039 (2) | 0.059 (3) | 0.040 (3) | -0.015 (2) | -0.007 (2) | 0.001 (3) |
| C5 | 0.058 (3) | 0.048 (3) | 0.054 (3) | -0.010 (3) | -0.019 (3) | 0.012 (3) |
| C6 | 0.056 (3) | 0.043 (3) | 0.055 (3) | -0.015 (3) | -0.021 (2) | 0.010 (3) |
| C7 | 0.035 (2) | 0.037 (3) | 0.042 (2) | -0.004 (2) | -0.0033 (19) | -0.002 (2) |
| C8 | 0.040 (2) | 0.046 (3) | 0.043 (3) | -0.008 (2) | -0.004 (2) | 0.004 (2) |
| C9 | 0.044 (3) | 0.047 (3) | 0.050 (3) | -0.017 (2) | -0.002 (2) | 0.001 (3) |
| C10 | 0.038 (2) | 0.041 (3) | 0.038 (2) | -0.006 (2) | -0.002 (2) | -0.002 (2) |
| C11 | 0.062 (3) | 0.042 (3) | 0.056 (3) | -0.010 (3) | -0.021 (3) | -0.001 (3) |
| C12 | 0.040 (2) | 0.039 (3) | 0.045 (3) | -0.013 (2) | -0.008 (2) | 0.004 (2) |
| N1 | 0.039 (2) | 0.043 (3) | 0.038 (2) | -0.0112 (18) | -0.0095 (16) | 0.0066 (19) |
| N2 | 0.043 (2) | 0.033 (2) | 0.049 (2) | -0.0095 (19) | -0.0146 (18) | 0.005 (2) |
| N3 | 0.067 (3) | 0.039 (3) | 0.081 (3) | -0.017 (3) | -0.044 (3) | 0.012 (3) |
| O2 | 0.064 (2) | 0.084 (3) | 0.055 (2) | -0.037 (2) | -0.0220 (18) | 0.015 (2) |
| S1 | 0.0527 (8) | 0.0359 (8) | 0.0871 (10) | -0.0128 (6) | -0.0365 (7) | 0.0107 (7) |
| O1A | 0.15 (3) | 0.056 (13) | 0.14 (2) | -0.027 (13) | -0.08 (2) | 0.014 (12) |
| O1B | 0.087 (6) | 0.125 (9) | 0.058 (4) | -0.065 (6) | -0.017 (4) | 0.011 (4) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|------------|-----------|-----------|-----------|
| C1—C2 | 1.480 (7) | C7—C8 | 1.393 (6) |
| C1—H1A | 0.9600 | C7—C10 | 1.482 (6) |
| C1—H1B | 0.9600 | C8—C9 | 1.375 (6) |
| C1—H1C | 0.9600 | C8—H8 | 0.9300 |
| C2—C3 | 1.479 (7) | C9—H9 | 0.9300 |
| C2—H2A | 0.9700 | C10—N1 | 1.285 (6) |
| C2—H2B | 0.9700 | C10—C11 | 1.502 (7) |
| C3—O1B | 1.234 (8) | C11—H11A | 0.9600 |
| C3—O1A | 1.242 (2) | C11—H11B | 0.9600 |
| C3—O2 | 1.327 (6) | C11—H11C | 0.9600 |
| C4—C9 | 1.363 (7) | C12—N3 | 1.305 (6) |
| C4—C5 | 1.362 (7) | C12—N2 | 1.351 (6) |
| C4—O2 | 1.410 (5) | C12—S1 | 1.679 (4) |
| C5—C6 | 1.386 (6) | N1—N2 | 1.369 (5) |
| C5—H5 | 0.9300 | N2—H2 | 0.84 (3) |
| C6—C7 | 1.394 (7) | N3—H3A | 0.85 (3) |
| C6—H6 | 0.9300 | N3—H3B | 0.80 (3) |
| C2—C1—H1A | 109.5 | C6—C7—C10 | 121.7 (4) |
| C2—C1—H1B | 109.5 | C9—C8—C7 | 120.9 (5) |
| H1A—C1—H1B | 109.5 | C9—C8—H8 | 119.6 |
| C2—C1—H1C | 109.5 | C7—C8—H8 | 119.6 |
| H1A—C1—H1C | 109.5 | C4—C9—C8 | 120.4 (5) |

| | | | |
|--------------|------------|---------------|------------|
| H1B—C1—H1C | 109.5 | C4—C9—H9 | 119.8 |
| C3—C2—C1 | 113.6 (5) | C8—C9—H9 | 119.8 |
| C3—C2—H2A | 108.8 | N1—C10—C7 | 114.6 (4) |
| C1—C2—H2A | 108.8 | N1—C10—C11 | 125.6 (4) |
| C3—C2—H2B | 108.8 | C7—C10—C11 | 119.7 (4) |
| C1—C2—H2B | 108.8 | C10—C11—H11A | 109.5 |
| H2A—C2—H2B | 107.7 | C10—C11—H11B | 109.5 |
| O1B—C3—O2 | 121.3 (5) | H11A—C11—H11B | 109.5 |
| O1A—C3—O2 | 113.3 (14) | C10—C11—H11C | 109.5 |
| O1B—C3—C2 | 124.9 (5) | H11A—C11—H11C | 109.5 |
| O1A—C3—C2 | 113.1 (12) | H11B—C11—H11C | 109.5 |
| O2—C3—C2 | 111.6 (5) | N3—C12—N2 | 116.7 (4) |
| C9—C4—C5 | 120.6 (4) | N3—C12—S1 | 122.8 (4) |
| C9—C4—O2 | 114.3 (4) | N2—C12—S1 | 120.6 (4) |
| C5—C4—O2 | 125.1 (5) | C10—N1—N2 | 119.1 (4) |
| C4—C5—C6 | 119.7 (5) | C12—N2—N1 | 118.2 (4) |
| C4—C5—H5 | 120.2 | C12—N2—H2 | 111 (3) |
| C6—C5—H5 | 120.2 | N1—N2—H2 | 131 (3) |
| C5—C6—C7 | 121.0 (5) | C12—N3—H3A | 122 (4) |
| C5—C6—H6 | 119.5 | C12—N3—H3B | 121 (4) |
| C7—C6—H6 | 119.5 | H3A—N3—H3B | 115 (4) |
| C8—C7—C6 | 117.4 (4) | C3—O2—C4 | 124.5 (4) |
| C8—C7—C10 | 120.9 (4) | | |
| C1—C2—C3—O1B | 20.2 (11) | C6—C7—C10—N1 | 154.4 (4) |
| C1—C2—C3—O1A | -47 (2) | C8—C7—C10—C11 | 158.8 (4) |
| C1—C2—C3—O2 | -176.3 (5) | C6—C7—C10—C11 | -22.2 (6) |
| C9—C4—C5—C6 | -0.9 (8) | C7—C10—N1—N2 | -176.1 (3) |
| O2—C4—C5—C6 | -178.1 (5) | C11—C10—N1—N2 | 0.3 (7) |
| C4—C5—C6—C7 | -1.8 (8) | N3—C12—N2—N1 | 7.4 (7) |
| C5—C6—C7—C8 | 3.6 (7) | S1—C12—N2—N1 | -171.5 (3) |
| C5—C6—C7—C10 | -175.4 (4) | C10—N1—N2—C12 | 175.4 (4) |
| C6—C7—C8—C9 | -2.8 (7) | O1B—C3—O2—C4 | -14.7 (11) |
| C10—C7—C8—C9 | 176.3 (4) | O1A—C3—O2—C4 | 52 (2) |
| C5—C4—C9—C8 | 1.8 (8) | C2—C3—O2—C4 | -178.9 (5) |
| O2—C4—C9—C8 | 179.2 (4) | C9—C4—O2—C3 | 161.2 (5) |
| C7—C8—C9—C4 | 0.2 (7) | C5—C4—O2—C3 | -21.5 (8) |
| C8—C7—C10—N1 | -24.6 (6) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------|----------|-------------|-------------|---------------|
| N3—H3B \cdots N1 | 0.80 (3) | 2.27 (5) | 2.588 (6) | 104 (4) |
| C5—H5 \cdots O1B | 0.93 | 2.32 | 2.812 (7) | 113 |
| N2—H2 \cdots S1 ⁱ | 0.84 (3) | 2.69 (3) | 3.525 (4) | 173 (4) |

| | | | | |
|----------------------------|----------|----------|-----------|---------|
| N3—H3A···S1 ⁱⁱ | 0.85 (3) | 2.55 (3) | 3.402 (5) | 177 (5) |
| C11—H11B···S1 ⁱ | 0.96 | 2.77 | 3.452 (5) | 128 |

Symmetry codes: (i) $-x-1, -y+1, -z$; (ii) $-x-1, -y+2, -z$.