$N$-Carbethoxy-$N'$-(3-phenyl-$1H$-$1,2,4$-triazol-$5$-yl)thiourea

Anton V. Dolzhenko, Geok Kheng Tan, Lip Lin Koh, Anna V. Dolzhenko and Wai Keung Chui


This open-access article is distributed under the terms of the Creative Commons Attribution Licence http://creativecommons.org/licenses/by/2.0/uk/legalcode, which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.

*Acta Crystallographica Section E: Structure Reports Online* is the IUCr’s highly popular open-access structural journal. It provides a simple and easily accessible publication mechanism for the growing number of inorganic, metal-organic and organic crystal structure determinations. The electronic submission, validation, refereeing and publication facilities of the journal ensure very rapid and high-quality publication, whilst key indicators and validation reports provide measures of structural reliability. In 2007, the journal published over 5000 structures. The average publication time is less than one month.

Crystallography Journals Online is available from journals.iucr.org
**N-Carbethoxy-N’-(3-phenyl-1H-1,2,4-triazol-5-yl)thiourea**

Anton V. Dolzhenko, Geok Kheng Tan, Lip Lin Koh, Anna V. Dolzhenko and Wai Keung Chui

Department of Pharmacy, Faculty of Science, National University of Singapore, 18 Science Drive 4, Singapore 117543, Singapore

Correspondence e-mail: phada@nus.edu.sg

Received 4 January 2010; accepted 19 January 2010

Key indicators: single-crystal X-ray study; \( T = 100 \) K; mean \( σ(C–C) = 0.002 \) \( \text{Å} \); \( R \) factor = 0.040; \( wR \) factor = 0.102; data-to-parameter ratio = 15.9.

The title compound [systematic name: ethyl \( N-[N-(3-phenyl-1H-1,2,4-triazol-5-yl)carbamothioyl]carbamate\), \( \text{C}_{12}\text{H}_{13}\text{N}_{5}\text{O}_{2}\text{S} \), exists in the 3-phenyl-thioureoide-1H,1,2,4-triazole tautomeric form stabilized by intramolecular hydrogen bonding between the endocyclic NH H atom and the thioureido S atom. The molecular structure is also stabilized by intramolecular \( N-H\cdots C \) hydrogen bonds arranged in an \( S(6) \) graph-set motif within the carbethothioureido moiety. The planes of the phenyl and 1,2,4-triazole rings make a dihedral angle of 7.61 (11)°. In the crystal, the molecules form two types of inversion dimers. Intermolecular hydrogen bonds are arranged in \( R_2^2(6) \) and \( R_5^2(8) \) graph-set motifs, together forming a network parallel to (111).

Related literature

For the synthesis, tautomerism and crystal structure studies of related 1,2,4-triazoles, see: Dolzhenko et al. (2007, 2009a,b,c). For the structures of related carbethothioureides, see: Huang et al. (2009); Lin et al. (2004, 2007); Su et al. (2006); Zhang et al. (2003, 2007). For the graph-set analysis of hydrogen bonding, see: Bernstein et al. (1995).

**Experimental**

Crystal data

\[ \begin{align*}
\text{C}_{12}\text{H}_{13}\text{N}_{5}\text{O}_{2}\text{S} \\
M_r &= 291.33 \\
\text{Triclinic, } P\bar{T} \\
a &= 5.9929 (3) \text{ Å} \\
b &= 9.4200 (5) \text{ Å} \\
c &= 12.2000 (7) \text{ Å} \\
\alpha &= 91.818 (1)^\circ \\
\beta &= 92.585 (1)^\circ \\
\gamma &= 101.083 (1)^\circ \\
V &= 674.62 (6) \text{ Å}^3 \\
Z &= 2 \\
\mu &= 0.25 \text{ mm}^{-1} \\
T &= 100 \text{ K} \\
\end{align*} \]

Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 2001)

\( T_{\text{min}} = 0.873, T_{\text{max}} = 0.971 \)

\( 3092 \) independent reflections

\( 194 \) parameters

\( \Delta P_{\text{max}} = 0.59 \text{ e Å}^{-3} \)

\( \Delta P_{\text{min}} = -0.20 \text{ e Å}^{-3} \)

**Table 1**

Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>D—A</th>
<th>D—D—A</th>
<th>D—H—A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N5—H5—S1</td>
<td>0.81 (2)</td>
<td>2.58 (2)</td>
<td>3.3739 (13)</td>
<td>166.0 (17)</td>
</tr>
<tr>
<td>N4—H4—O2</td>
<td>0.84 (2)</td>
<td>1.97 (2)</td>
<td>2.6448 (16)</td>
<td>137.3 (18)</td>
</tr>
<tr>
<td>N3—H3—N1</td>
<td>0.84 (2)</td>
<td>2.67 (2)</td>
<td>3.0926 (13)</td>
<td>113.0 (16)</td>
</tr>
<tr>
<td>N3—H3—N2&quot;</td>
<td>0.84 (2)</td>
<td>2.32 (2)</td>
<td>2.9838 (18)</td>
<td>136.5 (18)</td>
</tr>
</tbody>
</table>

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELX97 (Sheldrick, 2008); molecular graphics: SHELXL (Sheldrick, 2008); software used to prepare material for publication: SHELXL.

This work was supported by the National Medical Research Council, Singapore (NMRC/NIG/0019/2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GW2076).

**References**


supplementary materials
supplementary materials


**N-Carbethoxy-N’-(3-phenyl-1H-1,2,4-triazol-5-yl)thiourea**

**A. V. Dolzhenko, G. K. Tan, L. L. Koh, A. V. Dolzhenko and W. K. Chui**

**Comment**

Annular tautomerism of 1,2,4-triazoles in solutions (Dolzhenko et al., 2009a) and crystalline state (Dolzhenko et al., 2009b,c) is a subject of our continuous investigations. Recently, we reported the crystal structure of 3(5)-amino-5(3)-phenyl-1H-1,2,4-triazole (Dolzhenko et al., 2009b). Both 3-amino-5-phenyl- and 5-amino-3-phenyl-1H-1,2,4-triazole tautomeric forms were found to coexist in the crystal. Herein we study the related structure with carbethoxythiourea moiety presented instead of the amino group. Due to annular tautomerism, there is theoretical possibility for existence of three tautomeric forms viz. N-carbethoxy-N’-(3-phenyl-1H-1,2,4-triazol-5-yl)thiourea (A), N-carbethoxy-N’-(5-phenyl-1H-1,2,4-triazol-3-yl)thiourea (B) and N-carbethoxy-N’-(3-phenyl-4H-1,2,4-triazol-5-yl)thiourea (C) (Figure 2). Unlike 3(5)-amino-5(3)-phenyl-1H-1,2,4-triazole, only one tautomeric form A was identified in the crystal (Figure 3). The N3—H···S1 hydrogen bonds between the endocyclic N(3)H proton of the triazole ring and the thiourea sulfur S1 atom (Figure 3 and 4, Table 1) are arranged in a S(6) graph-set motif (Bernstein et al., 1995) stabilizing this tautomer. Interestingly, structurally similar carbethoxythioureido substituted pyrazole (Huang et al., 2009) does not possess this motif and crystallizes as a tautomer with the carbethoxythiourea moiety at position 5 of the ring.

The triazole ring is essentially planar with an r.m.s. deviation of 0.0058 Å. Its mean plane makes a dihedral angle of 7.61 (11)° with the phenyl ring.

The C—N bonds of the thiourea group have unequal lengths: the C9—N4 bond is significantly shorter (1.3440 (18) Å) compare to the C9—N5 bond (1.3811 (18) Å). The configuration of the carbethoxythiourea group of the title compound is similar to those reported for the similar structures (Huang et al., 2009; Lin et al., 2007; Lin et al., 2004; Su et al., 2006; Zhang et al., 2007; Zhang et al., 2003). The triazole ring and the thiocarbonyl lie in (Z)-configuration across the thiourea C9—N4 bond; while the carbethoxy and thiocarbonyl groups adopt (E)-configuration across the C9—N5 bond. This configuration is stabilized by an intramolecular N4—H···O2=C10 hydrogen bond (Figure 3 and 4, Table 1) making a S(6) graph-set motif, which is common for carbethoxythioureas (Huang et al., 2009; Lin et al., 2007; Lin et al., 2004; Su et al., 2006; Zhang et al., 2007; Zhang et al., 2003).

In the crystal, the molecules form two types of cyclic dimmers (Figure 4, Table 1). The N2—N3H sides of two molecules are connected by intermolecular hydrogen bonds making the R22(6) graph-set motif. Atom N5 is also involved in intramolecular N—H···S interactions with the thiocarbonyl atom S1 of adjacent molecule making another pair with the R22(8) graph-set motif similar to those observed in other carbethoxythioureas (Huang et al., 2009; Lin et al., 2007; Lin et al., 2004; Su et al., 2006; Zhang et al., 2007; Zhang et al., 2003). Together, these hydrogen bonds connect molecules in a network parallel to the (111) plane.
supplementary materials

Experimental

The title compound was synthesized by nucleophilic addition of 3(5)-amino-5(3)-phenyl-1H-1,2,4-triazole (Dolzhenko et al., 2007) to ethoxycarbonyl isothiocyanate in DMF solution at room temperature (Figure 1). Single crystals suitable for crystallographic analysis were grown by recrystallization from toluene.

Refinement

All the H atoms attached to the carbon atoms were constrained in a riding motion approximation [0.95 Å for Caryl—H, 0.99 Å for methylenic protons and 0.98 Å for methyl group; \( U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C_{\text{aryl}}), U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C_{\text{methylene}}) \) and \( U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C_{\text{methyl}}) \) while the N-bound H atoms were located in a difference map and refined freely.

Figures

Fig. 1. Synthesis of N-carbethoxy-N’-(3-phenyl-1H-1,2,4-triazol-5-yl)thiourea.

Fig. 2. Annular tautomerism in N-carbethoxy-N’-(3(5)-phenyl-l(4)H-1,2,4-triazol-5(3)-yl)thiourea.

Fig. 3. The molecular structure of N-carbethoxy-N’-(3-phenyl-1H-1,2,4-triazol-5-yl)thiourea, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 4. Crystal packing in the cell (view along axis a).

dimethyl N-[N-(3-phenyl-1H-1,2,4-triazol-5-yl)carbamothioyl]carbamate

Crystal data

C\(_{12}\)H\(_{13}\)N\(_{2}\)O\(_2\)S

\( M_r = 291.33 \)

Triclinic, \( \overline{P} \) \(

\( a = 5.9929 (3) \) Å
\( b = 9.4200 (5) \) Å
\( c = 12.2000 (7) \) Å
\( \alpha = 91.818 (1)^\circ \)
\( \beta = 92.585 (1)^\circ \)

\( Z = 2 \)

\( F(000) = 304 \)

\( D_\alpha = 1.434 \) Mg m\(^{-3}\)

Melting point: 454 K

Mo K\( \alpha \) radiation, \( \lambda = 0.71073 \) Å

Cell parameters from 4121 reflections

\( \theta = 2.7^\circ-27.5^\circ \)

\( \mu = 0.25 \) mm\(^{-1} \)

\( T = 100 \) K
\[ \gamma = 101.083 \, (1)° \]
\[ V = 674.62 \, (6) \, \text{Å}^3 \]

Rod, colourless

\[ 0.56 \times 0.24 \times 0.12 \, \text{mm} \]

**Data collection**

Bruker SMART APEX CCD
diffractometer

3092 independent reflections

Radiation source: fine-focus sealed tube

2828 reflections with \( l > 2\sigma(l) \)

graphite

\( R_{\text{int}} = 0.028 \)

\( \phi \) and \( \omega \) scans

\( \theta_{\text{max}} = 27.5°; \theta_{\text{min}} = 1.7° \)

Absorption correction: multi-scan

(SADABS; Sheldrick, 2001)

\( h = -7 \rightarrow 7 \)

\( k = -12 \rightarrow 12 \)

\( l = -15 \rightarrow 15 \)

**Refinement**

Refinement on \( F^2 \)

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

\( R[F^2 > 2\sigma(F^2)] = 0.040 \)

Hydrogen site location: inferred from neighbouring sites

\( wR(F^2) = 0.102 \)

\( w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.2404P] \)

\( P = (F_o^2 + 2F_c^2)/3 \)

3092 reflections

\( \Delta\rho_{\text{max}} = 0.59 \, \text{e Å}^{-3} \)

194 parameters

\( \Delta\rho_{\text{min}} = -0.20 \, \text{e Å}^{-3} \)

0 restraints

**Special details**

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

**Refinement.** Refinement of \( F^2 \) against ALL reflections. The weighted \( R \)-factor \( wR \) and goodness of fit \( S \) are based on \( F^2 \), conventional \( R \)-factors \( R \) are based on \( F \), with \( F \) set to zero for negative \( F^2 \). The threshold expression of \( F^2 > 2\sigma(F^2) \) is used only for calculating \( R \)-factors(gt) etc. and is not relevant to the choice of reflections for refinement. \( R \)-factors based on \( F^2 \) are statistically about twice as large as those based on \( F \), and \( R \)-factors based on ALL data will be even larger.

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

<table>
<thead>
<tr>
<th></th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{\text{iso}} )</th>
<th>( U_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.26167 (6)</td>
<td>0.64734 (4)</td>
<td>−0.02591 (3)</td>
<td>0.02072 (12)</td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>0.58945 (18)</td>
<td>0.44334 (11)</td>
<td>0.28112 (8)</td>
<td>0.0204 (2)</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>0.31338 (18)</td>
<td>0.55681 (11)</td>
<td>0.33852 (8)</td>
<td>0.0217 (2)</td>
<td></td>
</tr>
</tbody>
</table>
supplementary materials

<table>
<thead>
<tr>
<th></th>
<th>$U^{11}$</th>
<th>$U^{22}$</th>
<th>$U^{33}$</th>
<th>$U^{12}$</th>
<th>$U^{13}$</th>
<th>$U^{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0269 (2)</td>
<td>0.0220 (2)</td>
<td>0.01582 (19)</td>
<td>0.01013 (15)</td>
<td>0.00368 (14)</td>
<td>0.00310 (13)</td>
</tr>
<tr>
<td>O1</td>
<td>0.0255 (5)</td>
<td>0.0203 (5)</td>
<td>0.0183 (5)</td>
<td>0.0113 (4)</td>
<td>0.0017 (4)</td>
<td>0.0021 (4)</td>
</tr>
<tr>
<td>O2</td>
<td>0.0270 (6)</td>
<td>0.0238 (5)</td>
<td>0.0175 (5)</td>
<td>0.0120 (4)</td>
<td>0.0040 (4)</td>
<td>0.0029 (4)</td>
</tr>
<tr>
<td>N1</td>
<td>0.0203 (6)</td>
<td>0.0153 (6)</td>
<td>0.0188 (6)</td>
<td>0.0047 (5)</td>
<td>0.0010 (5)</td>
<td>0.0011 (5)</td>
</tr>
<tr>
<td>N2</td>
<td>0.0205 (6)</td>
<td>0.0206 (6)</td>
<td>0.0194 (6)</td>
<td>0.0083 (5)</td>
<td>0.0000 (5)</td>
<td>0.0019 (5)</td>
</tr>
<tr>
<td>N3</td>
<td>0.0212 (6)</td>
<td>0.0206 (6)</td>
<td>0.0174 (6)</td>
<td>0.0088 (5)</td>
<td>0.0035 (5)</td>
<td>0.0041 (5)</td>
</tr>
<tr>
<td>N4</td>
<td>0.0225 (6)</td>
<td>0.0187 (6)</td>
<td>0.0141 (6)</td>
<td>0.0078 (5)</td>
<td>0.0020 (5)</td>
<td>0.0025 (5)</td>
</tr>
<tr>
<td>N5</td>
<td>0.0220 (6)</td>
<td>0.0190 (6)</td>
<td>0.0174 (6)</td>
<td>0.0093 (5)</td>
<td>0.0039 (5)</td>
<td>0.0006 (5)</td>
</tr>
<tr>
<td>C1</td>
<td>0.0230 (7)</td>
<td>0.0193 (7)</td>
<td>0.0214 (7)</td>
<td>0.0074 (6)</td>
<td>-0.0003 (6)</td>
<td>0.0013 (5)</td>
</tr>
<tr>
<td>C2</td>
<td>0.0262 (8)</td>
<td>0.0251 (8)</td>
<td>0.0235 (8)</td>
<td>0.0068 (6)</td>
<td>0.0054 (6)</td>
<td>0.0001 (6)</td>
</tr>
<tr>
<td>C3</td>
<td>0.0224 (7)</td>
<td>0.0236 (8)</td>
<td>0.0317 (8)</td>
<td>0.0089 (6)</td>
<td>0.0014 (6)</td>
<td>-0.0037 (6)</td>
</tr>
<tr>
<td>C4</td>
<td>0.0220 (7)</td>
<td>0.0191 (7)</td>
<td>0.0313 (8)</td>
<td>0.0081 (6)</td>
<td>-0.0035 (6)</td>
<td>0.0004 (6)</td>
</tr>
<tr>
<td>C5</td>
<td>0.0214 (7)</td>
<td>0.0183 (7)</td>
<td>0.0211 (7)</td>
<td>0.0032 (5)</td>
<td>-0.0020 (5)</td>
<td>0.0024 (5)</td>
</tr>
<tr>
<td>C6</td>
<td>0.0168 (6)</td>
<td>0.0155 (7)</td>
<td>0.0201 (7)</td>
<td>0.0034 (5)</td>
<td>-0.0012 (5)</td>
<td>-0.0016 (5)</td>
</tr>
</tbody>
</table>

Atomic displacement parameters ($\AA^2$)
| C7   | 0.0172 (7) | 0.0159 (6) | 0.0185 (7) | 0.0039 (5)  | -0.0032 (5) | 0.0002 (5) |
| C8   | 0.0194 (7) | 0.0153 (6) | 0.0171 (7) | 0.0036 (5)  | 0.0000 (5)  | -0.0004 (5) |
| C9   | 0.0186 (7) | 0.0136 (6) | 0.0184 (7) | 0.0026 (5)  | 0.0005 (5)  | 0.0005 (5)  |
| C10  | 0.0213 (7) | 0.0135 (6) | 0.0199 (7) | 0.0042 (5)  | 0.0015 (5)  | 0.0023 (5)  |
| C11  | 0.0318 (8) | 0.0256 (8) | 0.0194 (7) | 0.0135 (6)  | -0.0016 (6) | 0.0021 (6)  |
| C12  | 0.0249 (8) | 0.0235 (8) | 0.0285 (8) | 0.0094 (6)  | -0.0008 (6) | 0.0042 (6)  |

**Geometric parameters (Å, °)**

| S1—C9 | 1.6632 (14) | C1—C6 | 1.394 (2) |
| O1—C10 | 1.3274 (17) | C1—H1 | 0.9500 |
| O1—C11 | 1.4568 (17) | C2—C3 | 1.390 (2) |
| O2—C10 | 1.2142 (18) | C2—H2 | 0.9500 |
| N1—C8 | 1.3194 (18) | C3—C4 | 1.386 (2) |
| N1—C7 | 1.3680 (18) | C3—H3 | 0.9500 |
| N2—C7 | 1.3260 (19) | C4—C5 | 1.385 (2) |
| N2—N3 | 1.3674 (17) | C4—H4 | 0.9500 |
| N3—C8 | 1.3345 (18) | C5—C6 | 1.397 (2) |
| N3—H3N | 0.84 (2) | C5—H5 | 0.9500 |
| N4—C9 | 1.3440 (18) | C6—C7 | 1.4685 (19) |
| N4—C8 | 1.3845 (18) | C11—C12 | 1.501 (2) |
| N4—H4N | 0.84 (2) | C11—H11A | 0.9900 |
| N5—C10 | 1.3803 (18) | C11—H11B | 0.9900 |
| N5—C9 | 1.3811 (18) | C12—H12A | 0.9800 |
| N5—H5N | 0.81 (2) | C12—H12B | 0.9800 |
| C1—C2 | 1.389 (2) | C12—H12C | 0.9800 |
| C10—O1—C11 | 115.00 (11) | C1—C6—C5 | 119.48 (13) |
| C8—N1—C7 | 102.43 (12) | C1—C6—C7 | 120.00 (13) |
| C7—N2—N3 | 102.54 (11) | C5—C6—C7 | 120.52 (13) |
| C8—N3—N2 | 109.22 (12) | N2—C7—N1 | 114.46 (13) |
| C8—N3—H3N | 131.7 (14) | N2—C7—C6 | 122.90 (13) |
| N2—N3—H3N | 118.4 (14) | N1—C7—C6 | 122.64 (13) |
| C9—N4—C8 | 128.91 (13) | N1—C8—N3 | 111.32 (12) |
| C9—N4—H4N | 117.6 (13) | N1—C8—N4 | 121.13 (13) |
| C8—N4—H4N | 113.1 (13) | N3—C8—N4 | 127.42 (13) |
| C10—N5—C9 | 127.10 (13) | N4—C9—N5 | 114.77 (12) |
| C10—N5—H5N | 116.8 (13) | N4—C9—S1 | 125.65 (11) |
| C9—N5—H5N | 115.5 (13) | N5—C9—S1 | 119.58 (11) |
| C2—C1—C6 | 120.04 (14) | O2—C10—O1 | 125.48 (13) |
| C2—C1—H1 | 120.0 | O2—C10—N5 | 125.13 (13) |
| C6—C1—H1 | 120.0 | O1—C10—N5 | 109.38 (12) |
| C1—C2—C3 | 120.18 (14) | O1—C11—C12 | 109.95 (12) |
| C1—C2—H2 | 119.9 | O1—C11—H11A | 110.3 |
| C3—C2—H2 | 119.9 | C12—C11—H11A | 110.3 |
| C4—C3—C2 | 119.88 (14) | O1—C11—H11B | 110.3 |
| C4—C3—H3 | 120.1 | C12—C11—H11B | 110.3 |
| C2—C3—H3 | 120.1 | H11A—C11—H11B | 108.6 |
| C5—C4—C3 | 120.28 (14) | C11—C12—H12A | 109.5 |
| C5—C4—H4 | 119.9 | C11—C12—H12B | 109.5 |
supplementary materials

C3—C4—H4 119.9  H12A—C12—H12B 109.5
C4—C5—C6 120.13 (14)  C11—C12—H12C 109.5
C4—C5—H5 119.9  H12A—C12—H12C 109.5
C6—C5—H5 119.9  H12B—C12—H12C 109.5

Hydrogen-bond geometry (Å, °)

\[
\begin{array}{cccc}
D—H\cdots A & D—H & H\cdots A & D\cdots A & D—H\cdots A \\
N5—H5N\cdots S1^i & 0.81 (2) & 2.58 (2) & 3.3739 (13) & 166.0 (17) \\
N4—H4N\cdots O2 & 0.84 (2) & 1.97 (2) & 2.6448 (16) & 137.3 (18) \\
N3—H3N\cdots S1 & 0.84 (2) & 2.67 (2) & 3.0926 (13) & 113.0 (16) \\
N3—H3N\cdots N2^ii & 0.84 (2) & 2.32 (2) & 2.9838 (18) & 136.5 (18) \\
\end{array}
\]

Symmetry codes: (i) −x+1, −y+1, −z; (ii) −x, −y+2, −z.
supplementary materials

Fig. 1

\[
\begin{array}{c}
\text{Ph} \quad \text{N} = \text{NH} \quad \text{NH}_2 \\
\text{Ph} \quad \text{N} = \text{NH} \quad \text{NH}_2 + \quad \text{S} \quad \text{N} \quad \text{C} = \text{O} \\
\quad \text{OEt} \\
\text{Ph} \quad \text{N} = \text{NH} \quad \text{NH} \quad \text{N} = \text{NH} \quad \text{S} \quad \text{C} = \text{O} \\
\quad \text{OEt}
\end{array}
\]
supplementary materials

Fig. 2

\[ \text{A} \overset{\text{Ph}}{\longrightarrow} \text{B} \overset{\text{Et}}{\longrightarrow} \text{C} \]
Fig. 3
Fig. 4