(E)-O-Ethyl N-(4-nitrophenyl)thiocarbamate

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The title compound, C_{9}H_{10}N_{2}O_{3}S, is effectively planar, adopts an E conformation about the central C—N bond and exists in the thione form. N—H···S and C—H···O hydrogen bonds link the molecules into ribbons. Layers of ribbons are connected to adjacent layers via C—H···O interactions. The crystal is a non-merohedral twin, with the twin law describing a rotation of 180° around the [T00] direction.

**Comment**

Compounds related to the title compound, (I), with general formula ROC(=S)N(H)R', have been shown in theory to prefer the E conformation about the central C—N bond, which has substantial double-bond character (Ho et al., 2005). Such a conformation allows for the formation of an |···H—N—C|=S] synthon. In structures where there are no competing functional groups for hydrogen bonding, this synthon is invariably observed (e.g. Taylor & Tiekink, 1994; Abraham et al., 1995; Ho et al., 2003, 2005; Kuan et al., 2005; Tadiboppa & Tiekink, 2005; Jian et al., 2006). In cases where competing functionality is present, other synths are observed in the solid state (e.g. Morales et al., 2000), but with retention of the E conformation. In contrast, competing synths can force the energetically unstable Z conformation in the structures of formula ROC(=S)N(H)R', where R = Me and Et, and R' is 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl (Zhang et al., 2001), and MeOC(=S)N(H)R', where R' is 2-(2-methyl-5-nitro-1H-imidazol-1-yl) (Bernardinelli et al., 1995).

![Chemical structure of (I)](image)

Compound (I) (Fig. 1) adopts an E conformation. The molecule, including the pendant groups, is essentially planar, as seen from the torsion angle data (Table 1). The geometric data collected in Table 1 show that the molecule exists in the thione form shown in the scheme. The thioamide |···H—N—C|=S] synthon is formed between centrosymmetric molecules, N1—H1···S1' (details in Table 2). Both nitro-O atoms are involved in C—H···O interactions, the first of these occurring between C4—H4 and O2\textsuperscript{\text{a}} (Table 2).
The result of these hydrogen-bonding interactions is the formation of ribbons, as highlighted in Fig. 2. Layers of such ribbons are connected to other layers via C–H⋯O interactions involving both O2 and O3 atoms (Table 2).

Table 2
Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D⋯A–H⋯A</th>
<th>D⋯H</th>
<th>H⋯A</th>
<th>D⋯A</th>
<th>D⋯H⋯A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1⋯H1⋯S1</td>
<td>0.88</td>
<td>2.70</td>
<td>3.4435 (19)</td>
<td>142</td>
</tr>
<tr>
<td>C1⋯H4⋯O2a</td>
<td>0.95</td>
<td>2.57</td>
<td>3.481 (3)</td>
<td>162</td>
</tr>
<tr>
<td>C8⋯H4a⋯O2a</td>
<td>0.99</td>
<td>2.57</td>
<td>3.345 (3)</td>
<td>135</td>
</tr>
<tr>
<td>C3⋯H3⋯O3a</td>
<td>0.95</td>
<td>2.54</td>
<td>3.275 (3)</td>
<td>135</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) –x,–y,–z; (ii) –x+1,–y+1,–z; (iii) x,y+1,z; (iv) x,y+1,z.

All H atoms were included in the riding-model approximation, with C–H = 0.95–0.99 Å and N–H = 0.88 Å, and with Uiso(H) = 1.5Ueq(C) or 1.2Ueq(N and remaining C).

Initial indexing of the unit cell provided evidence that the crystal was a non-merohedral twin, as the predicted reflection positions fit poorly to the actual positions and a large number of reflections were poorly indexed.
not predicted by the initial indexing result. Indexing with the Twin-Solve program (Rigaku/MSC & Prekat, 2006) clearly indicated two triclinic twin components. The twin law describes a rotation of 180° around the [001] direction, given by the matrix \( \begin{pmatrix} 1 & 0 & 0 \\ 0 & -0.674 & -1 \\ 0 & -0.016 & 0 \end{pmatrix} \). Integration of the intensities produces a reflection file with three types of reflections, namely component 1, component 2, and overlaps of 1 and 2. An absorption correction based on the measurement of equivalent reflections [multi-scan: ABSCOR (Higashi, 1995)] was applied; three constrained absorption surfaces were used, based on each of the three types of reflections.

Data collection: CrystalClear (Rigaku/MSC, 2005); cell refinement: TwinSolve (Rigaku Americas Corporation & Prekat, 2006); data reduction: TwinSolve; program(s) used to solve structure: SIR92 (Altomare et al., 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXL97.

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References


