Chien Ing Yeo and Edward R.T. Tiekink*

Crystal structure of the (E)-O-methyl-N-phenylthiocarbamate – 4,4′-bipyridine (1/1), C\textsubscript{18}H\textsubscript{17}N\textsubscript{3}O\textsubscript{S}

Abstract

C\textsubscript{18}H\textsubscript{17}N\textsubscript{3}O\textsubscript{S}, monoclinic, C\textsubscript{2}/c (no. 15), a = 13.4754(3) Å, b = 13.8997(3) Å, c = 18.0300(4) Å, β = 107.202(3)°, V = 3226.03(13) Å\textsuperscript{3}, Z = 8, R\textsubscript{gt}(F) = 0.0341, wR\textsubscript{ref}(F\textsuperscript{2}) = 0.0878, T = 100(2) K.

CCDC no.: 1825491

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement

Table 1: Data collection and handling.

<table>
<thead>
<tr>
<th>Crystal:</th>
<th>Colourless plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size:</td>
<td>0.24 × 0.20 × 0.04 mm</td>
</tr>
<tr>
<td>Wavelength:</td>
<td>Cu Kα radiation (1.54184 Å)</td>
</tr>
<tr>
<td>µ:</td>
<td>18.4 cm\textsuperscript{−1}</td>
</tr>
<tr>
<td>Diffractometer, scan mode:</td>
<td>SuperNova Dual, ω scans</td>
</tr>
<tr>
<td>2θ\textsubscript{max}, completeness:</td>
<td>150°, 98.6%</td>
</tr>
<tr>
<td>N(hkl)\textsubscript{measured}, N(hkl)\textsubscript{unique}, R\textsubscript{int}:</td>
<td>6551, 3285, 0.020</td>
</tr>
<tr>
<td>Criterion for I\textsubscript{obs}, N(hkl)\textsubscript{gt}:</td>
<td>I\textsubscript{obs} &gt; 2 σ(I\textsubscript{obs}), 2972</td>
</tr>
<tr>
<td>N(param)\textsubscript{refined}:</td>
<td>213</td>
</tr>
<tr>
<td>Programs:</td>
<td>Agilent programs [1], SHELX [2, 3], ORTEP [4]</td>
</tr>
</tbody>
</table>

Source of materials

4,4′-Bipyridine (Merck; bpy; 0.05 g, 0.32 mmol) and 2.1 mol equivalent of MeOC(S)=N(H)Ph [5] (0.11 g, 0.67 mmol), each in chloroform (10 mL), were mixed and stirred at 323 K for 3 h. The resulting mixture was left for evaporation at room temperature after which colourless blocks were deposited. 

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with U\textsubscript{iso}(H) = 1.2–1.5 U\textsubscript{eq}(C). The N-bound H-atom was refined with a distance restraint of N–H = 0.88 ± 0.01 Å, and U\textsubscript{iso}(H) = 1.2 U\textsubscript{eq}(N).

Comment

In the known co-crystals of alkoxycarbamothioamides, i.e. molecules of the general formula ROC(S)=N(H)R′, for R, R′ = alkyl/aryl, with bipyridyl-type molecules, e.g. 4,4′-bipyridine (bpy), thioamide-N–H···N(pyridyl) hydrogen bonds have proven to be a reliable supramolecular synthon [6–8]. This synthon serves to link molecules in their 2:1 co-crystals, [ROC(S)=N(H)R]\textsubscript{0.5}(bipyridyl-type molecule) into three-molecule aggregates. In continuation of these studies, it was of some surprise that despite being co-crystallized

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The Figure (70% displacement ellipsoids) shows the MeOC(=S)N(H)Ph molecule in the present report with those in its pure form [5] and in its (centrosymmetric) co-crystal with trans-1,2-bis(4-pyridyl)ethylene [6] shows the MeOC(=S)N(H)Ph molecules to be also twisted with dihedral angles of 60.92(4)° and 31.40(6)°, respectively, between the least-squares planes through the CNOS and phenyl residues. The key difference between the new and literature structures is in the relative orientations of the thioamide-N—H and thione-S atoms. Indeed, the overwhelming majority of alkoxycarbothioamide molecules [9], including those functioning as coformers in co-crystals have a syn-arrangement of thioamide-N—H and thione-S atoms [6–8], there being only three exceptional structures. Thus, in MeOC(=S)N(H)(4-(C liquor(OMe))Ph) [5], owing to the dihedral angles of 70.62(3)° and 31.40(6)° leading to centroymmetric, four-molecules supramolecular aggregates.

The central CNOS chromophore in the alkoxycarbothioamide molecule is planar as is expected, but what was not expected is the anti-disposition of the thioamide-N—H and thione-S atoms. The alkoxycarbothioamide molecule is twisted with the dihedral angle between the central residue and the pendent phenyl group being 43.46(4)°.

A comparison of the MeOC(=S)N(H)Ph molecule in the present report with those in its pure form [5] and in its (centrosymmetric) co-crystal with trans-1,2-bis(4-pyridyl)ethylene [6] shows the MeOC(=S)N(H)Ph molecules to be also twisted with dihedral angles of 60.92(4)° and 31.40(6)°, respectively, between the least-squares planes through the CNOS and phenyl residues. The key difference between the new and literature structures is in the relative orientations of the thioamide-N—H and thione-S atoms. Indeed, the overwhelming majority of alkoxycarbothioamide molecules [9], including those functioning as coformers in co-crystals have a syn-arrangement of thioamide-N—H and thione-S atoms [6–8], there being only three exceptional structures. Thus, in MeOC(=S)N(H)(4-(C=0)(OMe))Ph [5], owing to the dihedral angles of 70.62(3)° and 31.40(6)° leading to centroymmetric, four-molecules supramolecular aggregates.

The molecule packing, both thione-S and pyridyl-N atoms are available for forming supramolecular aggregation via weak hydrogen bonds and it is the latter that does so. Thus, methyl-C—H···O(carbonyl) hydrogen bonding, and in each of (4-pyridyl)-CH2O(=S)N(H)Ph [10] and (cinchonan-9-y1)OC(=S)N(H)X(2,4-MeO)2Ph [11], owing to the dihedral angles of 0.92(4)° and 31.40(6)°, respectively, between the least-squares planes through the CNOS and phenyl residues. The central CNOS chromophore in the alkoxycarbothioamide molecule is planar as is expected, but what was not expected is the anti-disposition of the thioamide-N—H and thione-S atoms. The alkoxycarbothioamide molecule is twisted with the dihedral angle between the central residue and the pendent phenyl group being 43.46(4)°.

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Acknowledgements: Sunway University is thanked for support of biological and crystal engineering studies of metal thiocarbamides.


