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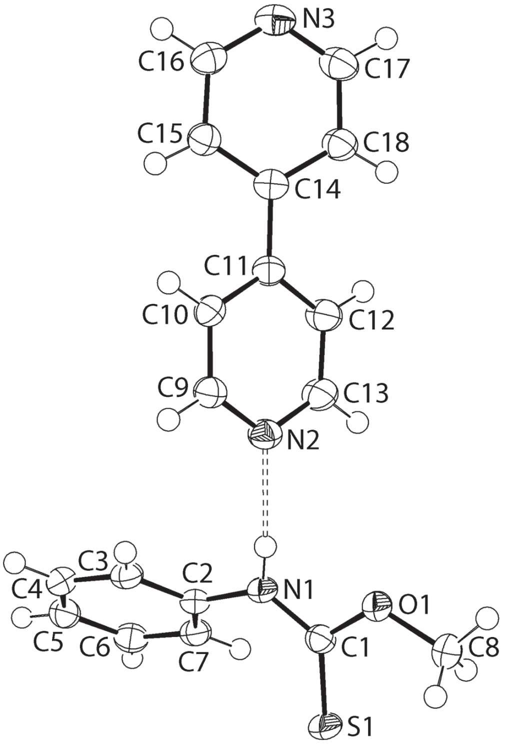
Crystal structure of the (*E*)-*O*-methyl-*N*-phenylthiocarbamate – 4,4′-bipyridine (1/1), $C_{18}H_{17}N_3OS$



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Abstract

$C_{18}H_{17}N_3OS$, monoclinic, $C2/c$ (no. 15), $a = 13.4754(3)$ Å, $b = 13.8997(3)$ Å, $c = 18.0300(4)$ Å, $\beta = 107.202(3)°$, $V = 3226.03(13)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0341$, $wR_{ref}(F^2) = 0.0878$, $T = 100(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	$0.24 \times 0.20 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	18.4 cm^{-1}
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	150°, 98.6%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6551, 3285, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2972
$N(param)_{refined}$:	213
Programs:	Agilent programs [1], SHELX [2, 3], ORTEP [4]

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. **Elem. Anal.** Calc. for $C_{18}H_{17}N_3OS$: C, 63.39; H, 5.73; N, 11.37%. Found: C, 63.12; H, 5.37; N, 11.17%. **IR** (cm^{-1}): 3178 (br) ν(N–H); 1593 (*s*) ν(C=C; bpy); 1447 (*s*) ν(C—N); 1411 (*m*) ν(C–N, bpy); 1205 (*s*) ν(C=S); 1059 (vs = very strong) ν(C—O).

Experimental details

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

Comment

In the known co-crystals of alkoxycarbothioamides, 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*]$_2$(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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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.67921(3)	1.01618(2)	0.31033(2)	0.02535(11)
O1	0.66639(8)	0.87788(7)	0.40900(5)	0.0211(2)
N1	0.65785(9)	0.82439(8)	0.29330(7)	0.0188(2)
H1N	0.6581(13)	0.7693(14)	0.3162(10)	0.024(4)*
C1	0.66688(10)	0.90365(10)	0.33706(8)	0.0186(3)
C2	0.65421(10)	0.82017(9)	0.21395(8)	0.0179(3)
C3	0.70866(11)	0.74577(10)	0.19136(8)	0.0196(3)
H3	0.7498	0.7029	0.2292	0.024*
C4	0.70268(11)	0.73438(10)	0.11340(8)	0.0215(3)
H4	0.7393	0.6834	0.0980	0.026*
C5	0.64337(11)	0.79728(10)	0.05817(8)	0.0225(3)
H5	0.6400	0.7901	0.0051	0.027*
C6	0.58893(11)	0.87097(10)	0.08097(8)	0.0220(3)
H6	0.5481	0.9138	0.0431	0.026*
C7	0.59355(10)	0.88269(10)	0.15838(8)	0.0199(3)
H7	0.5557	0.9329	0.1734	0.024*
C8	0.67688(13)	0.95279(11)	0.46615(8)	0.0265(3)
H8A	0.6668	0.9255	0.5135	0.040*
H8B	0.6246	1.0027	0.4456	0.040*
H8C	0.7464	0.9811	0.4782	0.040*
N2	0.62886(9)	0.63529(9)	0.34710(7)	0.0216(2)
N3	0.40921(9)	0.18236(9)	0.39977(7)	0.0253(3)
C9	0.67538(11)	0.55211(10)	0.33986(8)	0.0218(3)
H9	0.7391	0.5546	0.3274	0.026*
C10	0.63555(11)	0.46253(10)	0.34956(8)	0.0204(3)
H10	0.6719	0.4057	0.3441	0.025*
C11	0.54178(10)	0.45626(10)	0.36740(8)	0.0189(3)
C12	0.49238(11)	0.54286(11)	0.37386(9)	0.0252(3)
H12	0.4278	0.5426	0.3851	0.030*
C13	0.53828(11)	0.62903(10)	0.36371(9)	0.0251(3)
H13	0.5037	0.6871	0.3688	0.030*
C14	0.49654(10)	0.36184(10)	0.37897(8)	0.0193(3)
C15	0.52092(11)	0.27751(10)	0.34610(8)	0.0212(3)
H15	0.5684	0.2792	0.3163	0.025*
C16	0.47558(11)	0.19112(10)	0.35717(8)	0.0237(3)
H16	0.4924	0.1350	0.3333	0.028*
C17	0.38787(12)	0.26308(11)	0.43226(9)	0.0270(3)
H17	0.3422	0.2587	0.4635	0.032*
C18	0.42801(11)	0.35302(11)	0.42343(9)	0.0242(3)
H18	0.4090	0.4080	0.4474	0.029*

under analogous conditions as for previous experiments [6–8], the title 1:1 co-crystal, [MeOC(=S)N(H)Ph]$_2$(bpy), was isolated instead of the anticipated 2:1 co-crystal.

The Figure (70% displacement ellipsoids) shows the asymmetric unit, comprising one full molecule each of MeOC(=S)N(H)Ph and bpy, linked by a thioamide-N—H···N(pyridyl) hydrogen bond. The bpy molecule is significantly twisted as seen in the dihedral angle of 24.36(7)° between the pyridyl rings. 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(=O)Me)Ph) [5], owing to the dictates of thioamide-N–H···O(carbonyl) hydrogen bonding, and in each of (4-pyridyl)-CH$_2$OC(=S)N(H)Ph [10] and (cinchonan-9-yl)OC(=S)N(H)(2,4-MeO)$_2$Ph [11], owing to the dictates of thioamide-N—H···N(pyridyl) hydrogen bonding, anti-dispositions of the thioamide-N–H and thione-S atoms are observed. Calculations [5], showed the energy differences between *syn*- and anti-conformations in these molecules differed by as little as 4–8 kJ mol^{-1}. Thus, the surprising observation is the predominance of the *syn*-conformation.

In the molecular 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···N(pyridyl) contacts are noted [C8—H8a···N3^i = 2.59 Å and 159° for $1-x$, $1-y$, $1-z$] leading to centrosymmeric, four-molecule supramolecular aggregates in the crystal.

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