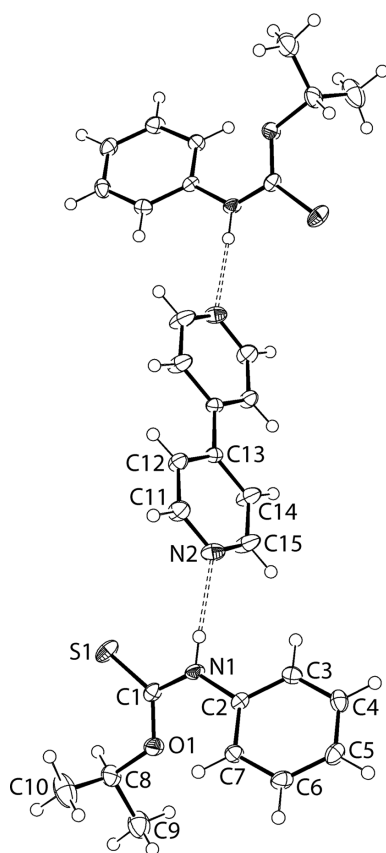


Chien Ing Yeo and Edward R.T. Tiekink*

Crystal structure of the co-crystal *O*-isopropyl phenylcarbamothioate – 4,4'-bipyridine (2/1), $C_{15}H_{17}N_2OS$

**Table 1:** Data collection and handling.

Crystal:	Block, colourless
Size:	0.10 × 0.05 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.22 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
θ_{\max} , completeness:	27.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5109, 3354, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2762
$N(\text{param})_{\text{refined}}$:	178
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

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

Source of material

4,4'-Bipyridine (Merck; bpy; 0.05 g, 0.32 mmol) and 2.1 mole equivalent of *i*-PrOC(=S)N(H)Ph [5] (0.11 g, 0.67 mmol), each in dichloromethane (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. Anal. Calc. for $C_{15}H_{17}N_2OS$: C, 65.90; H, 6.27; N, 10.25. Found: C, 63.28; H, 6.66; N, 10.24. IR (cm⁻¹): 3164 (br) ν (N–H); 1593 (s) ν (C=C; bpy); 1448 (s) ν (C–N); 1393 (s) ν (C–N, bpy); 1204 (s) ν (C=S); 1087 (vs) ν (C–O).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The N-bound H-atom was located in difference Fourier map but refined with a distance restraint of N–H = 0.88 ± 0.01 Å, and with $U_{\text{iso}}(\text{H})$ set to 1.2 $U_{\text{equiv}}(\text{N})$.

Discussion

The alkoxy-carbothioamides, i.e. molecules of the general formula ROC(=S)N(H)R' for R, R' = alkyl/aryl [6], find interest in crystal engineering endeavours in terms of their ability to form thioamide-N–H...S(thione) hydrogen bonds and the

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Abstract

$C_{15}H_{17}N_2OS$, triclinic, $P\bar{1}$ (no. 2), $a = 5.8595(3)$ Å, $b = 9.2967(4)$ Å, $c = 14.0545(8)$ Å, $\alpha = 83.320(4)$, $\beta = 89.240(4)$, $\gamma = 74.524(4)$, $V = 732.71(7)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0458$, $wR_{\text{ref}}(F^2) = 0.1231$, $T = 100$ K.

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Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my

Chien Ing Yeo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
S1	0.82329(9)	−0.06274(5)	0.19555(4)	0.02853(15)
O1	0.5643(2)	0.20073(14)	0.10848(10)	0.0257(3)
N1	0.4505(3)	0.13231(16)	0.25485(11)	0.0196(3)
H1N	0.456(4)	0.065(3)	0.3029(17)	0.028(6)*
C2	0.2515(3)	0.25973(18)	0.25604(12)	0.0167(3)
C3	0.0502(3)	0.23730(19)	0.30264(13)	0.0202(4)
H3	0.0485	0.1394	0.3304	0.024*
C4	−0.1482(3)	0.3574(2)	0.30864(13)	0.0232(4)
H4	−0.2847	0.3413	0.3406	0.028*
C5	−0.1476(3)	0.5007(2)	0.26827(13)	0.0244(4)
H5	−0.2834	0.5828	0.2720	0.029*
C6	0.0533(3)	0.5226(2)	0.22247(14)	0.0241(4)
H6	0.0539	0.6207	0.1947	0.029*
C7	0.2542(3)	0.40392(18)	0.21635(13)	0.0197(4)
H7	0.3915	0.4209	0.1855	0.024*
C1	0.6066(3)	0.09765(18)	0.18471(13)	0.0195(4)
C8	0.7202(3)	0.1838(2)	0.02449(14)	0.0279(4)
H8	0.7873	0.0747	0.0178	0.034*
C9	0.5605(4)	0.2597(3)	−0.06113(16)	0.0412(6)
H9A	0.4302	0.2126	−0.0643	0.062*
H9B	0.6521	0.2489	−0.1200	0.062*
H9C	0.4959	0.3666	−0.0544	0.062*
C10	0.9150(4)	0.2537(3)	0.03901(17)	0.0477(6)
H10A	1.0055	0.2036	0.0973	0.072*
H10B	0.8484	0.3605	0.0455	0.072*
H10C	1.0198	0.2432	−0.0161	0.072*
N2	0.4473(3)	−0.11967(17)	0.40417(12)	0.0265(4)
C11	0.6235(3)	−0.1965(2)	0.46444(15)	0.0271(4)
H11	0.7364	−0.1469	0.4818	0.033*
C12	0.6514(3)	−0.34441(19)	0.50318(14)	0.0230(4)
H12	0.7810	−0.3935	0.5455	0.028*
C13	0.4892(3)	−0.42063(17)	0.47995(12)	0.0171(3)
C14	0.3044(4)	−0.3405(2)	0.41794(16)	0.0315(5)
H14	0.1872	−0.3864	0.4001	0.038*
C15	0.2921(4)	−0.1928(2)	0.38220(16)	0.0346(5)
H15	0.1649	−0.1408	0.3394	0.042*

influence of this upon molecular conformation [5–7] as well as their propensity to form co-crystals [8]. As a continuation of the latter studies, the title 2:1 co-crystal was isolated.

As indicated from the figure (50% displacement ellipsoids), there is a thioamide-N—H···S(thione) hydrogen bond connecting the co-crystal cofomers [N1—H···S1 = 2.11(3) Å and 170(2)°]. The strictly planar 4,4'-bipyridyl molecule is situated about a centre of inversion with the unlabelled atoms of the figure related by the symmetry operation: 1−x, −1−y, 1−z. The three-molecule aggregate resembles that observed in the previously reported 2:1 co-crystal of the title carbothioamide with trans-1,2-bis(4-pyridyl)ethene [8]. Indeed, all known co-crystals of this type,

i.e. [ROC(=S)N(H)R']₂(bipyridyl)-type molecule), six in all, feature a similarly assembled three-molecule aggregate [8]. The *syn* disposition of the thioamide-N—H and thione-S atoms is consistent with that observed in the three other known structures containing the identical i-PrOC(=S)N(H)Ph molecule. An overlap diagram (not shown) of the molecule reported herein, the parent compound [5], the molecule in the 2:1 co-crystal with trans-1,2-bis(4-pyridyl)ethene [8] and that with the thione-S coordinating a (Ph₃P)₂CuCl entity [9] shows a remarkable consistency of conformation. The major difference arises, in fact, for the *i*-Pr group in the title compound which is rotated about the O—C axis by approximately 60° compared to the three literature molecules. The dihedral angles between the central CNOS residue and appended N-bound phenyl ring vary from approximately 28° in the copper(I) complex [9] to 47° in the co-crystal [8].

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