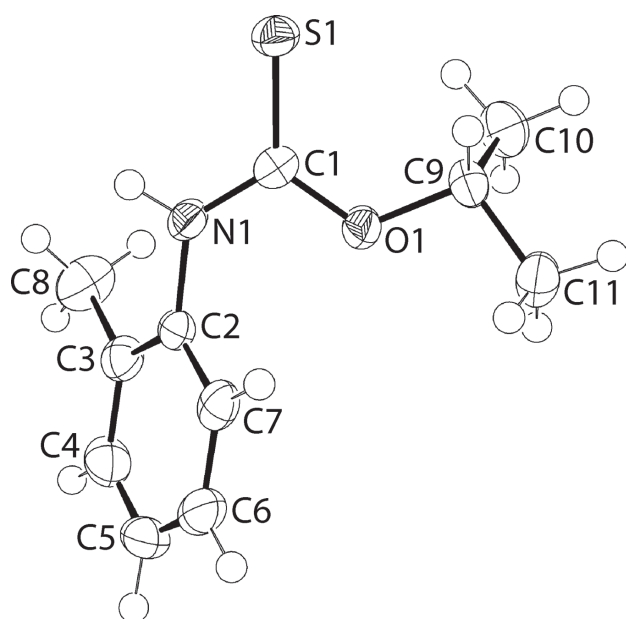


Chien Ing Yeo and Edward R.T. Tiekink*

Crystal structure of *N*-(2-methylphenyl)(propan-2-yloxy)carbothioamide, C₁₁H₁₅NOS

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

| | |
|--|--|
| Crystal: | Colourless block |
| Size: | 0.27 × 0.11 × 0.11 mm |
| Wavelength: | Mo K α radiation (0.71073 Å) |
| μ : | 0.25 mm ⁻¹ |
| Diffractometer, scan mode: | Bruker SMART APEX, ω |
| θ_{\max} , completeness: | 27.5°, >99% |
| $N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} : | 10515, 2649, 0.058 |
| Criterion for I_{obs} , $N(hkl)_{\text{gt}}$: | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2186 |
| $N(\text{param})_{\text{refined}}$: | 133 |
| Programs: | Bruker [1], SHELX [2–4], WinGX/ORTEP [5] |

Source of material

All chemicals and solvents were used as purchased without purification. All reactions were carried out under ambient conditions. The melting point was determined on a Krüss KSP1N melting point meter. The IR spectrum was obtained on a Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR spectrophotometer from 4000 to 400 cm⁻¹; abbreviation: s, strong. Elemental analyses were performed on a Perkin Elmer PE 2400 CHN Elemental Analyser.

o-Tolyl isothiocyanate (Sigma Aldrich; 2.5 mmol, 0.33 mL) was added to NaOH (Merck; 2.5 mmol, 0.10 g) in *i*PrOH (Merck; 5 mL) and the mixture was left stirring at room temperature for 2 h, followed by the addition of excess 5 M HCl solution. The resulting mixture was stirred for another 1.5 h. The final product was extracted with chloroform (Merck; 20 mL) and left for evaporation at room temperature, yielding colourless crystal after 4 weeks. *M*.pt: 323–324 K. IR (cm⁻¹): 3208 (s) ν (N–H), 1459 (s) ν (C–N), 1204 (s) (C=S), 1094 (s) ν (C–O). Anal. Calc. for C₁₁H₁₅NOS: C, 63.12; H, 7.22; N, 6.69%. Found: C, 63.15; H, 7.42; N, 6.92%.

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Abstract

C₁₁H₁₅NOS, monoclinic, $P2_1/n$ (no. 14), $a = 7.3979(4)$ Å, $b = 8.5384(4)$ Å, $c = 18.2771(10)$ Å, $\beta = 90.999(3)^\circ$, $V = 1154.32(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0409$, $wR_{\text{ref}}(F^2) = 0.1093$, $T = 100(2)$ K.

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The title 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.

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, Bandar Sunway 47500, 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, Bandar Sunway 47500, Selangor Darul Ehsan, Malaysia

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2–1.5U_{\text{eq}}(\text{C})$. The N-bound H-atom was located in a 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 $U_{\text{equiv}}(\text{N})$.

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

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{iso} [*] / <i>U</i> _{eq} |
|------|-------------|-------------|-------------|---|
| S1 | 0.31646(5) | 0.92776(5) | 1.08505(2) | 0.02241(14) |
| O1 | 0.08168(14) | 0.74832(13) | 1.00997(6) | 0.0207(3) |
| N1 | 0.30848(17) | 0.84343(16) | 0.94626(7) | 0.0204(3) |
| H1N | 0.4082(17) | 0.8953(19) | 0.9436(10) | 0.025* |
| C1 | 0.23022(19) | 0.83559(18) | 1.01114(8) | 0.0184(3) |
| C2 | 0.2401(2) | 0.78416(18) | 0.87761(8) | 0.0183(3) |
| C3 | 0.3557(2) | 0.69622(19) | 0.83442(9) | 0.0233(4) |
| C4 | 0.2909(3) | 0.6479(2) | 0.76591(10) | 0.0311(4) |
| H4 | 0.3679 | 0.5893 | 0.7351 | 0.037* |
| C5 | 0.1177(3) | 0.6831(2) | 0.74184(9) | 0.0340(4) |
| H5 | 0.0767 | 0.6491 | 0.6949 | 0.041* |
| C6 | 0.0044(2) | 0.7679(2) | 0.78616(10) | 0.0312(4) |
| H6 | -0.1154 | 0.7909 | 0.7700 | 0.037* |
| C7 | 0.0651(2) | 0.81951(19) | 0.85417(9) | 0.0228(3) |
| H7 | -0.0123 | 0.8787 | 0.8845 | 0.027* |
| C8 | 0.5424(2) | 0.6509(2) | 0.86049(11) | 0.0352(4) |
| H8A | 0.5997 | 0.5855 | 0.8234 | 0.053* |
| H8B | 0.5343 | 0.5922 | 0.9064 | 0.053* |
| H8C | 0.6149 | 0.7456 | 0.8687 | 0.053* |
| C9 | -0.0271(2) | 0.73030(19) | 1.07634(8) | 0.0209(3) |
| H9 | -0.0288 | 0.8313 | 1.1040 | 0.025* |
| C10 | 0.0529(2) | 0.6032(2) | 1.12380(10) | 0.0303(4) |
| H10A | 0.1774 | 0.6310 | 1.1377 | 0.045* |
| H10B | 0.0527 | 0.5042 | 1.0967 | 0.045* |
| H10C | -0.0192 | 0.5916 | 1.1680 | 0.045* |
| C11 | -0.2154(2) | 0.6921(2) | 1.04822(10) | 0.0287(4) |
| H11A | -0.2581 | 0.7762 | 1.0158 | 0.043* |
| H11B | -0.2970 | 0.6821 | 1.0896 | 0.043* |
| H11C | -0.2129 | 0.5932 | 1.0210 | 0.043* |

Comment

The title compound was investigated as part of continuing and systematic crystal chemical studies of alkoxy-carbothioamides [6–9], *i.e.* molecules of the general formula ROC(=S)N(H)R' (*R/R'* = alkyl and/or aryl). Continued synthesis of these molecules is also motivated by the exciting biological activity exhibited by their phosphanegold(I) derivatives, *e.g.* as anti-microbial [10] and anti-cancer [11] agents, and the observed dependence of biological potential upon the nature of *R* and *R'*. In the present communication, the crystal and molecular structures of the title compound, *iPrOC(=S)N(H)C₆H₄Me-2*, are described.

The molecular structure is shown in the figure (70% displacement ellipsoids) and features the normally observed [6–9] *syn*-disposition of the thione-S and thioamide-N–H atoms. The central residue is strictly planar with the [r.m.s. deviation of the S1, O1, N1, C1 atoms = 0.0011 Å] and forms a dihedral angle of 53.63(4)° with the appended 2-tolyl group. The key geometric parameters are C1–S1 = 1.6796(15) Å, C1–O1 = 1.3275(18) Å,

C1–N1 = 1.330(2) Å, S1–C1–O1 = 125.35(11)°, S1–C1–N1 = 121.88(12)° and O1–C1–N1 = 112.77(13)°. These follow the expected trends [6–9].

The molecular packing features thioamide-N–H···S(thione) hydrogen bonds [N1–H1n···S1ⁱ: H1n···S1ⁱ = 2.597(14) Å, N1···S1ⁱ = 3.4494(14) Å with angle at H1n = 170.0(15)° for symmetry operation (i) 1 – *x*, 2 – *y*, 2 – *z*] between centrosymmetrically related molecules to generate an eight-membered {···HNCS}₂ synthon. Globally, the dimeric aggregates thus formed stack in columns along the *a*-axis. The connections between the columns leading to a three-dimensional architecture are of the type tolyl-C–H···S(thione) [C5–H5···S1ⁱⁱ: H5···S1ⁱⁱ = 2.83 Å, C5···S1ⁱⁱ = 3.7218(19) Å with angle at H5 = 156°; C7–H7···S1ⁱⁱⁱ: H7···S1ⁱⁱⁱ = 2.85 Å, C7···S1ⁱⁱⁱ = 3.7374(16) Å with angle at H7 = 155°, for symmetry operations: (ii) -1/2 + *x*, 3/2 – *y*, -1/2 + *z*; (iii) – *x*, 2 – *y*, 2 – *z*].

The present structure determination completes the series of structures of general formula ROC(=S)N(H)C₆H₄Me-2, *i.e.* for *R* = Me [12] and Et [13]. While not isostructural, the three structures exhibit the same trends in geometric parameters and in their respective crystals, the formation of eight-membered {···HNCS}₂ synthons mediated by thioamide-N–H···S(thione) hydrogen bonds.

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