Crystal Structure of *a*-Phenyl-N-thioacetylmorpholine

İ. ÇELİK,*¹ M. AKKURT*², İ. DEMİRTAŞ,*³ R. ERENLER,*³ and K. GÜVEN*⁴

*¹ Department of Physics, Faculty of Arts and Sciences, Cumhuriyet University, 58140 Sivas, Turkey

*² Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey

*³ Department of Chemistry, Faculty of Arts and Sciences, Gaziosmanpaşa University, 60240 Tokat, Turkey

*⁴ Department of Physics, Faculty of Arts and Sciences, Kırıkkale University, Yahşıhan, 71450 Kırıkkale, Turkey

The title compound, C₁₂H₁₅NOS, consists of a thioamid and an α -substituted phenyl group. It crystallizes in the monoclinic space group *P*2₁/*c*. The unit-cell parameters at 293 K are *a* = 6.553(5), *b* = 23.362(5), *c* = 8.201(5) Å, β = 112.532(5)°, *V* = 1159.7(12) Å³, *D*_x = 1.268 g/cm³, *Z* = 4. The morpholine group takes a chair conformation.

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Thioamides are versatile compounds that have found wide applications in the synthesis of industrial and fine chemical products.¹ They are used as vulcanization accelerators, additives to lubricating oils, corrosion inhibitors, flotation agents, insecticides and fungicides, preservatives, and intermediates for preparation of certain vitamins (*e.g.* B₁) and other pharmaceutical products.² Thioamides have also attracted attention in peptide chemistry.³ Particularly, α -substituted thioacetamides are useful synthetic intermediates and would provide an alternative route to aryl propionic acids used in the synthesis of non-steroidal anti-inflammatory and analgesic drugs. Aryl and aryl alkyl thioamides and their corresponding carboxylic acids are useful organic compounds and are used as biologically active compounds such as pesticides⁴ or antiulcer agents.⁵

We therefore carried out the Willgerodt-Kindler reaction of acetophenone with sulfur and morpholine in reflux temperature. In this study, the crystal structure of the title compound was determined by X-ray analysis.

A mixture of ketone (1.5 g, 12.5 mmol), sulfur (0.5 g, 15.6 mmol), and morpholine (1.22 g, 14 mmol, 1.22 ml) in a Pyrex glass was refluxed for 5 h. The reaction was monitored with TLC. After cooling, the reaction product **4** was purified with silica gel chromatography by eluting with hexane-ethyl acetate (8:2) to give a colorless solid (2 g, 72%). M.p. 352 – 353 K. Analysis calculated for C₁₂H₁₅NOS: C 65.19, H 6.79, N 6.32 %; found: C 65.10, H 6.85, N 6.35%.

A summary of the crystallographic information is given in Table 1. The data were collected on a Rigaku AFC-7S diffractometer using graphite-monochromated Mo *K*_α radiation with the $\omega/2\theta$ scan mode. The collected data were reduced by

using the MSC/AFC Diffractometer Control Software and empirical absorption correction was carried out by using the TEXSAN program.⁶ The title compound was solved by direct methods and refined by full-matrix least-squares method on *F*². All H atoms were located geometrically, at distances of 0.93(CH) and 0.97(CH₂) from the parent atoms. They were refined by using a riding model and the *U*_{iso} values were constrained to be 1.2 times *U*_{eq} of the parent atom. The final conventional *R*(*F*) = 0.0450 and *wR*(*F*²) = 0.1263 or *I* ≥ 2 σ (*I*) with weighting scheme, *w* = 1/[$\sigma^2(F_o^2)$ + (0.0868*P*)² + 0.3367*P*]. The atomic coordinates and equivalent isotropic displacement parameters with estimated standard deviations for the other atoms except H are listed in Table 2. An ORTEP drawing of the title compound with atom numbering is shown in Fig. 2. X-ray results for geometrical parameters are given in Table 3.

The structure analysis of the title compound has revealed that the morpholine group takes a chair conformation with high stability [Puckering parameters: *Q* = 0.5483 Å, θ = 1.72° and ϕ

Fig. 1 Chemical diagram of the analyzed compound.

Table 1 Crystal and experimental data

Formula: C ₁₂ H ₁₅ NOS
Formula weight = 221.32
Crystal system: monoclinic
Space group: <i>P</i> 2 ₁ / <i>c</i> <i>Z</i> = 4
<i>a</i> = 6.553(5) Å
<i>b</i> = 23.362(5) Å
<i>c</i> = 8.201(5) Å
<i>V</i> = 1159.7(12) Å ³
<i>D</i> _x = 1.268 g/cm ³
No. of reflections used = 1877
2 θ _{max} = 59.96° with Mo <i>K</i> _α
<i>R</i> = 0.0450
(Δ <i>σ</i>) _{max} = 0.00
($\Delta\rho$) _{max} = 0.20 e Å ⁻³
($\Delta\rho$) _{min} = -0.36 e Å ⁻³
Measurement: Rigaku AFC-7S diffractometer
Program system: MSC/AFC Diffractometer control software
Structure determination: direct methods (SIR-97)
Refinement: full matrix least squares (SHELXL-97)

Fig. 2 An ORTEP view of the title molecule, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Fig. 3 A view of ORTEP the packing and the hydrogen contacts of the title molecule.

$= 1.2159^\circ$].⁷ The bond lengths and angles of the title compound are in good agreement with those in the literature. The six atoms of S1, N1, C7, C8, C9 and C12 form a plane with the maximum deviations of 0.008(3) Å for the C12 atom and of -0.008(3) Å for the C7 atom.

There are one C-H...O type-intermolecular contact and one C-H...S type-intramolecular hydrogen contact in the crystal structure of the title compound (Fig. 3 and Table 4). The crystal is not packed only by the inter-molecular hydrogen contact but also by non-parallel stacking of phenyl rings, as can be seen from Fig. 3. The angle between H...S-C is almost perpendicular; the very short C-H...S contact might be connected with the conjugation between S = C bond and N atom.

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Table 2 Atomic coordinates and temperature factors

Atom	x	y	z	$U_{eq}[\text{\AA}^2]$
S1	0.67469(14)	0.06145(3)	-0.16094(12)	0.0628(3)
O1	1.0104(4)	0.08766(10)	0.5141(3)	0.0659(7)
N1	0.6995(3)	0.06459(9)	0.1679(3)	0.0468(6)
C1	0.3483(4)	0.16227(11)	-0.0055(4)	0.0501(7)
C2	0.5300(5)	0.19829(11)	0.0405(5)	0.0603(9)
C3	0.5151(7)	0.25481(13)	0.0823(6)	0.0758(13)
C4	0.3185(8)	0.27642(17)	0.0773(7)	0.0922(15)
C5	0.1377(7)	0.2412(2)	0.0319(8)	0.106(2)
C6	0.1520(5)	0.18491(16)	-0.0068(6)	0.0766(13)
C7	0.3530(4)	0.10048(11)	-0.0554(4)	0.0527(8)
C8	0.5830(4)	0.07522(9)	-0.0050(4)	0.0428(7)
C9	0.9235(4)	0.03969(12)	0.2345(4)	0.0575(9)
C10	1.0805(5)	0.07808(15)	0.3770(5)	0.0666(10)
C11	0.7963(5)	0.11344(13)	0.4486(4)	0.0593(9)
C12	0.6269(4)	0.07643(12)	0.3083(4)	0.0526(9)

$U_{eq} = 1/3$ of the trace of the orthogonalized U tensor

Table 3 Selected bond distances (Å) and angles (°)

S1 - C8	1.640(3)	C1 - C7	1.504(4)
O1 - C10	1.386(5)	C2 - C3	1.377(4)
O1 - C11	1.429(4)	C3 - C4	1.370(7)
N1 - C8	1.351(4)	C4 - C5	1.372(7)
N1 - C9	1.475(4)	C5 - C6	1.364(6)
N1 - C12	1.431(4)	C7 - C8	1.521(4)
C1 - C2	1.387(4)	C9 - C10	1.519(5)
C1 - C6	1.387(5)	C11 - C12	1.525(4)
C10 - O1 - C11	110.2(2)	C4 - C5 - C6	120.8(5)
C8 - N1 - C9	122.9(2)	C1 - C6 - C5	120.8(4)
C8 - N1 - C12	125.5(2)	C1 - C7 - C8	114.8(2)
C9 - N1 - C12	111.6(2)	S1 - C8 - N1	123.6(2)
C2 - C1 - C6	117.9(3)	S1 - C8 - C7	119.0(2)
C2 - C1 - C7	123.5(3)	N1 - C8 - C7	117.3(2)
C6 - C1 - C7	118.7(3)	N1 - C9 - C10	109.7(2)
C1 - C2 - C3	120.9(3)	O1 - C10 - C9	112.5(3)
C2 - C3 - C4	120.1(4)	O1 - C11 - C12	111.8(2)
C3 - C4 - C5	119.5(4)	N1 - C12 - C11	110.3(2)

Table 4 Hydrogen-bond geometry (Å, °)

C7...H7A...O1 ⁱ	0.97	2.44	3.394(5)	168.
C9...H9A...S1	0.97	2.56	3.063(4)	112.

Symmetry operators: (i) $-1 + x, y, -1 + z$.

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