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MOLECULAR AND CRYSTAL STRUCTURE OF 5-BENZOYL-3-CYANO-2-ETHYLTHIO-6-TRIFLUOROMETHYLPYRIDINE*

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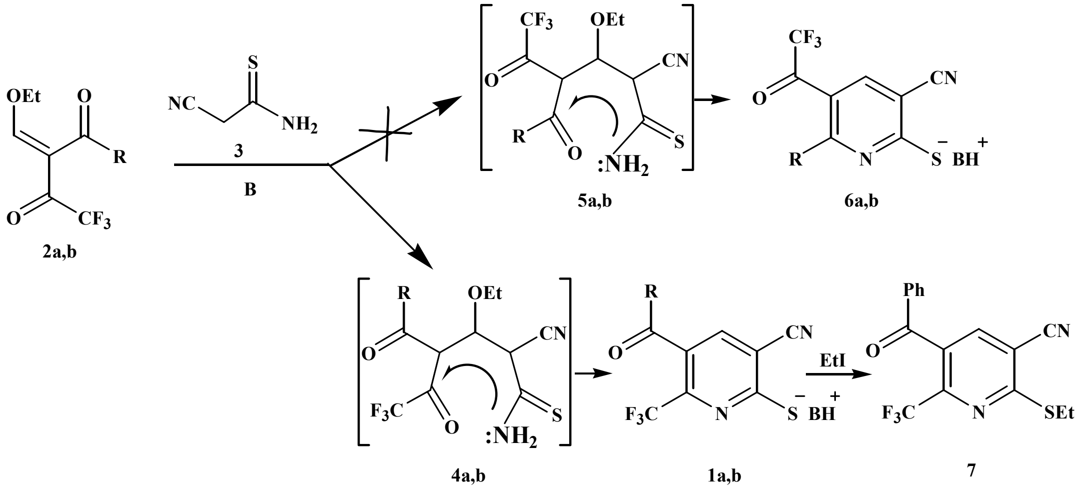
An X-ray diffraction structural analysis on 5-benzoyl-3-cyano-2-ethylthio-6-trifluoromethylpyridine was carried out to establish the regioselectivity of the reactions of ethoxymethylene derivatives of 1-aryl- and 1-hetaryl-3-trifluoromethyl-1,3-diketones with cyanothioacetamide and the alkylation pathway of the pyridinethiones obtained.

Keywords: 5-benzoyl-3-cyano-2-ethylthio-6-trifluoromethylpyridine, X-ray diffraction structural analysis.

In previous work [1], we have already reported the synthesis of N-methylmorpholinium 5-benzoyl-3-cyano-6-trifluoromethylpyridine-2-thiolate (**1a**) and N-methylmorpholinium 3-cyano-5-thenoyl-6-trifluoromethylpyridine-2-thiolate (**1b**) by the reaction of ethoxymethylene derivatives of benzoyltrifluoroacetone (**2a**) and thenoyltrifluoroacetone (**2b**) with cyanothioacetamide (**3**), proceeding through formation of adduct **4**, and cyclization of **4**, leading to thiolates **1a** and **1b**.



1, 2, 4–6 a R = Ph, **b** R = 2-thienyl; B = N-methylmorpholyl

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Since the formation of adduct **5**, which is isomeric to **4**, may occur during the reaction and, as a consequence, formation of salts **6a** and **6b**, unequivocal distinction between **1a, 1b** and **6a, 6b** by IR and ^{1}H NMR spectroscopy was impossible. An X-ray diffraction study was carried out on 5-benzoyl-3-cyano-2-ethylthio-6-trifluoromethylpyridine (**7**) (Figs. 1 and 2) obtained in the reaction of thiolate **1a** with ethyl iodide [1] in order to elucidate the regioselectivity of the reaction studied, the three-dimensional structure of the compounds obtained, and the pathways for the alkylation of these compounds.

The major geometric parameters of compound **7** are given in Table 1. The pyridine ring in **7** is planar to within ±0.023 Å. As a consequence of the steric conditions, $S_{(1)}$ and $C_{(7)}$ extrude from this ring by 0.084 and -0.083 Å, respectively, while $C_{(6)}$ and $C_{(8)}$ extrude from this ring by only -0.005 and 0.011 Å, respectively.

The $C_{(4)}C_{(5)}C_{(7)}$ bond angle (123.4(3)°) is much larger than the $N_{(1)}C_{(4)}C_{(7)}$ bond angle (112.8(3)°) due to intramolecular non-bonding interactions; the $F_{(2A)}\cdots C_{(8)}$ and $F_{(2A)}\cdots C_{(9)}$ contacts (3.047 Å) are much shorter than the sum of the van der Waals radii [2]. We should note that the $C_{(8)}$–$C_{(9)}$ bond (1.477(5) Å) is somewhat shorter than the $C_{(8)}$–$C_{(4)}$ bond (1.511(5) Å), probably due to different orientation of the π-system of the $C_{(8)}$=$O_{(1)}$ double bond relative to the benzene and pyridine aromatic rings. The $C_{(3)}C_{(4)}C_{(8)}O_{(1)}$ torsion angle is 63.1(4)°, while the

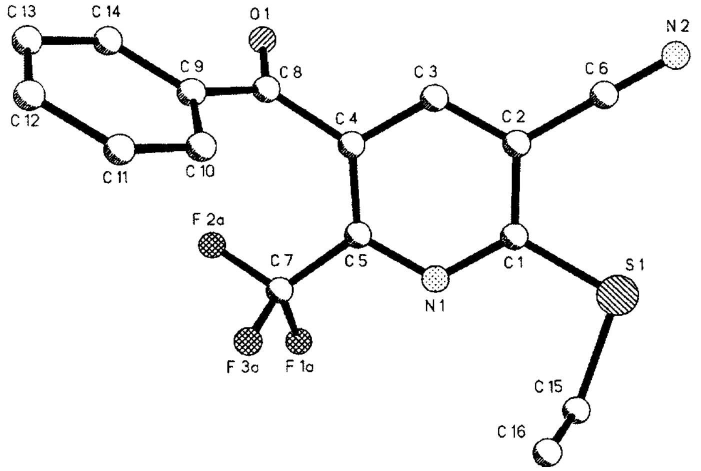

Fig. 1. General view of a molecule of compound **7**.

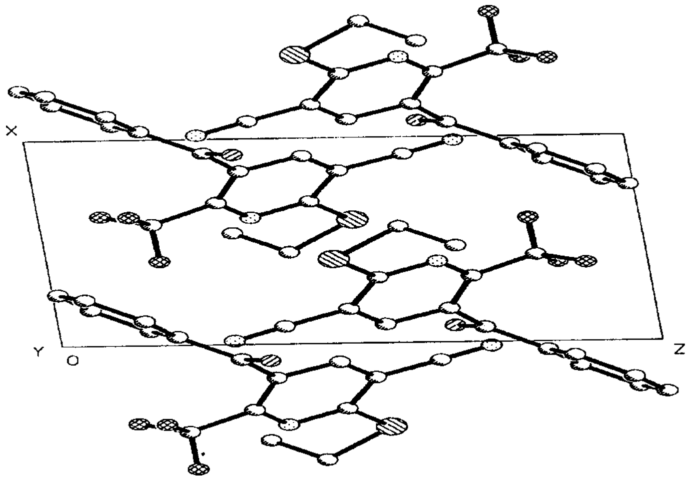

Fig. 2. Projection of the crystal structure of compound **7**.

TABLE 1. Bond Lengths (*d*) and Bond Angles (ω) in Molecule of Compound **7**

Bond	*d*, Å	Angle	ω, deg.
$S_{(1)}$–$C_{(1)}$	1.748(3)	$C_{(1)}S_{(1)}C_{(15)}$	101.8(2)
$S_{(1)}$–$C_{(15)}$	1.809(4)	$C_{(5)}N_{(1)}C_{(1)}$	119.2(3)
$O_{(1)}$–$C_{(8)}$	1.210(4)	$N_{(1)}C_{(5)}C_{(4)}$	123.9(3)
$N_{(1)}$–$C_{(5)}$	1.335(4)	$N_{(1)}C_{(5)}C_{(7)}$	112.8(3)
$N_{(1)}$–$C_{(1)}$	1.333(4)	$C_{(4)}C_{(5)}C_{(7)}$	123.4(3)
$N_{(2)}$–$C_{(6)}$	1.141(4)	$C_{(5)}C_{(4)}C_{(3)}$	116.5(3)
$C_{(3)}$–$C_{(2)}$	1.379(5)	$C_{(5)}C_{(4)}C_{(8)}$	127.2(3)
$C_{(2)}$–$C_{(1)}$	1.397(5)	$C_{(3)}C_{(4)}C_{(8)}$	116.2(3)
$C_{(4)}$–$C_{(3)}$	1.393(5)	$C_{(2)}C_{(3)}C_{(4)}$	120.2(3)
$C_{(5)}$–$C_{(4)}$	1.384(5)	$C_{(3)}C_{(2)}C_{(1)}$	119.0(3)
$C_{(5)}$–$C_{(7)}$	1.493(5)	$C_{(3)}C_{(2)}C_{(6)}$	119.9(3)
$C_{(4)}$–$C_{(8)}$	1.511(5)	$C_{(1)}C_{(2)}C_{(6)}$	121.1(3)
$C_{(2)}$–$C_{(6)}$	1.434(5)	$N_{(1)}C_{(1)}C_{(2)}$	121.0(3)
$C_{(8)}$–$C_{(9)}$	1.477(5)	$N_{(1)}C_{(1)}S_{(1)}$	119.4(2)
		$C_{(2)}C_{(1)}S_{(1)}$	119.6(3)
		$N_{(2)}C_{(6)}C_{(2)}$	178.4(4)
		$C_{(9)}C_{(8)}C_{(4)}$	119.6(3)

$C_{(14)}C_{(9)}C_{(8)}O_{(1)}$ torsion angle is only 8.3(5)°. The geometric parameters of the $C_{(1)}$–$S_{(1)}$–$C_{(15)}$ group ($S_{(1)}$–$C_{(15)}$, 1.809(4); $S_{(1)}$–$C_{(1)}$, 1.748(3) Å; $C_{(1)}S_{(1)}C_{(15)}$, 101.8(2)°) are ordinary. Thus, for example, the S–C(Me) (1.803(4) Å) and S–C(Ph) bond lengths (1.749(4) Å) in methyl phenyl sulfide agree within experimental error with the corresponding values found for compound **7**. There are no short intermolecular contacts in the crystal of **7**.

TABLE 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Parameters U_{eq} (Å$\times 10^3$) in the Structure of compound **7**

Atom	*x*	*y*	*z*	$U_{(eq)}$
$S_{(1)}$	4043(1)	7198(1)	4783(1)	59(1)
$F_{(1A)}$	5979(3)	5169(4)	8136(2)	99(1)
$F_{(2A)}$	3821(4)	3070(3)	8510(2)	104(1)
$F_{(3A)}$	3775(4)	5318(4)	8974(2)	115(1)
$O_{(1)}$	790(4)	116(3)	6596(2)	73(1)
$N_{(1)}$	3890(4)	5524(3)	6490(2)	49(1)
$N_{(2)}$	178(5)	4017(4)	2868(3)	71(1)
$C_{(5)}$	3152(4)	4235(4)	7014(3)	47(1)
$C_{(4)}$	1613(4)	2837(4)	6546(3)	44(1)
$C_{(3)}$	883(5)	2779(4)	5436(3)	48(1)
$C_{(2)}$	1634(4)	4099(4)	4882(3)	45(1)
$C_{(1)}$	3130(4)	5489(4)	5451(3)	46(1)
$C_{(6)}$	839(5)	4048(4)	3754(3)	53(1)
$C_{(7)}$	4184(5)	4449(5)	8155(3)	58(1)
$C_{(8)}$	702(5)	1325(4)	7075(3)	52(1)
$C_{(9)}$	-394(5)	1330(4)	8071(3)	52(1)
$C_{(10)}$	-676(5)	2666(5)	8504(3)	68(1)
$C_{(11)}$	-1729(7)	2608(7)	9426(4)	94(2)
$C_{(12)}$	-2454(7)	1254(10)	9916(4)	108(2)
$C_{(13)}$	-2198(7)	-60(8)	9490(5)	98(2)
$C_{(14)}$	-1159(6)	-59(5)	8565(4)	73(1)
$C_{(15)}$	5599(5)	8705(4)	5948(3)	61(1)
$C_{(16)}$	4635(6)	9308(5)	6840(4)	71(1)

EXPERIMENTAL

The X-ray diffraction structural analysis of a monocrystal of compound **7** was carried out at room temperature on an Enraf-Nonius CAD-4 automatic four-circle diffractometer using λMoKα radiation and graphite monochromator. The $\omega/2\theta$ scan rate ratio was 1.2, θmax = 22.5°, sphere segment $0 \leq h \leq 8$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$. The unit cell parameters and orientation matrix of a 0.18×0.30×0.46 mm crystal of **7** were found using 22 reflections with $12 < \theta < 13°$. A total of 2184 reflections were measured, of which 2007 were independent (R factor for averaging 0.037). The unit cell parameters of triclinic crystals of **7** are as follows: $a = 7.971(1)$, $b = 9.257(2)$, $c = 11.703(2)$ Å; $\alpha = 97.96(1)$, $\beta = 91.61(1)$, $\gamma = 114.78(1)°$; $V = 772.9(3)$ Å^3; $Z = 2$; $d_{\text{calc}} = 1.445$ g/cm^3; $m = 0.246$ mm^{-1}; $F(000)$ 344; space group $P1$ (No. 2). The structure was solved by the direct method and refined by the method of least squares anisotropically in the full-matrix approximation using the SHELXS and SHELXL-93 programs [4, 5]. A total of 1542 reflections and 209 parameters were used in the refinement. The number of reflections per parameter was 7.38. The weighting scheme $\omega = 1/[\sigma^2(Fo^2) + (AP)^2]$ was used where $P = (Fo^2 + 2Fc^2)/3$. The weighting scheme coefficients A (0.08) and B (0.270) were calculated using a standard program [5]. The ratios of the maximum and average displacements to the error in the final cycle were 0.056 and 0.008. A correction was introduced for anomalous absorption. Absorption corrections were not introduced. A total of 85% of the hydrogen atoms were located in the calculations, while the remaining hydrogen atoms were inserted geometrically. The hydrogen atoms were refined with fixed temperature and positional parameters. The final $R_1(F) = 0.0486$, $Rw(F^2) = 0.1255$, and GOF = 1.020. The residual electron density from the Fourier difference map was 0.30 and -0.20 e/A. All the structural calculations were carried out on a PC. The atomic coordinates are given in Table 2.

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