

Structure of 2-Thionyltrifluoroacetone Isonicotinyl Hydrazone

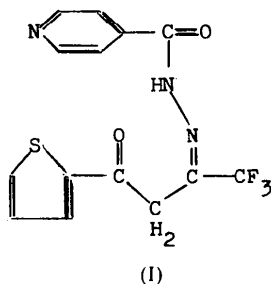
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(Received 7 August 1991; accepted 11 December 1991)

Abstract. $C_{14}H_{10}F_3N_3O_2S$, $M_r = 341.31$, orthorhombic, $Pbca$, $a = 8.604$ (2), $b = 14.290$ (4), $c = 24.924$ (4) Å, $V = 3064.4$ Å³, $Z = 8$, $D_x = 1.479$, $D_m = 1.480$ g cm⁻³ (floatation in CH₂Cl₂/CH₂I₂), $F(000) = 1392$, $T = 293$ K, $\lambda = 0.7107$ Å (Mo $K\alpha$), $\mu = 2.4$ cm⁻¹, final $R = 0.052$ for 2002 reflections. The molecule is in the keto form and has a folded conformation. The hydrogen bonds are intermolecular.

Introduction. The chemical and pharmacological properties of aryl hydrazones have been extensively investigated during recent years, owing to their potential application as antineoplastic, antiviral and anti-inflammatory agents (Wester & Palenik, 1973; Constable & Holmes, 1987). It is well recognized that superoxide $O_2^{\cdot-}$ and hydroxyl OH^{\cdot} radicals are produced in a wide range of biological reactions involved in the metabolism of oxygen. Activated oxygen has been implicated in the tissue and cell damage associated with inflammation and cancer. In this paper we report a new aryl hydrazone compound, 2-thionyltrifluoroacetone isonicotinyl hydrazone (I), which is an antioxidative agent and polydentate ligand of metals.



Experimental. A solution of 2-thionyltrifluoroacetone (0.02 mol, 4.6 g) in absolute ethanol (20 mL) was added to a refluxing solution of isonicotinyl hydrazone (0.02 mol, 2.8 g) in absolute ethanol (60 mL) followed by addition of 0.5 mL concentrated hydrochloric acid. The mixture was then refluxed for 4 h. After cooling to room temperature,

the white precipitate was separated out and recrystallized from absolute ethanol. Yield: 76%; m.p. 454–457 K. Anal.: C, 49.38; H, 2.91; N, 12.37%. Calc. for $C_{14}H_{10}F_3N_3O_2S$; C, 49.27, H, 2.93; N, 12.32%. The single crystals were obtained by slow evaporation of an acetone solution.

Superoxide radicals produced by the reaction of reduced coenzyme (I) with phenazine methasulfate were reacted with nitroblue tetrazolium to form a blue substance. The amount of $O_2^{\cdot-}$ radical and per cent inhibition to superoxide radical were then calculated *via* measurement of absorption of the reduced nitroblue tetrazolium by spectrophotometric analysis (Ponti, Dianzani, Cheeseman & Slater, 1978). OH^{\cdot} radicals produced when H_2O_2 reacts with ascorbate in the presence of Fe^{2+} -edta as a suitable metal catalyst were detected by ethylene formation from methional. Per cent inhibition was calculated *via* measurement of the amount of ethylene by gas chromatography (Winterbourn, 1979, 1981).†

A single crystal of dimensions $0.2 \times 0.25 \times 0.35$ mm was selected for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (50 kV, 20 mA, $\lambda = 0.7107$ Å). The unit-cell dimensions were obtained by least-squares fitting with 25 reflections in the range $20 \leq 2\theta \leq 30^\circ$. A total of 4180 reflections in the range $2 \leq 2\theta \leq 56^\circ$ were measured by an $\omega/2\theta$ scan at room temperature (293 ± 1 K); the scanning rate was $1-10^\circ$ min⁻¹. 2002 reflections with $I \geq 3\sigma(I)$ were used in the structure determination and refinement. All data were corrected for Lorentz and polarization effects, and empirical absorption corrections, based on the ψ scan, were applied (max. 0.9997, min. 0.9618; North, Phillips & Mathews, 1968). The structure was solved by direct methods with the *MULTAN82* program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), which determined the positions of all non-H atoms

† Tables of data for elimination of $O_2^{\cdot-}$ and OH^{\cdot} radicals, lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54961 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0380]

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Table 1. Final atomic coordinates and equivalent isotropic temperature factors

$$B_{eq} = (4/3)(B_{11}a^2 + B_{22}b^2 + B_{33}c^2).$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
S	1.0031 (2)	0.19497 (8)	0.02183 (5)	5.71 (2)
F(1)	0.5180 (3)	-0.0366 (2)	0.0775 (1)	8.23 (8)
F(2)	0.5590 (4)	-0.1385 (2)	0.1364 (1)	9.34 (8)
F(3)	0.3799 (3)	-0.0372 (2)	0.1478 (1)	8.60 (8)
O(1)	0.7293 (4)	0.1644 (2)	0.0933 (1)	6.93 (8)
O(2)	0.5276 (3)	0.1283 (2)	0.2956 (1)	4.76 (6)
N(1)	0.5915 (3)	0.0544 (2)	0.1984 (1)	3.84 (6)
N(2)	0.6929 (3)	0.1121 (2)	0.2247 (1)	3.81 (6)
N(3)	0.9609 (5)	0.3455 (3)	0.3423 (2)	6.37 (9)
C(1)	1.1666 (5)	0.1465 (4)	0.0019 (2)	5.6 (1)
C(2)	1.2001 (5)	0.0630 (3)	0.0247 (2)	4.95 (9)
C(3)	1.0842 (4)	0.0371 (3)	0.0615 (1)	3.97 (8)
C(4)	0.9664 (4)	0.1025 (2)	0.0643 (1)	3.72 (7)
C(5)	0.8228 (4)	0.1015 (3)	0.0953 (2)	4.07 (8)
C(6)	0.7977 (4)	0.0168 (2)	0.1308 (1)	3.69 (7)
C(7)	0.6402 (4)	0.0141 (2)	0.1563 (1)	3.70 (7)
C(8)	0.5216 (5)	-0.0486 (3)	0.1300 (2)	5.5 (1)
C(9)	0.6474 (4)	0.1485 (3)	0.2728 (1)	3.62 (7)
C(10)	0.7598 (4)	0.2175 (3)	0.2960 (1)	3.51 (7)
C(11)	0.8299 (5)	0.2863 (3)	0.2651 (2)	4.52 (8)
C(12)	0.9283 (5)	0.3492 (3)	0.2901 (2)	5.5 (1)
C(13)	0.8930 (6)	0.2777 (3)	0.3709 (2)	6.6 (1)
C(14)	0.7912 (5)	0.2138 (3)	0.3497 (2)	4.82 (9)
H(1)	1.257 (5)	0.155 (3)	-0.036 (2)	5.0*
H(N2)	0.786 (5)	0.115 (3)	0.208 (2)	5.0*
H(2)	1.292 (5)	0.018 (3)	0.018 (2)	5.0*
H(3)	1.085 (5)	-0.017 (3)	0.077 (2)	5.0*
H(6')	0.814 (5)	-0.037 (3)	0.107 (2)	5.0*
H(6)	0.885 (5)	0.017 (3)	0.157 (2)	5.0*
H(11)	0.811 (5)	0.297 (3)	0.229 (2)	5.0*
H(12)	0.978 (5)	0.399 (3)	0.267 (2)	5.0*
H(13)	0.918 (5)	0.278 (3)	0.408 (2)	5.0*
H(14)	0.742 (5)	0.170 (3)	0.368 (2)	5.0*

* Fixed.

mal factors for all non-H atoms and fixed isotropic parameters of 5\AA^2 for H atoms, which finally converged to $R = 0.052$ and $wR = 0.051$; $(\Delta/\sigma)_{\max} = 1.30$; $(\Delta\rho)_{\max} = 0.7$, $(\Delta\rho)_{\min} = -0.2 \text{ e \AA}^{-3}$. Positional parameters are given in Table 1 and bond lengths and angles in Table 2.

Discussion. From the observed bond lengths and angles and from the location of the H atoms in the difference Fourier synthesis, the molecule is shown

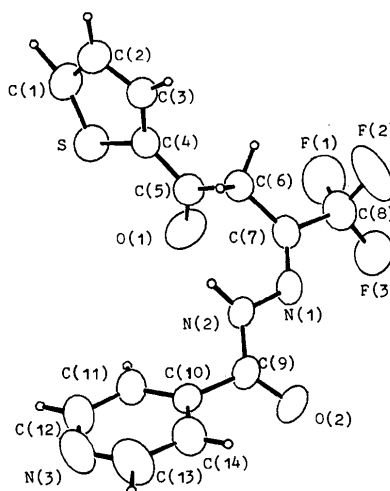


Fig. 1. An ORTEP drawing of the molecular structure.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

S—C(1)	1.646 (5)	N(1)—C(7)	1.268 (5)	C(5)—C(6)	1.515 (6)
S—C(4)	1.722 (4)	N(2)—C(9)	1.364 (4)	C(6)—C(7)	1.496 (5)
F(1)—C(8)	1.321 (5)	N(3)—C(12)	1.333 (6)	C(7)—C(8)	1.508 (6)
F(2)—C(8)	1.333 (5)	N(3)—C(13)	1.337 (7)	C(9)—C(10)	1.498 (5)
F(3)—C(8)	1.307 (5)	C(1)—C(2)	1.352 (6)	C(10)—C(11)	1.386 (5)
O(1)—C(5)	1.208 (5)	C(2)—C(3)	1.406 (5)	C(10)—C(14)	1.366 (5)
O(2)—C(9)	1.212 (4)	C(3)—C(4)	1.379 (5)	C(11)—C(12)	1.383 (6)
N(1)—N(2)	1.368 (5)	C(4)—C(5)	1.458 (5)	C(13)—C(14)	1.371 (6)
C(1)—S—C(4)	91.1 (2)	F(1)—C(8)—F(3)	107.3 (4)		
N(2)—N(1)—C(7)	117.4 (3)	F(2)—C(8)—F(3)	107.8 (4)		
N(1)—N(2)—C(9)	117.9 (3)	F(1)—C(8)—C(7)	111.6 (3)		
C(12)—N(3)—C(13)	117.2 (4)	F(2)—C(8)—C(7)	111.0 (3)		
C(1)—C(2)—C(3)	110.8 (4)	F(3)—C(8)—C(7)	114.2 (4)		
C(2)—C(3)—C(4)	112.1 (3)	O(2)—C(9)—N(2)	124.4 (3)		
C(3)—C(4)—C(5)	129.9 (3)	O(2)—C(9)—C(10)	121.7 (4)		
O(1)—C(5)—C(4)	122.3 (3)	N(2)—C(9)—C(10)	113.9 (3)		
O(1)—C(5)—C(6)	121.7 (3)	C(9)—C(10)—C(11)	122.2 (4)		
C(4)—C(5)—C(6)	116.0 (4)	C(9)—C(10)—C(14)	118.7 (3)		
C(5)—C(6)—C(7)	113.4 (3)	C(11)—C(10)—C(14)	119.1 (3)		
N(1)—C(7)—C(6)	129.7 (3)	C(10)—C(11)—C(12)	118.6 (4)		
N(1)—C(7)—C(8)	113.9 (3)	N(3)—C(12)—C(11)	122.8 (4)		
C(6)—C(7)—C(8)	116.3 (4)	N(3)—C(13)—C(14)	123.8 (5)		
F(1)—C(8)—F(2)	104.4 (4)	C(10)—C(14)—C(13)	118.5 (4)		
S—C(1)—C(2)	115.3 (3)	S—C(4)—C(3)	110.8 (3)		
S—C(4)—C(5)	119.3 (3)				

of the asymmetric unit. The coordinates of the H atoms were revealed by difference Fourier synthesis. The structure was refined with unit weights by full-matrix least-squares methods with anisotropic ther-

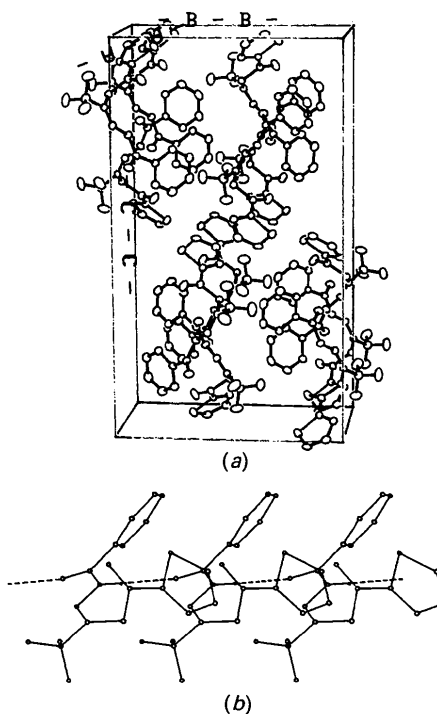


Fig. 2. (a) Molecular packing. (b) Intermolecular hydrogen bonds.

to be in keto tautomeric form [(I) and Fig. 1]. The hydrazone group $N2-N1=C7-C6$ is almost *cis*-planar (torsion angle 2.5°). Torsions at bonds adjacent to the double bond ($C7=N1-N2-C9$, -174° ; $N1=C7-C6-C5$, -83°) prevent formation of an intramolecular hydrogen bond $N2-H\cdots O1$, since the $H\cdots O1$ distance becomes 2.98 \AA . As shown in Fig. 1, the molecule has an overall V-shape. The thiophene and pyridine rings are each nearly planar, making a dihedral angle of 87.3° with each other. The molecular packing (Fig. 2) involves intermolecular hydrogen bonds (the $H\cdots O2$ distance and the $N2-H\cdots O2$ angle become 2.09 \AA and 156° , respectively) which link molecules to form chains.

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Acta Cryst. (1992). **C48**, 1297–1299

Structure of $BaCuSi_4O_{10}$ *

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(Received 30 September 1991; accepted 27 January 1992)

Abstract. Barium copper tetrasilicate, $BaCuSi_4O_{10}$, $M_r = 473.2$, tetragonal, $P4/ncc$, $a = 7.440(2)$, $c = 16.097(6) \text{ \AA}$, $V = 891.2(4) \text{ \AA}^3$, $Z = 4$, $D_x = 3.527 \text{ g cm}^{-3}$, $Mo K\alpha$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 73.59 \text{ cm}^{-1}$, $F(000) = 884$, $T = 296 \text{ K}$, $R = 0.0202$, $wR = 0.0167$ for 290 reflections with $I > 3\sigma(I)$. This royal-blue plate-like crystal, a by-product of the Tl-bearing superconductors, was identified by both electron microprobe and single-crystal diffraction to be the barium copper silicate $BaCuSi_4O_{10}$. The structure consists of rings of four-linked SiO_4 tetrahedra. Each ring is connected to four others to form a silicate layer in the *ab* plane. The compound is a synthetic isotype of the rare mineral gillespite ($BaFe-$

Si_4O_{10}) [Pabst (1943, 1958). *Am. Mineral.* **28**, 372–390; **43**, 970–980]. Two silicate phases with new structure types as by-products of the Tl-bearing oxide superconductors were recently reported by Finger, Hazen & Hemley [*Am. Mineral.* (1989), **74**, 952–959]. In this work we report the microanalysis results and the crystal structure of the said blue plate crystal.

Experimental. The title compound was obtained as royal-blue transparent plate crystals in an attempt to grow a crystal of ' $TlCa_3BaCu_3O_{8.5}$ ' by heating well mixed oxides of the said composition in a silica boat on a silver plate at 1193 K for 30 min, cooling at a rate of 18 K min^{-1} to 1129 K , and then turning the power off and allowing the furnace to cool to room temperature. Plate crystals about $2 \times 2 \times 0.05 \text{ mm}$, coated with a thin layer of carbon film, were first

* See also following paper [Janczak & Kubiak (1992). *Acta Cryst.* **C48**, 1299–1301].

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