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⋯O1, since the H⋯O1 distance becomes 2.98 Å. 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⋯O2 distance and the N2—H⋯O2 angle become 2.09 Å and 156°, respectively) which link molecules to form chains.

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SHORT-FORMAT PAPERS

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Structure of $BaCuSi_4O_{10}$*

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Abstract. Barium copper tetrasilicate, $BaCuSi_4O_{10}$, $M_r = 473.2$, tetragonal, $P4/ncc$, $a = 7.440$ (2), $c = 16.097$ (6) Å, $V = 891.2$ (4) Å³, $Z = 4$, $D_x = 3.527$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 73.59$ cm⁻¹, $F(000) = 884$, $T = 296$ 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 'TlCa₃BaCu₃O₈.₅' 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 × 2 × 0.05 mm, coated with a thin layer of carbon film, were first

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* See also following paper [Janczak & Kubiak (1992). *Acta Cryst.* C48, 1299–1301].
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Table 1. *Atomic coordinates* ($\times 10^4$) (*origin choice 2*) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$)

(a) BaCuSi$_4$O$_{10}$

	Position	x	y	z	U_{eq}*
Cu	4(c)	7500	−2500	−944 (1)	9(1)
Ba	4(b)	7500	2500	0	12 (1)
Si	16(g)	9822 (2)	−618 (2)	1543 (1)	9 (1)
O(1)	16(g)	7763 (5)	−7 (5)	1365 (2)	16 (1)
O(2)	8(f)	10247 (6)	−247 (6)	2500	31 (2)
O(3)	16(g)	4688 (5)	1130 (5)	909 (3)	17 (1)

(b) Gillespite BaFeSi$_4$O$_{10}$ (Pabst, 1943) (origin choice 1) [$a =$ 7.495 (1) Å, $c = 16.05$ (1) Å, $V = 90.6$ Å^3]

	Position	x	y	z
Fe	4(c)	0	5000	900
Ba	4(b)	0	0	0
Si	16(g)	2700	1750	1550
O(2)	16(g)	4650	2400	1400
O(1)	8(f)	2150	2150	2500
O(3)	16(g)	1350	2750	900

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Cu—O(3a)	1.922 (4)	Ba—O(1)	2.889 (4)
Ba—O(3)	2.749 (4)	Si—O(1)	1.624 (4)
Si—O(2)	1.596 (2)	Si—O(3b)	1.571 (4)

O(3a)—Cu—O(3c)	90.0 (1)	O(3a)—Cu—O(3d)	176.7 (3)
O(1)—Ba—O(3)	53.6 (1)	O(1)—Ba—O(1e)	125.4 (1)
O(3)—Ba—O(1e)	83.6 (1)	O(1)—Ba—O(1f)	81.0 (2)
O(3)—Ba—O(1f)	77.5 (1)	O(3)—Ba—O(1g)	157.1 (1)
O(1a)—Ba—O(1g)	80.9 (2)	O(3)—Ba—O(3h)	106.5 (1)
O(3)—Ba—O(3')	115.7 (2)	O(1)—Si—O(1j)	108.5 (3)
O(1)—Si—O(2)	108.0 (2)	O(1j)—Si—O(2)	108.9 (2)
O(1)—Si—O(3b)	110.3 (2)	O(1j)—Si—O(3b)	105.6 (2)
O(2)—Si—O(3b)	115.4 (3)		

Symmetry code: (a) $1 - x, 1 - y, -z$; (b) $1 - y, \frac{1}{2} + x, -z$; (c) $\frac{1}{2} + y, 1 - x, -z$; (d) $1 + y, \frac{1}{2} - x, -z$; (e) $\frac{1}{2} + y, 1 - x, -z$; (f) $\frac{3}{2} - x, \frac{1}{2} - y, z$; (g) $1 - y, x - \frac{1}{2}, -z$; (h) $\frac{3}{2} - x, \frac{1}{2} - y, z$; (i) $\frac{1}{2} + x, \frac{1}{2} + y, -z$; (j) $1 + y, \frac{1}{2} - x, -z$.

analyzed by EDS in a CamScan S-4 SEM. Only Si, Ba, and Cu were detected. No Ca, Tl, and Ag were traced. Further analysis was conducted on an ARL-EMX electron microprobe using SiO$_2$, BaSO$_4$, and CuFeS$_2$ as standards for Si, Ba, and Cu. Several different points gave the average stoichiometric composition Ba$_{0.96}$Cu$_{0.85}$Si$_{4.10}$O$_{10}$. A blue crystal of the title compound having dimensions 0.01 × 0.14 × 0.30 mm was selected for indexing and intensity data collection on a Nicolet *R3m/V* diffractometer with graphite-monochromated Mo *Kα* radiation (0.71073 Å) at room temperature. The unit-cell parameters were obtained by least-squares refinement of 19 reflections within the 2θ range 5 to 28°. Data collected by ω–2θ scans, scan width 1.10° + $K\alpha_1, \alpha_2$ separation and scan speed 2.93 – 14.65° min^{-1}. Total of 908 reflections measured with $(\sin\theta/\lambda)_{max} = 0.595$ Å^{-1} in the range of $0 < h < 8$, $0 < k < 8$, $0 < l < 18$. No significant variation in intensities of three standards monitored every 50 reflec-

Table 3. *Linkage motif and coordination numbers* (CN) *in* BaCuSi$_4$O$_{10}$

	4 O(1)	2 O(2)	4 O(3)	CN
Ba	4/1		4/1	8
Cu			4/1	4
4Si	2/2	1/2	1/1	4
CN	3	2	3	
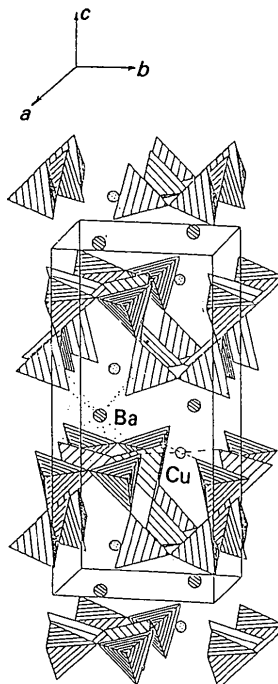
(a)
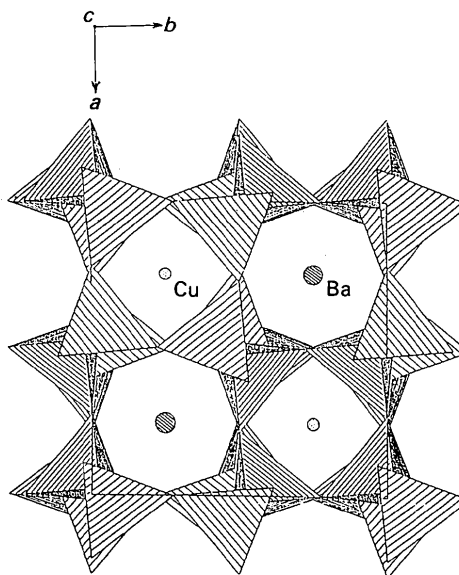
(b)

Fig. 1. Polyhedral plots of BaCuSi$_4$O$_{10}$. Projections approximately along (a) the a axis and (b) the c axis.

tions. The intensity data were corrected for absorption, Lorentz, and polarization effects. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90°. Max./min. transmission factors: 0.964/0.490. Systematic absences: $hk0$, $h + k = 2n + 1$; $0kl$, $l = 2n + 1$; hhl, $l = 2n + 1$. 290 unique reflections with $I > 3.0\sigma(I)$. Based on the statistical analysis of the intensity distribution, systematic extinctions, and the successful solution and refinement of the structure, the space group was determined to be $P4/ncc$ (No. 130). The structure was solved by direct methods and refined by full-matrix least squares based on F values. All of the atoms were refined with anisotropic temperature factors. At convergence $R = 0.0201$, $wR = 0.0167$, $w = [\sigma^2(F)]^{-1}$ [$\sigma^2(F)$ based on counting statistics], $(\Delta/\sigma)_{max} = 0.021$, $S = 1.64$, $(\Delta\rho)_{max} = 0.52$, $(\Delta\rho)_{min} = -0.58$ e Å^{-3}. Final atomic coordinates and thermal parameters are given in Table 1.* Atomic coordinates of gillespite BaFeSi₄O₁₀ and its lattice constants are also given in Table 1 for comparison. Selected bond distances and angles appear in Table 2. The linkage motif and the coordination numbers in BaCuSi₄O₁₀ are given in Table 3. The title compound is isotypic with BaFeSi₄O₁₀ (Pabst, 1943, 1958). Projections of the structure approximately along the a and c axes are shown in Fig. 1. The structure contains rings of four-connected SiO₄

tetrahedra. Each ring is connected to four others to form a silicate layer in the ab plane, as shown in Fig. 1(a). The Cu²⁺ and Ba²⁺ cations are located in the tunnels formed by rings of SiO₄ tetrahedra as shown in Fig. 1(b). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a DEC MicroVAX II computer system using the *SHELXTL-Plus* program (Sheldrick, 1990).

Related literature. The crystal structure of BaCuSi₄O₁₀ is isotypic with gillespite (BaFeSi₄O₁₀) which was reported by Pabst (1943, 1958). Both belong to the sheet silicate structure except that fourfold coordinated Fe²⁺ is substituted by fourfold coordinated Cu²⁺.

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54949 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BX0572]

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Refinement of the Structure of Barium Copper Silicate BaCu[Si₄O₁₀] at 300 K*

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Abstract. Barium copper tetrasilicate, BaCu[Si₄O₁₀], $M_r = 473.2$, tetragonal, $P4/ncc$, $a = 7.447$ (1), $c = 16.138$ (2) Å, $V = 895.0$ (2) Å³, $Z = 4$, $D_x = 3.512$ g cm⁻³, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 73.3$ cm⁻¹, $T = 300$ K, $F(000) = 884$, final $R = 0.030$, $wR = 0.023$, for 625 independent reflections. The crystals have been obtained during a study of the chemical reactivity of the '1-2-3' type superconductors. The structure BaCu[Si₄O₁₀] is of the BaFe[Si₄O₁₀] structure type, reported by Pabst [*Acta Cryst.* (1959), **12**, 733–739]. The structure contains SiO₄ tetrahedra which share corners to form four-membered rings which in turn are linked *via* four

* See also preceding paper [Lin, Liao & Wang (1992). *Acta Cryst.* C48, 1297–1299].