

Table 2. Geometric parameters (Å, °)

O1—C6	1.399 (4)	C7—C8	1.362 (5)
O1—C16	1.388 (4)	C8—C9	1.409 (4)
O2—C26	1.211 (5)	C9—C10	1.413 (4)
O3—C22	1.219 (5)	C12—C13	1.400 (5)
O4—C24	1.212 (5)	C13—C14	1.355 (5)
N1—C2	1.315 (4)	C14—C20	1.411 (4)
N1—C9	1.367 (5)	C15—C16	1.358 (5)
N11—C12	1.314 (4)	C15—C20	1.407 (4)
N11—C19	1.365 (4)	C16—C17	1.407 (5)
N23—C22	1.360 (4)	C17—C18	1.358 (4)
N23—C24	1.375 (5)	C18—C19	1.419 (4)
N25—C24	1.373 (5)	C19—C20	1.414 (5)
N25—C26	1.366 (4)	C21—C22	1.516 (5)
C2—C3	1.399 (5)	C21—C26	1.522 (5)
C3—C4	1.359 (6)	C21—C27	1.519 (5)
C4—C10	1.419 (5)	C21—C29	1.569 (6)
C5—C6	1.352 (5)	C27—C28	1.501 (7)
C5—C10	1.416 (5)	C29—C30	1.41 (1)
C6—C7	1.406 (5)		
C6—O1—C16	117.5 (2)	C15—C16—C17	121.8 (3)
C2—N1—C9	118.0 (3)	C16—C17—C18	119.5 (3)
C12—N11—C19	117.9 (3)	C17—C18—C19	120.9 (3)
C22—N23—C24	126.2 (4)	N11—C19—C18	118.9 (3)
C24—N25—C26	125.9 (3)	N11—C19—C20	122.5 (3)
N1—C2—C3	123.6 (4)	C18—C19—C20	118.6 (3)
C2—C3—C4	119.8 (3)	C14—C20—C15	123.4 (3)
C3—C4—C10	118.6 (3)	C14—C20—C19	116.8 (3)
C6—C5—C10	119.3 (4)	C15—C20—C19	119.8 (3)
O1—C6—C5	118.2 (3)	C22—C21—C26	113.8 (3)
O1—C6—C7	119.5 (3)	C22—C21—C27	108.9 (4)
C5—C6—C7	122.1 (3)	C22—C21—C29	107.5 (3)
C6—C7—C8	119.4 (4)	C26—C21—C27	109.0 (4)
C7—C8—C9	120.7 (4)	C26—C21—C29	105.2 (3)
N1—C9—C8	118.6 (3)	C27—C21—C29	112.7 (3)
N1—C9—C10	122.1 (3)	O3—C22—N23	119.9 (3)
C8—C9—C10	119.3 (3)	O3—C22—C21	121.4 (4)
C4—C10—C5	122.8 (4)	N23—C22—C21	118.7 (3)
C4—C10—C9	118.0 (3)	O4—C24—N23	121.3 (3)
C5—C10—C9	119.3 (3)	O4—C24—N25	122.1 (4)
N11—C12—C13	123.7 (3)	N23—C24—N25	116.6 (3)
C12—C13—C14	118.9 (3)	O2—C26—N25	120.2 (3)
C13—C14—C20	120.1 (3)	O2—C26—C21	121.3 (3)
C16—C15—C20	119.5 (3)	N25—C26—C21	118.6 (3)
O1—C16—C15	123.7 (4)	C21—C27—C28	114.2 (3)
O1—C16—C17	114.4 (3)	C21—C29—C30	114.7 (7)

A solution of sodium barbital (1 mmol) in 10 ml H₂O was added dropwise to a solution of 6,6'-diquinoyl ether (1 mmol) in 15 ml absolute alcohol at room temperature (294 K), with constant stirring for 2 h. Brown stick-like or plate-like crystals were grown from the mixed solution after 10 d. The crystals were filtered, washed with H₂O and absolute alcohol. Analysis: calculated for C₂₆H₂₄N₄O₄: C 68.40, H 5.30, N 12.28%; found: C 68.18, H 5.12, N 12.40%.

Structure analysis was performed with the *SDP* program on a PDP11/44 computer. The crystal structure was solved by direct methods. The positions of 34 non-H atoms in the asymmetric unit were determined with *MULTAN82* (Main *et al.*, 1982). The positions of all H atoms were determined by difference Fourier syntheses. The refinements were carried out with unit weights by full-matrix least squares for the coordinates of all atoms and anisotropic thermal parameters for the non-H atoms (isotropic thermal parameters for H atoms were fixed at 5 Å²).

Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55380 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0411]

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(E)-Methyl 2-Phenyl-2-(3-pyridyl)vinyl Sulfide

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Abstract

The unambiguous identification by X-ray diffraction of the (*E*) configuration of the title compound confirms a previous tentative assignment by NMR. The two planar rings (phenyl and pyridyl) are at an angle of about 70°. Crystal cohesion is ensured by a dense network of van der Waals contacts.

Comment

The structure determination of the *gem*-disubstituted vinyl sulfide was undertaken to confirm the (*E*) configuration suggested for this stereoisomer by ¹H NMR spectroscopy results. The stereochemistry of such prochiral vinyl sulfides (Madesclaire, Roche, Fauve & Veschambre, 1990) is of great interest as their asymmetric sulfoxidation yields chiral synthons which are widely used in organic synthesis (Solladié, 1988). In addition, these α,β -unsaturated sulfides possess antianoxia activity and may also act as free-radical scavengers which are useful in the cardiovascular field (Madesclaire, Roche & Duroux, unpublished). The angle between the phenyl and pyridyl rings is 69.4° and the plane containing the vinyl group (C1, C7, C13, C14) makes angles of 57.0 and 24.3° with the planes of the phenyl and pyridyl rings respectively. This relative disposition of the aromatic rings prevents delocalization of the π electrons.

The S—C bond lengths [S15—C14 1.752 (2), S15—C16 1.793 (3) Å] and the C—S—C and C=C—S angles [C14—S15—C16 100.1 (1), C13—C14—S15 124.9 (2)°] are comparable with published values for other vinyl sulfides [1.752 (10), 1.794 (12) Å, 102.5 (2), 127.0 (2)° (Derissen & Bijen, 1973); 1.759 (8), 1.795 (8) Å, 102.1 (5), 127.5 (7)° (Samdal, Seip & Torgriksen, 1979)]. The angle C10—N11—C12 is slightly smaller [116.4 (2)°] than the other angles in the pyridyl ring. Crystal cohesion is ensured by the three-dimensional network of van der Waals interactions listed in Table 2.

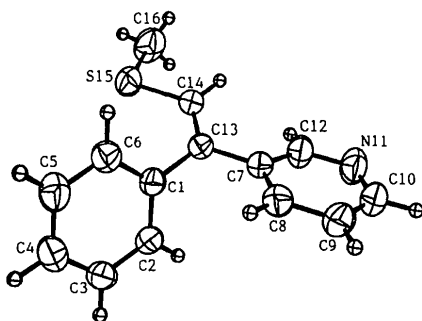


Fig. 1. ORTEP view of the title molecule showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels. H atoms are displayed as isotropic spheres with *B* values of 1.0 Å².

Experimental*Crystal data*C₁₄H₁₃NS*M_r* = 227.33

Monoclinic

*P*2₁/*b**D_x* = 1.259 Mg m⁻³*D_m* = 1.26 Mg m⁻³Mo *K*α radiation

λ = 0.71069 Å

a = 12.326 (2) Å*b* = 17.177 (1) Å*c* = 5.906 (2) Å

γ = 106.40 (1)°

V = 1199.56 Å³*Z* = 4

Cell parameters from 24

reflections

θ = 6–15°

μ = 0.23 mm⁻¹*T* = 293 K

Prism

0.48 × 0.26 × 0.06 mm

White

Data collection

Enraf-Nonius CAD-4

diffractometer

θ–2θ scans

Absorption correction:

none

7792 measured reflections

7792 independent reflections

2057 observed reflections

[*I* > 3σ(*I*), sinθ/λ < 0.8 Å⁻¹]*R*_{int} = 0θ_{max} = 39.95°*h* = 0 → 22*k* = –31 → 31*l* = 0 → 10

3 standard reflections

frequency: 60 min

intensity variation: 1%

*Refinement*Refinement on *F*Final *R* = 0.045*wR* = 0.044*S* = 2.2

2029 reflections

197 parameters

All H-atom parameters re-

fined

w = 1/σ²(*F*)(Δ/σ)_{max} = 0.02Δρ_{max} = 0.22 e Å⁻³Δρ_{min} = –0.23 e Å⁻³

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
C1	0.2344 (2)	0.3476 (1)	0.1315 (4)	3.15 (4)
C2	0.1983 (2)	0.2646 (1)	0.0863 (4)	3.65 (5)
C3	0.1306 (2)	0.2116 (1)	0.2391 (5)	4.13 (5)
C4	0.0970 (2)	0.2402 (1)	0.4375 (5)	4.40 (5)
C5	0.1328 (2)	0.3218 (2)	0.4847 (5)	4.59 (6)
C6	0.2012 (2)	0.3751 (1)	0.3341 (4)	4.03 (5)
C7	0.4142 (2)	0.3900 (1)	–0.1023 (4)	3.31 (4)
C8	0.4688 (2)	0.3470 (1)	0.0319 (5)	4.08 (5)
C9	0.5683 (2)	0.3333 (1)	–0.0439 (6)	4.88 (6)
C10	0.6113 (2)	0.3645 (2)	–0.2484 (6)	5.07 (6)
N11	0.5617 (2)	0.4058 (1)	–0.3836 (4)	5.28 (5)
C12	0.4647 (2)	0.4168 (1)	–0.3095 (5)	4.35 (5)
C13	0.3064 (2)	0.4053 (1)	–0.0323 (4)	3.13 (4)
C14	0.2757 (2)	0.4683 (1)	–0.1139 (4)	3.65 (5)
S15	0.1471 (1)	0.4887	–0.0555 (1)	4.71 (1)
C16	0.1440 (2)	0.5577 (2)	–0.2816 (6)	6.47 (7)

Table 2. Geometric parameters (Å, °)

C1—C2	1.394 (3)	C7—C12	1.391 (3)
C1—C6	1.390 (3)	C8—C9	1.386 (4)
C2—C3	1.383 (3)	C9—C10	1.366 (4)
C3—C4	1.379 (4)	C10—N11	1.327 (4)
C4—C5	1.375 (3)	N11—C12	1.336 (3)
C5—C6	1.379 (3)	C13—C14	1.334 (3)
C1—C13	1.487 (3)	C14—S15	1.752 (2)
C13—C7	1.483 (4)	S15—C16	1.793 (3)
C7—C8	1.382 (3)		

C2—C1—C6	118.2 (2)	C7—C8—C9	119.5 (2)
C2—C1—C13	121.0 (3)	C8—C9—C10	119.0 (3)
C6—C1—C13	120.8 (2)	C9—C10—N11	123.7 (2)
C1—C2—C3	120.5 (2)	C10—N11—C12	116.4 (2)
C2—C3—C4	120.4 (3)	C7—C12—N11	125.2 (2)
C3—C4—C5	119.6 (2)	C1—C13—C7	117.4 (2)
C4—C5—C6	120.4 (3)	C1—C13—C14	121.5 (2)
C1—C6—C5	121.0 (3)	C7—C13—C14	121.2 (2)
C8—C7—C12	116.2 (2)	S15—C14—C13	124.9 (2)
C8—C7—C13	122.0 (3)	C14—S15—C16	100.1 (1)
C12—C7—C13	121.7 (3)		
C2—C1—C13—C14	124.08	C13—C14—S15—C16	-162.27
C12—C7—C13—C14	-25.92		

van der Waals contacts

C3—C5 ⁱ	3.475 (3)	C6—C14 ⁱⁱⁱ	3.634 (4)
C9—C14 ⁱⁱ	3.531 (3)	N11—C12 ^{iv}	3.638 (4)
C10—C14 ⁱⁱ	3.537 (3)	C8—N11 ⁱⁱⁱ	3.687 (4)
C5—C14 ⁱⁱⁱ	3.543 (3)	C8—C10 ^v	3.718 (3)
C12—C12 ^{iv}	3.548 (4)	C2—C4 ⁱ	3.723 (3)
C3—C4 ⁱ	3.611 (4)	C3—C10 ^v	3.765 (4)
C5—C13 ⁱⁱⁱ	3.611 (3)	C6—C12 ⁱⁱⁱ	3.765 (3)

Symmetry codes: (i) $-x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, 1 - y, -z$;
 (iii) $x, y, z + 1$; (iv) $1 - x, 1 - y, -z - 1$; (v) $1 - x, \frac{1}{2} - y, \frac{1}{2} + z$.

Full-matrix least-squares refinements were performed using a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The figure and scheme were prepared on a Macintosh computer using *ORTEP* (Johnson, 1976).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55322 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1010]

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