

Fig. 1. The structure of (1) with atomic labeling scheme. 50% probability thermal ellipsoids.

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Structure of 18'-Epivinblastine

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Abstract. Methyl {3a*R*-[3a α ,4 β ,5 β ,5a β ,9(3*R**,-5*S**,7*R**,9*R**),10*bR*,13a α]}-4-(acetyloxy)-3a-ethyl-9-[5-ethyl-1,4,5,6,7,8,9,10-octahydro-5-hydroxy-9-(methoxycarbonyl)-2*H*-3,7-methanoazacycloundecino[5,4-*b*]indol-9-yl]-3a,4,5,5a,6,11,12,13a-octahydro-5-hydroxy-8-methoxy-6-methyl-1*H*-indolizino[8,1-*c,d*]carbazole-5-carboxylate methanol solvate, C₄₆H₅₈N₄O₉ · 2CH₃OH (1), *M_r* = 875.07, monoclinic, *P*2₁, *a* = 10.2759 (12), *b* = 22.353 (3), *c* = 10.4051 (12) Å, β = 106.502 (9)°, *V* = 2291.6 (5) Å³, *Z* = 2, *D_x* = 1.27 g cm⁻³, Mo *K* α radiation, λ = 0.7107 Å, μ = 0.8397 cm⁻¹, *F*(000) = 940, *T* = 198 K, *R* = 0.0470 for 2751 reflections, *F_o* \geq 4 σ (*F_o*). The *C* ring of the vindoline moiety is in the boat conformation with the hydroxy group and the tertiary N in the bowsprit positions resulting in a fairly short intramolecular hydrogen-bonding interaction. The relevant parameters for O3—H3···N9 are O···N 2.651 (6), H···N 1.94 (5) Å and O—H···N 147 (5)°. The *D* and *E* rings are in the sofa and envelope conformations, respectively. The piperidine ring of the catharanthine portion of the molecule assumes the chair conformation while the conformation of the azacyclononene ring is a boat-chair. An intramolecular hydrogen bond between the indolino NH of the catharanthine moiety and methoxy O (O25) of the vindoline moiety is also observed. The relevant parameters for N16'—H16'···O25 are N···O 2.827 (6), H···N2.14 (6) Å and O—H···N 136 (5)°.

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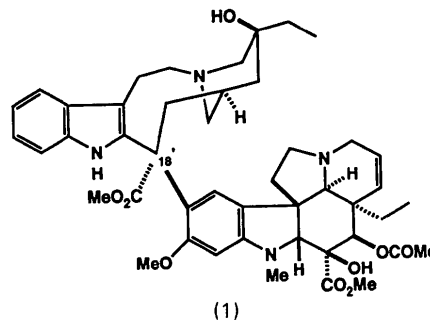
(1), the angles about each S atom are significantly smaller than in (2) [99.7 (1) at S(1), 100.4 (1)° at S(2), 100.5 and 101.7° at analogous atoms in (2)], and the disulfide bond is significantly longer in (1) [2.056 (1) Å] than in (2) (2.025 Å).

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Experimental. (1) was prepared during the course of a synthesis of the clinically important antitumor alkaloid vinblastine (Moncrief & Lipscomb, 1965; Magnus, Stamford & Ladlow, 1991). The absolute



configuration of (1) was assigned on the basis of internal comparison to the vindoline moiety (Moncrief & Lipscomb, 1966). Colorless crystals were obtained by slow evaporation of a methanol-water solution. The data crystal was separated from a cluster of smaller crystals and had approximate dimensions 0.17 × 0.34 × 0.43 mm. The data were collected on a Nicolet P3 diffractometer using a graphite monochromator and equipped with a Nicolet LT-2 low-temperature device. The lattice parameters were obtained by the least-squares refinement of 40 reflections with 18.2 < 2 θ < 21.2°.

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The data were collected from 4.0 to 50° in 2θ using the ω -scan technique, with a 1.2° scan range at 2–5° min⁻¹. 8740 reflections were measured, of which 4278 were unique ($R_{\text{int}} = 0.0195$), where h ranged from -12→12, k from 0→26 and l from -12→12. Four reflections (112, $\bar{1}\bar{5}\bar{1}$, $\bar{2}\bar{2}\bar{2}$, $\bar{1}\bar{4}\bar{0}$) were remeasured every 96 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 1.00–1.09. The data were also corrected for Lp effects but not absorption. Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (1527 reflections). Data reduction and decay correction were performed using the Nicolet XRD *SHELXTL-Plus* (Sheldrick, 1988) software package. The structure was solved by Patterson search methods using *PATSEE* (Egert & Sheldrick, 1985) and refined by full-matrix least squares (Sheldrick, 1988) with anisotropic thermal parameters for the non-H atoms. Most H atoms were located from a ΔF map and refined with isotropic thermal parameters. The H atoms on C3', C21', C23', C20, C21, C24, C25, C26 and C27 did not refine well and were idealized (C—H 0.96 Å) with isotropic U refined. The H atoms on the solvent methanol atoms (O1B, C2B, C2A) were idealized with isotropic U fixed at $1.2 \times U_{\text{eq}}$ of the relevant atom. The H atom on O1A (methanol O) could not be located and was omitted from refinement. $\sum w(|F_o| - |F_c|)^2$ was minimized where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$. The intensity, I , is given by $(I_{\text{peak}} - I_{\text{background}}) \times (\text{scan rate})$; where 0.02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times (\text{scan rate})]$. 725 independent parameters were refined in blocks of 362 and 364 parameters (a single overall scale factor was refined in all cycles) to a final $R = 0.0470$ for 2751 reflections, with $wR = 0.0405$ and goodness of fit, $S = 1.118$. The R value for all data was 0.0845, with $wR = 0.0488$. Max. $|\Delta/\sigma| < 0.1$ in the final refinement cycle and the min. and max. peaks in the final difference electron density map were -0.22, 0.22 e Å⁻³, respectively. The origin was defined along the 2_1 screw axis by the atom positions of the block not being refined. Neutral atom scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with the anomalous-dispersion corrections taken from the work of Cromer & Liberman (1970). The scattering factors for the H atom were obtained from Stewart, Davidson & Simpson (1965). Values used to calculate the linear absorption coefficient are from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55). All figures were generated using

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (Å²) for the non-H atoms of (1)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C1'	-0.1422 (5)	0.1507 (2)	0.4400 (6)	0.026 (2)
C2'	-0.2464 (6)	0.1122 (2)	0.4832 (6)	0.033 (2)
C3'	-0.3825 (6)	0.1446 (3)	0.4737 (6)	0.039 (2)
C4'	-0.3836 (5)	0.1901 (3)	0.5805 (6)	0.034 (2)
O4'	-0.3223 (5)	0.2448 (2)	0.5492 (5)	0.042 (2)
C5'	-0.2988 (7)	0.1680 (3)	0.7192 (6)	0.038 (2)
N6'	-0.1716 (5)	0.1440 (2)	0.7114 (4)	0.038 (2)
C7'	-0.0461 (7)	0.1526 (3)	0.8120 (6)	0.043 (3)
C8'	0.0677 (7)	0.1743 (3)	0.7532 (7)	0.038 (2)
C9'	0.1317 (5)	0.1276 (2)	0.6864 (5)	0.028 (2)
C10'	0.2555 (5)	0.0990 (3)	0.7580 (5)	0.030 (2)
C11'	0.3405 (6)	0.1035 (3)	0.8882 (6)	0.040 (2)
C12'	0.4571 (7)	0.0687 (3)	0.9267 (6)	0.049 (3)
C13'	0.4924 (7)	0.0299 (3)	0.8381 (6)	0.044 (3)
C14'	0.4100 (6)	0.0244 (3)	0.7087 (6)	0.041 (3)
C15'	0.2929 (5)	0.0591 (2)	0.6703 (5)	0.030 (2)
N16'	0.1940 (5)	0.0632 (2)	0.5504 (5)	0.030 (2)
C17'	0.0962 (5)	0.1043 (2)	0.5597 (5)	0.026 (2)
C18'	-0.0118 (5)	0.1184 (2)	0.4279 (5)	0.026 (2)
C19'	-0.1903 (7)	0.0910 (3)	0.6275 (6)	0.038 (2)
C20'	-0.5291 (7)	0.2051 (3)	0.5796 (7)	0.047 (3)
C21'	-0.5436 (7)	0.2476 (4)	0.6864 (7)	0.064 (3)
C22'	-0.0678 (5)	0.0607 (3)	0.3504 (5)	0.032 (2)
O22'	-0.0577 (4)	0.0115 (2)	0.3989 (4)	0.038 (2)
O23'	-0.1376 (4)	0.0736 (2)	0.2246 (4)	0.039 (2)
C23'	-0.1932 (7)	0.0225 (3)	0.1425 (7)	0.054 (3)
N1	0.2596 (4)	0.2680 (2)	0.1376 (4)	0.031 (2)
C2	0.2312 (5)	0.3291 (2)	0.1778 (5)	0.024 (2)
C3	0.1664 (5)	0.3685 (2)	0.0519 (5)	0.026 (2)
O3	0.1729 (4)	0.4299 (2)	0.0860 (4)	0.031 (2)
C4	0.0233 (5)	0.3457 (2)	-0.0142 (5)	0.025 (2)
O4	-0.0291 (3)	0.3806 (2)	-0.1351 (3)	0.029 (1)
C5	-0.0767 (5)	0.3479 (2)	0.0736 (5)	0.026 (2)
C6	-0.1739 (6)	0.3995 (3)	0.0382 (7)	0.038 (2)
C7	-0.1836 (6)	0.4437 (3)	0.1180 (6)	0.040 (3)
C8	-0.0856 (6)	0.4517 (3)	0.2535 (7)	0.039 (3)
N9	0.0347 (4)	0.4151 (2)	0.2634 (4)	0.030 (2)
C10	0.1367 (7)	0.4142 (3)	0.3955 (7)	0.045 (3)
C11	0.1968 (6)	0.3514 (3)	0.4101 (6)	0.032 (2)
C12	0.1382 (6)	0.3210 (2)	0.2739 (5)	0.028 (2)
C13	0.1279 (5)	0.2535 (2)	0.2816 (5)	0.026 (2)
C14	0.0597 (5)	0.2192 (3)	0.3527 (5)	0.029 (2)
C15	0.0612 (5)	0.1569 (2)	0.3460 (5)	0.024 (2)
C16	0.1391 (5)	0.1305 (2)	0.2685 (5)	0.026 (2)
C17	0.2084 (6)	0.1647 (2)	0.1990 (5)	0.030 (2)
C18	0.2012 (5)	0.2262 (2)	0.2050 (5)	0.025 (2)
C19	0.0002 (5)	0.3525 (2)	0.2235 (5)	0.026 (2)
C20	-0.1593 (6)	0.2882 (3)	0.0443 (6)	0.038 (2)
C21	-0.2678 (6)	0.2783 (3)	0.1163 (8)	0.054 (3)
C22	-0.0819 (6)	0.3502 (3)	-0.2498 (6)	0.036 (2)
O22	-0.1093 (4)	0.2984 (2)	-0.2551 (4)	0.049 (2)
C23	0.2494 (6)	0.3617 (3)	-0.0472 (6)	0.033 (2)
O23	0.2191 (4)	0.3303 (2)	-0.1456 (4)	0.047 (2)
C24	0.4441 (7)	0.3920 (3)	-0.1045 (7)	0.054 (3)
O24	0.3610 (4)	0.3949 (2)	-0.0143 (4)	0.039 (2)
C25	0.1678 (8)	0.0401 (3)	0.1550 (6)	0.053 (3)
O25	0.1448 (4)	0.0692 (2)	0.2694 (3)	0.034 (1)
C26	-0.1028 (8)	0.3906 (3)	-0.3671 (6)	0.061 (3)
C27	0.3915 (6)	0.2546 (3)	0.1216 (7)	0.051 (3)
O1A	0.5555 (5)	0.3497 (2)	0.4572 (5)	0.076 (2)
C2A	0.605 (1)	0.3639 (4)	0.3557 (9)	0.100 (4)
O1B	0.5871 (7)	0.4334 (3)	0.6620 (7)	0.125 (3)
C2B	0.495 (1)	0.4811 (4)	0.6281 (9)	0.117 (5)

SHELXTL-Plus (Sheldrick, 1988). The positional and thermal parameters for the non-H atoms are listed in Table 1.* The bond lengths and angles are

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles, H-bonding interactions and H-atom parameters and a unit-cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53891 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) for the non-H atoms of (1)

1	2	3	1-2	1-2-3
C2'	C1'	C18'	1.537 (9)	116.8 (4)
C18'	C1'		1.559 (8)	
C3'	C2'	C19'	1.553 (8)	106.8 (5)
C3'	C2'	C1'		114.2 (4)
C19'	C2'	C1'	1.523 (8)	111.3 (5)
C4'	C3'	C2'	1.509 (8)	117.5 (4)
O4'	C4'	C5'	1.455 (7)	108.3 (4)
O4'	C4'	C20'		107.4 (5)
O4'	C4'	C3'		107.9 (5)
C5'	C4'	C20'	1.539 (8)	111.6 (6)
C5'	C4'	C3'		110.7 (5)
C20'	C4'	C3'	1.529 (9)	110.8 (5)
N6'	C5'	C4'	1.437 (9)	110.4 (5)
C7'	N6'	C19'	1.424 (7)	119.4 (5)
C7'	N6'	C5'		123.8 (5)
C19'	N6'	C5'	1.451 (7)	111.8 (5)
C8'	C7'	N6'	1.55 (1)	112.4 (5)
C9'	C8'	C7'	1.505 (9)	116.3 (5)
C10'	C9'	C17'	1.430 (7)	106.6 (5)
C10'	C9'	C8'		120.7 (5)
C17'	C9'	C8'	1.367 (7)	132.6 (5)
C11'	C10'	C15'	1.392 (7)	117.8 (5)
C11'	C10'	C9'		134.0 (6)
C15'	C10'	C9'	1.404 (8)	108.2 (4)
C12'	C11'	C10'	1.389 (9)	119.4 (6)
C13'	C12'	C11'	1.39 (1)	121.7 (5)
C14'	C13'	C12'	1.377 (8)	120.1 (6)
C15'	C14'	C13'	1.391 (8)	118.2 (6)
N16'	C15'	C10'	1.370 (6)	106.3 (5)
N16'	C15'	C14'		131.0 (5)
C10'	C15'	C14'		122.8 (5)
C17'	N16'	C15'	1.386 (7)	110.2 (5)
C18'	C17'	C9'	1.531 (6)	135.4 (5)
C18'	C17'	N16'		115.4 (5)
C9'	C17'	N16'		108.6 (4)
C22'	C18'	C15'	1.543 (7)	110.1 (4)
C22'	C18'	C1'		103.1 (4)
C22'	C18'	C17'		111.3 (4)
C15'	C18'	C1'	1.547 (8)	110.4 (4)
C15'	C18'	C17'		105.5 (4)
C1'	C18'	C17'		116.4 (5)
C2'	C19'	N6'		106.7 (4)
C21'	C20'	C4'	1.50 (1)	115.9 (5)
O22'	C22'	O23'	1.202 (7)	124.5 (5)
O22'	C22'	C18'		124.8 (5)
O23'	C22'	C18'	1.333 (6)	110.5 (5)
C23'	O23'	C22'	1.443 (7)	115.1 (4)
C2	N1	C18	1.482 (7)	109.1 (5)
C18	N1	C27	1.401 (7)	118.0 (4)
C27	N1	C2	1.443 (8)	119.4 (4)
C3	C2	C12	1.561 (7)	114.0 (4)
C3	C2	N1		110.7 (4)
C12	C2	N1	1.578 (9)	106.0 (4)
O3	C3	C4	1.414 (6)	114.1 (4)
O3	C3	C23		105.7 (4)
O3	C3	C2		110.9 (4)
C4	C3	C23	1.523 (7)	108.4 (4)
C4	C3	C2		108.5 (4)
C23	C3	C2	1.520 (9)	109.0 (4)
O4	C4	C5	1.447 (6)	110.4 (4)
O4	C4	C3		106.6 (4)
C5	C4	C3	1.558 (8)	116.0 (4)
C22	O4	C4	1.346 (6)	117.1 (4)
C6	C5	C19	1.502 (8)	108.1 (5)
C6	C5	C20		108.7 (4)
C6	C5	C4		112.5 (5)
C19	C5	C20	1.539 (7)	110.5 (4)
C19	C5	C4		111.3 (4)
C20	C5	C4	1.563 (8)	105.8 (4)
C7	C6	C5	1.312 (9)	126.0 (5)
C8	C7	C6	1.493 (8)	122.4 (6)
N9	C8	C7	1.460 (8)	109.3 (5)
C10	N9	C19	1.473 (7)	107.5 (4)
C10	N9	C8		115.9 (5)
C19	N9	C8	1.474 (6)	112.3 (4)
C11	C10	N9	1.524 (8)	105.5 (5)
C12	C11	C10	1.533 (7)	105.9 (4)
C13	C12	C19	1.517 (7)	113.8 (4)
C13	C12	C2		102.2 (4)
C13	C12	C11		114.0 (4)
C19	C12	C2	1.536 (7)	113.4 (4)
C19	C12	C11		101.2 (4)
C2	C12	C11		112.7 (5)
C14	C13	C18	1.385 (8)	120.3 (5)

Table 2 (cont.)

1	2	3	1-2	1-2-3
C14	C13	C12		129.2 (5)
C18	C13	C12	1.384 (8)	110.5 (5)
C15	C14	C13	1.395 (7)	120.8 (5)
C16	C15	C18'	1.416 (8)	121.5 (4)
C16	C15	C14		117.4 (5)
C18'	C15	C14		120.9 (5)
C17	C16	O25	1.381 (9)	121.9 (5)
C17	C16	C15		121.8 (5)
O25	C16	C15	1.373 (6)	116.3 (5)
C18	C17	C16	1.380 (7)	119.0 (6)
N1	C18	C13		112.1 (5)
N1	C18	C17		127.3 (5)
C13	C18	C17		120.6 (5)
C5	C19	N9		111.3 (4)
C5	C19	C12		118.2 (5)
N9	C19	C12		102.4 (4)
C21	C20	C5	1.53 (1)	117.4 (5)
O22	C22	C26	1.188 (7)	125.2 (5)
O22	C22	O4		124.3 (5)
C26	C22	O4	1.484 (9)	110.5 (5)
O23	C23	O24	1.208 (7)	122.7 (6)
O23	C23	C3		125.0 (5)
O24	C23	C3	1.326 (7)	112.3 (5)
O24	C24		1.438 (9)	
C23	O24	C24		115.9 (5)
O25	C25		1.433 (8)	
C16	O25	C25		117.7 (4)
C2A	O1A		1.34 (1)	
C2B	O1B		1.40 (1)	

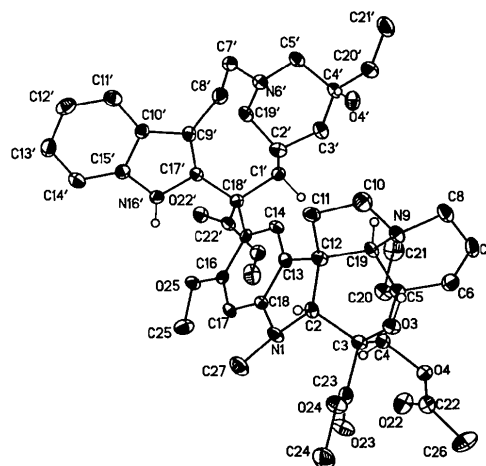


Fig. 1. View of $C_{46}H_{58}N_4O_9$ (1) showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Most H atoms were removed for clarity. H atoms represented as spheres of arbitrary size. The methanol molecules are not shown.

listed in Table 2. The atom-labeling scheme is shown in Fig. 1. Other computer programs used in this work are listed elsewhere (Gadol & Davis, 1982).

Related literature. Bisindole derivatives of (1) have been prepared previously (Kutney, Beck, Bylisma, Cook, Cretney, Fuji, Imhof & Treasurywala, 1975; Langlois, Gueritte, Langlois & Potier, 1976; Potier, 1980; Kuehne, Zebowitz, Bornmann & Marko, 1987; Kuehne & Bornmann, 1989).

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The Structure at 198 K of (1*R*,5*R*,15*R*,16*R*)-5-Isopropenyl-2-methyl-1-[*N*-(*trans*-2-phenylcyclohexyloxycarbonyl)amino]-2-cyclohexene

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Abstract. *trans*-2-Phenylcyclohexyl *N*-(5-isopropenyl-2-methyl-2-cyclohexan-1-yl)carbamate, C₂₃H₃₁NO₂, *M_r* = 353.50, orthorhombic, *P*2₁2₁2₁, *a* = 8.813 (2), *b* = 9.043 (2), *c* = 25.643 (5) Å, *V* = 2043.6 (8) Å³, *Z* = 4, *D_x* = 1.15 g cm⁻³ (198 K), Mo *Kα* radiation, λ = 0.7107 Å, μ = 0.6734 cm⁻¹, *F*(000) = 768, *T* = 198 K, *R* = 0.0547 for 1772 reflections [*F_o* ≥ 4σ(*F_o*)]. Molecules are H-bonded into infinite columns parallel to *a*. The H bond involves the NH group and the carbonyl O atom of the carbamate moiety with relevant parameters: N11—H11…O13 (related by ½ + *x*, ½ - *y*, -*z*); N…O 2.910 (5), H…O 2.11 (5) Å, N—H…O 159 (4)°.

Experimental. The carbamate (1) was prepared from the adduct formed from (*R*)-limonene with the *N*-sulfinylcarbamate of (1*R*)-*trans*-2-phenylcyclohexanol (Whitesell & Carpenter, 1987; Whitesell, Carpenter, Yaser & Machajewski, 1990) by reaction with hexamethyldisilazane followed by thermal rearrangement (Yaser, 1990). X-ray structural analy-

sis was used to confirm the stereochemistry of the chiral center bearing nitrogen (C1) and independently confirmed by internal comparison with the absolute stereochemistry of the *trans*-2-phenylcyclohexanol used (Whitesell & Lawrence, 1986). Crystals were obtained by slow evaporation from hexanes. The data crystal was a clear, colorless needle of approximate dimensions 0.11 × 0.11 × 0.29 mm; the data were collected on a Nicolet R3 diffractometer using a graphite monochromator and a Nicolet LT-2 low-temperature delivery system; lattice parameters were obtained from the least-squares refinement of 40 reflections with 20.2 < 2θ < 23.5°; ω scan technique with a 2θ range from 4.0–52.5° and a 1.2° ω scan at 5–10° min⁻¹ (*h* = -11 → 11, *k* = -12 → 12, *l* = 0 → 32). Two symmetry equivalent octants of data were collected (*hkl* and -*h*, -*k*, *l*) yielding a total of 4788 reflections of which 2417 were unique (*R_{int}* = 0.0198); four reflections (114, 132, 124, 125) were remeasured every 96 reflections to monitor instrument and crystal stability; a smoothed curve of the intensities of these check reflections was used to scale the data; the scaling factor ranged from 0.9912–1.014; the data were also corrected for Lp effects and absorption (based on crystal face measurements; transmission factor range was from 0.9832–0.9866). The data reduction, absorption and decay correction were applied using the Nicolet XRD *SHELXTL-Plus* software package (Sheldrick, 1988); reflections having *F_o* < 4σ(*F_o*) were considered unobserved (645

