

**Discussion.** The atomic coordinates are listed in Table 1,\* bond distances and bond angles are given in Figs. 1 and 2 for DBA and PMDA. The bonding geometry obtained for the PMDA molecule is in good agreement with that found in the low-temperature crystal structure determination for anthracene-PMDA (Robertson & Stezowski, 1978). The bond lengths in the DBA molecule are different from those given by Trotter (1958) for uncomplexed DBA, but because of the low accuracy of the latter work this comparison is not useful. The C—C bond distances in the DBA molecule are close to those found in unsubstituted uncomplexed anthracene (Lehmann & Pawley, 1972). Both molecules are planar, the maximum deviations from the mean planes of DBA and PMDA molecules (neglecting H atoms) being 0.007 and 0.009 Å respectively.

The crystal is built up of stacks along *a* of alternating donor DBA and acceptor PMDA molecules charac-

teristic of  $\pi$ - $\pi$  *D:A* complexes. The intrastack interplanar distance between donor and acceptor mean planes is 3.36 Å; the interplanar angle is 0.5°, those between the normals to the DBA and PMDA planes and the *a* axis are 20.1 and 19.6° respectively. The relative orientation of the molecules (Fig. 3) is very similar to that found in PMDA-anthracene (Robertson & Stezowski, 1978).

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\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43515 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Structure of *tert*-Butoxycarbonyl-L-alanyl-L-asparaginy-L-proline Benzyl Ester

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**Abstract.**  $C_{24}H_{34}N_4O_7$ ,  $M_r = 490.56$ , orthorhombic,  $P2_12_1$ ,  $a = 15.874$  (5),  $b = 18.080$  (8),  $c = 9.015$  (2) Å,  $V = 2588$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.253$  (2),  $D_x = 1.259$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 7.35$  cm<sup>-1</sup>,  $F(000) = 1048$ ,  $T = 297$  K,  $R = 0.058$  for 2516 independent reflections. The molecule adopts a folded conformation with Ala-Asn at the corner, although no intramolecular hydrogen bond is present. The proline ring has a type *B* conformation ( $\chi_1 = 19.4^\circ$ ). Cylindrical columns are formed along a diad screw axis by hydrogen bonds between the carbamoyl group of Asn and the backbone peptide groups.

**Introduction.** The tandemly repeating structure of Asn-Ala-Asn-Pro is found in the circum sporozoite (CS) protein of the human malaria parasite *Plasmodium falciparum* (Enea, Ellis, Zavala, Arnot, Asavanich, Masuda, Quakyi & Nussenzweig, 1984; Dame, Williams, McCutchan, Weber, Wirtz, Hockmeyer, Maloy, Haynes, Schneider, Roberts, Sanders, Reddy, Diggs & Miller, 1984) and is essential for the biological function of the CS protein (Ballou, Rothbard, Wirtz, Gordon, Williams, Gore, Schneider, Hollingdale, Beaudoin, Maloy, Miller & Hockmeyer, 1985). Three-dimensional studies of this repeating structure can provide useful information on conformational characteristics and on the possible application of artificial vaccines against *Plasmodium malaria*.

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As part of structure analyses of the repeating amino acid sequence, the present paper is concerned with the crystal structure of the tripeptide, *tert*-butoxycarbonyl-L-alanyl-L-asparaginyl-L-proline benzyl ester (Boc-Ala-Asn-Pro-OBzl).

**Experimental.** Synthesized by liquid-phase method. Colorless crystal,  $0.25 \times 0.35 \times 0.20$  mm, from ethyl acetate-hexane.  $D_m$  by flotation in benzene-carbon tetrachloride. Rigaku four-circle diffractometer with graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å). Cell parameters from 22 reflections with  $24 < \theta < 31^\circ$ . Intensity data measured by  $\omega$ - $2\theta$  continuous scan mode, scan speed  $5^\circ \text{ min}^{-1}$  ( $\theta$ ), scan range  $(1.2 + 0.15 \tan \theta)^\circ$ , 5 s stationary background counts.  $2\theta_{\text{max}} = 130^\circ$  ( $h$  0-18,  $k$  0-21,  $l$  0-10). Four reference reflections monitored every 100 reflections showed no significant variation in intensity during data collection ( $< 3\%$ ). 2516 independent reflections measured; 2277 with  $F_o > 3\sigma(F_o)$ . No absorption correction. Structure solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H atoms located on a difference map. Block-diagonal least-squares refinement with anisotropic temperature factors for C, N and O atoms and isotropic ones for H atoms converged at  $R = 0.058$ ,  $wR = 0.077$ ;  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = 0.35$  for  $F_o = 0.0$  and  $w = 1.0/[\sigma(F_o)]^2 -$

$0.0098|F_o| + 0.00227|F_o|^2$  for  $F_o > 0.0$ ;  $S = 1.59$ ;  $(\Delta/\sigma)_{\text{max}} = 0.45$  for non-H atoms;  $(\Delta\rho)_{\text{max}} = 0.28$ ,  $(\Delta\rho)_{\text{min}} = -0.18 \text{ e } \text{Å}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). All numerical computations performed on an ACOS 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University using *The Universal Crystallographic Computing System* (1979).

**Discussion.** The atomic parameters of the non-H atoms are given in Table 1.\* The bond lengths and angles are listed in Table 2. A perspective view of Boc-Ala-Asn-Pro-OBzl is shown in Fig. 1.

The bond lengths and angles agree reasonably well with those of similar oligopeptides. The torsion angles of the backbone chain, according to the definition of the IUPAC-IUB Commission on Biochemical

\* Lists of structure factors, anisotropic temperature factors, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43591 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

Table 1. Positional and equivalent isotropic thermal parameters of non-H atoms with e.s.d.'s in parentheses

	$x$	$y$	$z$	$B_{\text{eq}}(\text{Å}^2)$
$B_{\text{eq}} = \frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33})$				
N(1)	0.4981 (2)	0.5435 (2)	0.8322 (3)	3.7 (1)
C(1A)	0.4657 (2)	0.5531 (2)	0.9822 (4)	3.5 (1)
C(1B)	0.4205 (3)	0.6279 (2)	0.9917 (5)	5.0 (2)
C(1')	0.4054 (2)	0.4910 (2)	1.0276 (4)	3.2 (1)
O(1)	0.4061 (2)	0.4664 (2)	1.1540 (3)	4.3 (1)
N(2)	0.3534 (2)	0.4682 (2)	0.9223 (3)	3.5 (1)
C(2A)	0.3010 (2)	0.4032 (2)	0.9308 (4)	3.2 (1)
C(2B)	0.2106 (2)	0.4236 (2)	0.8874 (4)	3.3 (1)
C(2C)	0.1706 (2)	0.4698 (2)	1.0099 (4)	3.6 (1)
O(2D)	0.1699 (2)	0.4477 (2)	1.1391 (3)	4.8 (1)
N(2D)	0.1358 (3)	0.5320 (2)	0.9704 (4)	5.6 (2)
C(2')	0.3370 (2)	0.3460 (2)	0.8236 (4)	3.2 (1)
O(2)	0.3832 (1)	0.3646 (1)	0.7218 (3)	4.2 (1)
N(3)	0.3148 (2)	0.2751 (2)	0.8411 (3)	3.4 (1)
C(3A)	0.3473 (2)	0.2210 (2)	0.7332 (4)	3.7 (1)
C(3B)	0.3096 (3)	0.1480 (2)	0.7852 (5)	5.2 (2)
C(3C)	0.2373 (4)	0.1684 (3)	0.8809 (7)	7.1 (3)
C(3D)	0.2561 (2)	0.2428 (2)	0.9471 (5)	4.3 (2)
C(3')	0.3159 (2)	0.2422 (2)	0.5806 (4)	4.4 (2)
O(3)	0.2469 (2)	0.2648 (2)	0.5536 (3)	6.0 (1)
C(1)N	0.5531 (2)	0.4884 (2)	0.8019 (5)	4.0 (2)
O(2)N	0.5893 (2)	0.4529 (2)	0.8949 (4)	6.5 (2)
O(3)N	0.5637 (2)	0.4825 (2)	0.6555 (3)	4.8 (1)
C(4)N	0.6199 (3)	0.4261 (3)	0.5900 (6)	5.4 (2)
C(5)N	0.7091 (3)	0.4408 (3)	0.6318 (7)	7.3 (3)
C(6)N	0.5938 (4)	0.3497 (3)	0.6363 (9)	9.1 (4)
C(7)N	0.6077 (4)	0.4419 (5)	0.4240 (7)	9.6 (4)
O(8)C	0.3749 (2)	0.2305 (2)	0.4784 (3)	5.0 (1)
C(9)C	0.3493 (3)	0.2533 (3)	0.3300 (5)	6.4 (2)
C(10)C	0.4172 (3)	0.2331 (2)	0.2221 (4)	4.6 (2)
C(11)C	0.4327 (3)	0.1615 (2)	0.1857 (5)	5.2 (2)
C(12)C	0.4897 (3)	0.1426 (3)	0.0749 (6)	5.7 (2)
C(13)C	0.5292 (3)	0.1962 (3)	-0.0017 (5)	5.8 (2)
C(14)C	0.5162 (3)	0.2703 (3)	0.0320 (6)	6.2 (2)
C(15)C	0.4607 (3)	0.2870 (3)	0.1460 (6)	5.9 (2)

Table 2. Bond lengths (Å) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

N(1)-C(1A)	1.457 (5)	C(3B)-C(3C)	1.483 (8)
N(1)-C(1)N	1.353 (5)	C(3C)-C(3D)	1.501 (7)
C(1A)-C(1B)	1.533 (6)	C(3')-O(3)	1.194 (5)
C(1A)-C(1')	1.531 (5)	C(3')-O(8)C	1.331 (5)
C(1')-O(1)	1.223 (4)	C(1)N-O(2)N	1.203 (5)
C(1')-N(2)	1.324 (4)	C(1)N-O(3)N	1.335 (5)
N(2)-C(2A)	1.443 (4)	O(3)N-C(4)N	1.479 (6)
C(2A)-C(2B)	1.533 (5)	C(4)N-C(5)N	1.489 (8)
C(2A)-C(2')	1.526 (5)	C(4)N-C(6)N	1.50 (1)
C(2B)-C(2C)	1.523 (5)	C(4)N-C(7)N	1.54 (1)
C(2C)-O(2D)	1.231 (5)	O(8)C-C(9)C	1.458 (6)
C(2C)-N(2D)	1.303 (5)	C(9)C-C(10)C	1.498 (7)
C(2')-O(2)	1.222 (4)	C(10)C-C(11)C	1.358 (6)
C(2')-N(3)	1.340 (4)	C(10)C-C(15)C	1.377 (7)
N(3)-C(3A)	1.472 (5)	C(11)C-C(12)C	1.391 (7)
N(3)-C(3B)	1.457 (5)	C(12)C-C(13)C	1.345 (8)
C(3A)-C(3D)	1.524 (6)	C(13)C-C(14)C	1.390 (8)
C(3A)-C(3')	1.513 (5)	C(14)C-C(15)C	1.386 (8)
C(1A)-N(1)-C(1)N	120.2 (3)	C(3B)-C(3C)-C(3D)	107.5 (4)
N(1)-C(1A)-C(1B)	108.8 (3)	N(3)-C(3D)-C(3C)	103.0 (4)
N(1)-C(1A)-C(1')	112.4 (3)	C(3A)-C(3')-O(3)	125.0 (4)
C(1B)-C(1A)-C(1')	109.8 (3)	C(3A)-C(3')-O(8)C	111.0 (3)
C(1A)-C(1')-O(1)	120.7 (3)	O(3)-C(3')-O(8)C	124.0 (4)
C(1A)-C(1')-N(2)	115.2 (3)	N(1)-C(1)N-O(2)N	124.1 (4)
O(1)-C(1')-N(2)	124.1 (3)	N(1)-C(1)N-O(3)N	109.9 (3)
C(1')-N(2)-C(2A)	125.1 (3)	O(2)N-C(1)N-O(3)N	125.9 (4)
N(2)-C(2A)-C(2B)	109.3 (3)	C(1)N-O(3)N-C(4)N	121.7 (3)
N(2)-C(2A)-C(2')	107.6 (3)	O(3)N-C(4)N-C(5)N	110.5 (4)
C(2B)-C(2A)-C(2')	110.6 (3)	O(3)N-C(4)N-C(6)N	110.9 (5)
C(2A)-C(2B)-C(2C)	109.7 (3)	O(3)N-C(4)N-C(7)N	100.6 (4)
C(2B)-C(2C)-O(2D)	120.8 (3)	N(1)N-C(4)N-C(6)N	111.0 (5)
C(2B)-C(2C)-N(2D)	116.9 (3)	C(5)N-C(4)N-C(7)N	109.4 (5)
O(2D)-C(2C)-N(2D)	122.3 (4)	C(6)N-C(4)N-C(7)N	114.0 (5)
C(2A)-C(2')-O(2)	121.0 (3)	C(3')-O(8)C-C(9)C	113.2 (4)
C(2A)-C(2')-N(3)	118.3 (3)	O(8)C-C(9)C-C(10)C	109.0 (4)
O(2)-C(2')-N(3)	120.7 (3)	C(9)C-C(10)C-C(11)C	121.4 (4)
C(2')-N(3)-C(3A)	117.7 (3)	C(9)C-C(10)C-C(15)C	120.8 (4)
C(2')-N(3)-C(3D)	129.0 (3)	C(11)C-C(10)C-C(15)C	117.6 (4)
C(3A)-N(3)-C(3D)	113.0 (3)	C(10)C-C(11)C-C(12)C	121.7 (4)
N(3)-C(3A)-C(3B)	103.6 (3)	C(11)C-C(12)C-C(13)C	119.7 (5)
N(3)-C(3A)-C(3')	108.5 (3)	C(12)C-C(13)C-C(14)C	120.9 (5)
C(3B)-C(3A)-C(3')	111.7 (3)	C(13)C-C(14)C-C(15)C	117.7 (5)
C(3A)-C(3B)-C(3C)	105.4 (4)	C(10)C-C(15)C-C(14)C	122.3 (5)

Nomenclature (1970), are as follows:  $\phi_1 = -69.9$  (4),  $\psi_1 = -39.6$  (4),  $\omega_1 = 169.4$  (3) $^\circ$  for Ala,  $\phi_2 = -109.2$  (3),  $\psi_2 = 161.4$  (3),  $\omega_2 = 177.6$  (3) $^\circ$  for Asn, and  $\phi_3 = -60.7$  (4),  $\psi_3 = 141.8$  (3) $^\circ$  for Pro. The backbone chain of the compound takes a folded conformation at the Ala-Asn site. This conformation is different from the frequently observed  $\beta$ -turn form (Ashida, Yamane & Tanaka, 1980), and appears to be a new type of folding pattern. There is no intramolecular hydrogen bonding. The folded conformation without intramolecular hydrogen bonding has also been seen in Boc-Gly-Gly-Phe-OC<sub>2</sub>H<sub>5</sub> crystals (Ishida, Tanabe & Inoue, 1983).

The conformation of the Asn side chain is defined by two torsion angles  $\chi_1$ [N(2)–C(2A)–C(2B)–C(2C)] and  $\chi_2$ [C(2A)–C(2B)–C(2C)–N(2D)]. The observed value of  $-71.6$  (3) $^\circ$  for  $\chi_1$  corresponds to the most sterically favourable conformation with the carbamoyl

group *gauche* to the NH group and *trans* to the CO group (Benedetti, Morelli, Nemethy & Scheraga, 1983). However, the observed value  $\chi_2$ [ $-53.3$  (4) $^\circ$ ] deviates from most conformations observed in the Asn side chain of peptides ( $\approx -160^\circ$ ) (Benedetti, Morelli, Nemethy & Scheraga, 1983), and this is due to the participation of the carbamoyl group in hydrogen-bond formation.

The five-membered ring of the Pro residue has the torsion angles  $\chi_1$ [N(3)–C(3A)–C(3B)–C(3C)] =  $19.4$  (4) $^\circ$ ,  $\chi_2$ [C(3A)–C(3B)–C(3C)–C(3D)] =  $-27.9$  (5) $^\circ$ ,  $\chi_3$ [C(3B)–C(3C)–C(3D)–N(3)] =  $24.7$  (5) $^\circ$ ,  $\chi_4$ [C(3A)–N(3)–C(3D)–C(3C)] =  $-12.4$  (4) $^\circ$  and  $\theta$ [C(3D)–N(3)–C(3A)–C(3B)] =  $-4.2$  (4) $^\circ$ . Therefore the proline ring belongs to conformation *B*: in class *B*, the torsion angle  $\chi_1$  takes a positive value (Balasubramanian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran, 1971), and the ring puckering is defined as a *C<sub>s</sub>-C<sup>γ</sup>-endo-C<sup>β</sup>-exo* form (Ashida & Kakudo, 1974).

Hydrogen bonds are formed between the carbamoyl and peptide groups which are related by a diad screw axis parallel to the *c* direction (see Fig. 2) and consequently form an infinite cylindrical column. The hydrogen-bonding parameters are as follows: N(2)(*x*, *y*, *z*)...O(2D)(0.5–*x*, 1–*y*, *z*–0.5) =  $2.944$  (4) Å, H(2)...O(2D) =  $1.91$  (6) Å,  $\angle$ N(2)–H(2)...O(2D) =  $168$  (5) $^\circ$ ; N(2D)(*x*, *y*, *z*)...O(1)(0.5–*x*, 1–*y*, *z*–0.5) =  $2.929$  (5) Å, H(2Da)...O(1) =  $2.00$  (5) Å,  $\angle$ N(2D)–H(2Da)...O(1) =  $166$  (5) $^\circ$ ; N(2D)(*x*, *y*, *z*)...O(2)(0.5–*x*, 1–*y*, *z*+0.5) =  $2.953$  (5) Å, H(2Db)...O(2) =  $1.97$  (5) Å,  $\angle$ N(2D)–H(2Db)...O(2) =  $170$  (5) $^\circ$ . N(1) forms a short contact [ $= 3.189$  (4) Å] with a neighbouring O(2D) atom (0.5–*x*, 1–*y*, *z*–0.5), probably owing to an electrostatic interaction. The neighbouring columns contact with each other by van der Waals forces.

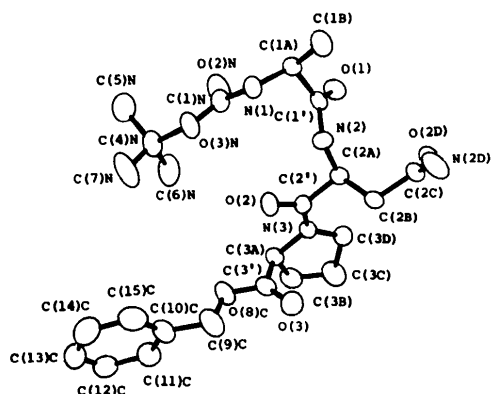


Fig. 1. A perspective view of Boc-Ala-Asn-Pro-OBzl, along with the atomic numbering.

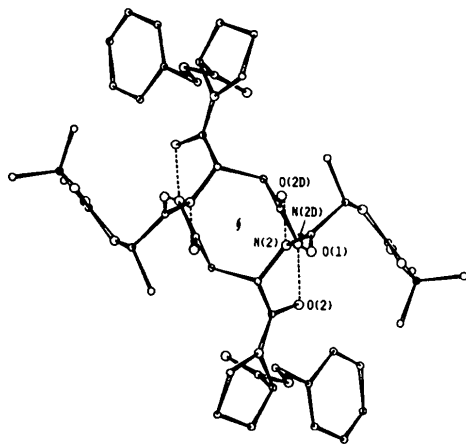


Fig. 2. Hydrogen-bonding mode observed in the crystal. The dotted lines represent hydrogen bonds.

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## A Dihydrothiocyanate Salt of a 14-Membered Tetraaza Macrocycle

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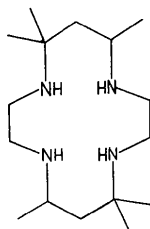
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**Abstract.**  $C_{16}H_{38}N_4^{2+} \cdot 2SCN^-$ ,  $M_r = 402.68$ , monoclinic,  $P2_1/c$ ,  $a = 7.512$  (7),  $b = 14.430$  (9),  $c = 10.691$  (8) Å,  $\beta = 104.0$  (1)°,  $U = 1124.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.15$  (2),  $D_x = 1.16$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 2.11$  cm<sup>-1</sup>,  $F(000) = 440$ , room temperature, final  $R = 0.071$  for 1039 [ $I > 3\sigma(I)$ ] independent observed reflections. The compound may be considered as a salt between hydrogen thiocyanate and the macrocyclic base *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*L*) in the form  $[LH_2]^{2+} \cdot 2[SCN]^-$ . Two of the N atoms (symmetry-related) in *L* are protonated. The thiocyanate ion is hydrogen bonded to two different macrocycles through the N and S atoms: N...N 2.78 (1) and S...N 3.50 (2) Å. There is also intramolecular hydrogen bonding to form a six-membered ring in the chair form with N...N 2.85 (2) Å.

**Introduction.** The macrocycle *L* (below) was first prepared by Curtis (1964) in a template reaction between nickel tris(ethylenediamine) and acetone; the free base was obtained by removing the metal ion from the resulting complex. Structure of the free base in the form of the dihydrate was reported by Gluźniński, Krajewski & Urbańczyk-Lipkowska (1980), while those of the salts are not known.



**Experimental.** Long crystals of the compound isolated as by-products in the preparation of the Fe<sup>II</sup> thiocyanate complex of the macrocycle. Slow recrystallization of the metal complex from chloroform-deposited crystals, the microanalysis of which showed that it was a salt of the macrocycle with hydrogen thiocyanate in the ratio of 1:2 [ $C_{16}H_{36}N_4 \cdot 2HNCS$ : Calc. % C = 53.7, H = 9.5, N = 20.9, S = 15.9; found % C = 53.5, H = 9.8, N = 20.6, S = 15.6; melting point 510 K (decomposed)].

Density measured by flotation in  $CCl_4$ /ligroin. Crystal of approximate size  $0.2 \times 0.2 \times 0.5$  mm mounted on Stoe STADI-2 diffractometer to rotate about the *a* axis. Cell dimensions calculated from  $2\theta$  measurements of 20 reflections in 30 to 40° range. Intensity data collected *via* variable-width  $\omega$  scan, background counts 20 s, step-scan rate  $0.033^\circ$  s<sup>-1</sup>, width  $(1.5 + \sin\mu/\tan\theta)$ . Absorption and extinction corrections not applied. Standard reflections *h*22 measured every 20 measurements for each layer: no significant change in intensity. 1947 reflections measured with  $2\theta_{\max} 50^\circ$ ,  $h$  0 to 6,  $k$  0 to 16 and  $l$  -12 to 12. 1548 unique reflections.  $R_{\text{int}} = 0.02$ . 1039 data with  $I > 3\sigma(I)$  used in subsequent calculations.

Structure solved by direct methods using *SHELX76* (Sheldrick, 1976) on Amdahl V7A computer. All non-hydrogen atoms refined anisotropically. Positional and thermal parameters of H atoms bonded to N – one to N(1) and two to N(4) – allowed to refine independently. H atoms bonded to the same C refined as rigid group with common thermal parameter and fixed C–H distance of 0.95 Å. Layers were given individual scale factors. Weighting scheme  $w = 1/[\sigma^2(F) + 0.002F^2]$ .  $\sigma(F)$  taken from counting statistics. Final  $R(F) = 0.071$  ( $wR = 0.080$ ,  $S = 1.878$ ) and final shift/e.s.d.  $< 0.03$ .