

responsible for the shortening of the (Cl)C—S bond (1.79 vs 1.84 Å). The present result confirms that stereoelectronic effects are not appreciable in (3b), a fact that could already be anticipated from the antiperiplanar arrangement of all the S—C—S—C moieties in the molecule. Among the bond angles, the C—S—C values are normal (Abrahams, 1956), as also occurs in (5) and (6). The same applies to the C—C—S angles. However, the S—C—S angle is significantly smaller than the corresponding value in (4) (101.4 vs 104°). If account is taken of the fact that the distance between S(2) and S(5) is only 2.82 Å, much smaller than the sum of van der Waals radii (3.70 Å), the small value of the S—C—S angle may indicate the existence of an attractive non-bonded interaction between the sulfur atoms. However, the possibility that the S—C—S angle could be forced to be small by the small intraannular C—S—C angles cannot be discounted. Finally, both six-membered rings have a slightly skew chair form. The S(2)—C(1)—C(1<sup>b</sup>)—S(5<sup>i</sup>) dihedral angle has a value of -66.4 (1)°, intermediate between that of 63.5° reported for 1,4-dithiane (5) and that of 70.9° reported for the S—CH<sub>2</sub>—CH<sub>2</sub>—S moiety of trans-2,3-dichloro-1,4-dithiane, (6). On the other hand, the peripheral S(2)—C(3)—C(4)—S(5<sup>i</sup>) dihedral angle has a very similar value of -68.1 (1)°. The discrepancy between this torsion angle and that calculated in solution by the *R*-value method (62.3°), can be attributed to the non-bonded attraction between the sulfur atoms in the crystal, which could be partially mitigated by solvation. It is worth noting that X-ray-measured and *R*-value-calculated torsional angles rarely differ by more than 1–2° over the range from 47 to 69°, so that a difference of 6° cannot be attributed to standard errors (Lambert, 1971). The asymmetry parameters (Duax, Weeks &

Rohrer, 1976) for the rings are  $\Delta C_m^1 = 6.1$ ;  $\Delta C_m^2 = 1.0$ ;  $\Delta C_m^3 = 5.9$ ;  $\Delta C_2^{1-2} = 7.5$ ;  $\Delta C_2^{2-3} = 6.9$  and  $\Delta C_2^{3-4} = 2.5^\circ$ .

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#### References

- ABRAHAMS, S. C. (1956). *Q. Rev. Chem. Soc.* **10**, 414–426.  
 BARRICELLI-BRAHDE, L. (1954). *Acta Chem. Scand.* **8**, 1145–1151.  
 BOESEKEN, J., TELLEGEN, F. & COHEN-HENRIQUEZ, P. (1931). *Recl Trav. Chim. Pays-Bas*, **50**, 909–911.  
 BORREMANS, F., ANTEUNIS, M., SHMUELI, U., SCHLEIFER, L., SHVO, H. & FUCHS, B. (1984). *Tetrahedron*, **40**, 257–258.  
 DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9. New York: John Wiley.  
 FUCHS, B. & ELLENWEIG, A. (1979). *Recl Trav. Chim. Pays-Bas*, **98**, 326–328.  
 FUCHS, B., GOLDBERG, I. & SHMUELI, U. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 357–364.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 KALFF, H. T. & ROMERS, C. (1965). *Acta Cryst.* **18**, 164–168.  
 LAMBERT, J. B. (1971). *Acc. Chem. Res.* **4**, 87–96.  
 LAMBERT, J. B. & SUN, H. (1977). *Org. Magn. Res.* **9**(11), 621–626.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 MARSH, R. E. & MCCULLOUGH, J. D. (1951). *J. Am. Chem. Soc.* **73**, 1106–1109.  
 PERICÁS, M. A., RIERA, A. & GUILERA, J. (1986). *Tetrahedron*, **42**, 2717–2718.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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## 2,2,4,4,6,6-Hexa(1-pyrrolyl)cyclotri(phosphazene)

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**Abstract.** C<sub>24</sub>H<sub>24</sub>N<sub>9</sub>P<sub>3</sub>, *M<sub>r</sub>* = 531.4, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 13.683 (2), *b* = 9.474 (1), *c* = 20.789 (3) Å, β = 104.05 (1)°, *V* = 2614 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.35 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71073 Å, μ = 2.5 cm<sup>-1</sup>,

*F*(000) = 1104, *T* = 293 (2) K, *R* = 0.041 for 2711 unique observed reflections. The PN ring is planar within 0.11 (1) Å with average P—N distances of 1.583 (6) Å, P angles of 117.7 (4)° and N angles of

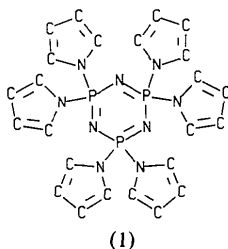
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121.1 (4)°. Exocyclic P–N distances average 1.671 (8) Å and NPN angles average 101.8 (5)°. The dihedral angles between the pyrrolyl rings and the PN ring vary from 63 (1) to 111 (1)°. The hybridization of the pyrrolyl N atoms varies from essential pure  $sp^2$  to a state with substantial pyramidalization.

**Introduction.** The synthesis of poly[di(pyrrolyl)phosphazene]  $[NP(NC_4H_4)_2]_x$  (PBPP) has recently been reported (Haddon, Stein, Chichester-Hicks, Marshall, Kaplan, Hellman & Bowmer, 1987). Subsequent electrochemical oxidation of PBPP was shown to produce fibrous black films of an electronically conducting polyphosphazene. Although the corresponding cyclic trimer, hexa(pyrrolyl)cyclotri(phosphazene) (1), was prepared over 25 years ago (McBee, Johncock, French & Braendlin, 1960), pyrrolylphosphazenes have received little mention in the open literature.

Compound (1)  $[NP(NC_4H_4)_2]_3$ , therefore provides an opportunity to examine aspects of the bonding and structure in pyrrolylphosphazenes, which may be of relevance in understanding the conformation and conductivity of PBPP.



**Experimental.** *Preparation of hexa(1-pyrrolyl)cyclotri(phosphazene) (1).* 5.9 g (0.15 mol) of potassium was refluxed with 20 ml (0.21 mol) of pyrrole in toluene (500 ml) with mechanical stirring, until all of the potassium had reacted. The slurry of potassium pyrrolide was allowed to cool, and a solution of 3.67 g (0.011 mol) of hexachlorocyclotri(phosphazene) in toluene (100 ml) was added drop-wise. At this point tetrabutylammonium bromide (1.0 g) was added and the mixture refluxed for 1 h and then allowed to stir overnight. The mixture was filtered and the solid washed with toluene. The filtrate was extracted twice with water and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator gave rise to a colorless solid. Recrystallization from heptane produced 2.74 g (47% yield) of large colorless crystals (suitable for crystallographic analysis). M.p. 475–477 K; lit. 471–473 K (McBee, Johncock, French & Braendlin, 1960).  $^1H$  NMR ( $CDCl_3, Me_4Si$ )  $\delta$  6.30(br), 6.84(br);  $^{13}C$  NMR ( $CDCl_3, Me_4Si$ )  $\delta$  113.5(br), 122.2(br);  $^{31}P$  NMR ( $CDCl_3, ext H_3PO_4$ )  $\delta$  2.82(br).

**Structure determination.** Colorless platelet data crystal 0.24 × 0.44 × 0.34 mm mounted on glass fiber.

Intensities measured with an Enraf–Nonius CAD-4 diffractometer using  $\omega$ - $2\theta$  scans of 4 to 16°  $min^{-1}$  in  $\theta$ . Unit cell determined from least-squares analysis of angle data for 16 reflections with  $12 < 2\theta < 16^\circ$ . Data collected to  $(\sin\theta)/\lambda$  of 0.60 Å $^{-1}$ ,  $0 \leq h \leq 13$ ,  $0 \leq k \leq 9$ ,  $-20 \leq l \leq 20$ . Three standard reflections (308, 537, 153) changed –1.9% over 42.1 h of data collection; no decay correction applied. 5125 reflections measured, 4598 unique ( $R_{int} = 0.04$ ), 1887 reflections with  $I < 3\sigma(I)$  considered unobserved. The analytical absorption correction ranged from 0.97 to 1.00. No extinction correction was made. Solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. Full-matrix least squares minimized  $\sum w(\Delta F)^2$ . H atoms found on difference Fourier maps and positions refined with constrained isotropic  $B = 1.2 \times B$  of bonded C atom. All non-H atoms refined anisotropically for 397 variables.  $R = 0.041$ ,  $wR = 0.047$ ,  $S = 1.26$ , where non-Poisson  $w^{-1} = [\sigma^2(I) + 0.0025I^2]/4F^2$ . Final  $(\Delta/\sigma)_{max} < 0.01$ ,  $\Delta\rho_{max} = 0.23$  (3) and  $\Delta\rho_{min} = -0.40$  (3)  $e \text{ \AA}^{-3}$  on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982) *SDP*.<sup>\*</sup> Table 1 gives the atom coordinates and Table 2 selected bond distances and angles. Fig. 1 shows the molecule with the numbering scheme.

**Discussion.** The preparation of (1) was found to be considerably improved by the use of a phase transfer catalyst (Austin, Riding & Allcock, 1983).

The phosphazene ring is planar within 0.11 (1) Å. The average P–N bond distance and the angles at P and N in the ring [1.583 (6) Å, 117.7 (4) and 121.1 (4)°, respectively] are comparable to the values found in other symmetrically substituted cyclotri(phosphazenes), *i.e.* 1.575 (4) Å, 118.4 (3) and 121.3 (4)° for the hexachloro (Bullen, 1971); 1.575 (2) Å, 117.3 (6) and 121.9 (6)° for the hexaphenoxy (Marsh & Trotter, 1971); 1.58 (3) Å, 119 (1) and 120 (2)° for the hexaimidazolyl (Ritchie, Fuller & Allcock, 1980); and 1.588 (5) Å, 116.7 (4) and 123.0 (4)° for the hexadimethylamino (Rettig & Trotter, 1973). The *exo* P–N bond distances average 1.671 (8) Å and are comparable to the 1.68 (1) Å distances found in the hexaimidazolyl molecule where the *exo*-N is also part of an aromatic ring (Ritchie, Fuller & Allcock, 1980), and longer than the 1.652 (4) Å values found in the

<sup>\*</sup> Tables of H-atom positions, anisotropic thermal parameters, intramolecular distances and angles, and observed and calculated structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44085 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hexadimethylamino (Rettig & Trotter, 1973). Paddock has concluded that in the cyclotetra(phosphazenes) the *exo* pyrazolyl group has a strong electron-withdrawing effect (Gallicano, Paddock, Rettig & Trotter, 1979). Based on the similarity in the  $^{31}\text{P}$  NMR chemical shifts, the same remarks may also apply to the cyclotri(phosphazenes):  $[\text{NP}(\text{pz})_2]_3$ ,  $0.3\sigma$  (Gallicano, Paddock, Rettig & Trotter, 1979);  $[\text{NP}(\text{imid})_2]_3$ ,  $2.2\delta$  (Ritchie, Fuller & Allcock, 1980);  $[\text{NP}(\text{pyrrolyl})_2]_3$ ,  $2.8\delta$ .

The one-center  $\pi$ -orbital-axis vector analysis (POAV1: Haddon & Scott, 1986; Haddon, 1986) of the pyrrolyl N atom (Table 3) shows that this atom exhibits considerable variability in its state of hybridization throughout the molecule. For example, the  $\sigma$ - $\pi$  bond angle ( $\theta_{\sigma\pi}$ ) spans almost  $6^\circ$  and the pyramidalization angle ( $\theta_{\sigma\pi} - 90$ ) ranges from  $0.8$  to  $6.7^\circ$ . Thus the hybridization of this atom varies from essentially pure  $sp^2$  to a state with substantial pyramidalization.

Table 1. Fractional atomic coordinates, equivalent isotropic thermal parameters and their *e.s.d.*'s

$$B_{\text{eq}} = \frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + acB_{13}\cos\beta).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
P(1)	0.27273 (6)	0.03406 (9)	0.09838 (4)	2.80 (2)
P(2)	0.09448 (6)	-0.02258 (9)	0.13315 (4)	2.75 (2)
P(3)	0.27633 (6)	-0.06799 (9)	0.22290 (4)	2.84 (2)
N(1)	0.1549 (2)	0.0072 (3)	0.0786 (1)	2.99 (6)
N(2)	0.1582 (2)	-0.0502 (3)	0.2065 (1)	3.05 (6)
N(3)	0.3336 (2)	-0.0156 (3)	0.1697 (1)	3.29 (6)
N(4)	0.3292 (2)	-0.0418 (3)	0.0444 (1)	3.23 (6)
N(5)	0.2919 (2)	0.2054 (3)	0.0868 (1)	3.14 (6)
N(6)	0.0162 (2)	-0.1563 (3)	0.1045 (1)	3.21 (6)
N(7)	0.0135 (2)	0.1057 (3)	0.1377 (1)	3.12 (6)
N(8)	0.3024 (2)	-0.2376 (3)	0.2421 (1)	3.38 (6)
N(9)	0.3306 (2)	0.0135 (3)	0.2939 (1)	3.19 (6)
C(1)	0.3237 (3)	0.0011 (4)	-0.0199 (2)	4.22 (9)
C(2)	0.3670 (3)	-0.0973 (5)	-0.0498 (2)	5.1 (1)
C(3)	0.3999 (3)	-0.2063 (5)	-0.0047 (2)	5.5 (1)
C(4)	0.3760 (3)	-0.1718 (4)	0.0523 (2)	4.57 (9)
C(5)	0.3858 (3)	0.2706 (4)	0.0977 (2)	4.9 (1)
C(6)	0.3734 (3)	0.4091 (4)	0.0933 (2)	5.2 (1)
C(7)	0.2723 (4)	0.4348 (5)	0.0801 (3)	8.0 (2)
C(8)	0.2222 (3)	0.3115 (4)	0.0757 (2)	5.9 (1)
C(9)	0.0435 (3)	-0.2753 (4)	0.0743 (2)	4.46 (9)
C(10)	-0.0209 (4)	-0.3791 (4)	0.0779 (2)	6.2 (1)
C(11)	-0.0920 (3)	-0.3267 (5)	0.1103 (2)	5.9 (1)
C(12)	-0.0676 (3)	-0.1933 (4)	0.1275 (2)	4.45 (9)
C(13)	0.0212 (3)	0.2024 (4)	0.1886 (2)	4.61 (9)
C(14)	-0.0499 (3)	0.3009 (4)	0.1691 (2)	5.7 (1)
C(15)	-0.1044 (3)	0.2687 (4)	0.1049 (2)	4.8 (1)
C(16)	-0.0652 (3)	0.1503 (4)	0.0864 (2)	4.19 (9)
C(17)	0.3977 (3)	-0.2970 (4)	0.2571 (2)	5.1 (1)
C(18)	0.3896 (3)	-0.4358 (4)	0.2667 (2)	5.6 (1)
C(19)	0.2887 (4)	-0.4643 (4)	0.2588 (2)	6.4 (1)
C(20)	0.2347 (3)	-0.3451 (4)	0.2432 (2)	4.8 (1)
C(21)	0.3323 (3)	-0.0325 (4)	0.3579 (2)	4.07 (8)
C(22)	0.3607 (3)	0.0759 (5)	0.3996 (2)	5.0 (1)
C(23)	0.3768 (3)	0.1933 (4)	0.3623 (2)	5.2 (1)
C(24)	0.3576 (3)	0.1559 (4)	0.2987 (2)	4.29 (9)

Since poly(phosphazenes) are generally insulators, the conductivity of oxidized PBPP (Haddon *et al.*, 1987) suggests that the pyrrolyl groups may have electro-polymerized to provide the conducting pathway. The distances and angles of (1) are therefore of interest in evaluating different linked pyrrolylphosphazene models. For models that involve the formation of C-C bonds between  $\alpha$ -C atoms of geminal pyrrolyl rings, the parameters of (1) show that these C atoms are separated by  $2.5\text{ \AA}$  when the rings are rotated to be coplanar. The formation of a  $1.5\text{ \AA}$  bond would require the *exo* N-P-N bond angle to close from  $103$  to  $81^\circ$ , or the P-N-C angle to close from  $126.6$  to  $105^\circ$  (or a combination). For models of PBPP involving a polyphosphazene backbone containing alternating *cis-trans* P-N linkages, the nearest contacts of  $\alpha$ -C atoms of pyrrolyl units on the same side of the backbone would be even longer at  $2.7\text{ \AA}$ . However, for the model of an all-*trans* (zigzag) polyphosphazene backbone with two rows of pyrrolyl groups each linked parallel to the backbone [the 'outrigger' model of Allcock (1985)], the  $\alpha$ -C atoms can achieve any separation from  $0.5$  to  $2.7\text{ \AA}$  by rotation of the *exo* P-N bond. Because the polyphosphazene linkage is easily flexed (Allcock, 1985), the polyphosphazene backbone can probably provide the support for a favorable polypyrrolyl chain.

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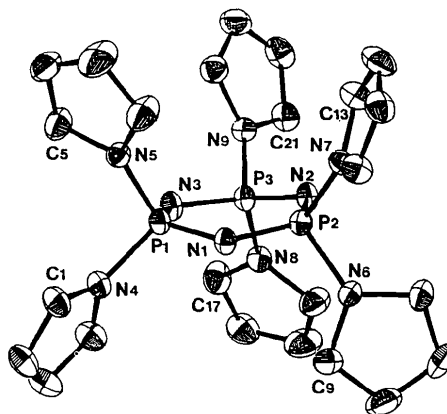


Fig. 1. ORTEP diagram (Johnson, 1976) and atom-numbering scheme. Ellipsoids at 30% probability level, H atoms omitted for clarity.

Table 2. Average values and ranges for intramolecular distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $[\text{NP}(\text{NC}_4\text{H}_4)_2]_3$

	Average	Range	Average	Range	
P-N ( <i>endo</i> )	1.583	1.577 (2)-1.585 (2)	N-P-N ( <i>endo</i> )	117.7	117.3 (1)-118.1 (1)
P-N ( <i>exo</i> )	1.671	1.663 (2)-1.673 (3)	N-P-N ( <i>exo</i> )	101.8	101.3 (1)-102.1 (1)
C-N	1.38	1.367 (4)-1.396 (4)	P-N-P	121.1	120.7 (2)-121.4 (2)
C-C (double)	1.34	1.324 (5)-1.346 (6)	C-N-C	106.8	106.2 (3)-107.2 (3)
C-C (single)	1.39	1.365 (6)-1.403 (6)	N-C-C	108	107.0 (4)-109.3 (4)
C-H	0.92	0.81 (4)-1.02 (4)	C-C-C	108	106.9 (4)-109.5 (4)

Table 3. Average values and ranges for the hybridization of the pyrrolyl N atoms in  $[\text{NP}(\text{NC}_4\text{H}_4)_2]_3$  from the POAV1 analysis (see text)

	Average	Range
$\theta_{\text{sp}}$	93.5°	90.8–96.7°
$m(\text{s}^m\text{p}, \pi)$	0.010	0.000–0.028
$\bar{n}(\text{sp}^n, \sigma)$	2.029	2.001–2.084

### References

- ALLCOCK, H. R. (1985). *Chem. Eng. News*, 18 March, pp. 22–36.  
 AUSTIN, P. D., RIDING, G. H. & ALLCOCK, H. R. (1983). *Macromolecules*, **16**, 719–722.  
 BULLEN, G. J. (1971). *J. Chem. Soc. A*, pp. 1450–1453.  
 Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.  
 GALLICANO, K. D., PADDOCK, N. L., RETTIG, S. J. & TROTTER, J. (1979). *Inorg. Nucl. Chem. Lett.* **15**, 417–420.  
 HADDON, R. C. (1986). *J. Am. Chem. Soc.* **108**, 2837–2842.

- HADDON, R. C. & SCOTT, L. T. (1986). *Pure Appl. Chem.* **58**, 137–142.  
 HADDON, R. C., STEIN, S. M., CHICHESTER-HICKS, S. V., MARSHALL, J. H., KAPLAN, M. L., HELLMAN, M. Y. & BOWMER, T. N. (1987) *Mater. Res. Bull.* **22**, 117–120.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht, The Netherlands.)  
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 MCBEE, E. T., JOHNCOCK, P., FRENCH, S. E. & BRAENDLIN, H. P. (1960). *US Gov. Res. Rep.* No. AD254,985.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN* 11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 MARSH, W. C. & TROTTER, J. (1971). *J. Chem. Soc. A*, pp. 169–173.  
 RETTIG, S. J. & TROTTER, J. (1973). *Can. J. Chem.* **51**, 1295–1302.  
 RITCHIE, R. J., FULLER, T. J. & ALLCOCK, H. R. (1980). *Inorg. Chem.* **19**, 3842–3845.

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## Structure of Vincamedine

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**Abstract.** Methyl 17-acetoxy-19,20-didehydroajmalan-16-carboxylate,  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_4$ ,  $M_r = 408.5$ , orthorhombic,  $P2_12_12_1$ ,  $a = 16.103$  (3),  $b = 11.836$  (2),  $c = 11.414$  (2) Å,  $V = 2175$  (1) Å<sup>3</sup>,  $D_x = 1.247$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 872$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 0.0917$  mm<sup>-1</sup>,  $T = 288$  K. The structure was solved by direct methods and refined by full-matrix least-squares method to  $R = 0.050$  ( $wR = 0.055$ ) for 1344 observed reflections. The absolute configuration was solved by the Bijvoet method. The indole ring has a chair form, with C(2) out of the plane defined by the remaining four atoms. The piperidine ring has a chair form, while the two six-membered rings of carbon atoms have a skew-sofa form. All the radical substituents are in *exo* sites.

**Introduction.** Vincamedine is an alkaloid isolated from *Vinca difformis*, with possible spasmolytic (Novikova,

Gotsiridze & Abuladze, 1984) and antiarrhythmic activity (Tagieva, Babaev & Aliev, 1979). An X-ray structural investigation of this compound has been carried out in order to elucidate the stereochemistry previously defined by Gosset-Garnier, Le Men & Janot (1961, 1965) and to correlate the structure to the pharmacological activity.

**Experimental.** Colourless prismatic crystals (0.1 × 0.1 × 0.15 mm). Philips PW 1100 diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation. Cell parameters from 25 reflections ( $5 \leq \theta \leq 12^\circ$ ), refined by least squares. Intensities from  $\omega$ -scan technique, scan width 0.8°, scan speed 0.03° s<sup>-1</sup>, 1496 independent reflections ( $2 \leq \theta \leq 25^\circ$ ), 1344 with  $I \geq 2.5\sigma(I)$ ,  $hkl$  range: 0 to 18, 0 to 13, 0 to 13. Three intensities were measured every 2 h as orientation and intensity control; significant intensity decay was not observed.  $L_p$