

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 |
|--------------------------------|---------|-------------|
| θ_{av} | 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 |

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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) Å³, $D_x = 1.247$ Mg m⁻³, $Z = 4$, $F(000) = 872$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.0917$ mm⁻¹, $T = 288$ 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 ω -scan technique, scan width 0.8° , scan speed $0.03^\circ \text{ s}^{-1}$, 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

corrections, absorption ignored. Structure solved by *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Isotropic and anisotropic full-matrix least-squares refinement (*SHELX76*, Sheldrick, 1976). $\sum w|F_o| - |F_c|^2$ minimized, where $w = [\sigma^2(F_o) + 0.0088|F_o|^2]^{-1/2}$. f , f' and f'' from *International Tables for X-ray Crystallography* (1974). 26 H (of 28) from $\Delta\rho$, which were refined with an overall isotropic temperature factor, anisotropic for the remaining atoms. Both enantiomorph configurations were refined. The absolute configuration was

Table 1. Comparison of observed and calculated values of $\Delta = (|F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|) / (|F_{hkl}| + |F_{\bar{h}\bar{k}\bar{l}}|)$ for the correct absolute configuration

| <i>h</i> | <i>k</i> | <i>l</i> | 1000 <i>A</i> _o | 1000 <i>A</i> _c | <i>h</i> | <i>k</i> | <i>l</i> | 100 <i>A</i> _o | 1000 <i>A</i> _c |
|----------|----------|----------|----------------------------|----------------------------|----------|----------|----------|---------------------------|----------------------------|
| 2 | 0 | 0* | 103.5 | -2.0 | 0 | 8 | 1 | -25.0 | -40.2 |
| 4 | 0 | 0* | 96.5 | -1.3 | 0 | 7 | 1 | -10.7 | -22.8 |
| 8 | 0 | 0* | -13.1 | 17.4 | 3 | 5 | 1 | -1.8 | -30.6 |
| 13 | 1 | 0 | -18.9 | -7.5 | 0 | 4 | 1 | -18.4 | -69.2 |
| 0 | 2 | 0 | 27.7 | 7.9 | 7 | 2 | 1 | 1.0 | 16.9 |
| 1 | 2 | 0 | -13.4 | -20.4 | 3 | 1 | 1 | 2.8 | 17.7 |
| 10 | 2 | 0 | -147.8 | -88.9 | 6 | 1 | 1 | -1.9 | -18.2 |
| 2 | 3 | 0 | -10.6 | -13.7 | 4 | 1 | 2 | 6.1 | 8.5 |
| 18 | 3 | 0 | 30.6 | 34.1 | 7 | 2 | 2 | -0.9 | -16.9 |
| 0 | 4 | 0 | -15.7 | -33.3 | 3 | 3 | 4 | -13.0 | -20.9 |
| 5 | 4 | 0 | 21.3 | 56.6 | 0 | 2 | 5 | 5.4 | 12.7 |
| 2 | 5 | 0 | -10.7 | -22.8 | 0 | 3 | 6 | 5.1 | 25.3 |
| 3 | 6 | 0 | -11.6 | -24.9 | 3 | 0 | 7 | 26.8 | 73.6 |
| 3 | 11 | 0 | -40.7 | -43.7 | 5 | 5 | 8 | 49.6 | 59.3 |
| 6 | 9 | 1 | -29.8 | 2.8 | 7 | 7 | 8 | 44.6 | 13.5 |

Table 2. Atomic parameters ($\times 10^4$) and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> _{eq} (Å ²) |
|-------|-----------|-----------|-----------|--|
| N(1) | -1481 (3) | 1764 (4) | 442 (4) | 4.0 (2) |
| C(2) | -1477 (3) | 595 (5) | 4 (5) | 3.5 (2) |
| C(3) | -1434 (3) | 428 (5) | -1322 (5) | 4.2 (3) |
| N(4) | -1334 (3) | -820 (4) | -1511 (4) | 4.1 (2) |
| C(5) | -614 (3) | -1253 (5) | -824 (5) | 3.7 (2) |
| C(6) | -806 (4) | -1231 (5) | 498 (6) | 4.1 (3) |
| C(7) | -754 (3) | 49 (4) | 704 (5) | 3.4 (2) |
| C(8) | -870 (3) | 631 (5) | 1877 (5) | 3.9 (2) |
| C(9) | -634 (4) | 365 (6) | 3005 (6) | 4.8 (3) |
| C(10) | -827 (5) | 1097 (7) | 3901 (7) | 5.8 (4) |
| C(11) | -1253 (4) | 2083 (7) | 3690 (7) | 5.7 (4) |
| C(12) | -1513 (4) | 2387 (6) | 2557 (6) | 4.8 (3) |
| C(13) | -1301 (3) | 1658 (5) | 1652 (5) | 4.1 (3) |
| C(14) | -734 (3) | 1089 (5) | -1908 (6) | 3.8 (2) |
| C(15) | -9 (3) | 264 (5) | -2120 (5) | 3.7 (2) |
| C(16) | 133 (3) | -435 (4) | -972 (5) | 3.7 (2) |
| C(17) | 110 (3) | 305 (5) | 159 (5) | 3.2 (2) |
| C(18) | 964 (6) | -376 (9) | -4416 (8) | 7.2 (5) |
| C(19) | 123 (5) | -831 (7) | -3991 (8) | 5.4 (4) |
| C(20) | -274 (4) | -536 (5) | -3048 (5) | 4.2 (3) |
| C(21) | -1138 (4) | -1004 (6) | -2759 (6) | 5.0 (3) |
| C(22) | 997 (4) | -966 (6) | -1087 (6) | 4.8 (3) |
| O(22) | 1610 (3) | -467 (5) | -1327 (6) | 7.1 (3) |
| C(23) | 1842 (5) | -2598 (8) | -932 (11) | 8.5 (5) |
| O(23) | 991 (3) | -2076 (4) | -868 (5) | 5.7 (2) |
| C(24) | 1279 (3) | 559 (6) | 1483 (5) | 4.0 (2) |
| O(24) | 724 (2) | -145 (3) | 984 (3) | 4.0 (2) |
| C(25) | 1862 (5) | -42 (8) | 2263 (7) | 6.3 (4) |
| O(25) | 1287 (3) | 1565 (4) | 1302 (4) | 5.8 (2) |
| C(26) | -2174 (4) | 2468 (6) | 95 (7) | 5.7 (3) |

determined by the Bijvoet difference method. 30 reflections with F_c differing significantly at the end of two refinements were remeasured with great care. Table 1 compares the observed and calculated values of

Table 3. Selected bond lengths (Å) and angles (°)

| | | | |
|-------------------|------------|-------------------|------------|
| C(2)-N(1) | 1.470 (7) | C(12)-C(11) | 1.407 (11) |
| C(13)-N(1) | 1.417 (8) | C(13)-C(12) | 1.388 (8) |
| C(26)-N(1) | 1.448 (8) | C(15)-C(14) | 1.541 (8) |
| C(3)-C(2) | 1.528 (9) | C(16)-C(15) | 1.566 (8) |
| C(7)-C(2) | 1.554 (7) | C(20)-C(15) | 1.484 (8) |
| N(4)-C(3) | 1.502 (8) | C(17)-C(16) | 1.560 (8) |
| C(14)-C(3) | 1.526 (8) | C(22)-C(16) | 1.532 (8) |
| C(5)-N(4) | 1.490 (7) | O(24)-C(17) | 1.466 (6) |
| C(21)-N(4) | 1.475 (9) | C(19)-C(18) | 1.536 (11) |
| C(6)-C(5) | 1.540 (9) | C(20)-C(19) | 1.300 (10) |
| C(16)-C(5) | 1.554 (7) | C(21)-C(20) | 1.533 (8) |
| C(7)-C(6) | 1.535 (7) | O(22)-C(22) | 1.183 (8) |
| C(8)-C(7) | 1.517 (8) | O(23)-C(22) | 1.338 (7) |
| C(17)-C(7) | 1.553 (7) | O(23)-C(23) | 1.505 (8) |
| C(9)-C(8) | 1.379 (9) | O(24)-C(24) | 1.347 (7) |
| C(13)-C(8) | 1.423 (8) | C(25)-C(24) | 1.477 (9) |
| C(10)-C(9) | 1.376 (10) | O(25)-C(24) | 1.209 (8) |
| C(11)-C(10) | 1.374 (11) | | |
| C(13)-N(1)-C(2) | 104.3 (5) | C(8)-C(13)-N(1) | 110.6 (5) |
| C(26)-N(1)-C(2) | 116.8 (5) | C(12)-C(13)-N(1) | 128.3 (6) |
| C(26)-N(1)-C(13) | 118.4 (5) | C(12)-C(13)-C(8) | 121.1 (6) |
| C(3)-C(2)-N(1) | 117.3 (5) | C(15)-C(14)-C(3) | 107.7 (5) |
| C(7)-C(2)-N(1) | 102.7 (4) | C(16)-C(15)-C(14) | 108.3 (4) |
| C(7)-C(2)-C(3) | 114.9 (4) | C(20)-C(15)-C(14) | 107.3 (5) |
| N(4)-C(3)-C(2) | 105.9 (5) | C(20)-C(15)-C(16) | 107.6 (4) |
| C(14)-C(3)-C(2) | 113.6 (5) | C(15)-C(16)-C(5) | 107.9 (4) |
| C(14)-C(3)-N(4) | 111.2 (5) | C(17)-C(16)-C(5) | 103.9 (4) |
| C(5)-N(4)-C(3) | 110.2 (4) | C(17)-C(16)-C(15) | 113.1 (4) |
| C(21)-N(4)-C(3) | 107.8 (5) | C(22)-C(16)-C(5) | 117.2 (5) |
| C(21)-N(4)-C(5) | 107.0 (5) | C(22)-C(16)-C(15) | 106.1 (5) |
| C(6)-C(5)-N(4) | 110.8 (5) | C(22)-C(16)-C(17) | 108.9 (5) |
| C(16)-C(5)-N(4) | 109.3 (4) | C(16)-C(17)-C(7) | 104.1 (4) |
| C(16)-C(5)-C(6) | 104.6 (4) | O(24)-C(17)-C(7) | 106.0 (4) |
| C(7)-C(6)-C(5) | 98.9 (5) | O(24)-C(17)-C(16) | 108.1 (4) |
| C(6)-C(7)-C(2) | 107.0 (4) | C(20)-C(19)-C(18) | 126.9 (8) |
| C(8)-C(7)-C(2) | 99.9 (4) | C(19)-C(20)-C(15) | 128.4 (6) |
| C(8)-C(7)-C(6) | 125.2 (5) | C(21)-C(20)-C(15) | 109.8 (5) |
| C(17)-C(7)-C(2) | 112.6 (4) | C(21)-C(20)-C(19) | 121.8 (6) |
| C(17)-C(7)-C(6) | 100.4 (4) | C(20)-C(21)-N(4) | 110.4 (5) |
| C(17)-C(7)-C(8) | 112.0 (4) | O(22)-C(22)-C(16) | 124.9 (6) |
| C(9)-C(8)-C(7) | 133.3 (5) | O(23)-C(22)-C(16) | 112.5 (6) |
| C(13)-C(8)-C(7) | 106.8 (5) | O(23)-C(22)-O(22) | 122.6 (6) |
| C(13)-C(8)-C(9) | 119.9 (5) | C(23)-O(23)-C(22) | 112.9 (6) |
| C(10)-C(9)-C(8) | 119.2 (7) | C(25)-C(24)-O(24) | 112.2 (6) |
| C(11)-C(10)-C(9) | 121.1 (7) | O(25)-C(24)-O(24) | 123.0 (5) |
| C(12)-C(11)-C(10) | 121.8 (7) | O(25)-C(24)-C(25) | 124.8 (6) |
| C(13)-C(12)-C(11) | 116.9 (7) | C(24)-O(24)-C(17) | 119.6 (4) |

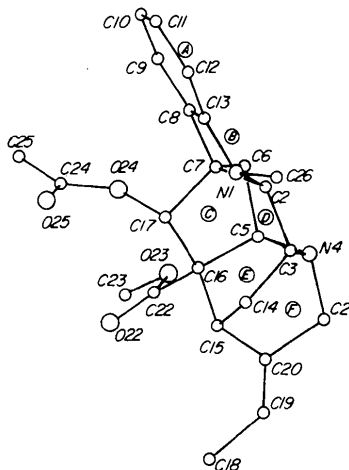


Fig. 1. View of the molecule with numbering of atoms.

$\Delta = (|F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|) / (|F_{hkl}| + |F_{\bar{h}\bar{k}\bar{l}}|)$ for the correct absolute configuration. It can be seen from Table 1 that the signs of Δ_c and Δ_o are the same for 27 reflections but there are three contradictions in the $h00$ reflections. These three are denoted by asterisks in Table 1. Final R was 0.050 ($wR = 0.055$) for all observed reflections. Max. shift/e.s.d. = 0.3 in x of H(C18). Max. and min. $\Delta\rho = 0.3$ and $-0.2 e \text{ \AA}^{-3}$, respectively. IBM-3083 computer. Final atomic coordinates are listed in Table 2, and bond lengths and angles in Table 3.* A view of the molecule is given in Fig. 1.

Discussion. The X-ray analysis confirms the stereochemistry given by Gosset-Garnier, Le Men & Janot (1961, 1965). The B ring [N(1), C(2), C(7), C(8) and C(13)] has a chair form with asymmetry parameter $\Delta C_m^2 = 0.5^\circ$, so the C(2) atom is out of the plane defined by the remaining four atoms. These four atoms are in the same plane as the benzene A ring. The D ring [C(2), C(3), N(4), C(5), C(6) and C(7)] has a chair form with asymmetry parameter $\Delta C_m^3 = 6.1^\circ$. The B and D rings are *trans*-fused. The C ring [C(5), C(6), C(7), C(16) and C(17)] has a skew-envelope form with asymmetry parameter $\Delta C_m^6 = 15.9^\circ$, while the two remaining six-membered rings [E : C(3), N(4), C(5), C(14), C(15) and C(16); F : C(3), N(4), C(14), C(15), C(20) and C(21)] have a skew-sofa form with asymmetry parameters $\Delta C_2^{4-21} = 28.7$, $\Delta C_2^3 = 19.7$, $\Delta C_2^5 = 20.6$ and $\Delta C_2^{3-4} = 25.2^\circ$. The stress between the C(15)–C(16) atoms produces a lengthening of this bond [1.566(8)] and C(16)–C(17) [1.560(8) Å]; the smallest

angles are C(7)–C(6)–C(5) [98.9(5)], C(8)–C(7)–C(2) [99.9(4)] and N(4)–C(3)–C(2) [105.9(5)°] and the largest C(8)–C(13)–N(1) [110.6(5)] and C(7)–C(2)–C(3) [114.9(4)°]. The values of C(8)–C(7)–C(2) and C(8)–C(13)–N(1) are 104.3(3) and 109.6(3)° in oxymetavincadiformine (Rodier, Ceolin, Croquelois, Kunesch & Poisson, 1978); 106(1)° in vincamine 2-oxoglutarate (Fayos & Martinez-Ripoli, 1981) and 107.3(2) and 107.3(2)° in vincamone (Chiesi-Villa, Gaetani Manfredotti, Guastini, Chiari & Viterbo (1973). The three substituent radicals occupy *exo* sites.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44079 (11 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 *N*-Methylaminoacetonitrile Hydrochloride

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Abstract. (Cyanomethyl)methylammonium chloride, $C_3H_7N_2^+Cl^-$, $M_r = 106.56$, orthorhombic, *Pbca*, $a = 11.518(1)$, $b = 10.201(1)$, $c = 9.166(1)$ Å, $V = 1076.9(2)$ Å³, $Z = 8$, $D_x = 1.314$ Mg m⁻³, $Mo K\alpha_1$, $\lambda = 0.70930$ Å, $\mu = 0.56$ mm⁻¹, $F(000) = 448$, $T = 295$ K, $R = 0.031$ for 1175 unique observed reflections

with $I \geq 3\sigma(I)$. The structure consists of centrosymmetric hydrogen-bonded dimers in which two $NCCH_2-NH_2CH_2^+$ cations are bridged by two Cl^- anions *via* N–H...Cl hydrogen bonds, $Cl \cdots H = 2.22(2)$ and $2.23(2)$ Å. The cation adopts a *gauche* conformation with respect to the central C(sp^3)–N(sp^3) bond.