

An intermolecular hydrogen bond involving the hydroxyl substituent at C(12) and the N atom of an adjacent molecule related by a twofold screw axis ( $x = \frac{1}{2}, y = \frac{1}{2}$ ) links the molecules into helices along *c*. The O(22)··N(4), O(22)—H(22) and H(22)··N(4) distances are 2.827 (4), 0.77 (5) and 2.07 (5) Å respectively [*cf.* distances of 2.85 (1), 0.98 (7) and 1.90 (7) Å in retrorsine] and the N(4)··H(22)—O(22) angle is 167 (3)° (162° in retrorsine). Similar interactions are observed in the jacobine crystal in which the comparable dimensions are 2.928 (5), 0.71 (5), 2.23 (5) Å and 167 (7)°. In senkirikine, H(22) is donated intramolecularly to O(20) in an asymmetric bifurcated hydrogen bond; the H(22)··O(20) and O(22)··O(2) distances are 2.22 (5) and 2.680 (3) Å respectively and the O—H··O angle 118 (2)°. Although the O(22)··O(20) distances in crystals of retrorsine hydrobromide ethanol solvate of 2.63 (2) Å and swazine methiodide of 2.69 Å are indicative of intramolecular hydrogen bonding, this could not be substantiated as the H(22) coordinates are not available. However, this distance is lengthened to 2.724 (4) Å in crystals of senecionine, 2.705 (10) Å in retrorsine and 2.711 (5) Å in jacobine where the hydroxyl substituent at C(12) is involved only in intermolecular hydrogen bonding.

The authors wish to thank Mr L. W. Smith, Division of Animal Health, CSIRO, for preparing the crystals of senecionine.

*Acta Cryst.* (1982). **B38**, 2758–2760

## Methyl 1,2-Bis(dimethylamino)-4-methyl-1*H*-pyrrolo[1,2-*a*]indole-3-carboxylate

BY GEORGE FERGUSON AND BRANKO KAITNER

*Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1*

W. BASIL WHALLEY

*The School of Pharmacy, The University, London WC1N 1AX, England*

AND DERYCK A. TAYLOR AND J. RICHARD LIDDELL

*Department of Chemistry, The University of Zimbabwe, Salisbury, Zimbabwe*

(Received 20 January 1982; accepted 7 May 1982)

**Abstract.** C<sub>18</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>, *M<sub>r</sub>* = 313.4, orthorhombic, *Pbca*, *a* = 8.349 (2), *b* = 23.465 (5), *c* = 17.387 (3) Å, *Z* = 8, *D<sub>c</sub>* = 1.22 g cm<sup>-3</sup>, *F*(000) = 1344, Mo *K*α radiation, λ = 0.71069 Å, μ(Mo *K*α) = 0.5 cm<sup>-1</sup>. Space group determined uniquely from systematic

0567-7408/82/102758-03\$01.00

### References

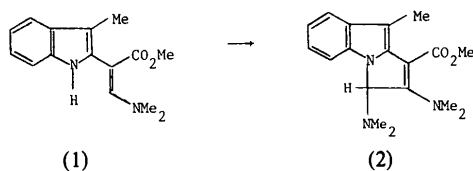
- BIRNBAUM, G. I. (1974). *J. Am. Chem. Soc.* **96**, 6165–6168.  
 BULL, L. B., CULVENOR, C. C. J. & DICK, A. T. (1968). *The Pyrrolizidine Alkaloids*. Amsterdam: North-Holland.  
 COLEMAN, P. C., COUCOURAKIS, E. D. & PRETORIUS, J. A. (1980). *S. Afr. J. Chem.* **33**, 116–119.  
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 CULVENOR, C. C. J. (1966). *Tetrahedron Lett.* pp. 1091–1099.  
 CULVENOR, C. C. J. & WOODS, W. G. (1965). *Aust. J. Chem.* **18**, 1625–1637.  
 HIKICHI, M., FURUYA, T. & IITAKA, Y. (1978). *Tetrahedron Lett.* pp. 767–770.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KROPMAN, M. & WARREN, F. L. (1949). *J. Chem. Soc.* pp. 2852–2854.  
 LAING, M. & SOMMERVILLE, P. (1972). *Tetrahedron Lett.* pp. 5183–5186.  
 PÉREZ-SALAZAR, A., CANO, F. H., FAYOS, J., MARTÍNEZ-CARRERA, S. & GARCÍA-BLANCO, S. (1977). *Acta Cryst.* **B33**, 3525–3527.  
 PÉREZ-SALAZAR, A., CANO, F. H., & GARCÍA-BLANCO, S. (1978). *Cryst. Struct. Commun.* **7**, 105–109.  
 SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 STOECKLI-EVANS, H. (1979). *Acta Cryst.* **B35**, 2798–2800.  
 STOECKLI-EVANS, H. & CROUT, D. H. G. (1976). *Helv. Chim. Acta*, **59**, 2168–2178.

absences. The structure was solved by direct methods and refined by full-matrix least-squares calculations; *R* = 0.059 for 786 reflections with *I* > 3σ(*I*). The analysis establishes the structure of this product from the reaction between the methyl ester of 3-methyl-

© 1982 International Union of Crystallography

indole-2-acetic acid and *N,N*-dimethylformamide/phosphoryl chloride. Molecular dimensions are normal; the molecule has slight intramolecular overcrowding.

**Introduction.** It has previously been reported (Jones, Taylor & Bower, 1974) that the Vilsmeier reaction between the methyl ester of 3-methylindole-2-acetic acid and *N,N*-dimethylformamide/phosphoryl chloride gives the derivative (1) together with smaller amounts of a more complex, orange-coloured product. This coloured product, to which the molecular formula C<sub>18</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> was assigned, is also formed (in greater yield) from (1) using further quantities of Vilsmeier reagent. The NMR data of this product did not permit the unequivocal assignment of a structure, which has now been defined by X-ray crystallography as (2), in agreement with previously recorded physical data (Jones *et al.*, 1974), including the molecular formula.



Crystals of (2) form orange needles on recrystallization from aqueous ethanol. Preliminary unit-cell data were obtained from Weissenberg and precession photographs; final values were obtained from a least-squares fit of the values of the setting angles for 12 general reflexions measured on a Hilger & Wats Y290 diffractometer.

The intensities of the unique reflexions with  $2 < \theta < 20^\circ$  (Mo  $K\alpha$ ) were measured in our usual way (Ferguson & Roberts, 1978). The intensities (1588) were corrected for Lorentz and polarization factors, but not for absorption, which is negligible. The 786 reflexions with  $I > 3\sigma(I)$  were labelled 'observed' and used in structure solution and refinement.

The structure was solved using the multiple-solution program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The first *E* map revealed the entire framework except the H atoms. Isotropic followed by anisotropic full-matrix refinement (Sheldrick, 1976) lowered *R* to 0.088. At this stage, a difference synthesis revealed small density maxima in positions consistent with the expected H-atom locations. These H atoms were then allowed for (with C–H 0.95 Å) but only an overall isotropic thermal parameter was refined. The refinement converged with  $R = 0.059$  and  $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0.064$  and a final difference synthesis was devoid of chemically significant features. In the early stages of the refinement unit weights were used and in the final cycles weights were derived from counting statistics. In the final cycle of refinement the largest coordinate shift/error ratio was 0.094 for the *z* coordinate of C(8).

The scattering factors of Cromer & Mann (1968) were used for non-H atoms and those of Stewart, Davidson & Simpson (1965) for H atoms. Final fractional coordinates for the non-H atoms are in Table 1.\* The molecular structure is shown in Fig. 1 along with the crystallographic-numbering scheme. Details of molecular geometry are in Table 2; these data, together with the location of the proton at C(11), establish the structure of (2) unequivocally.

\* The calculated H-atom coordinates, anisotropic thermal parameters and a listing of observed and calculated structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36913 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\times 10^3$ ) for the non-H atoms of C<sub>18</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$\bar{U}$ (Å <sup>2</sup> )*
C(1)	−1370 (9)	6950 (3)	5370 (6)	65 (5)
C(2)	−2400 (11)	7350 (4)	5694 (8)	90 (7)
C(3)	−2397 (15)	7431 (4)	6463 (9)	110 (9)
C(4)	−1380 (15)	7124 (4)	6953 (7)	111 (9)
C(5)	−354 (12)	6712 (4)	6644 (7)	99 (8)
C(6)	−367 (9)	6644 (3)	5870 (5)	64 (5)
C(7)	−1133 (8)	6746 (3)	4606 (6)	66 (6)
C(8)	5 (8)	6328 (3)	4647 (6)	62 (5)
C(9)	697 (9)	5853 (3)	4219 (5)	64 (5)
C(10)	1552 (9)	5522 (3)	4724 (6)	65 (5)
C(11)	1526 (9)	5775 (3)	5527 (5)	72 (6)
C(12)	−2050 (13)	6965 (4)	3918 (6)	104 (7)
C(13)	3315 (14)	5949 (6)	6624 (7)	164 (12)
C(14)	3934 (12)	6358 (4)	5347 (9)	140 (9)
C(15)	3016 (11)	4668 (4)	5209 (7)	97 (7)
C(16)	2841 (12)	4842 (4)	3818 (7)	112 (8)
C(17)	247 (9)	5738 (5)	3413 (6)	83 (7)
C(18)	−301 (13)	6187 (6)	2219 (8)	129 (10)
N(1)	511 (7)	6274 (3)	5409 (4)	68 (5)
N(2)	3160 (8)	5888 (3)	5787 (5)	92 (6)
N(3)	2418 (8)	5041 (3)	4590 (5)	80 (5)
O(1)	304 (7)	6218 (3)	2989 (4)	63 (5)
O(2)	−178 (9)	5283 (3)	3154 (4)	83 (5)

$$* \bar{U} = 0.333 (U_{11} + U_{22} + U_{33}).$$

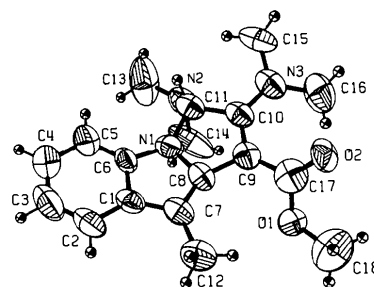


Fig. 1. View of the C<sub>18</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> molecule with the crystallographic-numbering scheme.

Table 2. *Interatomic distances (Å) and angles (°)*

## (a) Bond lengths

C(1)—C(2)	1.39 (1)	C(9)—C(17)	1.48 (1)
C(1)—C(6)	1.41 (1)	C(10)—C(11)	1.52 (1)
C(1)—C(7)	1.43 (1)	C(10)—N(3)	1.36 (1)
C(2)—C(3)	1.35 (2)	C(11)—N(1)	1.46 (1)
C(3)—C(4)	1.40 (2)	C(11)—N(2)	1.46 (1)
C(4)—C(5)	1.40 (1)	C(13)—N(2)	1.47 (1)
C(5)—C(6)	1.35 (1)	C(14)—N(2)	1.49 (1)
C(6)—N(1)	1.39 (1)	C(15)—N(3)	1.47 (1)
C(7)—C(8)	1.37 (1)	C(16)—N(3)	1.47 (1)
C(7)—C(12)	1.51 (1)	C(17)—O(1)	1.35 (1)
C(8)—C(9)	1.46 (1)	C(17)—O(2)	1.21 (1)
C(8)—N(1)	1.40 (1)	C(18)—O(1)	1.43 (1)
C(9)—C(10)	1.37 (1)		

## (b) Bond angles

C(2)—C(1)—C(6)	117.5 (10)	C(9)—C(10)—C(11)	111.0 (7)
C(2)—C(1)—C(7)	133.6 (10)	C(9)—C(10)—N(3)	129.5 (9)
C(6)—C(1)—C(7)	108.8 (7)	C(11)—C(10)—N(3)	119.4 (9)
C(1)—C(2)—C(3)	119.6 (11)	C(10)—C(11)—N(1)	101.1 (7)
C(2)—C(3)—C(4)	122.1 (11)	N(1)—C(11)—N(2)	116.1 (7)
C(3)—C(4)—C(5)	119.5 (11)	C(10)—C(11)—N(2)	110.0 (8)
C(4)—C(5)—C(6)	117.3 (11)	C(9)—C(17)—O(1)	110.9 (9)
C(1)—C(6)—C(5)	124.1 (9)	C(9)—C(17)—O(2)	126.1 (10)
C(1)—C(6)—N(1)	106.0 (8)	O(1)—C(17)—O(2)	122.9 (10)
C(5)—C(6)—N(1)	129.9 (10)	C(6)—N(1)—C(8)	109.4 (7)
C(1)—C(7)—C(8)	106.8 (8)	C(6)—N(1)—C(11)	136.5 (8)
C(1)—C(7)—C(12)	123.5 (8)	C(8)—N(1)—C(11)	112.4 (7)
C(8)—C(7)—C(12)	129.7 (10)	C(11)—N(2)—C(13)	114.0 (9)
C(7)—C(8)—N(1)	108.9 (8)	C(11)—N(2)—C(14)	112.4 (8)
C(9)—C(8)—N(1)	107.2 (8)	C(13)—N(2)—C(14)	113.5 (10)
C(7)—C(8)—C(9)	142.8 (10)	C(10)—N(3)—C(15)	123.2 (9)
C(8)—C(9)—C(10)	108.2 (8)	C(10)—N(3)—C(16)	123.4 (9)
C(8)—C(9)—C(17)	121.6 (9)	C(15)—N(3)—C(16)	113.4 (8)
C(10)—C(9)—C(17)	129.4 (9)	C(17)—O(1)—C(18)	117.2 (9)

## (c) Torsion angles

C(1)—C(2)—C(3)—C(4)	0.1	C(7)—C(1)—C(6)—N(1)	2.2
C(2)—C(3)—C(4)—C(5)	1.3	N(1)—C(8)—C(9)—C(10)	1.5
C(3)—C(4)—C(5)—C(6)	2.0	C(8)—C(9)—C(10)—C(11)	-2.1
C(4)—C(5)—C(6)—C(1)	1.7	C(9)—C(10)—C(11)—N(1)	1.8
C(5)—C(6)—C(1)—C(2)	0.6	C(10)—C(11)—N(1)—C(8)	0.8
C(6)—C(1)—C(2)—C(3)	0.3	C(11)—N(1)—C(8)—C(9)	-0.3
C(1)—C(6)—N(1)—C(8)	-3.0	C(2)—C(1)—C(6)—N(1)	179.3
C(6)—N(1)—C(8)—C(7)	2.8	C(7)—C(1)—C(6)—C(5)	-176.5
N(1)—C(8)—C(7)—C(1)	-1.3	C(7)—C(8)—N(1)—C(11)	170.4
C(8)—C(7)—C(1)—C(6)	0.5	C(6)—N(1)—C(8)—C(9)	-168.0

The standard deviations in torsion angles are in the range 1.2 to 1.6° for torsion angles near zero and 1.8 to 2.6° for those angles near 180°.

*Acta Cryst.* (1982). **B38**, 2760–2763

### 5-endo-(Bromomethyl)-1,2,4-trichloro-3,7,7-trimethoxynorborn-2-ene\*

BY D. VAN HEMELRIJK, A. T. H. LENSTRA AND H. J. GEISE

*University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium*

(Received 4 February 1982; accepted 26 April 1982)

**Abstract.** C<sub>11</sub>H<sub>14</sub>BrCl<sub>3</sub>O<sub>3</sub>, monoclinic, *P*2<sub>1</sub>/*n*, *Z* = 4, *a* = 7.988 (3), *b* = 15.672 (8), *c* = 11.949 (4) Å, β = 103.90 (3)°, *D*<sub>c</sub> = 1.74 Mg m<sup>-3</sup>; *R*<sub>w</sub> = 0.071 for 1478 observed reflections. The geometry of the title com-

**Discussion.** The molecule shows signs of intramolecular overcrowding. The benzene ring, C(1)—C(6), is close to being planar, but the five-membered ring N(1),C(8)—C(11) adopts a slight envelope conformation with C(9) at the flap, to reduce crowding between the CO<sub>2</sub>Me moiety on C(9) and the methyl atoms C(12) and C(16) [cf. C(11)—C(10)—N(3) 119.4 (9)°, C(9)—C(10)—N(3) 129.5 (9)° and C(1)—C(7)—C(12) 123.5 (8)° and C(8)—C(7)—C(12) 129.7 (10)°]. As a consequence, the molecule is slightly folded and there is a 12.5° angle between the benzene and N(1),C(8)—C(11) ring planes.

Molecular dimensions are normal within the accuracy of the analysis (e.g. mean aromatic C—C 1.40 Å, mean N—Me 1.50 Å). The bond lengths C(7)—C(8) 1.37 (1), C(8)—C(9) 1.46 (1), C(9)—C(10) 1.37 (1) Å, together with the orange colour of (2), and the UV spectrum (Jones *et al.*, 1974), suggest some delocalization involving the C(7), C(8) and C(9), C(10) double bonds with the benzenoid ring system. In the crystal structure, molecules are separated by normal van der Waals distances.

#### References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 FERGUSON, G. & ROBERTS, P. J. (1978). *Acta Cryst.* **B34**, 3083–3086.  
 JONES, C. F., TAYLOR, D. A. & BOWER, D. P. (1974). *Tetrahedron*, **30**, 957–961.  
 MAIN, P., HULL, S., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.  
 SHELDRIK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

\* Norbornane has been superseded by the name 8,9,10-trinorbornane.