

interacting solvents.\* Accordingly, the similar NMR behaviour of the carbonyl-C-atom chemical shifts of methyl 4-*X*- or 2,6-dimethyl-4-*X*-benzoates must be given a rationale which leaves only a minor conjugation effect between the COOMe group and the aromatic ring even in the 2,6-unsubstituted compounds Dell'Erba *et al.*, 1988).

The internal strain seems scarcely to affect the C(1)–C(7) bond distance, whose length [1.502 (3) Å] can be compared with the 41 corresponding bond distances for the 26 aforementioned 2,6-unsubstituted alkylbenzoates [average 1.487 (2) Å], with the six values reported for the four 2-chloro derivatives [average 1.496 (1) Å], and finally with the value found in the 2-chloro-6-methyl derivative [1.506 (3) Å] (Gillespie *et al.*, 1981). The increase in the hindrance and in the rotation angle of the methoxycarbonyl group seems thus to be accompanied by a small increase in the C(aromatic)–C(ester) bond length; the title compound is sited correctly in this sequence.

Intermolecular distances are in the normal range. There are only few contacts appreciably shorter than the sum of the van der Waals radii (Pauling, 1960):

\* This finding could be compared with results obtained through molecular-mechanics calculations (MM2), indicating a torsion angle of 54° for methyl 2,6-dimethylbenzoate (Baumstark, Balakrishnan, Dotrong, McCloskey, Oakley & Boykin, 1987).

C(9)··C(10) ( $-x, -\frac{1}{2}+y, -\frac{1}{2}-z$ ) 3.759 (4) Å;  
C(10)··C(10) ( $x, \frac{3}{2}-y, -\frac{1}{2}+z$ ) 3.799 (5) Å.

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#### References

- ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK, PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* **B35**, 2331–2339.
- BAUMSTARK, A. L., BALAKRISHNAN, P., DOTRONG, M., MCCLOSKEY, C. J., OAKLEY, M. G. & BOYKIN, D. W. (1987). *J. Am. Chem. Soc.* **109**, 1059–1062.
- BORTHWICK, P. W. (1980). *Acta Cryst.* **B36**, 628–632.
- DELL'ERBA, C., SANCASSAN, F., NOVI, M., PETRILLO, G., MUGNOLI, A., SPINELLI, D., CONSIGLIO, G. & GATTI, P. (1988). *J. Org. Chem.* **53**, 3564–3568.
- GILLESPIE, R. J., MURRAY-RUST, J., MURRAY-RUST, P. & PORTER, A. E. A. (1981). *Tetrahedron*, **37**, 743–746.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- KUHN, L. P. & CORWIN, A. H. (1948). *J. Am. Chem. Soc.* **70**, 3370–3375.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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## The Structure of an Alkaloid, Picrinine, from *Alstonia scholaris*

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**Abstract.** 2,5-Epoxy-1,2-dihydroakuammilan-17-oic acid, methyl ester, C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 7.065 (2), *b* = 8.117 (1), *c* = 28.834 (3) Å, *V* =

1653.53 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.37, *D<sub>x</sub>* = 1.36 g cm<sup>-3</sup>, *M<sub>r</sub>* = 338.40, *μ* = 7.037 cm<sup>-1</sup>, *F*(000) = 720, λ(Cu Kα) = 1.54184 Å. The structure was solved by direct methods and refined by least squares to *R* = 0.045 for 1555 independent reflections. Picrinine is a naturally

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Table 1. Fractional coordinates of non-H atoms with their *e.s.d.*'s in parentheses and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

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

	x	y	z	$U_{eq}$
O(1)	0.2013 (5)	0.1517 (3)	0.5560 (1)	0.0498
O(2)	0.4580 (5)	0.2117 (3)	0.5980 (1)	0.0563
O(3)	0.5827 (5)	-0.2940 (5)	0.6922 (1)	0.0480
N(1)	0.4731 (5)	-0.4124 (4)	0.6207 (1)	0.0428
N(2)	0.3183 (6)	-0.1751 (5)	0.7219 (1)	0.0479
C(1)	0.6191 (5)	-0.1751 (4)	0.5945 (1)	0.0324
C(2)	0.7382 (6)	-0.0866 (5)	0.5659 (1)	0.0396
C(3)	0.8506 (7)	-0.1685 (6)	0.5335 (1)	0.0521
C(4)	0.8395 (8)	-0.3395 (7)	0.5300 (2)	0.0548
C(5)	0.7166 (8)	-0.4308 (6)	0.5576 (2)	0.0508
C(6)	0.6076 (6)	-0.3477 (5)	0.5897 (1)	0.0393
C(7)	0.4409 (6)	-0.2918 (5)	0.6552 (1)	0.0362
C(8)	0.4797 (6)	-0.1204 (4)	0.6318 (1)	0.0300
C(9)	0.2990 (5)	-0.0513 (4)	0.6093 (1)	0.0299
C(10)	0.1211 (5)	-0.0501 (5)	0.6414 (1)	0.0341
C(11)	0.1346 (6)	0.0591 (6)	0.6842 (1)	0.0411
C(12)	0.2005 (7)	-0.0287 (6)	0.7282 (1)	0.0533
C(13)	0.2594 (7)	-0.2899 (6)	0.6836 (1)	0.0428
C(14)	0.5572 (6)	-0.0197 (5)	0.6737 (1)	0.0367
C(15)	0.5237 (7)	-0.1431 (6)	0.7130 (1)	0.0475
C(16)	0.0880 (6)	-0.2290 (5)	0.6567 (1)	0.0402
C(17)	0.3325 (6)	0.1188 (5)	0.5883 (1)	0.0365
C(18)	0.2162 (9)	0.3127 (6)	0.5336 (2)	0.0666
C(19)	0.0737 (8)	0.2140 (6)	0.6865 (2)	0.0573
C(20)	-0.0239 (9)	0.3125 (6)	0.6503 (2)	0.0704

occurring indole alkaloid. The structure is considered to have six fused rings. The phenyl ring (I) of the indole moiety is nearly planar. Its adjacent pyrrole ring (II) contains an  $sp^2$ -hybridized N atom and adopts a pure envelope conformation. The cyclohexane ring to which the carboxylate group is attached (III) has a distorted chair conformation. The other two five-membered heterocycles (V, VI) are puckered in distorted twist conformations. The six-membered heterocycle (IV) lies between ideal boat and twist boat conformations. Strain arising from steric factors is manifested in rings III and V by bond lengthening [C(7)–C(8) 1.570 (5), C(9)–C(10) 1.561 (5), N(2)–C(13) 1.504 (5), N(2)–C(15) 1.496 (6)  $\text{\AA}$ ]. Hyperconjugation is evident in the ethylidene moiety [C(20)–C(19) 1.485, C(19)=C(11) 1.331 (7)  $\text{\AA}$ ].

**Introduction.** Picrinine is an indole alkaloid isolated from the leaves of the plant *Alstonia scholaris*. The chemical structure of the compound was predicted from biogenetic considerations and NMR spectral data and has been supported by mass spectroscopy. The importance of the precise structure determination of picrinine arises from the biogenic significance of the molecule as it is considered to be an intermediate in the formation of the echitamine and echitamidine skeletons (Chatterjee, Mukharjee, Ray & Das, 1965). The present crystal structure analysis was carried out with a view to establishing the molecular structure, detailed stereochemistry of the molecule and the crystal packing arrangement.

**Experimental.** Crystals from acetone by slow evaporation, density measured by flotation in benzene–bromine mixture, crystal size 0.20  $\times$  0.40  $\times$  0.20 mm; intensity data collected on Philips PW 1100 diffractometer with graphite-monochromated Cu  $K\alpha$  radiation; cell parameters refined by the least-squares fitting of the setting angles of 25 high-angle reflections; 1606 independent reflections collected ( $0 \leq h \leq 8$ ,  $0 \leq k \leq 10$ ,  $0 \leq l \leq 35$ ,  $2\theta \leq 130^\circ$ );  $\omega/2\theta$  scan mode with scan speed 0.0668  $^\circ \text{s}^{-1}$ , scan width 0.80 to 0.35 $^\circ$ ; data corrected for Lp but not for absorption, space group from oscillation and Weissenberg photographs  $P2_12_12_1$  ( $h00$ ,  $h \neq 2n$ ;  $0k0$ ,  $k \neq 2n$ ;  $00l$ ,  $l \neq 2n$ ): structure solved by direct methods (MULTAN78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) with 200  $E$  values having  $E_{\min}$  1.46; correct model containing all the 25 non-H atoms was built up from successive Fourier syntheses using the program SHELX76 (Sheldrick, 1976);  $R$  value after full-matrix least-squares refinement of all the non-H atoms with anisotropic thermal parameters was 0.106; all the H atoms located from  $\Delta F$  synthesis. Each H atom was then assigned the isotropic temperature factor of the attached non-H atom. Final two cycles of refinement of the positional and anisotropic thermal parameters of the non-H atoms keeping all the parameters of the H atoms fixed with 1555 observed reflections [ $I \geq 2.5\sigma(I)$ ] led to a final  $R = 0.045$ , unit weights, number of parameters refined = 226; average and maximum  $\Delta/\sigma$  in final refinement 0.101 and 0.707, respectively.  $-0.22 \leq \Delta\rho \leq 0.29 \text{ e \AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The atomic coordinates of non-H atoms are listed in Table 1.

**Discussion.** The picrinine molecule consists of six fused rings, numbered I to VI as shown in Fig. 1, of which II,

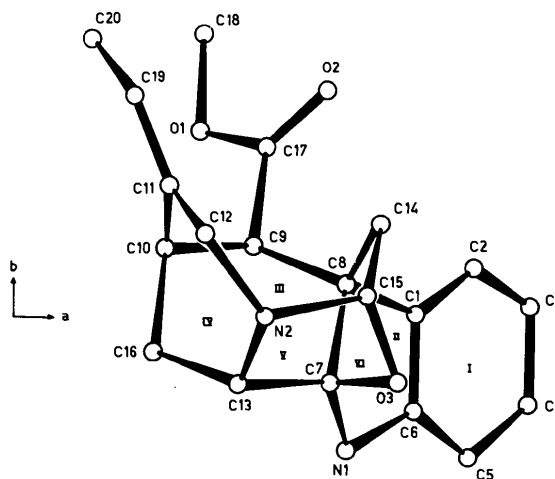


Fig. 1. A view of the picrinine molecule with the atom-numbering scheme.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

C(1)–C(2)	1.380 (5)	C(10)–C(11)	1.522 (5)
C(2)–C(3)	1.395 (5)	C(11)–C(12)	1.528 (5)
C(3)–C(4)	1.394 (7)	C(12)–N(2)	1.462 (6)
C(4)–C(5)	1.392 (8)	N(2)–C(13)	1.504 (5)
C(5)–C(6)	1.380 (7)	C(11)–C(19)	1.331 (7)
C(1)–C(6)	1.410 (5)	C(19)–C(20)	1.495 (8)
C(1)–C(8)	1.524 (5)	C(8)–C(14)	1.558 (5)
C(6)–N(1)	1.406 (5)	C(14)–C(15)	1.531 (5)
N(1)–C(7)	1.414 (5)	C(15)–N(2)	1.496 (6)
C(7)–C(8)	1.570 (5)	C(15)–O(3)	1.426 (6)
C(8)–C(9)	1.538 (5)	O(3)–C(7)	1.464 (5)
C(9)–C(10)	1.561 (5)	C(9)–C(17)	1.526 (5)
C(10)–C(16)	1.536 (6)	C(17)–O(2)	1.197 (5)
C(16)–C(13)	1.521 (6)	C(17)–O(1)	1.341 (5)
C(13)–C(7)	1.521 (6)	O(1)–C(18)	1.462 (6)
C(2)–C(1)–C(6)	119.6 (3)	C(10)–C(11)–C(12)	114.9 (3)
C(2)–C(1)–C(8)	131.6 (3)	C(10)–C(11)–C(19)	124.8 (3)
C(8)–C(1)–C(6)	108.7 (3)	C(12)–C(11)–C(19)	119.9 (3)
C(1)–C(2)–C(3)	120.0 (4)	C(11)–C(12)–N(2)	116.7 (3)
C(2)–C(3)–C(4)	119.4 (4)	N(2)–C(13)–C(7)	99.7 (3)
C(3)–C(4)–C(5)	121.6 (5)	C(7)–C(13)–C(16)	113.6 (3)
C(4)–C(5)–C(6)	118.1 (5)	N(2)–C(13)–C(16)	113.2 (3)
C(5)–C(6)–N(1)	128.4 (4)	C(8)–C(14)–C(15)	100.2 (3)
C(5)–C(6)–C(1)	121.3 (4)	N(2)–C(15)–C(14)	113.0 (4)
C(1)–C(6)–N(1)	110.3 (3)	O(3)–C(15)–C(14)	101.9 (3)
N(1)–C(7)–C(8)	106.4 (2)	N(2)–C(15)–O(3)	101.9 (3)
N(1)–C(7)–O(3)	113.2 (3)	C(10)–C(16)–C(13)	109.4 (3)
C(8)–C(7)–C(13)	111.7 (3)	C(9)–C(17)–O(2)	126.3 (3)
C(8)–C(7)–O(3)	101.8 (3)	O(1)–C(17)–O(2)	123.3 (3)
C(13)–C(7)–O(3)	100.6 (2)	C(9)–C(17)–O(1)	110.4 (3)
C(1)–C(8)–C(9)	110.2 (2)	C(11)–C(19)–C(20)	128.6 (5)
C(1)–C(8)–C(7)	99.1 (3)	C(6)–N(1)–C(7)	107.3 (3)
C(7)–C(8)–C(14)	101.1 (2)	C(12)–N(2)–C(13)	115.9 (3)
C(9)–C(8)–C(14)	115.3 (3)	C(13)–N(2)–C(15)	104.5 (3)
C(9)–C(8)–C(7)	111.1 (3)	C(12)–N(2)–C(15)	115.6 (4)
C(1)–C(8)–C(14)	118.2 (3)	C(18)–O(1)–C(17)	115.8 (4)
C(8)–C(9)–C(10)	114.9 (2)	C(7)–O(3)–C(15)	95.5 (3)
C(8)–C(9)–C(17)	111.6 (3)	C(9)–C(10)–C(11)	115.7 (3)
C(17)–C(9)–C(10)	110.8 (3)	C(9)–C(10)–C(16)	106.7 (3)
		C(11)–C(10)–C(16)	109.1 (3)

IV, V and VI are heterocyclic. The bond lengths and bond angles are listed in Table 2.\*

The phenyl ring I of the indole moiety is almost planar, the maximum deviation of an individual atom from the mean plane of the ring being 0.012 (6) Å for C(4). C(1) and C(6) rise above other atoms of the ring in the *c* direction so that the phenyl ring is slightly inclined to the *ab* plane. The mean value for the endocyclic angles in the ring is 120 (4)°. The average bond length is 1.392 (6) Å.

A torsion angle of  $-0.2$  (4)° for C(8)–C(1)–C(6)–N(1) indicates that these atoms in the five-membered ring II are planar. The deviation of C(7) from the mean plane of the ring is about 0.188 (4) Å, being 'pure envelope' (Cremer & Pople, 1975). The hydrogen atom

\*Tables of coordinates of H atoms, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles, least-squares planes and a list of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51259 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

H(N1) bonded to N(1) was unambiguously located on the difference electron density map. It lies in the same plane as C(6), C(7) and N(1). Thus the hybridization of N(1) is  $sp^2$ .

Ring III consists of C(7), C(8), C(9), C(10), C(13) and C(16); among these C(7), C(8), C(10) and C(16) lie almost in the *ab* plane while C(9) and C(13) are below and above the plane of these atoms, respectively. The ring is in a 'distorted chair' conformation (Ramakrishnan, 1980; Cremer & Pople, 1975). Four sides of this ring, C(7)–C(8), C(8)–C(9), C(9)–C(10) and C(7)–C(13), form part of the highly puckered eight-membered ring where C(10) is joined to C(13) through a  $-CH_2-$  bridge *via* C(16). The N(2) atom is folded back above ring III in the *ab* plane. C(7)–C(8) is slightly lengthened owing to the presence of bulky groups around C(7). Also the lengthening of C(9)–C(10) is due to the strain arising from the chain, O(2)–C(17)–O(1)–C(18), attached to C(9). All endocyclic angles in ring III except that at C(16) deviate significantly from the normal  $sp^3$  value.

The conformation of the six-membered ring IV, consisting of C(10), C(11), C(12), N(2), C(13) and C(16), is between 'ideal boat' and 'twist boat' (Cremer & Pople, 1975).

Both of the five-membered rings, V and VI, consisting of C(7), C(13), N(2), C(15), O(3) and C(8), C(14), C(15), O(3), C(7), respectively, assume puckered, distorted 'twist conformations' (Cremer & Pople, 1975). The lengthening of N(2)–C(13) and N(2)–C(15) bonds may be attributed to the strain arising from bulky group linked to C(13) and C(15).

The length of the C(19)–C(11) bond shows that this is a double bond. The sum of the valence angles around C(11) is about 360° which also suggests that this is an  $sp^2$  carbon atom. However, the bond angle of 128.6 (5)° at C(19) deviates significantly from the ideal  $sp^2$  value. Interaction of the methyl group at C(20) and the double bond C(19)–C(11) (hyperconjugation)

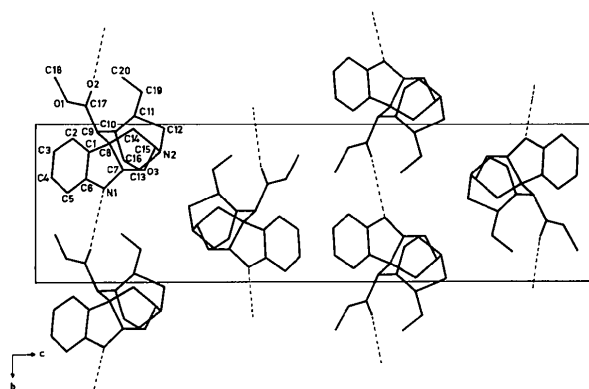


Fig. 2. A view of the crystal packing arrangement.

causes some shortening of the single bond C(19)–C(20) (Pauling, 1960).

The packing of the molecule viewed along *a* is shown in Fig. 2. The molecules are linked in chains by fairly strong hydrogen bonding between N(1)–H(N1)···O(2) [N(1)–H(N1) 1.040, N(1)···O(2) 3.122 (4), H(N1)···O(2) 2.19 Å, N(1)–H(N1)···O(2) 148.2°]. Parallel chains of hydrogen-bonded picrinine molecules are laterally displaced at regular intervals along the *c* direction. The hydrogen bonds together with the van der Waals forces associated with the other atoms represent the intermolecular interactions that stabilize the structure.

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#### References

- CHATTERJEE, A., MUKHERJEE, B., RAY, A. B. & DAS, B. (1965). *Tetrahedron Lett.* **41**, 3633–3637.
- CREMER, D. & POPLI, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, NY: Cornell Univ. Press.
- RAMAKRISHNAN, C. (1980). In *Computing in Crystallography*, edited by R. DIAMOND, S. RAMASESHAN & K. VENKATESHAN. Bangalore: Indian Academy of Sciences.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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## A DNA-Intercalating Compound Derived from 7H-Pyridocarbazole: the Structure of 10-Methoxy-2-Methyl-7H-pyrido[4,3-c]carbazolium Iodide

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**Abstract.** C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O<sup>+</sup>.I<sup>-</sup>, *M<sub>r</sub>* = 390.22, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.017 (2), *b* = 8.123 (5), *c* = 19.074 (4) Å, β = 95.86 (2)°, *V* = 1544 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.67 g cm<sup>-3</sup>, μ = 2.10 cm<sup>-1</sup>, λ(Mo Kα) = 0.7107 Å, *F*(000) = 768, *R* = 0.04 for 1236 unique reflections measured at 295 K. Dimensions of the ring system are similar to those found in 6*H*-pyridocarbazole analogues (ellipticine derivatives). The iodine ion and pyridocarbazolium system are linked by a hydrogen bond. The planar 7*H*-pyridocarbazole cations form stacks approximately parallel to *b*. Interactions between stacks occur by weak van der Waals forces.

**Introduction.** In the series of 6*H*-pyridocarbazoles, several compounds, mainly derivatives of ellipticines

(5,11-dimethyl-6*H*-pyrido[3,4-*b*]carbazole), show pronounced antitumor activity (Le Pecq, Dat-Xuong, Gosse & Paoletti, 1974). Activity on human tumors has been reported for some derivatives (Paoletti, Le Pecq, Dat-Xuong, Juret, Garnier, Amiel & Rouesse, 1980). This activity is related to the DNA-binding properties of this planar aromatic system. The mechanism involved in this interaction is an intercalation between adjacent base pairs in the DNA. Such properties are also found in the series of 7*H*-pyridocarbazoles, but if these derivatives are able to intercalate in DNA (Lauga, Delbarre & Roques, 1981), they show weak or no antitumor activity (Pelaprat, Oberlin, Le Guen, Roques & Le Pecq, 1980). The present study was undertaken to obtain more stereochemical information on this new