

## The Crystal and Molecular Structure of the Alkaloid Ambelline

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The crystal and molecular structure of the alkaloid ambelline,  $C_{18}H_{21}NO_5$ , has been determined by direct methods from three-dimensional diffractometer data. Absorption corrections were made. The unit cell is orthorhombic, space group  $P2_12_12_1$ , with four molecules per unit cell and  $a=11.729$ ,  $b=8.838$ ,  $c=15.306$  Å. The final value of  $R$  over 1542 independent reflexions is 6.1%. The thermal motion was analysed in terms of the rigid-body model; the hydrogen bonding is described.

### Introduction

Ambelline is one of the alkaloids found in *Amaryllidaceae*. Several plants of this family, which are used for local pharmacopoeia in Ivory Coast, are currently being examined by a research group of the University of Abidjan for their structural and medicinal properties. Ambelline has been extracted from bulbs of *Crinum jagus*, then purified and crystallized from chloroform. Chemical and mass-spectrum analysis confirmed the molecular formula  $C_{18}H_{21}NO_5$ . The absolute configuration of the aliphatic methoxyl (Fig. 1) had been chemically established (Fales & Wildman, 1960).

### Experimental

The crystals of ambelline are colourless lozenge-shaped plates bounded by well developed faces. The orthorhombic symmetry and the space group were determined from precession photographs. The unit-cell dimensions and their e.s.d.'s, presented in Table 1, were calculated from 15 high-angle  $Cu K\alpha$  reflexions centred on a Syntex  $P2_1$  four-circle diffractometer. Intensity data were collected at 294 K on a crystal with overall dimensions  $0.35 \times 0.35 \times 0.15$  mm which was mounted with  $a$  parallel to the  $\phi$  axis of the goniostat. 1782 symmetry-independent reflexions were collected with graphite monochromatized  $Cu K\alpha$  radiation up to  $2\theta=156^\circ$  by the  $\theta-2\theta$  variable-scan technique. Two reflexions measured every thirty reflexions did not show any significant crystal decomposition due to X-ray exposure. 1542 reflexions (87%) were considered as observed [ $I \leq 2\sigma(I)$ ]. The collection was completed by a  $\psi$  scan on twenty selected reflexions. The Lorentz and polarization corrections were applied as usual; with the  $\psi$ -scan data, absorption was corrected for according to the empirical method described by Kopfmann & Huber (1968). An overall temperature factor and

Table 1. Crystal data

Ambelline, $C_{18}H_{21}NO_5$ ; m.p. 532–536 K; M.W. 331.4	
$a=11.729$ (2)	$V=1587$ Å <sup>3</sup> [ $\alpha$ ] <sub>D</sub> =48°
$b=8.838$ (2)	$D_m=1.39$ g cm <sup>-3</sup> for $Z=4$
$c=15.306$ (3)	$D_x=1.38$ g cm <sup>-3</sup>
$\lambda(Cu K\alpha)=1.54178$ Å	$F(000)=704$
$T=294$ K	
Space group $P2_12_12_1$	

an absolute scale factor were computed by statistical methods.

### Structure determination

The structure was solved by applying a modification of the symbolic addition procedure (Karle & Karle, 1966). Three reflexions were fixed to define the origin of the cell; the numerical values of the phases of six additional reflexions were determined by the phase-function method (Riche, 1970, 1972). The phases of 224 reflexions were obtained by an iterative application of the tangent formula to the set of phases which gave the highest peaks in the phase-function map. The second  $E$  map readily displayed the whole molecular skeleton but one atom (C24) which was found by an electron density synthesis.

The starting set of phases is given in Table 2.

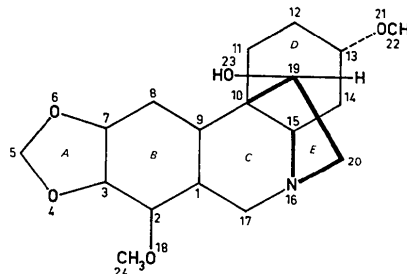


Fig. 1. The ambelline molecule.

Table 2. *Starting set*

<i>h</i>	<i>k</i>	<i>l</i>	$\varphi$ (cycle)	$ E $	} origin
10	0	1	0.250	3.83	
7	0	10	0.000	2.87	
0	7	8	0.250	2.45	
5	4	9	0.875	2.83	
3	8	3	0.125	2.79	
8	2	4	0.500	2.60	
4	5	7	0.000	2.49	
2	1	15	0.250	2.49	
0	3	5	0.250	2.18	

The signs of the *z* coordinates were changed to give the correct absolute configuration. Three cycles of least-squares block-diagonal refinement with isotropic parameters, followed by two cycles with anisotropic parameters improved the conventional *R* index to 10.5%. The H atoms were located on a difference electron density map; among them, five were slightly misplaced and their positions were corrected to give expected bond angles. At this point, full-matrix anisotropic cycles with H atom parameters held constant reduced the *R* value to 6.1%; the weighted residual  $R_w = [\sum w(|F_o| - |F_c|)^2 / (w|F_o|^2)]^{1/2}$  was 5.8%. The quantity minimized was  $\sum w|AF|^2$ . The relative shifts in the last cycle of refinement were less than 0.3 for all parameters. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Positional and thermal parameters are quoted in Tables 3(a), 3(b) and 4.\*

### Thermal motion analysis

Fig. 2 gives a stereoscopic view of the molecule and shows the shape and orientation of the thermal vibration ellipsoids. The thermal motion has been analysed according to the rigid-body model (Schomaker & Trueblood, 1968). **T, L, S** molecular tensors were derived from experimental anisotropic thermal parameters of 19 heavy atoms engaged in at least one ring (Table 5). The r.m.s. deviation of the observed thermal vibration

\* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31365 (4 pp.). Copies may be obtained through The Executive Secretary International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3(a). *Coordinates of heavy atoms ( $\times 10^5$ ) with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	50708 (48)	44926 (64)	6761 (38)
C(2)	50996 (51)	33257 (81)	12981 (41)
C(3)	41383 (51)	24631 (75)	14193 (38)
C(5)	28029 (54)	7670 (68)	18153 (45)
C(7)	31711 (49)	27523 (67)	9323 (37)
C(8)	31031 (46)	38739 (61)	3066 (34)
C(9)	40889 (45)	47255 (61)	1785 (33)
C(10)	41110 (43)	60165 (63)	-4842 (35)
C(11)	33109 (47)	58315 (64)	-12380 (36)
C(12)	35684 (50)	61946 (70)	-20519 (37)
C(13)	46802 (56)	68808 (62)	-23248 (36)
C(14)	54531 (47)	73008 (68)	-15605 (36)
C(15)	53712 (44)	62015 (64)	-8061 (35)
C(17)	61345 (48)	54432 (68)	5697 (37)
C(19)	39529 (49)	73529 (73)	50 (41)
C(20)	51553 (40)	78824 (50)	3753 (97)
C(22)	58072 (67)	64669 (95)	-36273 (47)
C(24)	62977 (62)	18886 (65)	22550 (47)
O(4)	39176 (41)	13306 (60)	20241 (34)
O(6)	23153 (33)	17714 (49)	11824 (27)
O(18)	61321 (40)	31378 (63)	17388 (39)
O(21)	52700 (43)	58249 (46)	-28896 (28)
O(23)	31252 (34)	75258 (49)	6742 (26)
N(16)	59608 (37)	67515 (54)	-107 (31)

Table 3(b). *Coordinates of hydrogen atoms ( $\times 10^4$ ) ( $B = 3.5 \text{ \AA}^2$  for all atoms)*

	<i>x</i>	<i>y</i>	<i>z</i>
H(151)	3019	0	1579
H(152)	2512	690	2448
H(8)	2392	4052	-36
H(11)	2528	5338	-1080
H(12)	2989	6133	-2449
H(13)	4489	7759	-2642
H(141)	6257	7324	-1769
H(142)	5223	8323	-1347
H(15)	5738	5345	-1018
H(171)	6770	4655	381
H(172)	6314	5871	1202
H(19)	3910	8341	-492
H(201)	5177	7932	985
H(202)	5555	8793	170
H(221)	5250	7105	-3953
H(222)	6146	5702	-4016
H(223)	6433	7204	-3435
H(23)	2355	7759	446
H(241)	6234	1099	1868
H(242)	7056	1906	2551
H(243)	5684	1815	2725

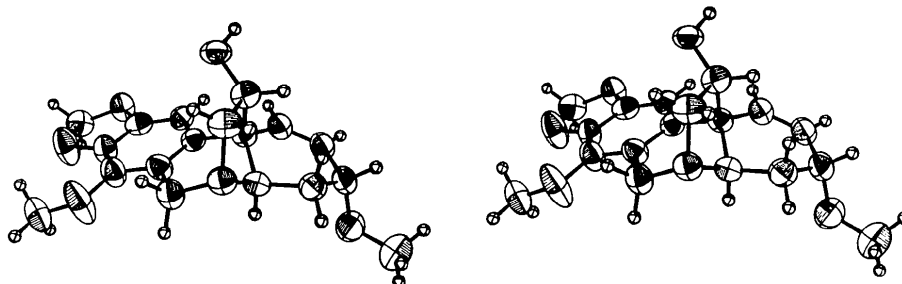


Fig. 2. Stereoscopic plot of the ambelline molecule. Thermal ellipsoids are scaled to include 50% probability.

Table 4. *Thermal parameters of heavy atoms (with e.s.d.'s in parentheses) ( $\times 10^5$ )*The parameters are in the form:  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	574 (41)	1354 (80)	516 (28)	8 (49)	-26 (31)	73 (42)
C(2)	688 (46)	1954 (110)	570 (31)	-65 (65)	-154 (35)	240 (52)
C(3)	803 (50)	1490 (93)	494 (29)	-113 (61)	-94 (32)	205 (44)
C(5)	974 (58)	1220 (84)	658 (34)	-135 (59)	41 (41)	46 (47)
C(7)	606 (42)	1415 (81)	493 (27)	-120 (55)	40 (29)	-147 (42)
C(8)	668 (42)	1178 (73)	396 (24)	-108 (54)	41 (27)	3 (35)
C(9)	588 (41)	1207 (72)	367 (23)	-14 (48)	19 (26)	-20 (35)
C(10)	535 (37)	1211 (74)	429 (24)	-23 (49)	-14 (26)	32 (38)
C(11)	686 (45)	1285 (75)	473 (26)	-29 (53)	-56 (31)	100 (41)
C(12)	788 (50)	1482 (85)	499 (28)	84 (59)	-74 (32)	140 (46)
C(13)	1005 (58)	1161 (77)	441 (27)	216 (60)	6 (33)	119 (39)
C(14)	701 (45)	1340 (80)	505 (28)	-57 (55)	43 (30)	87 (41)
C(15)	601 (41)	1164 (71)	457 (25)	59 (51)	-7 (28)	-34 (37)
C(17)	668 (46)	1589 (87)	524 (27)	-150 (55)	-68 (33)	163 (45)
C(19)	715 (47)	1420 (80)	462 (24)	-55 (56)	-6 (32)	-75 (41)
C(20)	720 (50)	1514 (97)	603 (33)	-122 (61)	9 (34)	-140 (48)
C(22)	1309 (75)	2292 (148)	603 (37)	-267 (92)	119 (46)	36 (64)
C(24)	1157 (71)	2120 (126)	652 (36)	240 (84)	-306 (45)	185 (62)
O(4)	1053 (45)	2402 (92)	925 (32)	-402 (57)	-269 (33)	821 (48)
O(6)	775 (34)	1664 (66)	605 (22)	-277 (43)	-73 (24)	207 (34)
O(18)	933 (42)	2697 (103)	1196 (38)	-375 (57)	-497 (35)	964 (56)
O(21)	1415 (53)	1323 (59)	595 (23)	130 (51)	200 (31)	25 (33)
O(23)	648 (30)	1863 (71)	525 (20)	255 (43)	34 (22)	-153 (34)
N(16)	544 (33)	1448 (70)	499 (22)	-131 (45)	-19 (25)	20 (37)

ellipsoids from those calculated is  $0.079 \text{ \AA}^2$ . This value and the criteria defined by Burns, Ferrier & McMullan (1968) show that the fit is only moderately good. This fit becomes better when the analysis is restricted to rings *B*, *C*, *D* and *E* (r.m.s. deviation  $0.046 \text{ \AA}^2$ ) which behave nearly as a rigid part. For out-of-ring atoms, it can be seen that O(23) and O(18) have some additional motion while C(24) has a smaller observed ellipsoid than calculated. The translational motion is almost isotropic with an average r.m.s. amplitude of  $0.21 \text{ \AA}$ ; the libration is limited by the molecular close-packing and the hydrogen-bond net.

Table 5. *Molecular tensors for ambelline (out-of-ring atoms are excluded), Schomaker-Trueblood analysis, centre of mass coordinates*

$\begin{bmatrix} 412 & 22 & 26 \\ & 413 & 41 \\ & & 483 \end{bmatrix}$	$\begin{bmatrix} 10.7 & -5.6 & 1.9 \\ & 6.0 & -0.9 \\ & & 4.6 \end{bmatrix}$	$\begin{bmatrix} -10 & 19 & 44 \\ & 6 & 3 & -30 \\ & -2 & 1 & 7 \end{bmatrix}$
T ( $\text{\AA}^2$ ) $\times 10^4$	L (deg $^2$ )	S ( $\text{\AA rad}$ ) $\times 10^4$

### Molecular structure and packing

The overall shape of the molecule is illustrated in Fig. 2. The bond lengths and valency angles are shown in Fig. 3. The mean value of the  $C(sp^3)-C(sp^3)$  bond distances amounts to  $1.537 \text{ \AA}$ , in good agreement with the commonly observed value of  $1.533 \text{ \AA}$  (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). Least-squares planes through selected fragments of the molecule were computed (Table 6). The aromatic ring *B* is planar with an average C-C bond length of  $1.388 \text{ \AA}$ . Ring *A* is slightly folded about the direction

O(4)···O(6), as in the lycorine molecule (Roques, Piquion, Fourme & André, 1974). Rings *C* and *D* are

Table 6. *Least-squares planes through selected parts of the ambelline molecule and displacements ( $\text{\AA}$ ) of the atoms from these planes*

Atoms excluded from the calculation of the least-squares plane are denoted by an asterisk.

	(a)	(b)	(c)	(d)
C(1)	-0.27	-0.01	0.11	
C(2)	-0.09	0.01		
C(3)	0.15	0.01		
C(5)	0.60	0.06		
C(7)	0.22	0.00		
C(8)	0.06	-0.01		
C(9)	-0.16	0.01	-0.02	
C(10)	-0.37		-0.25	-0.15
C(11)	0.30			-0.03
C(12)	0.91			0.08
C(13)	0.96			0.06
C(14)	0.11			-0.26
C(15)	0.09		0.46	0.31
C(17)	-0.56		0.05	
C(19)	-1.91		-1.74*	
C(20)	-2.21		-1.76*	
C(22)	2.74			1.32*
C(24)	0.20	0.28*		
O(4)	0.27	-0.06		
O(6)	0.44	-0.03		
O(18)	-0.17	0.05*		
O(21)	2.34			1.35*
O(23)	-2.72			
N(16)	-0.91		-0.35	

Equations of planes, where  $x, y, z$  are the fractional coordinates in the unit cell

(a)	$0.1886x - 0.7514y - 0.6323z = 2.2439$
(b)	$0.3235x - 0.6477y - 0.6898z = 1.3545$
(c)	$0.3638x - 0.7263y - 0.5832z = 1.4302$
(d)	$0.3319x - 0.9109y - 0.2452z = 2.9074$

distorted boats. Part *E* is a constrained pentagonal ring with two bond lengths significantly longer than the quoted standard value [ $C(10)-C(15)=1.567$ ,  $C(10)-C(19)=1.569$  Å] and valency angles between ( $sp^3$ ) carbon atoms ranging from  $99.8$  to  $103.1^\circ$ .

In the spatial packing, each molecule is linked to two neighbouring molecules by  $O(23)-H(23)\cdots N(16)$  linear hydrogen bonds to form infinite chains parallel to the *a* crystal axis, as can be seen in Fig. 4. The shortest intermolecular distances, which are approximately equal to the sum of van der Waals radii, are listed in Table 7. These contacts are fairly numerous. H(23), which is involved in the hydrogen bond, is in very close interaction with atoms C(14), C(15), C(17), C(20).

Calculations were performed on a UNIVAC 1110 computer (Centre de Calcul de l'Université Paris-Sud), using the Créteil terminal. A local version of the X-RAY 70 System of crystallographic programs (Stewart, Kundell & Baldwin, 1970) was used, including

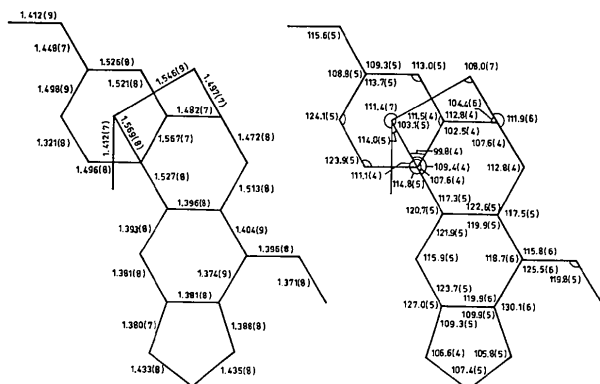


Fig. 3. Bond distances and angles in the ambelline molecule.

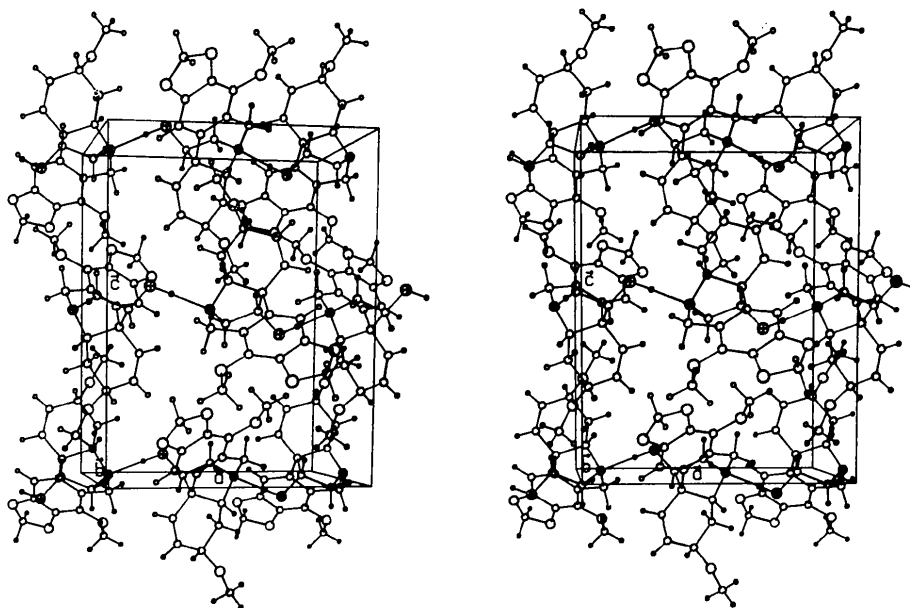


Fig. 4. Stereoscopic plot of the molecular packing. Atoms engaged in the hydrogen bonding have a distinct representation.

Table 7. *Intramolecular shortest distances and hydrogen bonding in the ambelline structure*

	Distance (Å)	
C(5)·····C(12) <sup>2</sup>	3.58	
C(7)·····H(15) <sup>5</sup>	2.89	
C(8)·····H(12) <sup>2</sup>	2.99	
C(24)·····C(22) <sup>8</sup>	3.57	
O(21)·····H(223) <sup>3</sup>	2.97	
O(23)·····H(142) <sup>8</sup>	2.57	
H(11)·····H(5) <sup>1</sup>	2.59	
H(141)·····H(241) <sup>5</sup>	2.32	
H(19)·····H(242) <sup>4</sup>	2.34	
H(23)·····H(222) <sup>7</sup>	2.22	
C(14) <sup>6</sup>	2.81	
C(15) <sup>6</sup>	2.56	
C(17) <sup>6</sup>	2.64	
C(20) <sup>6</sup>	2.93	

Hydrogen bond	Distance	Distance	Angle
O(23)-H(23)·····N(16) <sup>6</sup>	H·····N	O·····N	O-H-N
	1.82 Å	2.82 Å	178°

#### Symmetry code

(1)	$x, 1+y, z$	(5)	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$
(2)	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$	(6)	$-\frac{1}{2}+x, \frac{3}{2}-y, -z$
(3)	$\frac{3}{2}-x, 1-y, \frac{1}{2}+z$	(7)	$1-x, \frac{1}{2}+y, -\frac{1}{2}-z$
(4)	$\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$	(8)	$1-x, -\frac{1}{2}+y, -\frac{1}{2}-z$

*RIGBOD*, a program for the analysis of thermal motion (André, Fourme & Zechmeister, 1972), and *ABSORP*, program for empirical absorption correction (Kopfmann & Huber, 1968). The set of starting phases was chosen with the aid of *DEVIN*, written by C. Riche; the illustrations were prepared with *ORTEP* (Johnson, 1965).

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## The Structure of Aliphatic Amine Adducts of Uranyl Acetylacetonate. I. Dioxobis-(2,4-pentanedionato)mono-(2-*N*-methylaminopentan-4-one)uranium(VI)

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Crystals of the title compound are monoclinic with  $a=8.314$  (5),  $b=22.723$  (9),  $c=12.589$  (6) Å,  $\beta=123.0$  (2)°,  $Z=4$ , space group  $P2_1/c$ . The structure was determined by Patterson and Fourier methods and refined by full-matrix least squares to a final  $R$  of 0.030 for 2043 independent reflexions. The U atom has pentagonal bipyramidal coordination and the *N*-methylacetylacetonamine is bonded to U *via* O. There are two intramolecular N–H···O hydrogen bonds which govern the geometry of the adduct molecule.

#### Introduction

The reaction of uranyl nitrate with acetylacetonate (HAA) in the presence of ammonia and a variety of primary and secondary amines has recently been re-investigated (Haigh & Thornton, 1971). It was found that the product of the reaction of uranyl nitrate with acetylacetonate in the presence of methylamine could be formulated as the  $\beta$ -ketoamine adduct of uranylacetylacetonate,  $\text{UO}_2(\text{AA})_2[\text{CH}_3\text{-CO-CH=C}(\text{CH}_3)\text{-NHCH}_3]$ . The stoichiometry of the complex was deduced from IR and PMR measurements, and it was suggested that the structure was probably analogous to that established for the hydrate,  $\text{UO}_2(\text{AA})_2(\text{H}_2\text{O})$ , (Frasson, Bombieri & Panattoni, 1966), which is

pentagonal bipyramidal. It was suggested (Haigh & Thornton, 1971), that the adduct molecule would be bonded to U *via* the O atom, but no suggestions were made concerning the spatial arrangements of the three ring systems present in the complex. We are undertaking the structural determination of a series of compounds of this type to determine whether the adduct is bonded through O or N and to investigate the hydrogen bonding. The methylamine derivative was chosen first due to its crystalline excellence.

#### Experimental

The compound was prepared as previously described (Haigh & Thornton, 1971).

A single crystal was ground to a sphere of radius 0.14 mm and the lattice constants were obtained from a least-squares analysis of the settings of 25 reflexions measured on a four-circle diffractometer with Mo  $K\alpha$

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