

temperature, would lead to a dynamic situation at high temperature which could be frozen in at low temperature [as was observed and predicted in the anthracene-TCNB complex (Luty & Kuchta, 1986)]. On lowering the temperature the first case would lead to approximately the same apparent oscillation as at room temperature, but the second case would show a considerable reduction in the molecular oscillation. The third case might or might not lead to a significant reduction of thermal motion. Low-temperature structure determination is planned in order to establish which kind of disorder occurs in the acridine-TCNB complex.

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### Conformation of Multiflorine\*

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**Abstract.** C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O, *M<sub>r</sub>* = 246.3, monoclinic, *P*2<sub>1</sub>, *a* = 12.008 (2), *b* = 7.568 (2), *c* = 8.297 (2) Å, β = 114.70 (1)°, *V* = 685.0 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.19 (4) g cm<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å, μ =

5.55 cm<sup>-1</sup>, *F*(000) = 268, room temperature, *R* = 0.039 for 892 unique observed reflections. The configuration of both *A/B* and *C/D* ring junctions is *trans*. The γ-keto-α,β-enamine ring *A* adopts a slightly distorted half-chair conformation, ring *B* a distorted chair conformation, ring *C* is a boat and ring *D* is in almost ideal chair conformation. Protonation of the free base changes the *C/D*-junction configuration into *cis* and the *C*-ring conformation into chair.

\* 1,7,7a,8,9,10,11,13,14,14a-Decahydro-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1',2'-*e*][1,5]diazocin-2-one.

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**Introduction.** Multiflorine has been extracted with ethyl ether from alkaliized seeds of *Lupinus albus* cv. BAC (Wysocka & Brukwicki, 1988). Previously it was isolated from *L. varius* (Crow & Riggs, 1955) and *L. multiflorus* (Comin & Deulofeu, 1959).

The structure of multiflorine in solution has recently been determined by  $^{13}\text{C}$  NMR spectroscopy (Brukwicki & Wysocka, 1989); however, unequivocal confirmation of the conformation in the solid state was necessary.

**Experimental.** Crystal of approximate dimensions  $0.20 \times 0.15 \times 0.30$  mm, Syntex  $P2_1$  diffractometer, graphite monochromator,  $\text{Cu K}\alpha$  radiation. Accurate cell parameters refined from setting angles of 15 reflections ( $20 \leq 2\theta \leq 52^\circ$ ).  $\theta$ - $2\theta$  profiles measured and analysed according to the Lehmann & Larsen (1974) procedure. The intensities of two monitor reflections measured after every 30 reflections showed no significant change during the data collection. 1003 reflections measured with  $2\theta \leq 115^\circ$  ( $-13 \leq h \leq 11$ ,  $0 \leq k \leq 8$ ,  $0 \leq l \leq 9$ ). No absorption correction. 892 unique observed reflections with  $I \geq 2\sigma(I)$ . Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms generated geometrically. Full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976), function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w^{-1} = \sigma^2(F_o) + 0.0001F_o^2$ ,  $\sigma(F_o)$  based on counting statistics. Non-H atoms refined anisotropically, H atoms at calculated positions riding on their C atoms; isotropic temperature factors for H atoms, one value for each group of atoms attached to a common heavy atom. At final stages extinction corrections were performed, empirical isotropic extinction parameter  $x$  used to correct  $F_c$  according to  $F_c' = F_c(1 - xF_c^2/\sin\theta)$ ,  $x$  converged at 0.063 (3). Final refinement of 163 parameters converged at  $R = 0.039$ ,  $wR = 0.046$ ,  $S = 2.47$ ,  $(\Delta/\sigma)_{\text{max}} = 0.01$  in final cycle, largest peak in final  $\Delta F$  map  $0.09 \text{ e } \text{\AA}^{-3}$ , largest hole  $-0.11 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors those incorporated in *SHELX76*. Other computer programs used: local programs (Jaskólski, 1982), *ORTEP* (Johnson, 1976), *PLUTO78* (Motherwell & Clegg, 1978).

**Discussion.** Final positional parameters and  $U_{\text{eq}}$  for non-H atoms are given in Table 1.\* The molecule is shown in Fig. 1. The bond lengths and bond angles are listed in Table 2.

\* Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom parameters, asymmetry parameters, least-squares-planes data, intermolecular contacts and a molecular packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51661 (13 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 and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = \frac{1}{3}(U_{11}U_{22}U_{33}).$$

	x	y	z	$U_{\text{eq}}$
N(1)	0.8208 (3)	0.0863	-0.0003 (4)	0.058 (1)
C(2)	0.8023 (3)	0.1051 (8)	-0.1722 (5)	0.070 (2)
C(3)	0.8029 (3)	0.2606 (8)	-0.2529 (5)	0.073 (2)
C(4)	0.8141 (3)	0.4236 (7)	-0.1653 (5)	0.067 (2)
O(4)	0.8158 (3)	0.5689 (6)	-0.2296 (4)	0.096 (1)
C(5)	0.8157 (4)	0.4113 (7)	0.0174 (5)	0.064 (1)
C(6)	0.8707 (3)	0.2404 (6)	0.1145 (5)	0.054 (1)
C(7)	0.8524 (3)	0.2172 (5)	0.2856 (4)	0.050 (2)
C(8)	0.9170 (3)	0.0483 (6)	0.3777 (5)	0.060 (1)
C(9)	0.8483 (3)	-0.1030 (7)	0.2578 (5)	0.064 (2)
C(10)	0.8575 (4)	-0.0884 (6)	0.0805 (6)	0.072 (2)
C(11)	0.7146 (3)	-0.1108 (7)	0.2386 (5)	0.056 (1)
C(12)	0.6920 (4)	-0.2778 (6)	0.3218 (6)	0.079 (2)
C(13)	0.5627 (5)	-0.2848 (8)	0.3122 (7)	0.097 (2)
C(14)	0.5352 (4)	-0.1172 (8)	0.3887 (6)	0.085 (2)
C(15)	0.5621 (3)	0.0440 (7)	0.3036 (5)	0.074 (2)
N(16)	0.6887 (2)	0.0439 (6)	0.3231 (3)	0.056 (1)
C(17)	0.7156 (3)	0.2067 (6)	0.2502 (5)	0.055 (1)

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with their e.s.d.'s in parentheses

N(1)-C(2)	1.356 (5)	C(8)-C(9)	1.515 (6)
N(1)-C(6)	1.466 (4)	C(9)-C(10)	1.525 (7)
N(1)-C(10)	1.464 (4)	C(9)-C(11)	1.547 (5)
C(2)-C(3)	1.356 (8)	C(11)-C(12)	1.518 (7)
C(3)-C(4)	1.409 (7)	C(11)-N(16)	1.463 (6)
C(4)-O(4)	1.226 (7)	C(12)-C(13)	1.522 (7)
C(4)-C(5)	1.511 (6)	C(13)-C(14)	1.515 (8)
C(5)-C(6)	1.521 (6)	C(14)-C(15)	1.511 (8)
C(6)-C(7)	1.535 (6)	C(15)-N(16)	1.460 (4)
C(7)-C(8)	1.525 (5)	N(16)-C(17)	1.467 (6)
C(6)-N(1)-C(10)	117.2 (3)	C(8)-C(9)-C(11)	110.7 (4)
C(2)-N(1)-C(10)	117.5 (3)	C(8)-C(9)-C(10)	109.9 (3)
C(2)-N(1)-C(6)	116.3 (3)	C(10)-C(9)-C(11)	113.2 (3)
N(1)-C(2)-C(3)	125.3 (4)	N(1)-C(10)-C(9)	112.2 (3)
C(2)-C(3)-C(4)	121.6 (4)	C(9)-C(11)-N(16)	109.8 (3)
C(3)-C(4)-C(5)	115.0 (4)	C(9)-C(11)-C(12)	111.1 (3)
C(3)-C(4)-O(4)	125.2 (4)	C(12)-C(11)-N(16)	109.5 (3)
O(4)-C(4)-C(5)	119.8 (4)	C(11)-C(12)-C(13)	112.2 (4)
C(4)-C(5)-C(6)	113.9 (4)	C(12)-C(13)-C(14)	110.2 (4)
N(1)-C(6)-C(5)	111.3 (3)	C(13)-C(14)-C(15)	110.7 (4)
C(5)-C(6)-C(7)	112.9 (3)	C(14)-C(15)-N(16)	111.3 (3)
N(1)-C(6)-C(7)	109.4 (3)	C(11)-N(16)-C(15)	111.6 (3)
C(6)-C(7)-C(8)	112.5 (3)	C(15)-N(16)-C(17)	110.6 (3)
C(6)-C(7)-C(8)	108.7 (3)	C(11)-N(16)-C(17)	110.3 (3)
C(8)-C(7)-C(17)	109.3 (3)	C(7)-C(17)-N(16)	111.4 (3)
C(7)-C(8)-C(9)	106.3 (3)		

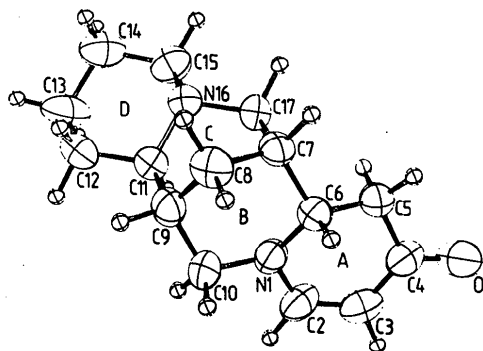


Fig. 1. A view of the molecule.

The bond lengths and bond angles are comparable, within experimental error, with those found in other sparteine derivatives with the exception of the values of ring *A*. The mean values for the  $C_{sp^2}-C_{sp^2}$  and  $C_{sp^2}-N_{sp^2}$  bonds are equal to 1.527 (4) and 1.464 (2) Å, respectively. In ring *A* the same pattern of bond-length distribution has been found as in the structure of multiflorine perchlorate hemihydrate (Pyżalska, Gdaniec, Borowiak & Wolińska-Mocydlarz, 1980), which indicates a noticeable conjugation in the N(1)–C(2)–C(3)–C(4)–O(4) bond system. This is confirmed by least-squares-plane calculations which indicate that the N(1), C(2), C(3), C(4), O(4) system is nearly planar.

The four-ring system has a *trans,trans* configuration at the *A/B* and *C/D* ring junctions: the torsion angles along the N(1)–C(6) bond are equal to +38.8 (4) and –49.3 (4)° in rings *A* and *B*, respectively; those along the C(11)–N(16) bond are +55.1 (3) and –59.3 (4)° in rings *C* and *D*, respectively.

The conformations of the *A*, *B* and *D* rings of multiflorine are similar to those of multiflorine perchlorate hemihydrate (Pyżalska *et al.*, 1980). Ring *A* is in a slightly distorted half-chair conformation. The displacements of C(5) and C(6) from the least-squares plane through N(1), C(2), C(3) and C(4) are –0.191 (4) and +0.392 (3) Å, respectively. The rotation symmetry along the line joining the midpoints of the C(2)–C(3) and C(5)–C(6) bonds is reflected in the small value [9 (1)°] of the  $\Delta C_2^{2,3}$  asymmetry parameter (Duax & Norton, 1975; Duax, Weeks & Rohrer, 1976). Ring *B* adopts a distorted chair conformation. The distortion involves the loss of the mirror plane,  $\Delta C_5^6 = 14.2$  (8)°, with retention of the rotation symmetry,  $\Delta C_2^{1,10} = 3.6$  (8)° (the ring is twisted). The asymmetry parameters of ring *D* have low values, showing nearly ideal chair conformation.

Ring *C* adopts a boat conformation, the torsion angles along the C(7)–C(17) and C(9)–C(11) bonds being equal to 3.1 (4) and 7.3 (4)°, respectively. The C(7), C(9), C(11), C(17) system is almost planar and the displacements of N(16) and C(8) from this plane equal –0.671 (3) and –0.730 (4) Å, respectively.

In the case of multiflorine perchlorate the protonation takes place on the N(16) atom. The lone pair on N(1) in the  $\gamma$ -keto- $\alpha,\beta$ -enamine system in ring *A* is involved in the above-mentioned conjugation and for this reason is inactive for protonation. It has also been shown that the N(1)···N(16) intramolecular hydrogen bond is impossible in the multiflorine monocation (Pyżalska *et al.*, 1980) for the same reason.

A comparative analysis of the conformational data for the present structure and for the structure of multiflorine perchlorate hemihydrate (Pyżalska *et al.*,

1980) indicates that the intermolecular hydrogen bond between the two crystallographically independent cations and one water molecule is probably the factor which determines the change of conformation of the *C/D* fragment from *trans/boat*–chair in the free base into *cis/chair*–chair in the monocation.

In the case of sparteine free base and its monocation a configurational–conformational change in the *C/D* quinolizidine system also takes place: from *trans/boat*–chair in the free base into *cis/chair*–chair in the monocation (Borowiak, Bokii & Struchkov, 1973; Brukwicki & Wysocka, 1989). The factor which determines this change is an intramolecular N(1)–H···N(16) hydrogen bond.

In conclusion, the protonation of multiflorine or sparteine free base causes a change of *C*-ring conformation into the chair form due to hydrogen-bond formation.

The crystal structure of multiflorine is stabilized by van der Waals forces. No short intermolecular contacts have been observed.

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