

The Structure of 4,4-Dimethylazacyclohexane-2,6-dione (4,4-Dimethyl-2,6-piperidinedione)*

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Abstract. C₇H₁₁NO₂, $M_r = 141.2$, orthorhombic, *Pccn*, $a = 10.553$ (3), $b = 19.536$ (3), $c = 7.338$ (1) Å, $V = 1512.8$ (5) Å³, $Z = 8$, $D_c = 1.12$ Mg m⁻³. Final $R = 0.065$ for 1137 reflections. The ring shows a half-boat conformation and the two methyl groups are in pseudo-equatorial and axial positions respectively. The molecules are joined in chains along [001] by N—H...O hydrogen bonds.

Introduction. The influence of the carbonyl function on the geometries of five- and six-membered rings is the object of a systematic study in progress in our laboratories to gain a better understanding of the nature of the electronic interactions between the C=O group and the rest of the molecule. Moreover, it seems interesting to compare the data obtained by X-ray analysis in the solid state with results obtained from solution studies, mostly by NMR spectroscopic methods, to deduce correlations between the preferred conformations of the rings.

The compound was recrystallized from benzene as white elongated prisms. One of them was cut to give a single crystal of dimensions 0.6 × 0.3 × 0.2 mm. The orthorhombic symmetry and preliminary cell dimensions were deduced by rotation and Weissenberg photographs. Cell parameters were then refined using the $(\theta, \chi, \varphi)_{hkl}$ values of 14 reflections accurately measured on a Siemens AED diffractometer.

Intensities were collected at room temperature, using Ni-filtered Cu K α radiation, for 2786 ($\pm hkl$) reflections with $\theta < 70^\circ$ which were merged to give 1437 independent reflections; 1137 with $I \geq 2\sigma(I)$ were considered observed and used in the analysis. Absorption was ignored.

The structure was solved by direct methods using *SHELX* (Sheldrick, 1975). Refinement was carried out

by full-matrix anisotropic least squares down to $R = 0.14$. A ΔF synthesis computed at this stage revealed six of the H atoms and the remainder were located after further anisotropic refinement cycles; all these atoms were then refined isotropically. Three reflections affected by non-systematic errors were omitted in the last cycles of refinement which converged to $R = 0.065$, $R_w = 0.058$ ($R_w = \sum |F_o - F_c| w^{1/2} / \sum F_o w^{1/2}$; $w = 0.005$).

The final atomic parameters and their estimated standard deviations are given in Table 1.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35811 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$ for O, N and C, $\times 10^3$ for H) and isotropic temperature factors

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

	x	y	z	B_{eq} (Å ²)
O(1)	1932 (1)	4891 (1)	2108 (2)	4.75
O(2)	804 (2)	6123 (1)	7015 (2)	6.28
N	1286 (1)	5498 (1)	4537 (2)	3.76
C(1)	1222 (1)	5331 (1)	2717 (2)	3.45
C(2)	262 (2)	5697 (1)	1589 (3)	4.06
C(3)	-67 (1)	6414 (1)	2264 (3)	3.86
C(4)	-396 (2)	6352 (1)	4300 (3)	4.37
C(5)	594 (2)	6002 (1)	5414 (2)	4.07
C(6)	-1206 (2)	6682 (1)	1197 (5)	6.16
C(7)	1061 (2)	6897 (1)	1995 (4)	4.89
H(1)	182 (2)	527 (1)	520 (4)	
H(2)	-43 (3)	537 (1)	165 (3)	
H(3)	60 (2)	577 (1)	33 (4)	
H(4)	-52 (2)	682 (1)	488 (4)	
H(5)	-114 (2)	605 (1)	453 (3)	
H(6)	-147 (3)	712 (1)	167 (4)	
H(7)	-195 (3)	637 (1)	147 (5)	
H(8)	-100 (3)	669 (1)	-17 (5)	
H(9)	86 (2)	735 (1)	240 (4)	
H(10)	117 (2)	693 (1)	56 (4)	
H(11)	186 (2)	679 (1)	261 (3)	

* Stereochemistry of Rings. III. Cyclohexane Derivatives. 1. Part II: Bocelli (1981).

The calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna) with financial support from the University of Parma.

Discussion. A view of the molecule is depicted in Fig. 1 which also gives the numbering scheme. Table 2 reports bond distances and angles with their standard deviations, and least-squares planes are given in Table 3.

The ring shows a half-boat conformation; following the Cremer & Pople (1975) notation, the values of the ring-puckering coordinates are: $Q = 0.46$ (1) Å, $\varphi = 183.8$ (4), $\theta = 49.2$ (5)° [using the atomic sequence N, C(1), C(2), C(3), C(4), C(5)], with C(2), C(1), N, C(5) almost coplanar. The displacement of C(4) from this plane is probably dependent on steric hindrance between this atom and the C(7) axial methyl group of the vicinal molecules.

The two methyl groups are in pseudo-equatorial and axial positions respectively, angles of 69.1 (4) and

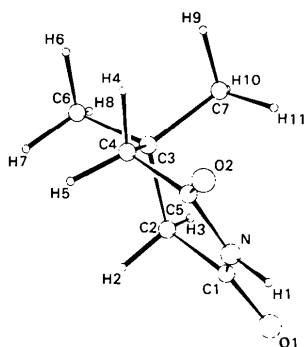


Fig. 1. Perspective view of the molecule.

Table 2. Bond distances (Å) and angles (°)

O(1)—C(1)	1.225 (2)	N—H(1)	0.87 (2)
O(2)—C(5)	1.219 (2)	C(2)—H(2)	0.97 (2)
N—C(1)	1.376 (2)	C(2)—H(3)	1.00 (3)
N—C(5)	1.385 (3)	C(4)—H(4)	1.02 (2)
C(1)—C(2)	1.491 (3)	C(4)—H(5)	1.00 (2)
C(2)—C(3)	1.526 (3)	C(6)—H(6)	0.96 (2)
C(3)—C(4)	1.539 (3)	C(6)—H(7)	1.01 (3)
C(3)—C(6)	1.527 (3)	C(6)—H(8)	1.03 (4)
C(3)—C(7)	1.532 (3)	C(7)—H(9)	0.96 (2)
C(4)—C(5)	1.492 (3)	C(7)—H(10)	1.06 (3)
		C(7)—H(11)	0.98 (2)
C(1)—N—C(5)	126.4 (1)	C(6)—C(3)—C(7)	109.5 (2)
O(1)—C(1)—N	119.4 (1)	C(4)—C(3)—C(7)	110.4 (2)
N—C(1)—C(2)	117.3 (1)	C(4)—C(3)—C(6)	110.3 (2)
O(1)—C(1)—C(2)	123.4 (2)	C(3)—C(4)—C(5)	114.2 (2)
C(1)—C(2)—C(3)	114.5 (2)	N—C(5)—C(4)	116.1 (2)
C(2)—C(3)—C(7)	110.3 (2)	O(2)—C(5)—C(4)	124.5 (2)
C(2)—C(3)—C(6)	109.1 (2)	O(2)—C(5)—N	119.4 (2)
C(2)—C(3)—C(4)	107.1 (2)		

Table 3. Equations of planes referred to orthogonal axes with distances (Å) of relevant atoms from the planes

The e.s.d.'s of the equations are calculated following Waser, Marsh & Cordes (1973).

Plane 1: N, C(1), C(2), C(3), C(4), C(5)

$$0.7920 (305)X + 0.5983 (512)Y - 0.1216Z = 7.0167 (61)$$

N 0.079 (2), C(1) -0.007 (2), C(2) -0.281 (2), C(3) 0.222 (2), C(4) -0.307 (2), C(5) 0.012 (2), O(1) 0.127 (2), O(2) 0.186 (2), C(6) -0.322 (2), C(7) 1.753 (2)

Plane 2: C(2), C(1), N, C(5)

$$0.6916 (695)X + 0.6867 (511)Y - 0.2241Z = 7.5831 (10)$$

C(2) -0.011 (2), C(1) 0.014 (2), N -0.015 (2), C(5) 0.012 (2), O(1) 0.042 (2), O(2) 0.064 (2), C(3) 0.600 (2), C(4) -0.058 (2)

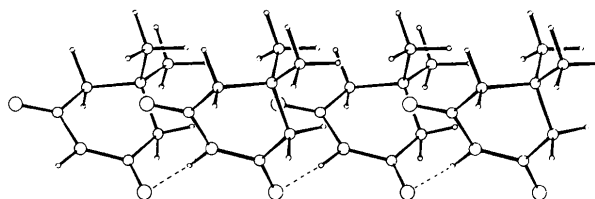


Fig. 2. Packing of the molecules.

1.4 (5)° being formed by the two bond lines [C(3)—C(6) and C(3)—C(7)] and the normal to the ring mean plane.

All bond distances and angles agree well with expected values but the C—N—C angle is significantly larger [126.4 (1)°] than a normal sp^2 angle. This large value, as previously observed in compounds containing similar molecular fragments (Egert, Lindner, Hillen & Gassen, 1978; Hamor, O'Leary & Walker, 1977, 1978; Srikrishnan & Parthasarathy, 1978; Porter & Voet, 1978), is in agreement with the observations of Singh (1965). Following the results of these observations, the enlargement of the angle at the N atom together with the C=O bond lengths [1.225 (2), 1.219 (2) Å] indirectly confirm the absence of an enolic tautomer in the solid state.

Fig. 2 shows the packing of molecules. Hydrogen bonds [O(1)⋯N = 2.916 (2), O(1)⋯H(1) = 2.06 (3) Å, N—H⋯O = 168.8 (4)°] link the molecules in chains running along the *c* axis, and slightly perturb the geometry of the ring, not sufficiently to affect the bond distances but giving an enlargement of the endocyclic C—C—N angle at the C attached to the O involved in the hydrogen bond.

There are no other unusually short non-bonded distances.

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The Structure of Decussine; A New Indole Alkaloid

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Abstract. C₂₀H₁₉N₃, orthorhombic, *P*2₁2₁2₁, *a* = 9.391 (1), *b* = 9.934 (1), *c* = 17.144 (2) Å, *V* = 1599.2 Å³, *Z* = 4, *D_x* = 1.251 Mg m⁻³, *T* = 297 K, *μ*(Mo *Kα*) = 0.07 mm⁻¹, final *R* = 0.061 for 1579 observed reflections. Decussine is a pentacyclic indole alkaloid composed of a tetrahydro-β-carboline skeleton with an azepino ring attached to a pyridine ring. The compound has been isolated from the bark of an African plant (*Strychnos decussata*) and has a pronounced muscle-relaxant effect. The molecules crystallize in a herring-bone pattern with only van der Waals interactions between them.

Introduction. A new indole alkaloid, named decussine, has been isolated from the stem bark of *Strychnos decussata* (Pappe) Gilg. collection No. Lg 10 797 collected in Karawa, Kenya. The alkaloid was shown to have a pronounced muscle-relaxant effect both *in vivo* and *in vitro* and the molecular and crystal structure is reported here. The chemical and pharmacological work has been described by Rolfsen, Olaniyi, Sandberg & Kvick (1980).

A slightly elongated crystal of maximum dimension 0.2 mm crystallized from methanol was used for the data collection on a CAD-4 diffractometer with graphite-monochromatized Mo *Kα* radiation and an *ω*/2*θ* scan method. A preliminary film investigation indicated orthorhombic symmetry and *P*2₁2₁2₁ as the

space group. The reflections in the octant *hkl* out to a maximal $\sin \theta/\lambda = 0.64 \text{ \AA}^{-1}$ were collected. Three reflections were monitored at regular intervals to provide a check on crystal and experimental stability. Only deviations expected from counting statistics were observed. A total of 2011 independent intensities were collected and corrected for background by a profile-analysis method (Lehmann & Larsen, 1974) and for Lorentz and polarization effects, but not for absorption ($\mu = 0.07 \text{ mm}^{-1}$). The structure was solved by direct methods with the program *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) and refined by least squares minimizing the quantity $\sum w(F_o^2 - k^2|F_c|^2)^2$ with the program *UPALS*. The weights were $w = \sigma^{-2}(F_o^2)$, and $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.05F_o^2)^2$ where $\sigma_c(F_o^2)$ is based on counting statistics. The standard deviation of an observation of unit weight is $S = [\sum w(F_o^2 - k^2|F_c|^2)^2/(m - n)]^{1/2} = 0.99$ where *m* is the total number of observations (1579 reflections with $F_o^2 > 0$) and *n* is the total number of parameters varied (284).

The 284 parameters included the scale factor, positional parameters for the 42 atoms, anisotropic thermal parameters for the 23 non-H atoms and 19 isotropic thermal parameters for the H atoms. The final agreement factors are $R(F^2) = \sum |F_o^2 - k^2|F_c|^2|/\sum |F_o^2| = 0.061$; $R_w(F^2) = [\sum w(F_o^2 - k^2|F_c|^2)^2/\sum wF_o^4]^{1/2} = 0.075$; $R(F^2) = 0.085$ if the 432 reflections with $F_o^2 < 0$ were included.

The scattering factors for neutral H, C, and N atoms were taken from *International Tables for X-ray Crystallography* (1974). The programs used have been

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