

Structure of 1,2,3,4-Tetrahydro-1-methyl-2-oxo-3-azocinecarbonitrile

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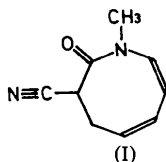
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Abstract. C₉H₁₀N₂O, orthorhombic, *Pbca*, *Z* = 8, *a* = 13.624 (5), *b* = 13.757 (3), *c* = 9.234 (2) Å, *D_m* = 1.21, *D_x* = 1.237 Mg m⁻³. The structure was solved by the symbolic-addition procedure; block-diagonal least-squares refinement led to a final *R* of 0.082 for 817 observed reflexions. Molecules are held together by van der Waals interactions. The azocine ring has an extremely distorted boat conformation; the single bond lying between the two C–C double bonds is fairly short (1.44 Å), indicating some conjugation between them. However, the large torsion angle (49°) formed by these bonds prevents conjugation. The bond angles of the C atoms in this part of the molecule are also large (ca 130°).

Introduction. On photoreaction of 2-pyridones with electrophilic ethylenes, 3-substituted 1,2,3,4-tetrahydro-2-oxoazocines and stereospecific [2 + 2] cyclo-adducts were obtained (Somekawa, Shimou, Tanaka & Kumamoto, 1975; Somekawa & Kumamoto, 1977). On the basis of PMR and mass spectra, the chemical structures of the former products were proposed to be of the type (I). The photochemical reactions are complicated and the PMR signals of 1-alkyl derivatives show unusual features. Therefore, the X-ray diffraction study of the title compound was carried out to confirm the presumed chemical structure and also to determine the precise molecular conformation.



The title compound was recrystallized from a benzene solution as colorless plates. Preliminary

Weissenberg photographs showed systematic absences indicating the space group to be *Pbca*. The unit-cell parameters were refined by a least-squares procedure using the 2θ values of 15 reflexions measured on a Syntex *P1* four-circle diffractometer. The density was measured by flotation in an aqueous KI solution. A single crystal (approximate dimensions: 0.25 × 0.19 × 0.17 mm) was used for intensity measurements. 2372 reflexions within a range of $2\theta \leq 55^\circ$ were collected by the θ - 2θ scan technique with a variable scan rate from 4.8 to 12.0° min⁻¹ (monochromated Mo *K* α radiation). 817 independent reflexions with $I > 2.33\sigma(I)$ were considered to be observed and they were used for the analysis. Corrections for Lorentz and

Table 1. Reflexions and their *E* values used as a starting set for phasing

<i>h</i>	<i>k</i>	<i>l</i>	<i>E</i>	Sign	
0	0	2	2.58	–	Known phases
0	0	4	2.09	+	
0	0	10	2.92	+	
0	4	0	1.85	–	
0	6	0	2.39	–	
0	10	0	2.71	+	
0	12	0	1.74	+	
2	0	0	1.61	+	
10	0	0	1.79	–	
10	4	0	1.68	+	
12	0	0	2.82	–	Origin set
12	0	4	2.79	–	
16	0	0	2.08	–	
0	8	3	3.89	+	Symbolic set
5	0	8	3.98	+	
6	11	2	3.61	+	
2	9	2	2.42	–	
5	2	7	3.11	–	
12	6	4	2.75	+	

polarization effects and for fluctuation of the monitored intensities were applied, but no absorption corrections were made.

The structure was solved by the direct method using the program *MULTAN* (Germain, Main & Woolfson, 1971). The phases of 13 reflexions were obtained by the Σ_1 relation and three reflexions to define the origin were selected automatically. Three additional reflexions were then allowed to assume all possible sign combinations. The combination shown in Table 1 gave the highest value of the figure of merit (1.28) which was used for phasing of 263 reflexions with $E \geq 1.5$. An E map calculated with those reflexions revealed all 13 non-hydrogen atoms as the largest 13 peaks in the asymmetric unit. An R value calculated with this model was 0.20 for all observed reflexions.

Block-diagonal least-squares refinement of the atomic coordinates and anisotropic thermal parameters reduced R to 0.116. A difference Fourier synthesis calculated at this stage gave all the H atom peaks. By introduction of these H atoms into the refinement the final R dropped to 0.082 for the observed reflexions. Shifts of the positional and thermal parameters of the non-hydrogen atoms were almost one tenth of the standard deviations. A final difference Fourier map had no peaks $>0.3 \text{ e } \text{Å}^{-3}$. The final atomic coordinates are listed in Table 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34075 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic coordinates with their estimated standard deviations in parentheses

	x	y	z
C(1)	0.0431 (5)	0.3966 (5)	0.2394 (8)
C(2)	0.0315 (5)	0.3409 (5)	0.0974 (8)
C(3)	0.0064 (6)	0.2343 (5)	0.1284 (9)
C(4)	0.0895 (7)	0.1786 (5)	0.1967 (9)
C(5)	0.1842 (6)	0.2017 (6)	0.2118 (10)
C(6)	0.2390 (6)	0.2885 (6)	0.1822 (9)
C(7)	0.2214 (5)	0.3784 (6)	0.2181 (8)
C(8)	-0.0507 (5)	0.3855 (6)	0.0163 (8)
Me	0.1497 (6)	0.4851 (6)	0.4079 (9)
N(1)	0.1355 (4)	0.4140 (4)	0.2863 (6)
N(2)	-0.1123 (5)	0.4167 (6)	-0.0490 (8)
O	-0.0291 (3)	0.4259 (4)	0.3054 (6)
H(C2)	0.097 (5)	0.341 (5)	0.030 (8)
H(1C3)	-0.060 (5)	0.235 (6)	0.191 (8)
H(2C3)	-0.016 (6)	0.201 (6)	0.029 (9)
H(C4)	0.070 (7)	0.108 (6)	0.233 (11)
H(C5)	0.230 (7)	0.138 (6)	0.248 (11)
H(C6)	0.307 (5)	0.277 (5)	0.120 (8)
H(C7)	0.267 (7)	0.435 (7)	0.193 (10)
H(1Me)	0.214 (6)	0.470 (5)	0.468 (8)
H(2Me)	0.097 (5)	0.485 (6)	0.478 (10)
H(3Me)	0.159 (6)	0.555 (6)	0.374 (9)

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Unit weights for all the observed reflexions were adopted in the least-squares refinement. All calculations were performed on the FACOM M-190 computer at the Computer Centre of Kyushu University with the *UNICS II* program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974).

Discussion. Fig. 1 shows the crystal structure of a cell projected along the c axis, together with the atom-numbering system, bond distances and angles. The molecules are held together by van der Waals forces.

The presence of an azocine ring suggested on the basis of the chemical evidence is confirmed by the results of the present structure analysis. The azocine

Table 3. Distances (Å) of atoms from the best least-squares plane

The equation of the molecular plane is $-0.2050X - 0.1810Y + 0.9619Z = 0.6431$, where X, Y, Z are expressed in Å along the crystallographic cell edges.

C(1)*	0.375	C(8)	-1.316
C(2)*	-0.715	Me	1.353
C(3)*	-0.104	N(2)	-1.802
C(4)*	0.410	O	1.090
C(5)*	0.221	H(C2)	-1.501
C(6)*	-0.411	H(1C3)	0.638
C(7)*	-0.267	H(2C3)	-0.842
N(1)*	0.491	H(C4)	0.964
		H(C5)	0.572
		H(C6)	-1.124
		H(C7)	-0.760
		H(1Me)	1.749
		H(2Me)	2.126
		H(3Me)	0.849

* Indicates atoms involved in the calculation of the least-squares plane.

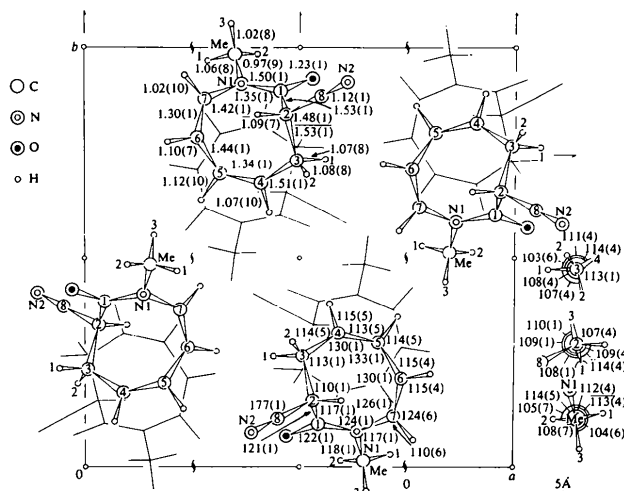


Fig. 1. The crystal structure projected along the c axis.

ring has an extremely distorted boat conformation as shown in Fig. 2 and Table 3. The ring consists of three parts: the two C—C double bonds [C(4)—C(5), C(6)—C(7)] connected by the single bond [C(5)—C(6)], the amide group [N(1),C(1)], and the two singly bonded C atoms [C(2),C(3)] with tetrahedral configurations. The H(1) and H(2) atoms attached to C(3) are in *gauche* positions with respect to C(8) and H(C2) respectively, and the cyano group [C(8),N(2)] is in the equatorial position of the ring.

The ring itself has some interesting and unusual features in its molecular geometry: the single bond C(5)—C(6) is fairly short (1.44 Å), indicating some conjugation with the adjacent double bonds in this part of the molecule. But the large torsion angle (49°) of C(4)—C(5)—C(6)—C(7) (Table 4), prevents the conjugation to some extent. Moreover, the bond angles in

this part are remarkably large (*ca* 130°) and also the C(6)—C(7) double bond is fairly short (1.30 Å). This unusual bonding behavior due to the large strain of the azocine ring is consistent with the fact that this compound is not subject to either Diels—Alder addition or bromination of the C(3) position by *N*-bromosuccinimide, which is characteristic of an ordinary conjugated C—C double bond (Paquette, 1964).

On the basis of the large torsion angle (51°) observed for C(6)—C(7)—N(1)—C(1) and fairly short N(1)—C(1) bond length (1.35 Å), it seems likely that the lone-pair electrons of N(1) are strongly conjugated with the carbonyl group but not with the C(6)—C(7) double bond. In other words, N(1) should be considered as a part of an amide group rather than that of an enamine group. In fact, a strong IR absorption band was observed in the region characteristic of amide groups.

Table 4. Torsion angles (°) of the ring

N(1)—C(1)—C(2)—C(3)	101
C(1)—C(2)—C(3)—C(4)	-112
C(2)—C(3)—C(4)—C(5)	13
C(3)—C(4)—C(5)—C(6)	-7
C(4)—C(5)—C(6)—C(7)	-49
C(5)—C(6)—C(7)—N(1)	7
C(6)—C(7)—N(1)—C(1)	51
C(7)—N(1)—C(1)—C(2)	5

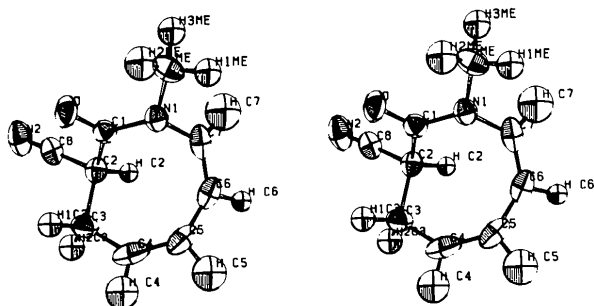


Fig. 2. A stereoview of the molecular conformation drawn with the program ORTEP (Johnson, 1965).

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Neutron Diffraction Study of Diaquaxonium 2,5-Dibromobenzenesulphonate*

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Abstract. [H₂O]₂[C₆H₃Br₂SO₃], monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 7.040 (2), *b* = 7.656 (1), *c* = 22.157 (2) Å, β = 96.73 (2)° [Lundgren (1972). *Acta Cryst.* **B28**, 475–

481]. Neutron wavelength 1.210 Å, μ(measured) = 0.083 mm⁻¹. Intensities were recorded at 294 K. The H₂O₂⁺ complex consists of an H₃O⁺ ion hydrogen bonded to two water molecules. The central H₃O⁺ ion is disordered, with two probable O atom positions separated by 0.68 Å. H atom positions associated with

* Hydrogen Bond Studies. CXXXVI. Part CXXXV: Nahrungsbauer, Lundgren & Andersen (1979).