

The crystal structure of 5 α -cyano-3-keto-10-methyl-octahydronaphthalene

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Abstract. 5 α -cyano-3-keto-10-methyl-octahydronaphthalene, C₁₂H₁₇NO, crystallizes in monoclinic space group $P2_1c$ with $a = 7.28(2)$, $b = 7.48(2)$, $c = 19.29(5)\text{\AA}$, $\beta = 88.0(2)^\circ$ and has four molecules per unit cell. The structure was solved by direct methods and refined to an R -value of 11.4% by block diagonal least-squares method for 565 observed reflections recorded by film method. The cyano group is *cis* to methyl group at C(10) and the fused rings have a chair conformation. The carbonitrile fragment is almost linear, the angle C-C \equiv N being $175.6(3.0)^\circ$.

Keywords. Crystal structure; octahydronaphthalene; conformation.

1. Introduction

The compound 7 α -cyano-3-keto-4, 10-dimethyl- Δ^4 -octahydronaphthalene, referred to as cyanoenone is obtained as an intermediate during the total synthesis of ethylene thioketal of the stereoisomer isocarissone of carissone by the addition of hydrogen cyanide to 3-keto-4, 10-dimethyl- $\Delta^{4,6}$ -hexahydronaphthalene (Angadi 1977). The structure proposed on the basis of chemical and other physical methods is shown in figure 1(a). Recrystallization by slow evaporation of hexane solution resulted in colourless, prismatic crystals.

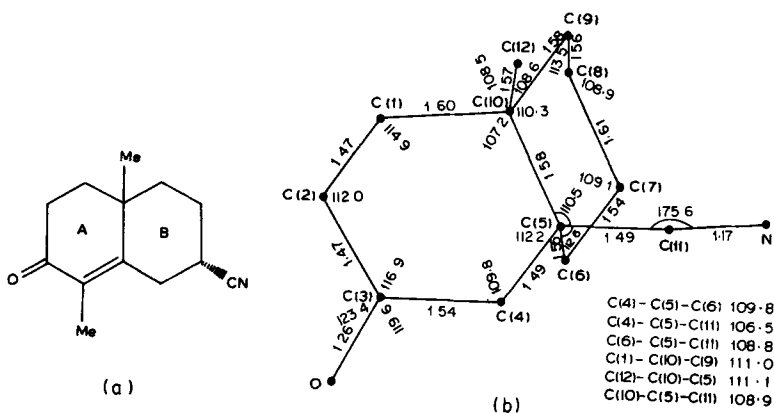


Figure 1. (a) Cyanoenone molecule. (b) Molecule viewed along 'b' axis with bond lengths and angles.

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Preliminary data of the compound were obtained from the rotation and equi-inclination Weissenberg photographs. The systematic absences $h0l$, ($l = 2n + 1$); $0k0$, $k = 2n + 1$, indicated the space group $P2_1/c$. The lattice parameters were refined using 13 reflections in the 2θ range $14-64^\circ$. The density of the crystal was measured by floatation technique using aqueous solution of sodium chloride. The disagreement between the measured density, 1.19 mg m^{-3} and the calculated density, 1.29 mg m^{-3} based on the molecular formula $\text{C}_{13}\text{H}_{17}\text{NO}$ (Angadi 1977) indicated the absence of one of the methyl groups in the molecule which was later confirmed from the difference Fourier maps. The compound investigated now is known as 5α -cyano-3-keto-10-methyl-octahydronaphthalene, $\text{C}_{12}\text{H}_{17}\text{NO}$. The crystal data is given in table 1.

2. Experimental

A single crystal of dimensions $0.31 \times 0.31 \times 0.5 \text{ mm}$ was used for data collection. The intensity data were recorded by taking multifilm equi-inclination Weissenberg photographs corresponding to reciprocal levels $l = 0$ to 6 using nickel filtered $\text{CuK}\alpha$ radiation. The intensities were estimated visually by comparison with a calibrated set of intensities of the 700 reflections accessible, the intensities of 565 reflections were measured. The data were corrected for Lorentz, polarization and spot shape (Phillips 1954) effects. The initial scale and temperature factor were determined from a Wilson plot (Wilson 1942).

The structure was solved by direct methods using MULTAN (Germain *et al* 1971) with 105 reflections having $E_{\min} \geq 1.34$. The E -map computed from the phase set having the highest figure of merit revealed the positions of six non-hydrogen atoms. Subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. The positional parameters of these atoms were refined with isotropic temperature factors giving an R -value of 20%. Further refinement with anisotropic temperature factors reduced the R -value to 16%. The positions of all the hydrogen atoms fixed from geometrical considerations were used in the structure factor calculations and their positional parameters were not refined. All the hydrogen atoms were

Table 1. Crystal data.

Chemical formula: $\text{C}_{12}\text{H}_{17}\text{NO}$	FW = 191.28
Crystal system: Monoclinic	F(000) = 416
Space Group: $P2_1/c$	$\lambda(\text{CuK}\alpha) = 1.5418\text{\AA}$
$a = 7.28(2)\text{\AA}$	$\mu(\text{CuK}\alpha) = 0.55 \text{ mm}^{-1}$
$b = 7.48(2)\text{\AA}$	$V = 1049.8\text{\AA}^3$
$c = 19.29(5)\text{\AA}$	$D_c = 1.20 \text{ mg m}^{-3}$
$\beta = 88.0(2)^\circ$	$D_m = 1.19 \text{ mg m}^{-3}$
$Z = 4$	

assigned a common isotropic temperature factor of 3.0\AA^2 . The final refinement resulted in an R -value of 0.114 for 565 observed reflections. The difference Fourier map taken at the end of final refinement was featureless thus supporting the absence of one of the methyl groups. Curickshank's (1965) weighting scheme was used in the final calculations and the weight of each reflection was calculated according to the formula

$$1/w = 2.914 - 0.1679 |F_o| + 0.0049 |F_o|^2.$$

The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The form factors for C, N and O are taken from Cromer and Waber (1965) and for hydrogens from Stewart *et al* (1965). The structure was refined on IBM 360/44 computer using crystallographic programs (Shiono and Reddy 1968). The final positional parameters of non-hydrogen atoms with ESD's in the parentheses are given in table 2.

3. Results and discussion

The structure obtained by x-ray methods along with bond lengths and angles is shown in figure 1(b). The ESD's in bond lengths vary from 0.04 to 0.05 \AA and for bond angles from 2.1 to 3 \Rightarrow respectively. The means C(sp³) - C(sp³) bond distance of 1.56(4) \AA is normal within the limits of experimental errors. The average value of the bond lengths C(2) - C(3) and C(3) - C(4) is 1.51(5) \AA and is in agreement with the value of 1.506(5) \AA associated with C(sp³) - C(sp²) single bond (Lide 1962). The observed bond length of 1.26(4) \AA for C = O bond compares with the value of 1.252 \AA proposed by Marsh and Donohue (1967). The C - C \equiv N chain is almost linear within the limits of experimental accuracy, the angle C - C \equiv N being 175.6(3.0) $^\circ$.

The torsional angles (table 3) for the rings A and B have an average value of 53(3) and 57(3) $^\circ$ respectively. These values are close to the range 52.9 - 57.1 $^\circ$ reported for cyclohexane derivatives (Dunitz and Strickler 1966; van

Table 2. Positional parameters ($\times 10^3$) with standard deviations for non-hydrogen atoms.

Atom	x	y	z
O	623(3)	218(2)	245(1)
N	319(5)	152(4)	-27(1)
C(1)	154(4)	285(4)	220(2)
C(2)	296(4)	183(4)	255(1)
C(3)	473(5)	188(4)	217(2)
C(4)	472(5)	143(4)	139(1)
C(5)	334(3)	256(3)	104(1)
C(6)	398(4)	454(4)	104(2)
C(7)	267(5)	579(4)	66(1)
C(8)	65(6)	569(4)	104(2)
C(9)	-2(4)	372(4)	105(1)
C(10)	136(4)	239(3)	140(2)
C(11)	327(4)	192(4)	32(1)
C(12)	59(5)	44(4)	133(2)

Table 3. Torsion angles(°) with ESD in parentheses.

C(1) - C(2) - C(3) - C(4)	- 50(4)
C(2) - C(3) - C(4) - C(5)	53(4)
C(3) - C(4) - C(5) - C(10)	- 55(3)
C(4) - C(5) - C(10) - C(1)	55(3)
C(5) - C(10) - C(1) - C(2)	- 52(3)
C(10) - C(1) - C(2) - C(3)	50(3)
C(10) - C(5) - C(6) - C(7)	- 58(3)
C(5) - C(6) - C(7) - C(8)	60(3)
C(6) - C(7) - C(8) - C(9)	- 57(3)
C(7) - C(8) - C(9) - C(10)	56(3)
C(8) - C(9) - C(10) - C(5)	- 55(3)
C(9) - C(10) - C(5) - C(6)	53(3)
C(12) - C(10) - C(5) - C(11)	54(3)

Remoortere and Boer 1971) and the rings have a chair conformation. The cyano group is *cis* to methyl group at C(10), the torsional angle C(12) - C(10) - C(5) - C(11) being 54(3)°. There is no intra- or inter-molecular hydrogen bonding and the molecules are loosely held by van der Waals interactions.

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