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4-Methylcinnoline

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Abstract. $C_9H_8N_2$, monoclinic, $P2_1/c$, $a = 11{\cdot}880$ (3), $b = 18{\cdot}258$ (5), $c = 7{\cdot}224$ (2) Å, $\beta = 107{\cdot}14$ (1)°, $V = 1497$ (1) Å^3, $Z = 8$, $D_x = 1{\cdot}28$ Mg m^{-3}; two molecules in the asymmetric unit; least-squares refinement technique; final R factor 8·0%, weighted R factor 3·1%; no absorption correction applied [μ(Mo $K\alpha$) = 0·074 mm^{-1}]. Differences greater than 2σ have been observed between the bond lengths and angles of the two independent molecules.

Introduction. In our laboratory the protonation behaviour of the diazanaphthalenes has been studied (van de Weijer, Thijsse & van der Meer, 1976). This group of compounds comprises ten isomers, of which six are symmetric from a chemical point of view, *i.e.* both N atoms are chemically equivalent. For these symmetric compounds there is no ambiguity about the site of protonation. With regard to the other four isomers, protonation can take place at two sites, *i.e.* at one of the two non-equivalent N positions. Calculations of the most probable protonation sites were carried out by van de Weijer, van der Meer & Koster (1975) using the molecular-potential method of Bonaccorsi, Scrocco & Tomasi (1971). The results of this method were in agreement with NMR experiments except for the case of cinnoline (1,2-diazanaphthalene) (van de Weijer, Thijsse & van der Meer, 1976). This discrepancy was attributed to the fact that the molecular potential was calculated on the basis of a naphthalene-like geometry. To verify this assumption we wanted to recalculate the molecular potential on the basis of the real cinnoline geometry. Unfortunately cinnoline did not yield crystals of sufficient quality; therefore we investigated the structure of the closely related 4-methylcinnoline.

Intensities and unit-cell dimensions were measured at room temperature (293 K) on a computer-controlled single-crystal diffractometer (Philips PW1100) using graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å). Details of the measurements are given in Table 1.

The calculation of the variances of the intensities has been performed according to McCandlish, Stout & Andrews (1975). The scaling factor K and its variance $S^2(K)$ were 1·00824 and 0·00018 respectively, indicating a stable measurement. The instability factor of the standards, P, was 0·0032.

The structure was solved with the aid of the program *MULTAN* (Germain, Main & Woolfson, 1971). The E map showed the positions of the C and N atoms. From a difference Fourier synthesis the positions of all the H atoms were found.

The refinement was carried out with a local version of the program *ORFLS* (Busing, Martin & Levy, 1962). The parameters used in the refinement were the positional parameters and anisotropic temperature factors of the C and N atoms, the positional parameters and isotropic temperature factors of the H atoms, a scaling factor and a secondary-extinction factor (Larson, 1969). The number of independent reflexions was 4318, of which only 2669 were greater than their estimated standard deviations. The function minimized was $\sum w(|F_o| - k|F_c|)^2$; the summation extends over all significant ($>1\sigma$) reflexions; k is the scaling factor; $|F_o|$ and $|F_c|$ are the observed and calculated structure factors; the weights w were taken to be $\sigma^{-2}(F_o)$. $\sigma^2(F_o) = [I + 0{\cdot}5S^2(I)]^{1/2} - I$ (Rees, 1976; de With, 1977), where I is the net intensity and $S(I)$ is its standard deviation. The scattering-factor tables for C and N were taken from *International Tables for X-ray Crystallography* (1974). The scattering-factor table for bonded H was taken from Stewart, Davidson & Simpson (1965). Including all significant reflexions, the final R factor was 8·0% and the weighted R factor 3·1% – a striking difference, due to a relatively large number of weak reflexions in the set.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34058 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Details of the measurements*

Scan mode	ω–2θ
Scan speed	0·04° s^{-1}
Scan width	1·6° + 0·5° tg θ
Detector aperture	
horizontal	2°
vertical	1°
Number of measured reflexions	4318
Radiation type	Mo $K\alpha$

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Table 2. *Fractional atomic coordinates*

Estimated standard deviations are in parentheses and refer to the last significant digits. The values for the C and N atoms are $\times 10^4$. The values for the H atoms are $\times 10^3$.

	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
N(1)	6300 (2)	5692 (1)	−1350 (3)	−1321 (2)	3036 (1)	3019 (3)
N(2)	6997 (2)	5121 (1)	−959 (3)	−2021 (2)	2467 (1)	2984 (3)
C(3)	7218 (2)	4783 (1)	784 (4)	−1589 (2)	1787 (2)	3006 (3)
C(4)	6780 (2)	4997 (1)	2241 (3)	−480 (2)	1609 (1)	3036 (3)
C(5)	5510 (2)	5926 (1)	3215 (4)	1480 (2)	2138 (2)	3091 (3)
C(6)	4775 (2)	6510 (1)	2690 (5)	2143 (3)	2736 (2)	3124 (4)
C(7)	4524 (2)	6816 (1)	840 (5)	1656 (3)	3439 (2)	3121 (4)
C(8)	5039 (2)	6550 (1)	−451 (5)	529 (3)	3530 (2)	3104 (3)
C(9)	5814 (2)	5941 (1)	26 (3)	−193 (2)	2908 (1)	3061 (3)
C(10)	6043 (2)	5618 (1)	1867 (3)	295 (2)	2203 (1)	3069 (3)
C(11)	7046 (4)	4573 (2)	4087 (5)	−115 (4)	827 (2)	3025 (6)
H(1)	780 (2)	433 (1)	97 (3)	−218 (2)	141 (1)	297 (3)
H(2)	572 (2)	567 (1)	452 (3)	176 (2)	161 (1)	315 (3)
H(3)	439 (2)	670 (1)	365 (4)	296 (2)	271 (1)	313 (3)
H(4)	394 (2)	723 (1)	49 (3)	214 (2)	387 (1)	320 (3)
H(5)	492 (2)	671 (1)	−171 (3)	10 (2)	398 (1)	306 (3)
H(6)	749 (2)	411 (1)	402 (4)	−73 (2)	51 (2)	311 (4)
H(7)	631 (2)	440 (1)	432 (4)	17 (2)	74 (2)	193 (4)
H(8)	737 (2)	487 (1)	513 (4)	60 (2)	77 (1)	412 (4)

Discussion. The atomic coordinates from the final refinement, including all significant reflexions, are given in Table 2. Bond lengths and angles of both molecules, including their differences, as calculated with the program *ORFFE* (Busing, Martin & Levy, 1964) are listed in Table 3. All covariances have been taken into account. Application of the χ^2 test to these differences shows that the probability that the molecular structures are identical is less than 0·1%.

In Table 4 the best planes of fit through the ring atoms and the atomic distances to these planes are given. Molecule 1 appears to be less flat than molecule 2.

ORTEP drawings (Johnson, 1965) of both molecules are shown in Fig. 1(*a*) and (*b*), illustrating that the thermal motions closely resemble one another.

Fig. 2 gives a stereo diagram of the molecular packing drawn with the program *POP*1 (van de Waal, 1978). It can be seen that the packing of molecules 1 differs from that of molecules 2. Molecules 1 are in a zigzag packing arrangement while molecules 2 are approximately antiparallel to each other.

A rigid-body analysis of the thermal motion, applied to the non-hydrogen atoms of both molecules (Schomaker & Trueblood, 1968), has been made. It has been found that the correction in bond lengths, due to librational motion, ranges from 0·006 to 0·010 Å. The librational motions of both molecules turned out to be virtually the same. As a consequence, the differences in the molecular structures cannot be explained by differences in thermal motion. The differences in packing (as discussed above) probably contribute to the calculated differences mentioned in Tables 3 and 4.

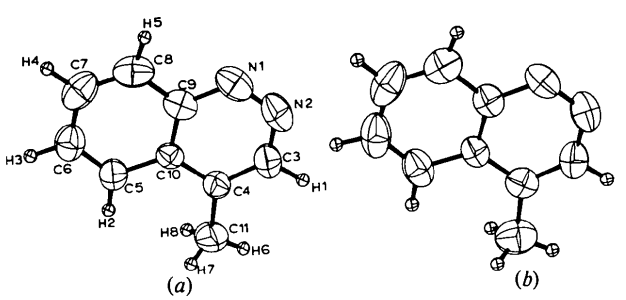

Fig. 1. Two independent molecules of 4-methylcinnoline. (*a*) Molecule 1, (*b*) molecule 2.

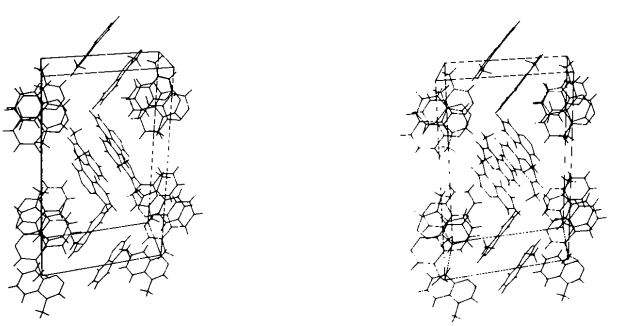

Fig. 2. Stereoscopic pair showing the molecular packing. Molecules 1 have been indicated by means of a dot on the C atom of the methyl group.

Calculation of the molecular potential on the basis of the present geometries indicated that protonation should occur at the β site. This is in agreement with the results of the NMR experiment.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *in the two molecules*

Estimated standard deviations are in parentheses and refer to the last digits.

	Molecule 1	Molecule 2	Δ*
N(1)–N(2)	1·310 (3)	1·326 (2)	16 (3)
N(2)–C(3)	1·357 (3)	1·343 (2)	−14 (4)
C(3)–C(4)	1·361 (5)	1·351 (2)	−10 (5)
C(5)–C(6)	1·359 (4)	1·343 (3)	−15 (4)
C(6)–C(7)	1·398 (4)	1·407 (3)	9 (5)
C(7)–C(8)	1·348 (5)	1·346 (3)	−2 (6)
C(9)–N(1)	1·366 (5)	1·351 (2)	−15 (5)
C(8)–C(9)	1·419 (3)	1·419 (3)	0 (4)
C(4)–C(10)	1·409 (3)	1·419 (2)	10 (4)
C(5)–C(10)	1·424 (5)	1·408 (2)	−16 (5)
C(9)–C(10)	1·406 (3)	1·411 (2)	4 (4)
C(4)–C(11)	1·493 (4)	1·493 (3)	0 (5)
C(3)–H(1)	1·07 (2)	0·98 (1)	−9 (2)
C(5)–H(2)	1·02 (2)	1·01 (2)	−1 (2)
C(6)–H(3)	1·00 (2)	0·97 (2)	−3 (2)
C(7)–H(4)	1·00 (2)	0·96 (2)	−4 (2)
C(8)–H(5)	0·93 (2)	0·96 (1)	4 (2)
C(11)–H(6)	1·01 (2)	0·95 (2)	−6 (3)
C(11)–H(7)	0·99 (2)	0·96 (2)	−3 (3)
C(11)–H(8)	0·92 (2)	0·98 (2)	6 (3)
C(9)–N(1)–N(2)	119·0 (2)	118·5 (2)	−5 (3)
N(1)–N(2)–N(3)	119·9 (3)	119·3 (2)	−5 (4)
N(2)–C(3)–C(4)	125·0 (2)	126·1 (2)	11 (3)
C(3)–C(4)–C(10)	116·1 (3)	116·2 (2)	1 (3)
C(4)–C(10)–C(9)	117·0 (3)	115·7 (2)	−14 (4)
C(10)–C(9)–N(1)	122·9 (2)	124·2 (2)	13 (3)
C(9)–C(10)–C(5)	118·7 (2)	119·1 (2)	5 (3)
C(10)–C(5)–C(6)	119·8 (3)	120·7 (2)	8 (3)
C(5)–C(6)–C(7)	121·3 (4)	120·2 (2)	−11 (4)
C(6)–C(7)–C(8)	120·3 (3)	121·4 (2)	11 (3)
C(7)–C(8)–C(9)	120·6 (3)	119·6 (2)	−10 (4)
C(8)–C(9)–C(10)	119·3 (4)	119·0 (2)	−3 (4)
C(3)–C(4)–C(11)	120·9 (2)	120·9 (2)	0 (3)
C(10)–C(4)–C(11)	123·0 (3)	122·9 (2)	0 (4)
N(1)–C(9)–C(8)	117·8 (3)	116·8 (2)	−10 (3)
C(4)–C(10)–C(5)	124·3 (2)	125·2 (2)	9 (3)
N(2)–C(3)–H(1)	114 (1)	112 (1)	−2 (1)
C(4)–C(3)–H(1)	121 (1)	121 (1)	1 (1)
C(10)–C(5)–H(2)	115 (1)	113 (1)	−1 (1)
C(6)–C(5)–H(2)	126 (1)	126 (1)	0 (1)
C(5)–C(6)–H(3)	118 (1)	123 (1)	5 (2)
C(7)–C(6)–H(3)	121 (1)	117 (1)	−4 (2)
C(6)–C(7)–H(4)	118 (1)	120 (1)	2 (2)
C(8)–C(7)–H(4)	121 (1)	118 (1)	−3 (2)
C(7)–C(8)–H(5)	126 (1)	128 (1)	2 (1)
C(9)–C(8)–H(5)	113 (1)	112 (1)	−1 (2)
C(4)–C(11)–H(6)	112 (1)	111 (1)	−1 (2)
C(4)–C(11)–H(7)	111 (1)	109 (1)	−1 (2)
C(4)–C(11)–H(8)	111 (1)	106 (1)	−5 (2)
H(6)–C(11)–H(7)	104 (2)	115 (2)	11 (2)
H(7)–C(11)–H(8)	103 (2)	103 (2)	0 (2)
H(8)–C(11)–H(6)	116 (2)	113 (2)	−4 (2)

* The differences (value in molecule 2 − value in molecule 1) $\times 10^3$ Å and $\times$ 10° for dimensions involving non-hydrogen atoms ($\times 10^2$ Å and $\times$ 1° for dimensions involving H atoms).

Table 4. *Atomic deviations* (Å) *from the best plane of fit through the* C *and* N *atoms [except* C(11)]

The intercept equation for molecule 1 is $0{\cdot}734x + 0{\cdot}966y + 0{\cdot}079z = 1$; that for molecule 2 is $-0{\cdot}103x - 0{\cdot}048y + 3{\cdot}309z = 1$.

	Molecule 1	Molecule 2
N(1)	0·020 (4)*	−0·005 (4)
N(2)	0·009 (5)	0·008 (4)
C(3)	−0·022 (5)	0·005 (5)
C(4)	−0·022 (4)	0·004 (5)
C(5)	0·026 (5)	−0·006 (6)
C(6)	0·007 (6)	−0·003 (7)
C(7)	−0·031 (6)	−0·002 (7)
C(8)	−0·009 (6)	0·010 (6)
C(9)	0·011 (5)	0·002 (4)
C(10)	0·011 (4)	0·004 (4)
C(11)	−0·103 (8)	−0·004 (8)
H(1)	−0·03 (4)	0·00 (4)
H(2)	0·03 (4)	0·04 (4)
H(3)	−0·02 (5)	−0·02 (4)
H(4)	−0·10 (4)	0·04 (4)
H(5)	−0·05 (4)	−0·02 (4)
H(6)	−0·25 (5)	0·07 (6)
H(7)	−0·89 (5)	−0·77 (6)
H(8)	0·60 (5)	0·74 (5)

* Errors, in the last significant digit, are twice the radius of the error sphere.

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