A Neutron Diffraction Study of the Crystal and Molecular Structure of Pyrazole, $C_3H_4N_2$

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The crystal and molecular structure of pyrazole has been rein-
vestigated using 770 independent three-dimensional single-crystal
neutron diffraction reflections with $\sin\theta/\lambda \leq 0.642$ Å^{-1}. A final dif-
ference Fourier map showed no evidence of tautomery with respect
to the two nitrogen atoms. Positional parameters and anisotropic
temperature factors for all atoms were refined by the full-matrix
least squares method to an R-value of 0.057, and a weighted R-value
of 0.057. Within experimental error (e.s.d. 0.01 Å) the two N−C
bond lengths are equal (1.33 Å) and so are the two C−C bond lengths
(1.38 Å). The N−N bond length equals 1.34 Å. The average value of
the C−H bond lengths is 1.09 Å, and that of the N−H bond lengths
1.02 Å. A discussion of corrections of bond lengths for thermal motion
is given. The range of standard deviations for the six independent
C−H bond lengths and the two independent N−H bond lengths is
0.014−0.020 Å.

The structure of pyrazole was determined previously by Ehrlich[1] from
photographically recorded X-ray diffraction data of the three projections.
The molecular formula of pyrazole with the numbering of the atoms is shown
in Fig. 1. The molecule was found to be planar with bond lengths compatible
with an aromatic system and with the shortest C−N bond length connected
with the pyrrole-type (>NH) nitrogen atom. Mighell and Reimann pointed
out[2] that their findings in the structure determination of the coordination
complex $Ni(C_3H_4N_2)_4Cl_2$[3] are at variance with this aspect of Ehrlich's structure.
Assuming that the pyrazole molecule is coordinated to the metal atom through
the pyridine-type (−N=) nitrogen atom they conclude that the shortest
C−N bond length is with this nitrogen atom.

We decided to settle the problem of the location of the hydrogen atoms
using neutron diffraction technique and we also aimed at comparison with

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an X-ray study based on diffractometer collected data, which is in progress in this laboratory. A microwave study of the gas phase of pyrazole is being done by L. Nygaard *et al.* in Chemical Laboratory V, University of Copenhagen, Copenhagen, Denmark.
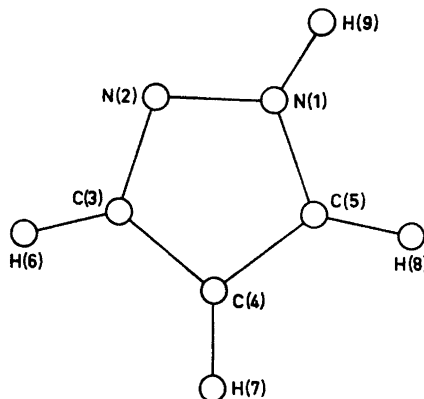

Fig. 1. The molecular formula of the pyrazole molecule. The numbers denote the numbering system used.

EXPERIMENTAL

Data collection. Two single crystals of approximately the same size were used during data collection. The shapes were cylindrical (diameter 2.6 mm, length 6.0 mm) with the axis of the cylinder parallel to the crystallographic c-axis. The crystals were grown from the melt. The melting point is 69.5 − 70°C. Because of the appreciable sublimation at room temperature the crystals were sealed in thinwalled boron-free glass tubes.

Sets of three-dimensional neutron diffraction intensity data were collected at room temperature using a Hilger-Ferranti automatic four-circle diffractometer at the Danish Reactor 3 at the Atomic Energy Research Establishment, Risø, Denmark. The wavelength of the monochromatic neutron beam reflected from the (002) planes of a Be single crystal was 1.011 Å. The neutron flux at the specimen was 0.93×10^6 n/cm²/sec.

The symmetrical A setting (Furnas and Harker) [4] and ω scan with total scan width of 1.10° was used in data collection. The counts were recorded for each step of 0.04° in the scan, and the counting time per reflection was 10 min. Reflection (3,1,1) was remeasured every 16 reflections as an internal standard. During data collection its intensity apparently increased, because of rapidly decreasing efficiency of a defective monitor counter, which was of a fission chamber type. Reflections were measured in sequence of increasing $\sin\theta$. All reflections with $l > 0$ and $\sin\theta/\lambda \leq 0.642$ were measured using a ³He proportional counter.

When about 2000 reflections had been collected, the first crystal was lost and the other crystal was mounted. About 1200 reflections more were collected with the second crystal, and the two data set were scaled together.

Data processing. Inspection of reflections indicated that the total scan width used in data collection had been rather narrow, and especially for reflections at higher angles the background count was poorly defined.

A mean background intensity function was evaluated using the measurements in the tails of the reflection profiles and averaging over symmetry related reflections.

The value of the background function was subtracted from each point in the reflection profile and the resulting peak counts were integrated. The Lorentz factor was applied to the 3203 intensities, and symmetry related reflections were averaged giving 875 independent intensities. 105 reflections had $|F_o|^2$ less than two times $\sigma(F_o{}^2)$ as evaluated according to statistics and were excluded from the final refinement.

The integrated intensities were corrected for absorption using a program written by Wells [6] ($\mu = 1.795$ cm^{-1}, measured experimentally). The correction factors varied from 0.64 to 0.68.

CRYSTAL DATA

The space group and unit cell dimensions used for data collection and refinement are the following as determined by Ehrlich.[1] Space group: $P2_1cn$ (equivalent to $Pna2_1$, No. 33 in *International Tables for X-ray Crystallography*).[5]

Unit cell: $a = 8.232 \pm 0.004$ Å, $b = 12.840 \pm 0.006$ Å, $c = 7.054 \pm 0.004$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$.

There are two crystallographically independent molecules in the asymmetric unit.

LOCATION OF HYDROGEN ATOMS AND LEAST SQUARES REFINEMENT

A Fourier map based on the carbon and nitrogen positions given by Ehrlich [1] showed unambiguously the locations of the 8 hydrogen atoms. The parameters of all atoms as found from the Fourier map were used as starting values for a least squares analysis. The scattering lengths used are the following: (in units of Fermi $= 10^{-13}$ cm): $b_H = -3.719$,[7] $b_C = 6.648$,[7] and $b_N = 9.57$.[8] Atomic coordinates and anisotropic temperature factor coefficients were refined in 9×9 matrices in a block diagonal least squares program, G403.[9] The weights used in the refinement were

$$w = 1/(\mu F)^2; \quad \mu F = \sqrt{\sigma(F_o{}^2)_{count} + (1 + p)F_o{}^2} - |F_o|$$

$\sigma(F_o{}^2)_{count}$ is the standard deviation estimated from counting statistics. p is a parameter introduced to account for errors other than from counting statistics. After each cycle of least squares refinement p was adjusted so that the average of $w(F_o - F_c)^2$ was nearly independent of the size of F. At the end of refinement $p = 0.0166$.

Reflections of high intensity were noticeably affected by extinction. At the R-value 0.067 an extinction correction based upon Zachariasen's 1963 paper [10] and using an approach as described by Larson [11] (eqn. (3)) was included in the refinement. Program G403 uses the equation in full length.

$$F_c{}^* = kF_c(1 + g\frac{p_2}{p_1} \cdot A\frac{dA^*}{d\mu} \cdot \frac{1}{\sin 2\theta} \cdot F_c{}^2)^{-\frac{1}{2}}$$

k is a scalefactor, g is Zachariasen's parameter for secondary extinction, $p_2/p_1 = 1$ for neutrons, $A^* = A^{-1}$ is the absorption factor, and μ is the linear absorption coefficient.

The quantity $A(dA^*/d\mu)$ is obtained from the absorption program.

Scale factor, overall temperature factor and extinction parameter are correlated, and so they are refined in a separate 3×3 matrix. After a few cycles the R-factor was 0.060. The refined value for the extinction parameter is $g = 2.22 \times 10^{-5}$. The data from the two crystals used in data collection were kept separate, but were all included in the least squares refinements. Uneven distribution of signs for $(F_o - F_c)$ indicated that the two sets of data had not

been properly scaled. A separate scale factor was introduced for each of the two sets of data, and the refinement was continued on the full matrix least squares program ORFLS [12] in Stewart's X-ray 63 system.[13] The final R-values (based on F) are $R = 0.0567$ and $R_w = 0.0569$. The final positional and thermal parameters are presented in Table 1, and the observed and calculated structure factors are listed in Table 2.

Table 1a. Atomic coordinates for the two crystallographically independent molecules in fractions of the unit cell dimensions. Least squares standard deviations $\times 10^4$ are given in parentheses. The atoms marked with a dash belong to a separate molecule. The x coordinate of C(3) was used to fix the position of the molecules in the polar space group.

Atom	x/a	y/b	z/c
N(1)	0.8531 (9)	0.1006 (3)	1.1452 (6)
N(2)	0.8558 (9)	0.1789 (3)	1.0196 (6)
C(3)	0.7222 (0)	0.1817 (4)	0.9322 (9)
C(4)	0.6191 (12)	0.1067 (5)	1.0013 (8)
C(5)	0.7080 (10)	0.0560 (5)	1.1396 (8)
H(6)	0.7064 (21)	0.2375 (12)	0.8207 (23)
H(7)	0.4957 (21)	0.0912 (12)	0.9557 (25)
H(8)	0.6776 (22)	−0.0092 (11)	1.2371 (20)
H(9)	0.9487 (15)	0.0880 (8)	1.2379 (16)
N(1′)	0.1477 (10)	0.1857 (3)	0.5018 (6)
N(2′)	0.1407 (10)	0.1033 (3)	0.3859 (6)
C(3′)	0.2884 (10)	0.0627 (4)	0.3902 (8)
C(4′)	0.3915 (11)	0.1186 (4)	0.5088 (8)
C(5′)	0.2962 (7)	0.1978 (4)	0.5762 (8)
H(6′)	0.3186 (20)	−0.0063 (10)	0.3089 (22)
H(7′)	0.5162 (15)	0.1017 (12)	0.5425 (23)
H(8′)	0.3228 (17)	0.2610 (12)	0.6772 (23)
H(9′)	0.0491 (16)	0.2322 (9)	0.5128 (19)

Table 1b. Anisotropic temperature factor parameters, u_{ij}, in Å^2. The expression for the temperature factor is $\exp[-2\pi^2(h^2a^{*2}u_{11} + k^2b^{*2}u_{22} + l^2c^{*2}u_{33} + 2\,hka^*b^*u_{12} + 2hlc^*a^*u_{13} + 2klb^*c^*u_{23})]$. The least squares standard deviations $\times 10^4$ are given in parentheses.

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
N(1)	0.0507 (13)	0.0660 (14)	0.0723 (17)	0.0035 (11)	−0.0072 (13)	0.0007 (13)
N(2)	0.0516 (14)	0.0709 (17)	0.0814 (21)	−0.0127 (12)	−0.0029 (14)	0.0010 (16)
C(3)	0.0651 (23)	0.0705 (24)	0.0652 (25)	−0.0040 (18)	−0.0089 (19)	0.0003 (21)
C(4)	0.0540 (19)	0.0702 (23)	0.0703 (25)	−0.0052 (18)	−0.0067 (20)	0.0022 (21)
C(5)	0.0534 (19)	0.0605 (22)	0.0737 (27)	−0.0062 (17)	−0.0038 (19)	0.0051 (22)
H(6)	0.1238 (80)	0.1162 (70)	0.0836 (64)	−0.0181 (61)	−0.0235 (62)	0.0430 (59)
H(7)	0.0939 (73)	0.1117 (69)	0.1264 (104)	−0.0349 (57)	−0.0512 (75)	0.0134 (71)
H(8)	0.1086 (78)	0.1035 (71)	0.1057 (78)	−0.0074 (61)	−0.0055 (69)	0.0562 (67)
H(9)	0.0629 (44)	0.0886 (60)	0.0838 (67)	0.0046 (45)	−0.0237 (51)	0.0038 (58)
N(1′)	0.0556 (14)	0.0672 (15)	0.0732 (17)	0.0041 (12)	0.0033 (13)	0.0020 (14)
N(2′)	0.0527 (13)	0.0658 (16)	0.0814 (20)	−0.0019 (11)	−0.0106 (13)	0.0032 (15)
C(3′)	0.0592 (22)	0.0587 (20)	0.0653 (25)	−0.0013 (17)	−0.0025 (19)	−0.0048 (20)
C(4′)	0.0443 (17)	0.0647 (21)	0.0710 (24)	0.0039 (15)	−0.0082 (17)	0.0016 (20)
C(5′)	0.0505 (19)	0.0613 (22)	0.0690 (23)	0.0025 (16)	0.0007 (18)	−0.0076 (21)
H(6′)	0.1021 (79)	0.0782 (56)	0.1150 (84)	0.0113 (53)	−0.0072 (71)	−0.0461 (60)
H(7′)	0.0438 (37)	0.1258 (96)	0.1303 (92)	0.0143 (47)	−0.0058 (49)	−0.0177 (77)
H(8′)	0.0819 (60)	0.1128 (87)	0.1039 (77)	−0.0052 (60)	−0.0086 (62)	−0.0466 (73)
H(9′)	0.0671 (45)	0.0866 (59)	0.0976 (71)	0.0086 (42)	0.0067 (52)	−0.0109 (57)

Table 2. Observed and calculated structure factors.

h	k	l	Fobs	Fcal	Phase

Table 2. Continued.

h	k	l	Fobs	Fcal	Phase

DISCUSSION

There is only one tautomeric form of the free pyrazole molecule, since a tautomeric shift of a hydrogen atom from one nitrogen atom to another is equivalent to rotating the molecule 180° around an axis in the plane of the molecule. In the crystalline state tautomery with respect to the two nitrogen atoms would show up as half a hydrogen atom connected to each of the two nitrogen atoms. A difference Fourier map based upon the final positions had maximum fluctuations of ± 0.45 Fermi/Å^3. Near the pyridine-type nitrogen atom at the possible hydrogen tautomeric position the fluctuations did not exceed ± 0.17 Fermi/Å^3 (5 % of a hydrogen nucleus). We conclude therefore that the hydrogen atom bonded to a nitrogen atom has little tendency to jump from one nitrogen atom to another.

Bond lengths and bond angles in the two crystallographically independent molecules are shown in Fig. 2. The two molecules are identical within experimental error. Table 3 presents a comparison of mean bond lengths between ring atoms as found with neutron and X-ray diffraction techniques. All values are averages over two crystallographically independent molecules. The three X-ray determinations cited are of molecular pyrazole,[1] $Ni(C_3H_4N_2)_4Cl_2$[3] and $Ni(C_3H_4N_2)_4Br_2$.[14] Compared with Ehrlich's X-ray determination[1] we have shifted a hydrogen atom from one nitrogen atom to the other, which supports the theory[2] that the longest $C-N$ bond length should be to the pyrrole-type nitrogen atom.
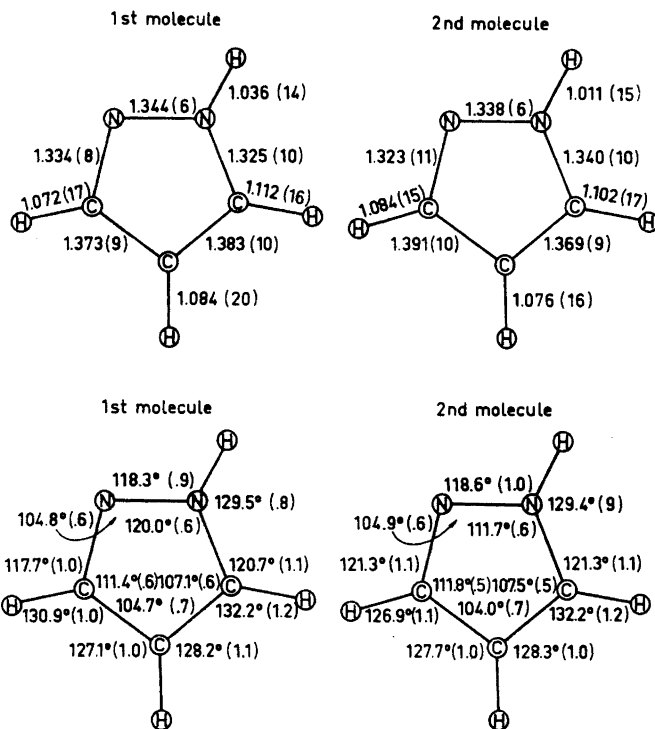
Fig. 2a, 2b. Uncorrected internuclear distances and angles of the two crystallographically independent molecules.

Table 3. Comparison of bond distances in the pyrazole molecule between the X-ray structure determinations of $C_3H_4N_2$,[1] $Ni(C_3H_4N_2)_4Cl_2$,[3] $Ni(C_3H_4N_2)_4Br_2$,[14] and the present neutron determination. All distances quoted are averages over two crystallographically independent bond lengths.

	Neutron	X-ray
N(1)—N(2)	1.341 (6)	1.361 (15)
		1.344 (5)
		1.344 (11)
N(2)—C(3)	1.329 (10)	1.314 (18)
		1.325 (5)
		1.322 (11)
C(3)—C(4)	1.382 (10)	1.414 (21)
		1.391 (7)
		1.389 (16)
C(4)—C(5)	1.376 (10)	1.335 (21)
		1.364 (6)
		1.351 (13)
C(5)—N(1)	1.333 (10)	1.346 (18)
		1.345 (4)
		1.352 (9)

Shifting a hydrogen atom in each of the two molecules does not alter the hydrogen bonding system as described by Ehrlich.[1] "The molecules are hydrogen-bonded together to form long chains. These chains form an arrangement which is related to the figure 8 as a helix is related to the figure 0, that is a translation perpendicular to the plane of the 8 takes place as the figure is described.

If we regard these 8 spirals as having a cylindrical form, then the crystal is a close-packed arrangement of cylinders. The principal axes of these cylinders are parallel to the crystallographic c axis."
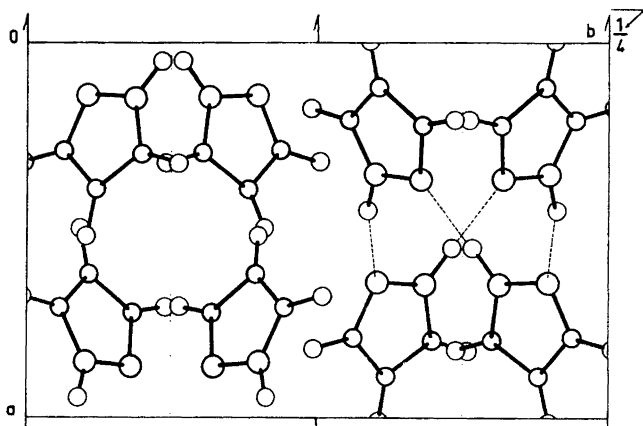

Fig. 3. The contents of a unit cell viewed down the c axis. Hydrogen bonds are denoted by dotted lines.

Fig. 3 shows the contents of a unit cell viewed down the c axis. The hydrogen bonds are denoted by dotted lines.

The temperature factor parameters were analyzed for indication of rigid body motion by using the Schomaker and Trueblood [15] method and program.
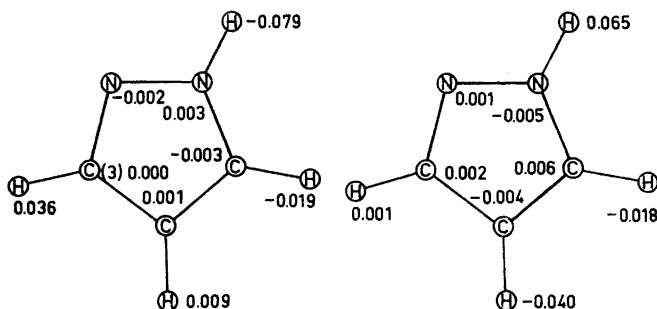

Fig. 4. Deviations in Å of the atoms from the least squares planes through the ring atoms and hydrogen atom H(7).

Table 4.

Molecule 1

Principal axes of L (librational tensor) and their direction cosines relative to a coordinate system with axes parallel with unit cell axes.

(Angles in degrees^2)	Angles in degrees	cos α	cos β	cos γ
82.09	9.06	−0.7047	0.3715	−0.6044
69.60	8.34	−0.5620	−0.8123	0.1561
35.82	5.99	−0.4330	0.4497	0.7812

Principal axes of T (translational tensor) and their direction cosines relative to a coordinate system with axes parallel with unit cell axes.

Mean square ampl. Å^2	RMS ampl. Å	cos α	cos β	cos γ
0.0600	0.245	0.0801	−0.7939	0.6028
0.0484	0.220	0.8288	−0.2829	−0.4828
0.0458	0.214	0.5538	0.5382	0.6353

Cross-tensor S transformed to principal axes of L.

−0.0020	0.0030	−0.0057
−0.0086	0.0015	−0.0043
0.0026	0.0026	0.0006

Molecule 2

Principal axes of L given as for molecule 1.

(Angles in degrees^2)	Angles in degrees	cos α	cos β	cos γ
83.09	9.12	−0.6591	0.7351	0.1590
69.07	8.31	−0.6978	−0.5190	−0.4936
33.26	5.77	−0.2803	−0.4363	0.8550

Principal axes of T given as for molecule 1.

Mean square ampl. Å^2	RMS ampl. Å	cos α	cos β	cos γ
0.0569	0.239	−0.0679	0.6949	0.7159
0.0473	0.218	−0.8349	0.3532	−0.4221
0.0414	0.203	−0.5462	−0.6224	0.5562

Cross-tensor S transformed to principal axes of L.

0.0020	0.0000	0.0057
−0.0008	−0.0002	0.0038
−0.0045	−0.0005	−0.0017

When the carbon and nitrogen ring atoms and hydrogen atom H(6) were included in the rigid body model, the root mean square displacements u_{ij} were adequately described, only two Δu_{ij}'s exceeding twice their standard deviations.

Table 4 shows the translational, librational, and screw tensors for the two pyrazole molecules, the rigid body model consisting of the carbon and nitrogen ring atoms and hydrogen atom H(6). The deviations in Å of the atoms from the least squares plane through these atoms are shown in Fig. 4. The hydrogen atoms deviating most from the plane are H(9) and H(9′) which take part in the hydrogen bonding system.

There are indications in the signs of the Δu_{ij}'s that the hydrogen atoms H(7) and H(8) bound to carbon atoms move more vigorously than the rigid body and that H(9) bound to the nitrogen atom and taking part in the hydrogen bonding system moves less, but altogether the rigid body motion seems a fair approximate description of the thermal movement of the pyrazole molecules, and all interatomic bond lengths are corrected accordingly.

Table 5. Mean values of bond lengths and bond angles corrected for rigid body motion. Distances within the ring were corrected using a rigid body model consisting of ring atoms and hydrogen H(6). C−H and N−H distances were corrected assuming all atoms moving as a rigid body.

Bond lengths in Å		Bond angles in degrees	
N(1)−N(2)	1.365	N(1)−N(2)−C(3)	104.8
N(2)−C(3)	1.350	N(2)−C(3)−C(4)	111.7
C(3)−C(4)	1.407	C(3)−C(4)−C(5)	104.4
C(4)−C(5)	1.398	C(4)−C(5)−N(1)	107.3
C(5)−N(1)	1.356	C(5)−N(1)−N(2)	111.9
C(3)−H(6)	1.094	N(2)−C(3)−H(6)	119.4
C(4)−H(7)	1.096	C(3)−C(4)−H(7)	127.5
C(5)−H(8)	1.125	N(1)−C(5)−H(8)	121.1
N(1)−H(9)	1.036	N(2)−N(1)−H(9)	118.3

Table 5 presents the mean values of the bond lengths and bond angles corrected for rigid body motion. Within experimental error the two C−N bonds have the same internuclear distances as similarly the two C−C inter-

Fig. 5. Comparison between neutron bond lengths and similar bond lengths for pyridine and pyrrole as determined by M.W. technique. The pyrazole molecule is divided in a "pyridine side" and a "pyrrole side". Bond lengths are given for N−C, C−C, C−H and N−H in pyridine and in pyrrole, respectively. The numbers in brackets are average values for pyrazole, corrected for thermal movements.
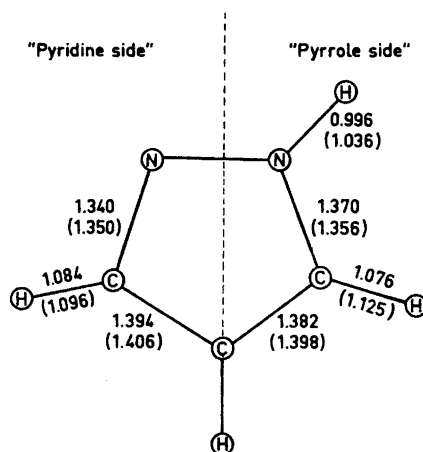
nuclear distances have equal values. This indicates a high degree of delocalisation of electrons over the entire ring system. There is little indication of alternative single bond double bond character distributed over the ring. We would therefore expect the bond lengths in pyrazole to be close to the average over similar bond lengths in the pyridine and pyrrole molecules. This is evident from Fig. 5 which shows a comparison between the neutron bond length for pyrazole and bond lengths found with M.W. technique for pyridine and pyrrole. On the "pyridine side" of the pyrazole molecule is shown pyridine [16] bond lengths, and on the "pyrrole side" pyrrole [17] bond lengths.

Fig. 5 also shows an example of how $N-H$ and $C-H$ bond lengths determined by neutron diffraction appear longer than similar ones found by M.W. technique.

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