3-Methyl-5-phenylpyrazole: A Neutron Diffraction Study

By **Frank H. Moore**, Australian Institute for Nuclear Science and Engineering, Lucas Heights, New South Wales
Allan H. White * and **Anthony C. Willis**, Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia

A single-crystal neutron diffraction study of the title compound (734 reflections, *R* 0.08) has located the tautomeric N–H hydrogen atoms; the two molecules in the asymmetric unit are closely related to a second pair generated by a crystallographic two-fold axis, the ' tautomeric ' protons bridging adjacent N · · · N groups to form a hydrogen bound cyclic tetramer. Within each of the three remarkably short independent N · · · N contacts, the tautomeric hydrogen atoms are almost linearly co-ordinated and symmetrically disposed.

A RECENT *X*-ray crystallographic study[1] of the title compound located all atoms except the ' tautomeric ' protons from the nitrogen atoms; since the structural asymmetric unit comprised a pair of molecules closely related to another pair by a two-fold crystallographic axis, with adjacent N · · · N pairs very closely spaced at distances $\lesssim 2.9$ Å, it was surmised that the molecules were linked by mobile tautomeric hydrogen bonds. The opportunity has recently arisen to reinvestigate the problem by single-crystal neutron diffraction and we report here the results of this study. The atomic numbering scheme adopted throughout is that of the *X*-ray study.

EXPERIMENTAL

A crystal 2 × 4 × 3 mm (grown by cooling a light petroleum solution slowly) was used for data collection, the cell dimensions used being taken from the *X*-ray study. Data were collected on the four-circle diffractometer at port 2TANB of the HIFAR reactor at the Australian Atomic Energy Commission research establishment at Lucas Heights, by use of monochromatic neutrons ($\lambda = 1.25$ Å). An initial complete data set in the range $2\theta < 60°$ was collected (754 reflections, all of which were used in the refinement). Data collection was extended beyond this limit but, as the intensities obtained were weak and diminished rapidly as a function of θ, probably as a consequence of the high thermal motion in the lattice, they were ultimately discarded. Refinement of the structure was carried out by least squares, those hydrogen atoms ' missing ' from the *X*-ray study being easily located in a difference map. The parameters of each molecule were refined as a full matrix, but in view of the rather limited data set the

---

[1] E. N. Maslen, J. R. Cannon, A. H. White, and A. C. Willis, *J.C.S. Perkin II*, 1974, 1298.

number of variables was restricted by approximating the carbon and nitrogen positions as invariants by use of the X-ray values. All thermal parameters were refined anisotropically according to the form used in the X-ray study. At convergence, no parameter shift exceeded 0.25σ. A weighting scheme of the form $w = (\sigma^2|F_o| + n|F_o|^2)^{-1}$ was used, a value of $n = 2 \times 10^{-3}$ being found appropriate. The final R was 0.080, R' [$= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] being 0.094. These values were adversely influenced by the large number of weak reflections in the data set, *e.g.* for the 114 reflections with $|F_o| > 14$, R was 0.044, while for the 117 with $|F_o| < 3$ it was 0.474. Scattering factors are taken from ref. 2.

Computation was carried out by use of a local adaptation of ref. 3 at the University of Western Australia on a CDC 6200 machine.

TABLE 1

Hydrogen atom positional co-ordinates ($\times 10^3$), and anisotropic thermal parameters ($\times 10^2$ Å^2 for H, $\times 10^3$ Å^2 for other atoms). Least-squares estimated standard deviations for neutron data in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Molecule (1)									
H(1)	677(1)	003(2)	699(2)	8(2)	7(2)	12(3)	−3(1)	3(2)	2(2)
H(2)	783(2)	−111(3)	696(3)	18(3)	17(3)	14(4)	9(3)	4(3)	5(3)
H(3)	888(1)	−025(3)	651(3)	10(2)	15(3)	17(4)	5(2)	−1(2)	−2(3)
H(4)	888(1)	174(3)	607(3)	5(2)	16(3)	26(5)	0(2)	0(2)	1(2)
H(5)	788(1)	289(2)	618(2)	7(2)	12(2)	18(4)	3(2)	6(2)	5(2)
H(8)	677(1)	372(2)	578(2)	7(2)	11(2)	11(3)	−1(1)	3(2)	2(2)
H(10)	513(4)	433(4)	580(5)	37(8)	12(3)	19(6)	8(4)	−20(6)	1(4)
H(10)	509(3)	472(5)	676(3)	17(4)	24(5)	13(4)	13(4)	6(3)	2(4)
H(10)	567(2)	515(4)	607(7)	16(4)	11(3)	57(12)	8(3)	4(6)	17(6)
Molecule (2)									
H(1)	430(1)	−170(3)	795(2)	12(2)	14(2)	7(2)	−6(2)	−2(2)	2(2)
H(2)	330(1)	−284(3)	829(2)	10(2)	14(3)	16(4)	−7(2)	−4(2)	1(2)
H(3)	312(1)	−352(3)	978(2)	5(2)	17(3)	10(3)	−6(2)	0(2)	2(2)
H(4)	397(2)	−295(3)	1 099(2)	19(3)	14(3)	8(3)	−10(2)	6(2)	3(2)
H(5)	497(1)	−179(2)	1 067(2)	15(2)	10(2)	5(3)	−2(2)	−4(2)	1(2)
H(8)	604(1)	−121(2)	1 026(2)	9(2)	12(2)	7(2)	2(2)	−5(2)	−1(2)
H(10)	694(1)	112(3)	961(6)	3(2)	6(2)	74(12)	2(1)	−4(3)	−12(4)
H(10)	729(2)	041(5)	887(3)	16(4)	29(6)	11(4)	−16(4)	2(3)	0(4)
H(10)	723(1)	−013(3)	975(4)	3(2)	20(4)	25(6)	−3(2)	−2(2)	9(4)
' Tautomeric ' hydrogen atoms									
H(A)	500(−)	270(4)	750(−)	20(5)	11(3)	15(5)		−3(4)	
H(B)	500(−)	−044(3)	750(−)	11(3)	4(2)	22(6)		8(3)	
H(C)	605(1)	102(3)	776(2)	3(1)	29(4)	16(3)	5(2)	−6(2)	−15(3)

Other atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Molecule (1)						
N(1)	41(6)	86(8)	52(9)	−12(5)	0(5)	7(6)
N(2)	38(6)	70(6)	35(8)	−6(5)	10(5)	6(5)
C(1)	76(9)	50(8)	77(14)	22(8)	22(8)	2(8)
C(2)	107(12)	48(9)	69(14)	21(8)	4(9)	6(8)
C(3)	43(9)	131(4)	107(16)	22(10)	15(9)	−5(12)
C(4)	54(9)	113(12)	84(14)	13(9)	26(8)	−2(11)
C(5)	44(8)	82(10)	99(15)	−5(7)	20(8)	−11(9)
C(6)	47(8)	76(9)	28(11)	16(8)	12(6)	3(8)
C(7)	44(8)	47(8)	54(12)	−2(7)	3(7)	−2(8)
C(8)	44(8)	65(9)	62(12)	−10(7)	5(7)	24(8)
C(9)	36(8)	80(11)	83(15)	−1(8)	−4(8)	−4(9)
C(10)	59(9)	50(8)	151(17)	−20(7)	−26(9)	30(9)
Molecule (2)						
N(1)	57(6)	57(6)	48(8)	1(5)	1(6)	13(6)
N(2)	62(6)	63(6)	30(8)	3(5)	−9(6)	12(6)
C(1)	75(10)	88(10)	19(11)	−12(8)	2(7)	−14(9)
C(2)	61(9)	88(10)	77(14)	−26(8)	−14(9)	16(11)
C(3)	117(12)	70(11)	81(17)	−32(9)	31(12)	−5(11)
C(4)	111(13)	85(11)	35(14)	−22(9)	6(9)	−10(10)
C(5)	58(8)	68(10)	58(13)	−23(7)	−10(9)	−19(9)
C(6)	67(9)	31(7)	19(11)	2(7)	−10(8)	4(8)
C(7)	35(7)	44(7)	30(11)	8(6)	−18(7)	9(7)
C(8)	70(10)	62(9)	39(13)	19(7)	−8(8)	24(8)
C(9)	65(10)	62(9)	21(11)	−2(7)	−13(7)	7(8)
C(10)	53(9)	115(11)	66(13)	1(8)	−4(7)	−26(10)

Structure-factor Tables are deposited as Supplementary Publication No. SUP 21340 (5 pp., 1 microfiche).[*] Results are shown in Tables 1—3. The atomic numbering scheme is as for ref. 1, *viz.* within each of the two independent

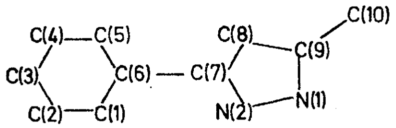
---

[*] For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, Index issue, 1974.

[2] G. E. Bacon, *Acta Cryst.*, 1972, **A28**, 357.

[3] ' X-Ray ' system of programs, version of June, 1972, Technical Report TR 192, Computer Science Centre, University of Maryland.

molecules the atoms are numbered as in (I), an additional preceding digit denoting molecule (1) or (2) in the Discussion or Tables where necessary; H(*i*) is attached to C(*i*).



(I)

TABLE 2

Hydrogen atom bond distances (Å) and angles (deg.), with estimated standard deviations in parentheses. Calculations are based on the neutron positional parameters and estimated standard deviations for the hydrogen atoms, and the *X*-ray parameters and estimated standard deviations for the remainder. Values for molecule (2) follow those for molecule (1)

C(1)–H(1)	1.10(2), 1.04(3)
C(2)–H(2)	1.13(4), 1.09(3)
C(3)–H(3)	1.12(3), 1.18(3)
C(4)–H(4)	1.06(3), 1.10(3)
C(5)–H(5)	1.06(3), 1.13(3)
C(8)–H(8)	1.07(3), 1.10(3)
C(10)–H(10)	0.96(7), 1.04(4)
C(10)–H(10)	1.03(5), 1.00(5)
C(10)–H(10)	0.94(6), 0.94(4)
H(5) · · · H(8)	2.47(3), 2.33(4)
H(8)–C(8)–C(7)	129(1), 129(1)
C(9)–C(10)–H(10)	108(3), 110(1)
C(9)–C(10)–H(10)	113(3), 118(3)
C(9)–C(10)–H(10)	116(3), 113(2)
H(1)–C(1)–C(2)	120(1), 121(2)
H(1)–C(1)–C(6)	119(1), 120(2)
H(2)–C(2)–C(3)	121(2), 118(2)
H(2)–C(2)–C(1)	119(2), 121(2)
H(3)–C(3)–C(2)	116(2), 118(1)
H(3)–C(3)–C(4)	123(2), 122(1)
H(4)–C(4)–C(3)	118(2), 119(2)
H(4)–C(4)–C(5)	121(2), 121(2)
H(5)–C(5)–C(6)	121(1), 119(2)
H(5)–C(5)–C(4)	118(1), 120(2)
H(8)–C(8)–C(9)	126(1), 125(1)
H(10)–C(10)–H(10)	99(5), 104(5)
H(10)–C(10)–H(10)	103(7), 110(5)
H(10)–C(10)–H(10)	115(5), 101(4)
'Tautomeric ' hydrogen contacts	
H(A) · · · N(11)	1.458(4)
H(B) · · · N(22)	1.413(4)
H(C) · · · N(12)	1.44(4)
H(C) · · · N(21)	1.41(4)
H(A) · · · N(11)–N(12)	124(2)
H(A) · · · N(11)–C(19)	127(2)
H(C) · · · N(12)–N(11)	120(1)
H(C) · · · N(12)–C(107)	132(1)
N(11) · · · H(A) · · · N(11$^{\text{I}}$)	176(4)
N(22) · · · H(B) · · · N(22$^{\text{I}}$)	175(2)
N(12) · · · H(C) · · · N(21)	178(3)
H(B) · · · N(22)–N(21)	116(1)
H(B) · · · N(22)–C(27)	132(1)
H(C) · · · N(21)–N(22)	118(1)
H(C) · · · N(21)–C(29)	132(1)

Superscript I denotes atom at $1 - x, y, 1\frac{1}{2} - z$.

DISCUSSION

Inspection of the thermal motion, as determined by the neutron diffraction study, shows that the vibrational amplitudes of the hydrogen atoms are, as expected, quite high, especially for the methyl hydrogens, indicating considerable oscillation about the C–Me bonds. It is of interest that in both molecules the angles C(7)–C(8)–H(8) [129(1)°] are found to be greater (significant at $>3\sigma$) than C(9)–C(8)–H(8): this may well be a consequence of the conflict between conjugation (requiring a planar molecule) and steric interaction between H(8) and the nearby H(5) resulting in a twist of the two aromatic rings with respect to each other about the C(6)–C(7) axis of 21.3 and 18.2°. The close H(5) · · · H(8) contact is found to be 2.47(3), in one molecule and 2.33(4) Å in the other (*cf.* the H · · · H van der Waals contact estimate of 2.4 Å).[4] No corresponding angular distortion is found about C(5).

TABLE 3

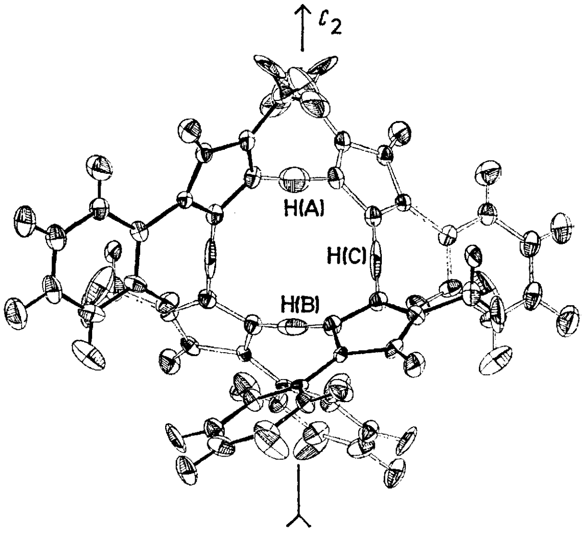
Deviations (Å) of the hydrogen atoms from the least-squares planes of ref. 1. Values for molecule (2) follow those for molecule (1)

Plane (*a*): C and N atoms of pyrazole ring

[H(8) −0.01, 0.03; H(A) −0.05, –; H(B) –, −0.35; H(C), 0.06, 0.30]

Plane (*b*): C atoms of phenyl ring

[H(1) −0.06, −0.06; H(2) 0.00, −0.08; H(3) 0.03, −0.03; H(4) −0.04, −0.04; H(5) 0.02, −0.04]



View of the hydrogen bonding and tetrameric configuration; 50% ellipsoids

As indicated by the *X*-ray study, the molecules are grouped about the two-fold axes, the asymmetric unit of two molecules generating two further molecules by the C_2 symmetry operation; the N–N portion of the pyrazole ring lies nearest the two-fold axis and this generates a cluster of four molecules with their N–N groups cyclically arrayed with remarkably short N · · · N contacts [N(11) · · · N(11) 2.913(1) and N(22) · · · N(22)

---

[4] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 261.

2.824(5) Å] across the two-fold axis and between the molecular pair of the asymmetric unit [N(12) · · · N(21) 2.852(5) Å]. It was surmised that the tautomeric hydrogen atoms, which could not be located by *X*-ray methods, caused these remarkably short contacts by a hydrogen-bonding mechanism, the hydrogen atoms lying in the N · · · N bonds. The estimated mean of such observed N · · · N hydrogen-bonded contacts in the literature is 3.07 ± 0.11.[5]

The location of the hydrogen atoms in the present structure confirms these expectations (Figure). Two of the hydrogen atoms are located on the two-fold axis, H(A) spanning N(11) and its rotation image at necessarily equal distances of 1.458(4) Å with an effectively linear N · · · H · · · N bond [176(4)°] and H(B) likewise spanning N(22) and its image at 1.413(4) Å, with N · · · H · · · N 175(2)°. H(C) Spans the pair N(21) and N(12) within the asymmetric unit almost symmetrically, in spite of the absence of a symmetry constraint, at 1.44(4) and 1.41(4), with N · · · H · · · N 178(3)°. The gross elongation of the thermal ellipsoid of H(C) along the N(12) · · · N(21) contact casts some doubt on the symmetry of its disposition; the possibility that it may represent a dumbell with a double minimum in the potential well rather than a true ellipsoid is not supported by the evidence of the final difference map. It thus seems that all hydrogen bridges in this structure are very short, strong, and symmetrical. The external angles at each nitrogen atom to these hydrogen atoms have a mean of 125°, within the range 116—132°; this value is to be expected in the exocyclic angles of a five-membered ring. The tautomeric hydrogen atoms H(A) and H(C) are almost coplanar with molecule 1; this is not so with molecule 2, where H(B) and H(C) have quite large deviations of —0.35 and 0.30 Å.

We thank the Australian Institute of Nuclear Science and Engineering for neutron diffraction facilities and financial support.

[4/1839 *Received*, 9*th September*, 1974]

---

[5] S. N. Vinogradov and R. H. Linnell, ' Hydrogen Bonding,' Van Nostrand–Reinhold, New York, 1970, p. 170.