Crystal Structure of 3-Methyl-5-phenylpyrazole

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The crystal structure of the tautomeric title compound, $C_{10}H_{10}N_2$, has been determined by direct methods from X-ray diffractometer data, and refined by least squares to R 0·060 (1614 reflections). Crystals are monoclinic, space group $C2/c$, $a = 19·841(6)$, $b = 12·000(2)$, $c = 15·079(4)$ Å, $\beta = 92·58(2)°$, $Z = 16$ (two independent molecules in the asymmetric unit).

The geometry of the molecule is as expected: interaction between the pyrazole substituents in each case imparts a twist (21·35 and 18·21°) about the bond between the phenyl and pyrazole rings. The molecules are clustered in groups of four about the two-fold axes of the cell with the pyrazole nitrogen atoms directed toward, or close to, that axis. It has not been possible to locate the NH hydrogen atoms, which are presumed to exist as a loose association within each molecular grouping.

THE pyrazoles are well known to exist as tautomers, as are the pyrazolones; in the former case, the location of the NH proton is considered to be indefinite as regards its association with one or other of the nitrogen atoms, whereas in the latter, the tautomerism is of the keto–enol type. Such judgements are almost invariably made on the basis of the behaviour of the compound in solution. Whereas a number of the more important pyrazolone

drugs have been studied structurally in the solid state, little is known about the pyrazoles proper, apart from the parent compound, which has been examined extensively.[1] In pyrazole itself, it was concluded that the tautomeric proton is localized in a definite association with one of the crystallographically distinct nitrogen atoms in the solid state and exhibits no detectable tendency to migrate to the other nitrogen. In order to examine whether this is invariably the case, the title compound has been studied structurally by X-ray methods.

EXPERIMENTAL

A needle section, a cube ca. 0·20 mm, was used for X-ray work. Cell dimensions were obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex PĪ diffractometer. A unique set of data in the range $2\theta < 100$, was collected by a conventional θ—2θ scan yielding 1838 independent reflections of which 1614, having $I > 2\sigma$ (I) were considered observed, and used in the structure determination and refinement with unit weights.

matrix. The final value of R was 0·060, and of R' 0·058 $\{R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|]^{\frac{1}{2}}\}$. Anisotropic thermal parameters were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Scattering factors were for the neutral atoms, no correction being applied for the effects of anomalous dispersion.[2] Hydrogen atoms for the benzene rings and methyl groups were located in a difference map; attempts to refine them positionally with fixed isotropic thermal parameters failed and they were positioned geometrically ($r_{\text{C-H}} = 1\cdot00$ Å) and included in the calculations of R, being readjusted after each least-squares cycle. In spite of the relatively good definition of these hydrogen atoms in difference maps, the location of the remaining protons associated with the nitrogen atoms of the pyrazole ring remains obscure (see Discussion section), and no other significant peaks were observed in the final difference map. Parameter shifts in the final least-squares cycle were $<0\cdot1\sigma$.

All data processing and computation was carried out on the CDC 6200 machine at this University, by use of a local adaptation of the ' X-Ray '72 ' program system.[3] Estimated hydrogen atom positions and structure factors are listed in Supplementary Publication No. SUP 21035 (9 pp.,

TABLE 1

Final atomic fractional ($\times 10^4$) cell and thermal ($\times 10^3$) parameters, with least squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Molecule (1)									
N(1)	5646(2)	2750(3)	7077(2)	62(3)	74(3)	71(3)	−2(2)	−6(2)	5(2)
N(2)	6130(2)	1942(3)	7165(3)	57(2)	73(3)	59(2)	−2(2)	2(2)	2(2)
C(1)	7251(3)	0432(5)	6817(3)	90(4)	79(4)	71(3)	10(3)	15(3)	2(3)
C(2)	7840(4)	−0198(5)	6775(4)	123(5)	85(4)	81(4)	26(4)	12(4)	3(3)
C(3)	8420(3)	0296(7)	6518(4)	92(5)	124(6)	94(4)	36(4)	9(3)	−11(4)
C(4)	8428(3)	1394(6)	6298(4)	72(4)	128(6)	115(5)	7(4)	18(3)	−7(3)
C(5)	7848(3)	2025(4)	6336(3)	73(4)	87(4)	91(4)	3(3)	9(9)	2(3)
C(6)	7254(2)	1552(4)	6604(3)	69(3)	76(4)	44(3)	−1(3)	3(2)	−3(2)
C(7)	6642(2)	2241(4)	6655(3)	62(3)	65(3)	49(3)	−8(3)	−3(2)	−5(2)
C(8)	6481(2)	3252(5)	6234(3)	65(3)	72(3)	71(3)	−10(3)	−6(2)	9(3)
C(9)	5853(2)	3534(4)	6520(3)	62(3)	69(3)	82(3)	−3(3)	−14(3)	4(3)
C(10)	5432(3)	4529(5)	6388(4)	83(4)	92(4)	135(5)	5(3)	−7(3)	23(4)
Molecule (2)									
N(1)	5952(2)	−0139(3)	3364(2)	68(3)	75(3)	52(2)	4(2)	−10(2)	3(2)
N(2)	5344(2)	0391(3)	3340(2)	66(3)	67(2)	50(2)	5(2)	−6(2)	−3(2)
C(1)	4248(3)	2001(4)	3586(3)	85(4)	82(4)	67(3)	15(3)	−7(3)	−8(7)
C(2)	3689(3)	2646(5)	3793(4)	86(4)	95(4)	93(4)	17(3)	−14(3)	3(3)
C(3)	3602(3)	2994(5)	4642(4)	93(4)	80(4)	96(4)	16(3)	17(4)	−1(3)
C(4)	4061(3)	2693(5)	5302(4)	106(4)	84(4)	79(4)	13(4)	14(3)	−9(3)
C(5)	4609(2)	2053(4)	5115(3)	89(4)	75(3)	59(3)	7(3)	−4(3)	−4(3)
C(6)	4714(2)	1694(3)	4259(3)	69(3)	51(3)	57(3)	−4(2)	−4(2)	0(2)
C(7)	5300(2)	1010(3)	4082(3)	62(3)	54(3)	50(3)	−4(2)	−4(2)	1(2)
C(8)	5897(2)	0861(4)	4600(3)	73(3)	69(3)	56(3)	−3(3)	−12(3)	−7(3)
C(9)	6287(2)	0144(4)	4134(3)	57(3)	72(3)	65(3)	−4(3)	−10(2)	8(3)
C(10)	6977(2)	−0324(5)	4356(3)	69(3)	104(4)	91(4)	−1(3)	−15(3)	8(3)

Crystal Data.—$C_{10}H_{10}N_2$, $M = 158\cdot3$. Monoclinic, $a = 19\cdot841(6)$, $b = 12\cdot000(2)$, $c = 15\cdot079(4)$ Å, $\beta = 92\cdot58(2)°$, $U = 3587(2)$ Å³, $D_m = 1\cdot17$, $Z = 16$, $D_c = 1\cdot17$, $F(000) = 1344$. Ni filtered Cu-$K_{\bar{\alpha}}$ radiation, $\lambda = 1\cdot5418$ Å; $\mu(Cu$-$K_{\bar{\alpha}}) = 5\cdot69$ cm⁻¹. Space group $C2/c$ (C_{2h}^6, No. 15).

In view of the constancy of μr throughout the data range, no absorption correction was applied. The structure was solved by direct methods and refined by least squares, the parameters of each molecule being refined as a single

* For details see Notice to Authors No. 7, in *J.C.S. Perkin II*, Index issue 1973.

[1] F. K. Larsen, M. S. Lehmann, I. Søtofte, and S. E. Rasmussen, *Acta Chem. Scand.*, 1970, **24**, 3244; J. Berthou, J. Elguero, and C. Kerat, *Acta Cryst.*, 1970, **B26**, 1880; H. W. W. Ehrlich, *ibid.*, 1960, **13**, 946.

microfiche).* Results are shown in Tables 1—3 and the Figure. There are two independent molecules in the asymmetric unit. Within each molecule, the atoms are numbered as shown in (I), but in the Discussion section and Tables the first digit (1 or 2) denotes molecule (1) or (2).

(I)
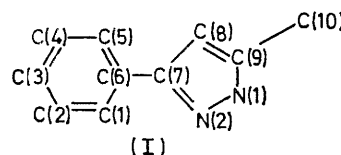
[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[3] X-Ray system of programs, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., 1972.

TABLE 2

Interatomic distances (Å) and angles (deg.); least squares
e.s.d. in the final digit in parentheses

(a) Distances

	Molecule (1)	Molecule (2)
C(1)–C(2)	1·396(9)	1·400(8)
C(2)–C(3)	1·366(9)	1·365(8)
C(3)–C(4)	1·360(11)	1·368(8)
C(4)–C(5)	1·381(8)	1·370(8)
C(5)–C(6)	1·386(7)	1·385(6)
C(1)–C(6)	1·382(7)	1·392(6)
C(6)–C(7)	1·474(7)	1·457(6)
C(7)–C(8)	1·400(7)	1·399(6)
C(8)–C(9)	1·378(7)	1·372(7)
C(9)–C(10)	1·491(7)	1·503(7)
C(7)–N(2)	1·350(6)	1·350(5)
C(9)–N(1)	1·338(6)	1·354(6)
N(1)–N(2)	1·367(5)	1·363(5)

(b) Angles

C(6)–C(1)–C(2)	120·3(5)	119·4(4)
C(1)–C(2)–C(3)	119·7(6)	120·9(5)
C(2)–C(3)–C(4)	120·6(6)	119·6(5)
C(3)–C(4)–C(5)	120·2(6)	120·4(5)
C(4)–C(5)–C(6)	120·6(5)	121·4(4)
C(5)–C(6)–C(7)	119·9(4)	120·0(4)
C(5)–C(6)–C(1)	118·6(5)	118·3(4)
C(1)–C(6)–C(7)	121·5(4)	121·7(4)
C(6)–C(7)–C(8)	129·4(4)	129·2(4)
C(6)–C(7)–N(2)	121·5(4)	122·9(4)
C(7)–C(8)–C(9)	105·2(4)	106·1(4)
C(8)–C(9)–C(10)	128·9(5)	130·5(4)
C(8)–C(9)–N(1)	109·4(4)	109·3(4)
C(10)–C(9)–N(1)	121·7(4)	120·3(4)
C(9)–N(1)–N(2)	108·9(4)	107·7(3)
C(7)–N(2)–N(1)	107·5(4)	109·0(3)
C(8)–C(7)–N(2)	109·0(4)	107·9(4)

(c) Non-bonding contacts

N(11) · · · N(11^I)	2·913(5)
N(12) · · · N(21^{II})	2·852(5)
N(22) · · · N(22^{III})	2·824(5)

Roman numerals denote the following transformations of the
asymmetric unit:

I $1 - x, y, 1\frac{1}{2} - z$ II $x, y, \frac{1}{2} + z$ III $1 - x, y, \frac{1}{2} - z$

TABLE 3

Equations of best least-squares planes in the form: $pX +$
$qY + rZ = s$.* Atomic deviations (Å) are given in
square brackets. Values for molecule (2) follow those
for molecule (1)

	p	q	r	s	σ
Plane (a): pyrazole ring					
	0·3958	0·4977	0·7718	14·113	0·001
	0·4297	0·7779	−0·4584	2·520	0·003

[N(1) 0·00, 0·00; N(2) −0·00, −0·00; C(7) 0·00, 0·00;
C(8) 0·00, 0·00; C(9) −0·00, −0·00; C(10) −0·00, −0·01;
C(6) 0·01, 0·01; C(1) −0·41, 0·38; C(5) 0·45, −0·35]

Plane (b): Ph ring					
	0·2023	0·2314	0·9516	12·713	0·004
	0·5340	0·8289	−0·1668	5·455	0·004

[C(1) −0·001, 0·00; C(2) −0·00, −0·00; C(3) 0·00, 0·00;
C(4) 0·00, 0·00; C(5) −0·00, −0·00; C(6) 0·00, 0·00;
C(7) 0·02, −0·01; C(8) −0·35, 0·32; N(2) 0·46, −0·36]

* x, y, and z are orthogonal (Å) co-ordinates, related to the
fractional cell by: $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$.

DISCUSSION

The asymmetric unit comprises two discrete molecules;
each molecule consists of two planar units, these being
the pyrazole and phenyl rings. Although the thermal
motion in the lattice is high and bond lengths and angles

are uncorrected, the ring geometries do not deviate
significantly from those expected. As is usual in
Ar–Ar' systems, the influence of conjugation is in-
sufficient to constrain a substantially planar geometry
throughout the whole molecule; in this case, the angle
between the two rings is rather similar for both molecules
(21·61 and 18·06°). The probable reason for the non-
planarity lies in the interactions of H(18) with H(15),
and H(28) with H(25), which are suggested by the in-
equality between C(16)–C(17)–C(18) and C(26)–C(27)–
C(28) [129·4 and 129·2(4)°], and C(16)–C(17)–N(12) and
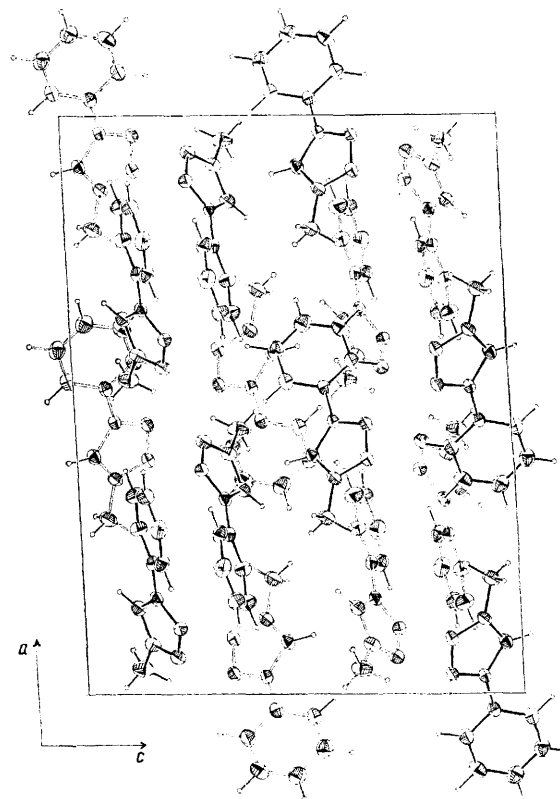
The unit cell contents, projected down b; 50% ellipsoids are
shown for the non-hydrogen atoms. Molecules in the ' upper '
half of the cell are shown with solid bonds

C(26)–C(27)–N(22) [121·5 and 122·9(4)°] which is con-
sistent in both molecules. The estimated distances
H(18) · · · H(15) and H(28) · · · H(25) are 2·44 and
2·38 Å; if the system were undistorted these would be
even less (taking the van der Waals radius of hydrogen as
1·2 Å).[4] A similar distortion is found about C(110)
and C(210) [C(18)–C(19)–C(110) and C(28)–C(29)–C(210)
128·9 and 130·5(4)°, C(110)–C(19)–N(11) and C(210)–
C(29)–N(21) 121·7 and 120·3(4)°].

The most interesting aspect of the structure is the
molecular packing and location of the nitrogen atoms.
Each molecule is positioned tilt-wise close to a crystallo-
graphic two-fold axis, e.g. $(0, y, \frac{1}{4})$; in each case the N–N
end of the pyrazole ring is directed towards that

⁴ L. Pauling, The Nature of the Chemical Bond, Cornell
University Press, Ithaca, New York, 1960, p. 261.

axis so that each molecule is distant from its rotation image by *ca.* 2·8—2·9 Å [(N(11) $\cdots$ N(11$^{\text{I}}$) 2·913(5), N(22) $\cdots$ N(22$^{\text{III}}$) 2·824(5) Å] and also from its pair in the asymmetric unit [N(12) $\cdots$ N(21$^{\text{II}}$) 2·852(5) Å]. All these contacts are remarkably short in comparison with the estimated van der Waals contact of *ca.* 3·0 Å,[4] and comprise a tightly bound aggregate of four molecules. Stoicheiometrically, this association also requires four hydrogen atoms; in spite of the clear resolution and the ready location of the other hydrogen atoms in both molecules, it was not possible satisfactorily to locate either of the independent tautomeric hydrogen atoms. It seems clear that a genuine solid-state tautomerisation does occur in the present system and that the molecular groupings are held together by indefinite associations of mobile hydrogen bonds. A neutron diffraction study has been initiated to clarify this point if possible.