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Structure of 4-Acetyl-5-methyl-2-phenylimidazole

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Abstract. $C_{12}H_{12}N_2O$, orthorhombic, *Pbca*, a = 23·067 (6), b = 13·344 (4), c = 7·088 (2) Å (from precession photographs and single-crystal diffractometry), D_m = 1·22, D_c = 1·22 g cm^{-3} for Z = 8, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, μ(Mo $K\bar{\alpha}$) = 0·86 cm^{-1}. The structure was solved by direct methods. The positional and thermal parameters were refined by the full-matrix least-squares procedure converging to a conventional R of 0·06 (R_w = 0·069) for 422 reflexions with $(\sin\theta/\lambda)_{\max}$ = 0·595 Å^{-1}.

Introduction. Single crystals of $C_{12}H_{12}N_2O$ (m.p. 200–201 °C), in the form of transparent prisms along **a**, were obtained by slow evaporation of the solvent from a solution in absolute ethanol.

The intensities were collected on a Philips PW 1100/15 four-circle diffractometer operating in the ω-scan mode (scan width = 1·5°, scan speed = 0·06° s^{-1}). 1919 independent reflections up to θ = 30° were measured, of which 422 had intensities greater than 2·5$\sigma(I)$, $\sigma(I)$ being calculated from the counting statistics of the measurements. During the data collection two standard reflections were measured every 180 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarization effects and were then converted to the absolute scale by Wilson's method. Absorption and extinction corrections were not applied.

Normalized structure factors were calculated and the 200 reflections with $E \geq 1·65$ were used in the phasing program *MULTAN* (Germain, Main & Woolfson, 1971). An E map was calculated as defined by Germain, Main & Woolfson (1971) and the structural solution was evident. The conventional R value was 0·28. The structure was refined by full-matrix least-squares methods and the R value reduced to 0·10. At this stage a difference map yielded the positions of all H atoms. These, with isotropic temperature factors equivalent to the anisotropic ones of the atoms to which they are bonded (Hamilton, 1959), were included in the refinement as 'fixed-atom' contributions to the F_c calculation (Stewart, 1965). The refinement was carried out minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = 3·70 + [(|F_o| - 45)/1·46]^2$ to give constant values of $w(|F_o| - |F_c|)^2$, independent of the value of $|F_o|$. The final R value for all observed reflections was 0·060 (R_w = 0·069).*

The calculations were carried out on the CYBER 76 computer of the 'Centro di Calcolo Interuniversitario dell'Italia Nord Orientale' with the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The scattering factors were those of Cromer & Mann (1968) for all atoms.

Discussion. The present compound was obtained during an investigation of the regiospecificity of reactions of nucleophiles with 3-(hydroxyimino)- and 3-(acyloxyimino)-2,4-diketones, upon reaction of 3-(hydroxyimino)pentane-2,4-dione with benzylamine.

This X-ray analysis demonstrates unequivocally that the derivative is 4-acetyl-5-methyl-2-phenylimidazole. A preliminary account of this molecular structure has already been given (Veronese, D'Angeli, Zanotti & Del Pra, 1977).

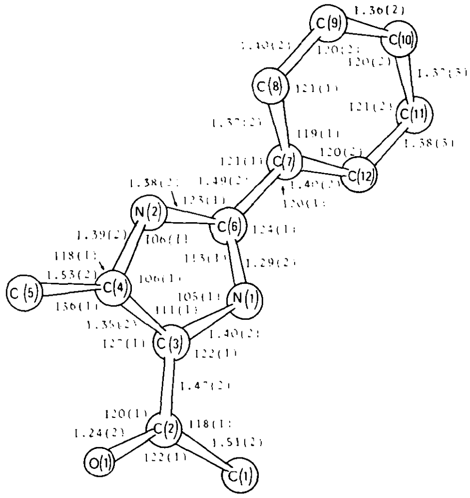

Fig. 1. Perspective view of the molecule with intramolecular bond distances (Å) and valence angles (°) (e.s.d.'s are in parentheses).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33401 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional parameters for non-hydrogen atoms with e.s.d.'s in parentheses*

	x	*y*	*z*
N(1)	0·6143 (5)	0·3441 (9)	0·140 (2)
N(2)	0·5458 (4)	0·4570 (9)	0·202 (2)
O(1)	0·5101 (4)	0·1454 (7)	0·226 (2)
C(1)	0·6106 (6)	0·125 (1)	0·146 (2)
C(2)	0·5569 (7)	0·186 (1)	0·185 (3)
C(3)	0·5622 (8)	0·296 (1)	0·185 (3)
C(4)	0·5199 (6)	0·363 (1)	0·218 (2)
C(5)	0·4558 (5)	0·359 (1)	0·272 (2)
C(6)	0·6030 (6)	0·439 (1)	0·158 (2)
C(7)	0·6465 (6)	0·520 (1)	0·132 (2)
C(8)	0·6360 (6)	0·615 (1)	0·195 (2)
C(9)	0·6776 (7)	0·691 (1)	0·172 (3)
C(10)	0·7288 (8)	0·670 (1)	0·086 (3)
C(11)	0·7393 (7)	0·575 (2)	0·018 (3)
C(12)	0·6990 (7)	0·500 (1)	0·040 (2)

Table 2. *Fractional coordinates for hydrogen atoms with e.s.d.'s in parentheses*

	x	*y*	*z*
H(C8)	0·602 (3)	0·632 (6)	0·25 (1)
H(C9)	0·672 (3)	0·756 (6)	0·21 (1)
H(C10)	0·757 (3)	0·717 (6)	0·06 (1)
H(C11)	0·775 (3)	0·560 (7)	−0·05 (1)
H(C12)	0·708 (3)	0·433 (7)	−0·02 (1)
H(N2)	0·529 (3)	0·509 (6)	0·22 (1)
H'(C5)	0·440 (3)	0·311 (6)	0·17 (1)
H''(C5)	0·457 (3)	0·315 (6)	0·40 (1)
H'''(C5)	0·426 (3)	0·408 (6)	0·29 (1)
H'(C1)	0·625 (3)	0·151 (6)	0·03 (1)
H''(C1)	0·642 (3)	0·145 (6)	0·24 (1)
H'''(C1)	0·607 (3)	0·052 (7)	0·14 (1)

Table 3. *Deviations* (Å) *of the atoms from some least-squares planes in the molecule with their dihedral angles*

The equations of the planes are in the form $PX + QY + RZ = S$ in orthogonal space with X parallel to **a**, Y perpendicular to **a** in the *ac* plane and Z perpendicular to the *ac* plane. Asterisks indicate the atoms not used in the plane calculations.

Plane 1: $0{\cdot}4095X - 0{\cdot}2437Y + 0{\cdot}8792Z = 5{\cdot}2304$

C(7)	0·008	C(10)	0·009
C(8)	−0·006	C(11)	−0·007
C(9)	−0·003	C(12)	−0·002
C(6)*	0·02		

Plane 2: $0{\cdot}2403X - 0{\cdot}0170Y + 0{\cdot}9705Z = 4{\cdot}3120$

N(1)	−0·02	C(4)	−0·01
C(2)	0·006	C(6)	0·02
C(3)	0·01	N(2)	0·001
O(1)*	0·04	C(5)*	0·007
C(1)*	0·05	C(7)*	0·06
H(N2)*	0·03		

The dihedral angle between planes 1 and 2 is 17·1°.

A perspective view of the molecule showing its conformation, the numbering system, and the intramolecular bond distances and angles is presented in Fig. 1. Final positional parameters (with e.s.d.'s) of the non-hydrogen and H atoms are reported in Tables 1 and 2 respectively. Some least-squares planes and torsion angles are given in Table 3.

In Table 4 the imidazole ring bonds are compared with the pattern of imidazole bond distances derived from a review of several observed structures (Guggenberger, 1975, and references therein); this review also shows the similarities of imidazole geometries in very different bonding situations, including the metal-bonded case.

Table 4 shows approximate agreement for the N(1)—C(3), C(3)—C(4) and C(4)—N(2) distances, whilst the agreement is poorer for the remainder. In particular, the difference between the values of N(1)—C(6) and N(2)—C(6) is unusually high in our structure. These data would indicate that resonance, although still present in the ring, is surely enhanced in the region of the molecule from N(2) to the acetyl

Table 4. *Comparison of imidazole distances* (Å)

	Present work	Mean value*	Range*
N(1)—C(3)	1·40	1·376	1·366–1·396
C(3)—C(4)	1·35	1·362	1·340–1·403
C(4)—N(2)†	1·39	1·371	1·352–1·390
N(2)†—C(6)	1·38	1·341	1·318–1·366
C(6)—N(1)	1·29	1·320	1·298–1·345

* These results are derived from the data in Table 6 of Guggenberger (1975). The e.s.d.'s of the distances are in the range 0·006–0·009 Å.

† The imidazole ring exists as the N(2)—H tautomeric form.

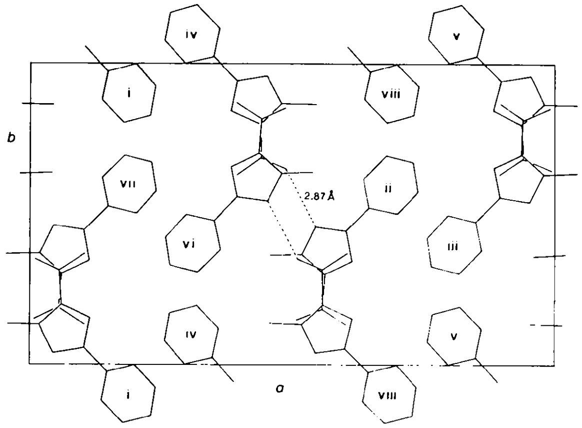

Fig. 2. The crystal structure projected down **c**. The symbols inside the phenyl rings represent the equivalent positions in space group *Pbca* (No. 61) [*i.e.* (i) x,y,z; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; (iii) $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$; (v) $\bar{x},\bar{y},\bar{z}$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (vii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (viii) $\frac{1}{2}+x, y, \frac{1}{2}-z$].

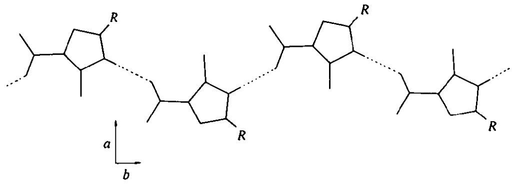

Fig. 3. View of the hydrogen bonding in the title compound (*R* represents the phenyl group).

group through C(4) and C(3). The C(6)–C(7) distance of 1·49 Å is close to a $C(sp^2)$–$C(sp^2)$ distance; this, together with the value of 17·1° for the dihedral angle between the phenyl and imidazole planes, is consistent with some reduction of delocalization between the two ring systems.

The crystal packing, which is presented in Fig. 2, is determined by hydrogen bonding and van der Waals interactions; in fact, while N(2) and O(1) are involved in hydrogen bonding the phenyl ring is involved in the conventional packing of planar aromatic rings. The molecules form chains (Fig. 3) in one dimension by N–H···O hydrogen bonds [N(2)–H···O(1): N(2)···O(1) 2·87, N(2)–H 0·81, H···O(1) 2·06 Å, ∠N(2)–H···O(1) 176·5°].

These data are in the range frequently observed (Donohue, 1968, and references therein). None of the remaining intermolecular contact distances are shorter than the sum of the van der Waals radii.

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8-Amino-5,7-dimethoxy-6-methylpyrrolo[1,2-*a*]indol-9-one

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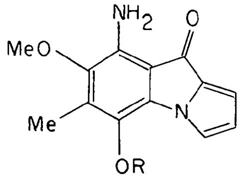
Abstract. $C_{14}H_{14}N_2O_3$, orthorhombic, $P2_12_12_1$, a = 8·955 (2), b = 16·250 (3), c = 8·794 (2) Å, V = 1274·7 (3) Å^3, Z = 4, D_x = 1·33, D_m = 1·29 g cm^{-3} (flotation in bromobenzene–*p*-xylene at 25 °C). The structure was solved by direct methods using 1448 diffractometer-measured independent observed reflections, and block-diagonal least-squares refinement led to R = 0·034 (observed reflections only) and R_w = 0·036. The molecules are linked by hydrogen bonding in chains parallel to **a**.

Introduction. Compound (I), with R = H, was prepared as a result of a metaphoto-Fries rearrangement of an amino lactone (Siuta, Franck & Ozorio, 1974). Since this product has potential application in mitomycin synthesis, it was decided to confirm the structure by X-ray crystallographic analysis of the methyl ether (R = CH_3). A preliminary report of the results of this work has been published along with a more detailed account of this metaphoto-Fries reaction (Crump *et al.*, 1977).



(I)

The crystals were red-gold, somewhat opaque, and had the form of slightly flattened prisms. X-ray data were collected with Cu *Kα* radiation (Ni-filtered) on an

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