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4(5)-(p-Methoxyphenylazo)-2-methylimidazole

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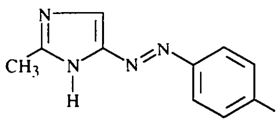
Abstract

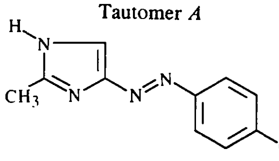
The two tautomers of the title compound, $C_{11}H_{12}N_4O$, form the asymmetric unit of the crystal structure as independent molecules. They form two independent chains *via* N—H···N hydrogen bonds and the chains are crosslinked by weak C—H···O contacts.

Comment

The structure of 4(5)-(p-methoxyphenylazo)-2-methylimidazole was determined as part of NMR and IR studies of imidazole derivatives (Maciejewska & Skulski, 1993; Maciejewska, 1995). The 2-arylazoimidazole fragment has attracted our attention because it plays a very important role in many drugs, dyes, indicators, polymers, *etc.* Due to a fast proton exchange between the N1 and N3 atoms, two tautomeric forms (*A* and *B*) are present in the crystalline state of the title compound.



Tautomer *A*



Tautomer *B*

The different localization of protons results in small differences in the geometry of the imidazole rings (Fig. 1). As a consequence, there is a small difference in aromatic character between these two rings as estimated by the HOMA model (Krygowski, 1993); 0.95 for tautomer *A* and 0.97 for tautomer *B*. This difference may be caused by the differences in the hydrogen bonds [N3···N1 3.053 (3) and 2.883 (3) Å in tautomers *A* and *B*, respectively (Fig. 2)]. Interestingly, molecules of the title compound form chains linked *via* hydrogen bonds between the analogous imidazole rings. There are only a few similar compounds reported in the Cambridge Structural Database (Allen *et al.*, 1991) which consist of two tautomers in the crystalline state, *i.e.* 5-(3,3-dimethyl-1-triazenyl)imidazole-4-carboxamide (Freeman & Hutchinson, 1979) and N-(4-chlorobenzylidene)-2-(4-imidazolyl)ethylamine (Bocelli & Cantoni, 1992). Other compounds similar to 2-methyl-4(5)-(p-R-phenylazo)imidazole (Anulewicz & Maciejewska, 1996) do not exhibit tautomerism.

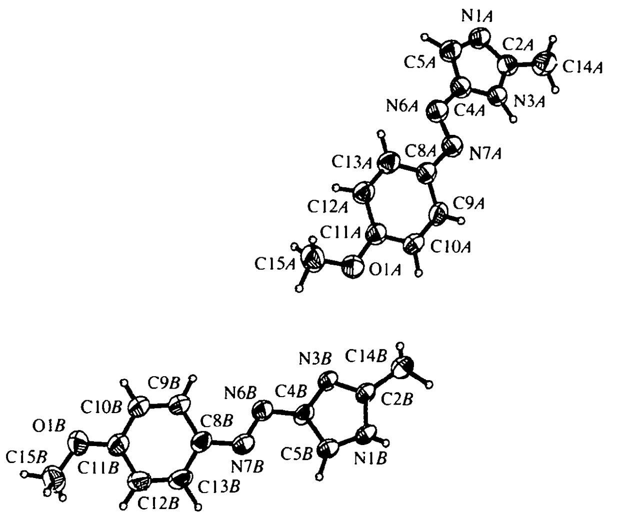


Fig. 1. The asymmetric unit of (I) composed of tautomers *A* and *B*. Displacement ellipsoids are drawn at the 50% probability level.

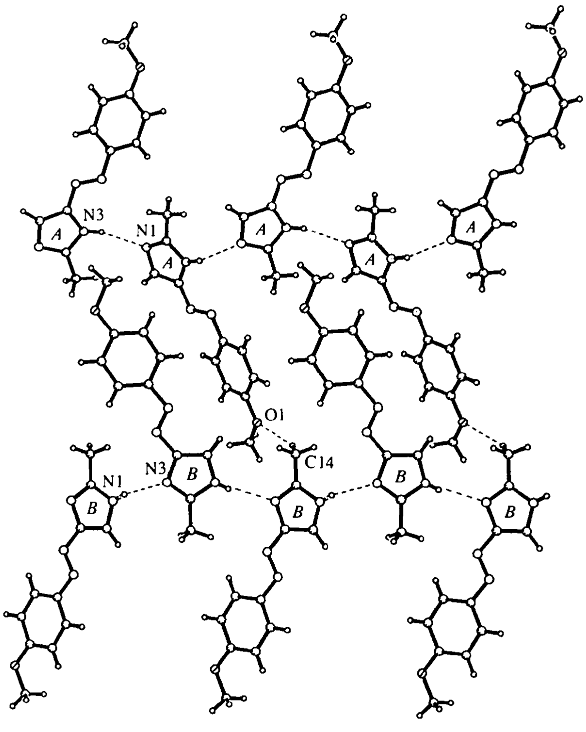


Fig. 2. The crystal packing diagram showing the hydrogen bonds.

Another interesting structural problem is associated with the bond angles in the imidazole ring (Table 2). The endocyclic angle at the C atom opposite the N atom bearing the lone pair is substantially smaller (105 << 110–111°) than those at the neighbouring C atoms. In other words, the endocyclic bond angles at the C atoms linked directly *via* C4—C5 are swapped in accordance with the position of the lone pair of electrons (*versus* H atom) (Kálmán & Argay, 1983). The different sequence of endocyclic bond angles substantiate the validity of the VSEPR (valence-shell/electron-pair repulsion) rules (Gillespie, 1963) for such planar rings.

Experimental

Crystal data

$C_{11}H_{12}N_4O$
$M_r = 216.24$
Monoclinic
$P2_1/c$
$a = 11.077\ (2)$ Å
$b = 9.631\ (2)$ Å
$c = 20.945\ (4)$ Å
$\beta = 93.53\ (3)°$
$V = 2230.2\ (7)$ Å^3
$Z = 8$
$D_x = 1.288$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 50 reflections
$\theta = 15.5–28.0°$
$\mu = 0.715$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.22 × 0.20 × 0.20 mm
Brown

Data collection

Kuma KM-4 diffractometer
ω/θ scans
Absorption correction: none
3736 measured reflections
3619 independent reflections
2649 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.1656$

$\theta_{\rm max} = 70°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 19$
3 standard reflections monitored every 100 reflections
intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0931$
$wR(F^2) = 0.2690$
$S = 1.023$
3603 reflections
320 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.2104P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.010$

$\Delta\rho_{\rm max} = 0.521$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.483$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0145 (19)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1*A*	0.0560 (2)	0.6717 (2)	−0.26775 (13)	0.0570 (6)
C2*A*	−0.0088 (3)	0.5567 (3)	−0.26096 (14)	0.0500 (6)
N3*A*	0.0515 (2)	0.4634 (2)	−0.22287 (12)	0.0500 (6)
C4*A*	0.1615 (3)	0.5204 (3)	−0.20412 (14)	0.0523 (7)
C5*A*	0.1613 (3)	0.6487 (3)	−0.2333 (2)	0.0591 (7)
N6*A*	0.2493 (2)	0.4673 (2)	−0.16174 (12)	0.0570 (6)
N7*A*	0.2188 (2)	0.3535 (2)	−0.13632 (12)	0.0534 (6)
C8*A*	0.3045 (3)	0.3026 (3)	−0.08927 (14)	0.0483 (6)
C9*A*	0.2669 (3)	0.1927 (3)	−0.0524 (2)	0.0566 (7)
C10*A*	0.3406 (3)	0.1414 (3)	−0.00271 (15)	0.0580 (7)
C11*A*	0.4531 (3)	0.1996 (3)	0.01169 (14)	0.0510 (6)
C12*A*	0.4914 (3)	0.3090 (3)	−0.02467 (15)	0.0557 (6)
C13*A*	0.4186 (3)	0.3599 (3)	−0.0749 (2)	0.0557 (6)
O1*A*	0.5171 (2)	0.1437 (2)	0.06264 (11)	0.0639 (6)
C15*A*	0.6349 (3)	0.1975 (4)	0.0798 (2)	0.0771 (10)
C14*A*	−0.1303 (3)	0.5319 (4)	−0.2910 (2)	0.0740 (10)
N1*B*	0.5227 (2)	−0.1930 (2)	0.26826 (13)	0.0540 (6)
C2*B*	0.5033 (3)	−0.0788 (2)	0.23082 (13)	0.0462 (6)
N3*B*	0.5633 (2)	0.0285 (2)	0.25653 (11)	0.0486 (6)
C4*B*	0.6208 (2)	−0.0194 (2)	0.31159 (14)	0.0468 (6)
C5*B*	0.5951 (3)	−0.1593 (3)	0.3192 (2)	0.0551 (7)
N6*B*	0.6928 (2)	0.0722 (2)	0.34940 (11)	0.0495 (6)
N7*B*	0.7355 (2)	0.0193 (2)	0.40044 (12)	0.0540 (6)
C8*B*	0.8083 (3)	0.1079 (3)	0.44002 (14)	0.0492 (6)
C9*B*	0.8486 (3)	0.2410 (3)	0.4227 (2)	0.0618 (8)
C10*B*	0.9205 (3)	0.3158 (3)	0.4653 (2)	0.0664 (9)
C11*B*	0.9559 (3)	0.2630 (3)	0.52514 (15)	0.0546 (7)
C12*B*	0.9177 (3)	0.1317 (3)	0.5420 (2)	0.0589 (7)
C13*B*	0.8455 (3)	0.0562 (3)	0.4990 (2)	0.0589 (7)
O1*B*	1.0277 (2)	0.3465 (2)	0.56363 (12)	0.0741 (7)
C15*B*	1.0837 (4)	0.2912 (4)	0.6203 (2)	0.0790 (10)
C14*B*	0.4268 (4)	−0.0779 (3)	0.1716 (2)	0.0719 (10)

Table 2. *Selected geometric parameters* (Å, °)

Tautomer *A*		Tautomer *B*	
N1*A*—C2*A*	1.331 (4)	N1*B*—C2*B*	1.360 (3)
N1*A*—C5*A*	1.352 (4)	N1*B*—C5*B*	1.335 (4)
C2*A*—N3*A*	1.351 (3)	C2*B*—N3*B*	1.325 (3)
N3*A*—C4*A*	1.372 (4)	N3*B*—C4*B*	1.363 (4)
C4*A*—C5*A*	1.379 (4)	C4*B*—C5*B*	1.388 (3)
C4*A*—N6*A*	1.374 (4)	C4*B*—N6*B*	1.401 (3)
N6*A*—N7*A*	1.273 (3)	N6*B*—N7*B*	1.250 (3)
N7*A*—C8*A*	1.413 (4)	N7*B*—C8*B*	1.408 (4)
C2*A*—N1*A*—C5*A*	105.0 (2)	C2*B*—N1*B*—C5*B*	109.2 (2)
N1*A*—C2*A*—N3*A*	111.5 (3)	N1*B*—C2*B*—N3*B*	109.8 (2)
C2*A*—N3*A*—C4*A*	107.5 (2)	C2*B*—N3*B*—C4*B*	106.0 (2)
N3*A*—C4*A*—C5*A*	104.8 (3)	N3*B*—C4*B*—C5*B*	109.7 (2)
N3*A*—C4*A*—N6*A*	128.1 (3)	N3*B*—C4*B*—N6*B*	119.0 (2)
C5*A*—C4*A*—N6*A*	127.0 (3)	C5*B*—C4*B*—N6*B*	131.3 (3)
N1*A*—C5*A*—C4*A*	111.2 (3)	N1*B*—C5*B*—C4*B*	105.2 (2)
N7*A*—N6*A*—C4*A*	113.3 (3)	N7*B*—N6*B*—C4*B*	113.5 (2)
N6*A*—N7*A*—C8*A*	114.0 (2)	N6*B*—N7*B*—C8*B*	115.4 (2)

Data collection: *Kuma KM*-4 *Software* (Kuma, 1991). Cell refinement: *Kuma KM*-4 *Software*. Data reduction: *Kuma KM*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Z)-2-(Benzoyl-*aci*-nitro)-2-phenylacetonitrile

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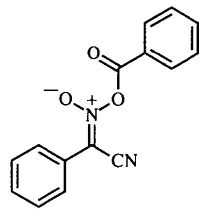
Abstract

The *aci*-nitro group of the title compound, $C_{15}H_{10}N_2O_3$, is almost coplanar with the phenylacetonitrile moiety [O11—N10···C1—C2 8.3 (2)°] and is almost perpendicular to the benzoyl group [O11—N10—O12—C13 84.7 (2)°]. The C—N=O angle of the *aci*-nitro group is distorted due to steric interaction with the neighboring *ortho*-H atom of the phenyl ring.

Comment

As part of an investigation of acyl-group transfer agents, carboxylic nitronic anhydrides (Nielsen, 1989) were examined. The title compound, (I), is an effective acylating agent under mild conditions (Thurston & Shriner, 1937). Its structure was determined in order to establish the conformation of the anhydride juncture.



(I)

The title compound exhibits a shortened C—N bond [C7—N10 1.318 (2) Å] and unequal N—O bond lengths [N10=O11 1.232 (2) and N10—O12 1.453 (2) Å] characteristic of an *aci*-nitro group (Nielsen, 1989). The difference in the O—N—C angles [O11=N10—C7 130.3 (2) and O12—N10—C7 114.00 (14)°] probably arises from non-bonded repulsion between the phenyl *ortho*-H2 atom and O11. Similar bond-angle distortions were seen in two silyl nitronates (Colvin *et al.*, 1980) and in *aci*-nitrodiphenylmethane (Bock *et al.*, 1993).

The title molecule assumes a conformation with two separate planar regions. The sp^2 character of the C7 atom causes the *aci*-nitro and phenylacetonitrile groups to form one almost planar region of the molecule as shown by the O11—N10···C1—C2 torsion angle of −8.3 (2)°. The benzoyl group is almost perpendicular to the *aci*-nitrophenylacetonitrile group as shown by the O11—N10—O12—C13 torsion angle of 84.7 (2)°. The roughly 90° orientation of the benzoyl plane with respect to the *aci*-nitro plane may reduce dipolar and/or steric repulsions between the carbonyl and both the *aci*-nitro and acetonitrile groups. There are no unusually short intermolecular contacts.

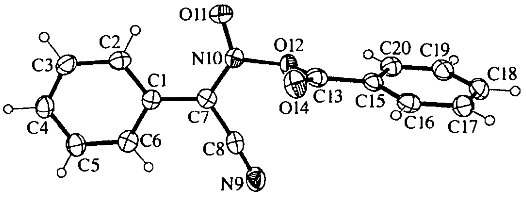


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids.

Experimental

The title compound was prepared according to the method of Thurston & Shriner (1937). Crystals were grown by vapor diffusion from a solution of 1,2-dichloroethane using pentane as the precipitant. Spectroscopic data: ^1H NMR (300 MHz, $CDCl_3$): δ 8.13 (*m*, 4H), 7.72 (*tt*, J = 8.94, 1.3 Hz, 1H), 7.56 (*m*, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 162.3 (C), 135.2 (CH), 132.1 (CH), 130.4 (CH), 129.2 (CH), 129.1 (CH), 127.8 (CH), 125.3 (C), 124.7 (C), 111.3 (C); IR (thin film): 2230, 1761, 1606, 1449, 1340, 1318, 1250, 1223, 975 cm^{-1}; HRMS (EI): calculated for $C_{15}H_{10}N_2O_3$ 266.0691, found 266.0691; m.p. (recrystallized from hexane) 389 K.