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Ethyl 3-(5-Amino-4-cyano-1-imidazolylamino)-2-butenoate: an Example of a Combined Inter- and Intramolecular Bifurcated Hydrogen Bond

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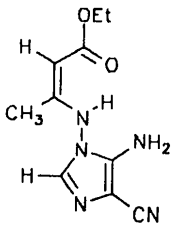
Abstract

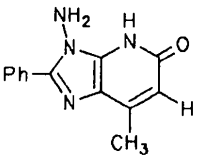
The imidazolyl ring is twisted out of the 2-butenoate plane (C—N—N—C) by 80.9 (4)° and delocalization occurs along a planar chain region extending from the amine to the carbonyl O atom. This O atom is also linked to the amine *via* an intramolecular hydrogen bond [O···N 2.747 (4), O···H 2.21 (3) Å, N—H···O 121 (3)°] which may explain why the ester carbonyl stretching vibration in the IR spectrum is shifted to lower frequency (1656 *cf.* 1730 cm^{-1} for a similar compound with no intramolecular hydrogen bonding). The same H and O atoms also take part in intermolecular hydrogen bonding around a crystallographic inversion centre [O···N 2.932 (4), O···H 2.19 (3) Å, N—H···O 144 (3)°].

Comment

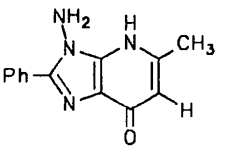
We have recently described a novel synthesis of 1,5-diamino-4-imidazolecarbonitrile (Alves, Booth, Freitas & Proença, 1992) and have investigated its reactions with β-ketoesters under acidic conditions. From the reaction with ethyl acetoacetate under acidic conditions it is clear from spectroscopic data (IR, ^1H and ^{13}C NMR spectroscopy under acidic conditions, and mass spectroscopy) that attack occurs at the keto carbonyl and that the ester group is unaffected. However, it was necessary to establish which of the two amino groups, *i.e.* that at the 1 or the 5 position, participated in the reaction. The X-ray structure establishes that the 1-amino group reacts in preference to that in the 5 position. This result, compound (1), is in contrast with a previous report (Bernardi, Viallefont & Zniber, 1978) that 1,5-diamino-2-phenylimidazole upon reflux with ethyl acetoacetate in xylene gives a major product identified as either (2) or (3).



(1)



(2)



(3)

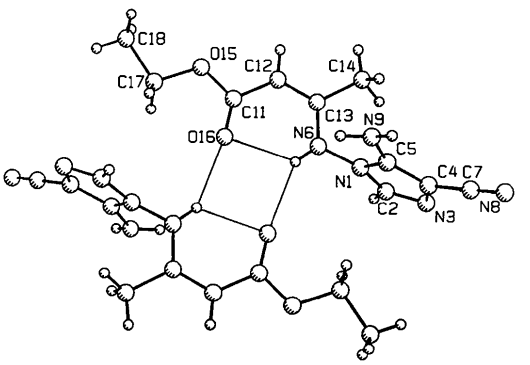


Fig. 1. Hydrogen bonding around 0.5,0,0. The title molecule, including the atomic numbering scheme, was drawn using *PLUTO* (Motherwell & Clegg, 1978).

Experimental

Crystal data

$C_{10}H_{13}N_5O_2$
M_r = 235.24
Monoclinic
$C2/c$
a = 14.619 (5) Å
b = 14.587 (8) Å
c = 12.024 (4) Å
β = 108.66 (3)°
V = 2429 (1) $Å^3$
Z = 8
D_x = 1.286 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 14.49–23.93°
μ = 0.0881 mm^{-1}
T = 296 K
Rods
0.35 × 0.20 × 0.20 mm
Colourless

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.92, T_{max} = 1.00
2305 measured reflections
2210 independent reflections
1041 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.053
θ_{max} = 25.0°
h = 0 → 16
k = 0 → 17
l = −13 → 13
3 standard reflections monitored every 150 reflections
intensity variation: −1.00%

Refinement

Refinement on F
Final R = 0.0376
wR = 0.0410
S = 1.448
1041 reflections
206 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.0119
$\Delta\rho_{max}$ = 0.10781 e Å^{-3}
$\Delta\rho_{min}$ = −0.22802 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*; *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984). .

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

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.3332 (2)	0.0345 (2)	0.1326 (2)	0.0451
C2	0.3523 (3)	0.0062 (3)	0.2462 (3)	0.0550
N3	0.2755 (2)	−0.0239 (2)	0.2654 (2)	0.0560
C4	0.2023 (2)	−0.0136 (2)	0.1587 (3)	0.0446
C5	0.2366 (2)	0.0229 (2)	0.0749 (3)	0.0406
N6	0.3978 (2)	0.0794 (2)	0.0880 (2)	0.0472
C7	0.1046 (3)	−0.0365 (3)	0.1438 (3)	0.0523
N8	0.0256 (2)	−0.0534 (3)	0.1297 (3)	0.0756
N9	0.1951 (2)	0.0493 (2)	−0.0370 (2)	0.0523
C11	0.5176 (2)	0.1769 (3)	−0.0213 (3)	0.0544
C12	0.4595 (3)	0.2186 (3)	0.0404 (3)	0.0608
C13	0.4037 (2)	0.1724 (2)	0.0908 (3)	0.0468
C14	0.3464 (3)	0.2219 (3)	0.1560 (4)	0.0665
O15	0.5637 (2)	0.2409 (2)	−0.0645 (2)	0.0821
O16	0.5260 (2)	0.0955 (2)	−0.0354 (2)	0.0572
C17	0.6245 (4)	0.2079 (3)	−0.1305 (5)	0.0937
C18	0.6557 (7)	0.2923 (6)	−0.1811 (9)	0.1384

Table 2. *Geometric parameters* (Å, °)

N1—C2	1.368 (4)	C5—N9	1.343 (4)
N1—C5	1.370 (3)	N6—C13	1.360 (4)
N1—N6	1.390 (3)	C11—C12	1.430 (5)
C2—N3	1.294 (4)	C11—O15	1.349 (4)
N3—C4	1.391 (4)	C11—O16	1.211 (4)
C4—C5	1.369 (4)	C12—C13	1.343 (4)
C2—N1—C5	108.4 (2)	N1—N6—C13	120.4 (3)
C2—N1—N6	125.5 (3)	C12—C11—O15	111.0 (3)
C5—N1—N6	125.5 (2)	C11—C12—C13	124.6 (3)
N3—C4—C7	122.5 (3)	N6—C13—C12	122.1 (3)
N1—C5—C4	103.7 (2)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D···H	H—A	D···A	D—H···A
N6—H6···O16	0.86 (3)	2.21 (3)	2.747 (4)	121 (3)
N6—H6···O16^{i}	0.86 (3)	2.19 (3)	2.932 (4)	144 (3)
N9—H9A···N3^{ii}	0.88 (3)	2.14 (3)	2.992 (4)	164 (3)
N9—H9B···N8^{iii}	0.92 (4)	2.17 (3)	3.060 (4)	161 (3)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $x, -y, z-\frac{1}{2}$; (iii) $-x, -y, -x$.

The title compound was prepared by the addition of a catalytic amount of perchloric acid (2 drops) to a suspension of 1,5-diamino-4-imidazolecarbonitrile (4.07 mmol) in ethyl acetoacetate (1 ml, 7.85 mmol) and ethanol (15 ml). The mixture was stirred for 7 d at room temperature to give the product as a white crystalline solid in 85% (3.48 mmol) yield. The crystals were purified by washing with diethyl ether.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71203 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1047]

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1,3,5-Triacetyl-2,4,6-triphenylbenzene: a Sterically Hindered Molecule

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Abstract

Steric congestion has twisted the acetyl and phenyl substituents out of conjugation with the central benzene ring with interplanar angles ranging from 59.5 to 80.2°. The molecular conformation is thus locked in the form of a rotor with two acetyl-O atoms projecting below and one above the benzene plane.

Comment

In the IR spectrum of the title 1,3,5 isomer (I) a single carbonyl stretching vibration at 1700 cm^{-1} is ob-