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Ethyl 6-nitro-2-phenylaminoimidazo[1,2-*a*]pyridine-3-carboxylate

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Key indicators

Single-crystal X-ray study
T = 168 K
Mean σ(C–C) = 0.003 Å
R factor = 0.052
wR factor = 0.088
Data-to-parameter ratio = 10.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In crystals of the title compound, $C_{16}H_{14}N_4O_4$, the molecule is found in an extended near-planar conformation, stabilized by intramolecular attractive interactions and electron delocalization. This analysis establishes an otherwise ambiguous spectroscopic assignment of the structure.

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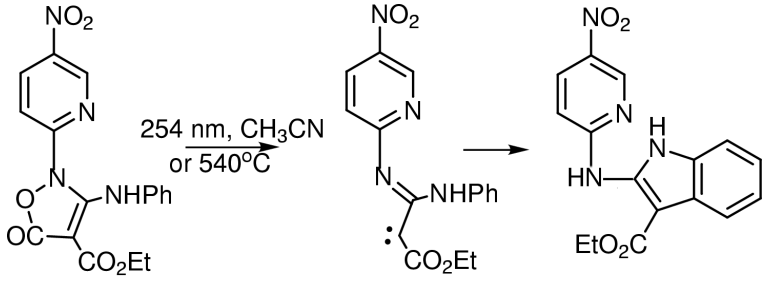
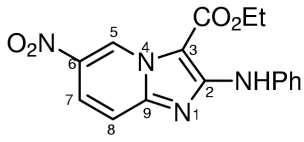
Comment

We have reported that brief photolysis or flash vacuum pyrolysis of the nitropyridylisoxazolone (1) gives a good yield of the indole (2) (Khalafy *et al.*, 1999) arising from the intramolecular cyclization of the carbene intermediate. Subsequently, we found that reaction of the isoxazolone (1) with a weak base in ethanol gave the same compound (2), by a sequence that is mechanistically different, and clearly incompatible with a carbenoid intermediate (Khalafy & Prager, 2000). During an extension of the latter reaction to a number of arylamino analogues, we encountered substrates that led to the formation of two products, one of which was analogous to the indole (2), and the other to the isomeric ethyl 6-nitro-2-phenylaminoimidazo[1,2-*a*]pyridine-3-carboxylate, (3). After comparison of the spectroscopic properties of the indole and imidazopyridine compounds, we suspected that the structure of the product (2) had been misassigned and that the product of all three reactions of (1) was the imidazopyridine (3). This suspicion has been clearly confirmed by the crystal structure determination of (3).



(1) (2)



(3)

In the crystal structure of the title compound, (3), the molecule is flat with all the non-H atoms within ±0.19 Å of a

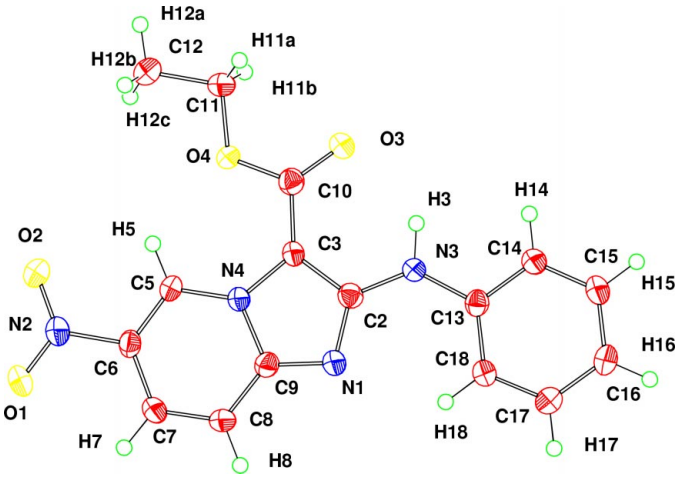


Figure 1
View of the title molecule, (3), showing the atom labels. Displacement ellipsoids are at the 50% probability level.

common plane (Fig. 1). This conformation is clearly stabilized by three attractive intramolecular contacts detailed in Table 2. This conformation is further stabilized by the electron delocalization that occurs. Seven C—N bonds in the molecule (omitting N2—C6) are of similar length, ranging from 1.328 (3) to 1.405 (3) Å, with C2—N3 notably 1.353 (3) Å (Table 1). Therefore, the C2—N3 bond has significant double-bond character which in turn would lead to higher acidity for H3 and a stronger N3—H···O3 hydrogen bond (Table 2). The molecules are arranged in sheets throughout the structure parallel to $(2\bar{1}2)$ and about 3.3 Å apart. There is an angle of 3.07 (7)° between the planes of the nitro group (C6, N2, O1 and O2) and the imidazopyridine moiety. There are 26 distinct examples of this imidazopyridine moiety, substituted in a variety of ways, in the April 2001 version of the Cambridge Structural Database (Allen & Kennard, 1993).

Experimental

Ethyl 2-(5-nitropyridin-2-yl)-5-oxo-3-phenylamino-2,5-dihydroisoxazole-4-carboxylate (Khalafy *et al.*, 1999) (0.020 g, 0.054 mmol) and potassium carbonate (0.037 g, 0.270 mmol) were refluxed in ethanol (2 ml) for 1 h. After 20 min the solution turned from orange to red. The solution was cooled, quenched with 1 *M* HCl (5 ml) and extracted with CH_2Cl_2 (3 × 25 ml). The combined extracts were washed with brine (1 × 20 ml), dried ($MgSO_4$) and the solvent was removed *in vacuo*, yielding a red solid which was recrystallized from ethanol to give the title compound (3) as yellow needles (0.012 g, 67%): m.p. 473–475 K; ν_{max} (film): 3330, 1667, 1619, 1604, 1576, 1344, 1310, 1212 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 9.87, *bs*, 1H; 8.93, *bs*, 1H; 8.15, *dd*, *J* = 9.6, 2.1 Hz, 1H; 7.72, *d*, *J* = 7.8 Hz, 2H; 7.52, *d*, *J* = 9.6 Hz, 1H; 7.38, *t*, *J* = 7.8 Hz, 2H; 7.07, *t*, *J* = 7.8 Hz, 1H; 4.56, *q*, *J* = 7.1 Hz, 2H; 1.55, *t*, *J* = 7.1 Hz, 3H,); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 160.8, 147.0, 139.4, 137.0, 129.2, 126.9, 122.9, 122.4, 118.8, 114.0, 98.9, 61.1, 14.6 (one carbonyl unsighted); *m/z*: 326 (*M*, 100%), 280 (54), 234 (27), 206 (10), 130 (11), 104 (17), 103 (15), 77 (36), 51 (13), 44 (15).

Crystal data

$C_{16}H_{14}N_4O_4$	Z = 2
M_r = 326.31	D_x = 1.466 Mg m^{-3}
Triclinic, $P\bar{1}$	Mo Kα radiation
a = 7.868 (4) Å	Cell parameters from 2508 reflections
b = 8.489 (4) Å	θ = 2.7–26.0°
c = 12.281 (6) Å	μ = 0.11 mm^{-1}
α = 104.38 (1)°	T = 168 (2) K
β = 92.30 (1)°	Plate, yellow
γ = 110.07 (1)°	0.57 × 0.05 × 0.04 mm
V = 739.2 (6) $Å^3$	

Data collection

Bruker *P*4 diffractometer	R_{int} = 0.03
ω scans	θ_{max} = 26.3°
9625 measured reflections	$h = -9 \rightarrow 9$
2989 independent reflections	$k = -10 \rightarrow 9$
2173 reflections with $F^2 > \sigma(F^2)$	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > \sigma(F^2)]$ = 0.052	$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]^{1/2}$
$wR(F^2)$ = 0.088	$(\Delta/\sigma)_{max} < 0.001$
S = 1.11	$\Delta\rho_{max}$ = 0.35 e $Å^{-3}$
2173 reflections	$\Delta\rho_{min}$ = −0.43 e $Å^{-3}$
217 parameters	

Table 1
Selected bond lengths (Å).

O1—N2	1.233 (3)	N4—C3	1.398 (3)
O2—N2	1.224 (3)	N4—C9	1.405 (3)
N1—C9	1.329 (3)	C2—C3	1.395 (3)
N1—C2	1.362 (3)	C3—C10	1.431 (3)
N2—C6	1.448 (3)	C5—C6	1.358 (3)
N3—C2	1.353 (3)	C6—C7	1.397 (3)
N3—C13	1.402 (3)	C7—C8	1.355 (3)
N4—C5	1.355 (3)	C8—C9	1.403 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O3	0.92	2.12	2.835 (2)	133
C5—H5···O4	0.95	2.28	2.832 (3)	116
C18—H18···N1	0.95	2.33	2.967 (3)	124

All H atoms were observed in a difference map but were placed at calculated positions.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *Xtal*3.7 *ADDREF SORTRF* (Hall *et al.*, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1994); program(s) used to refine structure: *Xtal*3.7 *CRYLSQ*; molecular graphics: *Xtal*3.7; software used to prepare material for publication: *Xtal*3.7 *BONDLA CIFIO*.

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References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Bruker (1997). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Hall, S. R., du Boulay, D. J. & Olthof-Hazekamp, R. (2000). Editors. *Xtal*3.7 *System*. University of Western Australia, Perth: Lamb.
Khalafy, J. & Prager, R. H. (2000). *J. Sci. I. R. Iran*, **11**, 32–38.
Khalafy, J., Prager, R. H. & Smith, J. A. (1999). *J. Chem. Res.* (*M*), pp. 518–536.