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Structures of Pyrazole Derivatives. III. 5-Amino-4-cyano-1-phenylpyrazole

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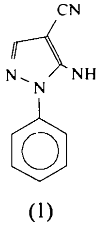
Abstract

The phenyl and pyrazole rings in the title compound, 5-amino-1-phenyl-4-pyrazolecarbonitrile, $C_{10}H_8N_4$, are planar and make a dihedral angle of 130.7 (1)°. The molecular packing involves an intermolecular hydrogen bond: $N(3)\cdots N(4^i) = 3.074\,(5)$, $N(3)—H'(N3) = 1.023\,(5)$, $N(4^i)\cdots H'(N3) = 2.060\,(5)$ Å, $N(3)—H'(N3)\cdots N(4^i) = 171.2\,(2)°$ [symmetry code: (i) $1-x, -y, 1-z$].

Comment

Following a research program aimed at synthesizing potentially bioactive functionalized pyrazoles (Iulek, Zukerman-Schpector, Barreiro & Freitas, 1993, and references therein), compound (1) was prepared (Freitas, 1991). In order to determine the overall conformation of (1) a three-dimensional crystal structure determination was undertaken.



(1)

As can be seen in Table 2, the internal and external angles of the pyrazole ring follow the set of empirical rules given by Bonati & Bovio (1990), such that (*a*) N(1)—N(2)—C(3) is smaller than N(2)—N(1)—C(5); (*b*) N(2)—C(3)—C(4) is larger than N(1)—N(2)—C(3), C(3)—C(4)—C(5) and N(1)—C(5)—C(4); (*c*) C(3)—C(4)—C(5) is not the largest internal angle; (*d*) N(2)—N(1)—C(7) is smaller than C(5)—N(1)—C(7); (*e*) N(2)—C(3)—H(C3) [124.2 (5)°] is larger than C(4)—C(3)—H(C3) [123.5 (5)°]; and (*f*) C(6)—C(4)—C(3) and C(6)—C(4)—C(5) are equal.

The C(4)—C(5) distance is marginally shorter than C(3)—C(4) as expected in neutral pyrazole rings (Zukerman-Schpector, Castellano, Oliva, Massabni & Pinto, 1984, and references therein). The pyrazole and phenyl rings are planar to within experimental accuracy, $\sigma_{\rm av}$ [defined as $(\sum_i^n d_i^2/N-3)^{1/2}$] being 0.003 and 0.006 Å, respectively.

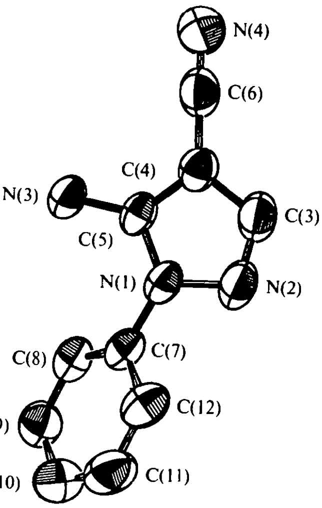


Fig. 1. The molecular structure of $C_{10}H_8N_4$ showing the atom labelling. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystal data

$C_{10}H_8N_4$
$M_r = 184.2$
Monoclinic
$P2_1/c$
$a = 11.007\,(2)$ Å
$b = 7.726\,(1)$ Å
$c = 12.194\,(2)$ Å
$\beta = 115.71\,(2)°$
$V = 934.3\,(7)$ Å^3
$Z = 4$
$D_x = 1.309$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 7–19°$
$\mu = 0.08$ mm^{-1}
$T = 292$ K
Irregular
0.30 × 0.28 × 0.01 mm
Yellowish
Crystal source: crystallized from ethanol

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1389 measured reflections
1318 independent reflections
705 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 25°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 14$
2 standard reflections
frequency: 30 min
intensity variation: ±0.9%

Refinement

Refinement on F
$R = 0.0429$
$wR = 0.0434$
$S = 1.33$
705 reflections
128 parameters
H-atom positions fixed, one overall $U_{\rm iso}$ refined

$w = 1/[\sigma^2(|F_o|) + 0.0003|F_o|^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

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

$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
N(1)	0.0604 (3)	0.1468 (4)	0.2234 (2)	4.5 (1)
N(2)	0.0778 (4)	0.2215 (4)	0.1277 (3)	5.8 (1)
N(3)	0.1891 (3)	0.0242 (4)	0.4192 (2)	4.8 (1)
N(4)	0.5303 (4)	0.0928 (6)	0.3936 (3)	8.4 (2)
C(3)	0.2079 (5)	0.2183 (6)	0.1628 (3)	5.9 (2)
C(4)	0.2772 (4)	0.1424 (5)	0.2782 (3)	4.6 (1)
C(5)	0.1788 (4)	0.0979 (5)	0.3144 (3)	4.1 (1)
C(6)	0.4170 (5)	0.1145 (6)	0.3422 (4)	5.7 (2)
C(7)	−0.0721 (4)	0.1321 (5)	0.2144 (3)	4.4 (1)
C(8)	−0.1022 (4)	0.1905 (5)	0.3065 (3)	5.0 (1)
C(9)	−0.2331 (5)	0.1820 (6)	0.2914 (4)	5.9 (2)
C(10)	−0.3323 (4)	0.1189 (6)	0.1855 (5)	6.9 (2)
C(11)	−0.3008 (5)	0.0600 (6)	0.0943 (4)	6.7 (2)
C(12)	−0.1704 (4)	0.0656 (5)	0.1075 (3)	5.6 (1)

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

N(1)—N(2)	1.388 (5)	N(1)—C(5)	1.348 (5)
N(1)—C(7)	1.419 (6)	N(2)—C(3)	1.305 (7)
N(3)—C(5)	1.358 (4)	N(4)—C(6)	1.139 (7)
C(3)—C(4)	1.405 (5)	C(4)—C(5)	1.379 (6)
C(4)—C(6)	1.408 (7)	C(7)—C(8)	1.377 (6)
C(7)—C(12)	1.382 (5)	C(8)—C(9)	1.373 (8)
C(9)—C(10)	1.369 (7)	C(10)—C(11)	1.378 (7)
C(11)—C(12)	1.374 (7)		
N(2)—N(1)—C(5)	111.8 (3)	N(3)—C(5)—C(4)	130.5 (3)
N(2)—N(1)—C(7)	118.7 (3)	N(4)—C(6)—C(4)	179.6 (5)
C(5)—N(1)—C(7)	129.4 (3)	N(1)—C(7)—C(8)	120.9 (4)
N(1)—N(2)—C(3)	104.4 (3)	N(1)—C(7)—C(12)	117.4 (3)
N(2)—C(3)—C(4)	112.2 (4)	C(8)—C(7)—C(12)	121.6 (4)
C(3)—C(4)—C(5)	105.3 (4)	C(7)—C(8)—C(9)	119.0 (4)
C(3)—C(4)—C(6)	127.4 (4)	C(8)—C(9)—C(10)	120.3 (4)
C(5)—C(4)—C(6)	127.3 (4)	C(9)—C(10)—C(11)	120.1 (5)
N(1)—C(5)—N(3)	123.2 (3)	C(10)—C(11)—C(12)	120.7 (4)
N(1)—C(5)—C(4)	106.2 (3)	C(7)—C(12)—C(11)	118.2 (4)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. H atoms were included as fixed contributors at the positions found by difference Fourier synthesis. One overall isotropic temperature factor for the H atoms was refined [$U_{\rm iso} = 0.091$ (5) Å^2]. The refinement was carried out by full-matrix least-squares methods. Programs used: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). Most of the calculations were performed at the Weizmann Institute of Science, Israel.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chemical Degradation of Spiroindolinonaphthoxazines: 8,13,13-Trimethyl-7a,8-dihydronaphtho[2,1-*b*]quinolino-[3,2-*e*][1,4]oxazine, $C_{22}H_{20}N_2O$

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Abstract

The molecular structure of the title compound consists of a naphthoxazine moiety fused to a tetrahydroquinoline fragment. The heterocyclic ring of the latter displays a 'boat' conformation. No geometrical differences from other similar compounds have been detected for the naphthoxazine system.

Comment

Spiroindolinonaphthoxazines have been extensively studied because their good photochromic properties (*i.e.* colorability and photochemical fatigue resistance) with respect to other organic photochromic compounds (Dürr,

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