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Crystal structure of ethyl 5-amino-1-(pyridin-2-yl)-1*H*-pyrazole-4-carboxylate, C₁₁H₁₂N₄O₂

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.22 × 0.21 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.10 mm ⁻¹
Diffractometer, scan mode:	PHOTON 100 CMOS, ω -scans
$\theta_{\max}$, completeness:	25°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11423, 5170, 0.048
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4346
$N(\text{param})_{\text{refined}}$:	463
Programs:	Bruker programs [1], SHELX [2]

Source of material

The compound we report here, ethyl 5-amino-1-(pyridin-2-yl)-1*H*-pyrazole-4-carboxylate, can be easily synthesized using a known synthetic procedure [3]. Evaporation at room temperature yielded colourless crystals of the desired compound.

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses. C–H hydrogen atoms were placed on calculated positions with the help of the SHELXL program [2] and refined using a riding model: C–H = 0.93 and 0.96 Å for aromatic and CH₃ H atoms, respectively, with $U_{\text{iso}}(\text{H}) = k$ times $U_{\text{eq}}(\text{N,C})$, where $k = 1.5$ for CH₃ H atoms and $= 1.2$ for all other H atoms.

Discussion

The title compound we report here is an important intermediate of pyrazolobenzotriazinone derivatives that act as COX inhibitors. Some COX inhibitors are used as nonsteroidal anti-inflammatory drug: they inhibit prostaglandin synthesis by blocking the cyclooxygenation of arachidonic acid to prostaglandin H₂, the common biosynthetic precursor to numerous prostaglandins including both the pro-inflammatory ones and those that provide protection for the gastric mucosa. The gastric damage is therefore strictly linked to the gastro-protective prostaglandin-synthesis inhibition. 3-Pyrazolyl-substituted benzotriazinones have attracted research interest, in particular the influence that the heterocyclic nuclei on the 3-position may have on anti-inflammatory, analgesic, ulcerogenic activities and acute toxicity. The molecular structure of the title compound is shown in the figure, the bond lengths and angles are within

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Abstract

C₁₁H₁₂N₄O₂, monoclinic, *Cc* (no. 9), $a = 16.146(5)$ Å, $b = 14.653(4)$ Å, $c = 14.621(4)$ Å, $\beta = 106.052(8)^\circ$, $V = 3324.3(16)$ Å³, $Z = 12$, $R_{\text{gt}}(F) = 0.0415$, $wR_{\text{ref}}(F^2) = 0.0965$, $T = 173(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
N1	0.7657(2)	0.4213(2)	0.7318(2)	0.0284(8)
N2	0.74237(19)	0.3972(2)	0.8789(2)	0.0260(8)
N3	0.7637(2)	0.4138(2)	0.9761(2)	0.0316(9)
N4	0.6384(2)	0.3108(2)	0.7613(2)	0.0303(8)
H4A	0.661391	0.338209	0.714311	0.036*
H4B	0.587991	0.276509	0.746211	0.036*
N5	0.5932(2)	0.4137(2)	0.3173(3)	0.0340(8)
N6	0.56904(19)	0.4313(2)	0.4645(2)	0.0273(8)
N7	0.5854(2)	0.4063(2)	0.5601(2)	0.0328(8)
N8	0.4761(2)	0.5316(2)	0.3533(3)	0.0408(10)
H8A	0.499328	0.501922	0.300396	0.049*
H8B	0.438947	0.577819	0.344591	0.049*
N9	0.2377(2)	0.5791(2)	0.2607(2)	0.0252(8)
N10	0.26017(19)	0.6038(2)	0.1128(2)	0.0225(8)
N11	0.2391(2)	0.5862(2)	0.0154(2)	0.0316(9)
N12	0.36327(19)	0.6906(2)	0.2317(2)	0.0260(8)
H12A	0.411092	0.730346	0.243990	0.031*
H12B	0.340756	0.667665	0.272427	0.031*
O1	0.53319(16)	0.21976(17)	0.86462(19)	0.0292(7)
O2	0.57231(16)	0.24424(17)	1.0237(2)	0.0289(7)
O3	0.37589(16)	0.62655(17)	0.45946(19)	0.0353(7)
O4	0.40109(17)	0.58416(18)	0.6137(2)	0.0351(7)
O5	0.46717(16)	0.78304(17)	0.12934(19)	0.0282(6)
O6	0.43160(16)	0.75870(18)	−0.0287(2)	0.0293(7)
C1	0.8057(3)	0.4668(3)	0.6762(3)	0.0318(10)
H1	0.790836	0.452235	0.610329	0.038*
C2	0.8666(3)	0.5330(3)	0.7095(3)	0.0343(11)
H2	0.893235	0.563399	0.667717	0.041*
C3	0.8883(3)	0.5543(3)	0.8046(3)	0.0346(11)
H3	0.930973	0.599214	0.829542	0.042*
C4	0.8478(2)	0.5101(3)	0.8642(3)	0.0292(10)
H4	0.860850	0.524333	0.930077	0.035*
C5	0.7871(2)	0.4439(2)	0.8231(3)	0.0236(9)
C6	0.6732(2)	0.3389(2)	0.8510(3)	0.0252(10)
C7	0.6505(2)	0.3162(3)	0.9332(3)	0.0237(9)
C8	0.7092(2)	0.3650(3)	1.0064(3)	0.0317(10)
H8	0.708899	0.362602	1.071232	0.038*
C9	0.5804(2)	0.2566(2)	0.9349(3)	0.0249(9)
C10	0.5043(3)	0.1823(3)	1.0299(3)	0.0315(10)
H10A	0.515273	0.120507	1.008479	0.038*
H10B	0.448005	0.203955	0.989232	0.038*
C11	0.5037(3)	0.1802(3)	1.1325(3)	0.0363(11)
H11A	0.559787	0.158989	1.171922	0.054*
H11B	0.458475	0.138561	1.139932	0.054*
H11C	0.492411	0.241671	1.152627	0.054*
C12	0.6346(3)	0.3732(3)	0.2606(3)	0.0380(10)
H12	0.619344	0.390001	0.195296	0.046*
C13	0.6973(3)	0.3094(3)	0.2913(3)	0.0397(11)
H13	0.723949	0.281237	0.248223	0.048*
C14	0.7212(2)	0.2866(3)	0.3866(3)	0.0382(10)
H14	0.765415	0.242858	0.410069	0.046*
C15	0.6809(2)	0.3274(2)	0.4477(3)	0.0326(10)
H15	0.696372	0.313241	0.513626	0.039*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C16	0.6161(2)	0.3906(2)	0.4079(3)	0.0273(9)
C17	0.5053(2)	0.4960(2)	0.4408(3)	0.0265(10)
C18	0.4810(2)	0.5146(3)	0.5228(3)	0.0283(10)
C19	0.5325(2)	0.4569(3)	0.5923(3)	0.0326(10)
H19	0.529445	0.454739	0.656205	0.039*
C20	0.4148(3)	0.5793(3)	0.5261(3)	0.0288(10)
C21	0.3330(2)	0.6464(3)	0.6203(3)	0.0354(10)
H21A	0.276467	0.623820	0.581437	0.043*
H21B	0.343123	0.707664	0.596988	0.043*
C22	0.3345(3)	0.6510(3)	0.7238(3)	0.0434(12)
H22A	0.323681	0.590106	0.745800	0.065*
H22B	0.289674	0.693134	0.731320	0.065*
H22C	0.390992	0.672721	0.761595	0.065*
C23	0.1985(3)	0.5347(3)	0.3167(3)	0.0281(10)
H23	0.214359	0.549011	0.382642	0.034*
C24	0.1361(3)	0.4691(3)	0.2836(3)	0.0290(10)
H24	0.110477	0.438070	0.325960	0.035*
C25	0.1118(3)	0.4494(3)	0.1870(3)	0.0309(10)
H25	0.068205	0.405517	0.161883	0.037*
C26	0.1515(2)	0.4942(3)	0.1279(3)	0.0278(10)
H26	0.136252	0.482053	0.061484	0.033*
C27	0.2150(2)	0.5579(2)	0.1690(3)	0.0232(9)
C28	0.2949(2)	0.6346(3)	−0.0139(3)	0.0294(10)
H28	0.296403	0.636464	−0.078351	0.035*
C29	0.3526(2)	0.6836(3)	0.0598(3)	0.0250(9)
C30	0.3287(2)	0.6624(2)	0.1412(3)	0.0209(9)
C31	0.4218(2)	0.7457(2)	0.0580(3)	0.0237(9)
C32	0.4984(3)	0.8222(3)	−0.0338(3)	0.0293(10)
H32A	0.554792	0.801277	0.007195	0.035*
H32B	0.486074	0.883221	−0.011567	0.035*
C33	0.5010(3)	0.8274(3)	−0.1351(3)	0.0331(11)
H33A	0.513633	0.766838	−0.156332	0.050*
H33B	0.545982	0.870362	−0.140298	0.050*
H33C	0.445028	0.848358	−0.175077	0.050*

normal ranges [4] and in good agreement with those found in the chemically related compound ethyl 1-acetyl-5-amino-1*H*-pyrazole-4-carboxylate [5]. The crystal structure analysis of the title compound revealed that the pyridine and pyrazole units in each of the three molecules present in the asymmetric unit A are not perfectly coplanar. The angles between the least-squares planes through the two ring systems are 6.8(2), 3.6(2) and 5.8(2)° for each of the three molecules in turn. In the crystal of the title compound, there are N—H···N and N—H···O intramolecular hydrogen bonds. Meanwhile, molecules are linked by C—H···O and N—H···O intermolecular hydrogen bonds to form a three-dimensional network. In the crystal structure, there are π–π stacking interactions, with centroid to centroid distances between ring centroids in the range of 3.983(3)–4.341(3) Å as calculated by the program PLATON [6].

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