Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 2,4-dimethylpyrido[1,2-*a*]benzimidazole-3-carboxylate

Ai Guo Zhu, Zhuo Ming Ma, Lin Jie Li, Tian Tian Wei and Yan Qing Ge*

School of Chemistry and Chemical Engineering, Taishan Medical University, Tai an 271016, People's Republic of China
Correspondence e-mail: yqge@yahoo.cn

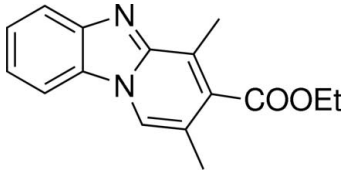
Received 12 September 2012; accepted 23 September 2012

Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.002 Å; R factor = 0.047; wR factor = 0.134; data-to-parameter ratio = 13.0.

The title compound, $C_{16}H_{16}N_2O_2$, was synthesized using a novel tandem annulation reaction between 1-(1*H*-benzo[*d*]i-]imidazol-2-yl)ethanone and ethyl (*E*)-4-bromobut-2-enoate under mild conditions. The dihedral angles formed by the mean plane of the five-membered imidazole ring with the dihydropyridin and benzene rings are 1.54 (9) and 1.85 (9)°, respectively.

Related literature

For the synthesis and characterization of pyrido[1,2-*a*]benz-]benzimidazole derivatives, see: Ge *et al.* (2009, 2011). For pharmaceutical applications of nitrogen-containing heterocyclic compounds, see: Badawey & Kappe (1999).



Experimental

Crystal data

$C_{16}H_{16}N_2O_2$
M_r = 268.31
Monoclinic, $P2_1/c$
a = 7.671 (4) Å
b = 13.174 (7) Å
c = 13.807 (7) Å
β = 102.680 (7)°
V = 1361.3 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 273 K
0.32 × 0.28 × 0.26 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.973, T_{max} = 0.978
6894 measured reflections
2389 independent reflections
2056 reflections with $I > 2\sigma(I)$
R_{int} = 0.086

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.134
S = 1.05
2389 reflections
184 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This study was supported by the Natural Science Foundation of Shandong Province (No. ZR2012BL04).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ5006).

References

Badawey, E. S. A. M. & Kappe, T. (1999). *Eur. J. Med. Chem.* **34**, 663–667.
Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Ge, Y. Q., Jia, J., Li, Y., Yin, L. & Wang, J. W. (2009). *Heterocycles*, **78**, 197–206.
Ge, Y. Q., Jia, J., Yang, H., Tao, X. T. & Wang, J. W. (2011). *Dyes Pigm.* **88**, 344–349.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2012). E**68**, o3032 [https://doi.org/10.1107/S1600536812040299]

Ethyl 2,4-dimethylpyrido[1,2-*a*]benzimidazole-3-carboxylate

Ai Guo Zhu, Zhuo Ming Ma, Lin Jie Li, Tian Tian Wei and Yan Qing Ge

S1. Comment

The synthesis of nitrogen-containing heterocyclic compounds has been a subject of great interest due to the wide application in pharmaceutical fields (Ge *et al.*, 2009; Ge *et al.*, 2011). Some pyrido[1,2-*a*]benzimidazole derivatives have been of interest for their biological activities, such as antineoplastic activity and central GABA-A receptor modulators for the treatment of anxiety (Badawey *et al.*; 1999).

The fused-ring system of the title compound (Fig. 1) is approximately planar, the dihedral angles formed by the mean planes through the imidazole ring with the dihydropyridine and benzene rings being 1.54 (9) and 1.85 (9)°, respectively. The mean plane defined by the carboxylate group (C3/C4/O1/O2) is tilted by 60.38 (5)° with respect to the plane of the benzene ring. The crystal structure is stabilized only by van der Waals interactions.

S2. Experimental

To a 50 ml round-bottomed flask were added 1-(1*H*-benzo[*d*]imidazol-2-yl)ethanone (1.00 mmol), (*E*)-ethyl 4-bromo-but-2-enoate (2.00 mmol), potassium carbonate (0.28 g, 2.05 mmol) and dry DMF (10 ml). The mixture was stirred at room temperature for 6 h. The solvent was removed under reduced pressure and the product was isolated by column chromatography on silica gel (yield 70%). Crystals of the title compound suitable for X-ray diffraction were obtained by allowing a refluxed solution of the product in ethyl acetate to cool slowly to room temperature (without temperature control) and allowing the solvent to slowly evaporate for 2 d.

S3. Refinement

All H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.93-0.97 Å and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for methyl H atoms. A rotating group model was applied to the methyl groups.

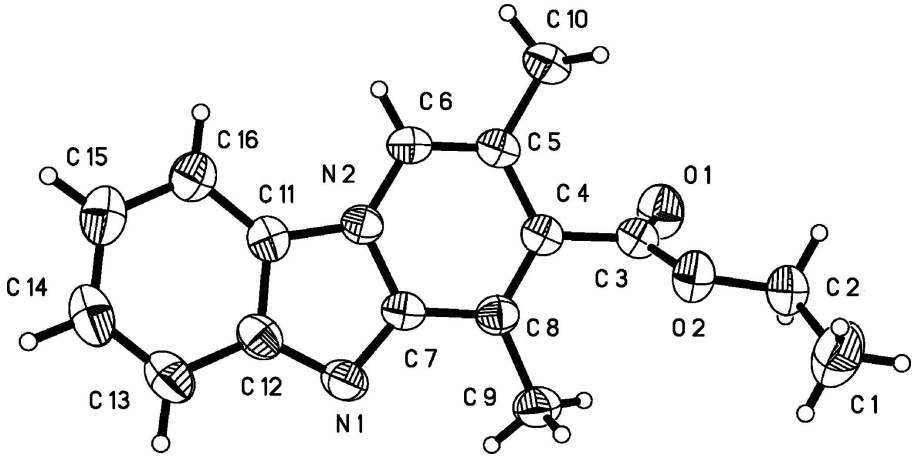


Figure 1

The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

Ethyl 2,4-dimethylpyrido[1,2-*a*]benzimidazole-3-carboxylate

Crystal data

$C_{16}H_{16}N_2O_2$
$M_r = 268.31$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.671$ (4) Å
$b = 13.174$ (7) Å
$c = 13.807$ (7) Å
$\beta = 102.680$ (7)°
$V = 1361.3$ (12) Å^3
$Z = 4$
$F(000) = 568$
$D_x = 1.309$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4261 reflections
$\theta = 3.0$–$28.2°$
$\mu = 0.09$ mm^{-1}
$T = 273$ K
Block, colourless
0.32 × 0.28 × 0.26 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.973$, $T_{max} = 0.978$
6894 measured reflections
2389 independent reflections
2056 reflections with $I > 2\sigma(I)$
$R_{int} = 0.086$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
$h = -5 \rightarrow 9$
$k = -15 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.134$
$S = 1.05$
2389 reflections
184 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 0.2415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.052$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.75792 (18)	−0.01609 (10)	0.27023 (9)	0.0440 (4)
N2	0.72152 (15)	−0.05514 (9)	0.10717 (9)	0.0351 (3)
O1	1.03253 (17)	0.23943 (10)	−0.01104 (10)	0.0594 (4)
O2	0.80757 (16)	0.30461 (8)	0.04828 (9)	0.0487 (3)
C1	0.7586 (4)	0.47805 (16)	0.07813 (19)	0.0802 (7)
H1A	0.6335	0.4681	0.0505	0.120*
H1B	0.7907	0.5467	0.0664	0.120*
H1C	0.7830	0.4654	0.1483	0.120*
C2	0.8641 (3)	0.40713 (12)	0.03063 (14)	0.0531 (5)
H2A	0.8429	0.4204	−0.0401	0.064*
H2B	0.9906	0.4155	0.0590	0.064*
C3	0.9069 (2)	0.22855 (11)	0.02743 (11)	0.0400 (4)
C4	0.84263 (19)	0.12847 (11)	0.05743 (10)	0.0365 (4)
C5	0.78468 (19)	0.05213 (11)	−0.01807 (10)	0.0360 (4)
C6	0.72718 (19)	−0.03754 (12)	0.00956 (10)	0.0373 (4)
H6	0.6910	−0.0881	−0.0376	0.045*
C7	0.77753 (19)	0.01635 (11)	0.18186 (10)	0.0358 (3)
C8	0.84377 (19)	0.11132 (11)	0.15597 (11)	0.0376 (4)
C9	0.9153 (2)	0.18433 (13)	0.23890 (12)	0.0505 (4)
H9A	1.0014	0.2284	0.2196	0.076*
H9B	0.9714	0.1471	0.2972	0.076*
H9C	0.8189	0.2241	0.2529	0.076*
C10	0.7900 (2)	0.07044 (13)	−0.12539 (11)	0.0460 (4)
H10A	0.7427	0.0123	−0.1643	0.069*
H10B	0.9113	0.0816	−0.1306	0.069*
H10C	0.7194	0.1291	−0.1495	0.069*
C11	0.66408 (19)	−0.13957 (11)	0.15187 (11)	0.0377 (4)
C12	0.6866 (2)	−0.11231 (12)	0.25233 (11)	0.0410 (4)
C13	0.6335 (2)	−0.18090 (14)	0.31784 (13)	0.0527 (5)
H13	0.6463	−0.1652	0.3847	0.063*
C14	0.5616 (2)	−0.27222 (14)	0.28027 (14)	0.0566 (5)
H14	0.5252	−0.3183	0.3229	0.068*
C15	0.5415 (2)	−0.29809 (13)	0.17999 (14)	0.0551 (5)
H15	0.4928	−0.3607	0.1577	0.066*
C16	0.5929 (2)	−0.23193 (12)	0.11366 (13)	0.0473 (4)

H16	0.5805	−0.2484	0.0470	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0471 (8)	0.0517 (8)	0.0327 (7)	−0.0038 (6)	0.0078 (5)	0.0015 (6)
N2	0.0331 (6)	0.0393 (7)	0.0329 (6)	0.0012 (5)	0.0070 (5)	−0.0004 (5)
O1	0.0582 (8)	0.0569 (7)	0.0723 (9)	−0.0017 (6)	0.0340 (7)	0.0058 (6)
O2	0.0493 (7)	0.0397 (6)	0.0601 (7)	0.0010 (5)	0.0186 (5)	0.0031 (5)
C1	0.0948 (17)	0.0504 (11)	0.1022 (18)	0.0057 (11)	0.0363 (14)	−0.0058 (11)
C2	0.0638 (11)	0.0409 (9)	0.0546 (10)	−0.0031 (8)	0.0126 (8)	0.0046 (8)
C3	0.0396 (8)	0.0440 (9)	0.0363 (8)	0.0011 (7)	0.0080 (6)	0.0016 (6)
C4	0.0319 (7)	0.0413 (8)	0.0366 (8)	0.0036 (6)	0.0085 (6)	0.0005 (6)
C5	0.0321 (7)	0.0438 (8)	0.0324 (7)	0.0057 (6)	0.0074 (6)	0.0000 (6)
C6	0.0366 (8)	0.0432 (8)	0.0314 (7)	0.0027 (6)	0.0055 (6)	−0.0043 (6)
C7	0.0333 (7)	0.0421 (8)	0.0318 (7)	0.0019 (6)	0.0064 (6)	−0.0017 (6)
C8	0.0355 (8)	0.0409 (8)	0.0360 (8)	0.0017 (6)	0.0069 (6)	−0.0024 (6)
C9	0.0584 (10)	0.0523 (10)	0.0397 (9)	−0.0096 (8)	0.0084 (7)	−0.0069 (7)
C10	0.0473 (9)	0.0566 (10)	0.0345 (8)	0.0042 (7)	0.0097 (7)	0.0030 (7)
C11	0.0311 (7)	0.0401 (8)	0.0419 (8)	0.0032 (6)	0.0081 (6)	0.0046 (6)
C12	0.0352 (8)	0.0488 (9)	0.0380 (8)	0.0030 (6)	0.0057 (6)	0.0067 (6)
C13	0.0480 (10)	0.0654 (11)	0.0432 (9)	−0.0023 (8)	0.0067 (7)	0.0143 (8)
C14	0.0476 (10)	0.0582 (11)	0.0622 (11)	−0.0028 (8)	0.0085 (8)	0.0237 (9)
C15	0.0480 (10)	0.0450 (9)	0.0711 (12)	−0.0029 (7)	0.0105 (8)	0.0066 (8)
C16	0.0449 (9)	0.0444 (9)	0.0534 (10)	−0.0003 (7)	0.0124 (7)	−0.0015 (7)

Geometric parameters (Å, º)

N1—C7	1.332 (2)	C6—H6	0.9300
N1—C12	1.381 (2)	C7—C8	1.425 (2)
N2—C6	1.3775 (19)	C8—C9	1.504 (2)
N2—C11	1.3899 (19)	C9—H9A	0.9600
N2—C7	1.393 (2)	C9—H9B	0.9600
O1—C3	1.2065 (19)	C9—H9C	0.9600
O2—C3	1.3283 (19)	C10—H10A	0.9600
O2—C2	1.455 (2)	C10—H10B	0.9600
C1—C2	1.480 (3)	C10—H10C	0.9600
C1—H1A	0.9600	C11—C16	1.389 (2)
C1—H1B	0.9600	C11—C12	1.406 (2)
C1—H1C	0.9600	C12—C13	1.401 (2)
C2—H2A	0.9700	C13—C14	1.377 (3)
C2—H2B	0.9700	C13—H13	0.9300
C3—C4	1.498 (2)	C14—C15	1.401 (3)
C4—C8	1.377 (2)	C14—H14	0.9300
C4—C5	1.446 (2)	C15—C16	1.383 (2)
C5—C6	1.345 (2)	C15—H15	0.9300
C5—C10	1.511 (2)	C16—H16	0.9300

C7—N1—C12	104.51 (12)	C4—C8—C9	124.71 (14)
C6—N2—C11	130.57 (13)	C7—C8—C9	117.46 (13)
C6—N2—C7	122.66 (13)	C8—C9—H9A	109.5
C11—N2—C7	106.78 (12)	C8—C9—H9B	109.5
C3—O2—C2	117.24 (13)	H9A—C9—H9B	109.5
C2—C1—H1A	109.5	C8—C9—H9C	109.5
C2—C1—H1B	109.5	H9A—C9—H9C	109.5
H1A—C1—H1B	109.5	H9B—C9—H9C	109.5
C2—C1—H1C	109.5	C5—C10—H10A	109.5
H1A—C1—H1C	109.5	C5—C10—H10B	109.5
H1B—C1—H1C	109.5	H10A—C10—H10B	109.5
O2—C2—C1	107.44 (15)	C5—C10—H10C	109.5
O2—C2—H2A	110.2	H10A—C10—H10C	109.5
C1—C2—H2A	110.2	H10B—C10—H10C	109.5
O2—C2—H2B	110.2	C16—C11—N2	131.97 (15)
C1—C2—H2B	110.2	C16—C11—C12	123.44 (14)
H2A—C2—H2B	108.5	N2—C11—C12	104.56 (13)
O1—C3—O2	123.88 (14)	N1—C12—C13	129.53 (15)
O1—C3—C4	124.72 (14)	N1—C12—C11	111.65 (13)
O2—C3—C4	111.39 (13)	C13—C12—C11	118.81 (15)
C8—C4—C5	122.15 (14)	C14—C13—C12	118.01 (17)
C8—C4—C3	119.11 (13)	C14—C13—H13	121.0
C5—C4—C3	118.72 (13)	C12—C13—H13	121.0
C6—C5—C4	118.31 (14)	C13—C14—C15	122.22 (16)
C6—C5—C10	119.97 (14)	C13—C14—H14	118.9
C4—C5—C10	121.71 (14)	C15—C14—H14	118.9
C5—C6—N2	120.53 (13)	C16—C15—C14	121.04 (17)
C5—C6—H6	119.7	C16—C15—H15	119.5
N2—C6—H6	119.7	C14—C15—H15	119.5
N1—C7—N2	112.50 (13)	C15—C16—C11	116.48 (16)
N1—C7—C8	129.02 (14)	C15—C16—H16	121.8
N2—C7—C8	118.48 (13)	C11—C16—H16	121.8
C4—C8—C7	117.80 (13)		