Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl 5-bromo-1*H*-indole-2-carboxylate

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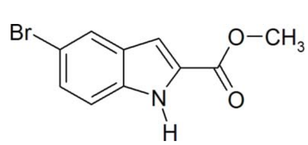
Received 1 July 2007; accepted 10 July 2007

Key indicators: single-crystal X-ray study; T = 103 K; mean σ(C–C) = 0.009 Å; R factor = 0.063; wR factor = 0.145; data-to-parameter ratio = 18.3.

The indole ring system in the title compound, $C_{10}H_8BrNO_2$, is planar. The sum of the angles around the indole N atom (359.9°) indicates sp^2-hybridization. The carboxylate group adopts a planar arrangement with respect to the indole ring system. The crystal structure is stabilized by intermolecular hydrogen-bond interactions.

Related literature

For related structures, see: Hu *et al.* (2005); Harrison *et al.* (2006); Butcher *et al.* (2006). For background, see: Murphy *et al.* (1997); Cavallini *et al.* (1958); Robinson (1969, 1982); Hughes (1993); Murakami (1999); Narayana *et al.* (2005, 2006); Singer & Shive (1957); Parmerter *et al.* (1958).



Experimental

Crystal data

$C_{10}H_8BrNO_2$
M_r = 254.08
Monoclinic, $P2_1/n$
a = 12.911 (12) Å
b = 3.907 (3) Å
c = 18.923 (18) Å
β = 105.460 (14)°
V = 920.0 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.44 mm^{-1}
T = 103 K
0.50 × 0.08 × 0.04 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.215, T_{max} = 0.843
6377 measured reflections
2339 independent reflections
1432 reflections with $I > 2\sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.145
S = 1.07
2339 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −1.44 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N—H0A···O1^{i}	0.88	1.96	2.815 (7)	163

Symmetry code: (i) $-x+1, -y-1, -z+1$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

BVA thanks Mangalore University for access to their research facilities. RJB acknowledges the Laboratory for the Structure of Matter at the Naval Research Laboratory for access to their diffractometers.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2177).

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doi:10.1107/S160053680703379X

supplementary materials

Acta Cryst. (2007). E**63**, o3505 [**doi:10.1107/S160053680703379X**]

Methyl 5-bromo-1*H*-indole-2-carboxylate

R. J. Butcher, J. P. Jasinski, H. S. Yathirajan, B. V. Ashalatha and B. Narayana

Comment

The synthesis of indole derivatives has long been a topic of fundamental interest to organic and medicinal chemists. The Fischer indole synthesis is the most widely used method for the preparation of indole derivatives (Robinson, 1969), and the chemistry of indoles, including its synthetic applications, has been published (Narayana *et al.*, 2006). In view of the importance of the title compound, $C_{10}H_8BrNO_2$ (I), its crystal structure is reported (Fig. 1).

The carboxyl group adopts a planar arrangement to the indole ring system. The N—O1 intramolecular distance of 2.80 (1) Å added to a C8–N–C1–C9 torsion angle of −178.7 (6)° indicates possible π-conjugation between the pyrrole double bond and the carbonyl group. Intermolecular hydrogen bonds (N–H0A···O1) stabilize the molecules as indicated in the packing diagram (Fig. 2).

Experimental

The title compound was prepared following the reported procedure for the synthesis of nitroindole esters (Narayana *et al.*, 2005, Fig. 3). Methylpyruvate-4-bromo-phenylhydrazone (0.0075 mol, 2 g) was taken in polyphosphoric acid (10 g) and kept under stirring for proper mixing. The entire reaction mass was slowly heated to 328–338 K and maintained for 4 h. Progress was monitored by TLC Water (100 ml) was added to the cooled solution to break the lumps until it became a slurry. The solid that separated was filtered and washed with water. The dried crude product was charcoalized in ethyl acetate, filtered over hyflo, slowly cooled to room temperature and kept overnight under stirring. Methyl-5-bromo-indole-2-carboxylate (I) was obtained as light-brown crystals with a yield of 70% by crystallization from ethyl acetate. Crystals of X-ray diffraction quality were obtained by recrystallization from acetone-toluene mixture (7:3); m.p. = 483 K.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.91 (s, 3H, $–CH_3$), 7.06 (s, 1H, Ar—H), 7.29 (d, J = 10.2 Hz, 1H, Ar—H), 7.39 (d, J = 8.7 Hz, 1H, Ar—H), 7.75 (s, 1H, Ar—H), 11.63 (s, 1H, –NH–, exchangeable with D_2O). ^{13}C NMR ($CDCl_3$ + DMSO, 75 MHz) δ 51.44, 106.73, 112.73, 114,123.84, 126.95, 128.13, 128.23, 135.76, 161.61. F T—IR (KBr): 3325 (–NH), 1697 (–C=O) cm^{-1}. Elemental analysis found: C, 47.10, H, 3.21, N, 5.48. $C_{10}H_8BrNO_2$ requires C, 47.27, H, 3.17, N, 5.51%.

Refinement

The H atoms were included in the riding model approximation with C—H = 0.95–0.98Å and N—H = 0.88 Å, and with U_{iso}(H) = 1.18–1.48U_{eq}(C, N). The maximum residual electron density peaks of 0.18 and −1.44 e Å^3, were located at 0.52 and 0.92Å from the C6 and Br atoms, respectively.

Figures

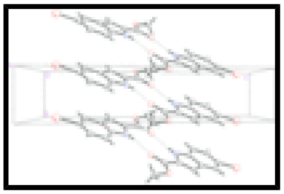

Fig. 1. Molecular structure of $C_{10}H_8BrNO_2$, (I), showing atom labeling and 50% probability displacement ellipsoids.
Fig. 2. Packing diagram of $C_{10}H_8BrNO_2$ viewed down the *a* axis. Dashed lines indicate N–H···O hydrogen bonds between N—H0A and O1 from inverted, in-plane adjacent molecules in (I).

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Crystal data

$C_{10}H_8BrNO_2$	F_{000} = 504
M_r = 254.08	D_x = 1.834 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 1647 reflections
a = 12.911 (12) Å	θ = 2.2–25.8º
b = 3.907 (3) Å	μ = 4.44 mm^{-1}
c = 18.923 (18) Å	*T* = 103 K
β = 105.460 (14)º	Needle, colorless
V = 920.0 (15) Å^3	0.50 × 0.08 × 0.04 mm
Z = 4	

Data collection

Bruker APEX II CCD area-detector diffractometer	2339 independent reflections
Radiation source: fine-focus sealed tube	1432 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.071
T = 103 K	θ_{max} = 28.6º
φ and ω scans	θ_{min} = 1.7º
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	*h* = −16→17
T_{min} = 0.215, T_{max} = 0.843	*k* = −5→4
6377 measured reflections	*l* = −25→25

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.063$	H-atom parameters constrained
$wR(F^2) = 0.145$	$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 5.6356P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2339 reflections	$\Delta\rho_{max} = 0.81$ e Å^{-3}
128 parameters	$\Delta\rho_{min} = -1.44$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.43279 (6)	0.06306 (19)	0.89203 (4)	0.0274 (2)
O1	0.6276 (4)	−0.3079 (13)	0.4996 (2)	0.0271 (11)
O2	0.7574 (3)	0.0016 (11)	0.5728 (2)	0.0250 (11)
N	0.5161 (4)	−0.2991 (15)	0.6079 (3)	0.0220 (12)
H0A	0.4795	−0.4091	0.5685	0.026*
C1	0.6148 (5)	−0.1513 (16)	0.6168 (3)	0.0211 (14)
C2	0.6482 (5)	−0.0043 (16)	0.6842 (3)	0.0243 (16)
H2A	0.7138	0.1144	0.7038	0.029*
C3	0.5657 (5)	−0.0635 (19)	0.7194 (3)	0.0248 (14)
C4	0.5518 (5)	0.0259 (17)	0.7874 (3)	0.0243 (15)
H4A	0.6056	0.1487	0.8222	0.029*
C5	0.4589 (5)	−0.0682 (19)	0.8022 (3)	0.0255 (14)
C6	0.3777 (5)	−0.2496 (18)	0.7533 (4)	0.0251 (15)
H6A	0.3144	−0.3107	0.7668	0.030*
C7	0.3888 (5)	−0.3407 (17)	0.6855 (3)	0.0250 (15)
H7A	0.3340	−0.4613	0.6511	0.030*
C8	0.4838 (5)	−0.2479 (17)	0.6701 (3)	0.0201 (14)
C9	0.6650 (5)	−0.1652 (17)	0.5576 (3)	0.0224 (15)
C10	0.8091 (6)	0.0175 (18)	0.5143 (4)	0.0297 (17)
H10A	0.8764	0.1463	0.5306	0.044*
H10B	0.7615	0.1320	0.4718	0.044*
H10C	0.8246	−0.2150	0.5005	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0362 (4)	0.0210 (3)	0.0275 (3)	0.0015 (4)	0.0126 (2)	−0.0016 (3)
O1	0.031 (3)	0.030 (3)	0.020 (2)	−0.005 (2)	0.0060 (19)	−0.007 (2)
O2	0.029 (2)	0.020 (3)	0.027 (2)	−0.006 (2)	0.0093 (19)	−0.0017 (18)
N	0.023 (3)	0.018 (3)	0.022 (3)	−0.003 (2)	0.001 (2)	−0.001 (2)
C1	0.026 (3)	0.006 (3)	0.030 (3)	−0.001 (3)	0.006 (3)	−0.001 (2)
C2	0.031 (3)	0.014 (4)	0.028 (3)	0.000 (3)	0.008 (3)	0.002 (2)
C3	0.029 (3)	0.017 (3)	0.029 (3)	0.002 (3)	0.007 (3)	−0.002 (3)
C4	0.030 (3)	0.014 (4)	0.028 (3)	−0.001 (3)	0.006 (3)	−0.002 (3)
C5	0.035 (4)	0.018 (3)	0.024 (3)	0.002 (3)	0.008 (3)	0.007 (3)
C6	0.026 (4)	0.013 (4)	0.034 (4)	−0.003 (3)	0.005 (3)	−0.002 (3)
C7	0.027 (4)	0.019 (4)	0.028 (3)	−0.005 (3)	0.005 (3)	−0.001 (3)
C8	0.023 (3)	0.010 (3)	0.025 (3)	0.003 (3)	0.003 (3)	0.003 (3)
C9	0.027 (4)	0.015 (4)	0.025 (3)	0.000 (3)	0.007 (3)	0.000 (3)
C10	0.034 (4)	0.022 (4)	0.037 (4)	−0.007 (3)	0.015 (3)	−0.001 (3)

Geometric parameters (Å, °)

Br—C5	1.890 (7)	C3—C8	1.408 (9)
O1—C9	1.212 (8)	C4—C5	1.354 (9)
O2—C9	1.322 (8)	C4—H4A	0.9500
O2—C10	1.439 (8)	C5—C6	1.393 (9)
N—C8	1.365 (8)	C6—C7	1.374 (9)
N—C1	1.368 (8)	C6—H6A	0.9500
N—H0A	0.8800	C7—C8	1.382 (9)
C1—C2	1.360 (9)	C7—H7A	0.9500
C1—C9	1.437 (9)	C10—H10A	0.9800
C2—C3	1.418 (9)	C10—H10B	0.9800
C2—H2A	0.9500	C10—H10C	0.9800
C3—C4	1.391 (9)		
C9—O2—C10	115.5 (5)	C7—C6—C5	120.3 (6)
C8—N—C1	108.7 (5)	C7—C6—H6A	119.9
C8—N—H0A	125.6	C5—C6—H6A	119.9
C1—N—H0A	125.6	C6—C7—C8	116.6 (6)
C2—C1—N	110.3 (6)	C6—C7—H7A	121.7
C2—C1—C9	130.5 (6)	C8—C7—H7A	121.7
N—C1—C9	119.2 (6)	N—C8—C7	129.5 (6)
C1—C2—C3	106.3 (6)	N—C8—C3	107.3 (6)
C1—C2—H2A	126.8	C7—C8—C3	123.1 (6)
C3—C2—H2A	126.8	O1—C9—O2	122.9 (6)
C4—C3—C8	118.8 (6)	O1—C9—C1	124.7 (6)
C4—C3—C2	133.8 (6)	O2—C9—C1	112.4 (5)
C8—C3—C2	107.4 (6)	O2—C10—H10A	109.5
C5—C4—C3	117.6 (6)	O2—C10—H10B	109.5
C5—C4—H4A	121.2	H10A—C10—H10B	109.5

C3—C4—H4A	121.2	O2—C10—H10C	109.5
C4—C5—C6	123.5 (6)	H10A—C10—H10C	109.5
C4—C5—Br	119.5 (5)	H10B—C10—H10C	109.5
C6—C5—Br	116.9 (5)		

C8—N—C1—C2	0.2 (7)	C1—N—C8—C3	−0.3 (7)
C8—N—C1—C9	−178.7 (6)	C6—C7—C8—N	−179.0 (6)
N—C1—C2—C3	0.0 (7)	C6—C7—C8—C3	−1.2 (10)
C9—C1—C2—C3	178.8 (7)	C4—C3—C8—N	179.2 (6)
C1—C2—C3—C4	−178.9 (8)	C2—C3—C8—N	0.3 (8)
C1—C2—C3—C8	−0.2 (8)	C4—C3—C8—C7	1.0 (10)
C8—C3—C4—C5	−0.5 (10)	C2—C3—C8—C7	−177.9 (6)
C2—C3—C4—C5	178.0 (7)	C10—O2—C9—O1	2.9 (9)
C3—C4—C5—C6	0.3 (11)	C10—O2—C9—C1	−176.2 (5)
C3—C4—C5—Br	−177.3 (5)	C2—C1—C9—O1	179.3 (7)
C4—C5—C6—C7	−0.6 (11)	N—C1—C9—O1	−2.0 (10)
Br—C5—C6—C7	177.1 (5)	C2—C1—C9—O2	−1.7 (10)
C5—C6—C7—C8	1.0 (10)	N—C1—C9—O2	177.0 (5)
C1—N—C8—C7	177.7 (7)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H0A···O1^{i}	0.88	1.96	2.815 (7)	163

Symmetry codes: (i) −*x*+1, −*y*−1, −*z*+1.

Fig. 1

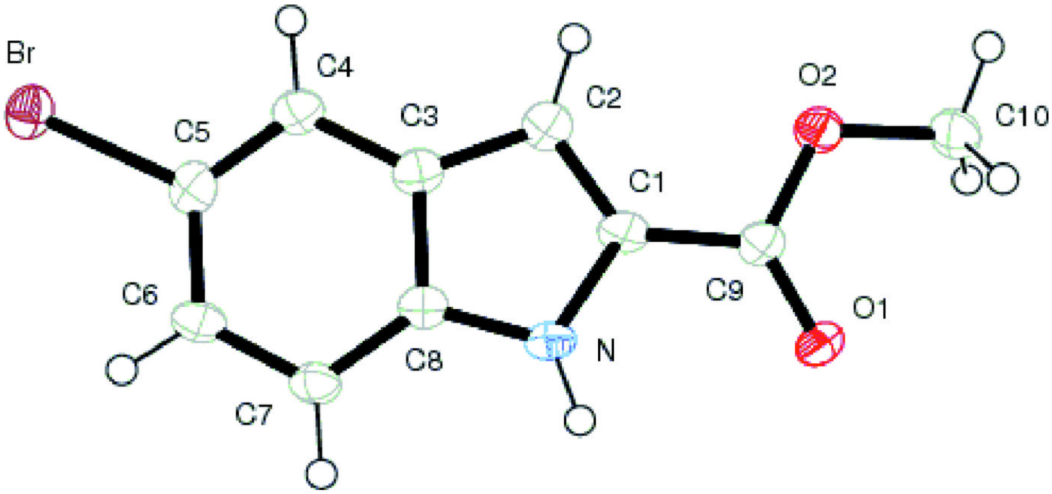

Fig. 2

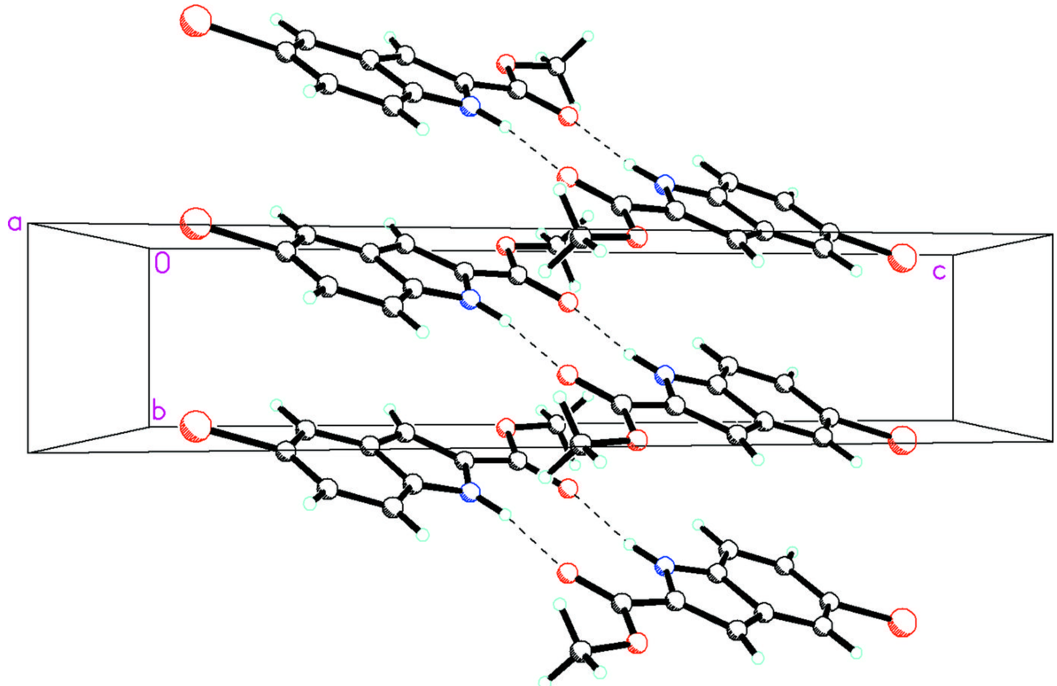

Fig. 3