

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

Ray J. Butcher,<sup>a</sup> Jerry P. Jasinski,<sup>b\*</sup> H. S. Yathirajan,<sup>c</sup> B. V. Ashalatha<sup>d</sup> and B. Narayana<sup>d</sup>

<sup>a</sup>Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, <sup>b</sup>Department of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA, <sup>c</sup>Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, and <sup>d</sup>Department of Chemistry, Mangalore University, Mangalagangotri 574 199, India  
Correspondence e-mail: jjasinski@keene.edu

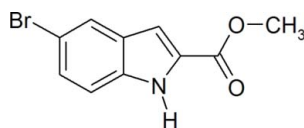
Received 1 July 2007; accepted 10 July 2007

Key indicators: single-crystal X-ray study;  $T = 103$  K; mean  $\sigma(\text{C}—\text{C}) = 0.009$  Å;  $R$  factor = 0.063;  $wR$  factor = 0.145; data-to-parameter ratio = 18.3.

The indole ring system in the title compound,  $\text{C}_{10}\text{H}_8\text{BrNO}_2$ , is planar. The sum of the angles around the indole N atom ( $359.9^\circ$ ) 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

$\text{C}_{10}\text{H}_8\text{BrNO}_2$	$V = 920.0$ (15) Å <sup>3</sup>
$M_r = 254.08$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 12.911$ (12) Å	$\mu = 4.44$ mm <sup>-1</sup>
$b = 3.907$ (3) Å	$T = 103$ K
$c = 18.923$ (18) Å	$0.50 \times 0.08 \times 0.04$ mm
$\beta = 105.460$ (14)°	

### 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  $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$

### Refinement

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

Table 1

Hydrogen-bond geometry (Å, °).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
$\text{N}—\text{H}0\text{A} \cdots \text{O}1^i$	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).

## References

- Bruker (2000). SHELXTL. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2006). APEX2. Bruker AXS Inc., Madison Wisconsin, USA.
- Butcher, R. J., Yathirajan, H. S., Ashalatha, B. V., Narayana, B. & Sarojini, B. K. (2006). *Acta Cryst.* **E62**, o3915–o3917.
- Cavallini, G., Ravenna, F. & Grasso, I. (1958). *Farmaco*, **13**, 113–120.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Harrison, W. T. A., Yathirajan, H. S., Ashalatha, B. V., Vijaya Raj, K. K. & Narayana, B. (2006). *Acta Cryst.* **E62**, o4050–o4051.
- Hughes, D. L. (1993). *Org. Prep. Proced. Int.* **25**, 609–632.
- Hu, S.-C., Tan, R.-X., Hong, K., Yu, Z.-N. & Zhu, H.-L. (2005). *Acta Cryst.* **E61**, o1654–o1656.
- Murakami, Y. (1999). *Yakugaku Zasshi*, **119**, 35–60.
- Murphy, J. A., Scott, K. A., Sinclair, R. S. & Lewis, N. (1997). *Tetrahedron Lett.* **38**, 7295–7298.
- Narayana, B., Ashalatha, B. V. & Vijayaraja, K. K. (2006). *J. Chem. Res.* pp. 309–311.
- Narayana, B., Ashalatha, B. V., Vijayaraj, K. K., Fernandes, J. & Sarojini, B. K. (2005). *Bioorg. Med. Chem.* **13**, 4638–4644.
- Parmerter, S. M., Cook, A. G. & Dixon, W. B. (1958). *J. Am. Chem. Soc.* **80**, 4621–4622.
- Robinson, B. (1969). *Chem. Rev.* **69**, 227–250.
- Robinson, B. (1982). *The Fischer Indole Synthesis*. New York: John Wiley and Sons.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). SADABS. University of Göttingen, Germany.
- Singer, H. & Shive, W. (1957). *J. Org. Chem.* **22**, 84–85.

**supplementary materials**

*Acta Cryst.* (2007). E63, 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<sub>10</sub>H<sub>8</sub>BrNO<sub>2</sub> (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  $\pi$ -conjugation between the pyrrole double bond and the carbonyl group. Intermolecular hydrogen bonds (N—H0A $\cdots$ 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-phenylhydrazine (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.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  3.91 (s, 3H, −CH<sub>3</sub>), 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<sub>2</sub>O). <sup>13</sup>C NMR (CDCl<sub>3</sub> + DMSO, 75 MHz)  $\delta$  51.44, 106.73, 112.73, 114, 123.84, 126.95, 128.13, 128.23, 135.76, 161.61. FT—IR (KBr): 3325 (−NH), 1697 (−C=O) cm<sup>−1</sup>. Elemental analysis found: C, 47.10, H, 3.21, N, 5.48. C<sub>10</sub>H<sub>8</sub>BrNO<sub>2</sub> requires C, 47.27, H, 3.17, N, 5.51%.

### Refinement

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

## Figures

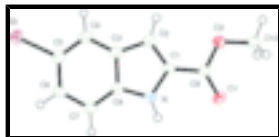


Fig. 1. Molecular structure of  $C_{10}H_8BrNO_2$ , (I), showing atom labeling and 50% probability displacement ellipsoids.

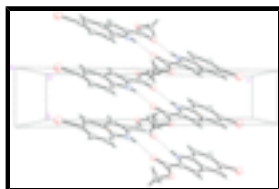


Fig. 2. Packing diagram of  $C_{10}H_8BrNO_2$  viewed down the  $a$  axis. Dashed lines indicate  $N-H\cdots O$  hydrogen bonds between  $N-H0A$  and  $O1$  from inverted, in-plane adjacent molecules in (I).



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

### Crystal data

$C_{10}H_8BrNO_2$

$M_r = 254.08$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1/n$

$a = 12.911\ (12)\ \text{\AA}$

$b = 3.907\ (3)\ \text{\AA}$

$c = 18.923\ (18)\ \text{\AA}$

$\beta = 105.460\ (14)^\circ$

$V = 920.0\ (15)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 504$

$D_x = 1.834\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1647 reflections

$\theta = 2.2\text{--}25.8^\circ$

$\mu = 4.44\ \text{mm}^{-1}$

$T = 103\ \text{K}$

Needle, colorless

$0.50 \times 0.08 \times 0.04\ \text{mm}$

### Data collection

Bruker APEX II CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 103\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

$T_{\min} = 0.215$ ,  $T_{\max} = 0.843$

6377 measured reflections

2339 independent reflections

1432 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$

$\theta_{\max} = 28.6^\circ$

$\theta_{\min} = 1.7^\circ$

$h = -16 \rightarrow 17$

$k = -5 \rightarrow 4$

$l = -25 \rightarrow 25$

### Refinement

Refinement on  $F^2$

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.063$$

$$wR(F^2) = 0.145$$

$$S = 1.07$$

2339 reflections

128 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 5.6356P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.44 \text{ e } \text{\AA}^{-3}$$

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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 ( $\text{\AA}$ , $^\circ$ )

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, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N—H0A $\cdots$ O1 <sup>i</sup>	0.88	1.96	2.815 (7)	163

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

Fig. 1

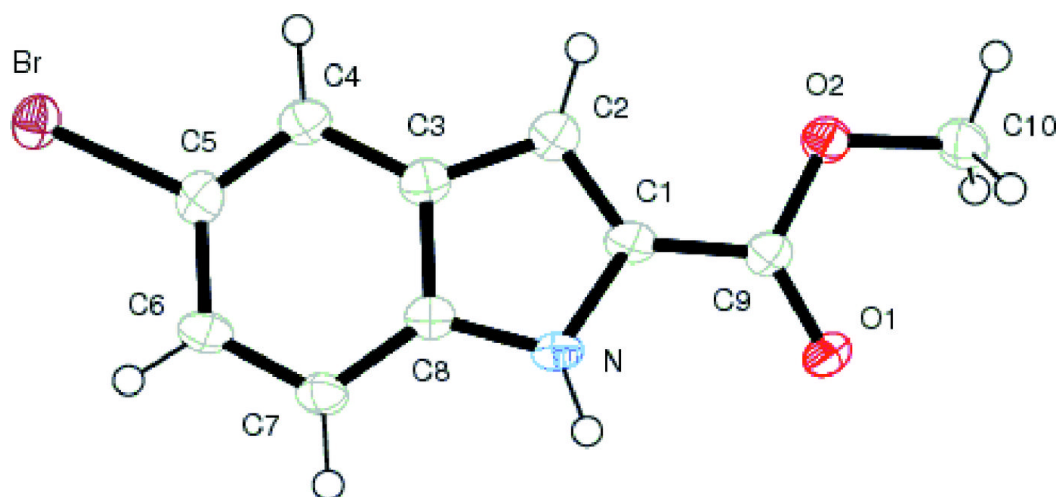




Fig. 2

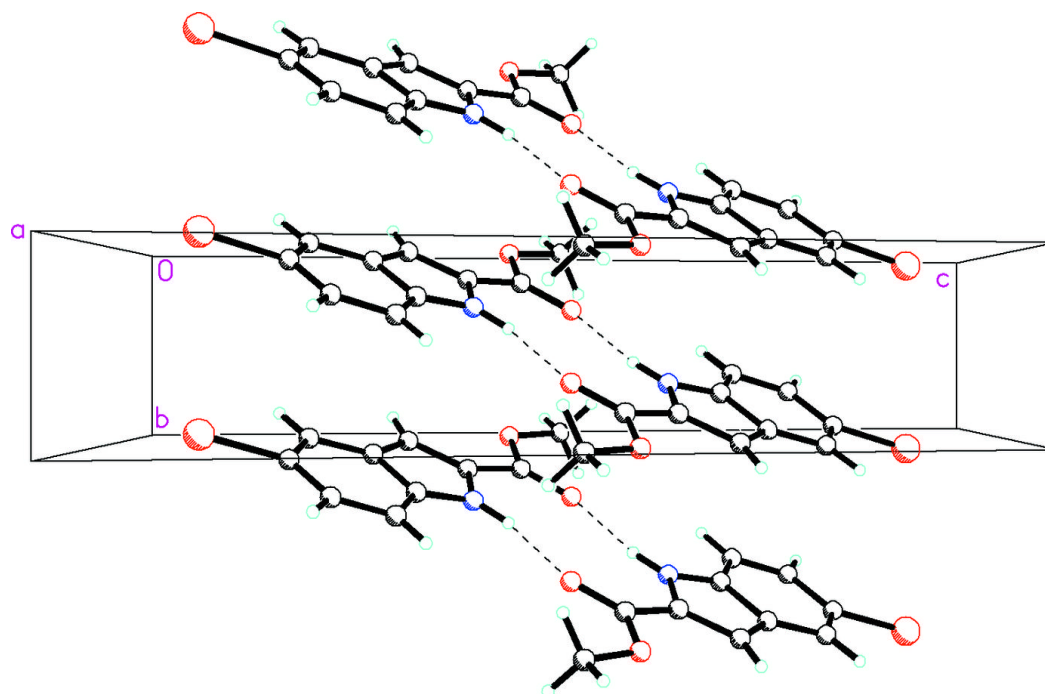


Fig. 3

