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# Dimethyl 4-iodopyridine-2,6-dicarboxylate

**Anusha D. Abhayawardhana, Masood Parvez and Todd C. Sutherland***

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4

Correspondence e-mail: sutherlt@ucalgary.ca

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**Key indicators**

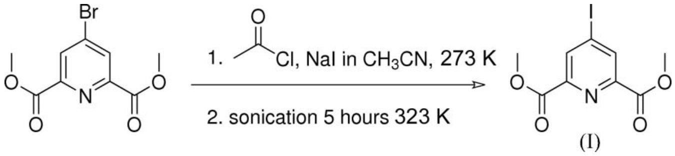
Single-crystal X-ray study
$T$ = 173 K
Mean $\sigma$(C–C) = 0.011 Å
$R$ factor = 0.050
$wR$ factor = 0.096
Data-to-parameter ratio = 13.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Two symmetry-independent but geometrically similar, essentially planar molecules of the title compound, $C_9H_8INO_4$, are linked *via* C—I···O=C interactions [I···O = 2.981 (6) and 3.006 (5) Å] into infinite chains running along the *b* axis. The independent molecules alternate within the chain, so that only one independent chain is formed in the crystal structure.

## Comment

The title compound, (I), is a precursor in the synthesis of 4-iodo-2,6-diaminopyridine. Diaminopyridine systems are effective in forming *D*—*A*—*D* hydrogen-bonding motifs for supramolecular studies, as shown by Shi *et al.* (2001) and Gray *et al.* (2004). The substitution of a 4-iodo group for a 4-bromo group is designed to optimize the subsequent Sonogashira coupling with a derivatized acetylene. The iodo-substituted molecule will allow further derivatization at position 4 and thus lead to a variety of new compounds, forming supramolecular materials showing similar hydrogen-bonding patterns.



(I)

The two independent molecules in the asymmetric unit (Fig. 1) have similar geometrical parameters. The non-H atoms in each of the molecules form roughly planar arrangements; only one of the carbomethoxy groups in one of the molecules, C30/O31/C32/O34, forms a significant dihedral angle of 14.8 (6)° with the plane of pyridine ring N21/C22–C26; the other three analogous dihedral angles are less than 6°.

The most significant feature of the crystal packing of the title compound is the existence of I···O interactions (Table 1). Similar I···O contacts were observed in a number of structures involving iodo-substituted aromatics together with the carbonyl groups (Leroy *et al.*, 2004; Cody, 1974; Britton & Young, 1997). Britton & Young (1997) attribute such contacts in the structure of *p*-iodobenzaldehyde to Lewis acid–Lewis base interaction. They emphasize, however, that such attribution would require the C=O···I and O···I—C angles to be close to 120 and 180°, respectively. This requirement is met only partially in the structure of the title compound, as both C=O···I angles in this case are substantially larger than 120° (see Table 1).

The I···O interactions link the molecules into infinite chains running along the *b* axis in the crystal structure. The

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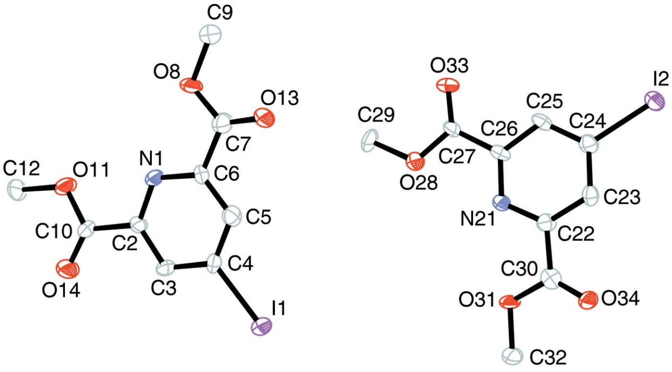

**Figure 1**
The asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level; H atoms have been omitted.

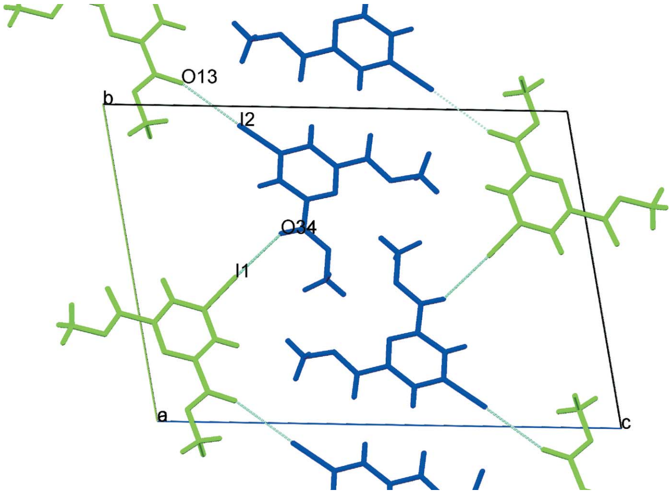

**Figure 2**
A view, down the *a* axis, of the packing of the title compound. The blue and green colours represent the two molecules of the asymmetric unit; the short intermolecular I$\cdots$O contacts are shown as dashed lines.

two independent molecules alternate in the chain, so that there is only one symmetry-independent chain in the crystal structure (Fig. 2).

## Experimental

The following procedure was adapted from Chessa *et al.* (2005). Acetyl chloride (10.9380 g, 10.9 mmol) was added to a mixture of dimethyl-4-bromopyridine-2,6-dicarboxylate (1.00 g, 3.65 mmol) and NaI (10.94 g, 73 mmol) in dry CH$_3$CN (24 ml) at 273 K. The reaction mixture was sonicated for 5 h under a nitrogen atmosphere in a 323 K water bath. After cooling to 273 K, saturated aqueous Na$_2$CO$_3$ (15 ml) and CH$_2$Cl$_2$ (30 ml) were added. The organic layer was washed with saturated aqueous Na$_2$S$_2$O$_3$ (10 ml) and water (2 × 10 ml), and dried over MgSO$_4$. The solvent was removed under reduced pressure. Crude dimethyl-4-iodopyridine-2,6-dicarboxylate was dissolved in hot methanol, then cooled in a refrigerator at 277 K for 24 h, where needles suitable for single-crystal X-ray analysis formed. The resulting translucent pale-yellow needles were filtered off, washed with cold methanol and dried under vacuum.

Both $^1$H NMR and mass spectrometry have confirmed the completion of the halogen exchange reaction presented in the scheme. The H atoms *ortho* to the halogen shifted downfield upon conversion to the iodo derivative ($\delta$ from 8.48 to 8.67 p.p.m.), and the mass spectrum (electrospray ionization-positive ion mode) showed only two peaks at 344 ($M$ + Na$^+$) and 360 ($M$ + K$^+$), consistent with the iodo derivative. No molecular ion was observed in either postive or negative mode. In addition, no isotopic distribution patterns that could be attributed to the Br derivative were observed.

*Crystal data*

C$_9$H$_8$INO$_4$
$M_r$ = 321.07
Triclinic, $P\overline{1}$
$a$ = 4.2120 (12) Å
$b$ = 13.359 (2) Å
$c$ = 19.236 (2) Å
$\alpha$ = 99.936 (5)°
$\beta$ = 94.326 (6)°
$\gamma$ = 96.790 (6)°
$V$ = 1053.6 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 3.03 mm$^{-1}$
$T$ = 173 (2) K
0.08 × 0.04 × 0.02 mm

*Data collection*

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min}$ = 0.793, $T_{\max}$ = 0.942
5334 measured reflections
3723 independent reflections
2296 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.096
$S$ = 1.02
3723 reflections
275 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.08 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.78 e Å$^{-3}$

**Table 1**
Geometry of the intermolecular I$\cdots$O contacts (Å, °).

| $C_a$ | I | O | $C_b$ | I$\cdots$O | $C_a$—I$\cdots$O | I$\cdots$O—$C_b$ |
|---|---|---|---|---|---|---|
| C4 | I1$^{\rm i}$ | O34$^{\rm ii}$ | C30 | 2.981 (6) | 177.6 (2) | 152.0 (6) |
| C24 | I2$^{\rm ii}$ | O13$^{\rm i}$ | C7 | 3.006 (5) | 175.5 (2) | 152.3 (6) |

Symmetry codes: (i) $-x, -y, 1 - z$; (i) $2 - x, 1 - y, 1 - z$.

The H atoms were located in a difference Fourier synthesis and included in the refinement in the riding-model approximation at geometrically idealized positions, with aromatic C—H = 0.96 Å, alkyl C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atom). The residual difference map contains one peak that is higher than 1 Å$^3$, which is located at a distance of 1.41 Å from atom C32.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

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## References

Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Britton, D. & Young, V. G. (1997). *Acta Cryst.* C**53**, 1359–1362.
Chessa, G., Canovese, L., Visentin, F., Santo, C. & Seraglia, R. (2005). *Tetrahedron*, **61**, 1755–1763.
Cody, V. J. (1974). *J. Am. Chem. Soc.* **96**, 6720–6725.
Fan, H.-F. (1991). *SAPI91*. Rigaku Corporation, Tokyo, Japan.

Farrugia, L. J. (1997). *J. Appl. Cryst* **30**, 565.

Gray, M., Goodman, A. J., Carroll, J. B., Bardon, K., Markey, M., Cooke, G. & Rotello, V. M. (2004). *Org. Lett.* **6**, 385–388.

Leroy, J., Schollhorn, B., Syssa-Magale, J.-L., Boubekeur, K. & Palvadeau, P. (2004). *J. Fluor. Chem.* **125**, 1379–1382.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Shi, X., Markigia, K. M., Fajer, J. & Drain, C. M. (2001). *J. Org. Chem.* **66**, 6513–6522.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.