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1,2,3-Trimethoxy-5,11-dihydroindolo[1,2-*b*]isoquinoline-5,11-dione

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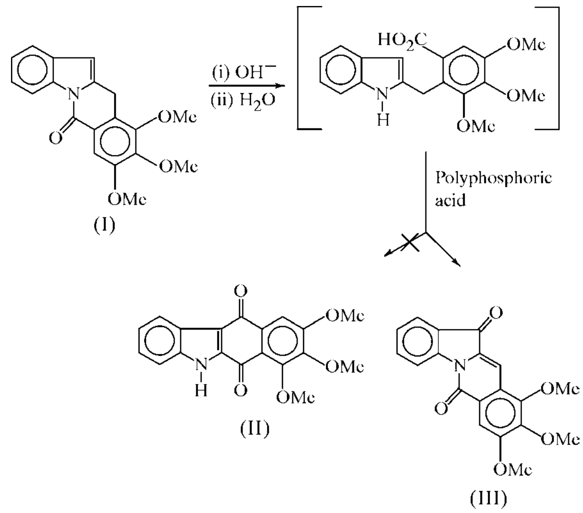
The title compound, $C_{15}H_{19}NO_5$, crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the asymmetric unit, which differ from each other in the orientation of their methoxy groups. Of the three methoxy groups in each molecule, one lies close to the plane of the molecule and the other two have an out-of-plane conformation where they point in opposite directions. In the crystal structure, four different types of π-stacks are observed and the molecules pack in two different types of stacking sheets, with alternating molecules *A* and *B* in one ribbon and alternating molecules *C* and *D* in the other. The supramolecular structure is supported by C—H···O and π–π interactions.

Comment

The structure determination of the title compound, (III), was undertaken as part of our investigations of the crystal packing and hydrogen-bonding network of substituted indole derivatives. Previous synthetic work in our laboratory has reported the formation of benzocarbazoloquinone from compound (I) by alkali followed by polyphosphoric acid treatment in air (Rajeswaran & Srinivasan, 1994) (see scheme). Crystal structure analysis of this product indicated that it is not compound (II) but the isomeric ketolactam, (III), which arises by the air oxidation of the indole 3-carbon as well as of the indole 2-carbon and the side-chain methylene unit. The title compound is useful as a key precursor for the synthesis of analogues of the kinamycin group of antibiotics (Sullivan *et al.*, 1992; Sato *et al.*, 1985; Sato & Gould, 1985). Pyrroloisoquinoline exhibits pharmaceutical activities, such as anti-leukaemic (Anderson *et al.*, 1998), muscarinic agonistic (Loesel *et al.*, 1998) and antidepressant (Elwan *et al.*, 1996).

The title compound contains four molecules in the asymmetric unit, designated *A*, *B*, *C* and *D*. Fig. 1 shows a displacement ellipsoid plot of two symmetry-independent molecules (*A* and *C*) of the asymmetric unit. The four rings of the molecule lie in a plane and the dihedral angles between the isoquinoline and indole moieties are 4.9 (1), 1.6 (1), 3.2 (1) and 4.4 (1)° for molecules *A*, *B*, *C* and *D*, respectively. The corresponding bond lengths and angles in all four molecules show that there are no significant differences, except those at the methoxy groups. The methyl group bonded to atom O4*A* is disordered over two positions, with an occupancy ratio of 0.59 (4):0.41 (4). The orientations of the three methoxy groups on the benzene ring are consistent with minimum steric interactions. Of the three methoxy groups, one group at C4 lies close to the plane of the molecule [the C17—O3—C4—C3 torsion angles are −4.5 (4), −2.5 (4), 2.9 (4) and 11.0 (4)° for molecules *A*, *B*, *C* and *D*, respectively], while the other two at C5 and C6 have an out-of-plane conformation where they point in opposite directions. Furthermore, the methoxy groups at C5 in molecules *A* and *B* point in the same direction, but this is opposite to what is observed in molecules *C* and *D* [the C18—O4—C5—C6 torsion angles are −70.4 (10), −105 (2), −69.3 (3), 88.5 (4) and 86.3 (3)° for molecules *A* (major and minor component), *B*, *C* and *D*, respectively]. At C6 in mol-



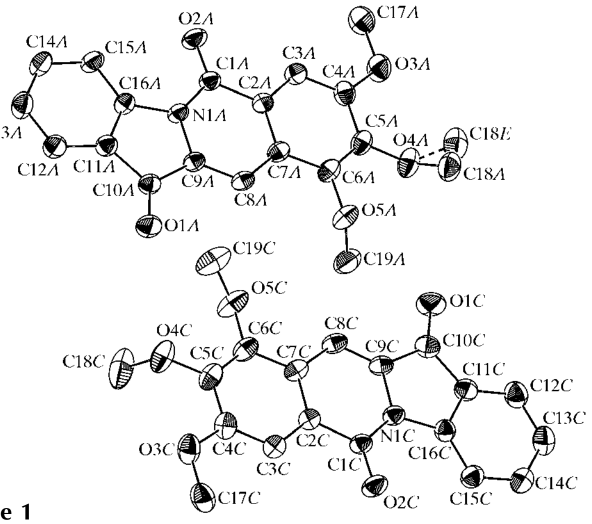


Figure 1
The asymmetric unit of (III), with the two crystallographically independent molecules, *A* and *C*, drawn with displacement ellipsoids at the 35% probability level. The minor disordered component of the methyl group (C18*E*) is also shown.

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ecules *A* and *B*, the methoxy groups point in the same direction, but point in opposite directions in molecules *C* and *D* [the C19—O5—C6—C5 torsion angles are −73.6 (3), −64.1 (3), 55.0 (4) and 62.0 (3)° for molecules *A*, *B*, *C* and *D*, respectively].

The centroids of the four rings of the molecules are *Cg*1 (N1/C9–C11/C16), *Cg*2 (N1/C1/C2/C7–C9), *Cg*3 (C2–C7) and *Cg*4 (C11–C16). In the crystal structure, molecules *A* and B^{viii}, *B* and A^{ix}, *C* and D^{ii}, and *D* and C^{x} are linked by C—H···O hydrogen bonds to form dimeric pairs (see Table 2 for symmetry codes). These pairs are further reinforced by stacking interactions. Adjacent pairs, translated along the *b* direction, are linked by C—H···O and stacking interactions. Thus, these molecules pack in two types of stacking ribbons involving four different types of π-stacks, with molecules *A* and *B* alternating in one ribbon (stack *AB*) [(*a*) AB^{viii} and the equivalent BA^{ix}; (*b*) AB^{vi} and the equivalent BA^{vii}], and molecules *C* and *D* alternating in the other ribbon (stack *CD*) [(*c*) *CD*; (*d*) CD^{ii} and the equivalent DC^{x}]. In stack *AB*, the centroids *Cg*1*A* and $Cg1B^{\mathrm{viii}}$ and *Cg*2*A* and $Cg2B^{\mathrm{viii}}$, and the equivalent pairs *Cg*1*B* and $Cg1A^{\mathrm{ix}}$ and *Cg*2*B* and $Cg2A^{\mathrm{ix}}$, are separated by 3.574 (2) and 3.621 (1) Å, respectively. The centroids *Cg*2*A* and $Cg2B^{\mathrm{vi}}$ and the equivalent pair *Cg*2*B* and $Cg2A^{\mathrm{vii}}$, are separated by 3.723 (1) Å. In stack *CD*, the centroids *Cg*2*C* and *Cg*2*D* are separated by 3.599 (1) Å. Centroids *Cg*2*C* and $Cg2D^{\mathrm{ii}}$ and the equivalent pair *Cg*2*D* and $Cg2C^{\mathrm{x}}$ are separated by 3.715 (1) Å. The ribbons propagate along the *b* direction and adjacent ribbons are interlinked by C—H···O interactions, resulting in a molecular sheet (Fig. 2). Thus, the supramolecular structure is supported by C—H···O and π–π interactions (Table 2). Fig. 3 shows the molecular packing along the *b* axis.

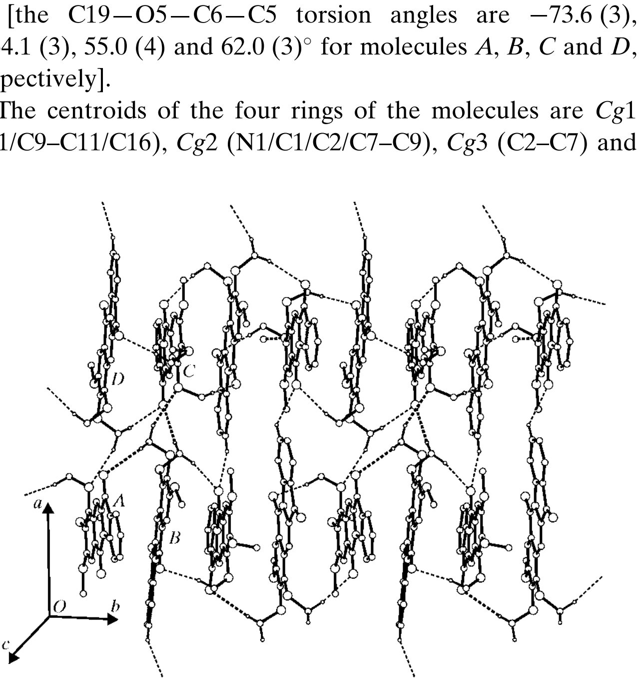

Figure 2
Part of the crystal structure of (III), showing the formation of ribbons running along the *b* direction. H atoms not involved in the interactions have been omitted for clarity. Symmetry-independent molecules *A*–*D* are also marked.

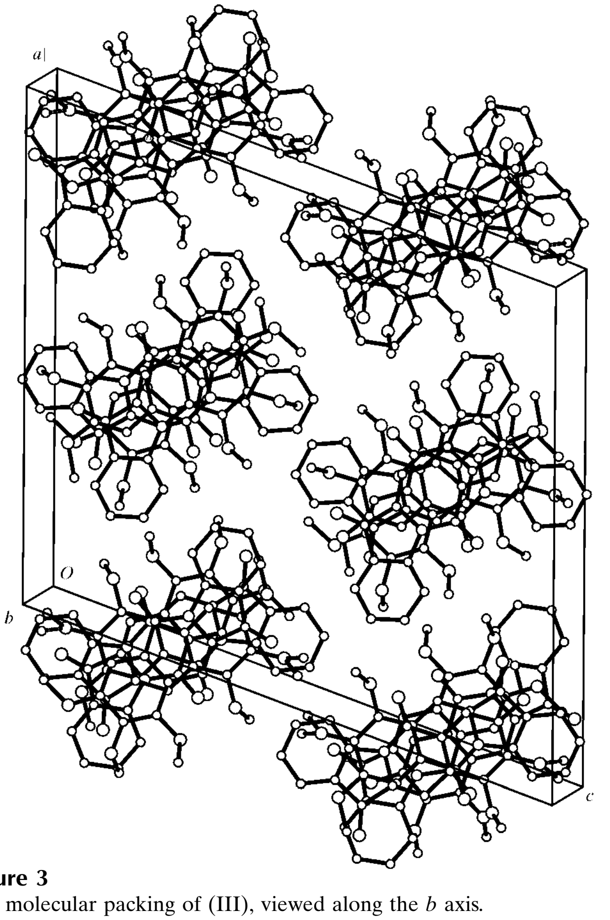

Figure 3
The molecular packing of (III), viewed along the *b* axis.

Experimental

Hydrolysis of 8,9,10-trimethoxy-11*H*-indolo[1,2-*b*]isoquinolin-6-one (0.64 g) ld to 0.58 g (85%) of the acid, which was reacted with polyphosphoric acid (7.5 ml) at 373 K for 2 h to afford compound (III) (yield 0.3 g, 35%). This work unambiguously supports the isomeric structure (III) (see scheme in *Comment*), instead of structure (II) as proposed in the original work (Rajeswaran & Srinivasan, 1994).

Crystal data

$C_{19}H_{15}NO_5$
$M_r = 337.32$
Monoclinic, $P2_1/c$
$a = 20.8934$ (4) Å
$b = 14.2400$ (3) Å
$c = 22.8886$ (4) Å
$\beta = 110.014$ (1)°
$V = 6398.6$ (2) Å^3
$Z = 16$
$D_x = 1.401$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 7530 reflections
$\theta = 1.1$–28.4°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Slab, yellow
0.44 × 0.34 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1996)
$T_{\min} = 0.739$, $T_{\max} = 0.980$
40492 measured reflections

15541 independent reflections
7962 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 28.3°$
$h = -27 \rightarrow 24$
$k = -19 \rightarrow 18$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.210$
$S = 1.09$
15541 reflections
924 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

O1A—C10A	1.221 (3)	O1C—C10C	1.215 (3)
O2A—C1A	1.220 (3)	O2C—C1C	1.225 (3)
N1A—C1A	1.381 (3)	N1C—C1C	1.378 (3)
N1A—C9A	1.407 (3)	N1C—C9C	1.407 (3)
N1A—C16A	1.425 (3)	N1C—C16C	1.422 (3)
C8A—C9A	1.350 (3)	C8C—C9C	1.332 (3)
O1B—C10B	1.220 (3)	O1D—C10D	1.221 (3)
O2B—C1B	1.229 (3)	O2D—C1D	1.220 (3)
N1B—C1B	1.385 (3)	N1D—C1D	1.395 (3)
N1B—C9B	1.412 (3)	N1D—C9D	1.403 (3)
N1B—C16B	1.414 (3)	N1D—C16D	1.422 (3)
C8B—C9B	1.337 (3)	C8D—C9D	1.335 (3)
C1A—N1A—C9A	123.9 (2)	C1C—N1C—C9C	123.5 (2)
C1A—N1A—C16A	126.8 (2)	C1C—N1C—C16C	127.0 (2)
C9A—N1A—C16A	109.2 (2)	C9C—N1C—C16C	109.6 (2)
C8A—C9A—C10A	131.1 (2)	C8C—C9C—C10C	131.2 (2)
C1B—N1B—C9B	123.2 (2)	C1D—N1D—C9D	123.3 (2)
C1B—N1B—C16B	127.2 (2)	C1D—N1D—C16D	126.8 (2)
C9B—N1B—C16B	109.6 (2)	C9D—N1D—C16D	109.9 (2)
C8B—C9B—C10B	131.4 (2)	C8D—C9D—C10D	130.8 (2)
C17A—O3A—C4A—C3A	−4.5 (4)	C17C—O3C—C4C—C3C	2.9 (4)
C18E—O4A—C5A—C6A	−105 (2)	C18C—O4C—C5C—C6C	88.5 (4)
C18A—O4A—C5A—C6A	−70.4 (10)	C19C—O5C—C6C—C5C	55.0 (4)
C19A—O5A—C6A—C5A	−73.6 (3)	C17D—O3D—C4D—C3D	11.0 (4)
C17B—O3B—C4B—C3B	−2.5 (4)	C18D—O4D—C5D—C6D	86.3 (3)
C18B—O4B—C5B—C6B	−69.3 (3)	C19D—O5D—C6D—C5D	62.0 (3)
C19B—O5B—C6B—C5B	−64.1 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C15A—H15A···O2A	0.93	2.39	2.926 (3)	116
C15B—H15B···O2B	0.93	2.41	2.939 (4)	116
C15C—H15C···O2C	0.93	2.40	2.929 (3)	116
C15D—H15D···O2D	0.93	2.38	2.920 (4)	117
C18A—H18C···O5A	0.96	2.49	3.053 (17)	117
C18B—H18I···O5B	0.96	2.50	3.109 (4)	121
C19A—H19C···O4A	0.96	2.55	3.096 (4)	117
C19B—H19F···O4B	0.96	2.38	3.026 (4)	124
C19C—H19G···O4C	0.96	2.50	2.919 (5)	106
C19D—H19J···O4D	0.96	2.34	2.981 (4)	123
C18D—H18N···O5A	0.96	2.54	3.439 (4)	156
C18D—H18O···O1C	0.96	2.60	3.372 (4)	138
C19D—H19K···O1A	0.96	2.57	3.502 (4)	164
C12A—H12A···O1C^{i}	0.93	2.56	3.345 (3)	142
C14B—H14B···O2C^{ii}	0.93	2.35	3.254 (4)	162
C14D—H14D···O2A^{iii}	0.93	2.53	3.201 (4)	129
C17C—H17H···O3A^{iv}	0.96	2.56	3.451 (4)	154
C17D—H17K···O3B^{v}	0.96	2.51	3.298 (4)	140
C18A—H18A···O1B^{vi}	0.96	2.32	3.278 (16)	173
C18B—H18G···O1A^{vii}	0.96	2.38	3.264 (4)	153
C18B—H18H···O5C^{vii}	0.96	2.50	3.420 (4)	160
C19A—H19A···O2B^{viii}	0.96	2.42	3.373 (4)	175
C19B—H19D···O2A^{ix}	0.96	2.33	3.240 (4)	158
C19C—H19I···O2D^{ii}	0.96	2.33	3.252 (5)	162
C19D—H19L···O2C^{x}	0.96	2.38	3.312 (4)	164

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+1, y, z$; (iv) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $-x, -y+1, -z$; (vi) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (vii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $x, y-1, z$; (ix) $x, y+1, z$; (x) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

H atoms were fixed geometrically and treated as riding on their parent C atoms, with aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$($\rm C_{methyl}$). The methyl group bonded to O4A was disordered and the occupancy factors of the two positions were refined, with their sum constrained to unity [C18A = 0.59 (4) and C18E = 0.41 (4)].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1262). Services for accessing these data are described at the back of the journal.

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