Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.315 (2)	N3—C1	1.360 (2)
N1—N2	1.391 (2)	N3—C2	1.371 (2)
N2—C1	1.297 (2)	N3—C9	1.437 (2)
N1—C2—C3—C8	−34.4 (2)	C1—N3—C9—C10	−67.3 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···N2^{i}	0.96 (2)	2.60 (2)	3.519 (2)	160 (1)
C15—H15*F*···N1^{ii}	0.96	2.60	3.544 (3)	170
C6—H6···π(Ring *C*)^{iii}	0.98 (2)	2.76 (2)	3.591 (3)	143 (1)
C10—H10···π(Ring *B*)^{iv}	0.98 (2)	2.73 (2)	3.552 (3)	143 (1)
C13—H13···π(Ring *B*)^{ii}	0.96 (2)	2.83 (2)	3.645 (3)	143 (1)
C15—H15*C*···π(Ring *C*)^{v}	0.96	3.15 (2)	4.056 (3)	158

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 + x, y, z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $1 - x, 1 - y, 2 - z$.

All H atoms were located from a difference map. The methyl group was found to be disordered, with two equally occupied orientations rotated from each other by 60°, and it was treated as an idealized disordered methyl group. The remaining H atoms were refined isotropically.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1079). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1138–1140

Methyl (5*SR*,6*SR*)-1,3-dichloro-8-diethylamino-5,6-dihydro-5-hydroxy-7-nitro-6-phenylisoquinoline-5-carboxylate

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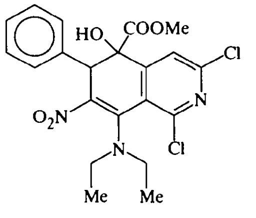
Abstract

In the title compound, $C_{21}H_{21}Cl_2N_3O_5$, the fused cyclohexadiene ring adopts a skew-boat conformation, with the methoxycarbonyl and phenyl groups attached in axial positions and the nitro and diethylamino groups attached equatorially. The mean plane through the cyclohexadiene ring forms dihedral angles of 23.30 (7) and 87.72 (8)° with the pyridine and phenyl rings, respectively. In the crystal, the inversion-related molecules exist as O—H···O hydrogen-bonded dimers.

Comment

The development of the tandem reaction process (Bunce, 1995), also called the domino reaction (Tietze, 1996), is a rapidly growing area of synthetic organic chemistry which allows the interlinking of several transformations in a single synthetic step. In conjunction with our work in this area, we have now uncovered a tandem Hamaguchi–Ibata and Diels–Alder reaction involving a crystalline diazoacetic ester (Sarkar *et al.*, 1999), and β-nitrostyrene in the presence of 1 mol% $Rh_2(OAc)_4$ in benzene under reflux conditions to give a substituted isoquinoline in high yield. The X-ray structure determination of the title compound, (I), was undertaken in order to elucidate the molecular conformation.



(I)

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The bond lengths and angles observed in (I) show normal values (Allen *et al.*, 1987). The pyridine ring is planar, with C8 deviating by a maximum of 0.054 (1) Å from its mean plane. The fused cyclohexadiene ring adopts a skew-boat conformation, with an asymmetry parameter ΔC_2(C4—C5) of 11.5 (2)° (Duax *et al.*, 1976); the methoxycarbonyl and phenyl groups are attached in axial positions, whereas the nitro and diethylamino groups are attached equatorially. The mean plane through the cyclohexadiene ring forms dihedral angles of 23.30 (7) and 87.72 (8)°, respectively, with the pyridine and phenyl rings. The nitro and methoxycarbonyl groups are individually planar and make dihedral angles of 46.31 (9) and 84.05 (8)°, respectively, with the attached ring. In the solid state, the inversion-related molecules exist as centrosymmetrically O3—H3*A*···O1(1 − *x*, 1 − *y*, −*z*) hydrogen-bonded dimers (Table 2). The crystal structure is stabilized by C—H···π interactions involving the phenyl rings and weak C—H···O contacts.

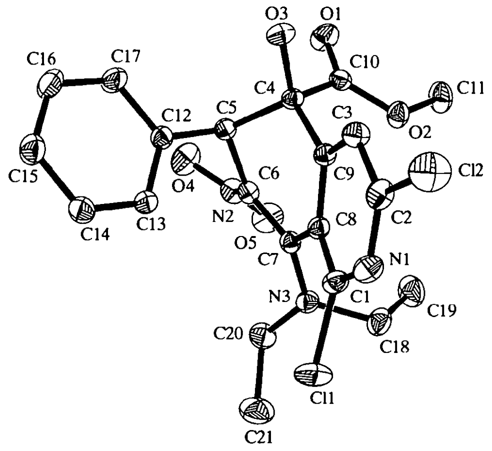

Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids and the atom-numbering scheme. The H atoms have been omitted for clarity.

Experimental

To a benzene solution (5 ml) containing $Rh_2(OAc)_4$ (1 mol%) and a twofold excess of nitrostyrene at 353 K, the diazoacetic ester in benzene (2 ml) was added *via* a syringe over a period of 2 h. After the addition was complete, the solution was refluxed for 20 min. The mixture was then purified by column chromatography and finally recrystallized from ethyl acetate to give orange crystals (m.p. 410 K).

Crystal data

$C_{21}H_{21}Cl_2N_3O_5$
$M_r = 466.31$
Monoclinic
$P2_1/c$
$a = 15.1789$ (6) Å
$b = 15.8689$ (6) Å
$c = 9.2735$ (3) Å
$\beta = 102.396$ (1)°
$V = 2181.7$ (1) Å^3
$Z = 4$
$D_x = 1.420$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1.37$–28.33°
$\mu = 0.336$ mm^{-1}
$T = 293$ (2) K
Slab
0.44 × 0.42 × 0.16 mm
Orange

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan, empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.87$, $T_{\max} = 0.95$

14 621 measured reflections
5389 independent reflections
4192 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 28.33°$
$h = -20 \rightarrow 19$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.108$
$S = 1.03$
5389 reflections
284 parameters
H atom: see below
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.6880P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.319 (2)	C3—C9	1.378 (2)
N1—C1	1.327 (2)	C6—C7	1.373 (2)
N3—C7	1.363 (2)	C7—C8	1.505 (2)
C2—C3	1.382 (2)		
O5—N2—C6—C7	−21.4 (2)	N3—C7—C8—C1	−30.1 (2)
O4—N2—C6—C5	−27.7 (2)	C9—C4—C10—O2	3.2 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O1$^{\rm i}$	0.82	2.03	2.837 (2)	169
C11—H11*B*···O4$^{\rm ii}$	0.96	2.56	3.381 (2)	144
C17—H17···O1$^{\rm i}$	0.93	2.51	3.366 (2)	152
C16—H16···π(Ph)$^{\rm iii}$	0.93	3.21	3.943 (2)	137
C21—H21*A*···π(Ph)$^{\rm iv}$	0.96	2.98	3.880 (2)	157

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

All the H atoms were placed at geometrically calculated positions and a riding model was used for their refinement; rotating-group refinement was used for the methyl groups.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1283). Services for accessing these data are described at the back of the journal.

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Trimethyl (5*SR*,6*SR*)-1,3-dichloro-8-diethylamino-5,6-dihydro-5-hydroxyisoquinoline-5,6,7-tricarboxylate

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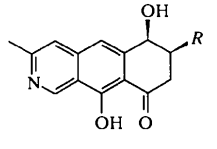
Abstract

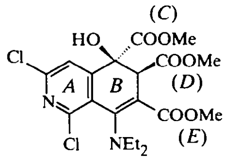
The title compound, $C_{19}H_{22}Cl_2N_2O_7$, has four independent molecules in the asymmetric unit with no pseudosymmetry. In each of the four molecules the fused cyclohexadiene ring adopts a skew-boat conformation, with two of the three methoxycarbonyl groups in the axial orientation and the third methoxycarbonyl and the diethylamino groups attached equatorially. The hydroxyl groups are involved in O—H···O intermolecular hydrogen bonds with carbonyl-O atoms to form infinite chains in the $[2\bar{1}0]$ direction.

Comment

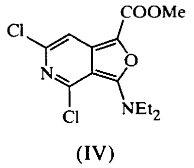
Pyrenophora teres, the causative fungus of net blotch disease, is a significant pathogen of barley (*Hordeum vulgare*). Net blotch disease occurs wherever barley is grown in temperate and humid regions of the world (Dickson, 1956). Diseases such as net blotch have received increasing attention in view of the growing popularity of barley (Shipton *et al.*, 1973). Several research groups have previously isolated bioactive compounds from *Pyrenophora teres* (Nukina *et al.*, 1980; Gordon & Webster, 1985; Smedegard-Peterson, 1977). Recently, two novel phytotoxic isoquinoline derivatives, pyrenoline A, (I), and pyrenoline B, (II), have been isolated from the culture fluid of *Pyrenophora teres* and characterized by spectroscopic and X-ray diffraction techniques (Coval *et al.*, 1990). In view of their significant biological activities, pyrenoline A and pyrenoline B are considered to be good candidates for a structure–activity relationship investigation. Accordingly, a synthetic program was undertaken which would allow preparation of large amounts of pyrenoline A and B and their congeners. During the course of this work, we have synthesized the title triester, (III), from the Diels–Alder reaction of (IV) (Sarkar *et al.*, 1999) with dimethyl fumarate. The X-ray structure determination of compound (III) was undertaken in order to establish the relative stereochemistry of the two stereogenic centres, which could not be ascertained by spectroscopic techniques.



(I) *R*=OMe
(II) *R*=H



(III)



(IV)

The asymmetric unit of compound (III) consists of four independent molecules, *A*, *B*, *C* and *D*, without

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