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Caulerpin

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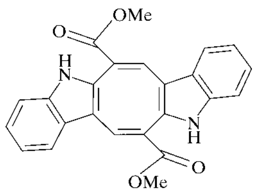
The crystal structure of caulerpin (dimethyl 6,13-dihydrodibenzo[*b*,*i*]phenazine-5,12-dicarboxylate, $C_{24}H_{18}N_2O_4$), an indole alkaloid, reported in space group *Cc* with an acute β angle, has been redetermined in the correct space group, *C*2/*c*. The molecule has twofold crystallographic symmetry and is composed of two essentially planar indole groups fused to an eight-membered cyclooctatetraene ring which adopts a boat conformation. The molecular dimensions are normal. The structure is stabilized by intermolecular and intramolecular interactions involving the indole N—H atom and carbonyl O atom [N···O 3.211 (4) and 2.836 (4) Å].

Comment

The species of genus Caulerpa have been investigated for their chemical constituents due to their utilization as salad delicacies in many countries (Santos, 1970). Caulerpin, (I), a plant-growth regulator (Raub *et al.*, 1987) and a non-toxic compound (Vidal *et al.*, 1984), was first isolated from *Caulerpa racemosa*. The crystal structure of (I) has been reported (Lu *et al.*, 1994) in a non-centrosymmetric space group (*Cc*) with an acute β angle [81.83 (2)°]. In this article, we describe the structure of (I) in the correct space group.



(I)

The structure of this novel indole alkaloid is composed of a molecules with twofold crystallographic symmetry wherein two essentially planar indole moieties [maximum deviation 0.018 (3) Å] are fused to an eight-membered cyclooctatetraene ring which adopts a boat conformation. The dihedral angle between the mean planes of the indole moieties is 73.2 (1)° and the rings are inclined at an angle of 36.6 (1)° with respect to the base of the cyclooctatetraene ring comprising C9, C10, C9^{i} and C10^{i} atoms [symmetry code: (i) $2 - x, y, \frac{3}{2} - z$]. The carboxylate groups are essentially planar, with the maximum deviation of any atom from the plane formed by O1, O2, C9, C11 and C12 being 0.007 (3) Å, and are oriented at 43.1 (1)° with respect to the base of the cyclooctatetraene ring.

The structure is stabilized by a network of intermolecular interactions involving the indole N—H atom and carbonyl O atom [N1···O1 3.211 (4) Å] forming chains of molecules extended along *a* axis which are also linked along the *b* axis. The carbonyl O and the indole N atoms are also involved in an intramolecular hydrogen bond of the type N—H···O [N···O 2.836 (4) Å].

A search of the Cambridge Structural Database (Allen & Kennard, 1993) did not show any structures related to this novel alkaloid, caulerpin.

Experimental

Caulerpa racemosa (Forsk.) was collected from Buleji coast near Karachi, Pakistan. The algae were washed with water, dried under shade and crushed. Dry powder (300 g) was soaked in ethanol for about two weeks. The ethanol extract was evaporated under vacuum at 310 K, the residue obtained was chromatographed on a column of silica gel and was eluted successively with, hexane, hexane–chloroform, chloroform–methanol and pure methanol. The fractions eluted with hexane–chloroform (1:1) afforded red crystals. They were recrystallized by dissolving in a drop of dichloromethane, followed by the addition of 1–2 ml of isooctane.

Crystal data

$C_{24}H_{18}N_2O_4$
$M_r = 398.40$
Monoclinic, *C*2/*c*
$a = 19.608$ (4) Å
$b = 4.786$ (2) Å
$c = 20.461$ (6) Å
$\beta = 97.91$ (2)°
$V = 1901.9$ (10) Å^3
$Z = 4$

$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.096$ mm^{-1}
$T = 293$ (2) K
Plate, red
0.65 × 0.30 × 0.07 mm

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
1736 measured reflections
1685 independent reflections
972 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\rm max} = 25°$

$h = 0 \rightarrow 22$
$k = 0 \rightarrow 5$
$l = -24 \rightarrow 24$
3 standard reflections every 200 reflections intensity decay: <0.10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.232$
$S = 1.19$
1685 reflections
136 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1325P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.206 (4)	N1—C1	1.371 (5)
O2—C11	1.328 (5)	N1—C8	1.381 (5)
O2—C12	1.434 (5)		
C11—O2—C12	116.3 (3)	C1—N1—C8	109.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.86	2.41	3.211 (4)	154.5
N1—H1···O1	0.86	2.43	2.836 (4)	109.6

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

The space group was determined from the systematic absences and confirmed by successful refinement.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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