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

O1—C9	1.364 (3)	C1—C2	1.506 (3)
O1—C10	1.429 (3)	C1—C22	1.515 (3)
O2—C11	1.418 (3)	C3—C4	1.470 (3)
O2—C12	1.414 (3)	C4—C9	1.400 (3)
O3—C13	1.433 (3)	C19—C20	1.473 (3)
O3—C14	1.367 (3)	C10—C11	1.491 (4)
N1—C2	1.456 (3)	C12—C13	1.488 (3)
N1—C3	1.256 (3)	C14—C19	1.398 (3)
N2—C20	1.256 (3)	C21—C22	1.520 (3)
N2—C21	1.455 (3)		
C9—O1—C10	118.7 (2)	O3—C13—C12	108.9 (2)
C11—O2—C12	111.3 (2)	O3—C14—C15	123.5 (2)
C13—O3—C14	117.9 (2)	O3—C14—C19	116.3 (2)
C2—N1—C3	116.6 (2)	C1—C22—C21	115.0 (2)
C20—N2—C21	119.0 (2)	O1—C9—C4	115.4 (2)
C2—C1—C22	112.5 (2)	O1—C9—C8	124.5 (2)
N1—C2—C1	112.1 (2)	O1—C10—C11	107.9 (2)
N1—C3—C4	123.3 (2)	C14—C19—C20	121.8 (2)
C3—C4—C5	121.3 (2)	C18—C19—C20	120.1 (2)
C3—C4—C9	119.9 (2)	N2—C20—C19	121.7 (2)
O2—C11—C10	110.2 (2)	N2—C21—C22	110.7 (2)
O2—C12—C13	109.8 (2)		

The structure was solved by direct methods. The H-atom positions were located by difference synthesis and refined isotropically.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1300). Services for accessing these data are described at the back of the journal.

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1-Nitrobenzo[*c*]cinnoline

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Abstract

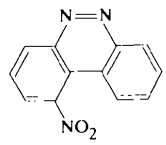
The title compound, $C_{12}H_7N_3O_2$, is a 1-nitro derivative of the ligand benzo[*c*]cinnoline. The rings in the benzo[*c*]cinnoline skeleton are close to planarity, while the skeleton itself is non-planar. The dihedral angles between the rings in the benzo[*c*]cinnoline skeleton are $\alpha\wedge\beta$ 4.0 (5), $\alpha\wedge\gamma$ 8.4 (2) and $\beta\wedge\gamma$ 4.5 (4)°; in benzo[*c*]cinnoline the $\alpha\wedge\gamma$ dihedral angle is 2.5°. The difference is caused by steric interactions between the nitro group and benzo[*c*]cinnoline skeleton.

Comment

Nitrobenzo[*c*]cinnolines are the starting materials for other benzo[*c*]cinnoline derivatives (Barton & Cocket, 1962; Kılıç & Tüzün, 1992). Benzo[*c*]cinnoline and some of its derivatives are known to have mutagenic (Leary *et al.*, 1983), antirheumatic (Matter, 1957; Erlenmeyer, 1958), herbicidal (Entwistle *et al.*, 1981) and carcinogenic (Ashby *et al.*, 1980) physiological activities. They have also been used as bleach catalysts in the processing of photographic silver-dye bleach materials (Jan, 1980). The structures of benzo[*c*]cinnoline (van der Meer, 1972) and octachlorobenzo[*c*]cinnoline (King *et al.*, 1983) have been described as complexes with bis(tricarbonyliron) (Doedens, 1970) and copper(I)-benzoato (Toth *et al.*, 1987). The structures of 1-morpholinobenzo[*c*]cinnoline (Hökelek *et al.*, 1990), 1- and 3-piperidinobenzo[*c*]cinnoline (Hökelek *et al.*,

1991*a*), 2- and 4-pyrrolidinobenzo[*c*]cinnoline (Hökelek *et al.*, 1991*b*) and 2-fluorobenzo[*c*]cinnoline (Hökelek, 1991) have been reported previously.

As far as we know, there are no reports on the structures of benzo[*c*]cinnolines substituted with alkyl, alkoxy, aminoalkyl or nitro groups. The structure determination of the title compound, (I), was undertaken in order to understand the effect of changing the type and position of the substituent, and to permit a comparison of its structure with those of previously reported benzo[*c*]cinnolines to be made.



(I)

Fig. 1 shows the compound (I) with the atomic numbering scheme. The benzo[*c*]cinnoline skeleton consists of almost planar rings. The maximum distances from the least-squares planes are 0.023 (2), 0.039 (2) and 0.023 (2) Å for rings α (C1,C2,C3,C4,C5,C14), β (C5,N6,N7,C8,C13,C14) and γ (C8,C9,C10,C11,C12, C13), respectively. The rings are twisted slightly with respect to each other. The dihedral angles between their least-squares planes are $\alpha\wedge\beta$ 4.0 (5), $\alpha\wedge\gamma$ 8.4 (2) and $\beta\wedge\gamma$ 4.5 (4)°. In benzo[*c*]cinnoline (van der Meer, 1972), the dihedral angle between the two benzenoid rings ($\alpha\wedge\gamma$) is 2.5°. The large corresponding dihedral angle in (I) probably results from steric interactions between the benzo[*c*]cinnoline and the nitro group at position 1. The dihedral angle $\alpha\wedge\gamma$ depends on the steric interaction with the substituents. The interaction is greatest with the substituents at position 1, as for 1-piperidinobenzo[*c*]cinnoline; the corresponding $\alpha\wedge\gamma$ angle in 3-piperidinobenzo[*c*]cinnoline (Hökelek *et al.*, 1991*a*) is 3.4 (1) and 1.8 (1)° in the two independent molecules. The corresponding $\alpha\wedge\gamma$ dihedral angles are 1.32 (6) and 4.95 (7)° in 2-pyrrolidino- and 4-pyrrolidinobenzo[*c*]cinnolines, respectively, (Hökelek *et al.*, 1991*b*) and 0.50 (7)° in 2-fluorobenzo[*c*]cinnoline (Hökelek, 1991).

The steric interaction between the H atom at C12 and the nitro group at C1 [N8···H121 = 2.39 (2) and O1···H121 = 2.50 (2) Å] generates an enlarged C13—C14—C1 angle [128.4 (1)°] and smaller ones at the opposite side of the benzo[*c*]cinnoline skeleton (see Table 1). It is well known that nitro substituents are a very strong electron-withdrawing group, so the endocyclic C14—C1—C2 angle [123.5 (2)°] is enlarged compared to corresponding ones in 1-morpholinobenzo-[*c*]cinnoline [119.0 (2)°; Hökelek *et al.*, 1990] and 1-piperidinobenzo[*c*]cinnoline [119.2 (3)°; Hökelek *et al.*, 1991*a*], where the morpholino and piperidino substituents are known electron-donating groups. The electron-withdrawing property of the nitro group is also effective on the C1—N8 bond length [1.467 (2) Å]; corresponding C—N bonds are 1.417 (2) Å in 1-morpholinobenzo[*c*]cinnoline (Hökelek *et al.*, 1990) and 1.419 (3) Å in 1-piperidinobenzo[*c*]cinnoline (Hökelek *et al.*, 1991*a*).

As a general trend, the C1—C2, C3—C4, C9—C10 and C11—C12 bonds in the benzo[*c*]cinnoline skeleton are shorter than the other bonds determined crystallographically in all of the benzo[*c*]cinnoline ligands. This determination is in agreement with the theoretical calculations made by Mulliken (1955).

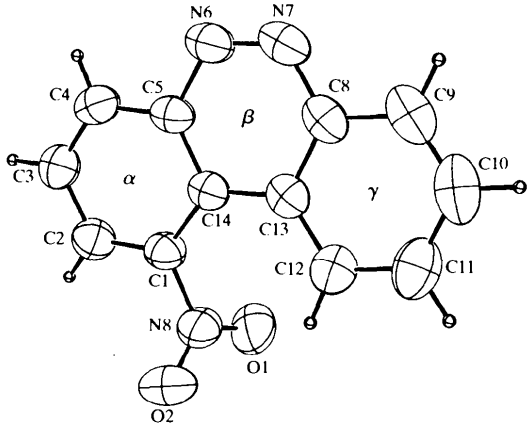


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Compound (I) was synthesized according to the literature method of Barton & Cocket (1962). Suitable crystals for X-ray crystallography were obtained from AcOH.

Crystal data

$C_{12}H_7N_3O_2$
M_r = 225.21
Monoclinic
$P2_1/n$
a = 7.894 (1) Å
b = 13.892 (1) Å
c = 9.556 (1) Å
β = 103.28 (2)°
V = 1019.9 (2) Å^3
Z = 4
D_x = 1.467 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–18°
μ = 0.1044 mm^{-1}
T = 298 K
Block
0.30 × 0.25 × 0.20 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans

1715 reflections with $F > 2\sigma(F)$
R_{int} = 0.018

Absorption correction:
empirical *via* ψ scans
(Fair, 1990)
T_{min} = 0.969, T_{max} = 0.979
2312 measured reflections
2062 independent reflections

θ_{max} = 26.3°
$h = 0 \rightarrow 9$
$k = -17 \rightarrow 0$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
R = 0.048
wR = 0.060
S = 1.68
1715 reflections
170 parameters
H atoms: see below
$w = 1/[\sigma(F)^2 + (0.02F)^2 + 1.0]$

$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

C14—C5	1.411 (2)	C3—C4	1.362 (3)
C14—C13	1.441 (2)	C9—C10	1.359 (3)
C14—C1	1.407 (2)	C1—C2	1.370 (3)
C5—N6	1.386 (2)	C2—C3	1.391 (3)
C4—C5	1.408 (3)	C1—N8	1.467 (2)
N6—N7	1.284 (3)	C11—C12	1.377 (3)
C8—C13	1.412 (2)	N8—O1	1.218 (2)
C8—C9	1.408 (3)	N8—O2	1.211 (2)
C8—N7	1.388 (2)	C10—C11	1.395 (3)
C13—C12	1.403 (3)		
C5—C14—C13	116.5 (1)	C8—C9—C10	120.0 (2)
C5—C14—C1	115.2 (2)	N6—N7—C8	120.6 (1)
C13—C14—C1	128.4 (1)	C1—C2—C3	119.6 (2)
C14—C5—N6	123.4 (2)	C14—C1—C2	123.5 (2)
C14—C5—C4	121.4 (1)	C14—C1—N8	120.8 (2)
N6—C5—C4	115.2 (2)	C2—C1—N8	115.6 (1)
C5—N6—N7	120.0 (2)	C4—C3—C2	119.7 (2)
C13—C8—C9	120.7 (2)	C13—C12—C11	121.0 (2)
C13—C8—N7	123.5 (2)	C1—N8—O1	117.6 (1)
C9—C8—N7	115.9 (2)	C1—N8—O2	118.1 (2)
C14—C13—C8	115.6 (1)	O1—N8—O2	124.2 (2)
C14—C13—C12	126.9 (2)	C9—C10—C11	120.3 (2)
C8—C13—C12	117.5 (2)	C12—C11—C10	120.4 (2)
C5—C4—C3	120.5 (2)		
C13—C14—C5—N6	5.2 (2)	C14—C5—C4—C3	−0.8 (3)
C13—C14—C5—C4	−176.2 (2)	C9—C8—C13—C12	4.0 (3)
C1—C14—C5—N6	−175.1 (2)	C14—C1—N8—O1	−65.7 (2)
C1—C14—C5—C4	3.6 (2)	C14—C1—N8—O2	116.1 (2)
C5—C14—C13—C8	−7.3 (2)	C2—C1—N8—O1	110.4 (2)
C13—C14—C1—N8	−8.1 (3)	C2—C1—N8—O2	−67.8 (2)

The structure was solved by direct methods. Most of the H-atom positions were located by difference synthesis and refined isotropically; the remaining ones were calculated geometrically and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1302). Services for accessing these data are described at the back of the journal.

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Homolycorine hydrochloride dihydrate†

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Abstract

The chirality of homolycorine has been determined by X-ray crystallographic analysis of the hydrochloride dihydrate, $C_{18}H_{22}NO_4^+ \cdot Cl^- \cdot 2H_2O$. Homolycorine is an

† Alternative name: 9,10-dimethoxy-1-methyllycorenan-7-one hydrochloride dihydrate.