2-Bromobenzo[c]cinnoline 6-oxide

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The title compound, $C_{12}H_7BrN_2O$, is a 2-bromo, N6-oxide derivative of the ligand benzo[c]cinnoline. The benzo[c]-cinnoline skeleton is nearly planar. The dihedral angle between the two benzenoid rings is 2.1 (1)°.

Comment

The structures of benzo[c]cinnoline derivatives with different substituents bonded at different positions of the benzo[c]-cinnoline skeleton have been the subject of much interest in our laboratory. Examples include 1-morpholinobenzo[c]-cinnoline, (II) (Hökelek et al., 1990), 1-piperidinobenzo[c]-cinnoline, (III), and 3-piperidinobenzo[c]cinnoline, (IV) (Hökelek et al., 1991a), 2-pyrrolidinobenzo[c]cinnoline, (V), and 4-pyrrolidinobenzo[c]cinnoline, (VI) (Hökelek et al., 1991b), 2-fluorobenzo[c]cinnoline, (VII) (Hökelek, 1991), and 1-nitrobenzo[c]cinnoline, (VIII) (Hökelek et al., 1999).

Benzo[c]cinnoline and some of its derivatives are known to have mutagenic (Leary et al., 1983), antirheumatic (Matter, 1957; Erlenmeyer, 1958), herbicidial (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 benzoatocopper(I) (Toth et al., 1987).


(I)
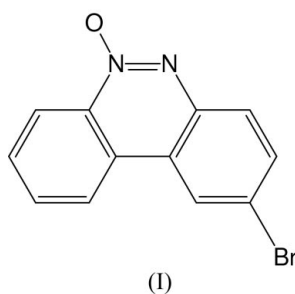
Benzo[c]cinnoline derivatives including N-oxides have been reviewed by Barton & Cockett (1962). As far as we know, there are no reports on the structures of benzo[c]cinnolines substituted with alkyl, alkoxy, aminoalkyl, nitro or N-oxide groups. The structure determination of the title compound, (I), was undertaken in order to understand the effects of changing the types and positions of the substituent and to permit a comparison of its structure with those of previously reported benzo[c]cinnolines.

Fig. 1 shows compound (I) with the atomic numbering. It is a 2-bromo, N6-oxide derivative of the ligand benzo[c]-

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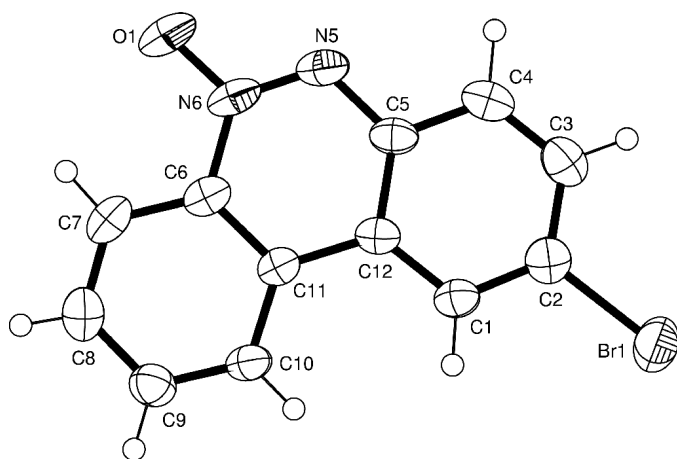
Figure 1
An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

cinnoline. The benzo[c]cinnoline skeleton consists of almost planar rings. The maximum distances from the least-squares planes are 0.014 (4), −0.013 (4) and −0.010 (4) Å for rings α(C1–C5,C12), β(C5,N5,N6,C6,C11,C12) and γ(C6–C11), respectively. The rings are twisted slightly with respect to each other. The dihedral angles between their least-squares planes are α–β = 2.2 (1)°, α–γ = 2.1 (1)° and β–γ = 0.5 (1)°. In benzo[c]cinnoline (Van der Meer, 1972), the dihedral angle between the two benzenoid rings is α–γ = 2.5°. The dihedral angle α–γ depends on the steric interactions between the benzo[c]cinnoline and the substituents at different positions. The interaction is greatest with the substituents at position 1. The corresponding α–γ angles are reported as 11.7° in (II), 14.32 (6) and 3.4 (1)° in (III), 1.8 (1)° in (IV), 1.32 (6)° in (V), 4.95 (7)° in (VI), 0.50 (7)° in (VII) and 8.4 (2)° in (VIII).

There are steric interactions between the H atoms at C1 and C10 (H1⋯H101 = 2.23 Å), and between the H atom at C7 and the O atom at N6 (O1⋯H71 = 2.38 Å). The benzo[c]cinnoline skeleton has enlarged C1—C12—C11 [124.6 (4)°] and C10—C11—C12 [124.9 (3)°] angles and smaller ones at the opposite side. The 6-oxide substituent generated enlarged N5—N6—C6 [124.1 (3)°], N6—C6—C7 [119.1 (3)°], C7—C6—C11 [122.2 (4)°] and N5—C5—C12 [124.2 (4)°], and narrowed N6—C6—C11 [118.7 (4)°] and C5—N5—N6 [117.6 (3)°] angles in the benzo[c]cinnoline skeleton with respect to the previously reported corresponding ones (Table 2).

The N6—O1 [1.268 (4) Å] bond length is highly shorter than the pyridine N-oxide N—O [1.304 (15) Å; Allen *et al.*, 1987], probably due to the electron resonating between the O atom and the benzo[c]cinnoline skeleton.

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 as determined crystallographically in all of the benzo[c]cinnoline ligands. This determination is in agreement with the theoretical calculations made by Mulliken (1955) and Hoffman (1963).

Crystal data

$C_{12}H_7BrN_2O$	$D_x = 1.813$ Mg m^{-3}
$M_r = 275.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 25
$a = 14.446$ (3) Å	reflections
$b = 3.963$ (1) Å	$\theta = 10-11°$
$c = 17.807$ (7) Å	$\mu = 4.05$ mm^{-1}
$\beta = 98.59$ (2)°	$T = 298$ K
$V = 1008.0$ (5) Å^3	Rod-shaped, yellow
$Z = 4$	$0.30 \times 0.10 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffract-ometer	$R_{int} = 0.014$
	$\theta_{max} = 26.3°$
$\omega/2\theta$ scans	$h = -18 \rightarrow 17$
Absorption correction: ψ scan (Fair, 1990)	$k = 0 \rightarrow 4$
	$l = 0 \rightarrow 22$
$T_{min} = 0.621$, $T_{max} = 0.667$	3 standard reflections
2420 measured reflections	frequency: 120 min
2031 independent reflections	intensity decay: 1%
1764 reflections with $F > 0$	

Refinement

Refinement on F	H-atom parameters constrained
$R = 0.058$	$w = 1 / [\sigma(F)^2 + (0.02\,F)^2 + 1.0]$
$wR = 0.051$	$(\Delta/\sigma)_{max} = 0.01$
$S = 1.12$	$\Delta\rho_{max} = 0.46$ e Å^{-3}
1764 reflections	$\Delta\rho_{min} = -0.51$ e Å^{-3}
145 parameters	

Table 1
Selected bond lengths (Å).

Br1—C2	1.892 (4)	C6—N6	1.426 (5)
N6—O1	1.268 (4)	C3—C4	1.359 (6)
C5—N5	1.377 (5)	C7—C8	1.358 (7)
N5—N6	1.298 (5)	C1—C2	1.368 (6)
C6—C7	1.389 (6)	C9—C10	1.367 (6)

Table 2
Comparison of the bond angles (°) in the benzo[c]cinnoline skeleton of (I) with the corresponding values in the related compounds (III), (IV), (V),(VI), (VII) and (VIII)..

Angles	(I)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
C5—C12—C11	116.9 (3)	115.1 (2)	117.7 (4)	116.0 (2)	116.1 (2)	117.0 (2)	116.5 (1)
C5—C12—C1	118.5 (4)	116.7 (2)	115.9 (4)	119.4 (2)	120.3 (2)	118.5 (3)	115.2 (2)
C11—C12—C1	124.6 (4)	128.0 (2)	126.3 (4)	124.7 (2)	123.7 (2)	124.5 (3)	128.4 (1)
C12—C11—C10	124.9 (3)	126.4 (2)	125.7 (4)	125.5 (2)	124.4 (2)	124.8 (2)	126.9 (2)
C12—C1—C2	119.6 (4)	119.2 (3)	121.6 (4)	120.6 (2)	118.4 (2)	117.7 (3)	123.5 (2)
C1—C2—C3	122.0 (4)	122.1 (3)	122.5 (4)	118.8 (2)	122.9 (2)	124.9 (3)	119.6 (2)
C2—C3—C4	118.7 (4)	119.8 (3)	116.6 (4)	120.8 (2)	121.6 (2)	118.3 (3)	119.7 (2)
C3—C4—C5	121.1 (4)	120.2 (3)	121.2 (4)	120.5 (2)	115.9 (2)	119.3 (3)	120.5 (2)
C6—C11—C12	118.4 (4)	117.3 (2)	116.7 (4)	116.3 (2)	127.1 (2)	116.4 (2)	115.6 (1)
C6—C11—C10	116.7 (4)	116.0 (2)	117.6 (5)	118.2 (2)	118.4 (2)	118.8 (3)	117.5 (2)
N5—N6—C6	124.1 (3)	119.6 (2)	119.5 (4)	119.7 (2)	119.9 (2)	120.5 (2)	120.6 (1)
N6—C6—C11	118.7 (4)	122.9 (2)	123.5 (4)	123.7 (2)	123.0 (2)	123.1 (3)	123.5 (2)
N6—C6—C7	119.1 (3)	115.2 (2)	115.4 (2)	116.2 (2)	116.2 (2)	116.7 (3)	115.9 (2)
C7—C6—C11	122.2 (4)	121.8 (2)	121.0 (5)	120.1 (2)	120.8 (2)	120.2 (3)	120.7 (2)
C5—N5—N6	117.6 (3)	121.5 (2)	121.1 (4)	120.3 (2)	121.5 (2)	120.2 (2)	120.0 (2)
N5—C5—C12	124.4 (4)	122.9 (4)	121.4 (4)	123.9 (2)	122.2 (2)	122.8 (3)	123.4 (2)

The positions of the H atoms were calculated geometrically at a distance of 0.95 Å from the corresponding C atom, and a riding model was used during their refinement.

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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