

hydrogène. La cohésion de la structure est due aux interactions de van der Waals.

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Structural Investigations of Benzo[c]cinnoline Derivatives. I. Structures of 1-Piperidinobenzo[c]cinnoline and 3-Piperidinobenzo[c]cinnoline

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Abstract. (1) $C_{17}H_{17}N_3$, $M_r = 263.34$, monoclinic, $P2_1/c$, $a = 8.473$ (3), $b = 11.556$ (4), $c = 13.933$ (6) Å, $\beta = 92.09$ (3)°, $V = 1363.3$ (3) Å³, $Z = 4$, $D_m = 1.27$, $D_x = 1.283$ g cm⁻³, $\lambda(Cu\text{ }K\alpha) = 1.54180$ Å, $\mu = 5.689$ cm⁻¹, $F(000) = 560$, $T = 293$ K, $R = 0.070$ for 1701 observed reflections [$I \geq 3\sigma(I)$]. (2) $C_{17}H_{17}N_3$, $M_r = 263.34$, triclinic, $P\bar{1}$, $a = 8.646$ (3), $b = 13.064$ (4), $c = 13.338$ (4) Å, $\alpha = 100.91$ (3), $\beta = 99.50$ (3), $\gamma = 106.03$ (3)°, $V = 1383.5$ (4) Å³, $Z = 4$, $D_m = 1.25$, $D_x = 1.264$ g cm⁻³, $\lambda(Cu\text{ }K\alpha) = 1.54180$ Å, $\mu = 5.606$ cm⁻¹, $F(000) = 560$, $T = 293$ K, $R = 0.059$ for 2040 observed reflections [$I \geq 3\sigma(I)$]. The rings in the benzo[c]cinnoline skeleton of (1) and (2) are close to planar, while the skeleton itself is non-planar. The dihedral angles between the rings in the benzo[c]cinnoline skeleton are between 6.59 (6) and 14.32 (6)° in (1) and between 1.0 (1) and 3.4 (1)° in the more planar (2). The difference is caused by steric interactions between the piperidino and benzo[c]cinnoline groups in (1). These interactions also cause the piperidino group in (1) to rotate out of the plane of the benzo[c]cinnoline group, while in (2) the whole molecule is close to planar.

The piperidino group adopts a slightly distorted chair conformation in both (1) and (2).

Introduction. Benzo[c]cinnoline and some of its derivatives can have mutagenic (Leary, Lafleur, Liber & Bleemann, 1983), antirheumatic (Matter, 1957; Erlenmeyer, 1958) and carcinogenic (Ashby, Styles & Paton, 1980) physiological properties. They have also been used as bleaching catalysts in the processing of photographic silver-dye bleach materials (Jan, 1980). The structure of benzo[c]cinnoline (van der Meer, 1972) has been reported previously. The crystal structures of 1-morpholinobenzo[c]cinnoline (Hökelek, Watkin, Kılıç & Tüzün, 1990) and 2- and 4-pyrrololidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991) have also been described. The structure determinations of the title compounds were undertaken to permit comparisons of the crystal structures of the benzo[c]cinnoline derivatives.

Experimental. (1): 1 mmol of 1-bromobenzo[c]cinnoline, prepared by bromination of benzo[c]cinnoline (Barton & Lapham, 1979), was mixed with 15 ml piperidine containing 5 ml Me₂SO and refluxed for 6 days. The product was purified by column chroma-

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tography and then recrystallized from *n*-hexane/ethanol and petroleum ether/diethyl ether, yielding yellow prismatic crystals. (2): 3-Bromo-benzo[c]cinnoline was obtained by reductive cyclization of 4-bromo-2,2'-dinitrobiphenyl (Barton & Lapham, 1979), 2 mmol was then mixed with 20 ml piperidine containing 10 ml Me₂SO and refluxed for 9 days. The product was purified by column chromatography and recrystallized first from *n*-hexane/ethanol and then from 2-propanol, yielding orange rod-shaped crystals. Experimental data, methods used to solve the structures and other related parameters and procedures are given in Table 1. No absorption correction was applied due to the low absorption coefficient for the compounds. Since difference syntheses did not clearly show the positions of the H atoms they were placed in calculated positions at a distance of 1.0 Å from the corresponding C atoms. A riding model was used in the refinement of the H positions. Isotropic displacement parameters of the H atoms were taken as *U* = 0.05 Å² in (1) and 1.3 times the corresponding displacement parameters of the connecting non-H atoms in (2). Initially a unit-weighting scheme was used, but in the final stages of the refinement the weights were assigned using the method described by Carruthers & Watkin (1979), as incorporated into the CRYSTALS package of programs (Watkin, Carruthers & Betteridge, 1985).

Discussion. The final coordinates and equivalent isotropic displacement parameters for (1) and (2) are given in Table 2.* Bond lengths and angles are given in Table 3 and the atom-numbering schemes in Fig. 1. The rings in the benzo[c]cinnoline group are planar in (2) with a maximum distance to the least-squares plane of 0.015 (4) Å. In (1) only ring α (C8—C9—C10—C11—C12—C13) is planar while the other two are close to planar, the maximum distance to the least-squares plane being 0.050 (3) Å for ring β (C5—N6—N7—C8—C13—C14) and 0.037 (3) Å for ring γ (C1—C2—C3—C4—C5—C14). The rings are also twisted with respect to each other. The dihedral angles between the least-squares planes are $\alpha - \beta = 7.74$ (9), $\alpha - \gamma = 14.32$ (6) and $\beta - \gamma = 6.59$ (6)°. In (2), the corresponding dihedral angles are smaller for both molecules. The values are $\alpha - \beta = 1.5$ (1) and 1.0 (1), $\alpha - \gamma = 3.4$ (1) and 1.8 (1), and $\beta - \gamma = 1.9$ (1) and 1.8 (1)°, for molecules *A* and *B*, respec-

Table 1. *Experimental data and structure-refinement parameters*

	(1)	(2)
Method of measuring <i>D_m</i>	Flotation in aqueous KI	
Crystal shape and size (mm)	Prismatic 0.25 × 0.25 × 0.6	Rod-shaped 0.1 × 0.2 × 0.5
Data-collection technique, diffractometer	ω -2θ scan, four-circle diffractometer (Enraf-Nonius CAD-4)	
Number and θ range (°) of reflections for measuring lattice parameters	25 reflections with $48 \leq 2\theta \leq 86$	7 ≤ 2θ ≤ 60
Max. ($\sin\theta/\lambda$) (Å ⁻¹)	0.617	
Range of <i>h</i> , <i>k</i> and <i>l</i>	$-1 \leq h \leq 10$, $-1 \leq k \leq 14$, $-17 \leq l \leq 17$ $16\bar{1}, \bar{1}1, \bar{1}\bar{2},$ $34\bar{2}, \pm 1$	$-1 \leq h \leq 10$, $-16 \leq k \leq 16$, $-16 \leq l \leq 16$ $\bar{2}10, 2\bar{1}0,$ $040, \pm 1$
Standard reflections and their intensity variation throughout experiment (%)		
Number of reflections measured	3871	6815
Number of unique reflections	2685	5428
Number of unobserved reflections	984	3388
Number of reflections used in the refinement	1701	2040
Criterion for recognizing unobserved reflections	$I \leq 3\sigma(I)$	
Method used to solve structure		Direct methods (see below)
Use of <i>F</i> or <i>F</i> ² magnitudes in least-squares refinement		<i>F</i>
Parameters refined	Coordinates and anisotropic temperature factors of non-H atoms	
Values of <i>R</i> , <i>wR</i>	181 0.070, 0.081 + 0.53, - 0.53	361 0.059, 0.075 + 1.55, - 1.55
Final residual electron densities (e Å ⁻³) for max. and min. peaks		
Max. (Δ/σ)	0.004	0.082
Source of atomic scattering factors		International Tables for X-ray Crystallography (1974, Vol. IV)
Computer programs used		SHELXS86 (Sheldrick, 1986), CRYSTALS (Watkins, Carruthers & Betteridge, 1985), SNOOPI (Davies, 1983)

tively. As can be seen from these values, the ring system is more twisted in (1) than in (2). In benzo[c]cinnoline (van der Meer, 1972) the dihedral angle between the two benzenoid rings is $\alpha - \gamma = 2.5^\circ$ which is close to the values found in (2). The large dihedral angles in (1) probably result from steric interactions between the benzo[c]cinnoline group and the piperidino group in position 1. This interaction is also clearly seen from the dihedral angle between ring β and the piperidino group which is 43.2 (1)° in (1) and 9.2 (1) and 15.7 (1)° in (2). In summary, this results in a rather planar appearance of (2) while in (1) the piperidino group is rotated out of the plane of the benzo[c]cinnoline group. The steric interaction between the H atom at C12 and the piperidino group at C1 in (1) and H atom in (2) also generates enlarged angles C12—C13—C14 and C13—C14—C1 and smaller angles at the opposite side of the benzo[c]cinnoline group (see Table 2). This effect is in

* Lists of structure factors, anisotropic thermal parameters bond lengths and angles including H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53224 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) with e.s.d.'s in parentheses

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
1-Piperidinobenzo[<i>c</i>]cinnoline (1)				
C1	2778 (3)	1035 (2)	4629 (2)	456 (13)
C2	2098 (3)	-16 (3)	4821 (2)	557 (15)
C3	2479 (3)	-640 (3)	5663 (2)	575 (17)
C4	3495 (3)	-185 (3)	6331 (2)	581 (17)
C5	4236 (3)	869 (2)	6163 (2)	504 (14)
N6	5257 (3)	1258 (2)	6897 (2)	593 (14)
N7	6081 (3)	2181 (2)	6805 (2)	591 (14)
C8	6023 (3)	2774 (2)	5935 (2)	478 (13)
C9	7121 (4)	3665 (3)	5862 (2)	559 (16)
C10	7251 (4)	4256 (3)	5014 (2)	588 (17)
C11	6270 (3)	3946 (3)	4231 (2)	544 (15)
C12	5170 (3)	3089 (2)	4291 (2)	469 (13)
C13	4990 (3)	2463 (2)	5155 (2)	419 (12)
C14	3961 (3)	1493 (2)	5290 (2)	436 (13)
N15	2345 (2)	1671 (2)	3789 (1)	468 (10)
C16	1605 (3)	1010 (2)	2991 (2)	540 (15)
C17	1534 (4)	1747 (3)	2090 (2)	615 (17)
C18	620 (4)	2858 (3)	2237 (2)	683 (20)
C19	1296 (4)	3505 (3)	3112 (2)	597 (17)
C20	1431 (3)	2724 (2)	3987 (2)	536 (15)

3-Piperidinobenzo[*c*]cinnoline (2)

Molecule A

C1	3836 (5)	4509 (3)	6240 (4)	780 (32)
C2	2935 (5)	4364 (3)	5264 (4)	725 (30)
C3	2692 (5)	5256 (3)	4863 (3)	649 (26)
C4	3492 (5)	6299 (3)	5507 (3)	655 (26)
C5	4435 (5)	6453 (3)	6502 (3)	637 (26)
N6	5202 (4)	7548 (3)	7089 (3)	806 (26)
N7	6083 (5)	7775 (3)	8025 (3)	924 (29)
C8	6267 (5)	6920 (4)	8475 (4)	763 (33)
C9	7240 (6)	7248 (5)	9508 (4)	985 (41)
C10	7471 (7)	6467 (6)	10027 (4)	1067 (45)
C11	6732 (7)	5357 (6)	9525 (5)	1176 (52)
C12	5803 (6)	5026 (4)	8513 (4)	960 (38)
C13	5545 (5)	5806 (4)	7956 (4)	731 (31)
C14	4620 (5)	5563 (3)	6915 (3)	657 (27)
N15	1754 (4)	5078 (2)	3864 (3)	728 (24)
C16	1402 (7)	6006 (4)	3555 (4)	1007 (40)
C17	613 (8)	5834 (4)	2464 (5)	1190 (49)
C18	-677 (7)	4758 (5)	1956 (4)	1127 (45)
C19	-259 (8)	3831 (4)	2278 (4)	1122 (43)
C20	541 (7)	4026 (4)	3377 (4)	1002 (38)

Molecule B

C21	3765 (5)	1301 (3)	5235 (3)	634 (26)
C22	4918 (5)	1388 (3)	6096 (3)	655 (27)
C23	4612 (5)	1560 (3)	7115 (3)	683 (29)
C24	3080 (5)	1663 (3)	7207 (3)	688 (29)
C25	1895 (5)	1570 (3)	6326 (3)	619 (28)
N26	383 (5)	1646 (3)	6517 (3)	740 (26)
N27	-805 (5)	1536 (3)	5746 (3)	756 (27)
C28	-607 (5)	1366 (3)	4713 (4)	648 (28)
C29	-1974 (5)	1270 (3)	3924 (4)	756 (32)
C30	-1852 (6)	1126 (3)	2920 (4)	855 (34)
C31	-385 (6)	1047 (4)	2647 (4)	864 (33)
C32	959 (5)	1119 (3)	3403 (3)	691 (28)
C33	880 (5)	1285 (3)	4459 (3)	600 (26)
C34	2186 (5)	1381 (3)	5313 (3)	560 (24)
N35	5834 (5)	1641 (3)	7971 (3)	865 (30)
C36	5433 (8)	1788 (6)	8992 (4)	1195 (57)
C37	6641 (12)	1902 (8)	9827 (5)	1621 (95)
C38	7713 (9)	1170 (6)	9716 (4)	1205 (54)
C39	8148 (8)	1065 (6)	8655 (4)	1246 (57)
C40	6897 (8)	957 (6)	7834 (4)	1175 (58)

Table 3. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

	(1)	(2A)	(2B)
C1—C2	1.375 (4)	1.352 (6)	1.355 (5)
C1—C14	1.436 (3)	1.407 (6)	1.417 (5)
C1—N15	1.419 (3)	—	1.415 (5)
C3—N15	—	1.382 (5)	1.388 (5)
C2—C3	1.405 (4)	1.422 (5)	1.391 (5)
C3—C4	1.351 (4)	1.383 (5)	1.387 (6)
C4—C5	1.395 (4)	1.386 (5)	1.403 (5)
C5—C14	1.425 (3)	1.413 (5)	1.399 (5)
C5—N6	1.389 (4)	1.407 (5)	1.284 (5)
N6—N7	1.283 (4)	1.284 (5)	1.400 (5)
N7—C8	1.393 (3)	1.397 (5)	1.407 (6)
C8—C9	1.393 (4)	1.410 (6)	1.409 (5)
C8—C13	1.417 (3)	1.401 (6)	1.342 (6)
C9—C10	1.373 (4)	1.376 (7)	1.401 (6)
C10—C11	1.393 (4)	1.393 (8)	1.376 (6)
C11—C12	1.365 (4)	1.373 (7)	1.399 (5)
C12—C13	1.418 (3)	1.413 (6)	1.426 (5)
C13—C14	1.436 (3)	1.411 (5)	1.451 (6)
N15—C16	1.470 (3)	1.442 (5)	1.457 (6)
N15—C20	1.474 (3)	1.432 (5)	1.349 (8)
C16—C17	1.517 (4)	1.449 (7)	1.509 (8)
C17—C18	1.517 (5)	1.484 (7)	1.515 (7)
C18—C19	1.524 (4)	1.473 (7)	1.362 (7)
C19—C20	1.517 (4)	1.456 (6)	—
C2—C1—N15	121.3 (2)	—	C22—C21—C34
C2—C1—C14	119.2 (3)	121.6 (4)	C21—C22—C23
C14—C1—N15	119.4 (2)	—	C22—C23—C24
C1—C2—C3	122.1 (3)	122.5 (4)	C22—C23—N35
C2—C3—C4	119.8 (3)	116.6 (4)	C24—C23—N35
C2—C3—N15	121.0 (4)	120.8 (4)	C23—C24—C25
C4—C3—N15	122.4 (4)	122.0 (4)	C24—C25—C34
C3—C4—C5	120.2 (3)	121.2 (4)	C24—C25—N26
C4—C5—N6	115.5 (2)	116.5 (4)	C34—C25—N26
C4—C5—C14	121.6 (3)	122.2 (4)	C25—N26—N27
N6—C5—C14	122.9 (3)	121.4 (4)	N26—N27—C28
C5—N6—N7	121.5 (2)	121.1 (4)	N27—C28—C33
N6—N7—C8	119.6 (2)	119.5 (4)	N27—C28—C29
N7—C8—C9	115.2 (2)	115.4 (5)	C29—C28—C33
N7—C8—C13	122.9 (2)	123.5 (4)	C28—C29—C30
C9—C8—C13	121.8 (2)	121.0 (5)	C29—C30—C31
C8—C9—C10	120.3 (2)	119.9 (6)	C30—C31—C32
C9—C10—C11	118.8 (3)	119.5 (6)	C31—C32—C33
C10—C11—C12	121.9 (3)	121.2 (6)	C28—C33—C34
C11—C12—C13	121.2 (2)	120.8 (5)	C32—C33—C28
C8—C13—C12	116.0 (2)	117.6 (5)	C32—C33—C34
C8—C13—C14	117.3 (2)	116.7 (4)	C21—C34—C25
C12—C13—C14	126.4 (2)	125.7 (4)	C21—C34—C33
C1—C14—C5	116.7 (2)	115.9 (4)	C25—C34—C33
C1—C14—C13	128.0 (2)	126.3 (4)	C23—N35—C36
C5—C14—C13	115.1 (2)	117.7 (4)	C23—N35—C40
C1—N15—C16	116.4 (2)	—	C36—N35—C40
C1—N15—C20	113.2 (2)	—	N35—C36—C37
C3—N15—C16	117.8 (4)	—	C36—C37—C38
C3—N15—C20	119.3 (4)	—	C37—C38—C39
C16—N15—C20	116.0 (2)	116.0 (4)	C38—C39—C40
N15—C16—C17	109.7 (2)	116.8 (4)	C39—C40—N35
C16—C17—C18	111.6 (3)	116.8 (5)	—
C17—C18—C19	110.1 (2)	113.0 (5)	—
C18—C19—C20	111.5 (2)	116.4 (5)	—
C19—C20—N15	111.4 (2)	117.2 (4)	—
accordance with what was found in benzo[<i>c</i>]cinnoline (van der Meer, 1972). The bond lengths C1—C2, C3—C4, C9—C10 and C11—C12 are generally shorter than the other bonds, which have also been shown by theoretical calculations (Mulliken, 1955; Hoffman, 1963) and experimentally determined in benzo[<i>c</i>]cinnoline (van der Meer, 1972). In both (1) and (2), the piperidino groups form a slightly dis-			

torted chair. The magnitude of the distortion can be described by the parameter $\theta = 5^\circ$ for the piperidino groups in (1) and (2) (Cremer & Pople, 1975); $\theta = 0^\circ$ for a perfect chair and 90° for a perfect boat. The high displacement parameters of many atoms in the piperidino groups of (2) indicate disorder in the positions of these groups. The location of the highest residual electron density is at the C37 position. The crystal packings, which are consistent with van der Waals interactions only, are shown in Fig. 2 for (1) and (2).

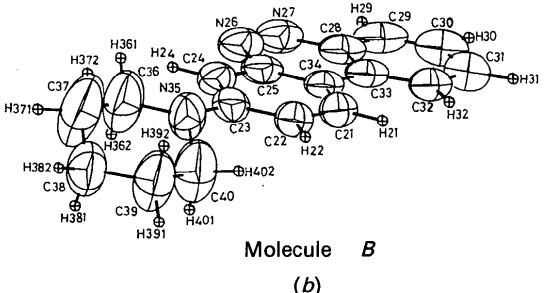
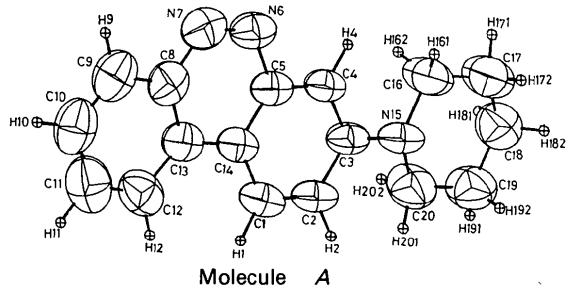
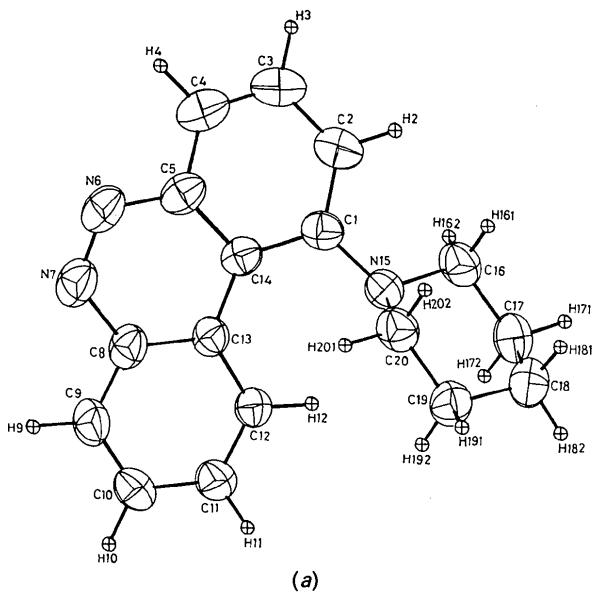


Fig. 1. SNOOPI (Davies, 1983) drawings of (a) (1) and (b) (2) with the atom-numbering schemes. The thermal ellipsoids are drawn at the 50% probability level.

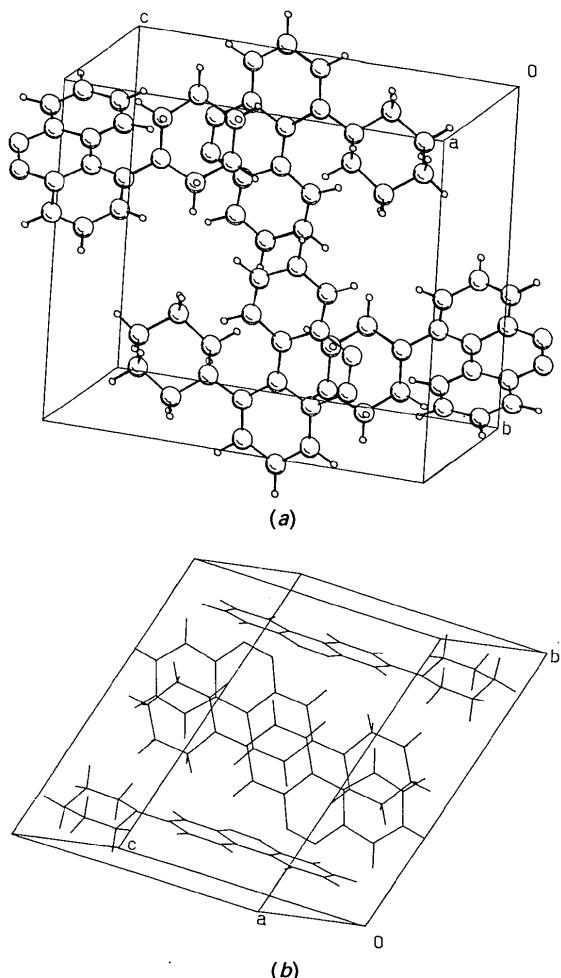


Fig. 2. The overall packing diagrams of the (a) (1) and (b) (2).

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Structural Investigations of Benzo[c]cinnoline Derivatives. II. Structures of 2-Pyrrolidinobenzo[c]cinnoline and 4-Pyrrolidinobenzo[c]cinnoline

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Abstract. (1) $C_{16}H_{15}N_3$, $M_r = 249.32$, monoclinic, $P2_1/c$, $a = 12.325$ (2), $b = 12.579$ (2), $c = 8.710$ (2) Å, $\beta = 106.41$ (1)°, $V = 1295.3$ (2) Å³, $Z = 4$, $D_m = 1.26$, $D_x = 1.278$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54180$ Å, $\mu = 5.726$ cm⁻¹, $F(000) = 528$, $T = 293$ K, $R = 0.056$ for 1817 observed reflections [$I \geq 3\sigma(I)$]. (2) $C_{16}H_{15}N_3$, $M_r = 249.32$, orthorhombic, $P2_12_12_1$, $a = 8.180$ (1), $b = 11.771$ (2), $c = 13.430$ (2) Å, $V = 1293.1$ (2) Å³, $Z = 4$, $D_m = 1.27$, $D_x = 1.281$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54180$ Å, $\mu = 5.734$ cm⁻¹, $F(000) = 528$, $T = 293$ K, $R = 0.039$ for 1253 observed reflections [$I \geq 3\sigma(I)$]. The rings in the benzo[c]cinnoline skeleton are close to planar in (1) with dihedral angles of 0.27 (7)–1.25 (6)° compared to angles of 2.1 (2)–4.95 (7)° in (2). The pyrrolidino ring in (1) is close to planar with a maximum deviation from the least-squares plane of 0.042 (3) Å. In (2), the pyrrolidino group adopts a puckered conformation with distances between –0.201 (2) and 0.507 (2) Å from the least-squares plane.

Introduction. Benzo[c]cinnoline and some of its derivatives can have mutagenic (Leary, Lafleur, Liber & Bleemann, 1983), antirheumatic (Matter, 1957; Erlenmeyer, 1958) and carcinogenic (Ashby, Styles & Paton, 1980) physiological activities. They have also been used as bleaching catalysts in the processing of photographic silver-dye bleach materials (Jan, 1980). The structures of benzo[c]cinnoline (van der Meer, 1972), 1-morpholinobenzo[c]cinnoline

(Hökelek, Watkin, Kılıç & Tüzün, 1990) and 1- and 3-piperidinobenzo[c]cinnolines (Hökelek, Kılıç & Tüzün, 1991) have been reported previously. The structure determinations of the title compounds were undertaken in order to study the effects of changing the positions of the substituents.

Experimental. 2-Bromobenzo[c]cinnoline was synthesized from 2-aminobenzo[c]cinnoline by the methods described by Holt & Oakland (1966) while 4-bromobenzo[c]cinnoline was isolated from a mixture obtained by bromination of benzo[c]cinnoline (Barton & Lapham, 1979). (1) and (2) were then obtained by mixing 1 mmol of the corresponding bromobenzo[c]cinnoline with 10 ml pyrrolidine and refluxing for 12 and 8 h, respectively. The crude products were recrystallized first from ethanol/water and then from ethanol (1), and from ethanol and dichloromethane/ethanol (2). Yellow prismatic crystals of (1) and yellow rod-shaped crystals of (2) were obtained within 2 days. Experimental data, the method used to solve structures and other relevant information are given in Table 1. Non-H atoms were included with anisotropic displacement parameters. Difference syntheses showed the location of some H atoms which were refined isotropically, the rest were placed in calculated positions (C—H = 1.0 Å). A riding model was used in the refinement of these H positions. Isotropic displacement parameters of H atoms, which cannot be obtained from difference syntheses, are taken as 1.3 times the corresponding displacement parameters of the connecting non-H

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