

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, $\lambda(Cu K\alpha) = 1.54180$ 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, $\lambda(Cu K\alpha) = 1.54180$ 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 & Blemann, 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-pyrrolidinobenzo[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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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
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
1-Piperidinobenzo[c]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)	C21—C22	1.355 (5)
C1—C14	1.436 (3)	1.407 (6)	C21—C34	1.417 (5)
C1—N15	1.419 (3)	—	C22—C23	1.415 (5)
C3—N15	—	1.382 (5)	C23—N35	1.388 (5)
C2—C3	1.405 (4)	1.422 (5)	C23—C24	1.391 (5)
C3—C4	1.351 (4)	1.383 (5)	C24—C25	1.387 (6)
C4—C5	1.395 (4)	1.386 (5)	C25—C34	1.403 (5)
C5—C14	1.425 (3)	1.413 (5)	C25—N26	1.399 (5)
C5—N6	1.389 (4)	1.407 (5)	N26—N27	1.284 (5)
N6—N7	1.283 (4)	1.284 (5)	N27—C28	1.400 (5)
N7—C8	1.393 (3)	1.397 (5)	C28—C29	1.407 (6)
C8—C9	1.393 (4)	1.410 (6)	C28—C33	1.409 (5)
C8—C13	1.417 (3)	1.401 (6)	C29—C30	1.342 (6)
C9—C10	1.373 (4)	1.376 (7)	C30—C31	1.401 (6)
C10—C11	1.393 (4)	1.393 (8)	C31—C32	1.376 (6)
C11—C12	1.365 (4)	1.373 (7)	C32—C33	1.399 (5)
C12—C13	1.418 (3)	1.413 (6)	C33—C34	1.426 (5)
C13—C14	1.436 (3)	1.411 (5)	N35—C36	1.451 (6)
C15—C16	1.470 (3)	1.442 (5)	N35—C40	1.457 (6)
N15—C20	1.474 (3)	1.432 (5)	C36—C37	1.349 (8)
C16—C17	1.517 (4)	1.449 (7)	C37—C38	1.509 (8)
C17—C18	1.517 (5)	1.484 (7)	C38—C39	1.515 (7)
C18—C19	1.524 (4)	1.473 (7)	C39—C40	1.362 (7)
C19—C20	1.517 (4)	1.456 (6)		
C2—C1—N15	121.3 (2)		C22—C21—C34	121.3 (4)
C2—C1—C14	119.2 (3)	121.6 (4)	C21—C22—C23	122.0 (4)
C14—C1—N15	119.4 (2)		C22—C23—C24	117.3 (4)
C1—C2—C3	122.1 (3)	122.5 (4)	C22—C23—N35	119.7 (4)
C2—C3—C4	119.8 (3)	116.6 (4)	C24—C23—N35	123.0 (4)
C2—C3—N15		121.0 (4)	C23—C24—C25	120.8 (4)
C4—C3—N15		122.4 (4)	C24—C25—C34	122.0 (4)
C3—C4—C5	120.2 (3)	121.2 (4)	C24—C25—N26	115.3 (4)
C4—C5—N6	115.5 (2)	116.5 (4)	C34—C25—N26	122.6 (4)
C4—C5—C14	121.6 (3)	122.2 (4)	C25—N26—N27	119.8 (4)
N6—C5—C14	122.9 (3)	121.4 (4)	N26—N27—C28	121.2 (4)
C5—N6—N7	121.5 (2)	121.1 (4)	N27—C28—C33	122.3 (4)
N6—N7—C8	119.6 (2)	119.5 (4)	N27—C28—C29	117.0 (4)
N7—C8—C9	115.2 (2)	115.4 (5)	C29—C28—C33	120.7 (4)
N7—C8—C13	122.9 (2)	123.5 (4)	C28—C29—C30	119.8 (4)
C9—C8—C13	121.8 (2)	121.0 (5)	C29—C30—C31	120.6 (5)
C8—C9—C10	120.3 (2)	119.9 (6)	C30—C31—C32	120.7 (5)
C9—C10—C11	118.8 (3)	119.5 (6)	C31—C32—C33	120.2 (4)
C10—C11—C12	121.9 (3)	121.2 (6)	C28—C33—C34	116.4 (4)
C11—C12—C13	121.2 (2)	120.8 (5)	C32—C33—C28	118.0 (4)
C8—C13—C12	116.0 (2)	117.6 (5)	C32—C33—C34	125.5 (4)
C8—C13—C14	117.3 (2)	116.7 (4)	C21—C34—C25	116.5 (4)
C12—C13—C14	126.4 (2)	125.7 (4)	C21—C34—C33	125.9 (4)
C1—C14—C5	116.7 (2)	115.9 (4)	C25—C34—C33	117.6 (4)
C1—C14—C13	128.0 (2)	126.3 (4)	C23—N35—C36	117.2 (4)
C5—C14—C13	115.1 (2)	117.7 (4)	C23—N35—C40	118.4 (4)
C1—N15—C16	116.4 (2)		C36—N35—C40	113.8 (4)
C1—N15—C20	113.2 (2)		N35—C36—C37	117.1 (6)
C3—N15—C16		117.8 (4)	C36—C37—C38	118.1 (6)
C3—N15—C20		119.3 (4)	C37—C38—C39	110.2 (5)
C16—N15—C20	111.0 (2)	116.0 (4)	C38—C39—C40	115.4 (6)
N15—C16—C17	109.7 (2)	116.8 (4)	C39—C40—N35	118.8 (5)
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[c]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[c]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 $\theta \approx 5^\circ$ 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).

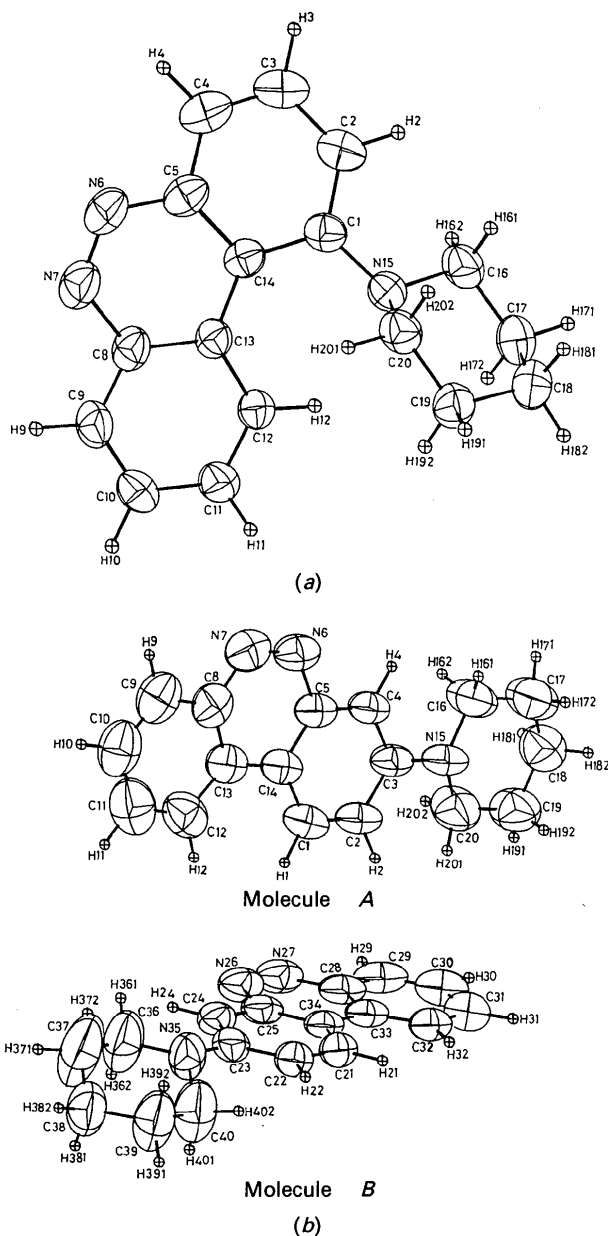


Fig. 1. *SNOOPI* (Davies, 1983) drawings of (a) (1) and (b) (2) with the atom-numbering schemes. The thermal ellipsoids are drawn at the 50% probability level.

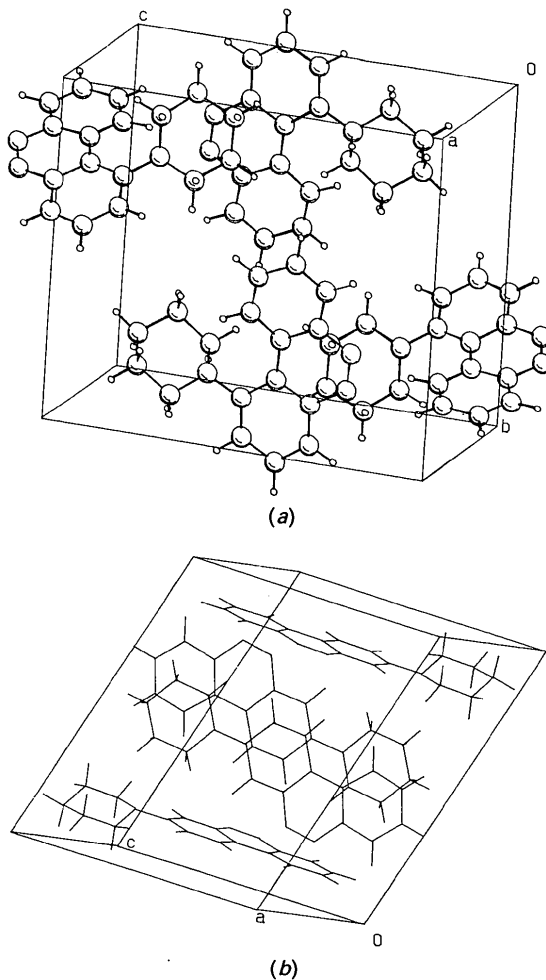


Fig. 2. The overall packing diagrams of the (a) (1) and (b) (2).

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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, $\lambda(\text{Cu } K\alpha) = 1.54180$ 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, $\lambda(\text{Cu } K\alpha) = 1.54180$ 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 & Blemann, 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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