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, $\beta = 92.09 (3)^{\circ}, V = 1363.3 (3) \text{ Å}^3, Z = 4, D_m = 1.27, D_x = 1.283 \text{ g cm}^{-3}, \lambda(\text{Cu } K\alpha) = 1.54180 \text{ Å}, \mu =$ 5.689 cm^{-1} , F(000) = 560, T = 293 K, R = 0.070 for1701 observed reflections $[I \ge 3\sigma(I)]$. (2) $C_{17}H_{17}N_3$, $M_r = 263.34$, triclinic, $P\overline{1}$, 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, $D_x = 1.264 \text{ g cm}^{-3}$, $D_m = 1.25$, $\lambda(Cu K\alpha) =$ $1.54180 \text{ Å}, \quad \mu = 5.606 \text{ cm}^{-1}, \quad F(000) = 560, \quad T = 1.54180 \text{ Å}, \quad \mu = 5.606 \text{ cm}^{-1}, \quad F(000) = 5.60, \quad T = 1.54180 \text{ Å}, \quad \mu = 5.606 \text{ cm}^{-1}, \quad F(000) = 5.60, \quad T = 1.54180 \text{ Å}, \quad \mu = 5.606 \text{ cm}^{-1}, \quad F(000) = 5.60, \quad T = 1.54180 \text{ Å}, \quad \mu = 5.606 \text{ cm}^{-1}, \quad F(000) = 5.60, \quad T = 1.54180 \text{ Å}, \quad \mu = 5.606 \text{ cm}^{-1}, \quad F(000) = 5.60, \quad T = 1.54180 \text{ Å}, \quad \mu = 5.606 \text{ cm}^{-1}, \quad F(000) = 5.606 \text{ cm}^{-1}, \quad F(000$ 293 K, R = 0.059 for 2040 observed reflections $I \ge 1$ $3\sigma(I)$]. The rings in the benzo clean 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 $3.4(1)^{\circ}$ 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 2and 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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tography and then recrystallized from *n*-hexane/ ethanol and petroleum ether/diethyl ether, yielding prismatic crystals. (2): 3-Bromoyellow 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 Å^2 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 $(C^{8}-C^{9}-C^{10}-C^{11}-C^{12}-C^{13})$ is planar α 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 $1.8(1)^{\circ}$, for molecules A and B, respec-

Table 1. Experimental data and structure-refinement parameters

Mahada Garaganing D	(1)	(2)				
Crystal shape and and size (mm)	Prismatic $0.25 \times 0.25 \times 0.6$	Rod-shaped $0.1 \times 0.2 \times 0.5$				
Data-collection technique, diffractometer	$\omega - 2\theta$ scan, four-circle diffractometer (Enraf-Nonius CAD-4)					
Number and θ range (°) of reflections for measuring lattice parameters	$25 ext{ reflecti}$ $48 \le 2\theta \le 86$	$7 \le 2\theta \le 60$				
Max. $(\sin\theta/\lambda)$ (Å ⁻¹)	0.617					
Range of h k and l	$-1 \le h \le 10$	$-1 \le h \le 10$.				
range of it, it and t	$-1 \le k \le 14$	$-16 \le k \le 16$				
	-17 < l < 17	$-16 \le l \le 16$				
Standard reflections and	161 1 17	710 210				
their intensity variation	347 + 1	040 + 1				
throughout experiment (%)	J42, ± 1	040, -1				
Number of reflections	3871	6815				
Number of unique	2685	5428				
reflections	2005	0.20				
Number of unobserved	984	3388				
reflections	284	5566				
Number of reflections wood	1701	2040				
Number of reflections used	1701	2040				
in the refinement	t = 2 - (D					
Criterion for recognizing	$I \leq 3\sigma(I)$					
unobserved reflections						
Method used to	Direct methods (see below)					
solve structure	_					
Use of F or F ² magnitudes in least-squares	F					
Parameters refined	Coordinates and ani	sotronic temperature				
ratanicers tenned	factors of n	tors of non-H atoms				
Maluar of DD		0.050 0.075				
values of <i>R</i> , <i>wR</i>	0.070, 0.081	0.039, 0.075				
Final residual electron densities (e $Å^{-3}$) for max, and min, peaks	+0.53, -0.53	+ 1.55, - 1.55				
Max (A/σ)	0.004	0.082				
Source of atomic	Internation	ternational Tables for X-ray				
scattering factors	Crystallogr	mhv (1974 Vol. IV)				
Computer programs	Crystatiography (1974, VOL IV) CHELYCS6 (Shaldrick 1094)					
weed	CRVSTALS (Watking Computance					
usuu	Betteridge 1985) SNOOPI (Day					
	benefuge, 19	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 $15.7(1)^{\circ}$ 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 $(\mathring{A}^2 \times 10^4)$ withTable 3. Bond lengths (\mathring{A}) and angles (\circ) with e.s.d.'s
in parentheses

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	e.s.d.'s in parentheses							(2, 1)		(2 D)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$U_{\rm eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$				C1—C2 C1—C14 C1—N15	(1) 1·375 (4) 1·436 (3) 1·419 (3)	(2 <i>A</i>) 1·352 (6) 1·407 (6)	C21—C22 C21—C34 C22—C23	(2B) 1·355 (5) 1·417 (5) 1·415 (5)		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	x y z			$U_{ m eq}$	C3—N15 C2—C3	 1·405 (4)	1·382 (5) 1·422 (5)	C23—N35 C23—C24	1·388 (5) 1·391 (5)		
Cl 2778 (b) 1653 (c) 4629 (c) 456 (c) C-C 477 (c) 1386 (b) 1386 (c) C2 -C 41 (c) 1496 (c) 1497 (c) 1387 (c) 1284 (c) 1497 (c) 1397 (c) 1284 (c) 1497 (c) 1597 (c) 15	I-Piperio	ainobenzo[c]cinn	oline (1)			C3—C4	1.351 (4)	1.383 (5)	C24—C25	1.387 (6)	
C2 2998 (3) -16 (3) 422 (2) 57 (15) C3-C14 1425 (3) 1431 (5) N23-C29 1394 (C5 4256 (3) -160 (3) 053 (2) 381 (10) N3-C2 1333 (3) 1336 (3) N23-C29 1400 (C5 4256 (3) -120 (5) 1234 (3) 1235 (2) 6372 (2) 333 (10) N3-C29 1400 (5) N23-C29 1400 (7) N3-C29 1400	Cl	2778 (3)	1035 (2)	4629 (2)	456 (13)	C4—C5	1.395 (4)	1.386 (5)	C25—C34	1.403 (5)	
$ \begin{array}{c} C_{1} & 2479 (3) & -640 (3) & 5663 (2) & 575 (17) & C_{2} - K6 & 1339 (4) & 1407 (6) & N26 - N27 & 1284 (4) \\ C_{3} & 4233 (3) & -183 (13) & 1284 (5) & N26 - N27 & 1284 (4) \\ C_{4} & 4233 (3) & 1284 (3) & 1284 (5) & N26 - N27 & 1407 (4) \\ C_{5} & 4233 (3) & 2774 (2) & 995 (2) & 491 (4) & C_{7} - C_{3} & 1337 (4) & 1397 (6) & C_{28} - C_{29} & 1407 (4) \\ C_{7} & 7124 (4) & 3456 (3) & 592 (2) & 599 (2) & 478 (13) & C_{7} - C_{3} & 1373 (4) & 1397 (6) & C_{28} - C_{29} & 1407 (4) \\ C_{9} & 7221 (4) & 4256 (3) & 592 (2) & 599 (6) & C_{10} - C_{11} & 1333 (4) & 1397 (6) & C_{28} - C_{21} & 1436 (6) \\ C_{11} & 2731 (4) & 4256 (3) & 592 (2) & 599 (1) & 446 (13) & C_{13} - C_{14} & 1436 (6) & 1411 (6) & N33 - C6 & 1431 (6) \\ C_{14} & 393 (13) & 4499 (2) & 2390 (2) & 446 (13) & C_{13} - C_{14} & 1436 (6) & 1411 (6) & N33 - C6 & 1431 (6) \\ C_{14} & 393 (13) & 4399 (2) & 4391 (2) & 440 (13) & N13 - C_{21} & 1438 (4) & 1431 (6) & C_{13} - C_{14} & 1436 (7) \\ C_{14} & 393 (13) & 4393 (2) & 2390 (2) & 446 (10) & C_{16} - C_{17} & 1337 (4) & 1449 (7) & C_{28} - C_{29} & 1515 (7) \\ N_{15} & 2345 (2) & 1677 (2) & 7799 (1) & 468 (10) & C_{16} - C_{17} & 1537 (4) & 1439 (7) & C_{28} - C_{29} & 1531 (2) \\ C_{14} & 1436 (13) & 113 - C & 397 (17) \\ C_{16} & 1605 (3) & 1100 (2) & 2990 (2) & 615 (17) & C_{18} - C_{18} & 1517 (6) & 1444 (7) & C_{28} - C_{29} & 1536 (1) \\ C_{14} & C_{$	C2	2098 (3)	- 16 (3)	4821 (2)	557 (15)	C5—C14	1.425 (3)	1.413 (5)	C25—N26	1.399 (5)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C3	2479 (3)	- 640 (3)	5663 (2)	575 (17)	C5—N6	1.389 (4)	1.407 (5)	N26—N27	1.284 (5)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4	3495 (3)	- 185 (3)	6331 (2)	581 (17)	N6—N7	1.283 (4)	1.284 (5)	N27—C28	1.400 (5)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C5	4236 (3)	869 (2)	6163 (2)	504 (14)	N7—C8	1.393 (3)	1.397 (5)	C28—C29	1.407 (6)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N6	5257 (3)	1258 (2)	6897 (2)	593 (14)	C8—C9	1.393 (4)	1·410 (6)	C28—C33	1.409 (5)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N7	6081 (3)	2181 (2)	6805 (2)	591 (14)	C8-C13	1.417 (3)	1.401 (6)	C29—C30	1.342 (6)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C8	6023 (3)	2774 (2)	5935 (2)	478 (13)	C9C10	1.373 (4)	1.376 (7)	C30C31	1.401 (6)	
Cli 231 (d) 225 (d) 425 (d) 501 (d) 588 (f) Cli -Cl2 1346 (d) 137 (Cli -Cl2 1346 (d) 138 (d) 141 (d) 15 (d) 33-Cd6 143 (d) 141 (d) 16 (d) 122 (d) 143 (d) 141 (d) 16 (d) 122 (d) 123 (d) 143 (d) 141 (d) 16 (d) 122 (d) 143 (d) 141 (d) 174 (d) 123 (d) 132 (d) 143 (d) 141 (d) 15 (d) 132 (d) 144 (d) 14	C9	7121 (4)	3665 (3)	5862 (2)	559 (16)	C10-C11	1.393 (4)	1.393 (8)	C31—C32	1.376 (6)	
C11 6270 (3) 3946 (3) 4231 (2) 544 (3) C12-C13 1418 (3) 413 (5) C33-C34 1426 (C) C12 5170 (3) 3946 (3) 245 (2) 515 (2) 419 (12) 713-C16 1470 (3) 1442 (5) 735-C36 1431 (C) C13 4490 (3) 2463 (2) 515 (2) 419 (12) 713-C16 1470 (3) 1442 (5) 735-C36 1431 (C) C15 244 (4) 714 (2) C12 C32 (2) 1414 (4) 714 (7) 714 (7) (7) (7) (7) (7) (7) (7) (7) (7) (7)	C10	7251 (4)	4256 (3)	5014 (2)	588 (17)	C11-C12	1·365 (4)	1.373 (7)	C32C33	1.399 (5)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CII	6270 (3)	3946 (3)	4231 (2)	544 (15)	C12—C13	1.418 (3)	1.413 (6)	C33—C34	1.426 (5)	
C13 4990 (3) 2463 (2) 5155 (2) 419 (12) N15-C16 1470 (3) 1432 (5) N15-C40 1437 (3) 1432 (5) N15-C40 1437 (7) 1438 (5) 1437 (7) C17-C38 1390 (7) 1466 (10) C16-C17 1517 (4) 1439 (7) C17-C38 1390 (7) 1466 (10) C16-C17 1517 (4) 1439 (7) C17-C38 1390 (7) 1466 (10) C16-C17 1517 (4) 1439 (7) C17-C38 1390 (7) 1360 (7) 1370 (7) 1360 (7) 1370 (7) 1360 (7) 1370 (7) 1360 (7) 1370 (7) 1360 (7) 1370 (7) 1360 (7) 1370 (7) 1360 (7) 1370	C12	5170 (3)	3089 (2)	4291 (2)	469 (13)	C13C14	1.436 (3)	1.411 (5)	N35—C36	1-451 (6)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CI3	4990 (3)	2463 (2)	5155 (2)	419 (12)	N15C16	1.470 (3)	1.442 (5)	N35C40	1.457 (6)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CI4	3961 (3)	1493 (2)	5290 (2)	436 (13)	N15-C20	1.474 (3)	1.432 (5)	C36—C37	1.349 (8)	
C10 100 (2) 100 (2) 200 (2) 340 (15 C17-C18 1517 (3) 1484 (7) C38-C39 1515 (C17 1534 (4) 1473 (7) C39-C40 1562 (C18 C30 (4) 2558 (3) 227 (2) 653 (20) C19-C20 1517 (4) 1435 (6) C19 C29 (143 (6) 227 (2) 2395 (2) 395 (2) 397 (2) 35 (15) C2-C1-N15 121 3 (2) C22-C21-C34 121 3 (2) C22-C1-C44 121 4 (2) C22-C1-C43 121 3 (2) C22-C1-C44 121 4 (2) C22-C1-C44 121 4 (2) C22-C1-C43 121 3 (2) C22-C1-C44 121 4 (2) C22-C1-C43 121 4 (2) C22-C1-C43 121 4 (2) C22-C1-C44 121 4 (2) C22-C1-C44 121 4 (2) C22-C1-C43 121 4 (2) C22-C1-C44 121 4 (2) C22-C1-C43 121 4 (2) C22-C1-C44 121 4 (2) C22-C1-C43 121 4 (2) C22-C1-C44 C13 121 4 (2) C1-C1-C12 C13 122 4 (2) C1-C1-C12 C13 121 4 (2) C1-C1-C12 C13 121 4 (2) C1-C1-C12 C13 121 4 (2) C1-C1-C12 C13 122 4 (2) C1-C1-C12 C13 121 4 (2	NIS	2345 (2)	1671 (2)	3789 (1)	468 (10)	C16-C17	1.517 (4)	1.449 (7)	C37—C38	1.509 (8)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CI6	1605 (3)	1010 (2)	2991 (2)	540 (15)	C17C18	1.517 (5)	1.484 (7)	C38—C39	1.515 (7)	
C18 $620(4)$ 2858(6) 227(2) 687(20) C19-C20 1517(4) 1456(6) C19 1296(4) 3305(5) 3112(2) 3997(2) 356(15) C2-C1-N15 1213(2) C22-C1-C34 1213(C) C2-C1-C14 1213(C) C22-C1-C34 1213(C) C2-C1-C14 1213(C) C22-C1-C34 1213(C) C22-C1-C34 1213(C) C22-C1-C14 1214(C) C12-C1-C12 1213(C) C12-C14-C15 1214(C) C12-C1-C14 1214(C) C12-C12-C13 1223(C) C12-C14-C13 1223(C) C13-C14 1213(C) C13-C14-C13 1213(C) C13-C14-C13 1213(C) C13-C14-C13 1213(C) C13-C14-C14 1214(C) C12-C14-C13 1213(C) C13-C14-C14 1214(C) C12-C14-C13 1214(C) C12-C13-C13 1202(C) C14-C14-C13 1214(C) C12-C13-C13 1202(C) C12-C13-C14 1214(C) C12-C13-C14 C14 124(C) C12-C13-C14 C14 124(C) C12-C13-C14 1214(C) C12-C13-C13 1202(C) C12-C13-C14 1214(C) C12-C13-C13 1202(C) C12-C13-C14 1214(C) C12-C13-C14 1214(C) C12-C13-C14 C14 1214(C) C12-C13-C13 1214(C) C12-C13-C14 C14 124(C)	CI/	1534 (4)	1747 (3)	2090 (2)	615 (17)	C18-C19	1.524 (4)	1.473 (7)	C39—C40	1.362 (7)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C18	620 (4)	2858 (3)	2237 (2)	683 (20)	C19—C20	1.517 (4)	1.456 (6)			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C19	1296 (4)	3505 (3)	3112 (2)	597 (17)	~ ~ ~					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C20	1431 (3)	2724 (2)	3987 (2)	536 (15)	C2-C1N15	121.3 (2)		C22—C21—C34	121.3 (4)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $						$C_2 \rightarrow C_1 \rightarrow C_1 4$	119.2 (3)	121.6 (4)	C21—C22—C23	122.0 (4)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2 Dimonia	din a han a falain n	-1:			CI4-CI-NIS	119.4 (2)	100 5 (4)	C22—C23—C24	117.3 (4)	
$ \begin{array}{c} \text{Molecule A} \\ \text{C2} & -2335 (5) & 4504 (3) & 5240 (4) & 780 (22) & (22C3V4 & 1199 (3) & 1106 (4) & (24C21-N3 & 1230 (4) \\ \text{C2} & 2335 (5) & 4504 (3) & 5264 (4) & 725 (30) & (22C3V15 & 11210 (4) & (23C24C25 & 128 (4) \\ \text{C3} & 2492 (5) & 5256 (3) & 4463 (3) & 5690 (3) & 659 (26) & (24C5V6 & 1135 (2) & 1105 (4) & (24C25-N26 & 1125 (2) \\ \text{C4} & 3492 (5) & 6493 (3) & 7090 (3) & 800 (3) & 806 (26) & V6C5C14 & 122 (3) & 1214 (4) & N26-N27C28 & 1212 (4) \\ \text{C4} & 5202 (4) & 7548 (3) & 7089 (3) & 800 (26) & N6C5C14 & 122 (3) & 1214 (4) & N27C28C3 & 122 3 (2) \\ \text{C6} & 6433 (5) & 7775 (3) & 8025 (3) & 994 (29) & 965 (4) & N7C8 & -C19 + 1215 (2) & 11214 (4) & N27C28C3 & 1122 (2) \\ \text{C7} & 740 (6) & 7748 (5) & 9908 (4) & 895 (4) & N7-C8C13 & 122 4 (2) & 1235 (4) & C28C39C30 & 1128 (2) \\ \text{C11} & 6732 (7) & 5357 (6) & 9525 (5) & 1167 (52) & 99C8C13 & 1214 (2) & 1154 (5) & C28C39C30 & 1128 (6) \\ \text{C11} & 6732 (7) & 5357 (6) & 9525 (5) & 1167 (52) & 69C1-C1 & 1128 (2) & 1124 (2) & 1204 (5) & C28C3C3 & 1129 (2) \\ \text{C12} & 5803 (6) & 9756 (4) & 7956 (4) & 771 (3) & 66 (4) & 7956 (4) & 771 (3) \\ \text{C14} & 4602 (5) & 5566 (3) & 6915 (3) & 728 (2) & 86 (-71-C12 & 1214 (2) & 1167 (4) & C28C39C30 & 1128 (2) \\ \text{C14} & 4602 (5) & 5566 (3) & 6915 (3) & 728 (2) & 86C12C13 & 1214 (2) & 1106 (5) & C28C33C34 & 1164 (6) \\ \text{N15} & 7754 (4) & 5078 (2) & 3864 (3) & 728 (2) & 86 (-71-C12 & 1214 (2) & 1127 (4) & C28C33C34 & 1164 (6) \\ \text{C15} & 5563 (3) & 6915 (3) & 7764 (3) & 728 (2) & 86C12C13 & 11214 (2) & 1176 (4) & C23C34C3 & 1125 (2) \\ \text{C16} & -115-C20 & 1110 (2) & 1156 (3) & 1223 (2) & N35C36C37 & 11174 (2) \\ \text{C16} & -115-C20 & 1110 (2) & 1156 (3) & 1226 (3) & C23R33C40 & 1184 (6) \\ \text{C18} & -677 (7) & 4726 (3) & 750 (3) & 653 (3) & 776 (3) & 755 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 716 (3) & 71$	5-Piperio	unobenzo[c]cinn	oline(2)			$C_1 - C_2 - C_3$	$122 \cdot 1 (3)$	122.5 (4)	C22—C23—N35	119-7 (4)	
C1 335 (5) 4509 (3) 6240 (4) 780 (32) C2-C3-N13 1210 (4) C3-C24-C2 128 (4) C3-C24-C2 128 (4) C3-C24-C2 128 (5) C4-C3-N15 122 (4) C4-C3-C34 122 (4) C3-C24-C2 115 (5) C3 20 (5) 525 (6) 466 (3) 649 (26) C3-C4-C5 112 (2) (3) 121 (2) (4) C4-C3-C34 122 (6) C4-C3-N26 115 (5) (2) 116 (4) C3-C24-C25 -N26 115 (2) 116 (4) C3-C24-C25 -N26 115 (2) 116 (4) C3-C24-C25 -N26 N7 119 (6) C3-C32-N26 N7 119 (6) C3-C34-C3 122 (6) C4-C5-N6 (1) 15 (2) 116 (4) C3-C24-C3 -N26 112 (2) (2) 116 (4) N27-C28-C3 112 (2) (2) 115 (4) N27-C28-C3 112 (2) (2) 115 (4) N27-C28-C3 112 (2) (2) 115 (4) N27-C28-C3 112 (2) (2) 116 (4) C3-C32-C3-C13 112 (2) (2) 115 (4) N27-C28-C3 112 (2) (2) 115 (4) (2) 115 (4) N27-C28-C3 112 (2) (2) 115 (4) (2) 115 (4) N27-C28-C3 112 (2) (2) 115 (4) (2) 112 (2) 115 (4) (2) 112 (2) 115 (4) (2) 112 (2) 115 (4) (2) 112 (2) 115 (4) (2) 112 (2)	Molecul	e A				$C_2 - C_3 - C_4$	119.8 (3)	116.6 (4)	C24—C23—N35	123.0 (4)	
C2 2935 (5) 4364 (3) 5264 (4) 725 (30) C3-C3-C14 121-6 (3) C24-C25-N26 1123 (2) C4-C3-N26 1135 (2) C4-C3-N26 (122 (4) N26-N27-C28 121 (4) N26-N27-C28 121 (2) (4) N26-N27-C28 (2) C3-N36 (2) N36-N7 (2) C3-N36	CI	3836 (5)	4509 (3)	6240 (4)	780 (32)	$C_2 = C_3 = N_{15}$		121.0 (4)	$C_{23} - C_{24} - C_{25}$	120.8 (4)	
C3 2692 (5) 2526 (3) 4863 (3) 649 (26) C=C=C=C=C 16 (10 ² C) 1212 (4) C3=-C2=-N26 1123 (5) C4=C5-N26 (1125 (3) 122 (4) C3=-C3=N26 1123 (5) C4=C5-N26 (1125 (3) 122 (4) C3=-N26 (1125 (2) 123 (4) C3=-N26 (1126 (3) 122 (4) C3=-N26 (1126 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) 123 (4) (23 (23 (24 (23 (11-C1) (1126	C2	2935 (5)	4364 (3)	5264 (4)	725 (30)	$C_4 - C_5 - N_{15}$	120 2 (2)	122.4 (4)	$C_{24} - C_{25} - C_{34}$	122.0 (4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C3	2692 (5)	5256 (3)	4863 (3)	649 (26)	$C_{4} - C_{5} - N_{6}$	120.2(3)	121.2(4)	C24—C25—N26	115.3(4)	
C5 4435 (3) 6433 (3) 6502 (3) 637 (26) CF C-C-L1 1210 (3) 1222 (4) C2=N3D-N27-C28 1212 (N7 6083 (5) 7775 (3) 8025 (3) 924 (29) C5-N6-N7 - C1 1952 (2) 1214 (4) N26-N27-C28 1212 (C5 027 (5) 6420 (4) 8475 (4) 754 (3) N6-N7-C3 1195 (2) 1154 (5) C29-C28-C3 127 (4) 127 (4) 1067 (45) N7-C3-C3 1152 (2) 1154 (5) C29-C30-C31 122 (5) (7) 170 (6) 745 (5) 9505 (6) 9505 (6) 170 (5) (5) C2 (-C3-C13 122 (2) 1154 (5) C29-C30-C31 120 (5) (7) 198 (5) 1067 (45) N7-C3-C3 112 (2) 123 (4) C28-C39-C30 1198 (5) (16 73 (7) 5357 (6) 9525 (5) 1176 (5) C2 (-C3-C13 121 (2) 120 (5) C29-C30-C31 120 (5) (7) 198 (6) 1027 (4) 1067 (45) N7-C3-C3 121 (2) 120 (5) C29-C30-C31 120 (5) (7) 198 (6) (12 3 5354 (5) 5806 (4) 7956 (4) 731 (3) C9-C10-C11 1188 (3) 1195 (6) C31-C32-C33 120 (2) (7) (13 5545 (5) 5806 (4) 7956 (4) 731 (3) C9-C10-C11 1188 (3) 1195 (6) C31-C32-C33 120 (2) (14 4620 (5) 5563 (3) 6915 (3) 657 (27) C10-C11-C12 1219 (3) 1212 (6) C32-C33-C34 1164 (15) (15 5334 (4) 2355 (4) 1007 (40) C8-C13-C12 1165 (5) C32-C33-C34 1164 (15 1190 (49) C8-C13-C14 1173 (2) 1167 (4) C21-C33 123 (2) (2) (2) 126 (3) (2) (2) (2) 126 (4) (2) (2) (2) (2) (2) (2) (2) (2) (2) (2	C4	3492 (5)	6299 (3)	5507 (3)	655 (26)	C4 - C5 - C14	$113^{1}3(2)$	110.5 (4)	C34-C25-N20	122.0 (4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CS	4435 (5)	6453 (3)	6502 (3)	637 (26)	N6-C5-C14	121.0 (3)	122.2(4)	N26 N27 C29	119.8 (4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	NO NZ	5202 (4)	7548 (3)	7089 (3)	806 (26)	$C_{5} N_{6} N_{7}$	122.9(3) 121.5(2)	121.4(4)	N27-C28-C33	121.2 (4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	IN /	6083 (5)	(020 (4)	8025 (3)	924 (29)	N6-N7C8	1215(2) 119.6(2)	119.5(4)	N27-C28-C33	122.5(4) 117.0(4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C8	6267 (5)	6920 (4)	84/5 (4)	/63 (33)	N7-C8-C9	1150(2)	115.4(5)	C^{20} C^{28} C^{23}	120.7(4)	
C10 $471(7)$ $4947(6)$ $1002/(4)$	C9 C10	7240 (6)	7248 (5)	9508 (4)	985 (41)	N7-C8-C13	122.9(2)	123.5(4)	$C_{29} = C_{20} = C_{30}$	110.8 (4)	
C11 0)22 (1) 0)25 (6) 0)25 (6) 0)25 (2) 110 (2) C8 - C9 - C10 120 3 (2) 119 (6) C30 - C31 - C32 - C33 120 2 (C13 5545 (5) 5563 (3) 691 (5) (3) 657 (27) C10 - C11 - 1188 (3) 119 5 (6) C31 - C32 - C33 - C34 116 4 (C14 4620 (5) 5563 (3) 691 (5) (3) 657 (27) C10 - C11 - C12 121 (9) (3) 121 2 (6) C32 - C33 - C34 125 (7) (1) 157 (4) (2) 117 (5) C32 - C33 - C34 125 (7) (1) 157 (4) (2) 117 (5) C32 - C33 - C34 125 (7) (1) 157 (4) (2) 117 (5) C32 - C33 - C34 125 (7) (1) 157 (4) (2) - C34 - C33 129 (2) (2) 116 (7) (4) C2 - C34 - C33 117 (6) (2) 117 (7) (4) C2 - C34 - C33 117 (6) (2) 117 (7) (4) C2 - C34 - C33 117 (6) (2) 117 (7) (4) C2 - C34 - C33 117 (6) (2) 117 (5) (2) 1159 (4) (2) - C34 - C33 117 (6) (2) - C14 - C13 128 (0) (2) 115 (2) (2) - N35 - C36 117 (2) (2) - C14 - C13 128 (0) (2) 115 (2) (2) - N35 - C36 117 (2) (2) - N35 - C36 (1) 110 (2) (2) - N35 - C36 (1) 110 (2) (2) - N35 - C36		/4/1 (/) 6722 (7)	0407 (0) 5257 (6)	10027 (4)	1067 (45)	C9-C8-C13	121.8(2)	123.9(4) 121.0(5)	$C_{20} = C_{20} = C_{30}$	120.6 (5)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0/32 (/) 5902 (ć)	5557 (0) 5036 (4)	9525 (5)	11/6 (52)	C8-C9-C10	120.3(2)	119.9 (6)	C_{30} C_{31} C_{32}	120.0(5) 120.7(5)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C12 C12	5605 (6)	5020 (4)	8313 (4)	900 (38)	C9-C10-C11	118.8 (3)	119.5 (6)	$C_{31} - C_{32} - C_{33}$	120.2(4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C13	3343 (3) 4630 (5)	56(0 (4)	(936 (4)	/31 (31)	C10-C11-C12	121.9 (3)	121.2(6)	$C_{28} - C_{33} - C_{34}$	116.4(4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N15	4020(3)	5078 (3)	0915 (3)	637 (27) 728 (24)	C11-C12-C13	$121 \cdot 2$ (2)	120.8 (5)	C32—C33—C28	118.0(4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CI6	1/34(4)	5078 (2) 6006 (4)	3604 (3)	1007 (40)	C8-C13-C12	116.0 (2)	117.6 (5)	C32-C33-C34	125.5 (4)	
C18 -677 (7) 4758 (5) 1956 (4) 1127 (45) $C12-C13-C14$ 1264 (2) 1257 (4) $C21-C34-C33$ 1259 (4) $C19$ -259 (8) 3831 (4) 2278 (4) 1122 (43) $C1-C14-C5$ 1167 (2) 1159 (4) $C25-C34-C33$ 1176 (6) $C1-C14-C13$ 1280 (2) 1263 (4) $C23-N35-C36$ 1172 (7) $C25-C14-C13$ 1151 (2) 1177 (4) $C23-N35-C36$ 1172 (7) $C2-C14-C13$ 1151 (2) 1177 (4) $C23-N35-C36$ 1184 (6) $C1-N15-C20$ 1164 (2) $C3-N15-C16$ 1178 (4) $C36-C37-C38$ 1184 (6) $C1-N15-C20$ 11323 (2) $N35-C36-C37$ 1171 (6) $C23-N15-C16$ 1178 (4) $C36-C37-C38$ 1184 (6) $C1-N15-C20$ 1193 (4) $C37-C38-C39$ 1102 (2) $C23-4612$ (2) 11550 (3) 7115 (3) 683 (29) $N15-C16-C17$ 1097 (2) 11668 (4) $C38-C39-C40$ 1154 (6) $C24-3080$ (5) 1663 (3) 7107 (3) 688 (29) $N15-C16-C17$ 1097 (2) 1168 (4) $C39-C40-N35$ 1188 (2) $C25-1895$ (5) 1570 (3) 6326 (3) 619 (28) $C17-C18-C19$ $110-1$ (2) 1130 (5) $C17-C18-C19$ $110-1$ (2) 1130 (5) $C17-C18-C19$ $110-1$ (2) 1130 (5) $C19-C20-N15$ $111-4$ (5) $C28-607$ (5) 1366 (3) 4713 (4) 648 (28) $C17-C18-C19$ $110-1$ (2) 1130 (5) $C19-C20-N15$ $111-4$ (2) 1172 (4) $C29-1974$ (5) 1270 (3) 3924 (4) 756 (32) $C19-C20-N15$ $111-4$ (2) 1172 (4) $C38-C39-C40-N35$ 1188 (2) $C19-C20-N15$ $111-4$ (2) 1172 (4) $C38-C39-C40-N35$ 1188 (2) $C19-C20-N15$ $111-4$ (2) 1172 (4) $C29-1974$ (5) 1283 (3) 4713 (4) 648 (28) $C17-C18-C19$ $110-1$ (2) 1130 (5) $C19-C20-N15$ $111-4$ (2) 1172 (4) $C38-C39-C40-N35$ 1188 (5) $C19-C10-N15$ $C10-C10$ $C3-C4$ $C9-C10$ and $C11-C12$ are general $C3-C38-C33$ (6) 1928 (6) 992 (7) 1920 (8) 9827 (5) 1621 (9) 1195 (57) 11920 (8) 9827 (5) 1621 (9) 1195 (57) 11920 (8) 9827 (5) 1621 (9) 1195 (57) 11920 (8) 1730 (8) 1730 (8) 1730 (8) 1730 (8) 1265 (7) 12610 (9) 11920 (C17	613 (8)	5834 (4)	2464 (5)	1190 (40)	C8-C13-C14	117.3 (2)	116.7 (4)	C21-C34-C25	116.5 (4)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C18	-677(7)	4758 (5)	1956 (4)	1127 (45)	C12-C13-C14	126.4 (2)	125.7 (4)	C21—C34—C33	125.9 (4)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C19	-259(8)	3831 (4)	2278 (4)	1122 (43)	C1C14C5	116.7 (2)	115.9 (4)	C25—C34—C33	117.6 (4)	
Molecule BC213765 (5)1301 (3)5235 (3)634 (26)C3-C14-C13115-1 (2)117-7 (4)C23-N35-C40113-8 (4)C213765 (5)1301 (3)5235 (3)634 (26)C1-N15-C16116-4 (2)C36-C37-C38113-1 (1)C224918 (5)1388 (3)6096 (3)655 (27)C3-N15-C16117-8 (4)C36-C37-C38118-1 (1)C234612 (5)1560 (3)7115 (3)688 (29)N15-C16-C17109-7 (2)116-8 (4)C38-C39-C40115-4 (1)C243080 (5)1663 (3)7207 (3)688 (29)N15-C16-C17109-7 (2)116-8 (4)C39-C40-N35118-8 (5)C251895 (5)1570 (3)6326 (3)619 (28)C17-C18-C19110-1 (2)113-0 (5)C39-C40-N35118-8 (5)N26383 (5)1646 (3)6517 (3)740 (26)C18-C19-C20111-5 (2)116-4 (5)C39-C40-N35118-8 (5)C28-607 (5)1366 (3)4713 (4)648 (28)C19-C20111-5 (2)116-4 (5)C39-C40-N35118-8 (5)C30-1852 (6)1126 (3)2920 (4)855 (34)caccordance with what was found in benzo[c]cinnolinC31-385 (6)1047 (4)2647 (4)864 (32)C19-C20111-4 (2)117-2 (4)C32959 (5)1119 (3)3403 (3)691 (28)C3-C4, C9-C10and C11-C12 are generalC342186 (5)1381 (3)5313 (3)560 (24)shorter than the other bonds, which have also beeC37 <t< td=""><td>C20</td><td>541 (7)</td><td>4026 (4)</td><td>3377 (4)</td><td>1002 (38)</td><td>CI-CI4-CI3</td><td>128.0 (2)</td><td>126.3 (4)</td><td>C23—N35—C36</td><td>117-2 (4)</td></t<>	C20	541 (7)	4026 (4)	3377 (4)	1002 (38)	CI-CI4-CI3	128.0 (2)	126.3 (4)	C23—N35—C36	117-2 (4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						C5-C14-C13	115-1 (2)	117.7 (4)	C23—N35—C40	118-4 (4)	
Molecule B $C1-N15-C20$ $1132 (2)$ $N35-C36-C37$ $117.1 (1)$ C213765 (5)1301 (3)5235 (3)634 (26) $C3-N15-C16$ $117.8 (4)$ $C36-C37-C38$ $118.1 (i)$ C224918 (5)1388 (3)6096 (3)655 (27) $C1-N15-C20$ $119.3 (4)$ $C37-C38-C39$ $110.2 (i)$ C234612 (5)1560 (3)7115 (3)683 (29) $N15-C16-C17$ $109.7 (2)$ $116.8 (4)$ $C39-C40-N35$ $118.8 (i)$ C243080 (5)1663 (3)7207 (3)688 (29) $N15-C16-C17$ $109.7 (2)$ $116.8 (4)$ $C39-C40-N35$ $118.8 (i)$ C251895 (5)1570 (3)6326 (3)619 (28) $C16-C17-C18$ $111.6 (3)$ $116.8 (5)$ $C19-C20-N15$ $111.4 (2)$ $117.2 (4)$ N27-805 (5)1536 (3)5746 (3)756 (27) $C18-C19-C20$ $111.5 (2)$ $116.4 (5)$ $C29-1974 (5)$ $1270 (3)$ $3924 (4)$ 756 (32)C30-1852 (6)1126 (3)2920 (4)855 (34)accordance with what was found in benzo[c]c]cinnolinC31-385 (6)1047 (4)2647 (4)864 (33) $(van der Meer, 1972)$. The bond lengths $C1-C$ C33880 (5)1285 (3)4459 (3)600 (26) $C3-C4$, $C9-C10$ and $C11-C12$ are generalC342186 (5)1381 (3)5313 (3)560 (24)N355834 (5)1641 (3)7971 (3)865 (30)C342186 (5)1788 (6)8992 (4)1195 (57)C376641 (12)1902 (8)						CI—N15—C16	116.4 (2)		C36—N35—C40	113.8 (4)	
C213765 (5)1301 (3)5235 (3) 634 (26) $C3-N15-C16$ $117\cdot8$ (4) $C36-C37-C38-C39$ $118\cdot1$ (iC224918 (5)1388 (3)6096 (3)655 (27) $C3-N15-C20$ $119\cdot3$ (4) $C37-C38-C39-C40$ $115\cdot4$ (6)C234612 (5)1560 (3)7115 (3)683 (29) $N15-C16-C17$ $109\cdot7$ (2) $116\cdot8$ (4) $C39-C40-N35$ $118\cdot8$ (6)C243080 (5)1663 (3)7207 (3)688 (29) $C16-C17-C18$ $111\cdot6$ (3) $116\cdot8$ (5) $C39-C40-N35$ $118\cdot8$ (5)C251895 (5)1570 (3)6326 (3)619 (28) $C16-C17-C18$ $111\cdot6$ (3) $116\cdot8$ (5) $C19-C20$ $111\cdot12$ (2) $113\cdot0$ (5)N26383 (5)1646 (3)6517 (3)740 (26) $C18-C19-C20$ $111\cdot5$ (2) $116\cdot4$ (5) $C29$ -1974 (5) 270 (3) 3924 (4)756 (22)C30-1852 (6)1126 (3)2920 (4)855 (34)accordance with what was found in benzo[c]c]cinnolinC31-385 (6)1047 (4)2647 (4)864 (33) $(van der Meer, 1972)$. The bond lengths $C1-C$ C33880 (5)1285 (3)4459 (3)600 (26) $C3-C4$, $C9-C10$ and $C11-C12$ are generalC342186 (5)1381 (3)5313 (3)560 (24)C355834 (5)1641 (3)7971 (3)865 (30)C365433 (8)1788 (6)8992 (4)1195 (57)C376641 (12)1902 (8)9827 (5)1621 (95)C387713 (9)170 (6)97	Molecul	e <i>B</i>				CI-N15-C20	113-2 (2)		N35—C36—C37	117.1 (6)	
C224918 (5)1388 (3)6096 (3) $655 (27)$ $C3-N13-C20$ $119-3 (4)$ $C3/-C38-C39-C40$ $110-2 (1)$ C234612 (5)1560 (3)7115 (3)683 (29) $C16-N15-C20$ $111-0 (2)$ $116-0 (4)$ $C38-C39-C40$ $115-4 (6)$ C243080 (5)1663 (3)7207 (3)688 (29) $N15-C16-C17$ $109-7 (2)$ $116-8 (4)$ $C39-C40-N35$ $118-8 (5)$ C251895 (5)1570 (3)6326 (3)619 (28) $C16-C17-C18$ $111-6 (3)$ $116-8 (5)$ N26383 (5)1646 (3)6517 (3)740 (26) $C18-C19-C20$ $111-5 (2)$ $116-4 (5)$ N27-805 (5)1536 (3)5746 (3)756 (27) $C18-C19-C20$ $111-4 (2)$ $117-2 (4)$ C28-607 (5)1366 (3)4713 (4)648 (28) $C19-C20-N15$ $111-4 (2)$ $117-2 (4)$ C30-1852 (6)1126 (3)2920 (4)855 (34)accordance with what was found in benzo[c]c]cinnolinC31-385 (6)1047 (4)2647 (4)864 (33)C32959 (5)1119 (3)3403 (3)691 (28)C33880 (5)1285 (3)4459 (3)600 (26)C342186 (5)1381 (3)5313 (3)560 (24)N355834 (5)1641 (3)7971 (3)865 (30)C365433 (8)1788 (6)8992 (4)1195 (57)C376641 (12)1902 (8)9827 (5)1621 (95)C387713 (9)1770 (6)9716 (4)1265 (57)<	C21	3765 (5)	1301 (3)	5235 (3)	634 (26)	$C_3 - NI_5 - CI_6$		117.8 (4)	$C_{36} - C_{37} - C_{38}$	118-1 (6)	
C234612 (5)1560 (3)7115 (3)683 (29) $C16-C17 - C18 - C19 - 110 - (2)$ $116 \cdot 0 (4)$ $C38-C.39-C40 - N35 - 115 \cdot 4 (1)$ C243080 (5)1663 (3)7207 (3)688 (29) $N15-C16-C17 - 109 \cdot 7 (2)$ $116 \cdot 8 (5)$ $C16-C17 - C18 - C19 - 7 (2)$ $116 \cdot 8 (5)$ C251895 (5)1570 (3)6326 (3)619 (28) $C16-C17 - C18 - C19 - 110 \cdot 1 (2)$ $113 \cdot 0 \cdot 5$ N26383 (5)1646 (3)6517 (3)740 (26) $C17-C18-C19 - 110 \cdot 1 (2)$ $113 \cdot 0 \cdot 5$ N27-805 (5)1536 (3)5746 (3)756 (27) $C18-C19-C20 - N15 - 111 \cdot 4 (2)$ $117 \cdot 2 \cdot 4$ C28-607 (5)1366 (3)4713 (4)648 (28) $C19-C20-N15 - 111 \cdot 4 (2)$ $117 \cdot 2 \cdot 4$ C30-1852 (6)1126 (3)2920 (4)855 (34)accordance with what was found in benzo[c]c]cinnolinC31-385 (6)1047 (4)2647 (4)864 (33)C32959 (5)1119 (3)3403 (3)691 (28)C33880 (5)1285 (3)4459 (3)600 (26)C342186 (5)1381 (3)5313 (3)560 (24)N355834 (5)1641 (3)7971 (3)865 (30)C365433 (8)1788 (6)8992 (4)1195 (57)Shown by theoretical calculations (Mulliken, 195C376641 (12)1902 (8)9827 (5)C387713 (9)1170 (6)9716 (4)1205 (54)C387713 (9)1170 (6)9716 (4)126 (57)C387713 (8) <td>C22</td> <td>4918 (5)</td> <td>1388 (3)</td> <td>6096 (3)</td> <td>655 (27)</td> <td>$C_{14} = N_{15} = C_{20}$</td> <td>111.0 (2)</td> <td>119.3 (4)</td> <td>$C_{37} - C_{38} - C_{39}$</td> <td>110.2 (5)</td>	C22	4918 (5)	1388 (3)	6096 (3)	655 (27)	$C_{14} = N_{15} = C_{20}$	111.0 (2)	119.3 (4)	$C_{37} - C_{38} - C_{39}$	110.2 (5)	
C243080 (5)1663 (3)7207 (3) $688 (29)$ $K13-C16-C17-C18$ $119-7 (2)$ $116-8 (4)$ $C39-C40-N35$ $118-8 (5)$ C251895 (5)1570 (3) $6326 (3)$ 619 (28) $C16-C17-C18$ $111-6 (3)$ $116-8 (4)$ $C39-C40-N35$ $118-8 (5)$ N26383 (5)1646 (3)6517 (3)740 (26) $C16-C17-C18$ $111-6 (3)$ $116-8 (4)$ $C39-C40-N35$ $118-8 (5)$ N27-805 (5)1536 (3)6517 (3)740 (26) $C17-C18-C19$ $110-1 (2)$ $113-0 (5)$ C28-607 (5)1366 (3)4713 (4)648 (28) $C19-C20$ $111-5 (2)$ $116-4 (5)$ C30-1852 (6)1126 (3)2920 (4)855 (34)accordance with what was found in benzo[c]c]cinnolinC31-385 (6)1047 (4)2647 (4)864 (33)(van der Meer, 1972). The bond lengths C1-CC33880 (5)1285 (3)4459 (3)600 (26)C3-C4, C9-C10 and C11-C12 are generalC342186 (5)1381 (3)5313 (3)560 (24)N355834 (5)1641 (3)7971 (3)865 (30)C365433 (8)1788 (6)8992 (4)1195 (57)C376641 (12)1902 (8)9827 (5)1621 (95)C387713 (9)1170 (6)9716 (4)1226 (57)C398148 (8)1065 (6)8655 (4)1246 (57)C398148 (8)1065 (6)8655 (4)1246 (57)C406897 (8)957 (6)7834 (4)1175 (58)C	C23	4612 (5)	1560 (3)	7115 (3)	683 (29)	C10-N15-C20	111.0(2)	116.0 (4)	$C_{38} - C_{39} - C_{40}$	115.4 (6)	
C251895 (5)1570 (3)6326 (3)619 (28) $C17-C18$ $C17-C18$ $C17-C18$ $C19$ $110-3$ (3) $110-3$ (3)N26383 (5)1646 (3)6517 (3)740 (26) $C17-C18$ $C19-C20$ $111-5$ (2) $113-0$ (5)N27-805 (5)1536 (3)5746 (3)756 (27) $C18-C19-C20$ $111-5$ (2) $116-4$ (4)C28-607 (5)1366 (3)4713 (4)648 (28) $C19-C20-N15$ $111-4$ (2) $117-2$ (4)C30-1852 (6)1126 (3)2920 (4)855 (34)accordance with what was found in benzo[c]c]cinnolinC31-385 (6)1047 (4)2647 (4)864 (33)(van der Meer, 1972).The bond lengths C1-CC33880 (5)1285 (3)4459 (3)600 (26)C3-C4,C9-C10and C11-C12 are generalN355834 (5)1641 (3)7971 (3)865 (30)shorter than the other bonds, which have also beeN355834 (5)1641 (3)7971 (3)865 (30)shown by theoretical calculations (Mulliken, 195C376641 (12)1902 (8)9827 (5)1621 (95)Hoffman, 1963) and experimentally determined ifC387713 (9)1170 (6)9716 (4)1265 (54)Hoffman, 1963) and experimentally determined ifC398148 (8)1065 (6)8655 (4)1246 (57)and (2), the piperidino groups form a slightly diC406897 (8)957 (6)7834 (4)1175 (58)and (2), the piperidino groups form a slightly di	C24	3080 (5)	1663 (3)	7207 (3)	688 (29)		109.7(2)	116.8 (4)	C39—C40—N35	118.8 (2)	
N26383 (5)1646 (3)6517 (3)740 (26) $C18-C19-C19-C19$ $1151 (2)$ $1150 (3)$ N27-805 (5)1536 (3)5746 (3)756 (27) $C18-C19-C20$ $1115 (2)$ $1164 (5)$ C28-607 (5)1366 (3)4713 (4)648 (28) $C18-C19-C20-N15$ $1114 (2)$ $117 (2)$ C30-1852 (6)1126 (3)2920 (4)855 (34)C31-385 (6)1047 (4)2647 (4)864 (33)C32959 (5)1119 (3)3403 (3)691 (28)C33880 (5)1285 (3)4459 (3)C342186 (5)1381 (3)5313 (3)560 (24)5834 (5)1641 (3)N355834 (5)1641 (3)C365433 (8)1788 (6)8992 (4)1195 (57)C376641 (12)1902 (8)9827 (5)C376641 (12)1902 (8)9827 (5)C387713 (9)C398148 (8)1065 (6)8655 (4)C398148 (8)1065 (6)8655 (4)C406897 (8)957 (6)7834 (4)1175 (58)and (2), the piperidino groups form a slightly di	C25	1895 (5)	1570 (3)	6326 (3)	619 (28)	C10 - C17 - C18	110.1(3)	112.0 (5)			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N26	383 (5)	1646 (3)	6517 (3)	740 (26)	C18 - C19 - C20	110.1(2)	115.0 (5)			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N27	- 805 (5)	1536 (3)	5746 (3)	756 (27)	C19 - C20 - N15	111.4(2)	117.2 (4)			
$\begin{array}{cccccc} C29 & -1974 (5) & 1270 (3) & 3924 (4) & 756 (32) \\ C30 & -1852 (6) & 1126 (3) & 2920 (4) & 855 (34) \\ C31 & -385 (6) & 1047 (4) & 2647 (4) & 864 (33) \\ C32 & 959 (5) & 1119 (3) & 3403 (3) & 691 (28) \\ C33 & 880 (5) & 1285 (3) & 4459 (3) & 600 (26) \\ C34 & 2186 (5) & 1381 (3) & 5313 (3) & 560 (24) \\ S135 & 5834 (5) & 1641 (3) & 7971 (3) & 865 (30) \\ C36 & 5433 (8) & 1788 (6) & 8992 (4) & 1195 (57) \\ C37 & 6641 (12) & 1902 (8) & 9827 (5) & 1621 (95) \\ C38 & 7713 (9) & 1170 (6) & 9716 (4) & 1226 (57) \\ C39 & 8148 (8) & 1065 (6) & 8655 (4) & 1246 (57) \\ C40 & 6897 (8) & 957 (6) & 7834 (4) & 1175 (58) \\ \end{array}$ accordance with what was found in benzo[c]cinnolin (van der Meer, 1972). In both (C28	-607 (5)	1366 (3)	4713 (4)	648 (28)	CI) C20 III5	111 4 (2)	11/2(4)			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C29	- 1974 (5)	1270 (3)	3924 (4)	756 (32)						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C30	- 1852 (6)	1126 (3)	2920 (4)	855 (34)	accordance v	vith what	t was fou	nd in benzo[c]c	innoline	
C_{32} $C_{39}(5)$ $C_{1119}(5)$ $3403(5)$ $691(28)$ (van der Meer, 1972). The bond lengths C1—C C_{33} $880(5)$ $1285(3)$ $4459(3)$ $601(26)$ $C3-C4$, C9—C10 and C11—C12 are general C_{34} $2186(5)$ $1381(3)$ $5313(3)$ $560(24)$ $N35$ $5834(5)$ $1641(3)$ $7971(3)$ $865(30)$ C_{36} $5433(8)$ $1788(6)$ $8992(4)$ $1195(57)$ C_{37} $6641(12)$ $1902(8)$ $9827(5)$ $1621(95)$ C_{38} $7713(9)$ $1170(6)$ $9716(4)$ $1205(54)$ C_{39} $8148(8)$ $1065(6)$ $8655(4)$ $1246(57)$ C_{40} $6897(8)$ $957(6)$ $7834(4)$ $1175(58)$ and (2), the piperidino groups form a slightly di	C31	- 385 (6)	104 / (4)	2647 (4)	864 (33)	(van der Ma	er 107) The	bond lengths (<u></u>	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C32	90 (S)	1119 (3)	5403 (3)	691 (28)	(van dei wieer, 1972). The bond lengths $CI - C2$,					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C33	000 (5)	1285 (3)	4459 (3)	600 (26)	$C_3 - C_4$, C_5	-C10	and Cl	I - C12 are g	generally	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C34 N25	2100 (3)	1381 (3)	5515 (5) 7071 (2)	200 (24)	shorter than	the othe	er bonds.	which have al	lso been	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C36	2024 (2) 5433 (9)	1041 (3)	(9/1 (3) 8002 (4)	803 (30)	shown by theoretical calculations (Mulliken 1055)					
C_{38} (12) (12) (12) (12) (12) (12) (12) (12)	C37	66 <u>41</u> (17)	100 (0)	0772 (4)	1621 (05)	II. Control 10		i calcula		i, 1755,	
C_{39} 8148 (8) 1065 (6) 8655 (4) 1246 (57) benzo[c]cinnoline (van der Meer, 1972). In both (C40 6897 (8) 957 (6) 7834 (4) 1175 (58) and (2), the piperidino groups form a slightly di	C38	7713 (9)	1170 (6)	9716 (4)	1205 (53)	Holiman, 19	(co) and	experin	ientally determ	ined in	
C40 6897 (8) 957 (6) 7834 (4) 1175 (58) and (2), the piperidino groups form a slightly di	C39	8148 (8)	1065 (6)	8655 (4)	1246 (57)	benzo[c]cinno	oline (va	n der M	eer, 1972). In l	both (1)	
$\langle , \rangle \langle , \rangle \langle , \rangle \langle , \rangle \rangle = \langle - \rangle $	C40	6897 (8)	957 (6)	7834 (4)	1175 (58)	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 Benzolclcinnoline 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, $\beta = 106.41 (1)^{\circ}, V = 1295.3 (2) \text{ Å}^3, Z = 4, D_m = 1.26, D_x = 1.278 \text{ g cm}^{-3}, \lambda(\text{Cu } K\alpha) = 1.54180 \text{ Å}, \mu = 1.54180 \text{ Å}, \lambda(\text{Cu } K\alpha) =$ 5.726 cm^{-1} , F(000) = 528, T = 293 K, R = 0.056 for1817 observed reflections $[I \ge 3\sigma(I)]$. (2) C₁₆H₁₅N₃, $M_r = 249.32$, 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, λ (Cu K α) = 1.54180 Å, $\mu = 5.734$ cm⁻¹, F(000) = 528, T = 293 K, R = 0.039 for 1253 observed reflections $|I| \ge 1$ $3\sigma(I)$]. The rings in the benzo[c]cinnoline skeleton are close to planar in (1) with dihedral angles of $0.27(7) - 1.25(6)^{\circ}$ compared to angles of 2.1(2)- $4.95(7)^{\circ}$ in (2). The pyrrolidino ring in (1) is close to planar with a maximum deviation from the leastsquares 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 4bromobenzo[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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