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

BY TUNCER HÖKELEK*

Department of Physics, Hacettepe University, 06532 Beytepe, Ankara, Turkey

AND EMİNE KILIÇ AND CELAL TÜZÜN

Department of Chemistry, Ankara University, Tandoğan, Ankara, Turkey

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, λ(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, λ(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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* To whom correspondence should be addressed.

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

	(1)	(2)
Method of measuring D_m	Flotation in aqueous KI	
Crystal shape and size (mm)	Prismatic $0.2 \times 0.3 \times 0.6$	Rod-shaped $0.5 \times 0.5 \times 0.4$
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 $11 \leq 2\theta \leq 31$	$12 \leq 2\theta \leq 36$
Absorption correction applied (max. and min. values)	Semi-empirical (North, Phillips & Mathews, 1968) $1.25, 1.16$	$1.28, 1.17$
Max. (sinθ/λ) (Å^{-1})	0.617	
Range of h, k and l	$-1 \leq h \leq 15$, $-1 \leq k \leq 15$, $-10 \leq l \leq 10$	$-1 \leq h \leq 10$, $-1 \leq k \leq 14$, $-1 \leq l \leq 16$
Standard reflections and their intensity variation throughout experiment (%)	$11\bar{3}, 266,$ $3\bar{6}6, \pm 1$	$301, \bar{1}15,$ $004, \pm 1$
Number of reflections measured	3429	2076
Number of unique reflections	2546	1479
Number of unobserved reflections	729	226
Number of reflections used in the refinement	1817	1253
Criterion for recognizing unobserved reflections	$I \leq 3\sigma(I)$	
Method used to solve structure	Direct methods (see below)	
Use of F or F^2 magnitudes in least-squares refinement	F	
Parameters refined	212	172
Values of R, wR	0.056, 0.071	0.039, 0.046
Method used to calculate w	Chebychev (Carruthers & Watkin, 1979)	
Final residual electron densities (e Å^{-3}) for max. and min. peaks	$+0.67, -0.67$	$+0.5, -0.5$
Max. (Δ/σ)	0.054	0.002
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	
Computer programs used	*SHELXS*86 (Sheldrick, 1986), *CRYSTALS* (Watkins, Carruthers & Betteridge, 1985), *SNOOPI* (Davies, 1983)	

atoms in (1), and as $U = 0.05$ Å^2 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.* The molecular structures with the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53227 (24 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* (Å$^2 \times 10^4$) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
2-Pyrrolidinobenzo[c]cinnoline (1)				
C1	8400 (2)	1890 (2)	2487 (3)	435 (11)
C2	8228 (2)	1230 (2)	3689 (3)	477 (12)
C3	7272 (2)	542 (2)	3317 (3)	586 (15)
C4	6563 (2)	491 (2)	1801 (3)	602 (15)
C5	6758 (2)	1123 (2)	578 (3)	483 (12)
N6	6000 (2)	1006 (2)	−922 (3)	569 (12)
N7	6104 (2)	1575 (2)	−2116 (2)	581 (12)
C8	6969 (2)	2314 (2)	−1877 (3)	484 (12)
C9	7016 (3)	2907 (2)	−3228 (3)	602 (16)
C10	7838 (3)	3640 (2)	−3115 (3)	643 (17)
C11	8656 (2)	3823 (2)	−1638 (3)	600 (14)
C12	8628 (2)	3249 (2)	−308 (3)	477 (12)
C13	7786 (2)	2481 (2)	−389 (2)	409 (11)
C14	7673 (2)	1842 (2)	928 (2)	420 (11)
N15	8959 (2)	1229 (2)	5191 (2)	522 (11)
C16	8856 (3)	531 (2)	6484 (3)	592 (16)
C17	9868 (3)	809 (3)	7860 (3)	791 (22)
C18	10558 (3)	1579 (3)	7327 (3)	788 (22)
C19	9948 (2)	1909 (2)	5652 (3)	521 (13)
4-Pyrrolidinobenzo[c]cinnoline (2)				
C1	1146 (3)	5976 (2)	7901 (2)	532 (12)
C2	−273 (3)	6589 (2)	8009 (2)	595 (13)
C3	−1506 (3)	6588 (2)	7304 (2)	548 (12)
C4	−1377 (3)	5952 (2)	6418 (1)	456 (9)
C5	75 (2)	5260 (2)	6321 (1)	409 (9)
N6	147 (2)	4538 (1)	5507 (1)	493 (9)
N7	1391 (2)	3880 (2)	5358 (1)	507 (9)
C8	2704 (3)	3907 (2)	6009 (1)	437 (9)
C9	4028 (3)	3187 (2)	5775 (2)	541 (11)
C10	5390 (3)	3186 (2)	6366 (2)	636 (14)
C11	5450 (3)	3883 (3)	7209 (2)	645 (14)
C12	4148 (3)	4568 (2)	7467 (2)	555 (11)
C13	2744 (3)	4598 (2)	6860 (1)	428 (9)
C14	1329 (3)	5298 (2)	7050 (1)	426 (9)
N15	−2578 (2)	6012 (2)	5722 (1)	493 (9)
C16	−2489 (3)	5641 (2)	4672 (2)	554 (11)
C17	−3807 (3)	6348 (2)	4156 (2)	618 (13)
C18	−5079 (3)	6500 (2)	4964 (2)	648 (14)
C19	−4045 (3)	6710 (2)	5886 (2)	576 (12)

atom-numbering schemes are shown in Fig. 1. Bond lengths and angles are given in Table 3, and molecular packing diagrams in Fig. 2.

The benzo[c]cinnoline skeletons in (1) and (2) consist of almost planar rings. The maximum distances from the least-squares planes are for (1) 0.003 (3), 0.007 (2) and 0.018 (2) Å for rings α (C8, C9, C10, C11, C12, C13), β (C5, N6, N7, C8, C13, C14) and γ (C1, C2, C3, C4, C5, C14), respectively. The corresponding distances in (2) are 0.023 (2), 0.027 (2) and 0.023 (3) Å, indicating greater deviations from planarity for (2). The benzo[c]cinnoline skeleton in (1) is also more planar than (2), which can be seen from the dihedral angles [for compound (2) in parentheses] $\alpha - \beta = 0.29$ (7) [2.1 (2)], $\alpha - \gamma = 1.32$ (6) [4.95 (7)] and $\beta - \gamma = 1.25$ (6)° [4.02 (6)°]. The dihedral angles depend on the steric interaction with the substituents. The interaction is greatest with the substituents in the position 1 as for 1-piperidino-

Table 3. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

	(1)	(2)		(1)	(2)
C1—C2	1·398 (3)	1·374 (3)	C8—C13	1·414 (3)	1·404 (3)
C1—C14	1·402 (3)	1·402 (3)	C9—C10	1·353 (4)	1·368 (4)
C2—C3	1·424 (3)	1·384 (3)	C10—C11	1·412 (4)	1·399 (4)
C2—N15	1·363 (3)		C11—C12	1·373 (3)	1·380 (3)
C3—C4	1·363 (3)	1·411 (3)	C12—C13	1·406 (3)	1·410 (3)
C4—C5	1·403 (4)	1·446 (3)	C13—C14	1·439 (3)	1·443 (3)
C4—N15		1·358 (3)	N15—C16	1·462 (3)	1·478 (2)
C5—C14	1·410 (3)	1·419 (3)	N15—C19	1·450 (3)	1·471 (3)
C5—N6	1·382 (3)	1·386 (2)	C16—C17	1·507 (4)	1·529 (3)
N6—N7	1·298 (3)	1·294 (2)	C17—C18	1·448 (5)	1·513 (4)
N7—C8	1·386 (3)	1·385 (3)	C18—C19	1·499 (3)	1·521 (4)
C8—C9	1·408 (4)	1·411 (3)			

	(1)	(2)		(1)	(2)
C2—C1—C14	120·6 (2)	118·4 (2)	C10—C11—C12	120·1 (3)	121·3 (2)
C1—C2—C3	118·8 (3)	122·9 (2)	C11—C12—C13	120·9 (2)	119·8 (2)
C1—C2—N15	121·3 (2)		C8—C13—C12	118·2 (2)	118·4 (2)
C3—C2—N15	119·9 (2)		C8—C13—C14	116·3 (2)	117·1 (2)
C2—C3—C4	120·8 (2)	121·6 (2)	C12—C13—C14	125·5 (2)	124·4 (2)
C3—C4—C5	120·5 (2)	115·9 (2)	C1—C14—C5	119·4 (2)	120·3 (2)
C3—C4—N15		120·0 (2)	C1—C14—C13	124·7 (2)	123·7 (2)
C5—C4—N15		124·2 (2)	C5—C14—C13	116·0 (2)	116·1 (2)
C4—C5—C14	119·8 (2)	120·9 (2)	C2—N15—C16	124·2 (2)	
C4—C5—N6	116·3 (2)	116·8 (2)	C2—N15—C19	122·8 (2)	
N6—C5—C14	123·9 (2)	122·2 (2)	C4—N15—C16		127·3 (2)
C5—N6—N7	120·3 (2)	121·5 (2)	C4—N15—C19		121·1 (2)
N6—N7—C8	119·7 (2)	119·9 (2)	C16—N15—C19	113·0 (2)	110·4 (2)
N7—C8—C9	116·2 (2)	116·2 (2)	N15—C16—C17	103·9 (2)	103·7 (2)
N7—C8—C13	123·7 (2)	123·0 (2)	C16—C17—C18	109·3 (2)	102·9 (2)
C9—C8—C13	120·1 (2)	120·8 (2)	C17—C18—C19	108·5 (3)	102·8 (2)
C8—C9—C10	120·4 (2)	119·7 (2)	C18—C19—N15	104·9 (2)	103·9 (2)
C9—C10—C11	120·3 (3)	119·9 (2)			

benzo[c]cinnoline where, for example, the angle $\alpha - \gamma$ = 14·4 (1)°, compared with the corresponding angle in 3-piperidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991), $\alpha - \gamma$ = 3·4 (1) and 1·8 (1)° for the two independent molecules.

The pyrrolidino group is quite planar in (1) but less so in (2). In (1) the displacements of the atoms in the pyrrolidino group from the least-squares plane are 0·009 (2), 0·005 (3), −0·034 (3), 0·042 (3) and −0·020 (3) Å for N15, C16, C17, C18 and C19, respectively. For (2) the corresponding distances are −0·145 (2), 0·045 (2), 0·507 (2), −0·201 (2) and
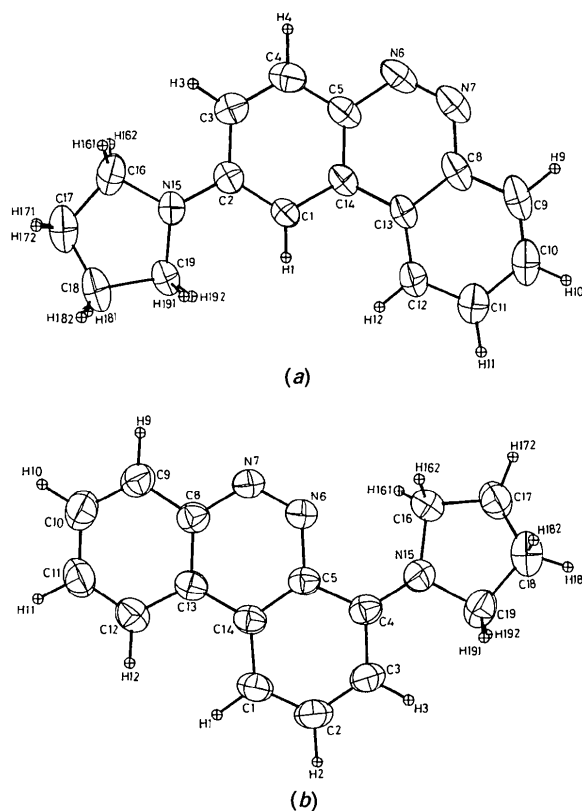

(a)

(a)

(b)

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.
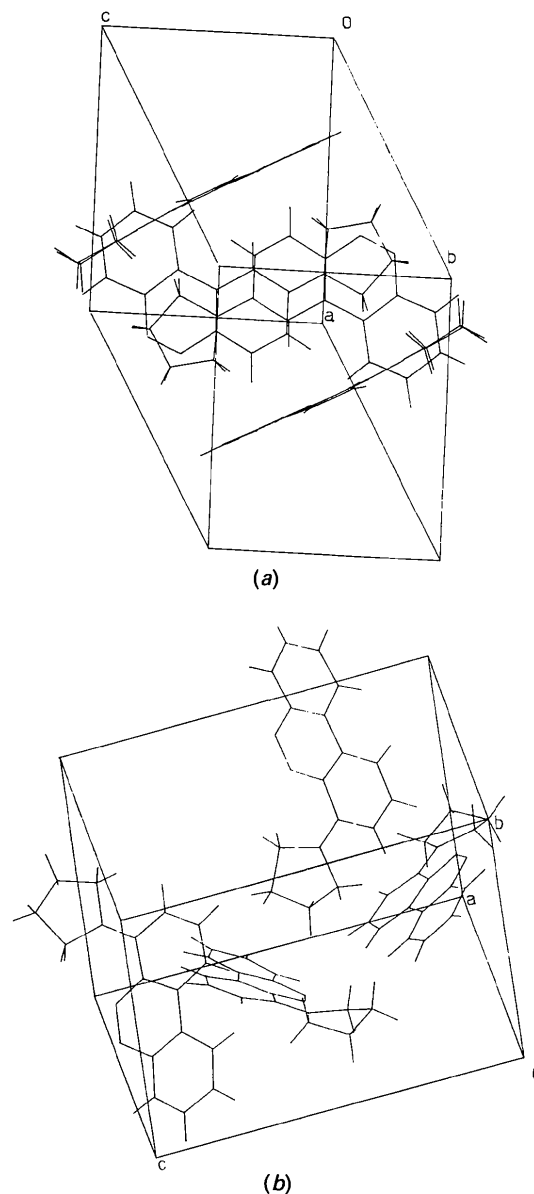

(b)

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

-0.080 (2) Å. This difference in planarity also results in generally smaller angles within the pyrrolidino ring in (2) compared with (1). The dihedral angle between the pyrrolidino group and ring γ in the benzo[c]cinnoline skeleton is 5·43 (5) in (1) and 6·80 (5)° in (2).

Back donation of the lone pair of electrons of the N15 atom affects the bond lengths and angles of ring γ in the benzo[c]cinnoline skeleton. The hybridization of N15 is close to $sp^2 + p$ which results in short bonds C2—N15 = 1·363 (3) in (1) and C4—N15 = 1·358 (3) Å in (2). In 1- and 3-piperidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991) the corresponding distances are C1—N15 = 1·382 (5) (molecule A) and 1·388 (5) Å (molecule B) which might be ascribed to a hybridization intermediate between sp^3 and $sp^2 + p$. The type and position of the substituent determine the shape of the benzo[c]cinnoline skeleton as well as the overall shape of the molecule.

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Formation of Methyl 11-Hydroxy-8-oxopentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecanecarboxylate by a Regiospecific and Stereospecific Reduction

BY WILLIAM H. WATSON* AND RAM P. KASHYAP

Department of Chemistry, Texas Christian University, Forth Worth, Texas 76129, USA

AND ALAN P. MARCHAND* AND S. PULLA REDDY

Department of Chemistry, University of North Texas, PO Box 5068, Denton, Texas 76203, USA

Abstract. Methyl 11-hydroxy-8-oxopentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecanecarboxylate (3), $C_{13}H_{14}O_4$, $M_r = 234\cdot26$, triclinic, $P\bar{1}$, $a = 7\cdot291$ (1), $b = 7\cdot441$ (1), $c = 10\cdot414$ (1) Å, $\alpha = 104\cdot56$ (1), $\beta = 90\cdot41$ (1), $\gamma = 99\cdot07$ (1)°, $V = 539\cdot3$ (1) Å³, $Z = 2$, $D_x = 1\cdot442$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot00$ cm⁻¹, $F(000) = 248$, $T = 295$ K, $R = 0\cdot0487$ for 2138 reflections. Compound (3) contains four five-membered rings and a four-membered ring fused to form an open-ended cage structure. The through-bond interaction of the π systems in the parent diketone is absent in compound (3), which is reflected in the reduction of bond lengths. Although one C—C bond is 1·579 (2) Å, it has been shortened significantly. A hydrogen bond is formed between the hydroxyl group and the carbonyl O atom of the ester.

Introduction. In connection with an ongoing study of the synthesis and chemistry of novel substituted pentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecanes (PCU's; Marchand, 1989), sodium borohydride reduction of compound (1) (Watson, Nagl, Marchand, Reddy & Reddy, 1989) has been investigated. Highly stereo-