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Structure of 1-Morpholinobenzo[*c*]cinnoline

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Abstract. $C_{16}H_{15}N_3O$, $M_r = 265{\cdot}316$, monoclinic, $P2_1/c$, $a = 10{\cdot}572\,(5)$, $b = 11{\cdot}954\,(6)$, $c = 11{\cdot}222\,(2)$ Å, $\beta = 108{\cdot}13\,(2)°$, $V = 1347{\cdot}8\,(1{\cdot}4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}30$, $D_x = 1{\cdot}307$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54180 Å, $\mu = 6{\cdot}373$ cm^{-1}, $F(000) = 560$, $T = 293$ K, $R = 0{\cdot}046$ for 2103 observed reflections. The two benzenoid rings are each planar but twisted with respect to each other with a torsion angle of 11·7°; in benzo[*c*]cinnoline the corresponding torsion angle is 2·5°.

Introduction. Benzo[*c*]cinnoline is known to be a mutagen (Leary, Lafleur, Liber & Blemann, 1983), and some of its derivatives are known to have antirheumatic (Matter, 1957; Erlenmeyer, 1958), herbicidal (Entwistle, Terence & Barton, 1981) and carcinogenic activity (Ashby, Styles & Paton, 1980). The structures of benzo[*c*]cinnoline (van der Meer, 1972) and octachlorobenzo[*c*]cinnoline (King, MacBride, Muir & Wright, 1983) have been described, as have those of benzo[*c*]cinnoline complexes with bis(tricarbonyliron) (Doedens, 1970) and copper(I) benzoato (Toth, Floriani, Chiesi-Villa & Guastini, 1987).

As far as we know, there are no reports on the structures of benzo[*c*]cinnolines substituted with alkyl, alkoxy, aminoalkyl or dialkylamino groups. The present paper is the first of a series devoted to structural studies on related pyrrolidino-, piperidino- and morpholinobenzo[*c*]cinnolines.

A structure determination of the title compound, which contains a morpholino group, was undertaken to permit a comparison of its structure with those of previously reported benzo[*c*]cinnolines to be made.

Experimental. 1-Bromobenzo[*c*]cinnoline was prepared by bromination of benzo[*c*]cinnoline (Barton & Lapham, 1979) obtained by reductive cyclization of 2,2′-dinitrobiphenyl with hydrazine hydrate using palladium on carbon as a catalyst. 1-Morpholinobenzo[*c*]cinnoline was synthesized from the reaction of 1 mmol 1-bromobenzo[*c*]cinnoline in 15 ml morpholine containing 5 ml dimethyl sulfoxide by refluxing for 96 h. After purification by column chromatography using silica gel and dichloromethane–diethyl ether, the product was recrystallized from petroleum ether. In about 3 d yellow prismatic crystals were obtained from *n*-hexane–diethyl ether. Experimental data, the method used to solve the structure and other related parameters and procedures are given in Table 1. Non-H atoms were included with anisotropic thermal parameters, while H atoms were located on difference syntheses and refined isotropically.

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

Method of measuring D_m	Flotation in aqueous KI
Crystal shape and size (mm)	Prismatic, 0·6 × 0·6 × 1·0
Diffractometer used and data-collection technique	Four-circle diffractometer (Enraf–Nonius CAD-4), ω–2θ scan
Number and θ range (°) of reflections used for measuring lattice parameters	25, $45 \leq 2\theta \leq 64$
Absorption correction applied, max. and min. values	Semi-empirical (North, Phillips & Mathews, 1968), 1·25 and 1·18
Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurements (Å^{-1})	0·638
Range of h, k and l	$-1 \leq h \leq 13$, $-1 \leq k \leq 14$, $-13 \leq l \leq 13$
Standard reflections and their intensity variation (%) throughout experiment	026, $0\bar{6}0$, 620; −1·2, 3, 3
Number of reflections measured	3717
Number of unique reflections	2632
Number of unobserved reflections	417
Criterion for recognizing unobserved reflections	$I \leq 3\sigma(I)$
Method used to solve structure	Direct methods
Use of F or F^2 magnitudes in least-squares refinement	F
Parameters refined	241
Values of R, wR	0·046, 0·057
Method used to calculate w	$w = 1$
Final residual electron densities (e Å^{-3}) for max. and min. peaks	+0·30 and −0·30
Max. Δ/σ	0·02
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974)
Computer programs used	*SHELXS*86 (Sheldrick, 1986), *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985), *SNOOPI* (Davies, 1983)

Discussion. The final coordinates and isotropic or equivalent isotropic thermal parameters are given in Table 2.* The structure of the title compound is shown in Fig. 1. The two benzenoid rings are each planar but twisted with respect to each other with a torsion angle of 11·7°; in benzo[*c*]cinnoline the corresponding torsion angle is 2·5°.

As can be seen from Table 3, the bond angles and lengths generally agree with those observed in benzo[*c*]cinnoline where the bond angles corresponding to H12—C12—C11, H12—C12—C13, C14—C13—C12, C1—C14—C13, C8—C13—C14 and C5—C14—C13 are 119 (2), 121 (2), 124·9 (2), 124·9 (2), 116·2 (2) and 117·0 (2)°, the C25—C26—H26 angle corresponding to C14—C1—N15 is 120 (2)° and the bond lengths corresponding to C13—C12, C13—C14 and C14—C1 in the title compound are 1·417 (4), 1·436 (3) and 1·417 (3) Å respectively.

The short H12 to N15 distance (2·3 Å) in the title compound is consistent with the ^{1}H NMR data. This close contact leads to increased twisting in the benzo[*c*]cinnoline system, as shown by the large torsion angle, and is the dominating effect in determining the molecular shape, since it generates large C14—C13—C12 and C13—C14—C1 angles (126·6 and 126·9° respectively) and smaller C8—C13—C14 and C5—C14—C13 angles (116·3 and 115·5° respectively). The bonds C12—C11, C11—C10, C10—C9, C1—C2, C3—C2 and C4—C3 are significantly shorter than the other bonds in the benzene rings.

Table 2. *Atomic coordinates* (× 10^4) *and isotropic or equivalent isotropic thermal parameters* (Å^2 × 10^4, × 10^3 *for* H) *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/U_{eq}
C1	7269 (2)	4287 (1)	2684 (1)	522
C2	7907 (3)	4951 (2)	3704 (2)	732
C3	7219 (4)	5593 (2)	4314 (2)	853
C4	5876 (4)	5567 (2)	3947 (2)	756
C5	5165 (2)	4931 (1)	2878 (2)	612
N6	3805 (2)	4981 (2)	2570 (2)	805
N7	3066 (2)	4498 (1)	1574 (2)	759
C8	3645 (2)	3954 (1)	767 (2)	566
C9	2759 (2)	3541 (2)	−357 (2)	683
C10	3217 (2)	3049 (2)	−1223 (2)	667
C11	4584 (2)	2955 (1)	−1007 (2)	579
C12	5476 (1)	3339 (1)	92 (1)	473
C13	5030 (1)	3842 (1)	1026 (1)	438
C14	5852 (2)	4320 (1)	2196 (1)	467
N15	7997 (1)	3588 (1)	2115 (1)	521
C16	7889 (2)	2397 (1)	2383 (2)	586
C17	8499 (2)	1696 (2)	1600 (3)	775
O18	9843 (1)	1986 (2)	1778 (2)	950
C19	9913 (2)	3122 (3)	1471 (3)	911
C20	9397 (2)	3870 (2)	2305 (2)	762
H2	8978 (27)	4962 (24)	3999 (25)	119 (9)
H3	7636 (29)	6134 (27)	5091 (30)	139 (10)
H4	5321 (24)	5925 (22)	4301 (23)	101 (7)
H9	1788 (23)	3620 (18)	−433 (19)	89 (6)
H10	2611 (24)	2753 (20)	−1975 (22)	97 (7)
H11	4910 (19)	2643 (16)	−1600 (18)	70 (5)
H12	6447 (16)	3306 (12)	187 (14)	47 (4)
H161	6936 (20)	2193 (16)	2205 (17)	68 (5)
H162	8359 (20)	2256 (17)	3259 (20)	79 (6)
H171	7982 (24)	1841 (20)	685 (22)	97 (7)
H172	8500 (22)	872 (22)	1884 (21)	97 (7)
H191	9409 (28)	3343 (23)	572 (27)	121 (9)
H192	10827 (31)	3291 (24)	1522 (26)	129 (9)
H201	9879 (25)	3750 (21)	3227 (24)	102 (7)
H202	9413 (21)	4691 (21)	2104 (21)	93 (7)

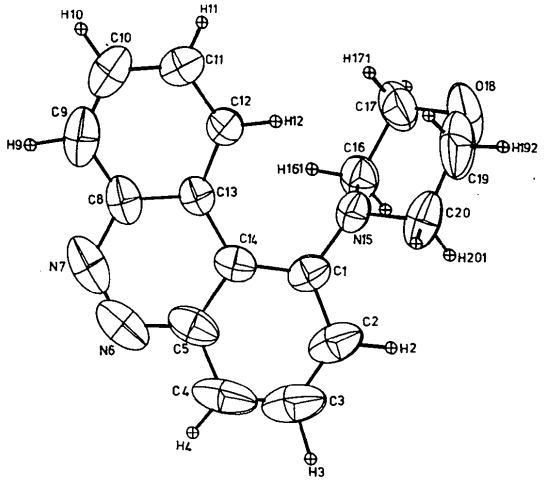

Fig. 1. A *SNOOPI* (Davies, 1983) drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52559 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C1—C14	1·426 (2)	C9—C10	1·349 (3)
C1—N15	1·417 (2)	C10—C11	1·394 (3)
C1—C2	1·384 (2)	C11—C12	1·377 (2)
C2—C3	1·378 (4)	C12—C13	1·411 (2)
C3—C4	1·350 (4)	C13—C14	1·447 (2)
C4—C5	1·421 (3)	N15—C16	1·467 (2)
C5—C14	1·412 (2)	N15—C20	1·466 (2)
C5—N6	1·372 (3)	C16—C17	1·498 (3)
N6—N7	1·284 (3)	C17—O18	1·415 (3)
N7—C8	1·402 (2)	O18—C19	1·409 (3)
C8—C13	1·407 (2)	C19—C20	1·514 (4)
C8—C9	1·406 (3)	C16—H161	0·99 (2)
C2—H2	1·08 (3)	C16—H162	0·97 (2)
C3—H3	1·06 (3)	C17—H171	1·02 (2)
C4—H4	0·91 (3)	C17—H172	1·04 (2)
C9—H9	1·01 (2)	C19—H191	1·02 (3)
C10—H10	0·95 (2)	C19—H192	0·97 (3)
C11—H11	0·92 (3)	C20—H201	1·01 (3)
C12—H12	1·00 (2)	C20—H202	1·01 (2)

C2—C1—C14	119·0 (2)	C10—C11—C12	120·9 (2)
C2—C1—N15	121·2 (2)	C11—C12—C13	120·9 (1)
C14—C1—N15	119·8 (1)	C8—C13—C14	116·3 (1)
C1—C2—C3	122·2 (2)	C12—C13—C8	117·0 (1)
C2—C3—C4	120·3 (2)	C12—C13—C14	126·6 (1)
C3—C4—C5	119·9 (2)	C13—C14—C5	115·5 (1)
C4—C5—N6	115·3 (2)	C13—C14—C1	126·9 (1)
C4—C5—C14	120·6 (2)	C1—C14—C5	117·5 (1)
N6—C5—C14	124·2 (2)	C1—N15—C16	113·2 (1)
C5—N6—N7	120·4 (2)	C1—N15—C20	117·7 (1)
N6—N7—C8	120·1 (2)	C16—N15—C20	109·4 (1)
N7—C8—C9	116·0 (2)	N15—C16—C17	110·3 (2)
N7—C8—C13	123·1 (2)	C16—C17—O18	112·2 (2)
C9—C8—C13	120·8 (2)	C17—O18—C19	109·1 (2)
C8—C9—C10	120·7 (2)	O18—C19—C20	111·2 (2)
C9—C10—C11	119·7 (2)	C19—C20—N15	108·5 (2)
H2—C2—C1	117·1 (15)	H162—C16—N15	109·2 (12)
H2—C2—C3	120·6 (15)	H162—C16—C17	108·7 (12)
H3—C3—C2	126·7 (16)	H171—C17—C16	107·6 (13)
H3—C3—C4	113·1 (16)	H171—C17—O18	107·6 (14)
H4—C4—C3	127·9 (16)	H171—C17—H172	115·0 (19)
H4—C4—C5	112·2 (16)	H172—C17—C16	108·1 (13)
H9—C9—C8	114·8 (12)	H172—C17—O18	106·5 (13)
H9—C9—C10	124·4 (12)	H191—C19—O18	116·2 (16)
H10—C10—C9	120·4 (14)	H191—C19—C20	106·3 (16)
H10—C10—C11	119·9 (14)	H191—C19—H192	102·1 (22)
H11—C11—C10	120·6 (12)	H192—C19—O18	108·1 (17)
H11—C11—C12	118·5 (12)	H192—C19—C20	112·7 (17)
H12—C12—C11	118·4 (9)	H201—C20—N15	106·3 (14)
H12—C12—C13	120·5 (9)	H201—C20—C19	112·6 (14)
H161—C16—N15	109·5 (11)	H201—C20—H202	109·2 (19)
H161—C16—C17	109·9 (11)	H202—C20—N15	106·1 (13)
H161—C16—H162	109·2 (16)	H202—C20—C19	113·7 (13)

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Structure of 2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane (TNSU), an Energetic Spiro Bicyclic Nitramine

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Abstract. $C_7H_{12}N_8O_8$, $M_r = 336{\cdot}22$, monoclinic, $C2/c$, $a = 12{\cdot}831\,(3)$, $b = 10{\cdot}726\,(3)$, $c = 19{\cdot}644\,(5)$ Å, $\beta = 108{\cdot}13\,(2)^\circ$, $V = 2569{\cdot}4$ Å^3, $Z = 8$, $D_x = 1{\cdot}739$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}47$ cm^{-1}, $F(000) = 1392$, $T = 291$ K, $R = 0{\cdot}049$ for 1509 reflections with $|F_o| > 3\sigma(F)$. Both rings of TNSU have chair conformations with two of the nitramine groups equatorial and two axial. The geometry of the nitramine groups in TNSU, with average N—N bond lengths of 1·383 (5) Å, average N—O bond lengths of 1·219 (7) Å, and average C—N bond lengths of 1·462 (15) Å, is typical of

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