Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HR1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Cyano-2-methylsparteine

IRENA WOLSKA AND TERESA BOROWIAK

Laboratory of Crystallography, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Abstract

In the title compound, [7S-(7α,7aα,14α,14aα)]-dodeca-hydro-4-methyl-7,14-methano-2H,6H-dipyrido[1,2-a:

1′,2′-e][1,5]diazocine-4-carbonitrile, $C_{17}H_{27}N_3$, the two quinolizidine moieties have been found to have *trans* A/B and *trans* C/D configurations. The piperidine rings A, B, C and D assume chair, chair, boat and chair conformations, respectively. The methyl substituent has been shown to adopt an equatorial orientation, with the cyano substituent in an axial position.

Comment

This work is a continuation of our studies on sparteine derivatives. Sparteine is the most common among the bisquinolizidine alkaloids isolated from lupine plants. It has been widely used as a model compound for the study of factors influencing conformational–configurational changes. The A/B ring system is not susceptible to conformational changes, whereas the C/D system is, owing to an easy inversion at the N16 atom.

Generally, free bases of sparteine derivatives have a *trans* configuration/boat–chair conformation of the C/D fragment, while the cations show a *cis* configuration/chair–chair conformation of this fragment, *e.g.* sparteine (Skolik, Krueger & Wiewiórowski, 1970) and the sparteine cation (Borowiak, Bokii & Struchkov, 1973), and 2-phenylsparteine (Katrusiak, Figas, Kałuski & Lesiewicz, 1989) and its cation (Kubicki, Borowiak & Boczoń, 1991). In these examples, the A/B fragment was found to have a *trans* configuration/chair–chair conformation in the free base as well as in the cation.

In this paper, we present the results of an X-ray structural analysis of 2-cyano-2-methylsparteine (I) (Fig. 1). The structure is similar to the examples cited above. The piperidine rings A, B and D adopt chair conformations with ring C having a boat conformation. The A/B junction is *trans* [torsion angles C2—N1—C6—C5 −52.5 (3) and C7—C6—N1—C10 56.5 (3)°], as is the C/D junction [torsion angles C9—C11—N16—C17 −54.0 (3) and C12—C11—N16—C15 59.0 (3)°]. The proper enantiomorph has been selected on the

(I)
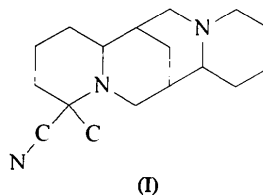
basis of the absolute configuration of naturally occurring sparteine derivatives (Klyne, Scopes, Thomas, Skolik, Gawroński & Wiewiórowski, 1974) to be C7-(S), C9-(S).

The methyl substituent occupies an equatorial position with torsion angles C4—C3—C2—C20 and C6—N1—C2—C20 of −178.9 (2) and 174.9 (2)°, respectively. The cyano group is axial with torsion angles C4—C3—C2—C18 64.2 (3) and C6—C1—C2—C18 −64.9 (3)°.
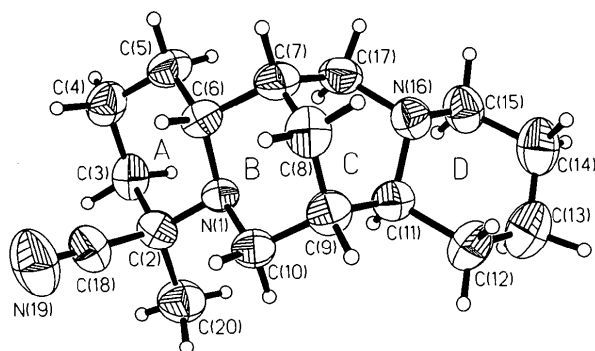
Fig. 1. A perspective view of the title molecule with displacement ellipsoids drawn at the 50% probability level.

The bond lengths and angles are similar to those found for other sparteine derivatives. The mean C_{sp^3}—C_{sp^3} bond length is 1.521 (4) Å and N1—C and N16—C have mean bond lengths of 1.469 (1) and 1.463 (6) Å, respectively. The range of C—H distances is 0.93 (3)–1.08 (3) Å, with B values in the range 0.043 (6)–0.11 (1) Å^2.

The crystal packing, presented in Fig. 2, shows no significant short contacts.
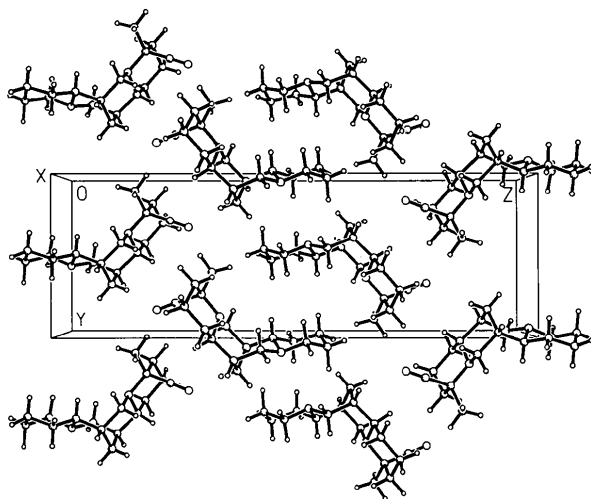

Fig. 2. Crystal packing along the [100] direction.

Experimental

Crystal data

$C_{17}H_{27}N_3$
$M_r = 273.42$
Orthorhombic
$P2_12_12_1$
$a = 7.146 (1)$ Å
$b = 8.635 (3)$ Å
$c = 25.500 (4)$ Å
$V = 1573.5 (6)$ Å^3

$Z = 4$
$D_x = 1.154$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 33 reflections
$\theta = 4.02$–$12.51°$
$\mu = 0.069$ mm^{-1}
$T = 293 (2)$ K
Prism

$0.7 \times 0.5 \times 0.2$ mm
Colourless
Crystal source: crystallized from ethyl alcohol

Data collection

KM-4 four-circle diffracto-meter
$\omega/2\theta$ scans
Absorption correction: none
1648 measured reflections
1648 independent reflections
1190 observed reflections
$[I > 2\sigma(I)]$

$\theta_{max} = 25.05°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 30$
2 standard reflections monitored every 100 reflections
intensity decay: 1.2%

Refinement

Refinement on F^2
$R(F) = 0.0311$
$wR(F^2) = 0.1161$
$S = 1.088$
1643 reflections
289 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.0640P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = <0.001$
$\Delta\rho_{max} = 0.168$ e Å^{-3}
$\Delta\rho_{min} = -0.117$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
N1	0.7139 (3)	0.3606 (2)	0.14976 (7)	0.0432 (5)
C2	0.7163 (4)	0.2309 (3)	0.18700 (10)	0.0508 (6)
C3	0.5175 (4)	0.1677 (3)	0.19500 (10)	0.0576 (7)
C4	0.3826 (4)	0.2917 (4)	0.21297 (12)	0.0630 (7)
C5	0.3861 (4)	0.4225 (4)	0.17427 (12)	0.0622 (7)
C6	0.5821 (3)	0.4840 (3)	0.16422 (10)	0.0490 (6)
C7	0.5801 (4)	0.6089 (3)	0.12101 (11)	0.0539 (6)
C8	0.7753 (4)	0.6800 (3)	0.11661 (12)	0.0587 (7)
C9	0.9009 (3)	0.5509 (3)	0.09905 (10)	0.0538 (6)
C10	0.9018 (3)	0.4242 (4)	0.14048 (11)	0.0542 (6)
C11	0.8423 (4)	0.4914 (3)	0.04475 (10)	0.0503 (6)
C12	0.9928 (5)	0.5214 (4)	0.00342 (12)	0.0674 (8)
C13	0.9333 (6)	0.4713 (5)	−0.05070 (14)	0.0842 (10)
C14	0.7460 (5)	0.5394 (4)	−0.06505 (13)	0.0785 (10)
C15	0.6040 (5)	0.5064 (4)	−0.02284 (11)	0.0652 (7)
N16	0.6667 (3)	0.5656 (2)	0.02776 (8)	0.0523 (5)
C17	0.5222 (4)	0.5455 (3)	0.06739 (11)	0.0546 (6)
C20	0.8418 (5)	0.0996 (4)	0.16792 (14)	0.0711 (8)
C18	0.7875 (4)	0.2837 (3)	0.23939 (11)	0.0616 (7)
N19	0.8392 (5)	0.3254 (4)	0.27906 (12)	0.0970 (10)

Table 2. *Selected geometric parameters* (Å, °)

N1—C2	1.468 (3)	C8—C9	1.499 (4)
N1—C6	1.470 (3)	C9—C10	1.521 (4)
N1—C10	1.470 (3)	C9—C11	1.535 (4)
C2—C18	1.500 (4)	C11—N16	1.474 (3)
C2—C20	1.525 (4)	C11—C12	1.528 (4)
C2—C3	1.535 (4)	C12—C13	1.507 (5)
C3—C4	1.512 (4)	C13—C14	1.507 (6)
C4—C5	1.500 (4)	C14—C15	1.507 (5)

$C_{17}H_{27}N_3$

C5—C6	1.520 (4)	C15—N16	1.459 (3)
C6—C7	1.542 (4)	N16—C17	1.455 (3)
C7—C8	1.528 (4)	C18—N19	1.136 (4)
C7—C17	1.530 (4)		
C2—N1—C6	113.5 (2)	C9—C8—C7	105.6 (2)
C2—N1—C10	112.2 (2)	C8—C9—C10	109.3 (2)
C6—N1—C10	110.8 (2)	C8—C9—C11	110.8 (2)
N1—C2—C18	110.4 (2)	C10—C9—C11	112.8 (2)
N1—C2—C20	111.6 (2)	N1—C10—C9	112.2 (2)
C18—C2—C20	108.1 (2)	N16—C11—C12	108.8 (2)
N1—C2—C3	110.2 (2)	N16—C11—C9	110.6 (2)
C18—C2—C3	107.7 (2)	C12—C11—C9	111.9 (2)
C20—C2—C3	108.8 (2)	C13—C12—C11	112.6 (3)
C4—C3—C2	112.3 (2)	C14—C13—C12	111.1 (3)
C5—C4—C3	108.8 (2)	C15—C14—C13	110.5 (3)
C4—C5—C6	112.9 (2)	N16—C15—C14	111.0 (3)
N1—C6—C5	112.3 (2)	C17—N16—C15	110.8 (2)
N1—C6—C7	109.5 (2)	C17—N16—C11	110.4 (2)
C5—C6—C7	110.9 (2)	C15—N16—C11	111.7 (2)
C8—C7—C17	109.0 (2)	N16—C17—C7	112.7 (2)
C8—C7—C6	109.0 (2)	N19—C18—C2	178.9 (3)
C17—C7—C6	113.0 (2)		

Data collection: *Kuma KM-4 User's Guide* (Kuma, 1992). Cell refinement: *Kuma KM-4 User's Guide*. Data reduction: *Kuma KM-4 User's Guide*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989). Software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

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Conformationally Defined Cyclohexyl Carnitine Analogs

WAYNE J. BROUILLETTE, GARY M. GRAY* AND ASHRAF SAEED

Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294-1240, USA

Abstract

Three diastereoisomers of racemic (3-carboxy-2-hydroxy-1-cyclohexyl)trimethylammonium chloride [$C_{10}H_{20}NO_3^+.Cl^-$; (1S,2S,3S) (2), (1R,2S,3S) (3) and (1S,2R,3S) (4)] were designed as rigid analogs for different low-energy conformational states of carnitine [(1), (3-carboxy-2-hydroxy-1-propyl)trimethylammonium chloride]. Structures (2)–(4) all assume a chair conformation in the solid state, in which the bulky trimethylammonio group occupies the equatorial position. As such, the orientations about C2—C3 in (2), (3) and (4) are all essentially the same as that found for (1) in the solid state (torsion angles for C1—C2—C3—N1 near 180°), while the orientations about C1—C2 in (2)–(4) are such that each diastereoisomer contains a different one of the three possible low-energy staggered conformations predicted for (1) in solution. Comparisons between (1) and (2)–(4) in the solid state revealed that diastereoisomers (2), (3) and (4) provide rigid models for the major low-energy conformations of carnitine.

Comment

(R)-Carnitine (1) is important in cellular metabolism as a substrate for several different carnitine acyltransferases. Structure (1) is conformationally flexible and determining the protein-bound conformation for (1) with each of the acyltransferases is of considerable pharmacological interest. Studies by others (Colucci & Gandour, 1988) have suggested that protein-bound (1) contains a *gauche* relationship between N1 and O3 [atoms were numbered as in (2)–(4) for easy comparison]. This conformation about C2—C3 also exists in the crystal structure of (1) (Tomita, Urabe, Kim & Fujiwara, 1974) and is favored in solution (Colucci, Gandour & Mooberry, 1986). However, the protein-bound conformation for (1) about C1—C2 has not been determined and two of the three possible low-energy staggered conformations are nearly equally favored in solution (Colucci, Gandour & Mooberry, 1986). As part of a study to address this question, we synthesized racemic cyclohexyl carnitine analogs (2), (3) and (4) (Brouillette, Saeed, Abuelyaman, Hutchison, Wolkowicz & McMillin, 1994).