C6	0.9131 (6)	−0.3943 (5)	0.2188 (5)	0.078 (2)
C7	0.8542 (5)	−0.3279 (5)	0.3043 (4)	0.0744 (14)
C8	0.7903 (5)	−0.2080 (4)	0.2936 (4)	0.0623 (13)
C8A	0.7835 (4)	−0.1505 (4)	0.1942 (3)	0.0489 (11)
O1	0.6297 (3)	0.1307 (3)	0.0594 (2)	0.0601 (8)
O2	0.8465 (4)	0.2761 (3)	0.0720 (3)	0.1012 (14)
C20	0.7126 (6)	0.2584 (5)	0.0551 (4)	0.0636 (13)
C21	0.6102 (6)	0.3612 (4)	0.0286 (4)	0.083 (2)
C1′	0.3086 (5)	0.0501 (4)	0.4077 (4)	0.0596 (12)
C2′	0.2211 (5)	−0.0689 (5)	0.3494 (4)	0.0670 (13)
C3′	0.2758 (5)	−0.1479 (5)	0.2665 (4)	0.0651 (13)
C4′	0.4176 (5)	−0.1090 (4)	0.2418 (3)	0.0579 (12)
C4′A	0.5097 (4)	0.0126 (4)	0.2995 (3)	0.0478 (11)
C5′	0.6592 (5)	0.0556 (4)	0.2709 (3)	0.0492 (11)
C6′	0.7454 (5)	0.1734 (4)	0.3280 (3)	0.0539 (11)
C6′A	0.6970 (5)	0.2563 (4)	0.4162 (3)	0.0481 (11)
N7′	0.7897 (4)	0.3699 (3)	0.4682 (3)	0.0513 (9)
C7′A	0.7405 (5)	0.4439 (4)	0.5521 (3)	0.0468 (10)
C8′	0.8338 (5)	0.5674 (4)	0.6103 (3)	0.0578 (12)
C9′	0.7865 (5)	0.6421 (4)	0.6951 (4)	0.0651 (13)
C10′	0.6446 (6)	0.6004 (5)	0.7273 (4)	0.0700 (13)
C11′	0.5528 (5)	0.4844 (4)	0.6728 (3)	0.0628 (13)
C11A	0.5972 (5)	0.4035 (4)	0.5837 (3)	0.0493 (11)
N12′	0.5020 (4)	0.2881 (3)	0.5290 (3)	0.0503 (9)
C12A	0.5511 (4)	0.2161 (4)	0.4465 (3)	0.0448 (10)
C12B	0.4552 (4)	0.0913 (4)	0.3844 (3)	0.0466 (10)

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

C4′A—C12B	1.401 (5)	N7′—C7′A	1.345 (4)
C4′A—C5′	1.460 (5)	C7′A—C11A	1.419 (5)
C5′—C6′	1.356 (5)	C11A—N12′	1.365 (5)
C6′—C6′A	1.424 (5)	N12′—C12A	1.323 (4)
C6′A—N7′	1.334 (4)	C12A—C12B	1.462 (5)
C6′A—C12A	1.433 (5)		

Refinement on F^2 for all reflections except for 2 with very negative F^2.

Data collection: *XSCANS* (Fait, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bader, A. R. (1951). *J. Am. Chem. Soc.* **73**, 3731–3732.
Fait, J. (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Raacke-Fels, I. D., Wang, C. H., Robins, R. K. & Christensen, B. E. (1950). *J. Org. Chem.* **15**, 627–630.
Sato, M., Oya, A. & Otani, S. (1980). *Cryst. Struct. Commun.* **9**, 811–813.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Wozniak, K., Kariuki, B. & Jones, W. (1991). *Acta Cryst.* C**47**, 1113–1114.

Acta Cryst. (1996). C**52**, 224–226

3,3-Dimethylglutaronitrile

Annie Héroux and François Brisse*

Département de Chimie, Université de Montréal, CP 6128,
Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7.
E-mail: brisse@tornade.ere.umontreal.ca

(*Received 15 March 1995; accepted 25 August 1995*)

Abstract

The X-ray determination of the title compound, 3,3-dimethylpentanedinitrile, $C_7H_{10}N_2$, was performed in order to characterize an intermediate product. The compound crystallizes in the *C*2/*c* space group, with one molecule in a general position and another molecule on a crystallographic twofold rotation axis.

Comment

The title compound, (I), was synthesized following the procedure previously described by Equi, Brown, Cooper, Ner, Watson & Robins (1991). The compound is an intermediate in the procedure used to obtain 3,3-dimethylpentanediamine from 3,3-dimethylglutaric acid. In the first reaction step, the acid function was protected with a mesylate (phenyl methanesulfonate) group (yield 83%). The product was then reacted with NaCN in DMSO to give the dinitrile compound. This last product was isolated by extraction according to Equi *et al.* (1991). A yellow liquid was obtained, from which a white solid appeared after distillation on a Kugelrhor apparatus (80 K/0.5 mmHg).

(I)

There are 12 molecules in the monoclinic unit cell of the *C*2/*c* space group, eight of which occupy general positions, while the other four possess a crystallographic twofold rotation axis passing through the central atom, C33. The bond distances and angles within the molecules are in good agreement with expected values. All C—H distances are in the range 0.96 (2)–1.02 (2) Å, while the C—C—H bond angles range from 105.7 (12) to 112.8 (10)° and the H—C—H angles range from 102.4 (16) to 114.3 (16)°. The environment of the central C atom deviates slightly from tetrahedral; the C—CH_2 and C—CH_3 bond lengths average 1.538 and 1.520 Å, respectively, while the CH_3—C—CH_3 and CH_2—C—CH_2 angles also show a marked difference, with values of 110.5 and 105.1°, respectively. The two groups of atoms N11, C11, C12, C13, C22, C21, N21 (r.m.s.

deviation 0.002Å) and C13, C14, C15 are planar. The dihedral angle between these planes is 89.9 (1)°. Atoms N31, C31, C32 and C33 of the molecule in a special position are also coplanar.

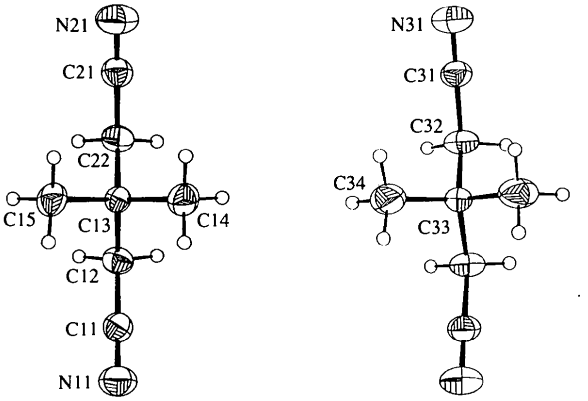


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the two molecules in the title compound and the atom-numbering scheme adopted. The ellipsoids are drawn at the 40% probability level, while the H atoms are represented by spheres of arbitrary size.

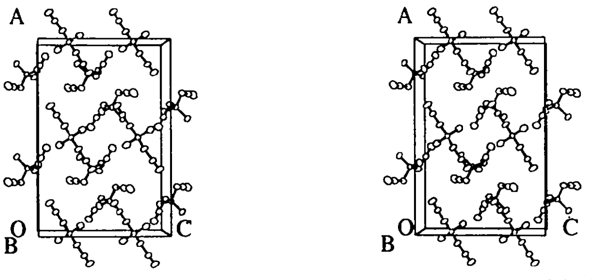


Fig. 2. Stereodiagram showing the relative disposition of the 3,3-dimethylglutaronitrile molecules within the unit cell.

Experimental

Crystals were obtained from tetrahydrofuran solution and the crystal used in the diffraction analysis was obtained directly after distillation of the solvent. The crystals are air sensitive at room temperature and decompose at low temperature (173 K) over a period of a few days.

Crystal data

$C_7H_{10}N_2$
$M_r = 122.17$
Monoclinic
$C2/c$
$a = 18.148\,(2)$ Å
$b = 10.424\,(2)$ Å
$c = 12.115\,(2)$ Å
$\beta = 90.15\,(2)°$
$V = 2292.0\,(7)$ Å^3
$Z = 12$
$D_x = 1.062$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 20$–$21.5°$
$\mu = 0.486$ mm^{-1}
$T = 223\,(5)$ K
Transparent plate
$0.38 \times 0.27 \times 0.09$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8077 measured reflections
2183 independent reflections
1804 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.038$
$\theta_{\rm max} = 69.81°$
$h = -21 \rightarrow 22$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
6 standard reflections monitored every 400 reflections
intensity decay: 5.88%

Refinement

Refinement on F^2
$R(F) = 0.0430$
$wR(F^2) = 0.1215$
$S = 1.065$
2183 reflections
184 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.4242P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$

$\Delta\rho_{\rm max} = 0.139$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.134$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0033 (4)
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)

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

	x	y	z	$U_{\rm eq}$
N11	0.05425 (8)	0.20873 (15)	0.92698 (12)	0.0711 (4)
C11	0.10631 (7)	0.17140 (13)	0.96903 (11)	0.0506 (4)
C12	0.17203 (7)	0.12179 (14)	1.02416 (12)	0.0475 (3)
C13	0.15853 (6)	−0.00804 (11)	1.08093 (9)	0.0383 (3)
C14	0.13574 (10)	−0.1089 (2)	0.99643 (13)	0.0572 (4)
C15	0.09953 (9)	0.0059 (2)	1.16961 (12)	0.0581 (4)
C22	0.23291 (7)	−0.04459 (14)	1.13354 (13)	0.0497 (4)
C21	0.22999 (8)	−0.16682 (14)	1.19244 (12)	0.0529 (4)
N21	0.22711 (9)	−0.26200 (14)	1.23766 (14)	0.0789 (5)
N31	0.16009 (7)	0.4503 (2)	0.09330 (12)	0.0734 (4)
C31	0.11508 (7)	0.50472 (14)	0.13864 (11)	0.0505 (4)
C32	0.05719 (8)	0.57357 (14)	0.19697 (13)	0.0509 (4)
C33	0	0.4836 (2)	1/4	0.0386 (4)
C34	0.03725 (10)	0.4021 (2)	0.3373 (2)	0.0750 (6)

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

N11—C11	1.141 (2)	C22—C21	1.461 (2)
C11—C12	1.460 (2)	C21—N21	1.135 (2)
C12—C13	1.538 (2)	N31—C31	1.137 (2)
C13—C14	1.524 (2)	C31—C32	1.457 (2)
C13—C15	1.526 (2)	C32—C33	1.541 (2)
C13—C22	1.539 (2)	C33—C34	1.514 (2)
N11—C11—C12	178.8 (2)	C21—C22—C13	112.7 (1)
C14—C13—C15	110.4 (1)	N21—C21—C22	179.3 (2)
C11—C12—C13	112.7 (1)	N31—C31—C32	179.6 (2)
C14—C13—C12	110.5 (1)	C31—C32—C33	113.0 (1)
C15—C13—C12	110.1 (1)	C34—C33—C32	109.4 (1)
C14—C13—C22	110.1 (1)	C34$^{\rm i}$—C33—C32$^{\rm i}$	109.4 (1)
C15—C13—C22	110.4 (1)	C34—C33—C32$^{\rm i}$	110.5 (1)
C12—C13—C22	105.2 (1)	C32—C33—C32$^{\rm i}$	105.0 (2)
C11—C12—C13—C14	61.1 (2)	C12—C13—C22—C21	179.6 (1)
C11—C12—C13—C15	−61.2 (2)	C31—C32—C33—C34$^{\rm i}$	−60.1 (2)
C11—C12—C13—C22	179.9 (1)	C31—C32—C33—C34	63.4 (2)
C14—C13—C22—C21	−61.3 (2)	C31—C32—C33—C32$^{\rm i}$	−178.0 (2)
C15—C13—C22—C21	60.9 (2)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The structure was solved in the *P*1 space group and *MISSYM* (Le Page, 1988) was used in order to detect a higher symmetry. The unit cell was ultimately found to be monoclinic.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: locally modified *NRC*-2 (Ahmed, 1968). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: BK1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahmed, F. R. (1968). *NRC Crystallographic Programs*. National Research Council of Canada, Ottawa, Canada.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Equi, A. M., Brown, A. M., Cooper, A., Ner, S. K., Watson, A. B. & Robins, D. J. (1991). *Tetrahedron*, **47**, 507–518.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Le Page, Y. (1988). *J. Appl. Cryst.* **21**, 983–984.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 226–228

2-Cyano-2-methylsparteine Perchlorate

MACIEJ KUBICKI,[a] TERESA BOROWIAK[a] AND WŁADYSŁAW BOCZOŃ[b]

[a]*Laboratory of Crystallography, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland, and* [b]*Laboratory of Stereochemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*

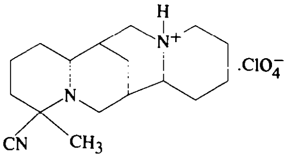
(*Received 23 May 1995; accepted 11 August 1995*)

Abstract

The cation of the title salt, $C_{17}H_{28}N_2^+.ClO_4^-$, is built up of two quinolizidine moieties and has a *trans-A/B* and *cis-C/D* configuration. All four rings adopt chair conformations. The protonation that takes place at the N16 atom and subsequent creation of an intramolecular N⁺—H···N hydrogen bond causes inversion of the N16 configuration compared with that of the free sparteine base. The perchlorate anion is disordered.

Comment

Sparteine is the most common among bis(quinolizidine) alkaloids isolated from lupine plants. Since the quinolizidine skeleton occurs in a number of natural compounds, sparteine is widely used as the model for studying the factors influencing the conformational/configurational changes. In this paper, we present the results of an X-ray structural analysis of 2-cyano-2-methylsparteine perchlorate, (I).



(I)

It has been shown that protonation of the free base is likely to cause inversion of configuration 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*/chair-chair combination, *e.g.* sparteine (Skolik, Krueger & Wiewiórowski, 1970) and the sparteine cation (Borowiak, Bokii & Strutchkov, 1973), and 2-phenylsparteine (Boczoń, 1981; Katrusiak, Figas, Kałuski & Lesiewicz, 1989) and its cation (Kubicki, Borowiak & Boczoń, 1991). The *A/B* fragment was found to be *trans*/chair-chair in the free base as well as in the cation. Due to its thermodynamic stability, it is not susceptible to configurational/conformational changes.

The title compound is another example of this tendency. All four rings adopt chair conformations, with the asymmetry parameters (Duax & Norton, 1975) showing greater distortions from ideal values for the central *B* and *C* rings than for the terminal *A* and *D* ones. The *A/B* junction is *trans* [C2—N1—C6—C5 −57.3 (5) and C7—C6—N1—C10 of 51.9 (4)°], while the *C/D* junction is *cis* [C9—C11—N16—C17 49.8 (4) and C12—C11—N16—C15 51.8 (5)°]. The intramolecular N16⁺—H16···N1 hydrogen bond [H16···N1 2.23 (4), N16···N1 2.841 (5) Å and N16—H16···N1 124 (3)°] stabilizes this system. This bond is signifcantly weaker that the one found in the 2-methylsparteine cation [N···N 2.710 (7) Å; Katrusiak, Hoser, Kałuski & Boczoń, 1980] and in the 2-phenylsparteine cation [2.742 (4) Å; Kubicki, Borowiak & Boczoń, 1991]. The protonation causes significant changes in the N—C bond lengths; the weighted mean values for atoms N1 and N16 are 1.490 (3) and 1.513 (5) Å, respectively. All other bond lengths and angles are typical, with a weighted mean value for the C_{sp^3}—C_{sp^3} bond length of 1.520 (2) Å.