Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.127$, $T_{\max} = 0.178$
10 786 measured reflections
5037 independent reflections
3815 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 29.97°$
$h = 0 \rightarrow 21$
$k = -20 \rightarrow 20$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 120 min^{-1}
intensity decay: 0.82%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.054$
$S = 1.880$
3815 reflections
209 parameters
H atoms riding [C—H 0.95 Å; U(H) = $1.3U_{\rm eq}$(C)]
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\max} = 0.029$
$\Delta\rho_{\max} = 1.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $9.2 (4) \times 10^{-8}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

I1—C1	2.094 (4)	C10—C14	1.534 (5)
I2—C8	2.083 (4)	C10—C15	1.489 (6)
O1—C9	1.209 (4)	C15—C16	1.185 (6)
O2—C10	1.423 (4)	C16—C17	1.440 (7)
C9—C12	1.479 (5)	C17—C18	1.345 (8)
C9—C13	1.479 (5)	C17—C19	1.486 (9)
C10—C11	1.527 (6)		
I1—C1—C2	116.1 (3)	C11—C10—C14	110.8 (3)
I1—C1—C13	122.6 (3)	C11—C10—C15	108.1 (3)
I2—C8—C7	116.4 (3)	C14—C10—C15	108.7 (3)
I2—C8—C12	122.2 (3)	C10—C15—C16	174.2 (4)
C12—C9—C13	115.3 (3)	C15—C16—C17	178.1 (5)
O2—C10—C11	110.4 (3)	C16—C17—C18	120.2 (5)
O2—C10—C14	107.0 (3)	C16—C17—C19	115.5 (5)
O2—C10—C15	111.9 (3)	C18—C17—C19	124.3 (5)
C13—C9—C12—C11	36.3 (5)	C11—C10—C14—C13	37.8 (5)
C12—C9—C13—C14	−37.4 (5)	C10—C11—C12—C9	2.0 (5)
C14—C10—C11—C12	−37.8 (5)	C9—C13—C14—C10	−1.8 (5)

The two largest peaks in the final difference map, both of density greater than 1 e Å^{-3}, were located less than 1 Å from the two I atoms.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. RKT also appreciates the Chancellor Student Aid Fund which made structure determination possible. Research was supported (or partially supported) by a Research Centers in Minority Institutions award (#G12RR03062) from the Division of Research Resources, National Institutes of Health and MBRS grant #GM08247.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1169). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Bayer, O. (1979). *Methoden der Organischen Chemie*, **7/3c**, 63–64.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Garcia, J. G., Asfaw, B. & Rodriguez, A. (1997). Unpublished results.
Garcia, J. G., Ramos, B., Pratt, L. & Rodriguez, A. (1995). *Tetrahedron Lett.* **36**, 7391–7394.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sygula, A., Sygula, R., Fronczek, F. R. & Rabideau, P. W. (1992). *J. Org. Chem.* **57**, 3286–3291.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1997). C**53**, 1139–1141

(1*S*,6*S*)-Tetrazolo[1,5-*g*]-7-aza-*trans*-himachal-2-ene†

Essedyia Lassaba,[a] Ahmed Benharref,[a] Michel Giorgi[b] and Marcel Pierrot[b]

[a]*Laboratoire de Chimie des Substances Naturelles et des Hétérocycles, associé au CNCPRST, Département de Chimie, Faculté des Sciences Semlalia, Université Cadi Ayyad, Marrakech, Morocco, and* [b]*LBS-UMR 6517, Faculté des Sciences et Techniques de Saint Jérôme, Avenue Escadrille Normandie Niemen, 13397 Marseille CEDEX 20, France. E-mail: mpie@ms432u04.u-3mrs.fr*

(Received 11 December 1996; accepted 5 March 1997)

Abstract

In the title compound, $C_{14}H_{22}N_4$, the tetrazole ring is fused with the eight-membered ring of the himachal-2-ene skeleton, which is in a *trans* conformation.

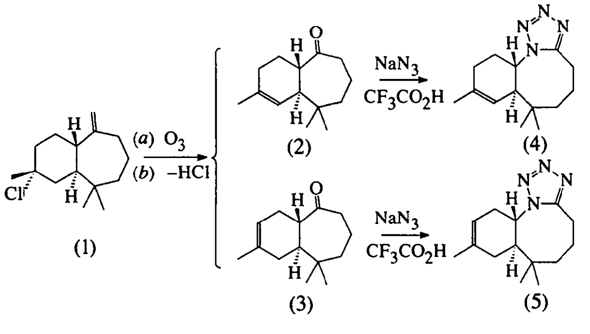
---

† Alternative name: (7a*S*,11a*S*)-4,5,6,7,7a,10,11,11a-octahydro-7,7,9-trimethyl-2-benzazocino[1,2-*d*]tetrazole.

Comment

Two sesquiterpenic hydrocarbons, α- and β-himachalene, are the main constituents of Atlas cedar (*Cedrus atlantica*) essential oils described by several authors (Joseph & Dev, 1968*a*; Plattier & Teisseire, 1974). In order to enhance the value and usefulness of the Atlas cedar essentials oils, we have undertaken a major program of research on this Moroccan natural product (Benharref, Bernardini, Fkih-Tetouani, Jacquier & Viallefont, 1981).

The action of HCl on a mixture of α- and β-himachalene in acetic acid leads to only one compound, 3,7-dichlorohimachalane, which on recrystallization from methanol yields 3-chlorohimachalane, (1) (Joseph & Dev, 1968*b*; Sasaki, Eguchi & Torut, 1971; Gelebe & Kaye, 1996). According to these authors, and as indicated below, the ozonolysis of (1) followed by a dehydrohalogenation leads to two sesquiterpenic ketones, (2) and (3). There are no data in the literature concerning the reactivity of (2) and (3), and we have studied the behaviour of these two compounds with respect to sodium azide. The action of two equivalents of NaN_3 on (2) or (3), in the presence of trifluoroacetic acid, leads to a 70% yield of (4) or (5), respectively. These compounds have been identified by mass spectrometry and NMR (^{1}H and ^{13}C).



The present crystallographic study of compound (4) allows us to assign the stereochemistry of the junction of the two rings in compounds (4) and (5) as *trans*. Several structures including a tetrazole ring are given in the Cambridge Structural Database (Allen & Kennard, 1993), but only a few of them correspond to a tetrazole ring fused with a five-, six- or seven-membered ring. A disordered occupancy of the N and C atoms located at the junction of the two rings is described in the structures of cyclopolymethylenetetrazoles, in the case of trimethylene, pentamethylene and butylpentamethylene (Ward, Wei, Smetana & Popov, 1979). The present structure is the first example of a tetrazole ring fused with an eight-membered ring. The eight-membered ring is composed of two planes and a twisted fragment: the planes [C6, N7, C8, C9 (r.m.s. deviation 0.011 Å) and C1, C6, C9, C10 (r.m.s. deviation 0.082 Å)] make an angle of 113.7 (2)° with one another. Atoms C11 and C12 are displaced by 0.526 (3) and −0.216 (2) Å, respectively, from the C1, C6, C9, C10 plane. The tetrazole ring [N7—C8—N4—N3—N2 (r.m.s. deviation 0.007 Å)] is essentially in the plane of the C6—N7—C8—C9 fragment, with a dihedral angle of 3.0 (2)°. C1 and C4 are in the plane of the C2=C3 double bond (C1—C2—C3—C4 r.m.s. deviation 0.019 Å), with C5 0.583 (3) and C6 −0.171 (2) Å from this plane.

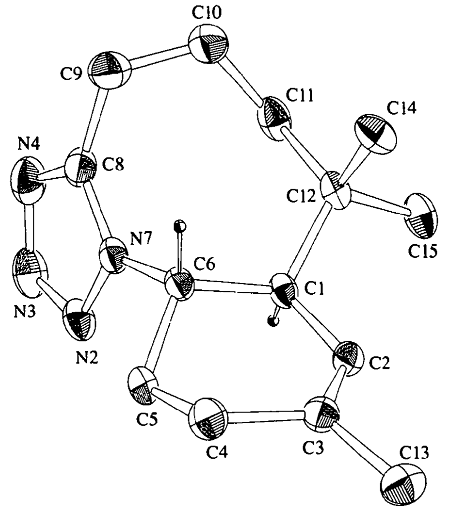


Fig. 1. The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Experimental

Crystals suitable for X-ray analysis were prepared by slow evaporation at room temperature from a hexane solution.

Crystal data

$C_{14}H_{22}N_4$
$M_r = 246.36$
Orthorhombic
$P2_12_12_1$
$a = 9.582\,(1)$ Å
$b = 10.495\,(2)$ Å
$c = 13.498\,(3)$ Å
$V = 1357.5\,(7)$ Å^3
$Z = 4$
$D_x = 1.21$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11\text{–}16°$
$\mu = 0.070$ mm^{-1}
$T = 294$ K
Cube
0.45 × 0.45 × 0.45 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1631 measured reflections
1454 independent reflections
1259 reflections with $I > 2.5\sigma(I)$

$R_{\rm int} = 0.067$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 0.8%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.068$
$S = 1.829$
1259 reflections
164 parameters
H atoms fixed
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0036F_o^4]$
$(\Delta/\sigma)_{\max} = 0.019$

$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.25×10^{-5}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

N2—N3	1.300 (4)	N7—C6	1.459 (3)
N2—N7	1.345 (3)	N7—C8	1.352 (4)
N3—N4	1.354 (4)	C1—C6	1.536 (3)
N4—C8	1.301 (4)	C8—C9	1.484 (5)
N3—N2—N7	106.1 (2)	C6—C1—C12	116.8 (2)
N2—N3—N4	111.0 (2)	N7—C6—C1	111.7 (2)
N3—N4—C8	106.1 (3)	N7—C6—C5	108.7 (2)
N2—N7—C6	122.0 (2)	C1—C6—C5	112.3 (2)
N2—N7—C8	107.9 (2)	N4—C8—N7	108.9 (3)
C6—N7—C8	130.1 (2)	N4—C8—C9	127.8 (3)
C2—C1—C6	109.3 (2)	N7—C8—C9	123.2 (3)
C2—C1—C12	110.3 (2)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1985). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1161). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 32–37.

Benharref, A., Bernardini, A., Fkih-Tetouani, S., Jacquier, R. & Viallefont, P. (1981). *J. Chem. Res.* (*S*), **12**, 372–373.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Gelebe, A. C. & Kaye, P. T. (1996). *J. Chem. Res.* (*S*), pp. 26–27.

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

Joseph, T. C. & Dev, S. (1968*a*). *Tetrahedron*, **24**, 3809–3827.

Joseph, T. C. & Dev, S. (1968*b*). *Tetrahedron*, **24**, 3853–3859.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.

Plattier, M. & Teisseire, P. (1974). *Recherches*, **19**, 131–144.

Sasaki, T., Eguchi, S. & Torut, T. (1971). *J. Org. Chem.* **36**, 2454–2457.

Ward, D. L., Wei, K.-T., Smetana, A. J. & Popov, A. I. (1979). *Acta Cryst.* B**35**, 1413–1419.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1997). C**53**, 1141–1143

2-(2-Bromo-4,5-dimethoxyphenyl)-2-(dimethylamino)acetonitrile

Raúl SanMartín,[a] Roberto Olivera,[a] Esther Domínguez,[a] José Luis Pizarro[b] and María Isabel Arriortua[b]

[a]*Departamento Química Orgánica, Universidad del País Vasco, Apdo 644, 48080 Bilbao, Spain, and* [b]*Departamento Mineralogía y Petrología, Universidad del País Vasco, Apdo 644, 48080 Bilbao, Spain. E-mail: npppisaj@lg.ehu.es*

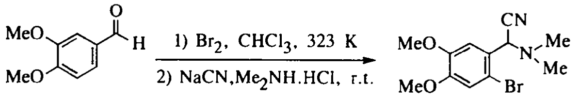
(*Received 31 October 1996; accepted 21 March 1997*)

Abstract

The regioselective synthesis, spectrometric data (^{1}H and ^{13}C NMR, and MS) and the X-ray crystal structure determination of the title compound, $C_{12}H_{15}BrN_2O_2$, are reported. In spite of the presence of a Br atom *ortho* to the bulky α-aminonitrile group, normal molecular dimensions have been found.

Comment

The title compound is a member of the α-aminonitrile family of derivatives, which are useful building blocks for the development of new synthetic methods in the field of α-amino acids (Davis, Portonovo, Reddy & Chiu, 1996), aminoamides (Taillades, Rossi, Garrel, Marull & Commeyras, 1996), thiadiazoles (Weinstock, Davis, Handelsman & Tull, 1967), imidazole derivatives (Matier, Owens & Comer, 1973) and oxazoles (Verschave, Vekemans & Hoornaert, 1984). In the course of the present investigations directed towards the preparation of a series of polyhalogenated deoxybenzoins, the α-aminonitrile (II) was synthesized.



(I) (II)

Taking into account that only the crystal structure determinations of a couple of aliphatic α-aminonitriles of type (II) have been reported (Parfonry, Tinant, Declercq & Van Meerssche, 1986; Parfonry, Declercq, Tinant & Van Meerssche, 1988), the X-ray structure of the title brominated aromatic α-aminonitrile, (II), was determined in order to expand the structural knowledge of this synthon.

Within experimental limits, the aromatic ring is essentially planar, with the methoxy groups at C6 and C7 slightly displaced out of the ring plane [deviations of 0.185 (5) and 0.115 (5) Å for C10 and C9, respectively].