Armishaw, O. A., Cox, P. J., Hassan, A. K. & Wardell, J. L. (1996). *J. Chem. Cryst.* **26**, 701–705.
Banert, K., Reissaus, E., Deiseroth, H.-J., Kluge, C. P. & Peters, E.-M. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 1164–1166.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hughes, N. A. & Speakman, P. R. H. (1966). *Carbohydr. Res.* **1**, 341–348.
Levene, P. A. & Raymond, A. L. (1933). *J. Biol. Chem.* **102**, 317–330.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Zsolnai, L. (1996). *ZORTEP. Interactive Graphics Program.* University of Heidelberg, Germany.

Acta Cryst. (1997). C**53**, 1941-1943

(5*R*/5*S*)-2,5-Diphenyl-7-[*trans*-(1*R*/1*S*,2*S*/2*R*)-2-phenylcyclohexyloxy]-2,3,5,8-tetrahydro-1*H*-1,2,4-triazolo[1,2-*a*]pyridazine-1,3-dione–Water (1/1): a Face-Selective Diels–Alder Reaction of 2-Alkoxy-1,3-butadiene

SANTIAGO GARCÍA-GRANDA,[a] RAFAEL SANTIAGO-GARCÍA,[a]
ANGEL SUÁREZ-SOBRINO[b] AND LUIS ANGEL LÓPEZ[b]

[a]*Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Avda. Julián Clavería 8, 33071 Oviedo, Spain, and* [b]*Instituto Universitario de Química Organometálica Enrique Moles, Unidad Asociada al CSIC, Universidad de Oviedo, Avda. Julián Clavería 8, 33071 Oviedo, Spain. E-mail: sgg@sauron.quimica.uniovi.es*

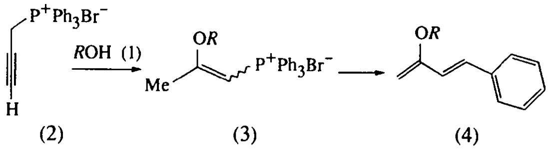
(*Received 13 March 1997; accepted 27 May 1997*)

Abstract

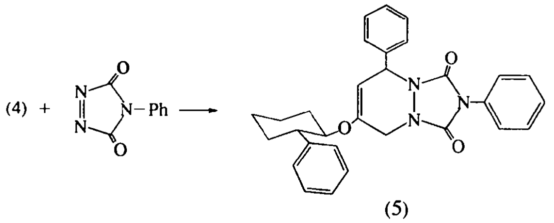
The title compound, $C_{30}H_{29}N_3O_3.H_2O$, is the final product in the Diels–Alder reaction between a 2-alkoxydiene and a reactive dienophile such as phenyltriazolinedione after recrystallization from methanol. The water molecule forms a hydrogen bond with a carbonyl O atom in one dione molecule and a weaker interaction with an N atom in a symmetry-related molecule, forming dimers linked by the water molecule. Atoms in the five-membered ring stemming from the dienophile molecule are related by a non-crystallographic C_2 axis through an N atom.

Comment

Chiral 2-substituted dienes are useful in Diels–Alder reactions. The role of chiral 2-alkoxy-1,3-butadienes in face-selective Diels–Alder reactions has recently been studied. The synthesis of substituted dienes has been reported as well as their [4+2] cycloaddition to hetero and carbo-dienophiles (Barluenga, Tomás, Suárez-Sobrino & López, 1995). The [4+2] cycloaddition of the racemic diene (4) (see reaction scheme below) to phenyltriazolinedione (PTAD) results in the formation of a new compound, (5), which is stable at room temperature. Knowledge of the structure of this Diels–Alder cycloadduct is a key for determining the stereochemical assignment of the other adducts in the cited work. The compound was crystallized from a methanol solution in the form of colourless crystals by slow evaporation.



(1) = (1*R*,2*S*/1*S*,2*R*)-*trans*-2-phenylcyclohexanol



In the title structure, most bond parameters are in the expected range. The O(3)—C(3) bond distance is shorter than the O(3)—C(13) distance due to conjugation with the double bond in the six-membered ring between atoms C(2) and C(3). The six-membered ring [C(1)–C(4), N(1) and N(2)] shows a half-chair conformation [$^6H_5$ in the notation of Boeyens (1978)]. The Cremer & Pople (1975) ring-puckering parameters are q_2 = 0.307 (3), q_3 = −0.284 (4), Q = 0.418 (3), φ = 92.5 (8)° and θ = 132.8 (3)°. The five-membered ring [N(1), N(2), C(6), C(5), N(3)] is almost planar. The sum of the bond angles is 538.2 (15)° and the maximum deviation from the least-squares plane is 0.069 (4) A, for C(5). A careful inspection of the internal Cartesian coordinates of the ring atoms shows that atoms C(6) and N(2) are related to C(5) and N(1), respectively, by $C2$ symmetry. The Cremer & Pople (1975) ring-puckering parameters for this ring are q_2 = 0.119 (3) and φ = 94 (1)°. The triply bonded N(3) atom is in a planar environment, the sum of the bond angles being 359.9 (9)°. The flattening is due to conjugation with the two carbonyl groups in the five-membered ring. Conjugation with the phenyl group is less important because of the unfavourable geometry. The dihedral angle between the least-squares planes formed by atoms C(25)–C(30) and the plane formed by atoms N(3), C(5), C(6), O(1) and O(2) is 45.06 (16)°. The maximum deviations from these two planes are C(27) 0.010 (5) and C(5) 0.040 (4) Å.

The six-membered ring formed by atoms C(13)–C(18) shows a chair conformation [$^1C_4$ in the notation of

Boeyens (1978)]. The Cremer & Pople (1975) ring-puckering parameters are q_2 = 0.019 (6), q_3 = 0.563 (5), Q = 0.563 (5), φ = 120 (16)° and θ = 2.0 (6)°. The ring formed by atoms C(7)–C(12) is planar, with a maximum deviation from the plane by C(10) of 0.003 (9) Å, and the ring formed by atoms C(19)–C(24) is also planar, with a maximum deviation from the plane by C(20) of 0.010 (5) Å.

The water molecule is linked by a hydrogen bond to the carbonyl O(1) atom (Table 2). A weaker interaction has been observed throughout H(50*B*) and the N atom N(3) in a symmetry-related molecule. The water molecule acts as a bridge between two molecules forming dimers as shown in Fig. 1.

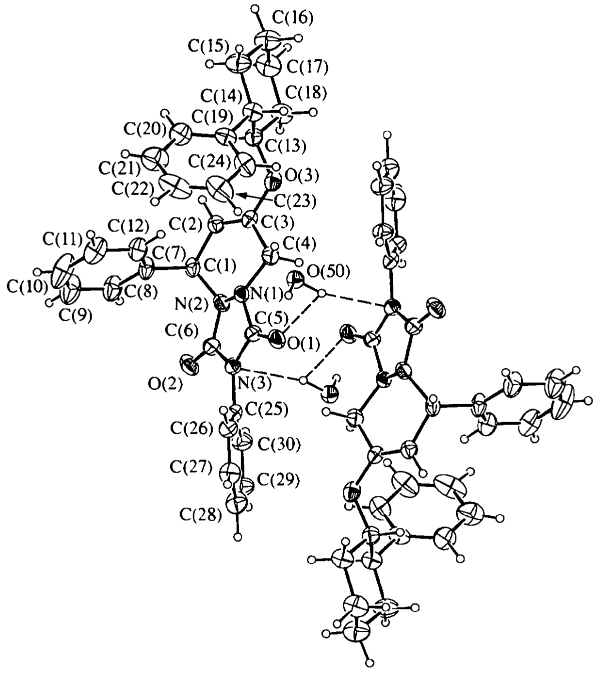


Fig. 1. *EUCLID* (Spek, 1982) plot (30% probability displacement ellipsoids) showing two molecules and the water molecules as a bridge between them forming dimers. The disordered water molecule is represented using an isotropic displacement parameter for clarity.

Experimental

To a solution of (1*R*,2*S*/1*S*,2*R*)-*trans*-2-phenylcyclohexanol, (1) (5.3 g, 30 mmol), in 150 ml toluene, prop-2-ynyltriphenyl phosphonium bromide, (2) (9.5 g, 25 mmol), was added. After stirring at 383 K for 48 h, the mixture was filtered. The filtrate was washed with ether–THF (5:1) and dried under vacuum to give a quantitative amount of the phosphonium salt, (3), used later without further purification. To a mixture of (3) (3.3 g, 5.9 mmol) and 50 ml THF, potassium hexamethyldisilazide (KHMDS) (toluene 0.5 *N*, 11.8 ml, 5.9 mmol) was added at 213 K under N_2. The mixture was warmed to room temperature, stirred for 1 h and cooled to 253 K, then benzaldehyde (0.6 ml, 5.9 mmol) was added. The mixture was stirred for 12 h at 333 K, then cooled and the solvent removed. The residue was purified by chromatography to give 1.4 g (93%) of the diene (4). The diene (500 mg, 1.6 mmol) was dissolved in 7 ml THF and the solution cooled to 173 K. A solution of phenyltriazolinedione (280 mg, 1.6 mmol) was slowly added. Solvent removal and chromatography of the residue gave 835 mg (91%) of the cycloadduct, which was further purified by recrystallization from methanol (m.p. 444–445 K). The exact mass calculated is 479.22089; found 479.21945.

Crystal data

$C_{30}H_{29}N_3O_3.H_2O$
M_r = 497.58
Monoclinic
$P2_1/c$
a = 13.972 (6) Å
b = 10.557 (4) Å
c = 18.596 (14) Å
β = 107.16 (2)°
V = 2621 (2) Å^3
Z = 4
D_x = 1.261 Mg m^{-3}
D_m not measured

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.084 mm^{-1}
T = 293 (2) K
Prismatic
0.30 × 0.23 × 0.20 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
4769 measured reflections
4611 independent reflections
2023 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.023

$\theta_{\max}$ = 25°
$h = -16 \rightarrow 15$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 22$
3 standard reflections every 200 reflections frequency: 60 min intensity decay: 4.19%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.186
S = 1.011
4610 reflections
425 parameters
H atoms riding with a common $U_{\rm iso}$

$w = 1/[\sigma^2(F_o^2) + (0.0832P)^2 + 0.2239P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.295 e Å^{-3}
$\Delta\rho_{\min}$ = −0.298 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N(1)—N(2)	1.410 (4)	N(3)—C(25)	1.434 (4)
N(1)—C(4)	1.456 (5)	C(1)—C(2)	1.511 (5)
N(2)—C(1)	1.481 (5)	C(2)—C(3)	1.315 (5)
N(3)—C(5)	1.386 (4)	C(3)—C(4)	1.489 (5)
N(3)—C(6)	1.401 (5)		
C(5)—N(1)—N(2)	107.7 (3)	C(3)—C(2)—C(1)	124.1 (4)
N(2)—N(1)—C(4)	114.4 (3)	C(2)—C(3)—O(3)	128.1 (3)
C(6)—N(2)—N(1)	108.8 (3)	C(2)—C(3)—C(4)	123.5 (3)
N(1)—N(2)—C(1)	116.0 (3)	O(3)—C(3)—C(4)	108.3 (3)
C(5)—N(3)—C(6)	110.4 (3)	N(1)—C(4)—C(3)	110.0 (3)
C(5)—N(3)—C(25)	126.1 (3)	N(1)—C(5)—N(3)	106.1 (3)
C(6)—N(3)—C(25)	123.4 (3)	N(2)—C(6)—N(3)	105.2 (3)
N(2)—C(1)—C(2)	107.1 (3)		

C(5)—N(1)—N(2)—C(6)	−14.2 (4)	C(2)—C(3)—C(4)—N(1)	14.6 (6)
C(4)—N(1)—N(2)—C(1)	61.2 (4)	N(2)—N(1)—C(5)—N(3)	11.7 (4)
N(1)—N(2)—C(1)—C(2)	−43.9 (4)	C(6)—N(3)—C(5)—N(1)	−5.4 (4)
N(2)—C(1)—C(2)—C(3)	15.8 (5)	N(1)—N(2)—C(6)—N(3)	10.4 (4)
C(1)—C(2)—C(3)—C(4)	−2.9 (6)	C(5)—N(3)—C(6)—N(2)	−3.2 (4)
N(2)—N(1)—C(4)—C(3)	−42.1 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(50)—H(50*B*)···O(1^{i})	0.96	2.71 (5)	2.91 (2)	93 (3)
O(50)—H(50*B*)···N(3^{ii})	0.96	3.36 (4)	4.22 (4)	148 (4)

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

From the first steps of the refinement, a residual electron density appeared. An unexpected water molecule could be modelled into the residual electron density. The water O atom was disordered [U_{eq} for the O atom = 0.575 (13) Å^2] and the H atoms must be geometrically placed. All non-H atoms in the asymmetric unit were anisotropically refined, and all H atoms except for the water molecule were located by a difference Fourier synthesis. A common displacement parameter was refined for all the H atoms. The final difference Fourier map showed no peaks higher than 0.29 e Å^{-3} and no deeper than −0.30 e Å^{-3}.

Data were collected by profile analysis over all reflections (Lehman & Larsen, 1974; Grant & Gabe, 1978) using Nonius CAD-4 diffractometer software. Cell refinement: *CRYSDA* (Beurskens *et al.*, 1992). Data reduction: *THE REFLEX* (Aguirre-Pérez, Gutiérrez-Rodríguez & García-Granda, 1997). The structure was solved using direct methods (*SHELXS*86; Sheldrick, 1985) and refined by anisotropic least-squares techniques using *SHELXL*93 (Sheldrick, 1993). Geometrical calculations were made with *PARST* (Nardelli, 1983) and molecular graphics incorporated *EUCLID* (Spek, 1982). *SHELXL*93 was used for preparing the material for publication and all calculations were made at the University of Oviedo on the Scientific Computer Centre and X-ray group VAX/AXP computers.

We thank DGICYT for support (PB93-0330) and MEC for a grant to RSG.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1480). Services for accessing these data are described at the back of the journal.

References

Aguirre-Pérez, A., Gutiérrez-Rodríguez, A. & García-Granda, S. (1997). *THE REFLEX*. To be published.
Barluenga, J., Tomás, M., Suárez-Sobrino, A. & López, L. A. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1785–1786.
Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Grant, D. F. & Gabe, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.
Lehman, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
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.
Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Acta Cryst. (1997). C**53**, 1943–1945

Cyclopropanation of a β-Himachalene Monoepoxide Derivative

E. LASSABA,[a] A. BENHARREF,[a] M. GIORGI[b] AND M. PIERROT[b]

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

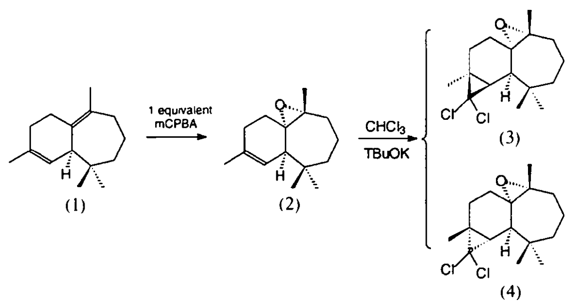
(*Received 12 May 1997; accepted 4 July 1997*)

Abstract

The stereochemistry of the title compound, (1*S*,2*R*,7*S*,8*S*,10*R*)-9,9-dichloro-1,2-epoxy-2,6,6,10-tetramethyltricyclo[5.5.0.0.^{8,10}]dodecane, $C_{16}H_{24}Cl_2O$, a derivative of β-himachalene, has been established. The epoxide bridge located at positions 1 and 2 on the seven-membered ring adopts a *cis* conformation with respect to the cyclopropane bridge located at positions 8 and 10 on the six-membered ring.

Comment

β-Himachalene, (1), is the main constituent of Atlas Cedar essential oils (Plattier & Teisseire, 1974). An early study (Joseph & Dev, 1968*a*) performed on Himalaya Cedar showed that (1) is a major component in its oils. The reactivity of this sesquiterpene has been widely investigated (Joseph & Dev, 1968*b*,*c*; Plattier & Teisseire, 1974) and this laboratory has studied its epoxidation and the reactivity of its derivatives.



Acta Crystallographica Section C
ISSN 0108-2701 © 1997