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Structure of a Tricyclo[3.2.1.$0^{2,7}$]octene Derivative: a Double Bridged Central Ring in an Octahydrobenz[*g*]-3-nitroindole

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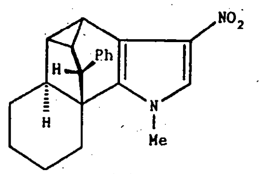
Abstract

The structure of *rac*-1-methyl-3-nitro{(1*R*,6*S*,8*S*)-6-phenyl-5,8-(tetramethylene)tricyclo[3.2.1.$0^{2,7}$]oct-3-eno}[4,3-*b*]pyrrole (1) has been determined. The compound, which is composed of a nitropyrrole annulated to a tricyclic octene, was prepared by an intramolecular Diels–Alder reaction.

Comment

Thermal ring closure of 2-(1-cyclohexenyl)-1-methyl-4-nitro-3-(4-phenyl-1,3-butadienyl)pyrrole in refluxing nitrobenzene yields two products: 3-nitro-5-(2-phenylethenyl)-6,7,8,9-tetrahydro-1-methylbenz[*g*]indole was obtained by electrocyclization of the triene system and the main product, the tricyclooctene derivative (1), by an intramolecular Diels–Alder reaction of the *ortho*-xylylene intermediate (Leusink, ten Have, van den Berg & van Leusen, 1992). The present structure determination excludes the alternate structure, the isomeric 2-phenyltricyclo[2.2.2.$0^{3,6}$]oct-7-ene which could not be ruled out by other spectroscopic means such as ^{1}H or ^{13}C NMR.



(1)

Compound (1) is composed of a 3-nitropyrrole unit. A search of the January 1992 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed no 3-nitropyrroles. The bond lengths and angles of the pyrrole are in general agreement with other pyrrole units in 4,5,6,7-tetrahydroindoles (Beddoes, Dalton, Joule, Mills, Street & Watt, 1986; Law, Lai, Sammes, Katritzky & Mak, 1984). The nitro group is coplanar with the pyrrole ring, the relevant torsion angle being 179.8(2)°. The structure most closely related to that of the tricyclic octene unit was found in the *C* ring of staphisine (Pelletier, DeCamp, Finer-Moore & Micóvić, 1980); the bond lengths and angles are in good agreement with those of this ring.

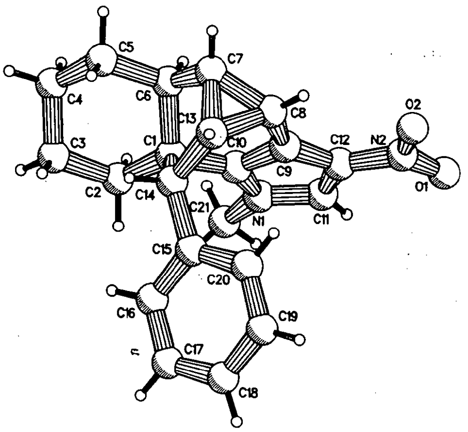


Fig. 1. *PLUTO* drawing of the molecule illustrating the puckering and the adopted numbering scheme.

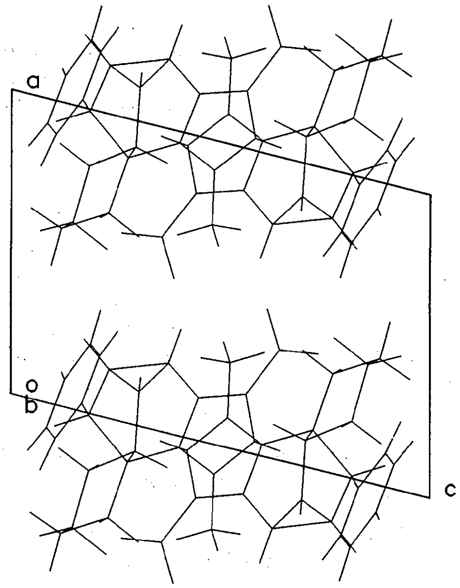


Fig. 2. Molecular packing viewed down [010].

Experimental

Crystal data

$C_{21}H_{22}N_2O_2$ D_x = 1.353 Mg m^{-3}

M_r = 334.42 Mo $K\bar{\alpha}$ radiation

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Triclinic
$P\bar{1}$
$a = 7.799\ (1)$ Å
$b = 9.872\ (1)$ Å
$c = 11.770\ (1)$ Å
$\alpha = 109.638\ (4)^\circ$
$\beta = 100.339\ (6)^\circ$
$\gamma = 97.756\ (6)^\circ$
$V = 820.77\ (15)$ Å^3
$Z = 2$

$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 15.54\text{–}18.97^\circ$
$\mu = 0.82$ mm^{-1}
$T = 130$ K
Parallelepiped
0.50 × 0.40 × 0.38 mm
Yellow

Data collection

Enraf-Nonius CAD-4F single-crystal diffractometer
$\omega/2\theta$ scans
4098 measured reflections
3569 independent reflections
3265 observed reflections $[I>2.5\sigma(I)]$

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 27.00^\circ$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 180 min
intensity variation: 0.9%

Refinement

Refinement on F_o
Final $R = 0.048$
$wR = 0.058$
$S = 0.751$
3265 reflections
315 parameters

All H-atom parameters refined
Calculated weights
$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\rm max} = 0.3840$
$\Delta\rho_{\rm max} = 0.443$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.392$ e Å^{-3}

Data collection: CAD-4 version 5.0 (Enraf-Nonius, 1988). Cell refinement: CAD-4 version 5.0, *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *EUCLID* (Spek, 1982). Program(s) used to solve structure: *SHELXS* (Sheldrick, 1990). Program(s) used to refine structure: *Xtal CRYLSQ* (Olthof-Hazekamp, 1990). Molecular graphics: *PLUTO* (Meetsma, 1992). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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

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

	x	y	z	$U_{\rm eq}$
O1	0.3808 (2)	0.26541 (19)	0.73573 (15)	0.0237 (5)
O2	0.4879 (2)	0.35510 (19)	0.61094 (16)	0.0241 (5)
N1	−0.0981 (2)	0.15941 (19)	0.48367 (16)	0.0123 (5)
N2	0.3615 (2)	0.2939 (2)	0.64030 (17)	0.0165 (5)
C1	−0.1276 (2)	0.2232 (2)	0.27936 (18)	0.0110 (5)
C2	−0.3266 (3)	0.1554 (2)	0.23197 (19)	0.0134 (6)
C3	−0.4151 (3)	0.1863 (2)	0.1192 (2)	0.0154 (6)
C4	−0.3859 (3)	0.3514 (2)	0.1480 (2)	0.0188 (6)
C5	−0.1871 (3)	0.4198 (2)	0.1867 (2)	0.0157 (6)
C6	−0.0866 (3)	0.3896 (2)	0.29776 (19)	0.0128 (5)
C7	0.1114 (3)	0.4243 (2)	0.30673 (19)	0.0147 (6)
C8	0.2286 (3)	0.3512 (2)	0.37667 (19)	0.0145 (6)
C9	0.1400 (3)	0.2782 (2)	0.44716 (19)	0.0132 (5)
C10	−0.0382 (3)	0.2170 (2)	0.40122 (18)	0.0116 (5)
C11	0.0408 (3)	0.1827 (2)	0.58036 (19)	0.0141 (6)
C12	0.1898 (3)	0.2550 (2)	0.55985 (19)	0.0137 (5)
C13	0.1588 (3)	0.2827 (2)	0.23474 (19)	0.0139 (6)
C14	−0.0069 (3)	0.1609 (2)	0.18688 (18)	0.0116 (5)
C15	0.0266 (3)	0.0083 (2)	0.17048 (18)	0.0124 (5)
C16	−0.1101 (3)	−0.1160 (2)	0.10616 (19)	0.0152 (6)
C17	−0.0812 (3)	−0.2570 (2)	0.0858 (2)	0.0189 (6)
C18	0.0888 (3)	−0.2769 (2)	0.1278 (2)	0.0201 (7)
C19	0.2269 (3)	−0.1548 (3)	0.1904 (2)	0.0202 (7)
C20	0.1961 (3)	−0.0138 (2)	0.2125 (2)	0.0163 (6)
C21	−0.2797 (3)	0.0923 (2)	0.4781 (2)	0.0169 (6)

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

O1—N2	1.235 (3)	C5—C6	1.539 (3)
O2—N2	1.248 (3)	C6—C7	1.512 (3)
N1—C10	1.395 (3)	C7—C8	1.530 (3)
N1—C11	1.355 (3)	C7—C13	1.505 (3)
N1—C21	1.461 (3)	C8—C9	1.469 (3)
N2—C12	1.414 (3)	C8—C13	1.536 (3)
C1—C6—C7	104.03 (17)	C7—C8—C9	115.3 (2)
C5—C6—C7	108.93 (18)	C7—C8—C13	58.79 (14)
C6—C7—C8	116.84 (18)	C9—C8—C13	115.76 (18)
C6—C7—C13	106.64 (18)	C8—C9—C10	117.65 (19)
C8—C7—C13	60.80 (14)	C8—C9—C12	136.3 (2)
C1—C6—C7—C13	27.3 (2)	C6—C7—C8—C13	94.9 (2)
C1—C6—C7—C8	−37.9 (2)	C9—C8—C13—C14	7.3 (3)
C5—C6—C7—C8	−158.16 (18)	C9—C8—C13—C7	105.2 (2)
C5—C6—C7—C13	−93.0 (2)	C7—C8—C13—C14	−97.8 (2)
C6—C7—C13—C8	−111.88 (19)	C7—C8—C9—C12	−145.8 (3)
C8—C7—C13—C14	109.42 (19)	C13—C8—C9—C10	−34.1 (3)
C13—C7—C8—C9	−106.0 (2)	C7—C8—C9—C10	31.8 (3)
C6—C7—C8—C9	−11.1 (3)	C13—C8—C9—C12	148.3 (3)
C6—C7—C13—C14	−2.5 (2)		

The crystal was placed into the nitrogen cold stream of the low-temperature unit (van Bolhuis, 1971) on the diffractometer. The radiation was graphite monochromated. Data were collected with scan width of $(1.05 + 0.34\tan\theta)^\circ$. The unit-cell parameters and orientation matrix were determined from a least-squares treatment of the *SET*4 setting angles (de Boer & Duisenberg, 1984). The unit cell was checked for the presence of higher lattice symmetry (Le Page, 1982; Spek, 1988). Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements (Le Page, 1987,1988).

The intensity data were corrected for Lorentz and polarization effects and scale variation, but an absorption correction was judged not to be necessary in view of the small observed variation in intensity of a 360 ° ψ scan of a close-to-axial reflection ($\bar{2}02$). The variance $\sigma^2(I)$ was calculated on the basis of counting statistics plus the term $(PI)^2$, where P (= 0.021) is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). Equivalent reflections were averaged and stated observed if satisfying the criterion $I \geq 2.5\sigma(I)$.

The structure was solved by direct methods (Sheldrick, 1990). H-atom positions were obtained from subsequent difference Fourier syntheses. The positional and anisotropic thermal displacement parameters for the non-H atoms and the isotropic thermal displacement parameters for the H atoms were refined using full-matrix least-squares techniques (Olthof-Hazekamp, 1990) minimizing the function $Q = \Sigma_h[w(2F_o^2 - k^2F_c^2)^2]$. Scattering factors were taken from Cromer & Mann (1968) and anomalous-dispersion factors from Cromer & Liberman (1970).

All calculations were carried out on the CDC-Cyber 962-31 computer at the University of Groningen using the program packages *Xtal* (Hall & Stewart, 1990) and *PLATON* (Spek, 1990) and a locally modified version of *PLUTO* (Meetsma, 1992; Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55756 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1037]

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Structure du (2*S*,6′*R*)-2-Amino-2-(1,2:3,4-di-*O*-isopropylidène-α-D-galactopyranos-6-yl)acétate de Méthyle

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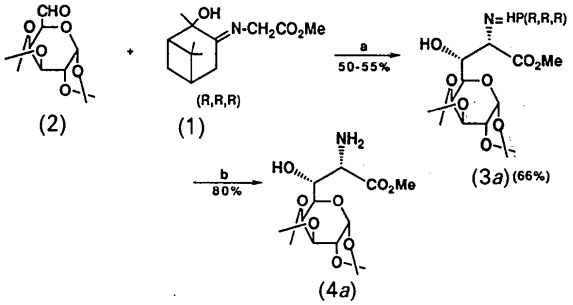
Abstract

The relative stereochemistry of the major synthetic product β-glycosyl-β-hydroxy-α-amino ester has been established as 2*S*,6′*R*. The two molecules of the asymmetric unit adopt a similar conformation whereby an intramolecular hydrogen bond N—H···O—H fixes the amino ester in a planar conformation. All intermolecular hydrogen bonds linking *A* to *A*, *B* to *B*, *A* to *B* and *B* to *A* form infinite chains along the *a* axis.

Commentaire

Nous avons décrit récemment la première synthèse de *C*-glycosyl-β-hydroxy-α-amino esters (El Hadrami, Lavergne, Viallefont, Riche & Chiaroni, 1992). L'action de l'énolate chiral dérivé de la glycine, préparé par action du tertiobutylate de potassium sur la base de Schiff (1), sur la fonction aldéhyde du 1,2:3,4-di-*O*-isopropylidène-α-D-*galacto*-hexadialdo-1,5 pyranose (2) est diastéréosélective. Elle conduit à deux diastéréoisomères dans la proportion 2:1. Le composé majoritaire (3*a*) a pu être isolé; il conduit après hydrolyse par l'acide citrique au β-glycosyl-β-hydroxy-α-amino ester (4*a*) dont la structure cristalline a été déterminée dans le but de préciser la stéréochimie de la chaîne.



a: ^{t}BuOK/THF, 195 K. b: acide citrique 15%, RT, 4 jours

La structure est représentée sur la Fig. 1 avec la configuration absolue déduite de celle du galactose de départ. La configuration absolue des atomes de carbone C2 et C3 est respectivement *S* et *R*. Les deux molécules indépendantes de l'unité asymétrique sont dans des conformations pratiquement identiques. Une comparaison systématique des longueurs de liaison, des angles de valence et des angles de torsion donne respectivement un écart type de 0,012 Å, 0,7 et 2,3°. Une liaison hydrogène intramoléculaire N7—H···O8 [N7*A*···O8*A* 2,715(6), N7*B*···O8*B* 2,706(6) Å] assure la planéité de l'ensemble N7, C2, C1, O8, O9 et C15 [écart maximum 0,034 (*A*) et 0,046 Å (*B*)].

L'empilement cristallin est représenté sur la Fig. 2. Les molécules *A* entre elles (*B* entre elles) forment des chaînes infinies le long de l'axe *a* reliées par des liaisons hydrogène entre l'amine N7 et l'hydroxyle O6 [N7—H···O6: N7*A*···O6*A* (1+*x*, *y*, *z*) 3,076(6), N7*B*···O6*B* (*x*−1, *y*, *z*) 3,074(5) Å]. Les molécules *A* et *B* sont reliées entre elles par des liaisons hydrogène O6*A*—H···N7*B* [1−*x*, *y*+1/2, 2−*z*; 2,767(6) Å] et O6*B*—H···N7*A* [2−*x*, *y*−1/2, 2−*z*; 2,743(5) Å]. Ces liaisons hydrogène ne forment pas un dimère mais une chaîne infinie le long de

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