

Fig. 2. View of the cation with methylene protons included.

2.555 (7) Å. This can be contrasted with the inside-protonated [5.4.3] diamine (White *et al.*, 1988) which has an N...N distance of 2.555 (3) Å, and an N—H—N angle of 160 (3)° with the inside proton essentially equidistant from both bridgehead nitrogens, the inside-protonated [6.4.3] diamine which has an N...N distance of 2.663 (4) Å (Alder, Orpen & White, 1988) with the inside proton localized near one of the bridgehead nitrogens, and the inside-protonated [4.4.4] diamine which has an intrabridgehead N...N distance of 2.526 Å and an apparently symmetrical N—H—N system (Alder, Orpen & Sessions, 1983). Close intermolecular contacts occur between the cation and anion, and between adjacent cations (see Table 2).

have similar conformations with $g^+g^-g^+g^-$ sequences of torsion angles (see Table 2) and with an approximate local plane of symmetry. This is similar to the conformation of the five-carbon bridge in the inside-protonated [5.4.3] diamine (White, Alder & Orpen, 1988). The two-carbon bridge is slightly twisted away from an eclipsed geometry [torsion angle = 15.7 (5)°]. The cation has an approximate twofold rotation axis bisecting the two-carbon bridge and the intrabridgehead N...N vector. The inside proton is localized near N(1) [N(1)—H = 1.09 (5), N(8)—H = 1.67 (5) Å], the N—H—N angle is 134 (5)° and the N...N distance is

References

- ALDER, R. W. (1983). *Acc. Chem. Res.* **16**, 321–327.
 ALDER, R. W., ORPEN, A. G. & SESSIONS, R. B. (1983). *J. Chem. Soc. Chem. Commun.* pp. 999–1000.
 ALDER, R. W., ORPEN, A. G. & WHITE, J. M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 949–950.
 ALDER, R. W., ORPEN, A. G. & WHITE, J. M. (1988). *Acta Cryst.* **C44**, 287–289.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 SHELDRIK, G. M. (1985). *SHELXTL*. Revision 5.1. Univ. of Göttingen, Federal Republic of Germany.
 WHITE, J. M., ALDER, R. W. & ORPEN, A. G. (1988). *Acta Cryst.* **C44**, 662–664.

Acta Cryst. (1988). **C44**, 666–668

(+)-7,9-O,O-(3,3-Dimethylglutaryl)heliotridine,* a Pyrrolizidine Alkaloid Analogue

BY ANDREW A. FREER,† DESMOND B. HAGAN AND DAVID J. ROBINS

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

(Received 27 October 1987; accepted 2 December 1987)

Abstract. $C_{15}H_{21}NO_4$, $M_r = 279.3$, orthorhombic, $P2_12_12_1$, $a = 6.115$ (1), $b = 7.989$ (1), $c = 29.986$ (2) Å, $V = 1465.0$ Å³, $Z = 4$, $D_x = 1.26$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 7.14$ cm⁻¹, $F(000) = 600$, $T = 291$ K, final $R = 0.056$ for 936 unique observed [$I \geq 3.0\sigma(I)$] reflections. The pyrrolizidine nucleus adopts an *exo-endo* conformation and the conformation of the ester carbonyl groups of the 11-membered macro-ring is antiparallel. The ester carbonyl group C(11)=O(11) is orientated in the same direction as C(8)—H.

* Heliotridine is (1*S*-*cis*)-2,3,5,7a-tetrahydro-1-hydroxy-1*H*-pyrrolizine-7-methanol (*Chemical Abstracts* name).

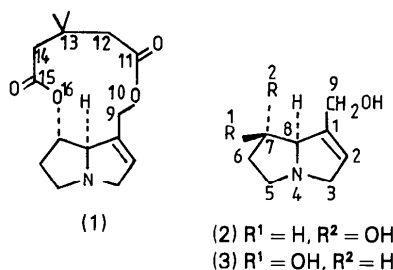
† To whom all correspondence should be addressed.

Introduction. Pyrrolizidine alkaloids continue to attract much attention because of their widespread occurrence and hepatotoxicity (Mattocks, 1986). The most toxic alkaloids are macrocyclic diesters of (+)-retronecine (3). Although many examples of monoesters and diesters of the epimeric base (+)-heliotridine (2) have been isolated, macrocyclic diesters of heliotridine have not yet been found to occur naturally (Robins, 1982). Recently, we reported the first synthesis of 11-membered macrocyclic diesters of heliotridine (Hagan & Robins, 1987). These pyrrolizidine alkaloid analogues were prepared from heliotridine and glutaric anhydride derivatives in readiness for a study of their toxicity. In order to gain more information about structure–biological-activity relationships in this area,

Table 1. Final positional parameters and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O(10)	0.3872 (7)	-0.3127 (6)	-0.0960 (1)	0.066
O(11)	0.2967 (14)	-0.5801 (7)	-0.0910 (2)	0.115
O(15)	0.1024 (11)	-0.1875 (6)	-0.2007 (2)	0.092
O(16)	-0.0547 (7)	-0.2678 (5)	-0.1376 (1)	0.061
N(4)	-0.1280 (10)	0.0322 (7)	-0.0501 (2)	0.059
C(1)	0.1883 (11)	-0.1307 (9)	-0.0463 (2)	0.056
C(2)	0.2284 (12)	0.0008 (10)	-0.0226 (2)	0.066
C(3)	0.0392 (16)	0.1170 (8)	-0.0232 (2)	0.078
C(5)	-0.2170 (14)	0.1313 (10)	-0.0879 (3)	0.079
C(6)	-0.2319 (12)	0.0077 (9)	-0.1267 (2)	0.067
C(7)	-0.0368 (11)	-0.1035 (7)	-0.1184 (2)	0.054
C(8)	-0.0344 (11)	-0.1219 (8)	-0.0680 (2)	0.050
C(9)	0.3324 (13)	-0.2804 (10)	-0.0502 (2)	0.073
C(11)	0.3657 (12)	-0.4639 (10)	-0.1127 (2)	0.063
C(12)	0.4365 (11)	-0.4741 (9)	-0.1601 (2)	0.064
C(13)	0.2750 (11)	-0.5512 (8)	-0.1934 (2)	0.054
C(14)	0.0403 (11)	-0.4811 (8)	-0.1872 (2)	0.057
C(15)	0.0336 (11)	-0.2949 (9)	-0.1775 (2)	0.056
C(17)	0.2612 (14)	-0.7412 (9)	-0.1872 (2)	0.076
C(18)	0.3585 (13)	-0.5180 (9)	-0.2399 (2)	0.077

we now report the X-ray structure of (+)-7,9-O,O-(3,3-dimethylglutaryl)heliotridine (1).



Experimental. Colourless plate-shaped crystals grown from cyclohexane, crystal ca $0.6 \times 0.5 \times 0.2$ mm used in data collection, CAD-4 diffractometer. Preliminary Weissenberg photographs indicate crystals to be orthorhombic, $P2_12_12_1$. 1790 independent intensities, θ limit 75° , $\omega/2\theta$ scan. Two standard intensities used to monitor variations in intensity data: $<4\%$ variation observed. No absorption corrections. h 0 to 7, k 0 to 10, l 0 to 37. Structure solution by direct phasing techniques using *MITHRIL* (Gilmore, 1984). Full-matrix least-squares refinement on F of coordinates and anisotropic thermal parameters for all non-H atoms converged to R and wR of 0.056 and 0.075 for 181 parameters. $w = 1/\sigma^2(F_o)$. H-atom coordinates, located from difference Fourier maps, included in structure-factor calculations, but not refined. 936 reflections, $I \geq 3.0\sigma_f$, used. $\Delta_{max}/\sigma = 0.23$; max. and min. heights in final difference Fourier map = 0.19 and $-0.22 e \text{\AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations on a Gould SEL 32/27 computer using Glasgow GX package (Mallinson & Muir, 1985).

Discussion. Final positional and equivalent isotropic thermal parameters are given in Table 1.* Bond lengths and angles with their standard deviations are given in Table 2. An *ORTEP* (Johnson, 1976) diagram, Fig. 1, shows the numbering scheme and absolute configuration of the molecule. The absolute configuration of (1) is known from chemical interrelationships and degradations (Warren, 1970, and references therein).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44592 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

O(10)-C(9)	1.437 (8)	O(10)-C(11)	1.315 (10)
O(11)-C(11)	1.210 (10)	O(15)-C(15)	1.182 (9)
O(16)-C(7)	1.438 (8)	O(16)-C(15)	1.329 (8)
N(4)-C(3)	1.467 (10)	N(4)-C(5)	1.486 (10)
N(4)-C(8)	1.460 (9)	C(1)-C(2)	1.293 (10)
C(1)-C(8)	1.512 (10)	C(1)-C(9)	1.490 (11)
C(2)-C(3)	1.484 (12)	C(5)-C(6)	1.530 (11)
C(6)-C(7)	1.508 (10)	C(7)-C(8)	1.518 (9)
C(11)-C(12)	1.489 (10)	C(12)-C(13)	1.533 (10)
C(13)-C(14)	1.552 (10)	C(13)-C(17)	1.531 (10)
C(13)-C(18)	1.508 (9)	C(14)-C(15)	1.517 (10)
C(9)-O(10)-C(11)	120.4 (6)	C(7)-O(16)-C(15)	118.6 (5)
C(3)-N(4)-C(5)	115.3 (6)	C(3)-N(4)-C(8)	108.6 (6)
C(5)-N(4)-C(8)	108.2 (5)	C(2)-C(1)-C(8)	111.7 (7)
C(2)-C(1)-C(9)	125.7 (7)	C(8)-C(1)-C(9)	122.4 (6)
C(1)-C(2)-C(3)	110.7 (7)	N(4)-C(3)-C(2)	105.2 (6)
N(4)-C(5)-C(6)	105.0 (6)	C(5)-C(6)-C(7)	102.0 (6)
O(16)-C(7)-C(6)	114.3 (6)	O(16)-C(7)-C(8)	108.2 (5)
C(6)-C(7)-C(8)	103.3 (6)	N(4)-C(8)-C(1)	103.5 (6)
N(4)-C(8)-C(7)	106.4 (5)	C(1)-C(8)-C(7)	116.2 (6)
O(10)-C(9)-C(1)	110.9 (6)	O(10)-C(11)-O(11)	122.3 (7)
O(10)-C(11)-C(12)	112.6 (7)	O(11)-C(11)-C(12)	125.0 (7)
C(11)-C(12)-C(13)	117.1 (6)	C(12)-C(13)-C(14)	112.0 (6)
C(12)-C(13)-C(17)	110.8 (6)	C(12)-C(13)-C(18)	108.2 (6)
C(14)-C(13)-C(17)	107.0 (6)	C(14)-C(13)-C(18)	111.1 (6)
C(17)-C(13)-C(18)	107.8 (6)	C(13)-C(14)-C(15)	113.7 (6)
O(15)-C(15)-O(16)	123.8 (7)	O(15)-C(15)-C(14)	126.1 (6)
O(16)-C(15)-C(14)	110.1 (6)		

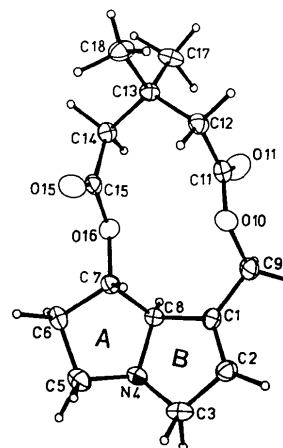


Fig. 1. An *ORTEP* diagram showing the numbering scheme with thermal ellipsoids at 50% probability.

Ring *A* is *exo*-buckled with a pucker angle of 33.2 (6)°. The angle of 124.2 (5)° between the planes defined by atoms C(1), C(8), N(4), C(3) and C(5), N(4), C(8), C(7) is characteristic of pyrrolizidine nuclei. Heliotridine itself (Gelbaum, Glinski, VanDerveer & Zalkow, 1985) and the two monoester heliotridine alkaloids lasiocarpine (Hay, Mackay & Culvenor, 1982) and heliotrine (Wodak, 1975) exist with ring *A* in the *endo*-buckled form. The addition of the macrocycle has therefore induced a conformational change to the more favoured *exo*-form which dominates other pyrrolizidine alkaloid bases. An exception to this is the 13-membered macrocyclic diester madurensine (Mackay, Sadek & Culvenor, 1984) which has the *endo*-buckled conformation due, most likely, to the attachment of the ester macrocycle at C(6).

The carbonyl bonds of the ester functions are antiparallel with an angle of 11.8 (6)° between the carbonyl bonds of the planar primary and secondary ester groups. The ester carbonyl group C(11)=O(11) is orientated in the same direction as C(8)—H. The alternative antiparallel conformation of the macro-ring has been found for the 11-membered retronecine diester trichodesmine (Tashkhodzhaev, Yagudaev & Yunusov, 1979) whilst the 11-membered macro-rings of the retronecine diesters of fulvine (Sussman & Wodak, 1973), axillarine (Stoekli-Evans & Crout, 1976), monocrotaline (Stoekli-Evans, 1979) and incanine (Tashkhodzhaev, Telezhenetskaya & Yunusov, 1979) all have the C(9) ester carbonyl bond directed below the plane of the macro-ring and synparallel to the C(7) ester carbonyl bond.

The transannular distance O(10)···O(16) of 2.998 (6) Å is similar to values found for other macrocyclic pyrrolizidine alkaloids where the ester

carbonyl bonds are antiparallel. There are no unusually short intermolecular contacts between any pairs of molecules.

We thank the Carnegie Trust for the Universities of Scotland for a Scholarship to DBH.

References

- GELBAUM, L. T., GLINSKI, J. A., VANDERVEER, D. & ZALKOW, L. H. (1985). *Acta Cryst.* C41, 1342–1345.
 GILMORE, C. J. (1984). *J. Appl. Cryst.* 17, 42–46.
 HAGAN, D. B. & ROBINS, D. J. (1987). *J. Chem. Soc. Perkin Trans.* 1. In the press.
 HAY, D. G., MACKAY, M. F. & CULVENOR, C. C. J. (1982). *Acta Cryst.* B38, 155–159.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 MACKAY, M. F., SADEK, M. & CULVENOR, C. C. J. (1984). *Acta Cryst.* C40, 1073–1077.
 MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* 18, 51–53.
 MATTOCKS, A. R. (1986). *Chemistry and Toxicology of Pyrrolizidine Alkaloids*. London: Academic Press.
 ROBINS, D. J. (1982). *Fortschr. Chem. Org. Naturst.* 41, 115–203.
 STOECKLI-EVANS, H. (1979). *Acta Cryst.* B35, 231–234.
 STOECKLI-EVANS, H. & CROUT, D. H. G. (1976). *Helv. Chim. Acta*, 59, 2168–2178.
 SUSSMAN, J. L. & WODAK, S. J. (1973). *Acta Cryst.* B29, 2918–2926.
 TASHKHODZHAEV, B., TELEZHENETSKAYA, M. V. & YUNUSOV, S. YU. (1979). *Khim. Prir. Soedin.* pp. 363–367.
 TASHKHODZHAEV, B., YAGUDAEV, M. R. & YUNUSOV, S. YU. (1979). *Khim. Prir. Soedin.* pp. 368–373.
 WARREN, F. L. (1970). In *The Alkaloids*, Vol. XII, edited by R. H. F. MANSKE, ch. 4. London, New York: Academic Press.
 WODAK, S. J. (1975). *Acta Cryst.* B31, 569–573.

Acta Cryst. (1988). C44, 668–671

Structure de la Nitro-7 Oxo-3 Benzoxaséléno-2,1-oxyde-1

PAR M. SBIT, L. DUPONT ET O. DIDEBERG

Laboratoire de Cristallographie, Institut de Physique B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgique

ET C. LAMBERT

Laboratoire de Chimie Organique, Institut de Chimie B6, Université de Liège au Sart Tilman, B-4000 Liège, Belgique

(Reçu le 2 septembre 1987, accepté le 7 décembre 1987)

Abstract. 7-Nitro-3-oxo-2,1-benzoxaselenole 1-oxide, C₇H₃NO₅Se, *M_r* = 260.063, orthorhombic, *Pbn̄b*, *a* = 11.442 (2), *b* = 14.569 (3), *c* = 19.904 (5) Å, *V* = 3317.9 (7) Å³, *Z* = 16, *D_x* = 2.082 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 62.51 cm⁻¹, *F*(000) = 2016, *T* = 290 K, m.p. = 490–493 K, final *R* = 0.055 for 1752

0108-2701/88/040668-04\$03.00

© 1988 International Union of Crystallography