Tableau 2. *Distances* (Å) *et angles de valence* (°), *avec les écarts-type*

C2—C1	1,393 (10)	C8—C7	1,544 (10)
C6—C1	1,386 (11)	O2—C7	1,422 (8)
O1—C1	1,376 (9)	C9—C8	1,524 (9)
C3—C2	1,391 (10)	N1—C8	1,550 (10)
C4—C3	1,390 (10)	N1—C10	1,525 (10)
C5—C4	1,396 (11)	N1—C11	1,519 (10)
C6—C5	1,375 (12)	N1—C12	1,513 (10)
C3—C7	1,534 (10)		
C6—C1—C2	121,2 (8)	O2—C7—C3	111,9 (7)
O1—C1—C2	121,1 (8)	O2—C7—C8	108,2 (6)
O1—C1—C6	117,7 (8)	C9—C8—C7	112,7 (6)
C3—C2—C1	119,3 (7)	N1—C8—C7	111,3 (6)
C4—C3—C2	119,9 (8)	N1—C8—C9	112,2 (6)
C7—C3—C2	118,2 (7)	C10—N1—C8	108,4 (6)
C7—C3—C4	121,9 (7)	C11—N1—C8	109,7 (6)
C5—C4—C3	119,7 (8)	C11—N1—C10	106,8 (6)
C6—C5—C4	120,8 (8)	C12—N1—C8	113,2 (6)
C5—C6—C1	119,1 (8)	C12—N1—C10	109,0 (7)
C8—C7—C3	108,5 (6)	C12—N1—C11	109,5 (8)

métriques de ces liaisons sont les suivants: O1···Cl1$^{\mathrm{i}}$ [(i) $-1-x$, $-0,5+y$, $-1,5-z$] 3,049 (6), O1—H10 1,07 (8), H10···Cl1$^{\mathrm{i}}$ 1,98 (6) Å, O1—H10···Cl1$^{\mathrm{i}}$ 180 (1)°; O2···O3 2,680 (7), O2—H20 1,05 (8), H20···O(3) 1,63 (8) Å, O2—H20···O3 172 (1)°; O3···Cl1$^{\mathrm{ii}}$ [(ii) $-x$, $-0,5+y$, $-1,5-z$] 3,100 (6), O3—H31 1,10 (8), H31···Cl1$^{\mathrm{ii}}$ 2,03 (6) Å, O3—H31···Cl1$^{\mathrm{ii}}$ 163 (1)°; O3···Cl1$^{\mathrm{iii}}$ [(iii) $-0,5-x$, $-1-y$, $0,5+z$] 3,119 (6), O3—H32 0,99 (8), H32···Cl1$^{\mathrm{iii}}$ 2,30 (6) Å, O3—H32···Cl1$^{\mathrm{iii}}$ 140 (1)°. La molécule d'eau et l'ion Cl^{-} sont donc chacun inclus dans trois liaisons hydrogène.

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Structure of the Lactonic Adduct from 2-Hydroxypinan-3-one and Glycine

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Abstract. 2,10,10-Trimethyl-3-oxa-6-azatricyclo[7.1.1.0^{2,7}]undec-6-en-4-one, $C_{12}H_{17}NO_2$, $M_r = 207.28$, monoclinic, $P2_1$, $a = 11.00$ (2), $b = 7.48$ (1), $c = 7.49$ (1) Å, $\beta = 114.3$ (1)°, $V = 562$ (3) Å^3, $Z = 2$, $D_x = 1.23$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 0.68$ mm^{-1}, $F(000) = 224$, $T = 294$ (1) K, final $R = 0.048$ for 888 independent reflexions. The structure allows the interpretation of the NMR spectrum observed in solution and of the stereochemistry on the C atom α to the lactone function in alkylation reactions.

Introduction. The synthesis of enantiomerically pure unnatural or naturally occurring but scarcely accessible α-amino acids has attracted considerable attention in recent years (Hoppe, 1982; Knowles, 1983; Schollkopf, 1983). In the laboratory we have developed a general method (El Achqar, Boumzebra, Roumestant & Viallefont, 1988) of synthesis of such compounds by creating the asymmetric centre, using 2-hydroxypinan-3-one as chiral auxiliary (Schmidt, 1960). This compound, after reaction with glycine derivatives led, under different experimental conditions, to the imine or to the lactone (El Achqar *et al.*, 1988).

In the ^{1}H NMR spectrum of this lactone, the two protons H(121) and H(122) (Fig. 1) do not present the same couplings: one proton is only coupled with the geminated proton, the other is coupled in addition with the two protons H(21) and H(22) (4.2 and 2.6 Hz). According to Atkinson & Perkins (1969) the maximum coupling is assigned to the protons whose

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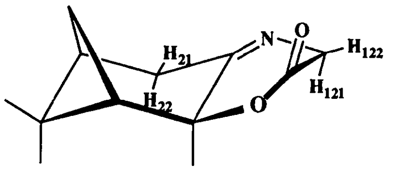
bonds are parallel to the π orbital of the C=N double bond. Molecular models show that the molecule can adopt two preferential conformations; one of these allows the interpretation of the NMR spectrum. The goal of the present work is to determine the conformation of the lactone (I) and to explain the stereochemistry observed on the α-C atom in alkylation reactions.



(I)

Experimental. Small colourless crystals were grown from ether. A crystal of dimensions 0.05 × 0.11 × 0.55 mm was used for data collection on an Enraf–Nonius CAD-3 diffractometer, with graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters were determined from the setting of 20 reflexions with $36 < \theta < 50°$. 1166 intensities were recorded by θ–2θ scan, and reduced to 1043 unique reflexions ($R_{\rm int} = 0.013$) and subsequently to 888 with $F_o > 3\sigma(F_o)$. One reference reflexion monitored every 60 reflexions showed no significant intensity variation. $3 < \theta < 65°$, index range $-12 \leq h \leq 11$, $0 \leq k \leq 8$, $0 \leq l \leq 8$. No absorption and extinction corrections were applied. The structure was solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). After refinement of non-H atoms with isotropic temperature factors, difference synthesis revealed all H atoms except H(81), H(101), H(102), H(103); positions of these atoms were calculated. $\sum w(F_o - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F) + 0.003416|F|^2]$. Strong reflexions 110 and 011, which had their intensities reduced by secondary extinction, and the spurious reflexion $\bar{5}56$, were excluded from the refinement [using *SHELX*76 (Sheldrick, 1976)]. Anisotropic temperature factors for C, N and O atoms and a unique isotropic temperature factor for all H atoms were used in the full-matrix least-squares refinement. Final $R = 0.048$, $wR = 0.055$, $S = 1.043$. $(\Delta/\sigma)_{\rm max} < 0.06$; $-0.16 < \Delta\rho < 0.15$ e Å^{-3}.* Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968) and values of f' and f'' for the anomalous-dispersion correction from Cromer & Liberman (1970).

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = (8/3)\pi^2(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$B_{\rm eq}$
C(1)	9198 (3)	5011 (8)	12622 (5)	3.8 (2)
C(2)	9308 (4)	4847 (8)	10677 (6)	4.3 (2)
C(3)	8079 (4)	3967 (7)	9151 (5)	3.4 (2)
C(4)	6786 (3)	4025 (7)	9449 (5)	3.2 (2)
C(5)	7139 (4)	4400 (7)	11625 (5)	3.3 (2)
C(6)	8432 (4)	3339 (8)	12870 (6)	4.0 (2)
C(7)	7959 (4)	6146 (7)	12411 (6)	3.7 (2)
C(8)	7732 (5)	7876 (8)	11228 (7)	5.0 (2)
C(9)	7967 (5)	6622 (8)	14435 (6)	5.2 (2)
C(10)	5694 (4)	5255 (8)	8062 (6)	4.1 (2)
C(11)	6177 (4)	1306 (7)	7536 (5)	3.3 (2)
C(12)	6960 (4)	2122 (8)	6478 (6)	4.5 (2)
N	8163 (3)	3048 (7)	7766 (5)	4.4 (2)
O(1)	6228 (3)	2194*	9129 (4)	3.7 (1)
O(2)	5567 (3)	−0078 (6)	7056 (4)	4.5 (1)

* Coordinate fixed to define origin on 2_1 axis.

Table 2. *Bond distances* (Å) *and bond angles* (°)

C(1)—C(2)	1.516 (6)	C(7)—C(9)	1.554 (6)
C(2)—C(3)	1.515 (6)	N—C(3)	1.279 (6)
C(3)—C(4)	1.528 (6)	N—C(12)	1.453 (6)
C(4)—C(5)	1.538 (5)	C(11)—C(12)	1.518 (8)
C(5)—C(6)	1.559 (7)	O(1)—C(11)	1.346 (5)
C(6)—C(1)	1.561 (8)	O(1)—C(4)	1.479 (5)
C(1)—C(7)	1.558 (6)	C(4)—C(10)	1.530 (7)
C(5)—C(7)	1.558 (7)	O(2)—C(11)	1.205 (7)
C(7)—C(8)	1.530 (8)		

C(2)—C(1)—C(6)	108.1 (4)	N—C(3)—C(4)	121.1 (4)
C(1)—C(2)—C(3)	111.2 (4)	N—C(3)—C(2)	120.4 (4)
C(2)—C(2)—C(4)	118.2 (4)	C(3)—N—C(12)	116.4 (4)
C(3)—C(4)—C(5)	108.4 (3)	N—C(12)—C(11)	113.7 (4)
C(4)—C(5)—C(6)	108.1 (4)	O(1)—C(11)—C(12)	116.0 (5)
C(1)—C(6)—C(5)	85.7 (4)	C(11)—O(1)—C(4)	117.6 (3)
C(6)—C(1)—C(7)	87.5 (3)	O(1)—C(4)—C(3)	107.4 (4)
C(1)—C(7)—C(5)	85.9 (4)	O(1)—C(4)—C(5)	104.3 (3)
C(6)—C(5)—C(7)	87.5 (4)	O(2)—C(11)—C(12)	123.8 (4)
C(1)—C(7)—C(9)	111.9 (4)	O(2)—C(11)—O(1)	120.2 (5)
C(5)—C(7)—C(9)	109.3 (4)	O(1)—C(4)—C(10)	106.8 (4)
C(1)—C(7)—C(8)	116.6 (4)	C(3)—C(4)—C(10)	115.8 (4)
C(5)—C(7)—C(8)	124.0 (4)	C(5)—C(4)—C(10)	113.3 (4)
C(8)—C(7)—C(9)	107.8 (4)		

Discussion. Atomic parameters are listed in Table 1. Bond distances and bond angles are given in Table 2. Fig. 1 shows the structure of the lactone. The crystal structure shows that the molecule adopts a preferential conformation which demonstrates the following features:

(i) Along the C(3)—C(4) bond a dihedral angle of 67.8 (5)° is formed between the C(3)—C(4)—O(1) and C(3)—C(4)—C(5) planes.

(ii) The two bonds C(12)—H(121) and C(2)—H(22) are parallel to the π orbital of the C=N double bond, so the coupling ($J = 4.2$ Hz) can be assigned to the protons H(121) and H(22) and the coupling ($J = 2.6$ Hz) to the protons H(121) and H(21). The proton H(122) does not exhibit a long-range coupling.

(iii) H(121) and the angular methyl group are very close: 1.92 (1) Å between H(121) and H(103); this

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55159 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0249]

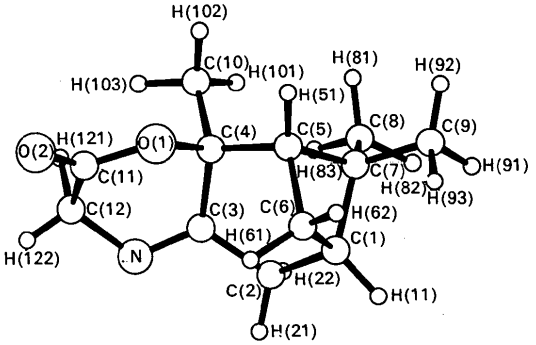

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the lactone (I) with atomic numbering. [Program adapted for the Macintosh by André & Michalowich (1991).]

face of the molecule is very crowded – it implies that the electrophile after the formation of the anion can only enter on the opposite face. These results are in good agreement with the observed stereochemistry.

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Structure du 2,3-Dihydro-3-(2-hydroxyéthylthio)benzo[*b*]thiophène 1-Oxyde, $C_{10}H_{12}O_2S_2$

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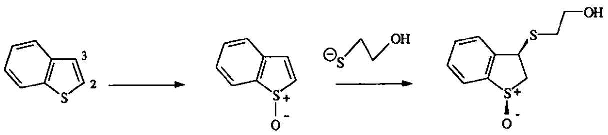
Abstract. 2,3-Dihydro-3-(2-hydroxyethylthio)-1-benzo[*b*]thiophene 1-oxide, $C_{10}H_{12}O_2S_2$, $M_r = 228.33$, monoclinic, $P2_1/a$, $a = 16.398$ (7), $b = 8.128$ (3), $c = 7.937$ (3) Å, $\beta = 92.13$ (4)°, $V = 1057.14$ Å^3, $Z = 4$, $D_x = 1.434$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 4.27$ mm^{-1}, $F(000) = 480$, $T = 295$ K, $R(F) = 6.2\%$ for 1259 reflexions. The O atom of the sulfoxide and the SCH_2CH_2OH group are *syn* to each other. In the racemic diastereoisomer (R^*,S^*), the molecules of the same sign are linked together by hydrogen bonds forming two chains in the lattice.

Introduction. L'oxydation métabolique par des microsomes du foie de rat du benzothiophène en présence de mercaptoéthanol conduit au benzothiophène sulfoxyde et au 2,3-dihydro-3-(2-hydroxyéthylthio)benzo[*b*]thiophène 1-oxyde (1). Leur identification a été faite en comparant des échantillons préparés par oxydation du benzothiophène par H_2O_2 dans CF_3COOH et par le traitement du benzothiophène sulfoxyde ainsi obtenu avec du mercaptoéthanolate dans le méthanol. Les thiophènes-*S*-oxydes sont une nouvelle classe de réactifs métaboliques. Le métabolisme et les effets toxiques possibles des dérivés du thiophène sont à l'étude (Mansuy, Valadon, Erdelmeier, Lopez-Garcia, Amar, Girault & Dansette, 1991).



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