1·527 (2), C—C = 1·515 (2) Å. The bond angles at the N atoms show a significant deviation from tetrahedral geometry, with the angles in each cation bisected by the S_4 axis being compressed to an average of 106·2 (2)°, possibly as a result of $CH_3\cdots CH_2$ intra-ion repulsions; the other C—N—C angles average 110·9 (2)°, and the N—C—C angles average 114·8 (1)°, perhaps a little larger than normal values as a result of the repulsions.

The thiosulfate anion has symmetry close to C_{3v} (Table 2), with S—S = 2·028 (1), mean (standard deviation of mean calculated from r.m.s. differences) S—O = 1·481 (2) Å (corrected for libration), S—S—O = 108·6 (5), O—S—O = 110·3 (1)°; the values are within the ranges normally found in thiosulfates (*e.g.* Teng, Fuess & Bats, 1984): S—S = 1·987–2·031, S—O = 1·473–1·489 Å. The anions are linked into chains along **a** by hydrogen bonds from the water molecules (Fig. 1, Table 2). O(4) forms two normal nearly linear bonds, O—(H)···O = 2·817 (3) Å and O—(H)···S = 3·458 (2) Å [an additional O(4)—H(O4*a*)···O(3^{i}) contact of 3·387 (3) Å and 134 (3)° may represent some minor bifurcation of the O—(H)···S bond]; O(5) forms a normal nearly linear O—(H)···S bond, 3·349 (3) Å, and a bifurcated $\text{O—H}\begin{matrix}\cdot\cdot\text{O}\\ \cdot\cdot\text{O}\end{matrix}$ bond, O···O = 3·121 (4) and 3·154 (4) Å. The shortest interionic distances involving the cation are H···S(2) = 2·86 (4), H···O = 2·52 (4), H···H = 2·10 (5) Å.

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Structure of Diethyl 9-Hydroxy-7-methyl-2,4-diphenyl-3-oxa-7-aza-1,5-bicyclo[3.3.1]nonanedicarboxylate

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Abstract. $C_{26}H_{31}NO_6$, $M_r = 453{\cdot}5$, monoclinic, $P2_1/c$, $a = 11{\cdot}504\ (4)$, $b = 14{\cdot}009\ (3)$, $c = 15{\cdot}564\ (4)$ Å, $\beta = 109{\cdot}80\ (3)°$, $V = 2360{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}276$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}844$ cm^{-1}, $F(000) = 968$, room temperature, $wR = 0{\cdot}037$ for 4701 reflections $[I > 1{\cdot}5\sigma(I)]$. The oxacyclohexanone part of the molecule is in a boat conformation, and the piperidine part shows a chair conformation. The OH group is inclined towards the phenyl-substituted part of the molecule and forms an intramolecular hydrogen bond [O···O = 2·726 (2) Å] to one of the carboxylate groups.

Introduction. Heterocyclic bicyclo[3.3.1]nonan-9-ols containing a piperidinol ring are of pharmacological interest because of their relation to opioid analgesics (Casy & Parfitt, 1986). To understand the pharmacological properties, it is important to know the stereogeometry of the molecule. 3-Oxa-7-aza-bicyclo[3.3.1]nonan-9-ones are obtained through a Mannich reaction by condensing a diethyl 4-oxo-2,6-diphenyl-1-oxa-3,5-cyclohexanedicarboxylate with formaldehyde and methylamine (Mannich & Mück, 1930; Haller & Unholzer, 1971). Two isomers are isolated (see Fig. 1), one showing a boat–chair conformation with the boat structure in the oxacyclohexanone ring containing the two benzene rings in a quasi-equatorial position, and the other isomer showing a chair–chair structure with the benzene rings in equatorial position (Küppers, Hesse, Ashauer-Holzgrabe, Haller & Boese,

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1987). Reduction of the boat–chair 3-oxa-7-azabicyclo[3.3.1]nonanone with sodium borohydride in methanol produces only one alcohol whereas the chair–chair bicyclononanone leads to two alcohols. One product of the chair–chair ketone reduction has the same physical properties as the alcohol derived from the boat–chair ketone, the other has different properties. In a preliminary paper (Haller & Ashauer, 1985) a chair–chair conformation has been postulated for both alcohols and the configuration of the hydroxyl group has been proposed from NMR data and the course of the reduction; however, the interpretation of the ^1H and ^{13}C NMR data was still unsatisfactory. Therefore, an X-ray crystal structure analysis of the alcohol derived from the boat–chair ketone was desirable to determine the configuration of the reduction product.

Experimental. Crystals were grown by evaporation of a methanolic solution of the bicyclononanol, prepared as described above. The sample used for crystallographic study was approximately isometric with edges *ca* 0·30 mm. Lattice parameters were determined by a least-squares fit to 60 diffractometrically measured Bragg angles (θ range: 6–34°). 7331 intensities were collected with a Philips PW 1100 diffractometer in the θ range 2–30°, θ–2θ scan technique. 5935 unique reflections, $R_{\rm int} = 0{\cdot}021$. Index ranges h −20/20, k 0/18, l 0/15. Two standard reflections ($\bar{8}00$ and $\bar{1}4\bar{2}$) monitored every 26 reflections showed no systematic decay, coefficients of variation 0·0016 and 0·0006, respectively. No absorption correction. Scattering factors for neutral atoms from Cromer & Mann (1968). The positions of non-H atoms were determined by direct methods. Approximate positions of the H atoms were generated geometrically and were refined afterwards. Refinement (based on F) using 4701 reflections with $I > 1{\cdot}5\sigma(I)$ yielded a final $wR = 0{\cdot}037$ ($R = 0{\cdot}061$). $w = 1/\sigma^2$. Anisotropic temperature factors for non-H atoms and individual isotropic temperature factors for H atoms. Isotropic extinction parameter $g = 4{\cdot}4\,(1) \times 10^{-7}$ [$F' = F(1 - gF^2/\sin\theta)$]. Max. $|\Delta/\sigma| = 0{\cdot}7$. Residual electron density between −0·30 and 0·40 e Å^{-3}. Programs used: *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986), *ORFFE* (Busing, Martin & Levy, 1964), *PLATON*87 (Spek, 1987), *ORTEP*II (Johnson, 1976).

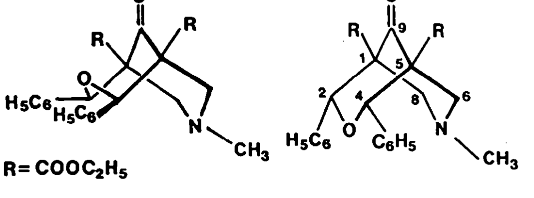

Fig. 1. Boat–chair and chair–chair isomers of the 3-oxa-7-azabicyclo[3.3.1]nonan-9-one.

Atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1; interatomic distances and angles are given in Table 2.*

Discussion. The packing of the molecules is shown in a stereoscopic *ORTEP* plot in Fig. 2. H atoms have been omitted for clarity, except for H(10) (with arbitrary diameter) which forms an intramolecular hydrogen bond (dashed). Since the molecules are attracted merely by van der Waals interactions a comparatively small density results ($D_x = 1{\cdot}276$ g cm^{-3}), which is in accord with the densities of two related bicyclononanones without hydrogen bonding ($D_x = 1{\cdot}251$, $1{\cdot}275$ g cm^{-3}; Küppers, Hesse *et al.*, 1987), and which is significantly lower than the density of a related diazaadamantanol ($D_x = 1{\cdot}350$ g cm^{-3}; Küppers, Samhammer & Haller, 1987) where an intermolecular hydrogen bond provides further intermolecular attraction.

Fig. 3 shows the stereogeometry of the molecule [H atoms omitted, except H(10)]. The oxacyclohexanone part of the bicyclononane skeleton is in a boat conformation with the benzene rings in a quasi-equatorial position, whereas the piperidine part has a chair conformation. The hydroxyl group is inclined towards the phenyl-substituted part of the molecule (*syn* configuration). The full designation of the compound is, therefore, diethyl 9-*syn*-hydroxy-7-methyl-2-*exo*,4-*exo*-diphenyl-3-oxa-7-aza-1,5-bicyclo[3.3.1]-nonanedicarboxylate. This stereogeometry differs distinctly from that proposed by Haller & Ashauer (1985) from NMR spectra.

The *syn* configuration of the OH group seems to be the consequence of the steric structure of the ketone; the rigid boat conformation of the oxacyclohexanone part of the bicyclononanone prevents the attack of the hydride from this side of the molecule to the carbonyl at C(9) (Fig. 4). Therefore, the hydride is added from the piperidine side of the molecule and the alcohol with *syn* configuration is formed with great stereoselectivity.

The H(10) atom of the hydroxyl group forms an intramolecular hydrogen bond to the acceptor carbonyl O(13) atom with the following geometry: O(10)—H(10) = 0·823 (19), H(10)—O(13) = 2·078 (18), O(10)—O(13) = 2·726 (2) Å, O(10)—H(10)···O(13) = 135·4 (1·5)°.

The stereogeometry of the molecule is clarified by the following angles between least-squares planes. The plane made up by C(2), O(3) and C(4) makes an angle of 49·6 (1)° with the best plane through benzene ring C(31) to C(36) and an angle of 62·8 (1)° with the best plane through benzene ring C(41) to C(46). The carboxylic groups are nearly coplanar with the plane

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* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51045 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (Å^2 × 10^4) *of non*-H *atoms*

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	7548 (1)	6119 (1)	−112 (1)	362 (4)
C(2)	6632 (1)	6250 (1)	442 (1)	370 (4)
O(3)	7048 (1)	5711 (1)	1275 (1)	407 (3)
C(4)	7178 (1)	4709 (1)	1156 (1)	372 (4)
C(5)	8059 (1)	4512 (1)	588 (1)	366 (4)
C(6)	7323 (1)	4084 (1)	−353 (1)	402 (5)
N(7)	6349 (1)	4724 (1)	−882 (1)	380 (4)
C(8)	6858 (1)	5633 (1)	−1031 (1)	399 (5)
C(9)	8619 (1)	5454 (1)	413 (1)	392 (4)
O(10)	9420 (1)	5852 (1)	1246 (1)	544 (4)
C(11)	5619 (2)	4288 (1)	−1743 (1)	478 (5)
C(12)	8039 (2)	7076 (1)	−307 (1)	460 (6)
O(13)	9044 (1)	7386 (1)	105 (1)	684 (5)
O(14)	7221 (1)	7521 (1)	−1004 (1)	605 (4)
C(15)	7522 (2)	8475 (1)	−1260 (2)	730 (9)
C(16)	6885 (3)	9193 (2)	−923 (2)	940 (13)
C(17)	9038·(2)	3768 (1)	1052 (1)	448 (5)
O(18)	135 (1)	3871 (1)	1316 (1)	645 (4)
O(19)	8474 (1)	2938 (1)	1102 (1)	502 (4)
C(20)	9224 (2)	2179 (2)	1648 (2)	688 (8)
C(21)	8392 (3)	1351 (2)	1594 (2)	912 (11)
C(31)	6452 (1)	7255 (1)	726 (1)	392 (5)
C(32)	7362 (2)	7709 (1)	1424 (1)	523 (6)
C(33)	7190 (2)	8619 (1)	1698 (1)	652 (7)
C(34)	6094 (2)	9082 (1)	1280 (1)	695 (8)
C(35)	5173 (2)	8647 (1)	586 (1)	637 (7)
C(36)	5357 (2)	7731 (1)	310 (1)	484 (6)
C(41)	7582 (1)	4287 (1)	2105 (1)	404 (5)
C(42)	6844 (2)	3628 (1)	2341 (1)	503 (6)
C(43)	7227 (2)	3217 (1)	3201 (1)	649 (8)
C(44)	8351 (2)	3447 (2)	3825 (1)	726 (9)
C(45)	9083 (2)	4108 (2)	3606 (1)	703 (7)
C(46)	8699 (2)	4536 (1)	2748 (1)	549 (5)

Table 2. *Interatomic distances* (Å) *and angles* (°) *of non*-H *atoms* (*except benzene rings*) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·583 (2)	C(1)–C(12)	1·525 (2)
C(2)–O(3)	1·435 (2)	C(12)–O(13)	1·197 (2)
O(3)–C(4)	1·429 (2)	C(12)–O(14)	1·327 (2)
C(4)–C(5)	1·579 (3)	O(14)–C(15)	1·469 (3)
C(5)–C(6)	1·544 (2)	C(15)–C(16)	1·444 (4)
C(6)–N(7)	1·453 (2)	C(5)–C(17)	1·524 (2)
N(7)–C(8)	1·454 (2)	C(17)–O(18)	1·196 (2)
C(8)–C(1)	1·540 (2)	C(17)–O(19)	1·348 (2)
C(1)–C(9)	1·541 (2)	O(19)–C(20)	1·449 (2)
C(5)–C(9)	1·533 (2)	C(20)–C(21)	1·487 (4)
C(9)–O(10)	1·424 (2)	C(2)–C(31)	1·511 (2)
N(7)–C(11)	1·454 (2)	C(4)–C(41)	1·511 (2)
C(2)–C(1)–C(8)	109·3 (1)	C(4)–C(5)–C(9)	109·7 (1)
C(2)–C(1)–C(9)	109·9 (1)	C(4)–C(5)–C(17)	111·4 (1)
C(2)–C(1)–C(12)	111·5 (1)	C(6)–C(5)–C(9)	107·1 (1)
C(8)–C(1)–C(9)	107·1 (1)	C(6)–C(5)–C(17)	105·2 (1)
C(8)–C(1)–C(12)	108·2 (1)	C(9)–C(5)–C(17)	112·7 (1)
C(9)–C(1)–C(12)	110·7 (1)	C(5)–C(6)–N(7)	111·6 (1)
C(1)–C(2)–O(3)	110·6 (1)	C(6)–N(7)–C(8)	110·9 (1)
C(1)–C(2)–C(31)	116·7 (1)	C(6)–N(7)–C(11)	110·9 (1)
O(3)–C(2)–C(31)	105·3 (1)	C(8)–N(7)–C(11)	111·0 (1)
C(2)–O(3)–C(4)	114·7 (1)	N(7)–C(8)–C(1)	110·3 (1)
O(3)–C(4)–C(5)	111·0 (1)	C(1)–C(9)–C(5)	107·8 (1)
O(3)–C(4)–C(41)	105·6 (1)	C(1)–C(9)–O(10)	113·7 (1)
C(5)–C(4)–C(41)	115·9 (1)	C(5)–C(9)–O(10)	110·9 (1)
C(4)–C(5)–C(6)	110·5 (1)		

through C(1), C(9) and C(5). The deviations are 21·6 (1)° [C(1),C(12),O(13),O(14)] and 5·3 (1)° [C(5),C(17),O(18),O(19)]. The former carboxylic group seems to be tilted out of the coplanar arrangement by means of the attractive effect of the intramolecular hydrogen bond.

Table 3 presents a comparison of the ^{13}C NMR data of the ketone of the oxaazabicyclononane skeleton with those of the corresponding alcohol. The small upfield shift of C(2) and C(4) (0·5 p.p.m.) together with the large upfield shifts of C(1) and C(5) (13·4 p.p.m.) and C(6) and C(8) (5·1 p.p.m.) (Table 3) are in qualitative agreement with measurements of Jeyaraman, Jawaharsingh, Avila, Ganapathy, Eliel, Manoharan & Morris-Natschke (1982) on 3-aza-7-thiabicyclononanone and the corresponding alcohol (1·4, 12·7, 3·3 p.p.m., respectively).

In the crystalline state, the hydroxyl group forms an intramolecular bond to one of the carbonyl groups. The IR spectrum of powdered crystals in KBr shows a broad absorption band with a maximum at *ca* 3480 cm^{-1} which is assumed to be caused by the OH group within this intramolecular hydrogen bond. The IR spectrum of the alcohol dissolved in CCl_4 was obtained at four different concentrations (0·025, 0·01,

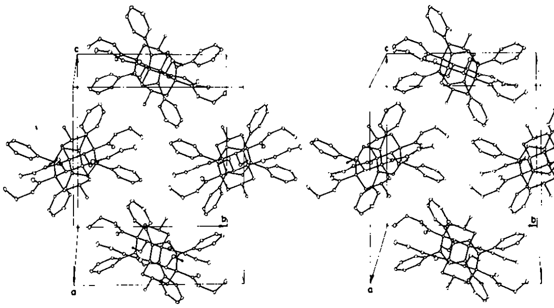

Fig. 2. Stereoscopic view of the unit cell parallel to **a*** (*ORTEP*II; Johnson, 1976).

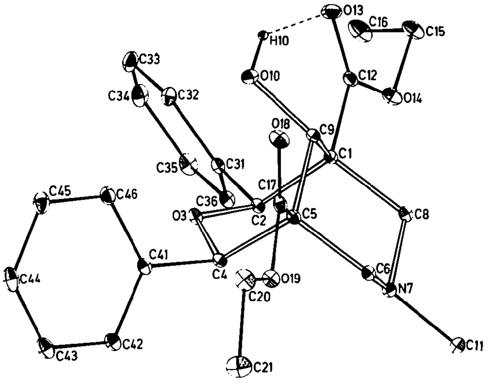

Fig. 3. *ORTEP*II (Johnson, 1976) plot of the molecule.

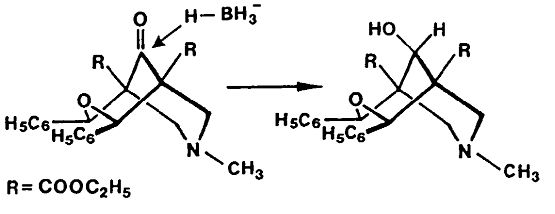

Fig. 4. Reduction of the boat–chair 3-oxa-7-azabicyclo[3.3.1]-nonan-9-one.

Table 3. ^{13}C *NMR data of the ketone and the alcohol*

Chemical shifts in p.p.m., TMS as internal standard

	C(1),C(5)	C(2),C(4)	C(6),C(8)
Ketone	65·6	82·8	65·8
Alcohol	52·2	82·3	60·7

0·005, and 0·001 *M*). At high concentrations a broadened signal at 3540 cm^{-1} is observed. Upon dilution this broadened absorption band disappears in favour of a sharp band appearing at 3640 cm^{-1} indicating a free OH group (Aaron, 1979). The results in CS_2 are similar. From this observation, it can be concluded that the alcohol exhibits an intermolecular hydrogen-bonded OH group in highly concentrated solutions.

This communication is dedicated to the memory of Professor Dr R. Haller who died on 6 April 1987 and who initiated the research on this class of compounds and gave various and valuable stimulations to this work.

Parts of the structure determination were performed in the course of a workshop in Göttingen, 1987, arranged by Professor G. M. Sheldrick. Further thanks are due to K.-F. Hesse for collecting the intensities, and to Mrs U. Bennewitz for retouching the drawings.

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Structure of *O,S*-Dibenzoylthiamin

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Abstract. 4-{*N*-[(4-Amino-2-methyl-5-pyrimidinyl)-methyl]formamido}-3-benzoylthio-3-penten-1-yl benzoate, $C_{26}H_{26}N_4O_4S$, $M_r = 490{\cdot}6$, triclinic, $P\bar{1}$, $a = 8{\cdot}139\,(1)$, $b = 14{\cdot}903\,(2)$, $c = 12{\cdot}107\,(1)$ Å, $\alpha = 109{\cdot}63\,(1)$, $\beta = 107{\cdot}87\,(1)$, $\gamma = 66{\cdot}19\,(1)°$, $V = 1240$ Å^3, $Z = 2$, $D_x = 1{\cdot}284$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 13{\cdot}87$ cm^{-1}, $F(000) = 516$, $T = 295$ K, $R = 0{\cdot}055$ for 2368 reflections with $I > 3\sigma(I)$. The *N*-formyl and ethylenic planes are nearly perpendicular to each other and the N(3)—C(4) bond retains single-bond character as observed characteristically in other ring-opened disulfide derivatives of thiamin. However, there is no intramolecular N(4′α)—H···O(2α) hydrogen bond which has been observed in the disulfide derivatives. The molecules related by a centre of symmetry form a dimer *via* N(4′α)—H···N(3′) hydrogen bonds [2·999 (5) Å]. Two *S*-benzoyl groups intercalate between the pyrimidine base-pair planes without any strong stacking interactions.

Introduction. Thiamin (vitamin B_1) is labile against acid, alkali and heat (Dwidevi & Arnold, 1973). The thiazolium ring in thiamin is easily hydrolyzed in mildly alkaline solution to give various thiol or disulfide derivatives which, in turn, can be easily converted to thiamin upon acidification (Hopmann, 1982). Some of the ring-opened disulfide derivatives have been used either as prodrugs or as starting materials for other thiamin derivatives. The crystal structures of three thiamin disulfide derivatives have been determined. These include thiamin propyl disulfide (TPD; Nishikawa, Kamiya, Asahi & Matsumura, 1969), thiamin tetrahydrofurfuryl disulfide (TTFD; Shin & Kim, 1986*a*) and thiamin disulfide dinitrate (TDD; Shin &

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