Table 3. *Intermolecular distances* (Å) *less than* 3·5 Å *between the non-hydrogen atoms, and hydrogen bonding*

C(3)···O(1^{i})	3·40 (2)	C(2)···O(1^{ii})	3·440 (12)
C(2)···C(3^{i})	3·35 (2)	O(3)···C(3^{ii})	3·35 (3)
O(1)···C(4^{i})	3·34 (2)	O(1)···C(7^{ii})	3·27 (3)
O(1)···O(1^{ii})	3·477 (10)	O(3)···O(1^{ii})	3·35 (3)
C(13)···O(1^{ii})	3·415 (14)	C(10)···O(3^{iii})	3·199 (14)
C(2)···O(3^{ii})	3·38 (4)	C(13)···O(4^{iii})	3·487 (17)
O(1)···C(1^{ii})	3·36 (3)		

Hydrogen bond: O(4)–H(5)···O(2^{iv}) 2·627 (13); O(4)–H(5) 1·09; H(5)···O(2^{iv}) 1·61 Å; ∠O(4)–H(5)–O(2) 153°.

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $1 - x$, $1 - y$, $\bar{z}$; (iii) $\bar{x}$, $1 - y$, $\bar{z}$; (iv) $\bar{x}$, $1 - y$, $1 - z$. Short intermolecular distances due to dimerization (iv) have been omitted.

hydrogen bond, which binds the molecules into centrosymmetric dimers, through carboxyl groups. The O(2)···O(4) hydrogen-bond distance of 2·627 (13) Å is in the range normally observed for aromatic carboxylic acid dimers. The carboxyl group is approximately coplanar with the benzene ring to which it is bonded. The dihedral angle between the least-squares plane of the ring and the carboxyl group is only about 2°. Both benzene rings are planar within experimental error and are nearly perpendicular to each other, making a dihedral angle of 89°.

Fig. 1 shows the packing in the crystal viewed along **c**. C(2) and O(1) in the molecules related by the symmetry operations $1 - x$, $1 - y$, $1 - z$ and $1 - x$, $1 - y$, $\bar{z}$ are located above O(1) and C(2) respectively. Because of this overlapping many close intermolecular contacts occur (Table 3), but none of these is substantially shorter than the sum of the van der Waals radii of the atoms concerned.

The author would like to thank Professor J. Gronowska for supplying the crystal before the publication of her experimental results and for a valuable discussion, Dr M. Główka (Institute of General Chemistry, Łódź) for advice on the use of the XRAY system of crystallographic programs, Mgr T. Cieplak for installing the XRAY system on a Riad-32 computer, and Mgr B. Walentynowicz for technical assistance.

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Acta Cryst. (1980). B**36**, 2814–2816

Structure of a Diastereoisomer of 1,9-Dimethyl-8-azabicyclo[4.3.0]nonane-3,7-dione. Proof of the Stereochemistry of a Synthetic Intermediate in the Synthesis of Vitamin B_{12}

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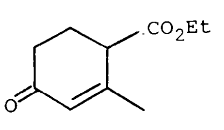
(*Received* 19 *May* 1980; *accepted* 27 *June* 1980)

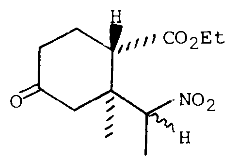
Abstract. $C_{10}H_{15}NO_2$, monoclinic, $P2_1$, $a = 7{\cdot}060\ (3)$, $b = 6{\cdot}510\ (3)$, $c = 10{\cdot}240\ (4)$ Å, $\beta = 100{\cdot}51\ (5)°$, $U = 462{\cdot}74$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ Mg m^{-3}, $F(000) = 196$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}091$ mm^{-1}. The structure was solved by direct methods and refined to $R = 0{\cdot}056$ for 809 observed reflections. Molecules are linked by hydrogen bonds to form columns down the screw axis.

Introduction. During studies of the synthesis of vitamin B_{12} the anion of nitroethane was added by a Michael reaction to a Hageman's ester (2-methyl-4-oxo-2-cyclohexene-1-carboxylate) (1) to give a racemic mixture of diastereoisomers (2) in 65% yield (Begbie, 1970).

The relative stereochemistry (*trans*) of the Michael addition was proved by synthetic comparison with a



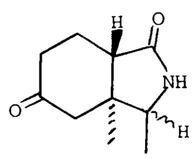
(1)



(2)

compound of known relative stereochemistry. Separation of the diastereoisomers and the conversion of each by the Nef reaction to the same ketone proved that the difference in stereochemistry was at the nitro carbon (Begbie, Bowman & Golding, 1980).

The stereochemistry of both diastereoisomers was assigned after detailed conformational analysis. In order to obtain independent proof of the stereochemistry both epimers of (2) were converted to the corresponding bicyclic amides (3) by reduction (with Raney-nickel and hydrogen) of the nitro group to the amine and subsequent ring closure by refluxing in toluene.



(3)

NMR analysis showed that the relative stereochemistry had not been altered during the conversion. Assignment of the relative stereochemistry by lanthanide-shift NMR or nuclear Overhauser effects was precluded by the extreme insolubility of the (*R*)-diastereoisomer of (3).

To confirm the assignment of stereochemistry, the structure of the (*R*)-diastereoisomer of (3) was determined by X-ray crystallography.

Acicular crystals were grown from acetone and data were collected on a Stoe automatic Weissenberg diffractometer, scanning in ω. Mo $K\alpha$ radiation (graphite monochromator) was used with $2\theta_{max} = 50°$, allowing the measurement of 890 unique reflections of which 809 were classed as observed $[I/\sigma(I) > 3]$. Lorentz and polarization corrections were applied but no corrections were made for absorption or extinction.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971), and refined by full-matrix least squares to $R = 0.056$.* Non-hydrogen atoms were allowed anisotropic thermal parameters but the H atoms were placed in calculated positions and not refined. In the final cycles the weighting scheme $w = 1/(1.5 + 1.0F)$ was employed. Scattering factors for C, N and O were those of Cromer & Mann (1968) and for H of Stewart, Davidson & Simpson (1965). All calculations were carried out with the XRAY system (1972) implemented at the University of Manchester Regional Computer Centre.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35419 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for the non-hydrogen atoms*

	x	y	z	B_{eq} (Å^2)*
C(1)	−55 (8)	6097 (46)	8038 (5)	2·6
C(2)	−1211 (7)	4385 (47)	8528 (5)	2·4
C(3)	−1621 (9)	2474 (46)	7684 (7)	3·4
C(4)	81 (8)	1704 (47)	7049 (5)	2·7
C(5)	1023 (7)	3549 (46)	6528 (5)	2·2
C(6)	1732 (7)	5152 (46)	7602 (4)	1·9
C(7)	2878 (7)	6589 (45)	6817 (5)	2·4
C(8)	2748 (8)	3317 (46)	5830 (5)	2·5
C(9)	3091 (8)	4240 (46)	8821 (5)	2·4
C(10)	4404 (8)	7947 (45)	7597 (6)	3·2
N(1)	3710 (7)	5072 (46)	5997 (5)	2·8
O(1)	−1851 (6)	4576 (46)	9559 (4)	3·6
O(2)	3107 (6)	1794 (45)	5194 (4)	3·7
H(11)	−866	6811	7268	
H(12)	365	7111	8768	
H(31)	−2003	1304	8239	
H(32)	−2734	2734	6934	
H(41)	1035	958	7740	
H(42)	−403	694	6309	
H(51)	30	4193	5812	
H(71)	1896	7504	6258	
H(81)	3740	5663	5101	
H(91)	2381	3110	9218	
H(92)	4232	3593	8516	
H(93)	3559	5250	9526	
H(101)	3785	8822	8218	
H(102)	5377	7015	8175	
H(103)	5149	8872	7114	

* B_{eq} is given by $\frac{1}{3}(B_{11} + B_{22} + B_{33})$.

Table 2. *Bond lengths* (Å) *and their e.s.d.'s*

C(1)–C(2)	1·52 (3)	C(5)–C(8)	1·53 (1)
C(1)–C(6)	1·54 (2)	C(6)–C(7)	1·55 (3)
C(2)–C(3)	1·51 (3)	C(6)–C(9)	1·55 (2)
C(2)–O(1)	1·23 (1)	C(7)–C(10)	1·51 (2)
C(3)–C(4)	1·55 (2)	C(7)–N(1)	1·49 (3)
C(4)–C(5)	1·52 (3)	C(8)–N(1)	1·32 (3)
C(5)–C(6)	1·53 (3)	C(8)–O(2)	1·24 (3)

Discussion. The final atomic coordinates are listed in Table 1, bond lengths and angles in Tables 2 and 3. The molecular structure and atom numbering are shown in Fig. 1; Fig. 2 shows the unit-cell contents.

The structure consists of molecules linked by two crystallographically equivalent hydrogen-bonded contacts to form columns down the screw axis with N(1)···O(2) = 2·96 (1) Å. The columns themselves are linked by normal van der Waals forces. The

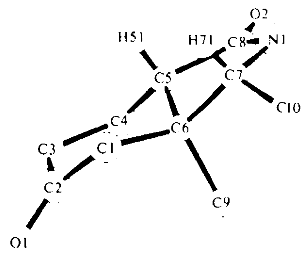


Fig. 1. The molecular structure and atom numbering.

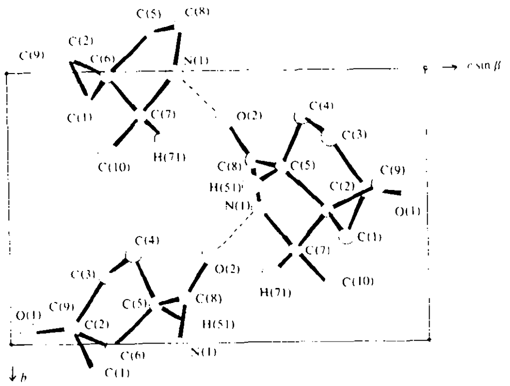


Fig. 2. The unit-cell contents projected down **a**. Hydrogen bonds are shown by broken lines.

molecule has a chair conformation in the six-membered ring *trans*-fused to a five-membered lactam. The structure also indicates that there is considerable steric interaction between the two *cis*-methyl groups, C(9)···C(10) [2·94 (3) Å]. The lactam ring reveals the expected shortening of the N(1)—C(8) amide bond

Table 3. *Bond angles (°) and their e.s.d.'s*

C(2)—C(1)—C(6)	108·7 (22)	C(5)—C(6)—C(7)	100·0 (9)
C(1)—C(2)—C(3)	118·2 (9)	C(5)—C(6)—C(9)	113·0 (21)
C(1)—C(2)—O(1)	120·9 (24)	C(7)—C(6)—C(9)	110·1 (8)
C(3)—C(2)—O(1)	120·8 (24)	C(6)—C(7)—C(10)	118·0 (7)
C(2)—C(3)—C(4)	115·1 (13)	C(6)—C(7)—N(1)	100·9 (21)
C(3)—C(4)—C(5)	108·3 (21)	C(10)—C(7)—N(1)	111·8 (8)
C(4)—C(5)—C(6)	113·2 (9)	C(5)—C(8)—N(1)	106·8 (19)
C(4)—C(5)—C(8)	121·6 (22)	C(5)—C(8)—O(2)	125·7 (21)
C(6)—C(5)—C(8)	102·7 (12)	N(1)—C(8)—O(2)	127·5 (10)
C(1)—C(6)—C(5)	107·6 (9)	C(7)—N(1)—C(8)	113·6 (10)
C(1)—C(6)—C(7)	116·1 (21)		
C(1)—C(6)—C(9)	109·8 (6)		

[1·32 (3) Å] compared with the normal N(1)—C(7) single-bond [1·49 (3) Å]. All other bonds and angles are as expected.

We thank Dr D. R. Russell for assistance in the data collection and for use of the diffractometer at Leicester University.

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Acta Cryst. (1980). B**36**, 2816–2819

Thieleanine

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(*Received* 8 *April* 1980; *accepted* 1 *July* 1980)

Abstract. $C_{15}H_{18}O_3$, M_r = 246·13, orthorhombic, $P2_12_12_1$, a = 6·843 (2), b = 28·219 (10), c = 6·789 (3) Å, V = 1311·0 (8) Å^3, Z = 4, d_c = 1·247 Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1324 reflexions led to a final R of 0·055. Thieleanine is a guaianolide-type sesquiterpene lactone composed of fused five- and seven-membered rings and a *trans*-fused α,β-unsaturated γ-lactone. The five- and seven-membered rings occur in flattened

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0567-7408/80/112816-04$01.00