Karagiannidis, 1984) and *N*-(2-diethylaminoethyl)-dithiocarbamic acid, in which $\Delta$(C—S) = 0·032 (7) Å (Kokkou, Cheer, Rentzeperis & Karagiannidis, 1988).

$\Delta$(C—S) values for dithiocarbamic acids are comparable with values for dithiocarbamate salts of strongly positive ions or groups which interact weakly with the S atoms of the $S_2CN$— moiety. The most characteristic of these are: $(N_2H_5)(H_2NNHCS_2)$ with $\Delta$(C—S) = 0·028 (8) Å (Braibanti, Manotti Lanfredi, Tiripicchio & Logiudice, 1969), $Na[S_2CN(CH_2)_4]$.-$2H_2O$ with $\Delta$(C—S) = 0·023 (3) Å (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980), $Na(S_2CNMe_2)$.-$2H_2O$ with $\Delta$(C—S) = 0·027 (3) Å (Oskarsson & Ymén, 1983), $K(S_2CNHCOH)$ with $\Delta$(C—S) = 0·057 (11), 0·028 (13), 0·063 (13), 0·044 (11) Å for the four molecules in the asymmetric unit (Gerner, Kiel & Gattow, 1985), although in this case the mesomeric effect also probably influences the molecular conformation, and $[N(n\text{-}C_4H_9)_4][S_2CN(CH_3)CSH]$ with $\Delta$(C—S) = 0·032 (3) Å (Gerner & Kiel, 1986).

The ammonium nitrogen N(2) is bonded to three C atoms and one H atom in an approximately tetrahedral coordination. The distance of N(2) from the plane of the C atoms is 0·447 (5) Å. H(N2) interacts with both S atoms of a neighbouring molecule (Table 2, Fig. 2). This results in bifurcated $N—H\cdots S_2$ hydrogen bonds interconnecting molecules to form infinite zigzag chains parallel to the *b* axis. In addition, the carbamate $H(N1^i)$ is strongly hydrogen bonded to S(2) (Fig. 2). This normal $N—H\cdots S$ hydrogen bond and its inversion equivalent form centrosymmetric eight-membered rings interconnecting the chains of molecules described above. The IR spectrum of DMAE in KBr disk exhibits two discrete bands $\bar{\nu}$(NH) and $\bar{\nu}$(N$^+$H) at 3160(*s*) and 2600(*m*) cm$^{-1}$ correspondingly.

Thanks are due to the University of Thessaloniki for the use of its computing facilities.

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*Acta Cryst.* (1989). C**45**, 142–145

# Structure of 2-Hydroxy-5-methyl-5-nitro-2-oxo-1,3,2$\lambda^5$-dioxaphosphorinane Monohydrate

By O. Johnson, D. W. Jones and R. S. Edmundson

*Department of Chemistry and Chemical Technology, University of Bradford, Bradford BD7 1DP, England*

(*Received* 2 *June* 1988; *accepted* 18 *August* 1988)

**Abstract.** $C_4H_8NO_6P.H_2O$, $M_r = 215$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 6{\cdot}142\ (2)$, $b = 8{\cdot}851\ (1)$, $c = 16{\cdot}493\ (2)$ Å, $U = 896{\cdot}7$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}58\ (1)$ (carbon tetrachloride/hexane flotation), $D_x = 1{\cdot}59$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}306$ mm$^{-1}$, $F(000) = 448$, $T = 298$ K, final $R = 0{\cdot}037$ over 634 unique diffractometer data $[I_o > 3\sigma(I_o)]$. The 5-nitro and 2-hydroxyl groups are both axial with respect to the dioxaphosphorinane chair ring, which is more evenly puckered than in some 1,3,2-dioxaphosphorinanes: chair planes O(1)—P—O(3) and C(3)—C(2)—C(1) are inclined at angles 136 (1) and 134 (1)° to the central O(1)—C(1)—C(3)—O(3) ring plane. The water oxygen is an acceptor for a hydrogen bond to the 2-hydroxyl [O(4)···O(5) = 2·40 (1) Å with angle O(4)—H(401)···O(5) = 156 (2)°], while the

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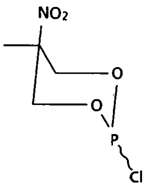
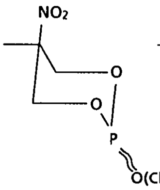
water hydrogens form hydrogen bonds of 2·66 (1) and 2·76 (1) Å to phosphoryl oxygens in different asymmetric units.

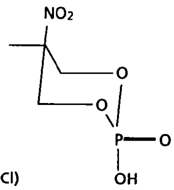
**Introduction.** The stereochemistries of substituted cyclic esters of tetracoordinate phosphorus acids, analogues of potential antitumour agents, have received appreciable NMR spectroscopic (in solution) and crystallographic study (Bartle, Edmundson & Jones, 1967; Edmundson, Johnson, Jones & King, 1985; Maryanoff, Hutchins & Maryanoff, 1979). For 1,3,$2\lambda^5$-diheterophosphorinanes, typically in flattened chair form, with bulky or electron-withdrawing groups on the phosphorus, the combination of 1,2 steric interaction with oxygen lone pairs and anomeric effects (Jeffrey, Pople & Radom, 1972) of antiperiplanar lone pairs adjacent to a polar bond favours the axial over equatorial isomer. 2-Chloro-5-methyl-5-nitro-1,3,$2\lambda^5$-dioxaphosphorinane 2-oxide appears to hydrolyse (Edmundson, 1965) more readily than the corresponding 5,5-dimethyl compound (Billman, Meisenheimer & May, 1966) to the monohydrate of the acid, 2-hydroxy-5-methyl-5-nitro-1,3,$2\lambda^5$-dioxaphosphorinane 2-oxide (or 2-hydroxy-5-methyl-5-nitro-2-oxo-1,3,$2\lambda^5$-dioxaphosphorinane, MNOH). An X-ray analysis enables the ring conformation and relative disposition of 2- and 5-substituents in MNOH to be established.



(I)



MNCl



MNOH

**Experimental.** Reaction between diol $HOCH_2CMeNO_2CH_2OH$ and freshly distilled $PCl_3$ in cooled ethanol-free $CHCl_3$ containing 2 mole $Et_3N$ yielded a residue of geometrical isomers of tervalent chloride (I). Oxidation with $N_2O_4$ in $CCl_4$ of the later (more soluble) chlorophosphite fractions successively crystallized ($CHCl_3$) from (I) yielded the less-stable higher-melting (m.p. 474–477 K) isomer of the pentavalent cyclic phosphoryl chloride, MNCl, recrystallized from $CHCl_3$. Aqueous hydrolysis then yielded (Billman, May & Heard, 1968) the acid MNOH monohydrate, recrystallized from methyl cyanide as needles with *a*-axis elongation (m.p. 442–444 K).

Single crystal of dimensions 0·13 × 0·10 × 0·53 mm used to confirm photographically determined cell dimensions (25 reflections, $18 < 2\theta < 30°$) and for intensity data collection with graphite-monochromatized Mo $K\alpha$ radiation on an Enraf–Nonius CAD-4 four-circle diffractometer at Queen Mary College, London University, England; intensity data measured by $\omega/2\theta$ variable scan over $2\theta$ range 3–50°, maximum acquisition time 60 s per scan, for one octant (index ranges $h$ 0/7, $k$ 0/10, $l$ 0/19), no significant drift in intensity standard reflections $00\bar{8}$, $0\bar{3}\bar{6}$ and 046, checked hourly; orientation controls 060 and $3\bar{4}2$ monitored every 200 reflections. 962 observations from data reduction yielded 854 unique data of which 634 had $I \geq 3\sigma(I)$.

Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) from highest 197 of $E$ values, first with a $C_4O_3NPCl$ input derived from *trans*-2-chloro-4-isopropyl-5,5-dimethyl-1,3,$2\lambda^5$-dioxaphosphorinan-2-one (*trans*-MMiprCl) (Edmundson *et al.*, 1985) and then for weighted Fourier recycling with a $C_4O_4NP$ fragment to yield a 12-atom structure initially expected to be MNCl, $C_4O_5NPCl$. Emergence, after least-squares refinement with *CRYSTALS* (Carruthers, 1978) and $F_o$ synthesis at $R = 0{\cdot}25$, of a water O(5) peak led to reinterpretation of the structure as a 2-hydroxy monohydrate. After anisotropic full-matrix least-squares refinement [$\sum w(|F_o| - |F_c|)^2$ minimized] of this 13-atom structure to $R = 0{\cdot}042$ (with methylene and methyl H atoms placed geometrically: C—H = 1 Å and $U_{\rm iso} = 0{\cdot}05$ Å$^2$) Fourier difference synthesis revealed peaks (> 2 e Å$^{-3}$) ascribed to the water and PO—H H-atoms. For the final stages of full-matrix least-squares refinement, anisotropic for 13 non-H atoms, isotropic for the three hydroxyl H, riding (C—H = 1·0 Å) for other H [fixed $U_{\rm iso} = 0{\cdot}08$ Å$^2$ for C(4)methyl H, $U_{\rm iso} = 0{\cdot}05$ Å$^2$ for methylene H atoms], coefficients 1·37 and 0·91 in two-term truncated Chebyshev series weighting scheme (Carruthers & Watkin, 1979), eight weakest reflections ($1 \leq |F_o| \leq 4$) excluded, final residuals $R = 0{\cdot}037$, $wR = 0{\cdot}043$, for 131 parameters and 634 contributing reflections, $(\Delta/\sigma)_{\rm max} = 0{\cdot}5$. Final $\Delta F$ synthesis showed maximum absolute function value |0·21| e Å$^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1962). No corrections for absorption or extinction.

**Discussion.** Final fractional coordinates of the non-hydrogen atoms are in Table 1,* bond lengths and bond angles in Table 2.

Fig. 1 shows the atom numbering and molecular conformation; the 2-nitro group [atoms N(1), O(11) and O(12) are coplanar with ring atoms C(2) and C(3)] and the 2-hydroxyl group are both axial. Dipole and NMR measurements (Arbuzov, Arshinova, Guseva, Zyablikova, Kozlov & Shermergorn, 1975) imply an

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* Lists of structure factors, anisotropic thermal parameters, parameters of H atoms, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51351 (7 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 and equivalent isotropic temperature factors* (Å$^2$× 10$^2$) *for the* C, N, O *and* P *atoms* (*e.s.d.'s in parentheses*)

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| P(1) | 0·7543 (3) | 0·4760 (2) | 0·9096 (1) | 4·5 (1) |
| O(1) | 0·8115 (7) | 0·3270 (5) | 0·9565 (2) | 4·8 (3) |
| O(2) | 0·8745 (8) | 0·6055 (6) | 0·9430 (4) | 7·6 (3) |
| O(3) | 0·8321 (8) | 0·4412 (4) | 0·8211 (3) | 5·4 (3) |
| O(4) | 0·5077 (7) | 0·4872 (6) | 0·9086 (4) | 6·0 (3) |
| O(5) | 0·2812 (10) | 0·7043 (7) | 0·9290 (5) | 7·5 (3) |
| N(1) | 1·0582 (8) | 0·1389 (6) | 0·8418 (4) | 4·7 (3) |
| O(11) | 1·1206 (9) | 0·0350 (7) | 0·8823 (3) | 7·9 (4) |
| O(12) | 1·1744 (9) | 0·2195 (6) | 0·8015 (4) | 9·1 (4) |
| C(1) | 0·7318 (12) | 0·1879 (7) | 0·9230 (3) | 4·8 (4) |
| C(2) | 0·8104 (9) | 0·1648 (7) | 0·8370 (4) | 3·7 (3) |
| C(3) | 0·7610 (13) | 0·3002 (7) | 0·7847 (4) | 4·8 (3) |
| C(4) | 0·7115 (10) | 0·0223 (8) | 0·8005 (5) | 6·1 (4) |

Table 2. *Bond lengths* (Å) *and angles* (°) (*e.s.d.'s in parentheses*)

| | | | |
|---|---|---|---|
| P(1)—O(1) | 1·569 (5) | C(2)—C(1) | 1·512 (9) |
| P(1)—O(3) | 1·566 (5) | C(2)—C(3) | 1·507 (8) |
| P(1)—O(2) | 1·471 (5) | C(2)—C(4) | 1·524 (8) |
| P(1)—O(4) | 1·518 (4) | C(2)—N(1) | 1·541 (8) |
| O(1)—C(1) | 1·436 (7) | N(1)—O(11) | 1·199 (7) |
| O(3)—C(3) | 1·452 (7) | N(1)—O(12) | 1·209 (7) |
| O(4)—H(401) | 0·86 (8) | O(5)—H(51) | 0·7 (1) |
| | | O(5)—H(52) | 0·9 (1) |
| | | | |
| O(1)—P(1)—O(2) | 110·9 (3) | C(1)—C(2)—C(4) | 110·8 (5) |
| O(1)—P(1)—O(3) | 103·1 (2) | C(1)—C(2)—N(1) | 106·7 (6) |
| O(1)—P(1)—O(4) | 106·5 (3) | C(4)—C(2)—N(1) | 106·9 (5) |
| O(2)—P(1)—O(4) | 117·0 (3) | C(4)—C(2)—C(3) | 110·6 (5) |
| O(2)—P(1)—O(3) | 110·5 (3) | C(3)—C(2)—N(1) | 110·3 (6) |
| O(3)—P(1)—O(4) | 107·9 (3) | C(2)—N(1)—O(11) | 117·3 (6) |
| C(1)—O(1)—P(1) | 117·0 (4) | C(2)—N(1)—O(12) | 117·8 (6) |
| C(3)—O(3)—P(1) | 117·5 (4) | O(11)—N(1)—O(12) | 124·8 (6) |
| C(2)—C(1)—O(1) | 111·6 (5) | P(1)—O(4)—H(401) | 114 (5) |
| C(2)—C(3)—O(3) | 112·7 (5) | H(51)—O(5)—H(52) | 105 (11) |
| C(1)—C(2)—C(3) | 111·4 (5) | | |

axial–axial structure for the more stable MNCl isomer (m.p. 435–436 K) (Billman *et al.*, 1966). The water-molecule oxygen accepts a hydrogen bond from the 2-hydroxyl group with O(4)···O(5) = 2·40 (1) Å and O(4)—H(401)···O(5) = 156 (2)°; the water hydrogens H(51) and H(52) form hydrogen bonds of 2·66 (1) and 2·76 (1) Å to phosphoryl oxygens O(2) in different (screw-related) asymmetric units (Fig. 2). In both 2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane (II), designated propane-1,3-diol cyclic phosphate (Mazhar-ul-Haque, Caughlan & Moats, 1970), and 2-hydroxy-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (III) (Murayama & Kainosho, 1969), chains of hydrogen bonds [2·44 (5) Å long in (II)] link hydroxyl or phosphoryl oxygens in different molecules.

In most 1,3,2-dioxaphosphorinanes, angle β between O(1)—P—O(3) and C(1)—O(1)—C(3)—O(3) appreciably exceeds angle α between C(1)—C(2)—C(3) and C(1)—O(1)—C(3)—O(3); thus in *trans*-MMIprCl, for example, α = 125 (1) and β = 143 (1)° and in 2-cyclohexyl-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-oxide (MM cyclo) (Edmundson, Johnson & Jones, 1988), α = 127 (1) and β = 143 (1)°. With a small axial substituent at P and lower 1,3-transannular interaction with axial H(11) and H(31), MNOH has β = 136 (1)° and, no doubt influenced by the orientation of the nitro group, α = 134 (1)°, so that the chair is almost undistorted. Within the ring, oxygen angles are closer to trigonal than tetrahedral values, the angle O(1)—P(1)—O(3) of 103·1 (2)° is smaller than in *cis*- and *trans*-MMiprCl [106·7 (1)°], while C(1)—C(2)—C(3) at 111·4 (5)° is larger than in *cis*- and *trans*-MMiprCl [106·8 (3)°]; corresponding pairs of bond lengths are within 1σ [2·5σ for C(1)—O(1) and C(3)—O(3)] of each other.

We thank Dr M. B. Hursthouse (QMC) and the SERC for data, and the Yorkshire Cancer Research Campaign for financial support.

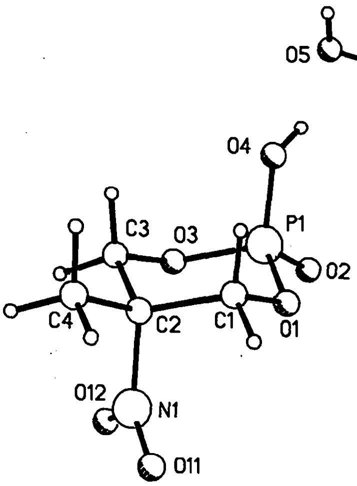

Fig. 1. Molecular conformation and atom numbering of the asymmetric unit.

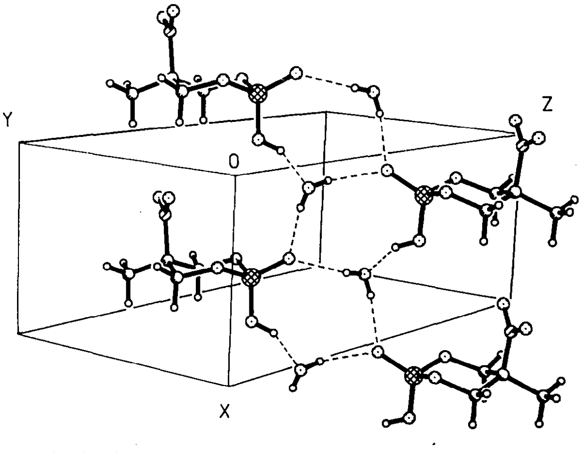

Fig. 2. View of the unit cell showing hydrogen bonding.

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*Acta Cryst.* (1989). C**45**, 145–148

# Structure of a Tricyclic Lactone – an Important Intermediate for the Total Synthesis of Dihydromevinolin

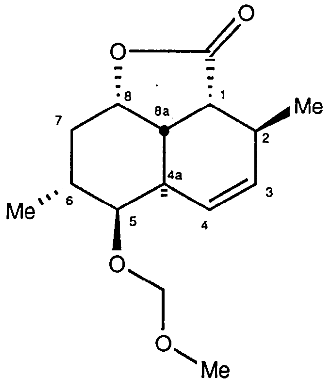
By Francine Bélanger-Gariépy, Patrick Roy, Stephen Hanessian and François Brisse

*Département de Chimie, Université de Montréal C.P.* 6128, *Succ. A, Montréal, Québec, H*3*C* 3*J*7, *Canada*

(*Received* 1 *June* 1988; *accepted* 18 *August* 1988)

**Abstract.** (1*R*,2*S*,4a*R*,5*S*,6*R*,8*S*,8a*S*)-5-Methoxymethoxy-2,6-dimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1,8-carbolactone, $C_{15}H_{22}O_4$, $M_r = 266{\cdot}34$, monoclinic, $P2_1$, $a = 9{\cdot}806\,(6)$, $b = 5{\cdot}758\,(3)$, $c = 12{\cdot}879\,(8)$ Å, $\beta = 92{\cdot}87\,(5)^\circ$, $V = 726{\cdot}27$ Å$^3$, $D_x = 1{\cdot}218$ Mg m$^{-3}$, $Z = 2$, $\lambda(\mathrm{Cu}\,K\bar{\alpha}) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\,K\bar{\alpha}) = 0{\cdot}674$ mm$^{-1}$, $F(000) = 288$, $T = 218$ K, $R = 0{\cdot}0458$ for 2633 observed reflections. The title compound, $C_{15}H_{22}O_4$, contains a *trans*-fused hexahydronaphthalene system, with a C=C bond at C(3)—C(4), and with a $\gamma$-lactone ring *cis*-fused across C(1)···C(8). The cyclohexane ring exhibits a flattened-chair conformation, the cyclohexene ring has the 1,3-diplanar conformation, and the five-membered $\gamma$-lactone has a C(8a)-envelope conformation. The molecule also contains a methoxymethoxy substituent axial at C(5), *trans* to a C(6) methyl group, and another methyl substituent at C(2) *trans* to the C atom of the $\gamma$-lactone.

**Introduction.** During the course of synthetic work aimed at the elaboration of the octahydronaphthalene portion of dihydromevinolin from optically active starting materials, it became necessary to use an intramolecular Diels–Alder reaction. Inspection of models had shown a preference for an *exo*-transition state leading possibly to the desired product. However, in view of the unknown stereochemistry at a secondary alcohol group produced in a previous step, it became imperative to seek definitive evidence for the structure of the Diels–Alder product. We report herein the crystal structure of this tricyclic product, $C_{15}H_{22}O_4$, which is a crucial intermediate in the total synthesis of the antihypercholesteremil agent dihydromevinolin (Albers-Schonberg *et al.*, 1981).



**Experimental.** Crystals of $C_{15}H_{22}O_4$ were recrystallized from hexane solution. Crystal fragment is a triangular

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