one type of interaction. The same monovalent I atom rarely participates in both short I...I and short I...O or I...N contacts. In the CSD there are 1559 compounds containing both an I atom and either an O or an N atom. In many of these structures there are short intermolecular distances involving I atoms, but only 16 structures contain monovalent I atoms 'close' to both an I and an O or N atom. In all but two of these 16 structures the O or N atom is multiply bonded to a C atom.

References


Structure of 4-Aminolactivinic Acid

BY Y. WADA, M. TAKAMOTO, S. TSUBOTANI AND K. KAMIYA

Central Research Division, Takeda Chemical Industries Ltd, Jusohonmachi, Yodogawa-ku, Osaka 532, Japan

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Abstract. 2-(4-Ammonio-3-oxo-1,2-oxazolidin-2-yl)-5-oxotetrahydrofuran-2-carboxylate, C₈H₈N₂O₆, Mₑ= 230.2, orthorhombic, P2₁2₁2₁, a = 7.833 (3), b = 21.577 (5), c = 5.565 (2) Å, V = 940.6 (5) Å³, Z = 4, Dₐ = 1.63 gcm⁻³, 2(Mo Kα) = 0.71069 Å, μ = 1.5 cm⁻¹, F(000) = 480, room temperature. Final R = 0.065 for 530 observed reflections. The title compound is a derivative of the new antibiotic lactivicin. The molecule consists of two five-membered rings (3-isoxazolidone and γ-lactone) directly connected by a C—N bond. The isoxazolidone ring exhibits a half-chair conformation and the γ-lactone ring is in an envelope form.

Introduction. Lactivicin (LTV) is a novel antibiotic isolated from culture filtrates of Empedobacter lactamgenus sp. nov. YK-258 and Lysobacter albus sp. nov. YK-422 (Nozaki, Katayama, Ono, Tsubotani, Harada, Okazaki & Nakao, 1987). An X-ray analysis as part of the structural study of this compound (Harada, Tsubotani, Hida, Ono & Okazaki, 1986) was undertaken for the determination in particular of the relative stereochemistry and the absolute configuration.

Among various derivatives and salts of LTV examined in an attempt to obtain suitable crystals, 4-aminolactic acid gave tolerable crystals for X-ray analysis.

Table 1. Positional parameters (×10⁴) and Ueq(A²×10²) for non-hydrogen atoms with e.s.d.'s in parentheses

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<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
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<td>8080 (11)</td>
<td>1382 (4)</td>
<td>1482 (18)</td>
<td>42 (5)</td>
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<td>N(2)</td>
<td>6920 (13)</td>
<td>1037 (5)</td>
<td>3064 (18)</td>
<td>31 (6)</td>
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<td>714 (5)</td>
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<td>35 (5)</td>
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<td>735 (5)</td>
<td>3932 (21)</td>
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<tr>
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<td>37 (7)</td>
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<td>6519 (16)</td>
<td>43 (5)</td>
</tr>
</tbody>
</table>

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Experimental. Recrystallization at 278 K from aqueous solution, colorless plates, crystal 0.2 x 0.2 x 0.01 mm; Rigaku AFC-5 diffractometer, graphite-monochromated Mo Kα radiation; cell parameters from least-squares refinement of 59 reflections in the range 21 < 2θ < 31°; 2θ-ω scan, 769 reflections with 2θ ≤ 45°, three standard reflections (011, 230, 340) monitored for each 60 reflections collected, standard reflections within 1.8% variation throughout the data collection, index range h = 0 to 8, k = 0 to 23, l = 0 to 5, 751 unique reflections, of which 530 with F > 3σ(F) considered observed and used for all calculations; Lorentz, polarization but no absorption corrections applied; structure solved by direct methods, H-atom positions from difference Fourier maps, unweighted full-matrix least-squares refinement of atomic coordinates and anisotropic temperature factors for all non-H atoms and isotropic temperature factors for H atoms, minimizing \( \sum (F_o - F_c)^2 \); final R = 0.065, wR = 0.070, S = 1.60. Max. Δ/σ = 0.024; max. difference-map peak 0.40 e Å⁻³. The main cause of the relatively high R index is the small size of the crystal. Atomic scattering factors from XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Computer programs MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and XRAY76. The final atomic positional parameters and Ueq values are given in Table 1,* bond distances and angles in Fig. 1 and the atomic numbering scheme in Fig. 2.

Discussion. The structure was confirmed as (I), in which 3-isoxazolidone and γ-lactone rings were directly linked through the N(2)-C(6) bond. Though the isomerization at the lactone moiety easily occurs in aqueous solution, the configuration at C(4) of 3-isoxazolidone is kept as S (Harada, Tsubotani, Hida, Ono & Okazaki, 1986). Therefore, as for the present crystal, the absolute configuration at C(6) is deduced to be R. Figures are drawn to show the correct configuration.

The 3-isoxazolidone ring is in a half-chair form and O(1), C(5) deviate from the plane formed by N(2), C(3) and C(4). Atoms O(1), C(6) are situated at one side and C(5), N(12) at the other side of the plane. The γ-lactone ring is in an envelope conformation in which C(10) is the flap and is displaced from the plane formed by the other four atoms to the same side as C(11) and opposite to N(2). These two five-membered rings are almost perpendicular to each other, and N(2)-C(3) and C(6)-C(10), N(2)-O(1) and C(6)-C(11) are s-trans with respect to the N(2)-C(6) bond.

![Fig. 1. Bond distances (Å) and angles (°). Small digits show e.s.d.'s.](image1)

![Fig. 2. Perspective view of the molecule. The numbering scheme is also shown.](image2)

![Fig. 3. Packing diagram.](image3)
The amino nitrogen N(12) presents a quaternary character: this quaternization is produced by proton transfer from the carboxyl group to N(12); thus, a 'zwitterion' structure is present, with the carboxyl group deprotonated and the amino N protonated. The distances of 2.75 (1), 2.74 (1) and 2.86 (1)/\AA between N(12) and O(11A) of the molecule at (1.5-x, -y, 0.5+z), O(11A) at (1+x, y, z) and 0(3) at (1.5-x, -y, -0.5+z) indicate the presence of three independent intermolecular hydrogen bonds. Fig. 3 shows the molecular packing.

The authors thank Dr Y. Oka for helpful discussion and Ms K. Higashikawa for technical assistance.

References


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The Stereochemistry of the Phosphorus–Selenium Bond. VI.* Structure of 5,5-Dimethyl-2-methylseleno-1,3,2-dioxaphosphorinane 2-Selenide

BY TADEUSZ J. BARTCZAK† AND WOJCIECH WOLF

Institute of General Chemistry, Technical University of Łódź, Zwirki 36, 90-924 Łódź, Poland

AND PAUL N. SWEPSTON‡ AND LIN ZERONG

Department of Chemistry, Northwestern University, Evanston, IL 60201, USA

(Received 25 November 1986; accepted 21 April 1987)

Abstract. \(C_2H_{10}O_2PSe_2\), \(M_r=306.06\), monoclinic, \(P2_1/n\), \(a=6.9528\) (5), \(b=12.234\) (1), \(c=12.235\) (2)/\AA, \(\beta=93.77\) (1)°, \(U=1038.4\) (2)/\AA\(^3\), \(Z=4\), \(D_m=1.94\) (by flotation in aqueous KI solution), \(D_x=1.958\) \(\text{Mg} \text{m}^{-3}\), \(\lambda=0.71073\) /\AA, \(\mu=7.16\) \(\text{mm}^{-1}\), \(F(000)=592\), \(T=133\) K, \(R=0.021\) for 1649 observed reflections \(|I|>3\sigma(I)\). The dioxaphosphorinane ring exists in the solid state in a flattened chair conformation with P-Se [2.071 (1)/\AA] positioned equatorially and P-Se [2.227 (1)/\AA] in the axial position. The geometrical features compare well with those of other 1,3,2-dioxaphosphorinane 2-selenides.

Introduction. Reactions of Na derivatives of \(O,O\)-diallylphosphoroanilidates and their thio and seleno analogues with CS\(_2\) give the corresponding phosphoroselenoates and phosphorodiselenoates (Lesiak, Lesnikowski, Stec & Zielinska, 1979). In the case of chiral phosphoroanilidates the PN → PSe conversion proceeds with high stereospecificity and the configuration at the P atom is retained. It seemed desirable to investigate the title compound, synthesized in the course of the above research, by means of X-ray crystallography to reveal the conformation of the 1,3,2-dioxaphosphorinane ring in the presence of two Se atoms bonded to the P atom. Here we report the results of this study, which forms a continuation of investigations of 1,3,2-dioxaphosphorinane 2-selenides performed at the Institute of General Chemistry, Technical University of Łódź, since 1975 (Bartczak, Christensen, Kinas & Stec, 1975a, b, 1976; Bartczak & Wolf, 1983; Bartczak, Galdecki, Trezeżwińska & Wolf, 1983; Bartczak, Galdecki, Wolf, Lesiak & Stec, 1986).

Experimental. Colourless crystal shaped to sphere ca 0.03 mm in diameter, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo Ka radiation; 2θ–ω scan mode; low-temperature system based on a design by Huffman (1974); lattice constants refined by least-squares fit of 25 reflections in the θ range 16.5–24.1°; empirical absorption correction (North, Phillips & Mathews, 1968) based on ω scan, transmission factors 0.999 max. and 0.919 min.; h–8→8,

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