

of an atom from plane *B* is 0.052 (3) Å, compared with 0.005 (5) Å for plane *A*. In ring *C* O(1) lies 0.396 (2) Å above the mean plane of the other four atoms [r.m.s. deviation for plane *C'* 0.027 (3) Å]. This configuration maximizes the O(1)··O(1') distance [4.396 (4) Å] at the expense of reducing C(1)··C(6') to 3.156 (3) Å. Studies of a model show that the molecule is potentially very flexible. There is only a small energy barrier between the observed position and the configuration with O(1) about 0.4 Å below the plane *C'*, for which O(1)··O(1') would be 3.2 Å and C(1)··C(6') 4.6 Å. However, the thermal ellipsoid of O(1) is small and shows no sign that this 'breathing' vibration of the molecule is important in the crystal. It appears that the observed configuration minimizes the effective molecular volume and gives the lowest packing energy, in spite of the short C(1)··C(6') distance.

The phenyl group *F* adopts a position of minimum steric interaction, with the torsion angle C(8)–C(7)–C(13)–C(14) 84.9 (3)°. Examination of the thermal ellipsoids of the ring shows that the main motion is a wagging about C(13) normal to the plane of the ring and not a rotation about C(13)–C(7). Fig. 2 shows the results of packing potential-energy calculations, using *OPEC* (Gavezzotti, 1983) for these two motions. There is very little energy change involved in either motion over the angular range of *ca* 2° which would correspond to thermal motion in the crystal. Over a larger angular range the rotation involves a change of only 8.4 kJ mol<sup>-1</sup> out to 20° whereas the wagging motion involves the loss of almost two thirds of the packing energy. As a scale for these calculations oscillation of the whole molecule about C(14)–C(14') was also considered. The energy profile is very much steeper than for either of the motions possible for the phenyl groups.

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## Structure of a Benzofuranone Oxime

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**Abstract.** (1*R*,2*S*,3*R*,4*S*,3'*R*)-1-(2,3,4,5,6,7-Hexahydro-2-hydroxyimino-4-oxo-3-benzo[*b*]furyl)-1,2,3,4,5-pentanepentayl pentaacetate, C<sub>23</sub>H<sub>29</sub>NO<sub>13</sub>, *M<sub>r</sub>* = 527.5, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>1, *a* = 10.669 (1), *b* = 28.112 (2), *c* = 8.432 (1) Å, *V* = 2529.0 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.37, *D<sub>x</sub>* = 1.38 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 0.107 mm<sup>-1</sup>, *F*(000) = 1112, *T* = 300 K, final *R* =

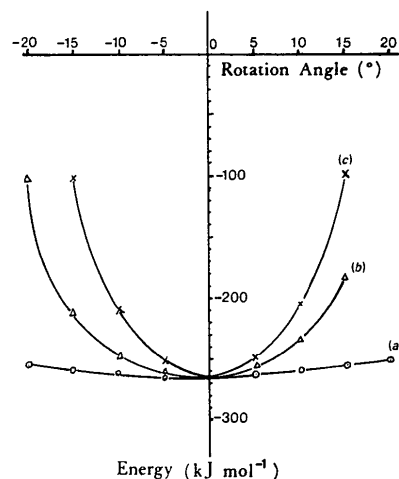


Fig. 2. Packing potential energy as a function of rotation. (a) Rotation of the phenyl group *G* about the C(7)–C(13) bond. The remainder of the molecule and all adjacent molecules at rest. (b) Wagging of the phenyl group *G* about C(13) as pivot and normal to rest position of the ring. The remainder of the molecule and all adjacent molecules at rest. (c) Rotation of the whole molecule about C(14)–C(14'), adjacent molecules at rest.

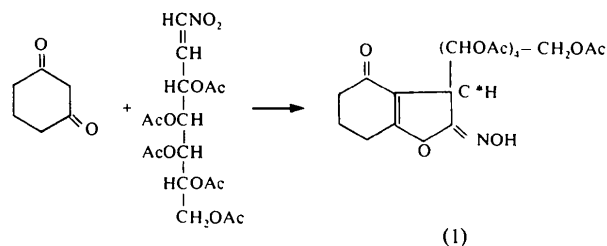
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0.073 for 2525 observed [*I* ≥ 2σ(*I*)] independent reflections. The form of the oxime is *Z*. The cyclohexene ring conformation is intermediate between half-boat and half-chair and the dihedral angle between the planar part of the cyclohexene ring and the furan plane is 5.8 (3)°. There is some electron delocalization along the resonance system O=C–C=C–C of the

cyclohexenone group. The configuration around the chiral centres of the sugar chain is *R,S,R* and *S* respectively, that is *D-galacto*. The new chiral centre C(3') is *R*. Packing is governed by an intermolecular hydrogen bond between the oxime hydrogen and an acetate oxygen, which stabilizes the crystal structure. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

**Introduction.** Crystals were prepared by Gómez-Sánchez & Galán (1985). They reported an easy way of obtaining (3*R*)-3-(*D-galacto*-pentaacetoxypropyl)-6,7-dihydro-2-hydroxyimino-4(5*H*)-benzofuranone by an abnormal Michael reaction of cyclohexane-1,3-dione with pentaacetoxy-1,2-dideoxy-1-nitrohept-1-enitol.



The compound (1) is a substance of considerable interest as a precursor of *C*-glycosyl benzofuranones. A new chiral centre is produced (marked with an asterisk) and two diastereoisomers could result although only one product has been isolated and detected chromatographically. Analytical and spectroscopic data do not give a definite conclusion so an X-ray crystallographic determination was undertaken in order to establish the crystal and molecular structure and the stereochemistry of this compound.

**Experimental.** Crystals are colourless needles with well shaped faces (0.4 × 0.3 × 0.4 mm).  $D_m$  by flotation. Enraf-Nonius CAD-4 diffractometer, Mo  $K\alpha$  radiation, graphite monochromator. Unit-cell parameters from least-squares refinement of 25 reflections in range  $2 < \theta < 10^\circ$ . 4120 independent reflections ( $0 \leq h \leq 15$ ,  $0 \leq k \leq 39$ ,  $0 \leq l \leq 11$ ) measured in  $2\theta < 60^\circ$  range,  $\omega$ - $2\theta$  mode. Two standard reflections (060 and  $0\bar{6}0$ ) monitored every 100 reflections showed only statistical fluctuations. 2525 reflections considered observed [ $I \geq 2\sigma(I_o)$ ] and used for structure determination; corrections for Lorentz and polarization, absorption and extinction ignored. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares on  $F$  with anisotropic thermal parameters for all non-H atoms ( $w = 1/\sigma^2$ ). All H atoms located on difference Fourier map and refined isotropically. Further least squares including positional parameters of H atoms produced convergence with  $R = 0.073$ ,  $wR = 0.070$  and  $S =$

3.36. Final difference Fourier synthesis showed  $\Delta\rho = \pm 0.3 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1962).  $(\Delta/\sigma)_{\text{max}} = 0.10$ . The absolute configuration was assumed on the basis of the compound used in the synthesis. *XRAY* system (Stewart, Kundell & Baldwin, 1970) used.\*

**Discussion.** The positional and isotropic thermal parameters for non-H atoms are given in Table 1. Fig. 1 shows a schematic view of the molecule with the atom numbers, bond distances and angles. C—H bond distances range from 0.96 (9) to 1.07 (11) Å with an average value of 1.01 (11) Å. The O—H bond length is 0.96 (6) Å. The results reveal an oxime structure. The lengths of the C(2)—N(2) and N(2)—O(2) bonds, 1.240 (9) and 1.403 (8) Å, are in agreement with those

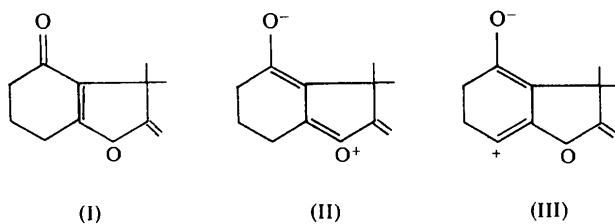
\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42527 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^3$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos(\mathbf{a}_i, \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
O(1)	11055 (5)	8656 (2)	2612 (6)	46 (2)
C(2)	9949 (7)	8524 (2)	3383 (8)	39 (2)
N(2)	9467 (6)	8124 (2)	3268 (8)	47 (2)
O(2)	10180 (6)	7833 (2)	2263 (7)	60 (2)
C(3)	9414 (7)	8957 (2)	4252 (8)	36 (2)
C(4)	10406 (8)	9828 (3)	4178 (9)	45 (2)
O(4)	9669 (6)	10018 (2)	5071 (8)	58 (2)
C(5)	11410 (9)	10101 (3)	3281 (12)	57 (3)
C(6)	12585 (10)	9827 (3)	2911 (13)	70 (4)
C(7)	12308 (8)	9360 (3)	2092 (10)	54 (3)
C(8)	11253 (7)	9133 (2)	2910 (9)	41 (2)
C(9)	10401 (7)	9320 (2)	3834 (8)	36 (2)
C(11)	9150 (6)	8915 (2)	6042 (7)	32 (2)
C(12)	7833 (6)	8747 (2)	6418 (7)	30 (2)
C(13)	7513 (6)	8798 (2)	8185 (7)	33 (2)
C(14)	6220 (6)	8599 (2)	8586 (7)	31 (2)
C(15)	5834 (7)	8706 (3)	10279 (8)	41 (2)
O(111)	10036 (4)	8597 (2)	6786 (5)	36 (1)
O(112)	10862 (7)	9197 (2)	8182 (10)	85 (3)
C(111)	10806 (7)	8779 (3)	7893 (9)	43 (2)
C(112)	11527 (7)	8406 (3)	8721 (10)	51 (2)
O(121)	7691 (4)	8251 (2)	6056 (5)	35 (1)
O(122)	6427 (6)	8430 (2)	4015 (7)	57 (2)
C(121)	6964 (7)	8143 (3)	4781 (9)	42 (2)
C(122)	6904 (9)	7619 (3)	4549 (11)	54 (3)
O(131)	7570 (5)	9310 (2)	8459 (6)	38 (1)
O(132)	8566 (8)	9206 (3)	10764 (8)	90 (3)
C(131)	8215 (8)	9456 (3)	9728 (10)	52 (3)
C(132)	8396 (10)	9983 (4)	9656 (15)	77 (4)
O(141)	5325 (4)	8806 (2)	7488 (6)	36 (1)
O(142)	4453 (5)	8093 (2)	7035 (8)	60 (2)
C(142)	3746 (9)	8764 (3)	5570 (11)	63 (3)
C(141)	4516 (7)	8518 (3)	6770 (9)	41 (2)
O(151)	4698 (5)	8453 (2)	10682 (6)	46 (2)
O(152)	5842 (6)	7787 (2)	10819 (7)	56 (2)
C(151)	4869 (8)	7981 (3)	10985 (9)	47 (2)
C(152)	3660 (10)	7746 (4)	11457 (14)	83 (4)

reported for 6,7-dihydro-6,6-dimethyl-3-phenylbenzofuran-2,4(3*H*,5*H*)-dione 2-oxime (Jones & Chaney, 1972), and also compare well with values ranging from 1.22 (3) to 1.33 (1) Å and 1.357 (18) to 1.439 (39) Å for the same bond in other oximes (Ansell, Moore & Nielsen, 1971). These, together with the value of 0.2 (9)° for the torsion angle O(2)–N(2)–C(2)–O(1), show that the oxime group corresponds to the *Z* conformation. The distribution of bond lengths indicates some electron delocalization in the fragment O(4), C(4), C(9), C(8), C(7) and O(1). The lactone oxime group can, in fact, be considered as a resonance hybrid of (I), (II) and (III).



Bond lengths and angles in other moieties appear to be normal.

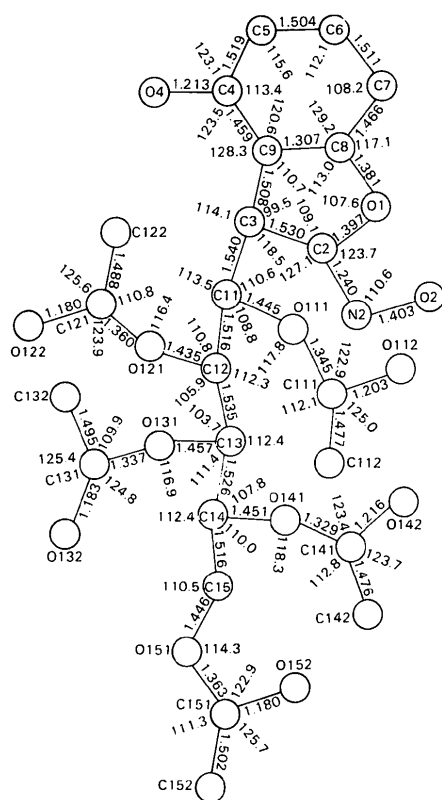


Fig. 1. View of the molecule with atom numbering, bond lengths (Å) and angles (°); e.s.d.'s are 0.009–0.013 Å and 0.5–0.8°.

The five-membered furan ring is nearly planar with each atom deviating < 0.012 (7) Å from the best plane. C(11) is out of the plane by –1.100 (6) Å and N(2) by 0.070 (6) Å. The cyclohexene ring conformation is intermediate between half-boat and half-chair. Cremer & Pople's (1975) puckering parameters for the sequence C(4)–C(5)–C(6)–C(7)–C(8)–C(9) are  $\theta = 52 (1)^\circ$ ,  $\psi = 110 (1)^\circ$ ,  $q_2 = 0.328 (8)$ ,  $q_3 = 0.255 (9)$ ,  $Q = 0.42 (1) \text{ \AA}$  and the asymmetry parameters of Nardelli (1983) are  $\Delta C_3[C(6)] = 0.0416 (49)$  and  $\Delta C_2[C(6)–C(5)] = 0.0622 (38)$ . The C(4), C(9), C(8) and C(7) atoms are in a plane [maximum deviation 0.001 (7) Å] and the angle between this plane and that of the five-membered ring is 5.8 (3)°. The sugar chain C(11)–C(12)–C(13)–C(14)–C(15) is nearly planar [maximum deviation from the mean plane 0.068 (8) Å]. The five acetoxy groups are roughly planar [maximum deviation 0.016 (7) Å]. The torsion angles defining the orientation of the acetoxy groups with respect to the sugar chain are: C(15)–C(14)–O(141)–C(141) = –104.8 (7), C(14)–C(13)–O(131)–C(131) = 106.5 (7), C(13)–C(12)–O(121)–C(121) = 128.8 (6), C(12)–C(11)–O(111)–C(111) = –117.7 (6)°.

The Newman projections corresponding to the C–C bonds of the sugar chain are shown in Fig. 2. According to the Klyne & Prelog (1960) rules the

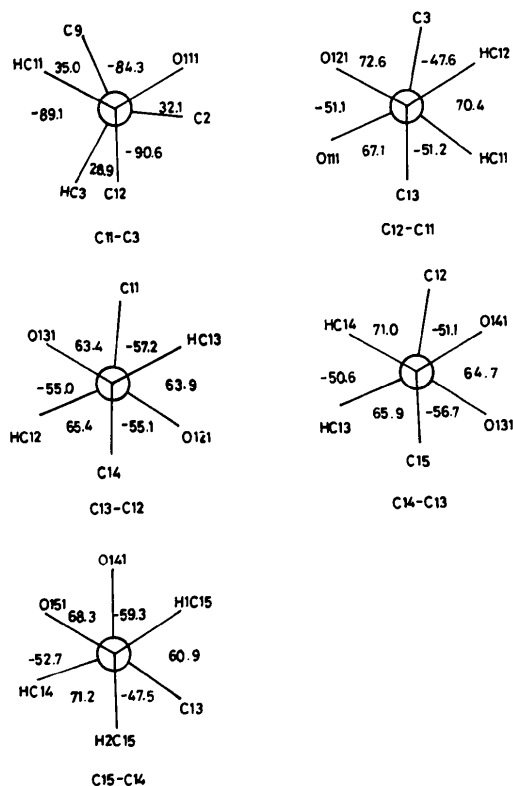


Fig. 2. Some Newman projections. Torsion angles in °; e.s.d.'s are in the range 0.4–1.0° (excluding those involving H atoms).

configurations around the chiral centres C(14), C(13), C(12) and C(11) are *R,S,R* and *S* respectively, in accord with the *D-galacto* constitution. The new chiral centre C(3) is *R*.

The packing is governed by an intermolecular hydrogen bond O(2)—H...O(142) ( $\frac{1}{2}+x$ ,  $\frac{3}{2}-y$ ,  $1-z$ ) = 2.780 (8) Å, O(2)—H = 0.98 (6) Å, H...O(142) = 1.86 (6) Å, O(2)—H...O(142) = 154 (5)°, which stabilizes the crystal structure. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

The authors thank Professor Gómez-Sánchez and Dr Galán for supplying the crystals. The present work is part of a wider research project supported by the Government through the Comisión Asesora de Investigación Científica y Técnica. This paper also forms part of the doctoral thesis of one of us (MJD).

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## Structure of 5,5-Dimethyl-2-ethylamino-1,3,2-dioxaphosphorinane 2-Selenide

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**Abstract.** C<sub>7</sub>H<sub>16</sub>NO<sub>2</sub>PSe, *M<sub>r</sub>* = 256.2, monoclinic, *I*2/*c*, *a* = 19.783 (4), *b* = 7.684 (1), *c* = 15.657 (2) Å, β = 104.41 (7)°, *Z* = 8, *V* = 2305 (1) Å<sup>3</sup>, *D<sub>m</sub>* = 1.46, *D<sub>x</sub>* = 1.48 Mg m<sup>-3</sup>, Cu *Kα*, λ = 1.54178 Å, μ = 5.52 mm<sup>-1</sup>, *F*(000) = 1040, *T* = 293 K, *R* = 0.035 for 1463 observed reflections. The dioxaphosphorinane ring adopts a slightly flattened chair conformation with the P=Se bond lying in the axial and the P—N bond in the equatorial position. The P=Se and P—N bond lengths are 2.081 (1) and 1.599 (3) Å respectively.

**Introduction.** The structure of the title compound has been determined to elucidate the influence of substituents with different electronegativities and steric interactions on the conformation of the dioxaphosphorinane ring and on the P-atom coordination sphere.

In this and in former studies (Bartczak & Wolf, 1983; Bartczak, Gałdecki, Trzeźwińska & Wolf, 1983) we have sought to define for 2-NHR-5,5-dimethyl-

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1,3,2-dioxaphosphorinane 2-selenides the effect of variation in the nature of the substituent *R* on the conformation properties of the dioxaphosphorinane ring system and on the spatial orientation of the substituents attached to the P atom. It has been well demonstrated that in the dioxaphosphorinane ring system 2-arylamino substituents tend to occupy an axial position (Bartczak, Gałdecki, Trzeźwińska & Wolf, 1983, and references cited therein), regardless of *X* in the adjacent P=*X* (*X*=O,S,Se), while dialkylamino groups prefer an equatorial position (Grand & Robert, 1978). However, to the best of our knowledge there is no evidence based on X-ray crystallographic data about the spatial orientation of the 2-monoalkylamino group attached to the P atom incorporated in the 1,3,2-dioxaphosphorinane ring system. For this reason, the title compound (1) was synthesized and its structure determined. Structural features of this compound are discussed in comparison with those recently reported for 2-anilino-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-selenide (2) (Bartczak, Gałdecki, Trzeźwińska & Wolf, 1983).

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