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

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

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

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#### Abstract

C}_{7} \mathrm{H}_{16} \mathrm{NO}_{2} \mathrm{PSe}, M_{r}=256 \cdot 2\), monoclinic, $I 2 / c$, $a=19.783$ (4),$\quad b=7.684$ (1), $\quad c=15.657$ (2) Á, $\beta=104.41$ (7) ${ }^{\circ}, Z=8, V=2305$ (1) $\AA^{3}, D_{m}=1.46$, $D_{x}=1.48 \mathrm{Mg} \mathrm{m}^{-3}, \quad \mathrm{Cu} K \alpha, \quad \lambda=1.54178 \mathrm{~A}, \quad \mu=$ $5.52 \mathrm{~mm}^{-1}, F(000)=1040, T=293 \mathrm{~K}, R=0.035$ for 1463 observed reflections. The dioxaphosphorinane ring adopts a slightly flattened chair conformation with the $\mathrm{P}=\mathrm{Se}$ bond lying in the axial and the $\mathrm{P}-\mathrm{N}$ bond in the equatorial position. The $\mathrm{P}=\mathrm{Se}$ and $\mathrm{P}-\mathrm{N}$ bond lengths are 2.081 (1) and 1.599 (3) $\AA$ 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, Galdecki, 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 $\mathrm{P}=X(X=\mathrm{O}, \mathrm{S}, \mathrm{Se})$, 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 synthetized and is 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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Experimental. Preparation by the reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane with ethylamine and subsequent addition of elemental selenium (Lesiak, Leśnikowski, Stec \& Zielińska, 1979); colourless crystals grown by slow evaporation from 1:1 mixture of chloroform and $n$-hexane; crystal used in analysis cut from a larger prism, dimensions $0.3 \times$ $0.4 \times 0.5 \mathrm{~mm}$; Syntex $P 2_{1}$ four-circle automated diffractometer, graphite-monochromatized Mo Ka radiation; accurate cell dimensions derived by leastsquares calculations from angular settings of 15 reflections measured at $21<\theta<31^{\circ} ; \theta / 2 \theta$ scan mode; 1550 unique reflections collected up to $2 \theta=115^{\circ}$; $h: 0 \rightarrow 32, k: 0 \rightarrow 10, l:-19 \rightarrow 19$ indices given in space group $C 2 / c$; no significant intensity variation of two standard reflections; Lp and empirical absorption corrections applied; secondary-extinction correction, $G=6.04(5) \times 10^{-3} ; 1459$ reflections according to the criterion $F_{o}>3 \sigma\left(F_{o}\right)$ assumed to be observed and applied for further calculations; structure solved by direct methods; structure refined using $F$ 's by standard full-matrix least-squares methods and difference electron density syntheses; last stages of refinement performed in space group $I 2 / c$ to avoid severe correlations which occurred when refining in the space group $C 2 / c$ owing to the large value of $\beta=$ $137.048(8)^{\circ}$; all H atoms located from $\Delta F$ maps, except $H(12), H(22)$ and $H(23)$ whose positions were calculated geometrically; final conventional $R=0.035$, $w R=0.039$ for observed reflections; max. $\Delta / \sigma=$ -0.09 for $z$ of $\mathrm{C}(2)$; largest peak in final $\Delta F$ map 0.50 e $\AA^{-3}$, largest minimum -0.40 e $\AA^{-3}$ (both near $\mathrm{Se}) ; w=1 / \sigma^{2}\left(F_{o}\right)$; scattering factors from International Tables for X-ray Crystallography (1974); all calculations performed using programs written by Sheldrick (1976).*

[^1]Discussion. The atom numbering is shown in Fig. 1. Final positional and equivalent isotropic thermal parameters are given in Table 1. Bond distances and angles are in Table 2. The dioxaphosphorinane ring adopts a slightly flattened chair conformation (Figs. 2 and 3). The $P=S e$ bond points in the axial direction and the $\mathrm{P}-\mathrm{N}$ bond adopts the equatorial position.

Table 1. Fractional atomic parameters $\left(\times 10^{4}\right)$ and $U_{\mathrm{eq}}\left(\AA^{2} \times 10^{3}\right)$ for the nonhydrogen atoms, with e.s.d.'s in parentheses

$$
U_{\mathrm{eq}}=\left(U_{11}+U_{22} \sin ^{2} \beta+U_{33}+2 U_{13} \cos \beta\right) / 3\left(1-\cos ^{2} \beta\right) .
$$

|  | $x$ | $y$ | $z$ | $U_{\text {eq }}$ |
| :---: | :---: | :---: | :---: | :---: |
| Se | 2661.9 (3) | 5531.4 (6) | -1798.3 (3) | 67.6 (4) |
| P | 3265 (1) | 3723 (1) | -949 (1) | 42.0 (5) |
| O(1) | 4040 (1) | 4354 (4) | -527 (2) | 51 (1) |
| O (3) | 2996 (1) | 3274 (3) | -107 (2) | 48 (1) |
| N | 3351 (2) | 1888 (4) | -1392 (2) | 58 (1) |
| $\mathrm{C}(4)$ | 3085 (2) | 4595 (6) | 577 (3) | 53 (2) |
| C(5) | 3842 (2) | 5084 (6) | 923 (3) | 54 (2) |
| C(6) | 4116 (2) | 5696 (6) | 156 (3) | 59 (2) |
| C(7) | 4262 (3) | 3568 (8) | 1390 (3) | 90 (2) |
| C(8) | 3881 (3) | 6612 (7) | 1557 (4) | 84 (2) |
| C(1) | 3736 (3) | 390 (6) | -952 (4) | 69 (2) |
| C(2) | 4350 (3) | -41 (9) | -1313 (5) | 128 (4) |

Table 2. Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$

| $\mathrm{P}-\mathrm{Se}$ | $2.081(1)$ | $\mathrm{O}(1)-\mathrm{P}$ | $1.587(3)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{O}(3)-\mathrm{P}$ | $1.577(3)$ | $\mathrm{N}-\mathrm{P}$ | $1.599(3)$ |
| $\mathrm{C}(6)-\mathrm{O}(1)$ | $1.465(5)$ | $\mathrm{C}(4)-\mathrm{O}(3)$ | $1.454(5)$ |
| $\mathrm{C}(1)-\mathrm{N}$ | $1.456(5)$ | $\mathrm{C}(5)-\mathrm{C}(4)$ | $1.509(6)$ |
| $\mathrm{C}(6)-\mathrm{C}(5)$ | $1.511(6)$ | $\mathrm{C}(7)-\mathrm{C}(5)$ | $1.509(7)$ |
| $\mathrm{C}(8)-\mathrm{C}(5)$ | $1.527(6)$ | $\mathrm{C}(2)-\mathrm{C}(1)$ | $1.500(6)$ |
|  |  |  |  |
| $\mathrm{O}(1)-\mathrm{P}-\mathrm{Se}$ | $113.7(1)$ | $\mathrm{O}(3)-\mathrm{P}-\mathrm{Se}$ | $114.9(1)$ |
| $\mathrm{O}(3)-\mathrm{P}-\mathrm{O}(1)$ | $102.2(1)$ | $\mathrm{N}-\mathrm{P}-\mathrm{Se}$ | $114.7(1)$ |
| $\mathrm{N}-\mathrm{P}-\mathrm{O}(1)$ | $104.7(2)$ | $\mathrm{N}-\mathrm{P}-\mathrm{O}(3)$ | $105.3(2)$ |
| $\mathrm{C}(6)-\mathrm{O}(1)-\mathrm{P}$ | $115.6(2)$ | $\mathrm{C}(4)-\mathrm{O}(3)-\mathrm{P}$ | $117.3(2)$ |
| $\mathrm{C}(1)-\mathrm{N}-\mathrm{P}$ | $126.3(3)$ | $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{O}(3)$ | $111.5(3)$ |
| $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(4)$ | $108.2(3)$ | $\mathrm{C}(7)-\mathrm{C}(5)-\mathrm{C}(4)$ | $111.0(4)$ |
| $\mathrm{C}(7)-\mathrm{C}(5)-\mathrm{C}(6)$ | $111.2(4)$ | $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(4)$ | $108.1(4)$ |
| $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(6)$ | $107.9(4)$ | $\mathrm{C}(8)-\mathrm{C}(5)-\mathrm{C}(7)$ | $110.3(4)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{O}(1)$ | $111.7(3)$ | $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{N}$ | $111.9(4)$ |



Fig. 2. Flattening of the 1,3,2-dioxaphosphorinane ring illustrated by the dihedral angles $\left({ }^{\circ}\right)$.


Fig. 3. The torsion angles $\left(^{\circ}\right.$ ). Asymmetry parameters (Duax \& Norton, 1975) are: $\Delta C_{s}^{\mathrm{p}}=0.9(2), \Delta C_{s}^{\mathrm{C}(6)}=5.3(2), \Delta C_{s}^{\mathrm{o}(1)}$ $=6 \cdot 3(3), \Delta C_{2}^{\mathrm{C}(5), \mathrm{C}(6)}=5.4(4), \Delta C_{2}^{\mathrm{P} .0(1)}=5.8(4), \quad C_{2}^{\mathrm{O}(1) . \mathrm{C}(6)}=$ $6.3(4)^{\circ}$.

In terms of stereoelectronic and steric effects being considered as the major factors which govern the spatial orientation in these and related cyclic systems (Kirby, 1983) it is most interesting to compare the structural features of the title compound (1) with those obtained for compound (2), where the anilino group occupies an axial position.

The axial $\mathrm{P}-\mathrm{N}$ bond $\mid 1.599$ (3) $\AA \mid$ in compound (2) is longer than the equatorial one in (1), and the length of the $\mathrm{P}=\mathrm{Se}$ bond shows the same tendency: the axial $\mathrm{P}=\mathrm{Se}$ bond in compound (1) $\mid 2.081$ (1) $\AA \mid$ is slightly longer than the equatorial one in (2) $\mid 2.068$ (1) $\AA \mid$. However, it is also worth pointing out that the $\mathrm{N}-\mathrm{C}$ bond in (1) is longer $\mid 1.456$ (5) $\AA \mid$ than the $\mathrm{N}-\mathrm{C}$ bond in (2) $\mid 1-422$ (6) $\AA \mid$. This comparison may indicate a substantial $p_{\pi}-p_{\pi}$ interaction between the $s p^{2}$-hybridized N lone pair and the phenyl-ring $\pi$ system in compound (2). Thus repulsive interactions of the filled $p$ orbital on an axial N atom bearing a phenyl substituent, as in (2),
with the endocyclic $\mathrm{P}-\mathrm{O}$ bonding orbitals are weaker than the corresponding interaction of the axially oriented $\mathrm{P}=\mathrm{Se}$ bond orbitals, and this accounts for the axial orientation of the anilino group in (2). However, if the exocyclic N atom bearing the ethyl group were to occupy an axial position, the repulsive interactions of its $p$ orbital with the endocyclic $\mathrm{P}-\mathrm{O}$ bonding orbital could be stronger than those between the endocyclic $\mathrm{P}-\mathrm{O}$ bonding orbitals and the $\mathrm{P}=\mathrm{Se}$ bond orbital and for this reason the ethylamino group prefers to occupy the equatorial position as found in (1).

All other bonds and angles have typical values for this class of compounds and will not be discussed in detail.

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# Dimethylammonium Picrate: Geometry and Interactions of the Picrate Ion 

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#### Abstract

C}_{2} \mathrm{H}_{8} \mathrm{~N}^{+} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N}_{3} \mathrm{O}_{7}^{-}, \quad M_{r}=274 \cdot 2\), orthorhombic, $P b 2_{1} a$ (non-standard setting of $P c a 2_{1}$ ), $a$ $=10.001$ (1), $b=11.087$ (4), $c=21.332$ (2) $\AA, \quad V=$ $2365.3 \AA^{3}, \quad Z=8, \quad D_{x}=1.54 \mathrm{~g} \mathrm{~cm}^{-3}, \quad \lambda($ Mo $K \alpha)=$ $0.71069 \AA, \mu=1.28 \mathrm{~cm}^{-1}, F(000)=1136, T=293 \mathrm{~K}$. Final $R=0.049$ from 1494 observed reflections. The


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structure is composed of alternating sheets of cations and anions. There are two picrate ions in the asymmetric unit and adjacent anion sheets are related by a pseudo crystallographic twofold axis. Aromatic bond lengths in the picrate ring range between 1.45 and $1.36 \AA$ and can be explained by a resonance description of the picrate ion.
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[^1]:    * Lists of structure factors, anisotropic thermal parameters, H -atom parameters and bond distances involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42549 ( 13 pp .). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

