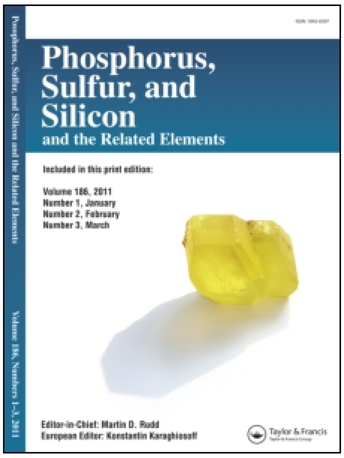

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND X-RAY STRUCTURE OF 6-CYANO-2,10-DIOXA-1-PHOSPHABICYCLO [4.4.0]DECANE-1-OXIDE

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To cite this Article Vinogradova, Natalya M. , Lyssenko, Konstantin A. , Odinets, Irene L. , Petrovskii, Pavel V. , Mastryukova, Tatyana A. and Kabachnik, Martin I.(1998) 'SYNTHESIS AND X-RAY STRUCTURE OF 6-CYANO-2,10-DIOXA-1-PHOSPHABICYCLO [4.4.0]DECANE-1-OXIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 132: 1, 265 — 269

To link to this Article: DOI: 10.1080/10426509808036992

URL: http://dx.doi.org/10.1080/10426509808036992

Phosphorus, Sulfur and Silicon, Vol. 132, pp. 265-269
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SYNTHESIS AND X-RAY STRUCTURE OF 6-CYANO-2,10-DIOXA-1–PHOSPHABICYCLO [4.4.0]DECANE-1-OXIDE

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(Received 18 September, 1997)

Bis(ω-chloropropyl)dialkoxyphosphonylacetonitriles **4** were established to undergo intramolecular bisdealkylation during distillation affording 6-cyano-2,10-dioxa-1-phosphabicyclo[4.4.0]decane-1-oxide **5** in high yield. The molecular structure of **5** was determined by the single crystal X-ray diffraction method. The molecule consists of cis-fused six-membered rings both in chair conformation.

Keywords: phosphabicyclo[4.4.0]decane-1-oxide; dealkylation; X-ray diffraction method

INTRODUCTION

Earlier two representatives of bicyclic 2,10-dioxa-1-phosphabicyclo[4.4.0]decane-1-oxides having a hydrogen atom **1**[1,2] or a metoxycarbonyl group **2**[3] in 6-position obtained by multistage process were described. Unlike their organic analogues-decaline and 2,10-dioxabicyclo[4.4.0]decane existing both in cis and in trans-isomer forms[4,5], bicyclic 1,2-oxaphosphorinanes represent cis-isomers* solely, the molecular structure being confirmed by X-ray data[1,3].

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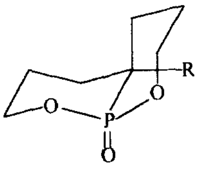
* Corresponding Author.

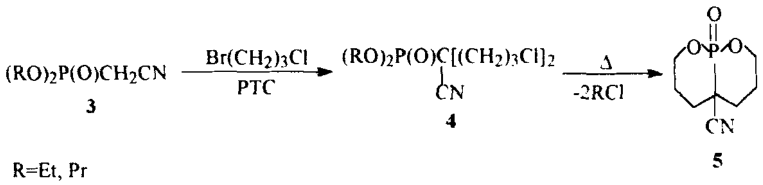
† According to the unpublished data of T.M.Lane et al., they recently succeded in the synthesis of the trans-isomer of 1[6].



1: R=H
2: R=COOMe

RESULTS AND DISCUSSION

We established that the 6-cyanosubstituted analogue **5** of these compounds formed in high yield from **4** during distillation as a result of intramolecular bisdealkylation. The phosphonate precursor **4** was obtained by alkylation of **3** by 1,3-chlorobromopropane under phase transfer catalysis (PTC) conditions.



According to X-ray data the molecule **5** as well as the molecules of above mentioned **1** and **2** consist of cis-fused six-membered rings both in chair conformation. The structure **5** with the atomic numbering scheme, the main bond lengths and angles are presented in Figure 1. Bond lengths and angles in **5** are similar to the corresponding values in **1** and **2**. In this series **(1, 2, 5)** the P-C bond length increases from 1.793(4) Å in **1** to 1.814(3) Å in **2** and to 1.836(4) Å in **5** (bond lengths in **1** and **5** were used with the account of libration correction). Such elongation is probably connected not only with the steric repulsion between P=O and the group in 6-position but also with the increasing of the electronwithdrawing character of these groups. The difference between the bond lengths ($\Delta_{5,1}$ = 0.04 Å and $\Delta_{2,1}$=0.02 Å) in these compounds is in good correspondence with σ values for CN and CO_2Me (0.58 and 0.20)[7]. The torsion angle 0(3)P(1)C(4)C(8) in **5** is equal to –42.96° (the similar torsion angle in **2** is equal to 46.4°). In the structure **5** as well as in **2** and **1** the cyclic oxygen atoms O(1) and O(2) are non-equivalent (C(1)O(1)P(1) 120.3(1)°, C(5)O(2)P(1) 116.7(1)°). May be one of the reasons of this non-equivalence of O(1) and O(2) atoms can be connected with the difference of the oxygens lone electron pairs orientation with respect to the P=O group (torsion angles O(3)P(1)O(1)C(1) 169.0° O(3)P(1)O(2)C(5) –65.8°). In the case of the O(2) atom one of the lone electron pairs have antiperiplanar orientation. The pseudotorsion angle of the other lone electron pairs of the O(1) and O(2) atoms with the P(1)=O(3) group fall in the range ±60±10°.

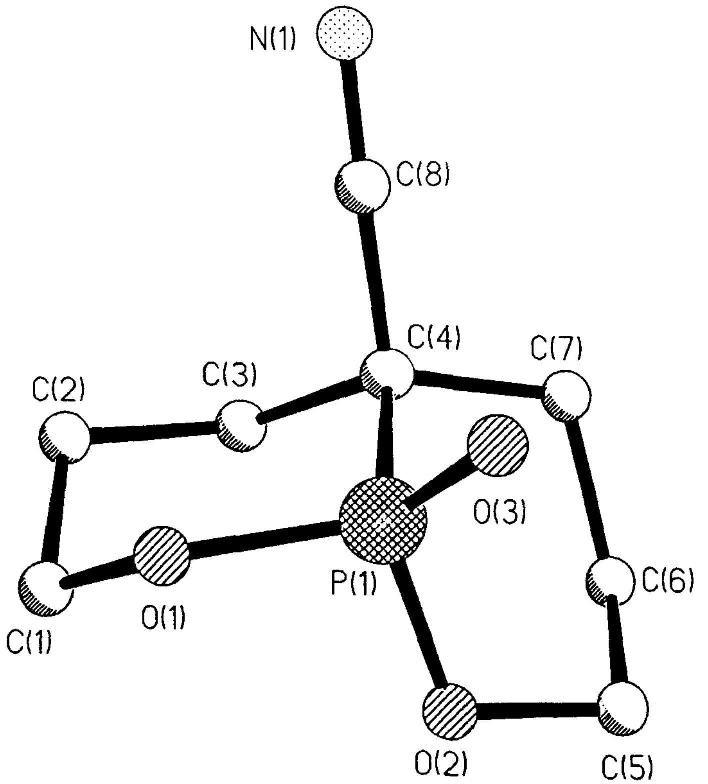


FIGURE 1 Molecular structure of 6-cyano-2,10-dioxa-1-phosphabicyclo[4.4.0]decane-1-oxide **5**. The main bond lengths (Å) and angles (deg): P(1)-O(3) 1.459(2), P(1)-O(1) 1.563(1), P(1)-O(2) 1.576(1), P(1)-C(4) 1.826(2), O(1)-C(1) 1.467(3), O(2)-C(5) 1.470(2); O(3)-P(1)-O(1) 112.55(9), O(3)-P(1)-O(2) 116.39(8), O(1)-P(1)-O(2) 103.79(7), O(1)-P(1)-C(4) 106.59(7), O(2)-P(1)-C(4) 101.58 (7), C(1)-O(1)-P(1) 120.3(1), C(5)-O(2)-P(1) 116.7(1), O(3)P(1)C(4)C(8)-42.96

To establish the reasons of the cis-conformation preferences we carried out the calculations by molecular mechanics method using force field MMX both for the cis and trans isomers. According to these calculations, in the case of the structure **1** the cis-isomer is more stable (ΔE=7.84 kca/mol). The instability of the trans-isomer is mainly connected with the steric repulsion of the CN group with the hydrogen atoms of the rings, the shortest C···H distance is similar to 2.45 Å (the sum of van der waals radii of C and H is equal to 2.82 Å)[8].

EXPERIMENTAL

Synthesis

General

The NMR spectra were recordered on a Bruker WP-200SY and AMX-400 in C_6D_6, $CDCl_3$ solutions using TMS (^1H,^{13}C) and 85% H_3PO_4 (^{31}P) as external standart. The initial compounds were prepared by the literature method[9].

Bis(3-chloropropyl)dialkoxyacetonitriles (4)

To a stirred solution of 7.5 mL 50% aq. NaOH and 0.83 g (3 mmol) TEBA a mixture of 6 g (30 mmol) of **3** and 5.67 g (36 mmol) of 1,3-chlorobromopropane was added. The resulting mixture was stirred for 3 h at rt. After dilution by 15 mL of water it was extracted by ether (4 × 10 mL). The extract was dried over sodium sulfate, concentrated and passed through a silica gel layer (40–100, eluent-petrol ether), affording 2.5 g (23%) of crude **4**, containing 5–7% chlorobromopropane. NMR ^1H (C_6D_6) δ 0.83 (t, 6 H), 1.48–1.56 (m, 12 H), 3.19 (t, 4 H), 4.02 (dt, 4 H), $^3J_{HH}$=6.67 Hz, $^3J_{PH}$=8.15 Hz. NMR ^{31}P (C_6D_6) δ 20.5.

6-Cyano-2,10-dioxa-1-phosphabicyclo[4.4.0]decane-1-oxide (5)

Crude **4** was distilled in vacuo affording 1.0 g (71%) **5**. Bp 215–220/1 mm Hg, mp 109–110°C (CH_2Cl_2-ether, 4:1). NMR ^1H ($CDCl_3$) δ 4.18–4.54 (m, 4H), 2.11–2.45 (m, 4H), 1.88–1.95 (m, 4 H). NMR ^{13}C (C_6D_6) δ 119.63, $^2J_{PC}$= 7.96 Hz, 70.45 , $^2J_{PC}$=6.57 Hz, 35.20, $^2J_{PC}$=114.8 Hz, 30.05, $^2J_{PC}$=5.7 Hz, 22.44, $^3J_{PC}$ = 5.5 Hz. ^{31}P ($CDCl_3$) δ 8.5. Anal. calcd.

for $C_8H_{12}NO_3P$. C, 47.76; H, 5.97; N, 6.97; P, 15.42. Found: C, 47.97; H, 5.77; N, 6.85; P, 15.33.

X-ray Crystal Structure Determination

Single crystals of (**5**) $C_8H_{12}N_1O_3P$ were grown from CH_2Cl_2-ether (4:1). Experimental data was obtained at 293K using a four-circle "Cad4 Enraf-Nonius" diffractometer (monochromatized MoKa radiation, $(\theta/5/3)\theta$ -scan, $2\theta<50°$). Crystals of **5** are monoclinic at 293K: a=9.213(2) Å, b=10.625(2) Å c=9.732(1) Å, β=93.64(1)°, V=950.7(3) $Å^3$, Z=4, space group C2/c, μ = 0.264 mm^{-1}, F(000)=424, d_{calc}=1.405 gcm^{-3}. The total number of measured reflections was 2849. The structure of **5** was solved by direct methods and refined by a full-matrix least squares in the anisotropic-isotropic (H-atoms) approximation. All hydrogen atoms were located by the electron difference electron density synthesis. The results of the refinement for **5** using 1281 independent reflections with $I>2\sigma(I)$ were: R1=0.0302; wR2=0.0695 and GOF=1.033 for all 1387 measured independent reflections. All calculations were performed with an PC/AT computer using SHELXTL programs package (version 3).

Acknowledgements

This work was supported by Russian Fundamental Research Foundation (grants Nos. 96–03–32992, 96–15–97298).

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