

Solid-State Conformations of Medium-Sized-Ring Phosphorus Heterocycles: Preparation and X-ray Crystal Structure of a Benzo-Fused 1,3,2-Dioxaphosphepane in a Twist Conformation

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ABSTRACT

The crystal and molecular structure of the benzo-fused seven-membered-ring phosphorus heterocycle, 2-phenyl-2-oxo-5,6-benzo-1,3,2-dioxaphosphepane, has been determined by single-crystal X-ray techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions $a = 13.312(1)$ Å, $b = 7.6132(8)$ Å, $c = 12.119(2)$ Å, and $\beta = 95.990(9)^\circ$. Full-matrix least-squares refinement led to $R = 4.4\%$ and $R_w = 5.9\%$. The conformation adopted by the 1,3,2-dioxaphosphepane ring is a twist with approximate C_2 symmetry.

INTRODUCTION

We have been interested in the conformational consequences of heteroatom substitution for carbon atoms in cycloalkanes, especially the conformational

properties of phosphorus heterocycles, using NMR and X-ray techniques. A great deal of conformational analyses have been carried out on six-membered-ring phosphorus heterocycles (phosphorinanes) [1]. Recently we have expanded our conformational studies to include five-membered-ring phosphorus heterocycles (phospholanes) [2] and seven-membered-ring phosphorus heterocycles (phosphepanes) [3].

Conformational and stereochemical analysis of seven-membered-ring phosphorus heterocycles is still relatively unexplored. The 1,3,2-dioxaphosphepane ring system, **1**, has, however, received some attention in terms of its conformational properties [4]. Unsaturation, benzo ring fusion, or cis ring fusion at C(5)–C(6) would serve to impart planarity in that part of the ring, favoring the chair conformation over the twist-chair [4]. In addition to the chair, two other conformations, the twist and twist-boat, have been suggested to be energetically feasible [4a]. Arbuzov and co-workers have concluded, based upon ^1H NMR, dipole moment, and Kerr effect data, that flexible twist forms are important if not predominant conformations in the equilibria of these compounds [5].

Sato and Goto [6], based upon proton NMR analysis, have concluded that a chair-chair equilibrium exists for **2**, **3**, and **4**. In a more recent analysis using ^1H NMR, dipole moment, and Kerr effect data, Arbuzov and co-workers [7] have concluded that **2** exists in a three-component equilibrium that in-

Dedicated to Professor Dr. Leopold Horner on the occasion of his eightieth birthday.

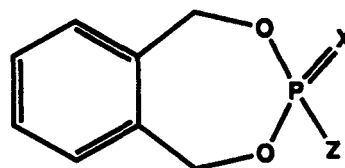
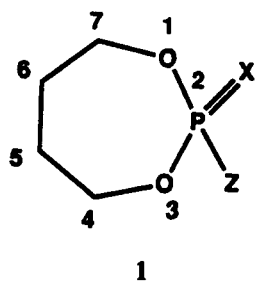
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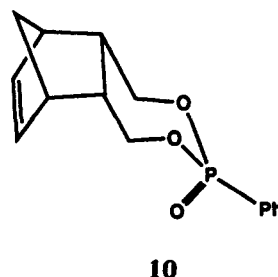
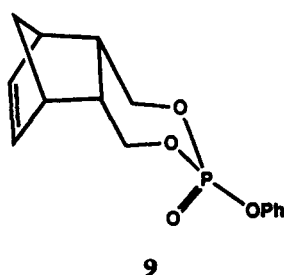
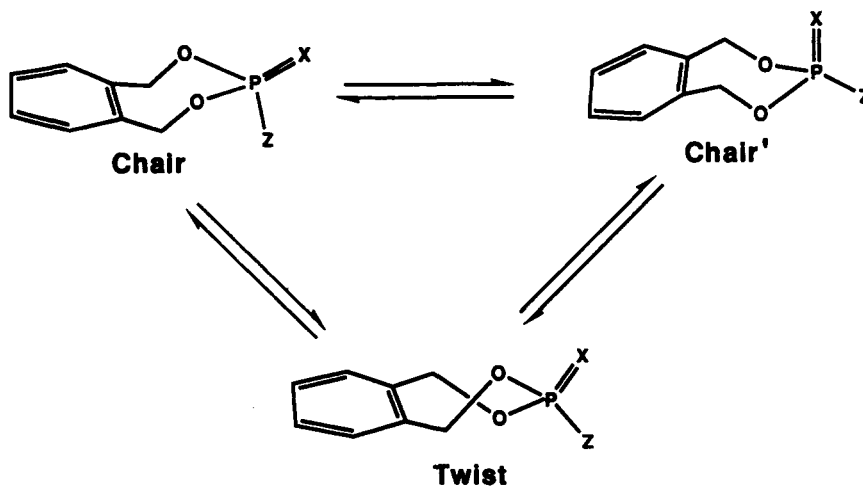
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cludes a flexible twist conformation as well as the two chair forms. It has been concluded that the methoxy analog, **3**, may also involve a twist conformation in equilibrium with the two chair forms [8]. In **5** and **6**, X-ray crystallographic analysis indicates a chair conformation with axial P=S [9], and ¹H NMR analysis is consistent with this conformation in solution [10]. It has been concluded, however, that for **6** and **7**, dipole moment and Kerr effect data indicate some (20–30%) population of twist form [11].

In this paper we report the synthesis and the crystal and molecular structure of 2-phenyl-2-oxo-5,6-benzo-1,3,2-dioxaphosphepane, **8**, a benzo-fused 1,3,2-dioxaphosphepane that adopts a twist conformation in the solid state. This represents, to our knowledge, the first example of a torsionally constrained dioxaphosphepane ring adopting a twist conformation in the solid state. All other crystal structures of analogous compounds show chair conformations, including the benzo-fused compounds **5** and **6** [9], as well as the norbornene-fused compounds **9** and **10** [3].

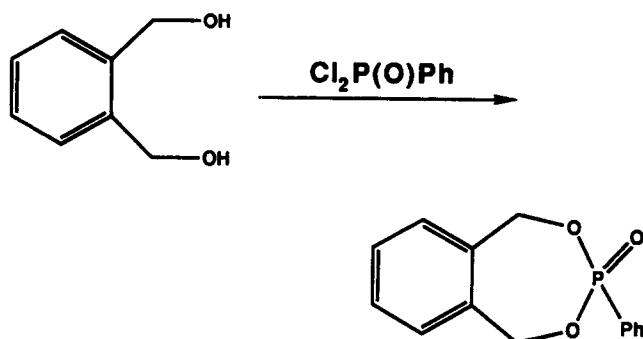


- 2, X = O, Z = Cl
- 3, X = O, Z = OMe
- 4, X = O, Z = OPh
- 5, X = S, Z = Me
- 6, X = S, Z = NMe₂
- 7, X = O, Z = NMe₂
- 8, X = O, Z = Ph



RESULTS AND DISCUSSION

The 1,3,2-dioxaphosphepane **8** is conveniently prepared by reaction of 1,2-benzenedimethanol with phenylphosphonic dichloride:

TABLE 1 Crystal Data for Dioxaphosphepane **8**

Molecular formula	C ₁₄ H ₁₃ PO ₃
Molecular weight	260.23
Space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i> (No. 14)
Cell dimensions	
<i>a</i> , Å	13.312(1)
<i>b</i> , Å	7.6132(8)
<i>c</i> , Å	12.119(2)
β , deg	95.990(9)
<i>V</i> , Å ³	1221.6(4)
<i>Z</i>	4
<i>d</i> _{calcd.} , g cm ⁻³	1.415
No. of unique data	1979
No. of obsd. data	1489
Absorption coeff., cm ⁻¹	19.78
<i>R</i>	4.4%
<i>R</i> _w	5.9%

The crystal data for **8** are listed in Table 1. The final atomic parameters for the compound are compiled in Table 2. A perspective view of the molecule, along with the labeling scheme, is given in Figure 1. Selected bond lengths, bond angles, and torsion angles for the compound are listed in Table 3 [12].

The conformation adopted by the dioxaphosphepane ring in compound **8** is a twist with approximate C₂ symmetry. The C(4)–O(3)–P(2)–C(12) and C(7)–O(1)–P(2)–O(2) dihedral angles are similar (69.7(2)° and 65.3(2)°, respectively) as are the C(4)–O(3)–P(2)–O(2) and C(7)–O(1)–P(2)–C(12) torsion angles (–164.5(2)° and –170.0(2)°, respectively). Neither the phenyl substituent nor the phosphoryl (P=O) group appear to be axial seeking in this structure. A twist conformation in **8** is in complete agreement with ¹H NMR analysis of the compound [13] and supports the general predictions and assessments of Arbuzov and Arshinova and their

co-workers for benzo-fused 1,3,2-dioxaphosphepanes [5].

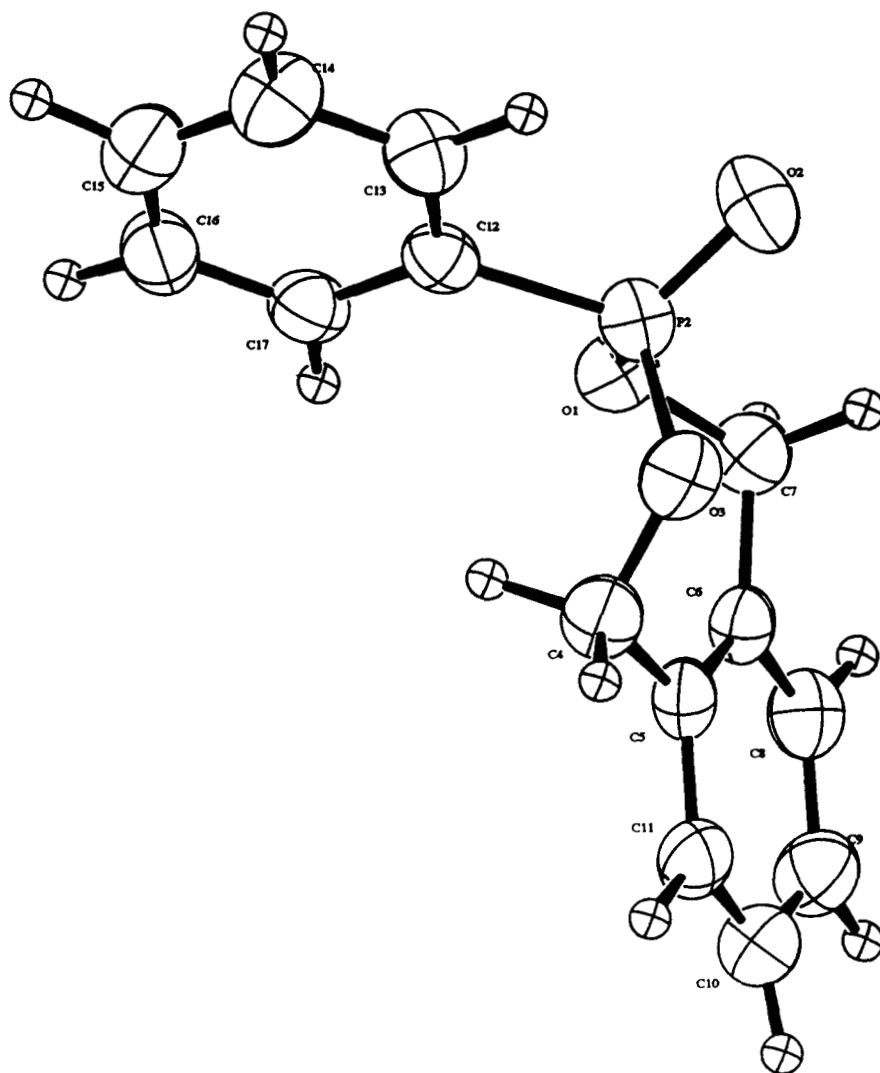
The analogous norbornene-fused 1,3,2-dioxaphosphepane, **10**, has been found to adopt a chair conformation in the solid state. The differences in conformation between **8** and **10** are likely the result of steric effects in **10** that are not possible in **8**. Note that a twist conformation in **10**, according to molecular models, may suffer from repulsive steric interactions between an axial proton on one of the methylene carbons of the phosphonate ring and the norbornene ring as well as steric interactions between ring oxygen and the norbornene ring. Thus, a twist conformation for the norbornene-fused 1,3,2-dioxaphosphepane ring may be less accessible, because of steric interactions, than in the benzo-fused system.

The phenyl moiety on phosphorus in **8** is neither coplanar nor perpendicular to the phosphoryl (P=O)

TABLE 2 Final Atomic Parameters for Dioxaphosphepane **8**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
P(2)	0.21992(6)	0.1923(1)	0.35115(6)	3.46(4)
O(1)	0.2197(2)	0.1645(3)	0.2219(2)	3.5(1)
O(2)	0.2671(2)	0.3529(3)	0.3987(2)	4.8(1)
O(3)	0.2800(2)	0.0268(3)	0.4028(2)	3.9(1)
C(4)	0.2641(2)	–0.1428(4)	0.3492(3)	4.0(2)
C(5)	0.3314(2)	–0.1734(4)	0.2584(2)	3.3(1)
C(6)	0.3497(2)	–0.0474(4)	0.1784(2)	3.2(1)
C(7)	0.3170(2)	0.1412(4)	0.1795(3)	3.7(1)
C(8)	0.4073(3)	–0.0955(5)	0.0936(3)	4.1(1)
C(9)	0.4484(3)	–0.2620(5)	0.0880(3)	4.8(2)
C(10)	0.4299(3)	–0.3847(5)	0.1674(3)	4.7(2)
C(11)	0.3725(2)	–0.3404(4)	0.2518(3)	4.1(2)
C(12)	0.0885(2)	0.1750(4)	0.3686(2)	3.2(1)
C(13)	0.0557(3)	0.2564(5)	0.4611(3)	4.1(2)
C(14)	–0.0452(3)	0.2489(3)	0.4781(3)	4.8(2)
C(15)	–0.1145(3)	0.1622(5)	0.4035(3)	4.5(2)
C(16)	–0.0817(3)	0.0833(5)	0.3112(3)	4.3(2)
C(17)	0.0195(2)	0.0897(4)	0.2936(3)	3.8(1)

FIGURE 1 ORTEP perspective drawing of dioxaphosphepane **8**.



group but rather bisects the P–O bonds (Figure 2). In 2-aryl-2-oxo-1,3,2-oxazaphosphorinanes, when the aryl group is equatorial it tends to be coplanar with the phosphoryl (presumably the result of conjugation) [14], but an axially disposed aryl group in this six-membered ring system, in order to avoid transannular 1,3-diaxial steric interactions, tends to be perpendicular [14]. In **10**, a seven-membered ring with an equatorial phenyl substituent, the phenyl group is seen to be coplanar with the phosphoryl group [3].

In compound **8**, the phenyl group may best be described as adopting an isoclinal disposition [15]; it is neither axial nor equatorial. A perpendicular arrangement of the phenyl moiety with the phosphoryl precludes conjugation, whereas a completely coplanar arrangement would suffer from steric interactions between the axial hydrogen on C(4) and the hydrogen on C(17). This geometrical arrangement also allows interaction of the aryl π -

system with the P(2)–O(3) antibonding orbital; and *exo-anomeric* interaction [16]. Note that there is also an *endo-anomeric* interaction between a *p*-orbital on O(3) and the P(2)–C(12) antibonding orbital.

Apart from the conformation of the phosphonate ring and the phenyl substituent on phosphorus, the geometrical features of compound **8** are very similar to those in the norbornene-fused analog **10**. The geometry at the phosphorus atom in **8** is, as expected, a distorted tetrahedron. The two aromatic rings appear to be completely regular.

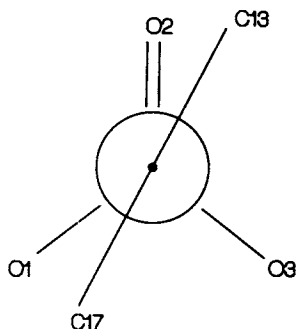
EXPERIMENTAL

Methods and Materials

All reagents were obtained from Aldrich Chemical Company, Milwaukee, WI. Solvents were dried using standard techniques. Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

TABLE 3 Selected Geometrical Parameters in Dioxaphosphepane **8**

<i>Bond Lengths (Å)</i>			
P(2)–O(1)	1.580(2)	C(8)–C(9)	1.385(5)
P(2)–O(2)	1.465(2)	C(9)–C(10)	1.382(5)
P(2)–O(3)	1.586(2)	C(10)–C(11)	1.381(5)
P(2)–C(12)	1.789(3)	C(5)–C(11)	1.390(4)
O(1)–C(7)	1.455(4)	C(12)–C(13)	1.391(4)
O(3)–C(4)	1.451(4)	C(13)–C(14)	1.382(5)
C(4)–C(5)	1.507(4)	C(14)–C(15)	1.388(5)
C(5)–C(6)	1.403(4)	C(15)–C(16)	1.380(5)
C(6)–C(7)	1.501(4)	C(16)–C(17)	1.387(5)
C(6)–C(8)	1.394(4)	C(12)–C(17)	1.384(4)
<i>Bond Angles (deg)</i>			
O(1)–P(2)–O(3)	103.5(1)	P(2)–O(3)–C(4)	119.1(2)
O(1)–P(2)–O(2)	117.3(1)	P(2)–O(1)–C(7)	117.2(2)
O(1)–P(2)–C(12)	101.9(1)	O(3)–C(4)–C(5)	113.3(3)
O(2)–P(2)–O(3)	109.3(1)	C(4)–C(5)–C(6)	123.9(3)
O(2)–P(2)–C(12)	113.5(1)	C(5)–C(6)–C(7)	125.2(3)
O(3)–P(2)–C(12)	110.7(1)	C(6)–C(7)–O(1)	112.9(2)
<i>Torsion Angles (deg)</i>			
O(1)–P(2)–O(3)–C(4)	–38.8(2)	O(1)–P(2)–C(12)–C(17)	22.1(3)
P(2)–O(3)–C(4)–C(5)	86.9(3)	O(2)–P(2)–C(12)–C(17)	149.2(3)
O(3)–C(4)–C(5)–C(6)	–44.2(4)	O(3)–P(2)–C(12)–C(17)	–87.4(3)
C(4)–C(5)–C(6)–C(7)	8.4(5)	C(4)–O(3)–P(2)–C(12)	69.7(2)
C(5)–C(6)–C(7)–O(1)	–35.7(4)	C(4)–O(3)–P(2)–O(2)	–164.5(2)
C(6)–C(7)–O(1)–P(2)	89.2(3)	C(7)–O(1)–P(2)–O(2)	65.3(2)
C(7)–O(1)–P(2)–O(3)	–55.0(2)	C(7)–O(1)–P(2)–C(12)	–170.0(2)

**FIGURE 2** Newman projection down the C(12)–P(2) bond.

Melting points are uncorrected. NMR coupling constants were measured at 200 MHz on 100 Hz SW expansions, 32K data base, 9.044-s acquisition times, and are probably accurate to ± 0.2 Hz. Phosphorus-31 NMR spectra were made at 81.015 MHz under proton noise decoupling conditions.

Preparation of 2-Phenyl-2-oxo-5,6-benzo-1,3,2-dioxaphosphepane, **8**

A solution of 1,2-benzenedimethanol (2.04 g, 14.78 mmol), anhydrous triethylamine (4.0 mL, 29 mmol), and sufficient anhydrous ethyl acetate to dilute to 80 mL, and a solution of phenylphosphonic di-

chloride (1.85 mL, 14.78 mmol) and sufficient anhydrous ethyl acetate to dilute to 80 mL, were added simultaneously by dropwise addition to a three-necked flask containing 150 mL anhydrous ethyl acetate. The reaction mixture was allowed to stir for 48 h, the triethylamine hydrochloride filtered off, the solid washed with ethyl acetate, and the solvent removed from the filtrate under reduced pressure to give a yellow oil that crystallized overnight. The solid residue was recrystallized from toluene to give 1.96 g (50.7% yield) of pure **8** as a colorless crystalline solid: mp 128.5°C; ^1H NMR (acetone- d_6) δ 5.09 (dd, 2H, $-\text{CH}_2\text{O}-$, $J_{\text{HH}} = 13.7$ Hz, $J_{\text{PH}} = 17.5$ Hz), 5.68 (dd, 2H, $-\text{CH}_2\text{O}-$, $J_{\text{HH}} = 13.7$ Hz, $J_{\text{PH}} = 12.7$ Hz), 7.22–7.88 (m, 9H, aromatic); ^{31}P NMR (acetone- d_6) δ 23.38; IR (KBr) 3060, 3030, 2880, 1500, 1448, 1439, 1380, 1292, 1275, 1250 (s, P=O), 1206, 1129 (s), 1062 (s), 1024 (s), 1014 (s), 1004 (s), 986 (s), 946, 867, 842 (s), 809 (s), 754 (s), 693 (s), 626, 615, 560, 530, 500, 479, 429, 394, 313. Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{PO}_3$: C, 64.62; H, 5.03; P, 11.90. Found: C, 64.23; H, 5.17; P, 11.66

X-ray Crystal Structure of **8**

X-ray quality crystals of **8** were grown by solvent diffusion of hexane into a saturated solution of the compound in ethyl acetate. A clear colorless plate (cut to cube) having approximate dimensions of

0.2 × 0.2 × 0.2 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $75.23 < 2\theta < 79.22^\circ$, corresponded to a monoclinic cell with the dimensions given in Table 1.

The data were collected at a temperature of $21 \pm 1^\circ\text{C}$ using the ω - 2θ scan technique. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.27° . The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 600.0 mm.

The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.95 to 1.00. The data were corrected for Lorentz and polarization effects. Data with $I > 3.00\sigma(I)$ were considered observed and were used in the solution and refinement of the structure.

The structure was solved by direct methods [17]. The nonhydrogen atoms were refined anisotropically. All hydrogen atoms were located in a difference Fourier but their coordinates and isotropic temperature factors were not refined. The final cycle of full-matrix least-squares refinement converged with

$$R = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.044$$

$$R_w = [(\sum\omega(|F_o| - |F_c|)^2 / \sum\omega F_o^2)]^{1/2} = 0.059$$

The standard deviation of an observation of unit weight [18] was 2.07. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum\omega(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.17 and $-0.33 \text{ e}^-/\text{A}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber [19]. Anomalous dispersion effects were included in F_c [20]; the values of $\Delta f'$ and

$\Delta f''$ were those of Cromer [21]. All calculations were performed using the TEXSAN [22] crystallographic software package of Molecular Structure Corporation.

ACKNOWLEDGMENTS

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$$[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$$

where N_o = number of observables, N_v = number of variables.

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