



Review

Chiral configurations in cyclophosphazene chemistry



Aylin Uslu*, Serkan Yeşilot**

Department of Chemistry, Gebze Technical University, Gebze 41400, Kocaeli, Turkey

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Abbreviations: NMR, nuclear magnetic resonance; HPLC, high performance liquid chromatography; TLC, thin layer chromatography; Ph, phenyl; Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; CSA, chiral solvating agents; CSR, chiral shift reagents; BN, 2,2'-dioxynaphthyl; BP, 2,2'-dioxynaphthyl.

* Corresponding author. Tel.: +90 262 6053009.

** Corresponding author. Tel.: +90 262 6053014.

E-mail addresses: aylin@gyte.edu.tr (A. Uslu), yesil@gyte.edu.tr (S. Yeşilot).

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ABSTRACT

The pentavalent phosphorus atoms in cyclophosphazenes (NPXY)_{*n*} are tetra-coordinated and their potential centers of chirality are analogous to those for tetrahedral carbon derivatives. Although the possibility of optical isomerism in cyclophosphazene derivatives was first discussed over 50 years ago, the stereogenic properties of substituted cyclophosphazene compounds have only been investigated systematically for about 15 years. This review summarizes the recent work reported on the stereogenic properties of cyclophosphazenes. The review will also cover those previously published compounds where the centers of chirality were not explicitly recognized, in order that the stereogenic properties of new compounds will be taken into account in future studies.

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1. Introduction

The stereogenic properties of molecules are very important in chemistry [1] and have major implications in catalysis, biochemistry and pharmacology [2]. The chirality of molecules may be described in terms of axial, central and planar chirality [3] for molecules containing carbon [1] and metal atoms [4]. Chiral phosphorus compounds (*P*-chiral) are also important and attract great interest [5–7] because of their wide use as chiral solvating agents [8,9], chiral ligand in solutions [10] and enzyme inhibitors [11].

Cyclophosphazenes and their derivatives have been of considerable interest for a number of years, partly because of their versatile chemistry [12–16] and partly because it is possible to use them to design materials with special properties such as thermal stability, catalytic properties, electrical conductivity, liquid crystals and biomedical activity [17–20]. A large part of the literature of cyclophosphazene chemistry deals with symmetrically substituted moieties (NPX₂), in which the tetra-coordinated pentavalent phosphorus atoms is not a center of chirality and it was only when unsymmetrically substituted phosphazene units (NPXY) were considered that the possibility of optical isomerism in cyclophosphazene derivatives was realized in 1962 [12]. In terms of chiral configurations the tetra-coordinated pentavalent phosphorus moiety in cyclophosphazenes (NPXY) is analogous to the tetrahedral carbon atom (Cabcd). However, it was about forty years between the first discussions of chiral configurations in cyclophosphazenes and their systematic investigation [21], which lead to a number of reports in the literature with incorrect conclusions because stereogenic properties were neither considered nor understood. There were also many published reports on cyclophosphazenes where the centers of chirality were not explicitly recognized.

The aim of the present review is to cover the recent work on cyclophosphazene derivatives having one, two or more

centers of chirality, outline the methods used to determine chirality of cyclophosphazenes. In order that the stereogenic properties of new derivatives of cyclophosphazenes will be taken into account in future studies, the review will also cover many previously published reports where the centers of chirality were not explicitly recognized, even though their structures were characterized by X-ray crystallography. Organic chemists are usually aware of the stereogenic consequences of their work and it is hoped that this review will encourage inorganic chemists working with cyclophosphazenes to take into consideration, and even exploit, the stereogenic properties of their compounds and systems.

2. Chirality of cyclophosphazenes and representations of structures

The possibility of optical isomerism was first discussed in a review in 1962 for derivatives of cyclotriphosphazene and cyclotetraphosphazene [12]. In that work the structures were represented with planar projections of the rings and substituents either above (in bold lines) or below (dotted lines) the plane [12]. In general that structural representation has not been adopted by other workers and so it is necessary to discuss other representations of cyclophosphazene derivatives, especially ones that are suitable for derivatives with centers of chirality.

2.1. Cyclotriphosphazenes

The basic cyclotriphosphazene compound is hexachlorocyclotriphosphazatriene (**1**) (NPXY)₃ with X = Y = Cl, whose chemical structure is shown in Fig. 1a. X-ray crystallographic studies of **1** at room [22] and low temperature [23] and most of its derivatives in the Cambridge Structural Database [24] show that the cyclophosphazene ring is approximately planar. It has been conventional to

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