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Review

Gyroscopes and the chemical literature: 1852–2002☆

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Contents

Abstract

A brief history of mechanical gyroscopes and their applications is followed by a summary of properties that are desirable in molecular gyroscopes. Molecules to which the descriptor gyroscope has been applied are then reviewed through early 2002. Syntheses as well as structural and dynamic properties of the macrocyclic platinum complexes *trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_{2n+2}PPh_2$) (n = 4, 5, 6, 8, 9), in which a single methylene chain spans the *trans* phosphorus atoms, are subsequently analyzed. No part of the Cl-Pt-C_6F_5 moiety can rotate through the macrocycle when it consists of 13 atoms; however, the chloride ligand can pass through macrocycles of ≥15 atoms, and the pentafluorophenyl ligand through macrocycles of ≥21 atoms. Analogous complexes in which two methylene chains span the *trans* phosphorus atoms are also discussed.

Keywords: Gyroscope; Alkene metathesis; Porphyrins; Cucurbituril; Phosphines; Turnstiles; Crystallography; Dynamic NMR

1. Introduction

The first device that closely resembled a modern mechanical gyroscope was described in 1817 by Johann von Bohnenberger, a Professor of mathematics and astronomy at the University of Tübingen in Germany [1,2]. However, credit for the discovery of the gyroscope is most widely attributed to the French scientist Jean Foucault in 1852 [1]. He sought to develop an instrument that would help visualize the rotation and precession of the Earth about its axis. Foucault coined the name for his invention from two Greek words—"gyros", meaning circle or rotation, and "skopein", meaning to view. A replica is depicted in Fig. 1 (left).

Since that time, gyroscopes have come to play very important roles in society and technology [1]. Most individuals are probably first introduced to gyroscopes as toys (Fig. 1, middle). However, there are many practical applications, such as anti-roll stabilizers in ships and high-speed trains, gyrocompasses and airplane autopilots, space station orientation and navigational systems, virtual reality headsets, and wireless computer pointing devices [4]. Gyroscopes – both macroscopic and molecular

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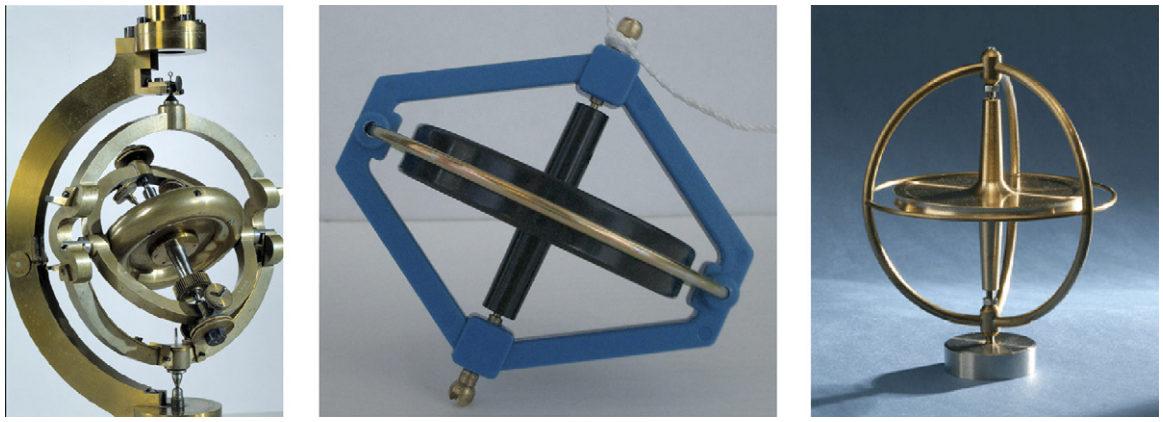

Fig. 1. Foucault gyroscope (left) and present-day toy versions or models (middle, right).

– can nearly always be dissected into two components, a rotator and a stator [3]. The latter is considered to be static, and the former spinning. However, motion is always a function of the reference frame of the observer. For this reason, the component with the greater moment of inertia is taken as the stator.

The purpose of this introductory review is not to present a detailed account of the complicated physics of a gyroscope. Rather, we seek to orient the reader intuitively with respect to common toy gyroscopes. Target properties for molecular models for gyroscopes are first proposed. We then review all cases where some type of molecule/gyroscope connection has been claimed in the literature, up to the beginning of our own efforts in 2002 [5,6]. These reports are evaluated with respect to the proposed target properties. This coverage corresponds to the sesquicentennial of Foucault's disclosure. However, it stops short of the important work of Garcia-Garibay [7,8], who has synthesized and characterized a variety of excellent models for molecular gyroscopes, a few of which are described in passing below.

2. Target properties, molecular gyroscopes

We have proposed that molecular gyroscopes should have the following properties: [5a]

(1) There should be a *functional* axis of rotation, which allows an interior domain of the molecule (the rotator) to rotate independently of an exterior domain (the stator).
(2) The exterior domain should sterically shield and optimally encase the rotator with "spokes", analogously to a common toy gyroscope. Although the physics of a gyroscope is not dependent upon an external assembly (simple toy spinning tops can also be regarded as gyroscopes), to our knowledge all gyroscopes used in real-world applications are enclosed in protective housings, for the logical purpose of insulating them from their environments.
(3) They should closely model the connectivity and symmetry of a toy gyroscope. For those in Fig. 1, the point groups are D_{2h} (middle) and D_{3h} (right).

Systems with the above features would still have one shortcoming vis-à-vis real world gyroscopes. Namely, the rotators would not rotate unidirectionally. Rather, rotation would be Brownian—random, in both clockwise and counterclockwise directions. Although rotations of $\geq 360^\circ$ would be statistically possible, they would not be as frequent as simple back/forth movements. The obvious question remains: what can be done on a molecular level that is analogous to "pulling the string" on a toy gyroscope?

One answer is to introduce a dipole moment on the rotator. Dipole moments interact with electric fields. The rotator could then be oriented by a static electric field. Garcia-Garibay has termed such systems molecular compasses [7,8]. A rotating electric field could then be used to drive unidirectional rotation, the molecular-level physics for which has been well worked out [3]. However, the introduction of a dipole moment necessitates a desymmetrization. The point group D_{nh} would no longer be possible.

Perhaps other means of achieving unidirectional rotation in molecules with features (1)–(3) will be realized in the future. However, in view of this problem, we commonly refer to such systems as "gyroscope-like". We also extend this terminology to assemblies with (a) dipolar rotators, but where the groups on the rotator are roughly isosteric, such that the shape is nearly of D_{nh} symmetry, and (b) stators of one symmetry (e.g., three identical "spokes" defining equal angles) and rotators of another (e.g., an axis with two identical ligands at a 180° angle).

These codicils are a logical reflection of a rapidly developing field. As noted by a reviewer, functional characteristics may ultimately be more important than restrictive symmetry requirements. Hence, some evolution in the preceding target properties can be anticipated.

3. Porphyrin systems of Rose [9]

Starting with the picket fence series of Collman, designer porphyrins have often been given rather colorful names. The first molecules we are aware of to which the descriptor "gyroscope" was applied were reported by Rose in 1985 [9]. The "double picket fence" porphyrin **1** shown in Scheme 1 was initially synthesized. Then bridges were introduced below and/or above the plane of the porphyrin ring system, giving **2**–**4**. The properties of these gyroscope porphyrins were contrasted with those of the