

Contents lists available at [SciVerse ScienceDirect](#)

Polyhedron

journal homepage: www.elsevier.com/locate/poly

What role has organic chemistry played in the development of molecule-based magnets?

Hiizu Iwamura*

College of Science and Technology, Nihon University, 3-11-3 Kanda-Surugadai, Chiyoda-ku, 101-8308 Tokyo, Japan

ARTICLE INFO

Article history:

Received 8 January 2013

Accepted 7 March 2013

Available online xxxx

Keywords:

Molecule-based magnets

Olivier Kahn

Radicals

Carbenes

Non-Kekulé hydrocarbons

Magnetic properties

ABSTRACT

Contributions of organic chemistry to the interdisciplinary science of molecule-based magnets are discussed in reference to transition metal coordination chemistry carried out successfully by Olivier Kahn and other scientists. Typical organic molecules have closed-shell structures and therefore organic compounds are usually diamagnetic. Organic chemists had to start with the design and construction of more-or-less stable open-shell organic molecules. Only then it became possible to study how to let their electron spins exchange-couple strongly by means of spin delocalization and polarization within a molecule and among molecules. Non-Kekulé π -systems were chosen to make the triplet carbene species to interact ferromagnetically. Approaches by means of synthetic organic chemistry proved effective. Magnetic susceptibility measurements revealed that such tetracarbene and nonacarbene have ground $S = 4$ and $S = 9$ states, respectively. Thus, the open-shell hydrocarbon molecules have been shown to have higher magnetic moments than those of $S = 5/2$ Fe(III) and $S = 7/2$ Gd(III) ions. Stable aminoxyl radicals played various roles in generating organic ferromagnets by controlling the exchange coupling between molecules in crystal, or by forming the metal/aminoxyl radical hybrid systems that were made on the basis of the supramolecular approaches and led to a number of ferro- and ferrimagnets. Metal/pyridylcarbene hybrid systems generated photochemically not only revealed the mode of the exchange coupling between the spins of metal d-orbital and those residing in organic π -orbital, but also suggested the route to novel photoresponsive magnetic materials. Most of the organic and metal/organic magnets discussed in the 80s and early 90s were trying to mimic conventional magnets by molecular materials. It is only after the advent of the single-molecule magnets when molecule-based magnets became molecular materials in their own right in the area of nano-science. Here again, novel organic molecules are used as useful, functional ligands for making single ion magnets and single chain magnets.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

This overview article is based on the Olivier Kahn Memorial Lecture at the International Conference on Molecule-based Magnets (ICMM 2012) in Orlando, Florida during October 7–11, 2012. The author had a number of occasions to see Olivier in person other than at the earlier ICMM meetings. The first encounter was in Paris when the author was invited by Olivier who organized for the first time a session of molecule-based magnets at the ICM meeting in 1988. The author arranged the first visit of Olivier to Japan as the distinguished scientist of the Japan Society for the Promotion of Science at the University of Tokyo. The author helped a student choose his graduate course under Kahn's supervision and eventually served together with Joel Miller as an external examiner of his Ph.D. thesis. Olivier Kahn was a brilliant and enthusiastic scientist and teacher, deeply concerned to encourage peers including

this author and talented young scientists. He proved himself a pioneer in molecular magnetism [1]. The materials discussed in this article are mostly published during his life, but the author would like to dedicate this paper to the memory of Olivier Kahn by emphasizing the contributions of organic chemistry to the interdisciplinary science of molecule-based magnets. It looks like a personal account [2–4] but the author tried to make it an objective review article as much as possible [5].

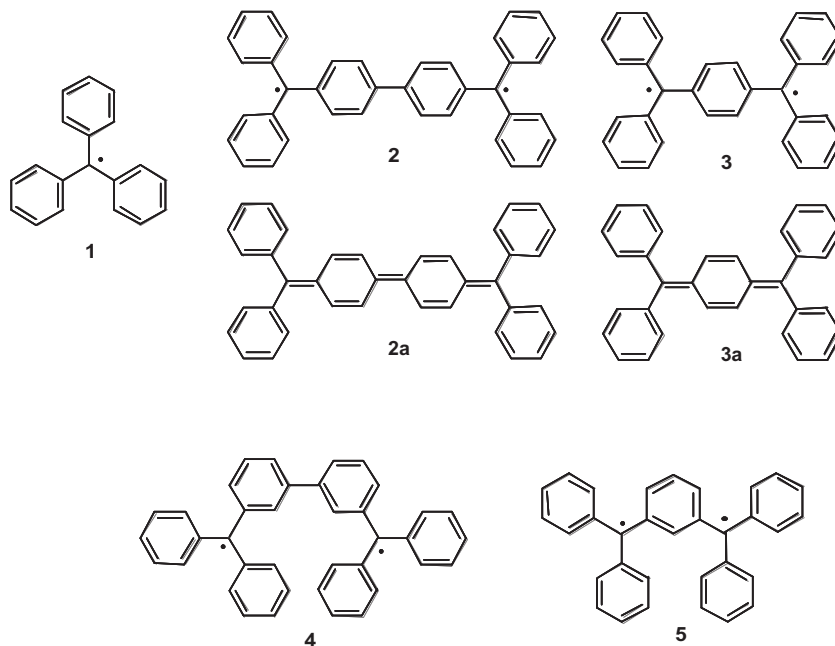
2. Organic molecules having unpaired electrons

The large majority of organic molecules have closed-shell electronic structures, i.e., they have a singlet ground state with equal numbers of electrons having α (up) and β (down) spins. Most organic compounds are therefore diamagnetic. Thus chemists had to start with the creation of the organic molecules called free radicals that have open-shell structures where not all electrons are paired. One of the first examples of free radicals that have a lifetime usable to experimental organic chemists can be traced to

* Tel./fax: +81 3 3259 0468.

E-mail address: iwamura.hiizu@nihon-u.ac.jp

triphenylmethyl radical (**1**) prepared by Gomberg in 1900 [6]. It took more than 30 years before it was found to be paramagnetic indeed. Inter alia, Müller made a series of 24 publications on the measurements of the paramagnetic susceptibility of **1**, some other radicals and diradicals at 293, 195 and 90 K corresponding to room, dry ice and liquid air temperatures, respectively, by means of a Gouy balance in 1934–1945 [7], in advance of the era of EPR spectroscopy. The Chichibabin (**2**) and Thiele hydrocarbons (**3**) were found to be diamagnetic and therefore should be represented by structures **2a** and **3a**. On the other hand, Schlenk hydrocarbon (**4**) was found to be at least 6% diradical. Schlenk–Braun hydrocarbon (**5**) was too unstable to study under these conditions.



3. Alignment of two or more spins of the unpaired electrons within a molecule

Unbiased radical centers have strong tendencies to react each other within molecules and between molecules to form chemical bonds as we learn from the potential energy curve for the formation of a hydrogen molecule from two hydrogen atoms in the introductory chemistry. Pauli's principle dictates the cancellation of α - and β -spins of the unpaired electrons cancel each other out in the chemical bond formation. Under special conditions, the electron spins can align in diradical and polyradical molecules in accordance with the exchange interaction represented in the absence of external magnetic field by effective spin Hamiltonian (Eq. (1)):

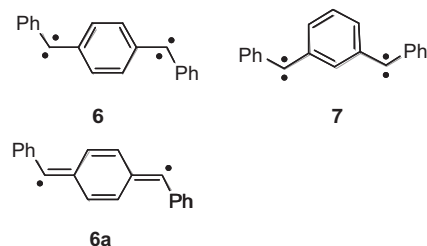
$$H_{\text{ex}} = -2 \sum J_{ij} S_i S_j \quad (1)$$

where J_{ij} represents the effective exchange interaction parameters for the magnetic centers i and j that have total quantum spin numbers S_i and S_j , respectively. When J_{ij} is positive the two spins tend to be parallel to each other in the ground state and the magnetic coupling is ferromagnetic. On the contrary, if J_{ij} is negative the two spins align in an antiparallel fashion and the interaction is antiferromagnetic.

The middle of 1960s has marked the beginning of the science of modern molecular magnetism of organic compounds. Three seminal papers from two research groups appeared one after another. They showed by the analyses of EPR fine structures how the two triplet carbene units interacted each other through the framework

of a benzene ring. In the first paper [8], the scientists of Bell Laboratories found for the para isomer **6** EPR fine structures characteristic of triplet species **6a** with the zero-field splitting parameters: $S = 1$, $D = 0.0521$, $|E| < 0.002 \text{ cm}^{-1}$ on which a dipolar interaction model suggested the separation of the unpaired electrons to be approximately 4 Å. They were, however, unable to show if the triplet is the ground state or degenerate with the singlet state in **6a**. The EPR spectrum of the *m*-dicarbene **7** was too complex for them to analyze. Wasserman et al. carried out photolysis of the precursor diazo compound on a sample in frozen organic solvents and, therefore, the generated dicarbene molecules were randomly oriented [9]. Perturbational theory to solve the fine structure Hamiltonian

was applied and by using the observed highest and next highest field features, they obtained the zfs parameters: $S = 2$, $D = 0.0701$, $E = 0.020 \pm 0.002 \text{ cm}^{-1}$ with some ambiguity in the E value. Itoh's analysis was more rigorous and complete in that the sample molecules of **7** were effectively oriented in host benzophenone crystals and the angular dependence of the observed two sets of four resonance positions was carefully analyzed to give $S = 2$, $D = 0.07131$, $E = 0.01902 \text{ cm}^{-1}$ without ambiguity as there were two sites for the quintet molecules present [10].



Thus the idea of having high-spin organic molecules by combining two concepts of the spin alignment in organic molecules, namely, the periodicity of the molecular orbitals in the π -system on the one hand, and the orthogonality of the orbitals carrying unpaired electron at the divalent carbon on the other, was established. The periodicity of the π -orbitals in isomeric quinodimethanes (**8**) is discussed either by their Kekulé structure, MO, and valence bond

Download English Version:

<https://daneshyari.com/en/article/7766436>

Download Persian Version:

<https://daneshyari.com/article/7766436>

[Daneshyari.com](https://daneshyari.com)