

Diamagnetic Anisotropy: Two Iron Complexes as Laboratory Examples

Ignacio Fernández*

Department of Organic Chemistry, University of Almería, Carretera de Sacramento s/n, E-04120 Almería, Spain

*ifernan@ual.es

Jorge Fernando Fernández Sánchez

Department of Analytical Chemistry, University of Granada, C/Fuentenueva s/n, E-18071, Granada, Spain

Nuclear magnetic resonance (NMR) is an important analytical tool in structural analysis, and thus undergraduate chemistry students are trained how to utilize ^1H and ^{13}C NMR data for structure elucidation. NMR, however, has many uses that go beyond simple structure analysis. Consequently, many chemistry laboratory courses incorporate experiments that expose the students to these techniques.

We have developed a student-friendly experiment using iron(II) phthalocyanine (PcFe) (*1*) that highlights an important concept of NMR found in almost every sample—*diamagnetic anisotropy*. It is worth mentioning that 605 articles on NMR have been published in this *Journal* since 1957 but none involve the NMR features of phthalocyanine complexes (*2*). Systems with pronounced diamagnetic anisotropy are typically aromatic where the induced ring currents are usually underestimated as a source of information. Ring-current effects produce a shielding or deshielding of protons resulting from their orientation with respect to an applied external magnetic field. The circulating π electrons create an induced magnetic field that opposes or reinforces the applied magnetic field in different magnetic zones. The zone where opposition to the applied magnetic field occurs is the shielding (+) zone. Protons located in this region have upfield chemical shifts (lower δ values). On the other hand, protons located in the zone of reinforcement are in the deshielded (−) zone and have downfield chemical shifts (higher δ values). A detailed explanation of this topic can be found in any organic chemistry or spectroscopic textbook (*3*). In this experiment, students synthesize two bis(amine) iron(II) phthalocyanine and examine various NMR spectra.

Procedure

Decylamine and benzylamine are used in this experiment. Both of these reagents are inexpensive and are commercially available. The iron(II) phthalocyanine complexes are prepared in a straightforward one-pot manner by reaction of PcFe with 2 equiv of the appropriate amine in deuterated tetrahydrofuran.¹ Yields of ca. 98% are typical if pure PcFe (available from Fluka) is used (*4*). The metal complex can be synthesized in 30–60 min. By using a relatively high metal complex concentration (ca. 30 mg in 0.75 mL THF-*d*₈) and optimized parameters, the NMR experiments (^1H , ^{13}C , gCOSY, and gHMQC) can be completed

in 1–2 h. The data processing to yield quality spectra is followed with standardized processing protocols allowing the students to process and print spectra with minor difficulties. This experiment integrates two important laboratory concepts: inorganic coordination synthesis and NMR spectroscopy, which further allowed the instructor to teach basic NMR concepts such as phase correction, integration, spectral window (i.e., large enough to cover all the signals), and spin systems and to demonstrate the versatility of NMR by the combination of standard one- and two-dimensional methods. A class of 12 students working in groups of two can successfully complete the experiment in a single laboratory session divided in two parts: sample preparation and data collection on a previously programmed instrument.

Hazards

The experiment should be performed in a fume hood using standard protective equipment: goggles, gloves, and lab coat. Decylamine is skin irritant and harmful if swallowed. Benzylamine is corrosive and harmful in contact with skin or if swallowed. Tetrahydrofuran is a highly flammable solvent, is an irritant, and is harmful if ingested. HCl methanolic 10% solution is corrosive. Iron(II) phthalocyanine may be irritating to the eyes, skin, and respiratory tract. In proximity to the NMR instrument a strong magnetic field is present that could cause health problems to persons with implanted or attached medical devices.

Results and Discussion

The structures of $[\text{PcFe}(\text{decylamine})_2]$ and $[\text{PcFe}(\text{benzylamine})_2]$ are shown in Figure 1. The differences between these two diamagnetic complexes are reflected in their NMR spectra. In the ^1H NMR spectra, integration of the signals in the phthalocyanine region relative to the amine signals confirms that the new structures contain 2 equiv of amine. Given the wealth of conformations that can exist in solution and that only sharp signals are observed, chemical exchange processes are necessarily fast with respect to the NMR time scale. The interesting low frequency signals for the amines that appear between ca. 0.5 ppm and −7 ppm arise as a consequence of the local diamagnetic anisotropy effects associated with the phthalocyaninato structure (*5*). The alkyl and benzyl chains are assumed to be extended