Synthesis and magnetic property of a nitroxide based on C\textsubscript{60}

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Abstract  The compounds containing stable nitroxide radicals possess magnetic properties for the free radical have net magnetic moment. Oxidization of the [60]fulleropyrrolidine obtained from the reaction of C\textsubscript{60} with diketone and 2-aminoisobutyric acid by m-chloroperoxybenzoic acid gives a new nitroxide integrated with C\textsubscript{60}. The stable nitroxide based on C\textsubscript{60} is confirmed to be antiferromagnetism with quantum design superconducting quantum interference device (SQUID).

Keywords: ferromagnet, fullerene, nitroxide, 1,3-dipolar circle addition reaction.

The ferromagnetism of the poly-1,2-bis-(2,2,6,6-tetramethyl-4-oxy-4-piperidyl-1-oxy)-butadiin (BIPO)\textsuperscript{1}\textsuperscript{1} firstly reported by Ovchinnikov has attracted the attention to study pure organic ferromagnets
because of the special favorable conditions of organic compounds in diversification of the molecular structure and physical processing. The function of the materials can be improved by building the model of functional molecular block and synthesizing target molecules. A lot of work have been done in designing and preparing organic ferromagnet in recent years.

The free radical is an important kind of spin source of organic compound, thus ferromagnetic interaction can take place through the interaction between those molecules, which is assisted by the special conjugated \( \pi \) bonds of \( C_{60} \). Reaction of \( C_{60} \) with tetrakis(dimethyl-amino)ethylen (TDAE) led to the formation of charge transfer (CT) complexes which showed interesting ferromagnetic properties\(^2\). We have also studied the formation of charge transfer complex based on \( C_{60} \), and reported the magnetic properties of those complexes\(^3\). We are interested in synthesizing a kind of novel organofullerenes containing stable nitroxide moieties and in studying the phenomenon of intermolecular and intramolecular charge transfer to find the relation of physical properties and abilities with molecular structure and to obtain an organoferromagnet with high Curie temperature and strong coercive force.

Cycloaddition reaction represents the most important and convenient approach in fullerene functionalization. The 1,3-dipolar cycloaddition reaction of azomethine ylides with \( C_{60} \) has been widely used to prepare N-substituted and N-unsubstituted fulleropyrrolidine derivatives of \( C_{60} \)\(^4,5\). One of the routes to obtain azomethine is to have aldehyde (or ketone) react with \( \alpha \)-amino acid, which was used to synthesize [60]fulleropyrrolidine by Maggini\(^6\), followed by other groups\(^7,8\). We have studied the relative subjects and reported firstly the [60]fulleropyrrolidine obtained by reaction of bialdehyde and \( \alpha \)-amino acid with \( C_{60} \)\(^9\). According to the conditions\(^10\) for the formation of stable nitroxides, i.e. oxidation of a secondary amine which has no \( \alpha \)-H, we made 2-aminoisobutyric acid and diketone react with \( C_{60} \) via 1,3-dipolar cycloaddition to yield [60]fulleropyrrolidine 1. Furthermore, [60]fulleropyrrolidine 1 was oxidized with \( m \)-chloroperbenzoic acid (MCPBA) at r.t. to give a stable nitroxide 2 (scheme 1).

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\begin{align*}
\text{CH}_3\text{COOH} + \text{CH}_3\text{NH}_2 & \quad \xrightarrow{\text{CO}_2, \text{H}_2\text{O}} \quad \text{O} \quad \text{O} \quad \text{COO} \quad \text{NH}\text{CH}_3 \\
\text{CH}_3\text{N}\text{H}_2 & \quad \xrightarrow{\text{C}_{60}, \text{N}_2} \quad \text{N}\text{H} \\
\text{CH}_3\text{CH}_3 & \quad \text{CH}_3\text{CH}_3 \\
\text{CH}_3\text{N} \text{H} & \quad \xrightarrow{\text{MCPBA}} \quad \text{CH}_3\text{CH}_3 \\
\end{align*}
\]

Scheme 1

\( \text{I} \quad \text{II} \)

1 Experimental

The \( C_{60} \) used in this experiment is more than 99% in purity, and \( \alpha \)-amino acid, ethyl 3-oxobutanoate, ethanol, ethyl ether, 1,6-dibromopentane, chlorobenzene used are AR reagents.

\((i)\) Preparation of 2,1,1-dioxododecane. Sodium (4.6 g) was dissolved in anhydrous ethanol (120 mL), to which ethyl 3-oxobutanoate (26.0 g) was then added, followed by 1,6-dibromopentane (24.4 g). The mixture was refluxed for 47 h and then solvent was removed. Water was added to the remainder to produce an oil, which was dissolved in ether. On removal of the solvent from the dried ethereal solution a viscous yellow oil (30.1 g) was obtained. This was hydrolysed with aqueous ethanolic sodium hydroxide (14.0 g, 300 mL 50% aqueous ethanol) by heating under reflux for 4 h. The EtOH was removed and a brown yellow oil was separated, which was solidified on cooling and was purified by recrystallization from petroleum ether (b.p. 60°–90°). The product obtained was colourless.