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Facile, Scalable, Regioselective Synthesis of C_{3v} $C_{60}H_{18}$ Using Organic Polyamines

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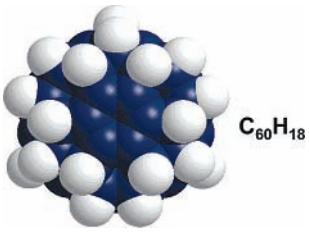
ABSTRACT



Organic polyamines are efficient reagents for the regioselective hydrogenation of [60]fullerene. When [60]fullerene is heated in diethylenetriamine, a known $C_{60}H_{18}$ isomer with C_{3v} symmetry is produced and isolated in good purity without the need for chromatographic separation. The reaction can be scaled upward to multigram levels without impacting yield or quality of product.

Numerous methods exist to hydrogenate [60]fullerene, including the Birch reduction,[1] zinc/acid reduction,[2] borane reduction,[3] transfer hydrogenation,[4] and catalytic hydrogenation.[5] Using these methods, one can prepare a range of hydrogenated [60]fullerene molecules from $C_{60}H_2$ to $C_{60}H_{36}$ to even more highly[5] hydrogenated adducts. Most of these methods produce mixtures of hydrogenated [60]fullerenes that are challenging to separate.[6] Extensive use of preparative or semipreparative high pressure liquid chromatography (HPLC) is typically required to isolate small quantities of purified hydrogenated [60]fullerene.

We now report the use of polyamines as effective, efficient reagents for the formation of hydrogenated [60]fullerenes. Cheap, commercially available diethylenetriamine is an especially effective hydrogenation reagent producing $C_{60}H_{18}$ in excellent yield and good purity without the need for HPLC or any other separation method. The reaction may be scaled to multigram levels.

Fullerenes are known to be readily aminated in primary and secondary aliphatic amine solution.[7] There is evidence

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that the reaction involves a single electron transfer from amine to [60]fullerene,[7a,e] and that amination reactions are facilitated by light,[8] presumably because photoexcited [60]-fullerene is a better electron acceptor.[9] In the presence of oxygen, the reactions between [60]fullerene and secondary aliphatic amines take a slightly different course,[10] producing in some cases tetrakisamino[60]fullerene compounds with additional epoxide function. This chemistry has since been optimized[8,11] such that multigram quantities of tetrakisamino-[60]fullerene epoxide products can be prepared in excellent yield.

While the chemistry between [60]fullerene and amines continues to attract considerable interest, there has been comparatively little attention[12] paid to the reactions between [60]fullerene and polyamines larger than diamines.[13] Our studies indicate that polyamines aminate [60]fullerene at room temperature to produce complex mixtures of products, analogous to reactions run in neat amine.[7] Upon moving to higher temperatures and ultimately subjecting [60]fullerene to neat high-boiling polyamine, we observe the formation of hydrogenated [60]fullerenes. In a typical reaction, [60]-fullerene is heated to boiling in a neat polyamine such as 1,3-propanediamine (bp 140 °C), diethylenetriamine (bp 209 °C), or triethylenetetramine (bp 267 °C) for 14−20 h under nitrogen in the dark. While hydrogenated [60]fullerene is produced in all cases, reactions run in boiling triethylene-tetramine and 1,3-diaminopropane produce complex mixtures of hydrogenated [60]fullerene. Conversely, reactions run in boiling diethylenetriamine produce an orange solid that, following cooling, filtering, and water washing, analyzes for C_{3v} $C_{60}H_{18}$. The reaction is highly regioselective and represents a simple method to produce C_{3v} $C_{60}H_{18}$ in excellent yield. No chromatographic separation of any kind is required. Moreover, the reaction is scalable. Table 1 illustrates the results obtained when running this reaction on a 0.1, 1.0, and 5.0 g scale.

Table 1. [60]Fullerene Hydrogenation Reactions Run in Neat Boiling Diethylenetriamine[a]

mass C_{60} (mg)	mL of DET[b]	time (h)	mass $C_{60}H_{18}$ (mg)	% yield
100	7	14	83	81
1000	50	16	919	90
5000	100	20	4674	91

[a] All reactions were run in boiling DET under nitrogen in the dark. [b] DET: diethylenetriamine.

The spectroscopic characteristics of our $C_{60}H_{18}$ produced in diethylenetriamine are identical to those reported by Taylor[14] for a $C_{60}H_{18}$ molecule produced by M.E.R. Corporation (Tucson, Az) using an ill-described high-temperature, high-pressure hydrogenation chemistry. Taylor assigned a C_{3v} crown structure (Figure 1) to this molecule based upon an analysis of its UV−vis, EI−MS, IR, and ^{1}H NMR spectra. The ^{1}H NMR spectrum, in particular, provides persuasive structural evidence for the proposed C_{3v} crown structure. Four ^{1}H NMR multiplets are observed, consistent with three equivalent ABB′CDD′ spin systems.

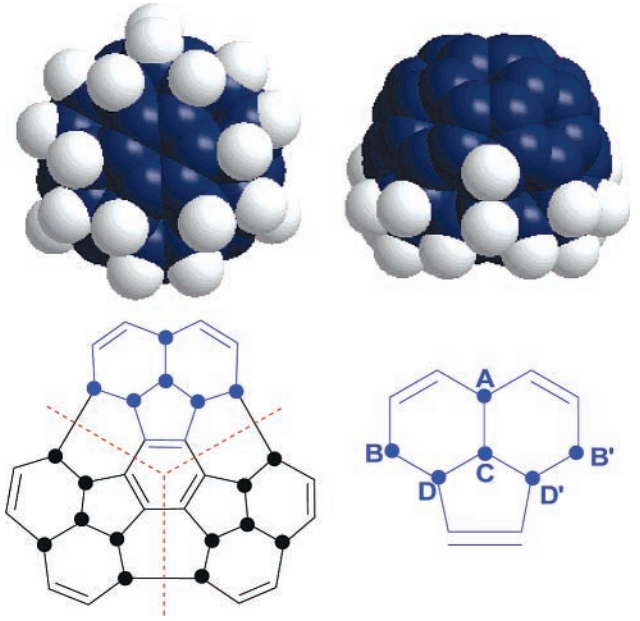

Figure 1. Structure of $C_{60}H_{18}$ produced in diethylenetriamine. Top: top view (left) and side view (right) of an MM2 minimized C_{3v} symmetric $C_{60}H_{18}$ structure. Bottom: the positions of all 18 hydrogen atoms can be divided into three equivalent ABB′CDD′ spin systems.

Although the ^{1}H NMR data are persuasive, we sought and found additional evidence for the proposed C_{3v} crown structure through the acquisition of ^{13}C NMR and 2D COSY NMR data. The ^{13}C NMR spectrum run in *o*-$C_6D_4Cl_2$ shows four sp^3 ^{13}C signals at 37.0, 37.7, 43.2, and 43.5 ppm and six sp^2 ^{13}C signals at 133.6, 141.3, 146.1, 149.3, 151.3, and 151.5 ppm, completely consistent with Taylor's proposed C_{3v} structure. A COSY spectrum (Figure 2) indicates strong cross-peaks between A and C protons, C and D protons, and

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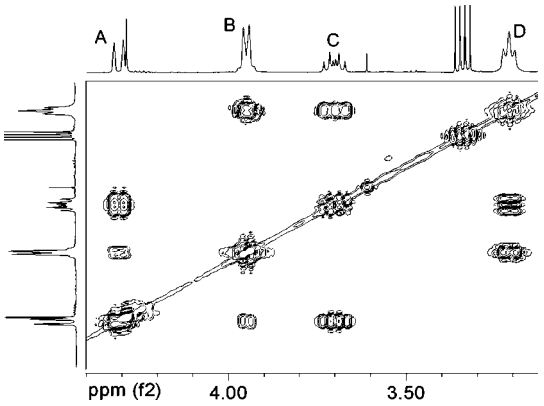

Figure 2. COSY spectrum of the C_{3v} symmetric $C_{60}H_{18}$ produced in boiling diethylenetriamine. The weak cross-peak observed between A and B protons is real and corresponds to a $^5J_{HH}$ of 3.0 Hz. The large quartet at ~3.3 ppm is due to residual solvent.

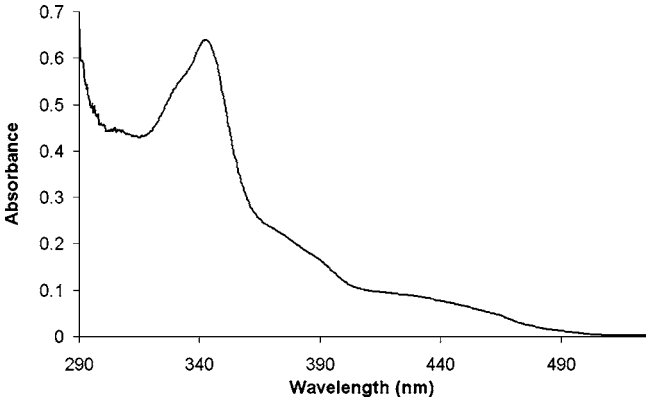

Figure 3. UV−vis trace of C_{3v} $C_{60}H_{18}$ showing a distinct maximum at 341 nm.

B and D protons, also consistent with Taylor's C_{3v} structure. Most revealing, however, is the relatively weak cross-peak observed between A and B protons. A phase-sensitive COSY spectrum (not shown) highlights this weak correlation and reveals the corresponding $^5J_{HH}$ coupling constant to be 3.0 Hz, consistent with other $^5J_{HH}$ coupling constants on hydrogenated [60]fullerene compounds.[15] A UV−vis spectrum for C_{3v} $C_{60}H_{18}$ reveals a distinct maximum at 341 nm and multiple shoulders between 330 and 480 nm (Figure 3). Cumulatively, the analytical data provide compelling evidence for Taylor's proposed C_{3v} crown structure for $C_{60}H_{18}$.

The mechanism for [60]fullerene hydrogenation in boiling polyamine is currently under investigation. Our preliminary data indicate that high-boiling monoamines (e.g., 1-aminooctane, bp 180 °C, and 1-aminododecane, bp 248 °C) do hydrogenate [60]fullerene, but only to a small extent. By contrast, hydrogenation of [60]fullerene in polyamine is facile and may proceed via a cooperative effect involving multiple amine functions.

In summary, we report the facile hydrogenation of [60]-fullerene in neat boiling polyamine solution including the scalable, regioselective synthesis of C_{3v} $C_{60}H_{18}$ in boiling diethylenetriamine.

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