

WATER-SOLUBLE FULLERENE DERIVATIVES, SYNTHESIS AND CHARACTERIZATION OF β -ALANINE C_{60} ADDUCTS

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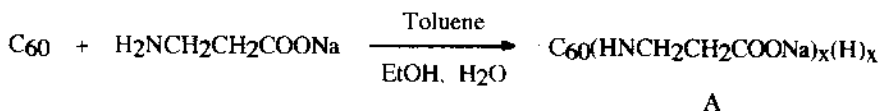
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Abstract β -alanine sodium salt reacts with C_{60} to give a water-soluble derivative A. Acidification of A yields derivative B $C_{60}(\text{NHCH}_2\text{CH}_2\text{COOH})_x(\text{H})_x$. Elemental analysis suggest x is equal to 9. ^1H and ^{13}C NMR spectra are consistent with the addition of amino acid through its amino group. These amino acid derivatives are air-stable and may be used as precursors for further functionalization.

Fullerenes are much more reactive than previously thought. They may undergo a variety of reactions such as hydrogenation,¹ halogenation,² osmylation³ and radical reaction.⁴ Benzene and toluene are the most common solvents employed in these studies because fullerenes easily dissolve in these organic solvents. In contrast water is seldom used, and a few water-soluble fullerene derivatives are known. Aqueous C_{60} solution was formed upon embedding C_{60} into γ -cyclodextrine⁵ and artificial lipid membranes⁶. Aqueous acid chemistry efficiently transform fullerenes into fullerols, water-soluble polyhydroxylated fullerene derivatives.⁷ Ethylenediamine reacts with C_{60} to form water-soluble "Hairyball", for which a stepwise amino addition mechanism was suggested involving the addition of the amino group NH_2 onto the double bonds of C_{60} .⁸ We found that the amino groups of amino acids can also react with C_{60} to form water-soluble products. Here we report the synthesis and characterization of β -alanine C_{60} derivatives.

β -alanine (3.0g) and sodium hydroxide (1.7g) was dissolved in 4ml water, 40ml ethanol was added, the resulting solution was added to a C_{60} toluene solution (84mg, 70ml) dropwise. The solution was stirred at room temperature, its color changed gradually from purple to dark brown. After stirring for one hour, the organic layer turned almost colorless. To make sure the reaction is complete the solution was stirred for 5 days. The aqueous layer was separated from the colorless organic layer, filtered, diluted with water to 10ml, 60ml ethanol was then added to cause the precipitation of product A, which was further reprecipitated from $\text{H}_2\text{O}/\text{EtOH}$. Ninhydrin test showed no free β -alanine present in the product. Derivative B was obtained upon acidification of derivative A with dilute HCl.

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Derivative A readily dissolves in water to form a strongly basic red brown solution. Elemental analysis suggests several sodium carbonate molecules per fullerene derivative are present which may come from the sodium hydroxide used to neutralize β -alanine. Because the basic character of A and the low solubility of sodium carbonate in ethanol, the above work-up procedure is not very effective in the complete removal of sodium carbonate. Titration of derivative A with HCl resulted in partial precipitation at pH around 5, along with the evolution of some bubbles indicating the presence of sodium carbonate. At pH around 3, the largest amount of precipitate was formed. Further acidification redissolves some of the precipitate. This solubility change indicates β -alanine is attached to C₆₀ through its amino group rather than the carboxyl group. If the latter, the free amino group would form ammonium salt in acidic solution, thus becomes more soluble in acidic solution than in basic solution. Unlike that of pure β -alanine which has one clear equivalent point, the titration curve of derivative A is flat with no clear equivalent points.

The precipitate from the titration was separated at pH about 3 to give derivative B. B is scarcely soluble in water, but becomes very soluble when some base such as sodium carbonate is added. Elemental analysis showed a carbon: nitrogen ratio of 9.6:1, which correlates to an average of nine β -alanine moieties per C₆₀ molecule. X-ray photoelectron spectroscopic (XPS) measurement gave a carbon:nitrogen:oxygen ratio of 9.12:1:2.18, close to the elemental analysis result.

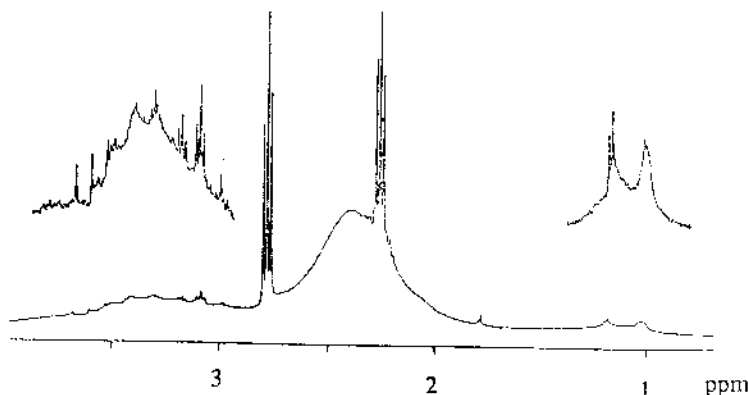


Fig. 1 400 MHz ¹H NMR spectrum of derivative A in D₂O solution, δ relative to DOH

The 400 MHz ¹H NMR spectrum in D₂O exhibits two triplets at 2.25 and 2.77 ppm (relative to DOH), assignable to the two methylene groups of β -alanine. Pure β -alanine exhibits two triplets at 2.53 and 3.15 ppm. The small shift of 0.3 ppm is not significant considering that the ¹H chemical shifts of β -alanine like other aminoacids are dependent on the pH value of the solution and could change as much as 1 ppm. Besides the two triplets, there are three broad peaks centered at 1.1, 2.3, 3.3 ppm respectively. Since the spectrum was run in D₂O, these signals can not be due to hydroxyl OH or amino NH protons. They are probably protons on the C₆₀ molecule. The broad feature of these peaks reflects the heterogeneous molecular distribution of derivative A. The ¹H NMR spectrum of derivative B is basically the same as that in Fig 1. Because the low solubility of B,

some sodium carbonate was added in its D₂O solution. The added carbonate is clearly shown on its ¹³C[¹H] NMR spectrum at 158.1 ppm in Fig 2 (relative to TMS). The relatively sharp peak at 31.6 ppm is due to the methylene carbon adjacent to the carboxyl group of β-alanine (CH₂COO). The intense broad peak at 34.7 ppm corresponds to the carbons bonded to the amino group, NHCH₂ of β-alanine. The carboxyl carbons of β-alanine appears at 177.0 ppm as a broad signal, indicating the heterogeneous molecular distribution and the added effect of the equilibrium between COO⁻ and COOH in the D₂O solution. The unsymmetrical broad peak around 145 ppm are unreacted olefinic carbons of C₆₀. The spectrum provides strong evidence for the addition of β-alanine on C₆₀ through its amino group.

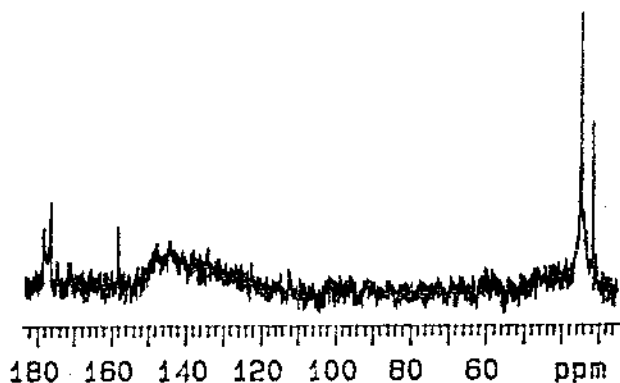


Fig. 2 ¹³C[¹H] NMR spectrum of derivative B in D₂O solution, δ relative to TMS

The infrared spectrum of both A and B showed strong broad bands centered at 3350 cm⁻¹ due to OH and NH moieties. While derivative A showed two more strong bands at 1597, 1407 cm⁻¹, derivative B showed several strong bands at 1717, 1631, 1401, 1216, 1045 cm⁻¹. The band at 1717 corresponds to the carbonyl stretching of the carboxylic acid group COOH, it shifted to 1597 in derivative A where the carboxylic group exists as the sodium salt COONa. This shift is characteristic of carboxylic groups, providing further evidence for the attachment of β-alanine on C₆₀ through its amino group. The mass spectrum is less informative. Laser-desorption mass spectrum of derivative B showed three major peaks at 1486, 1108 and 720 with the most intensive peak at 720.

Other amino acids react similarly with C₆₀. As the steric hindrance increases, the reaction is much slower for α-amino acids. The remarkable solubility of these derivatives in water makes them good precursors for further derivatization study, such as complexation with metal ions especially rare earth metal ion. Further purification and characterization of these products are currently underway.

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