

Sonochemical Reaction of Fullerene Oxides, [C₇₀(O)_n](n ≥ 1) with Aromatic Amines

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방향족 아민 화합물과 풀러렌 산화물의 [C₇₀(O)_n](n ≥ 1)의 초음파 화학 반응

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ABSTRACT : Sonochemical reaction of fullerene oxides, [C₇₀(O)_n] (n ≥ 1) with several aromatic amines such as 4-nitroaniline, 3-nitroaniline, and 4-isopropylaniline, in the presence of FeCl₃ were investigated under ultrasonic irradiation. This method is applicable to a wide variety of aromatic amines especially ring deactivated, to afford the corresponding cleavage products under mild conditions. The aminated fullerenes were confirmed by MALDI-TOF-MS and UV-vis spectra.

요약 : FeCl₃를 첨가한 초음파 조건에서 4-nitroaniline, 3-nitroaniline, and 4-isopropylaniline 등의 방향족 아민 화합물과 풀러렌 산화물 [C₇₀(O)_n] (n ≥ 1)을 반응시켰다. 이 반응은 방향족 아민 화합물을 사용한 풀러렌 산화물 쪼개짐 반응이다. MALDI-TOF-MS and UV-vis spectra를 사용하여 생성된 화합물이 아민화 풀러렌 유도체임을 확인하였다.

Keywords : fullerene oxides, aromatic amines, FeCl₃, ultrasonic irradiation, aminated fullerenes.

I . Introduction

A variety of synthetic methods¹⁻⁶ are currently at hand to introduce epoxide functionality into fullerenes. Fullerene oxides [C₇₀(O)_n](n ≥ 1) show an interesting reaction behavior both with themselves and in reactions with pure fullerene, case in point, the increased difficulty of oxidation of C₇₀ compared to C₆₀.⁷ The reason of the conceded difficulty is revealed to be the availability of less reactive double bonds present in C₇₀ as compared to with C₆₀.⁸ The

fullerene oxides [C₇₀(O)_n](n ≥ 1) are interesting precursors to the formation of other fullerene-based materials and starting materials for the formation of odd-numbered fullerene derivative species.⁹ β-Amino alcohols have been synthesized by opening of the epoxide ring with an excess of several different aromatic amines at elevated temperatures.¹⁰ Ultrasonic irradiation has been extensively studied and proven a useful synthetic technique for chemical reactions¹¹ with a large number of transformations reported the successful using in recent literatures.¹² It is well documented in the literatures that an ultrasonic irradiation not only accelerates chemical reactions but

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also reduces the number of steps required for normal reactions. The application of ultrasound has gained popularity among synthetic chemists not only because it improves classic chemical reactions by shortening reaction times and improving yields, but also by promoting new reactions.¹³ In this study we report the use of ultrasonic irradiation for the opening of fullerene oxides, $[C_{70}(O)_n](n \geq 1)$ through reaction with an excess of several aromatic amines, such as 4-nitroaniline, 3-nitroaniline, and 4-isopropylaniline in the presence of $FeCl_3$.

II. Experimental

Fullerene $[C_{70}]$ used in this work was of 99.0% purity and obtained from Tokyo Chemical Inc. (TCI). The oxidant used was 3-chloroperoxy benzoic acid (Fluka, 99.0%). Aromatic amines used were 4-nitroaniline (Aldrich, 99%), 3-nitroaniline (Aldrich, 99%), and 4-isopropylaniline (Aldrich, 99%). All samples were analyzed by MALDI-TOF-MS (Voyager DE STR) with a cyano-4-hydroxy cinnamic acid matrix. The electronic absorption spectra was obtained by UV-visible spectrophotometer (Shimadzu UV-1601 PC).

1. Reaction of fullerene $[C_{70}]$ with 3-chloroperoxy benzoic acid

A solution of C_{70} (20 mg, 0.024 mmol) and 3-chloroperoxy benzoic acid(96 mg, 2.56 mmol) in 60 ml of benzene was refluxed for 5 h. The sample of resulting solution was evaporated. The remaining solid material was washed with methanol to remove excess 3-chloroperoxy benzoic acid and then dried in a vacuum oven to yield the fullerene oxides $[C_{70}(O)_n](n \geq 1)$.

2. Reaction of fullerene oxides, $[C_{70}(O)_n](n \geq 1)$ with 4-nitroaniline under ultrasonic irradiation

A solution of $[C_{70}(O)_n](n \geq 1)$ (10 mg, 0.012 mmol) and 4-nitroaniline (18 mg, 0.13 mmol) in 30

ml of tetrahydrofuran was reacted in the presence of $FeCl_3$ (2.0 mg, 0.012 mmol) under ultrasonic irradiation for 24 h. The ultrasonic irradiation of all samples was conducted in a continuous mode with an Ultrasonic Generator UG 1200 made by Hanil Ultrasonic Co., Ltd. The ultrasonic equipment employed in this research had a frequency of 20 kHz and a power of 750 W. The configuration of the equipment was a horn-type system. And the size of the horn tip was 13 mm in diameter. The horn of the ultrasonic generator system was placed in a large reaction container, with the horn partially immersed in the solution (H_2O). The round bottom flask containing above reactants was placed in the reaction container. The round bottom flask was not in direct contact with the horn (they were at least 6 cm apart). The temperature was maintained between 25 and 4 $^{\circ}C$ for all ultrasonic irradiation treatments. The sample of resulting solution was evaporated and the remaining material was obtained as solid state products.

3. Reaction of fullerene oxides, $[C_{70}(O)_n](n \geq 1)$ with 3-nitroaniline under ultrasonic irradiation

A solution of $[C_{70}(O)_n](n \geq 1)$ (10 mg, 0.012 mmol) and 3-nitroaniline (18 mg, 0.13 mmol) in 30 ml of tetrahydrofuran was reacted in the presence of $FeCl_3$ (2.0 mg, 0.012 mmol) under ultrasonic irradiation for 24 h. The ultrasonic irradiation of all samples was conducted in a continuous mode with the Ultrasonic Generator at the same condition mentioned above.

4. Reaction of fullerene oxides, $[C_{70}(O)_n](n \geq 1)$ with 4-isopropylaniline under ultrasonic irradiation

A solution of $[C_{70}(O)_n](n \geq 1)$ (10 mg, 0.012 mmol) and 4-isopropylaniline (18 mg, 0.13 mmol) in 30 ml of tetrahydrofuran was reacted in the presence of $FeCl_3$ (2.0 mg, 0.012 mmol) under ultrasonic irradiation for 24 h. The ultrasonic irradiation of all

samples was conducted in a continuous mode with the Ultrasonic Generator UG1200 under the same operating conditions and test temperature.

III. Results and Discussion

In our early studies, we reported several methods for oxidation of fullerenes with various oxidants under ultrasonic irradiation.¹⁴

The oxidation of fullerene $[C_{70}]$ may proceed through a nucleophilic attack of the oxidant to a 6-6 bond (6-6 ring junction) of the fullerene, followed by heterolytic cleavage of the oxidant O-O bond. The common mechanism for fullerene oxidation involves oxygen atom transfer to the fullerene $[C_{70}]$ and it is often suggested that fullerene oxides, $[C_{70}(O)_n](n \geq 1)$, may be used as oxygen-transferring materials. Furthermore, fullerene oxides, $[C_{70}(O)_n](n$

$\geq 1)$, are interesting starting materials for the formation of other fullerene based entities.¹⁴

Using MALDI-TOF-MS, we identified a $[C_{70}(O)_n](n \geq 1)$ that formed in the reaction of C_{70} with 3-chloroperoxy benzoic acid. The formation of $[C_{70}(O)_n](n \geq 1)$ is identified from MALDI-TOF-MS analysis data which show the peaks at m/z : 840(C_{70}), 856($C_{70}O_1$), 872($C_{70}O_2$), 888($C_{70}O_3$), and 904($C_{70}O_4$). The most intense peak in Figure 1 occurred at m/z 840, due to the unreacted fullerene $[C_{70}]$ and the fragmentation of fullerene oxides, $[C_{70}(O)_n](n \geq 1)$.

Kmal et al. reported a limited success for the cleavage of epoxides by aromatic amines,¹⁰ whereas the present synthetic method has found a success with 4-nitroaniline.¹⁵

In continuation of these efforts, it was considered of interest to investigate the ring opening of fullerene oxides, $[C_{70}(O)_n](n \geq 1)$, with amino nucleo-

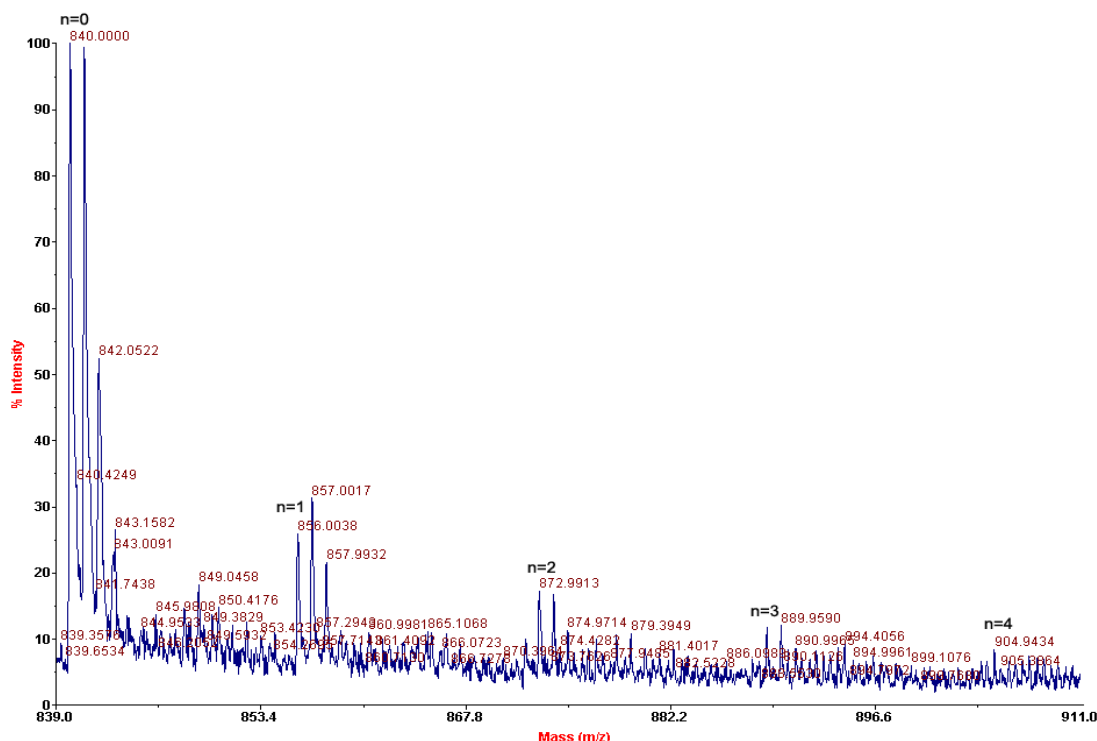
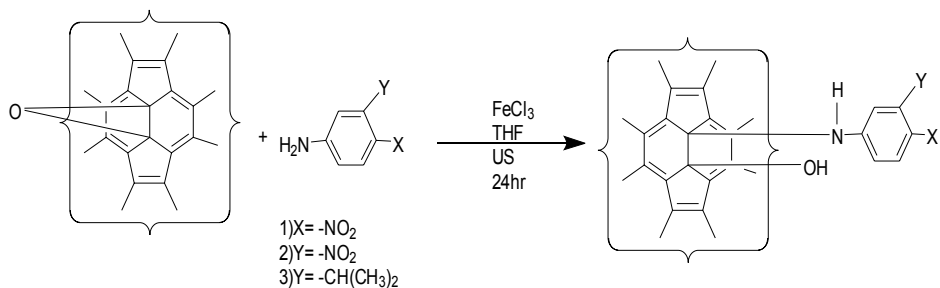


Figure 1. MALDI-TOF-MS spectrum of $[C_{70}(O)_n](n \geq 1)$.



Scheme 1.

philes under ultrasonic irradiation. Herein we wish to report an efficient cleavage of fullerene oxide rings with aromatic amines to produce aminofullerenols in the presence of FeCl₃ under ultrasonic irradiation for the first time (Scheme 1).

However, there are reports on the use of FeCl₃ as a catalyst for the alcoholysis of epoxides.^{16,17} We examined the reaction of fullerene oxides [C₇₀(O)_n] (n ≥ 1) with various aromatic amines in the presence of FeCl₃ by ultrasound in tetrahydrofuran (THF). As seen from the results, a number of aromatic amines have been employed for the cleavage of different epoxides, particularly ring deactivated amines such as 4-nitroaniline, 3-nitroaniline, and 4-isopropylaniline. This reaction was carried out in the absence of ultrasound. It is presumed that the opening of the epoxide with the amino functionality in the presence of ultrasonic irradiation is facilitated by acoustic cavitation in the reaction medium. The MALDI-TOF-MS analysis reported in Figure 2 (a)-(c) showing the formation of various aminofullerenols with peaks at: m/z = 994 (C₇₀OH(NHC₆H₄p-NO₂)) in 4-nitroaminofullerenol m/z = 994 (C₇₀OH(NHC₆H₄m-NO₂)) in 3-nitroaminofullerenol, and m/z = 991 (C₇₀OH(NHC₆H₄p-C(CH₃)₂)) in 4-isopropylaminofullerenol.

The electronic absorption bands (λ_{max}) of [C₇₀(O)_n] (n ≥ 1) and pure C₇₀ in tetrahydrofuran are shown in Figure 3. Due to the breaking of the conjugated 6-6 ring junction by addition of oxygen to fullerene [C₇₀], the bands shifted blue (379 nm → 375 nm) in the UV-visible spectrum. Also, the λ_{max} of several kinds of aminofullerenols in tetrahydrofuran were

observed at 339 nm in 4-nitroaminofullerenol at 336 nm in 3-nitroaminofullerenol, and at 363 nm in 4-isopropylaminofullerenol in Figure 4 (a)-(c).

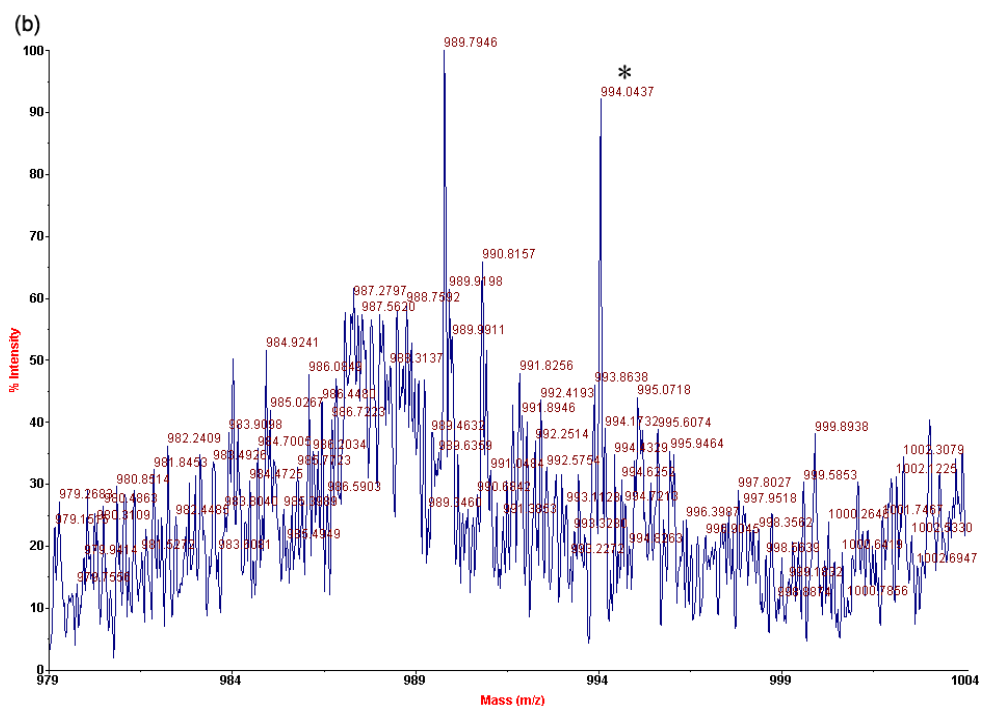
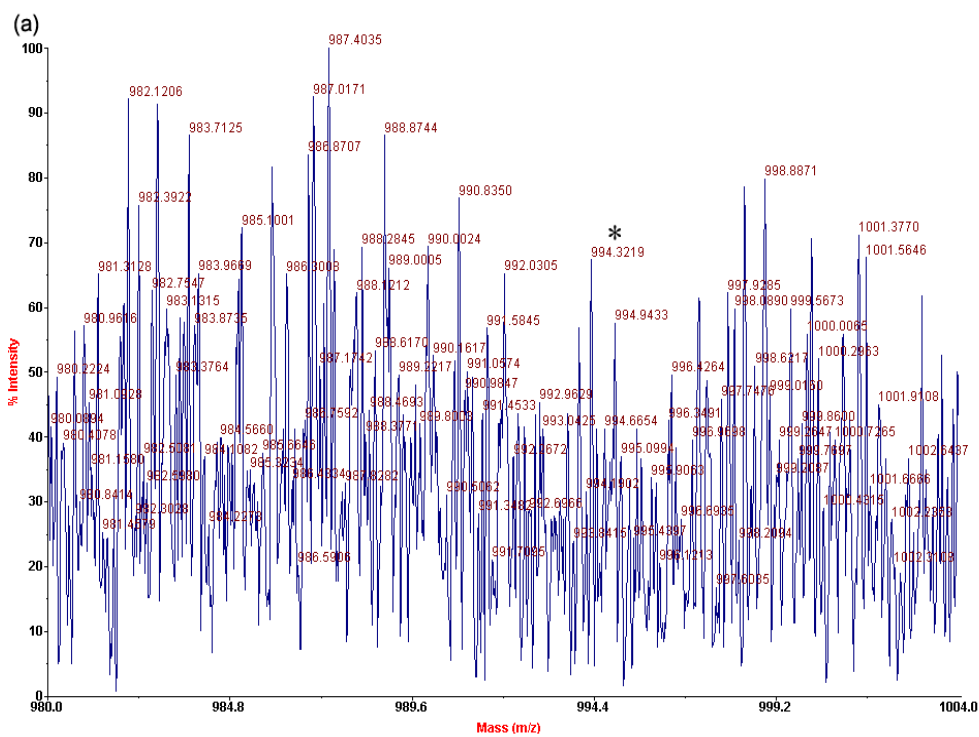
When ultrasound was not used, the rate of reaction of fullerene oxides with various aromatic amines was slower than with ultrasound, indicating that ultrasound increases the reaction efficiency in mild conditions.

IV. Conclusion

We have investigated an efficient method for the cleavage of fullerene oxides [C₇₀(O)_n] (n ≥ 1) with several aromatic amines such as 4-nitroaniline, 3-nitroaniline, and 4-isopropylaniline in the presence of FeCl₃ under ultrasonic irradiation. This method is applicable to a variety of aromatic amines that especially ring deactivated to afford the corresponding cleavage products under mild conditions. We are presently attempting to broaden the scope of this process to include other nucleophiles and epoxides and to study the influence of ultrasonic irradiation.

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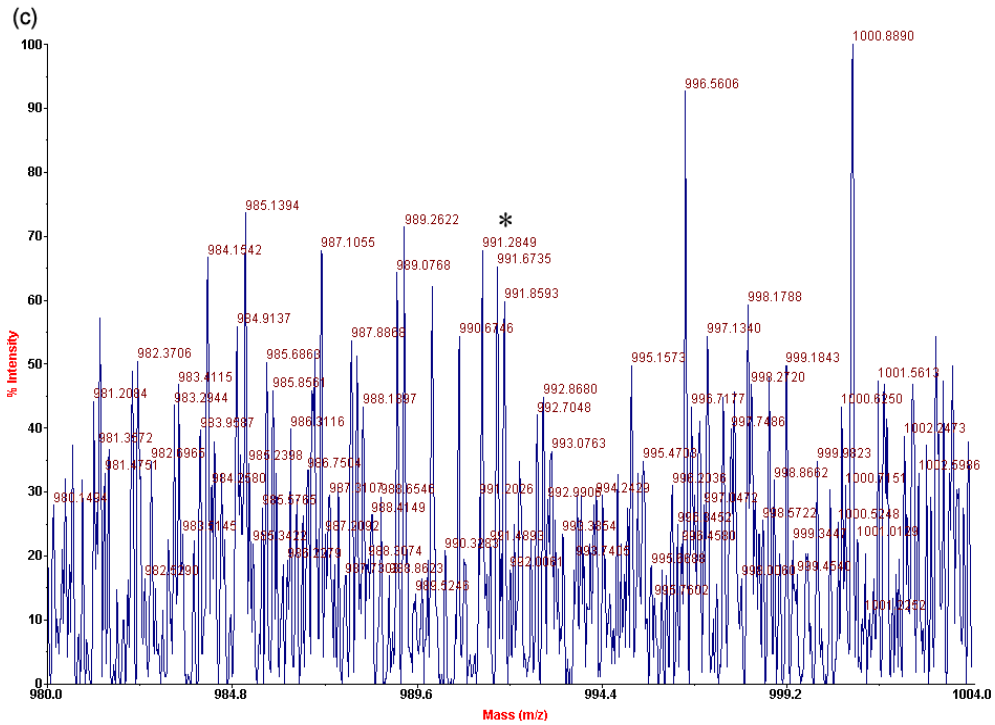


Figure 2. MALDI-TOF-MS spectra of various aminofullerenol; (a) 4-nitroaminofullerenol (b) 3-nitroaminofullerenol (c) 4-isopropylaminofullerenol.

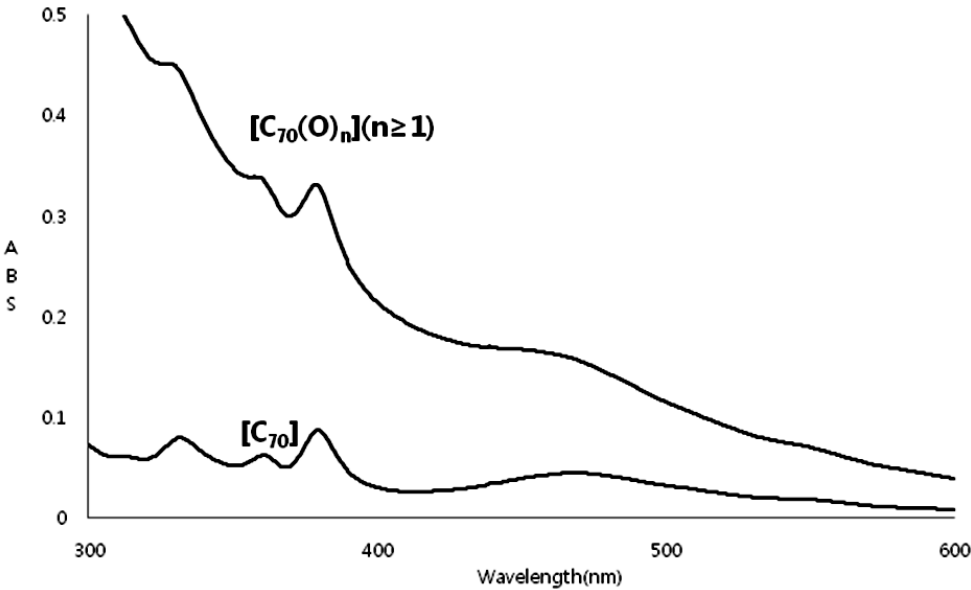


Figure 3. UV-visible spectra of fullerene[C₇₀] and fullerene oxide [C₇₀(O)_n](n ≥ 1) in the tetrahydrofuran.

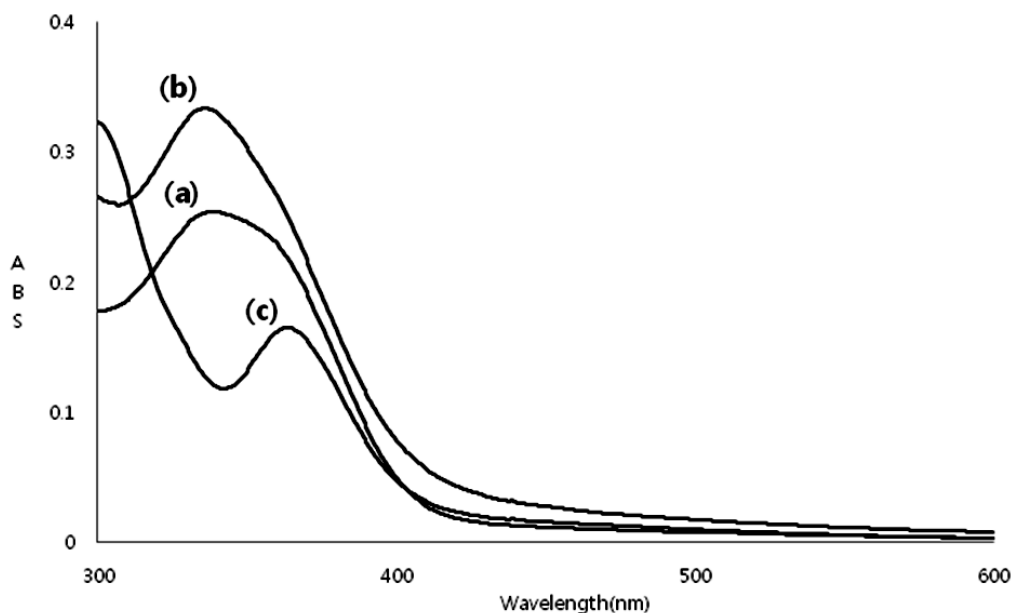


Figure 4. UV-visible spectra of various aminofullerenols in tetrahydrofuran; (a) 4-nitroaminofullerenol (b) 3-nitroaminofullerenol (c) 4-isopropylaminofullerenol.

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