

# Liquid chromatographic separation of all-carbon molecules C<sub>60</sub> and C<sub>70</sub> with multi-legged phenyl group bonded silica phases

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## ABSTRACT

The separation of C<sub>60</sub> and C<sub>70</sub> all-carbon compounds has been examined using new multi-legged phenyl group bonded silicas as the stationary phase in liquid chromatography. Two-legged biphenyl bonded silica gave the best separation because this phase offers the most suitable cavity-like structure to retain the C<sub>70</sub> molecule, and this provides good separation between C<sub>60</sub> and C<sub>70</sub>.

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## INTRODUCTION

The most attractive and interesting compounds in organic chemistry today are all-carbon molecules, called "buckminsterfullerenes" or "fullerenes" for short, which are produced in large quantities in the vaporization of graphite or in soot extracts. The major species have been identified as molecular C<sub>60</sub> and C<sub>70</sub> by NMR, mass spectrometry (MS) and other spectroscopic tools [1–4]. To isolate these interesting compounds, it is important to separate both compounds by chromatographic techniques, especially liquid chromatography (LC). The technique could be used on the preparative scale for the mass production of the compounds. There have been some studies using LC techniques in which both compounds have been separated. Taylor *et al.* [5] used an alumina column, and Ajie *et al.* [6] and Allemand *et al.* [7] used silica gel as the stationary phase. However, the separation was incomplete in those cases.

Cox *et al.* [8] discussed the chromatographic characteristics of C<sub>60</sub> and C<sub>70</sub>, which should closely resemble planar molecules with the corresponding "molecular footprints". They used nitroanilino-propyl silica (DNAP) as the stationary phase with an *n*-hexane to 50% dichloromethane gradient as the mobile phase. And they found that the retention of C<sub>60</sub> on the DNAP phase is very similar to that of triphenylene, a C<sub>18</sub> planar molecule, while the C<sub>70</sub> retention lies somewhere between the five-ring benzo[*a*]pyrene and the six-ring coronene compounds. Thus they assumed that C<sub>60</sub> may be considered an extreme example of the effect of non-planarity on retention time, which has been well documented with smaller polycyclic aromatic hydrocarbons in reversed-phase LC by several authors [9–11]. Therefore, it is reasonable to consider that stationary phases which can offer non-planarity recognition capability for these polycyclic aromatic hydrocarbons should be the best choice for the purpose of separation of C<sub>60</sub> and C<sub>70</sub>.

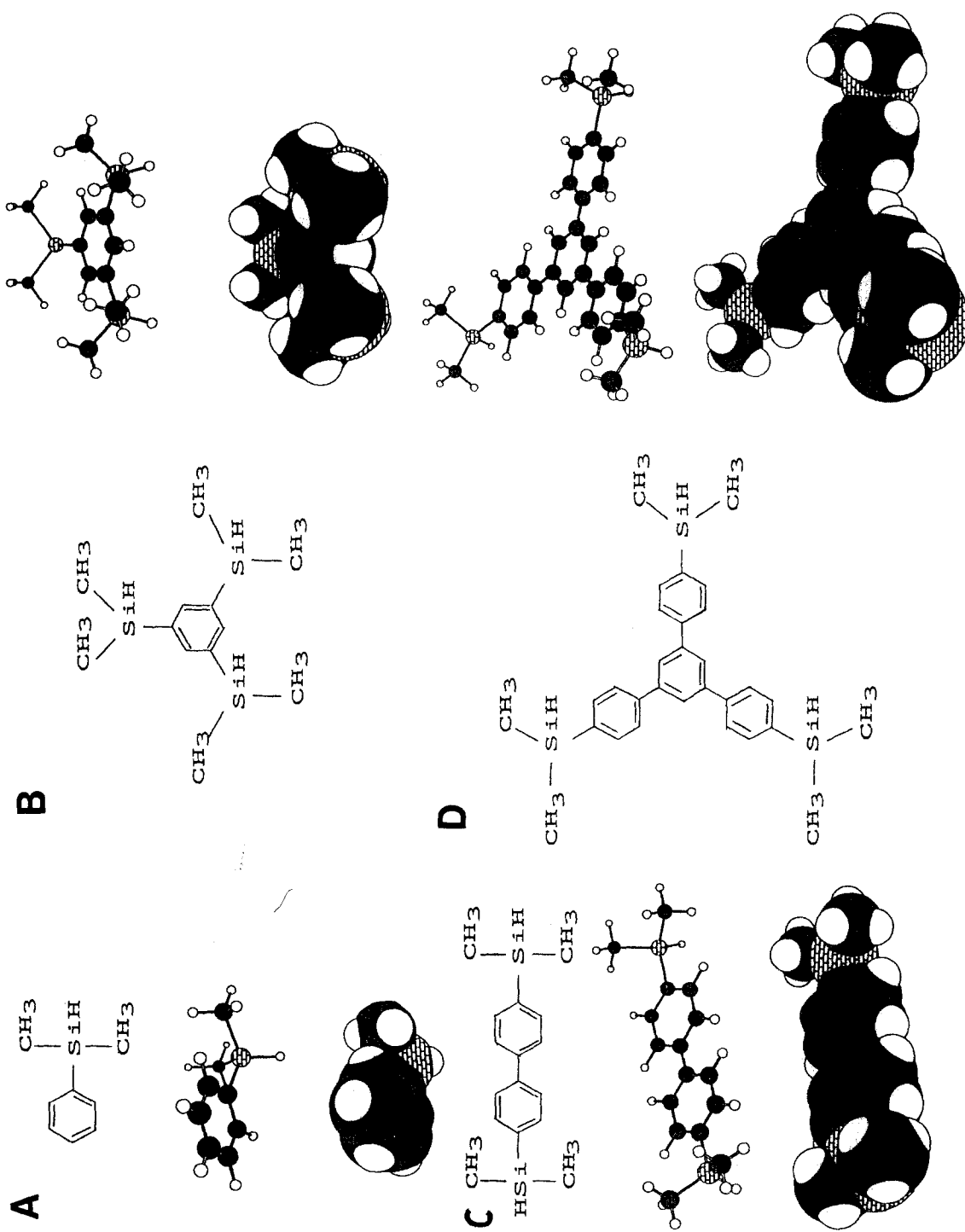


Fig. 1. Multi-legged phenyl group bonded phases used in this work. (A) P, (B) TP, (C) BP, (D) QP.

Hawkins *et al.* [12] thought that a stationary support containing  $\pi$ -acids might increase the retention and promote the discrimination of these  $\pi$ -basic aromatic clusters. They found that Pircle's phenylglycine-based LC column, which was originally designed for the separation of enantiomers by interactions that include the attraction between  $\pi$ -basic aromatic groups on substrates and  $\pi$ -acidic dinitrobenzamide groups on the stationary support, was useful for separating C<sub>60</sub> and C<sub>70</sub> [12].

In the above-mentioned situation of the problem of separating C<sub>60</sub> and C<sub>70</sub>, one would expect "multi-legged" phenyl group bonded silica phases [13] to be useful. These phases have a different cavity-like space size formed by the methyl and phenyl groups, and the separation is based on molecular-molecular interactions between the phenyl ring(s) and the methyl groups of the stationary phase and the solutes [13]. As the separation factor between *o*-terphenyl (non-planar) and triphenylene (planar) can be useful for indicating the molecular planarity recognition capability of stationary phases in reversed-phase LC mode, the phases were evaluated on this point. For example, typical octadecylsilica (ODS) phases (both polymeric and monomeric types) have planarity recognition capability, and therefore triphenylene elutes later than *o*-terphenyl with those phases. However, in a previous work [13], it was found that the typical multi-legged phase 1,3,5-tris(dimethylphenyl) (TP) as shown in Fig. 1B elutes *o*-terphenyl later than triphenylene. Therefore, it appeared that this phase has strong molecular non-planarity recognition capability based on the molecular-molecular interaction between the phase and the solutes. In this work, we will describe the preliminary experimental results of the separation of C<sub>60</sub> and C<sub>70</sub> by the novel multi-legged phenyl group bonded phases which use a different space cavity to recognize differences in the size and shape of C<sub>60</sub> and C<sub>70</sub>.

## EXPERIMENTAL

The LC system consisted of a JEOL CAP-G03 intelligent cascade pump (Tokyo, Japan) with a Model GAP G02 control unit, a Kontron capillary LC detector 433 (Amsterdam, Netherlands) and a Rheodyne injector 7513 (Cotati, CA, USA) of 0.5  $\mu$ l volume.

The multi-legged phenyl group bonded phases were synthesized using reactions developed in our laboratory [13]. Base silica was obtained from Shiseido (Yokohama, Japan). The particle diameter is *ca.* 5  $\mu$ m and very few metal impurities are present. The surface area of the silica is *ca.* 270 m<sup>2</sup>/g. These new materials are *p*-bis(dimethyldiphenyl) (BP); TP; and 1,1',1''-tris(dimethylquaternaryphenyl) (QP) bonded silicas.

For comparison, polymeric ODS (Vydac 201 TPB5 [10,11], Separations Groups, Hesperia, CA, USA), which is considered to have a strong molecular planarity recognition capability, was also evaluated. Because of its polymeric nature, the "slot-adsorption" model proposed by Wise and Sander [9] is rationalized, and because fullerenes such as C<sub>60</sub> and C<sub>70</sub> are sterically bulky, non-planar compounds the separation of C<sub>60</sub> and C<sub>70</sub> on the Vydac column is not expected to be better than on monomeric ODS phases and on the "multi-legged" phases. A monomeric-type ODS phase, Develosil-ODS, was also evaluated.

The synthesized phases were evaluated by cross-polarization magic angle spinning (CP-MAS) solid-state NMR spectroscopic measurements and Fourier-transform IR measurements. As shown in Fig. 1, TP, BP and QP phases have a unique structure which covers the silica surface horizontally, while the ODS phase is attached vertically to the silica surface by siloxane bonding.

All the phases were packed into fused-silica capillaries of 100–150 mm  $\times$  0.53 mm I.D. by a slurry technique. The mobile phase system was *n*-hexane. The sample probe C<sub>60</sub> and C<sub>70</sub> were obtained from a soot extract.

## RESULTS AND DISCUSSION

The molecular sizes of C<sub>60</sub> and C<sub>70</sub> are approximately 8 Å  $\times$  8 Å with the carbon atoms arranged like a soccer ball and 10 Å  $\times$  7 Å like a rugby ball, respectively, as shown in Fig. 2. Therefore, one would expect that the space size of the TP phase (the size of the space is *ca.* 5 Å  $\times$  5 Å), in which methyl groups and one phenyl ring form the cavity, would not be able to accept either solute, and thus the retention behaviour should be almost similar for both. The experimental results clearly agree with this hypothesis. With the BP phase, in contrast, the size

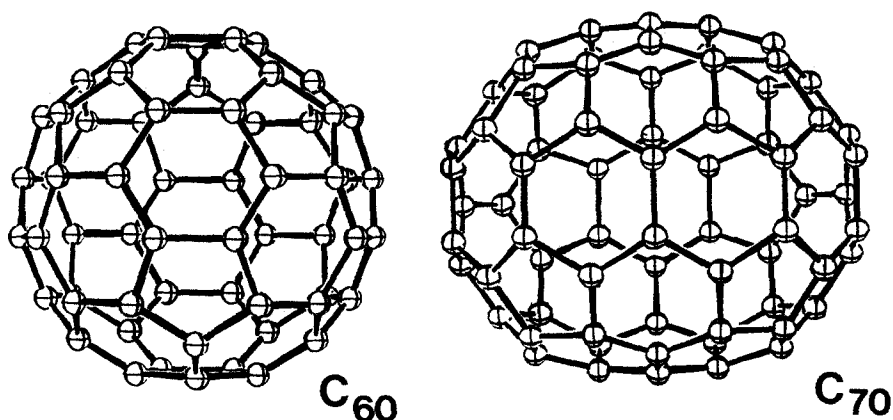


Fig. 2. Structures of  $C_{60}$  and  $C_{70}$ .

of  $C_{70}$  fits well into the pan-like space of the phase, while  $C_{60}$  is not large enough to fit well in the space, because the BP phase has *ca.* 11 Å between the methyl groups bonded to both silicon atoms. Therefore,  $C_{70}$  should have a longer retention than  $C_{60}$  with the BP phase. The result shown in Fig. 3A indicates excellently that this expectation is true. Also, as both solutes are retained because of the interaction between the BP phase and the solutes in the sense of molecular recognition, the BP phase clearly offers a large relative retention of the solutes and large capacity factors for both solutes. The interpretation of these results also means that the concept of this molecular-molecular interaction is useful in the design of new stationary phases which offer specific and/or selective separation of other fullerenes such as  $C_{76}$ ,  $C_{78}$  and others which are thought to exist in soot extracts. In addition to those

two phases, the QP phase was also tested. However, the space in this phase is too large to catch both solutes on its flat phenyl ring surface and, therefore, the phase cannot retain and recognize well the size difference between  $C_{60}$  and  $C_{70}$ . The experimental result with the QP phase shown in Table I suggests that this mechanism is present, although Cox *et al.* [9] and Hawkins *et al.* [12] suggested that a  $\pi$ - $\pi$  interaction mechanism should be useful for the separation of  $C_{60}$  and  $C_{70}$ .

In Table I, the retention data obtained by various separation systems are summarized. It is apparent that the BP phase gave very high separation factor values with an *n*-hexane mobile phase system. With the polymeric ODS phase, although high separation factor values can be obtained, the absolute retention value is not large enough for a good separation. As expected, monomeric ODS, Develosil, offered a

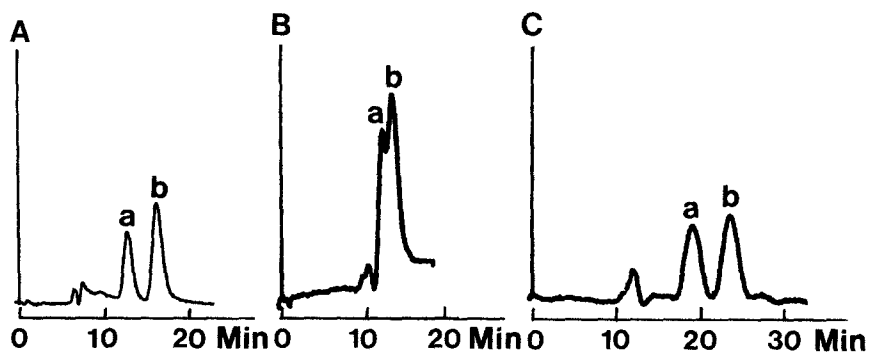


Fig. 3. Chromatograms for the separation of  $C_{60}$  and  $C_{70}$ . (A) BP, (B) Vydac, (C) Develosil. Mobile phase: *n*-hexane, 2  $\mu$ l/min. Peaks: a =  $C_{60}$ ; b =  $C_{70}$ .

TABLE I  
CAPACITY FACTORS AND SEPARATION FACTORS  
FOR C<sub>60</sub> AND C<sub>70</sub> WITH VARIOUS STATIONARY  
PHASES

Mobile phase: *n*-hexane at room temperature.

Stationary phase	Capacity factor		Separation factor
	C <sub>60</sub>	C <sub>70</sub>	
P	0.302	0.396	1.31
TP	0.107	0.126	1.18
BP	0.752	1.223	1.63
QP	No retention		
Vydac	0.171	0.284	1.66
Develosil	0.585	0.962	1.65

better separation factor than Vydac with larger capacity factors. Therefore, it is also possible to conclude that if one would like to use ODS phases for the separation of fullerenes, monomeric ODS should be a more feasible and better stationary phase. It should be mentioned here that the Vydac phase is a very powerful stationary phase for the separation of polycyclic aromatic hydrocarbons based on its high molecular planarity recognition capability [10,11]. Fig. 3 compares the separation of C<sub>60</sub> and C<sub>70</sub> with the BP phase (Fig. 3A), Vydac (Fig. 3B) and Develosil (Fig. 3C) with *n*-hexane as the mobile phase. The separation with Vydac is not very good because of the low retention of the compounds. However, this is not because of the low surface area of this phase.

It should also be mentioned here that separation of actual soot extracts yielded a number of fullerenes larger than C<sub>70</sub>, and the identification of those compounds is in progress.

In conclusion, the molecular-molecular interaction mechanism with multi-legged phenyl group bonded phases can achieve higher separation capability for these all-carbon compounds. Although the

separation obtained with the BP phase is not better than those reported phases discussed in the first part of this article, it has been shown that the BP phase can be useful as the stationary phase for preparative work because it offers larger retention and separation factor for C<sub>60</sub> and C<sub>70</sub>. For the separation of larger fullerenes such as C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub> one can use the concept of the multi-legged phases to design more suitable stationary phases which have an appropriate cavity size to catch the fullerenes once the size and shape of those compounds are found by computer calculations. Such work is under way in our laboratory.

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