

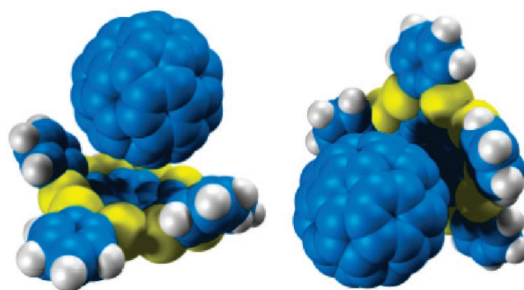
Concave Polyarenes with Sulfide-Linked Flaps and Tentacles:
New Electron-Rich Hosts for Fullerenes

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Pentakis(1,4-benzodithiino)corannulene (**6**) in CS₂ formed the strongest 1:1 complexes with C₆₀ and C₇₀ of any corannulene derivative yet reported. The 1,3,5,7,9-pentakis(propylthio)corannulene (**4b**) formed weaker 1:1 complexes with C₆₀ and C₇₀ in CS₂, whereas the decakis(propylthio)-corannulene (**5b**) and unsubstituted corannulene (**1**) showed no evidence for complexation with either C₆₀ or C₇₀ in CS₂.

Introduction

The concave surface of corannulene (**1**) has almost exactly the right degree of curvature to bring all 20 carbon atoms of the polyarene bowl into contact with the more steeply curved convex surface of C₆₀, when allowance is made for the van der Waals thickness of the two π -systems (Figure 1).¹ Such geometric complementarity looks ideal for a “contact lens” style supramolecular association of corannulene and substituted corannulene with the parent C₆₀ and its functionalized derivatives. A significant binding constant would be expected, however, only if the two surfaces exert some level of electronic attraction toward one another. Indeed, such a π -donor/ π -acceptor interaction ought to exist. The electron-deficient nature of the convex C₆₀ surface (good π -acceptor) has been amply demonstrated by the ease with which nucleophiles add (e.g., cyanide ion), by the ability of C₆₀

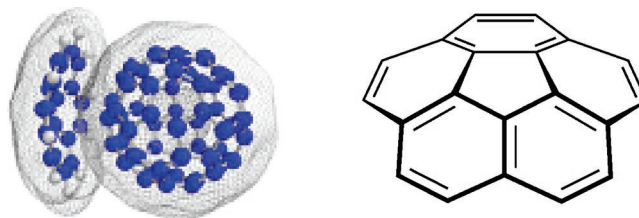


FIGURE 1. Corannulene (C₂₀H₁₀). Left: Molecular modeling of van der Waals contact with C₆₀. Right: Structural formula.

to serve as a dienophile toward electron-rich dienes (e.g., anthracene), and by the propensity of C₆₀ to form complexes with electron-rich metals (e.g., Pt(PEt₃)₂). Concave π -surfaces, by contrast, are calculated to exhibit electrostatic potentials that are even more negative (good π -donor) than those of their planar counterparts.²

Our initial studies³ in this area revealed that corannulene derivatives **2a**, **2b**, and **3** all form supramolecular complexes with C₆₀ in toluene-*d*₈ ($K_{\text{assoc}} = 2.8\text{--}4.5 \times 10^2$

(2) (a) Klärner, F.-G.; Panitzky, J.; Preda, D.; Scott, L. T. *J. Mol. Mod.* **2000**, *6*, 318–327. (b) Ansems, R. B. M.; Scott, L. T. *J. Phys. Org. Chem.* **2004**, *17*, 819–823.

(3) Mizyed, S.; Georghiou, P.; Bancu, M.; Cuadra, B.; Rai, A. K.; Cheng, P.; Scott, L. T. *J. Am. Chem. Soc.* **2001**, *123*, 12770–12774.

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[§] Boston College.

(1) (a) The C–C distance between adjacent layers of graphite is 3.35 Å: Franklin, R. E. *Acta Crystallogr.* **1951**, *4*, 253–261. (b) The shortest C–C distance between adjacent molecules of C₆₀ in the crystal is 3.11 Å: Buerger, H. B.; Blanc, E.; Schwarzenbach, D.; Liu, S.; Lu, Y. J.; Kappes, M. M.; Ibers, J. A. *Angew. Chem., Int. Ed.* **1992**, *31*, 640–643.

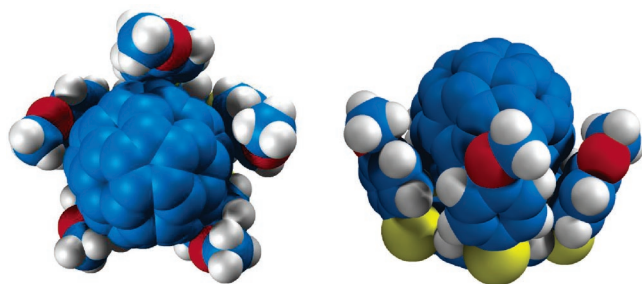
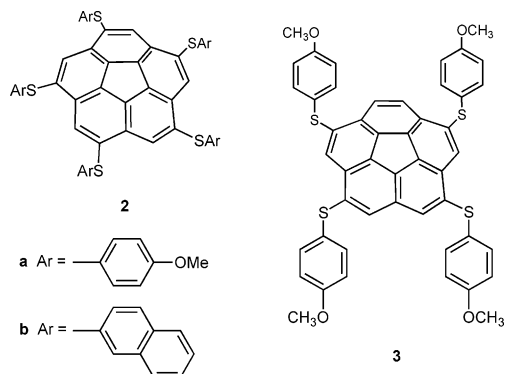


FIGURE 2. Top (left) and side (right) views of corannulene derivative **2a** embracing C_{60} with maximal contact (hypothetical structures; not an X-ray).

M^{-1}). For the strongest of these complexes, **2a**: C_{60} , a downfield shift in the 1H NMR signal for the *para*-methoxy groups at the termini of the five appendages suggests that the arms swing up and embrace the C_{60} , either all at once (Figure 2) or in combinations that rapidly equilibrate.

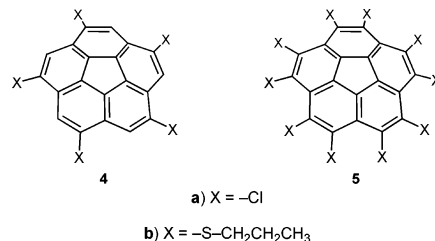


The new studies reported here were designed to probe (a) whether the aryl groups on the arms actually play a critical role in the binding, (b) to what extent the number of sulfur atoms attached to the corannulene core affects the strength of the binding, and (c) whether C_{70} will be attracted with a greater or a lesser affinity than C_{60} to such corannulene hosts. As discussed below, new insights into the steric requirements for these convex–concave supramolecular associations have also been brought to light.

Results

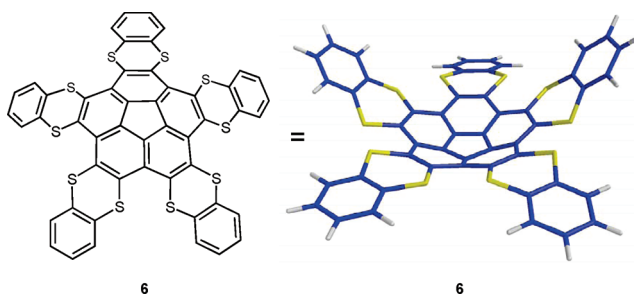
To learn whether the pendant aryl groups are required for complexation of C_{60} by the corannulene derivatives **2a**, **2b**, and **3**, the 1,3,5,7,9-pentakis(S- $CH_2CH_2CH_3$) derivative (**4b**),⁴ which lacks electron-rich π -systems on the arms but retains the geodesic polyarene core and the five attached sulfur atoms, was tested. Decakis(1-propylthio)corannulene **5b**,⁴ a poly(alkylthio) derivative with twice the number of sulfur atoms attached to the corannulene core, was also tested. Preliminary attempts to synthesize the corresponding pentakis- and decakis-(methylthio)corannulenes (**4** and **5**, X = SMe) gave products that were too insoluble to use in the subsequent NMR titration experiments, but the 1-propylthio chains were found to impart acceptable levels of solubility. The pentakis- and decakis(alkylthio)corannulenes with *n*-hexyl and *n*-dodecyl chains⁴ show even greater solubility

in organic solvents, but **4b** and **5b** were the only poly-(alkylthio) derivatives used for complexation studies.



Structures of 4a,b and 5a,b

The conformational motions that are available to the five flexible flaps on the poly(arylthio)- host with 10 sulfur atoms on the corannulene core, pentakis(1,4-benzodithiino)corannulene (**6**),⁴ resemble those of a Venus fly trap,⁵ and this compound emerged as the best host for fullerenes among all the corannulene derivatives we have studied to date. Per(arylthio)aromatic compounds have previously been observed to complex guests in the solid state;⁶ however, the complexes reported here are the first of their kind to be studied in solution.



Complexation Studies

The solubilities of pentakis(propylthio)-corannulene (**4b**), “fly trap”-corannulene (**6**), and of C_{60} and C_{70} (2.99 – 4.44×10^{-3} and 1.27 – 1.70×10^{-3} M, respectively)⁷ were too low in toluene- d_8 to allow for the unambiguous determinations of K_{assoc} values on the basis of 1H NMR complexation-induced chemical shifts. Preliminary 1H NMR titration experiments⁸ in toluene- d_8 at the low concentrations imposed by these solubility limitations revealed only very small chemical shift differences ($\Delta\delta$). Attempts to determine either the complexation stoichiometries or association constants (K_{assoc}) by UV–vis spectroscopic titration experiments at these low concentrations in toluene were also equivocal, since both host and guest molecules are colored, making the unambiguous assignment of any charge-transfer bands difficult.

(4) Bancu, M.; Rai, A. K.; Cheng, P.-C.; Gilardi, R. D.; Scott, L. T. *Synlett* **2004**, 173–176.

(5) Very recently, a revealing study of the mechanism of action of the Venus flytrap (*Dionaea muscipula*) entitled *How the Venus Flytrap Snaps* was reported: Forterre, S.; Skotheim, J. M.; Dumais, J.; Mahadevan, L. *Nature* **2005**, 433, 421–425.

(6) (a) Henderson, R. K.; MacNicol, D. D.; McCormack, K. L.; Rowan, S. J.; Yufit, D. S. *Supramol. Chem.* **1998**, 10, 27–32. (b) Downing, G. A.; Frampton, C. S.; Gall, J. H.; MacNicol, D. D. *Angew. Chem., Int. Ed.* **1996**, 35, 1547–1549.

(7) Tables 2.1 and 2.2. in: *Fullerenes: Chemistry, Physics and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; John Wiley & Sons: New York, 2000; pp 55–56.

(8) Fielding, L. *Tetrahedron* **2000**, 56, 6151–6170.

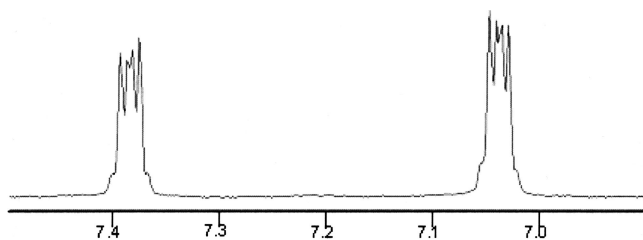


FIGURE 3. ^1H NMR of **6** showing the AA'BB' multiplets.

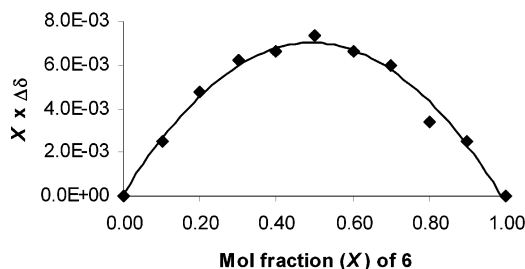


FIGURE 4. Job plot showing the 1:1 stoichiometry of C_{60} vs **6**.

In carbon disulfide, however, the solubilities of both the host molecules and the fullerenes employed in this study are higher: e.g., C_{60} and C_{70} in CS_2 have solubilities that are reported to be in the range of $7.2\text{--}16.4 \times 10^{-3}$ and $11.8\text{--}18.2 \times 10^{-3}$ M, respectively.⁷ CS_2 therefore became our solvent of choice; the concentrations of **4b** and **6** in CS_2 used in the ^1H NMR studies reported herein were both approximately 7.9×10^{-4} M. The use of CDCl_3 as an external lock was not suitable, as it did not provide a sufficiently stable lock and required long instrumental time usage in order to obtain the best precision for determining the chemical shift changes. When used as an internal lock, up to 20% v/v of CDCl_3 in the CS_2 was needed to achieve a stable lock and observe chemical shifts with an acceptable level of precision of ± 0.001 ppm from repeat measurements. At these elevated concentrations of CDCl_3 , however, the solubilities of both C_{60} and C_{70} were compromised (e.g., the solubility of C_{60} fullerene in chloroform is reported to be only in the range $0.22\text{--}0.71 \times 10^{-3}$ M). A far superior external lock was achieved with $\text{DMSO-}d_6$, which contains a higher percentage of deuterium per mole (14.4%) than does CDCl_3 (1.67%). All of the experimental results reported herein and presented in Figures 3–7 were therefore conducted in CS_2 solution using $\text{DMSO-}d_6$ as the external lock.

Complexation Studies of 6 with C_{60} and C_{70} :
(a) With C_{60} . The ^1H NMR spectrum of **6** (Figure 3) consists of only the orthophenylene ring hydrogen atoms, which appear as a pair of AA'BB' multiplets with four main overlapping signals each, one set having chemical shifts at $\delta = 7.393, 7.384, 7.382,$ and 7.374 ppm and the other at $\delta = 7.045, 7.139, 7.034,$ and 7.027 ppm. A Job plot (“method of continuous variation”)⁹ was employed to determine the stoichiometry of the complexation between **6** and C_{60} (Figure 4). As well, a subsequent mole ratio plot of $\Delta\delta$ versus guest-to-host molar ratios confirmed the 1:1 stoichiometry.

Preliminary experiments were conducted next to determine the optimum solution concentration ranges on the basis of the Job plot and mole ratio plot observations. The most consistent data were obtained when C_{60} or C_{70}

was added as a solid aliquot to solutions of **6** in NMR tubes followed by sonication to ensure complete dissolution. Two final determinations were then conducted, one in which the mole ratios of C_{60} to **6** ranged from 0.36 to 3.74 (“low ratios” in which $[\mathbf{6}] \sim 7.86 \times 10^{-4}$ M) and another in which the mole ratios of C_{60} to **6** ranged from 9.9 to 29.8 (“high ratios” in which $[\mathbf{6}] \sim 1.05 \times 10^{-4}$ M). These experiments yielded similar K_{assoc} values, which when averaged were 1420 ± 64 and 1420 ± 54 M^{-1} , respectively (Table 1, entries 1 and 2; Figures 5a and 5b, respectively), as determined by the double-reciprocal or “Benesi–Hildebrand” (B–H)¹⁰ data treatment and Scatchard–Foster–Fyfe (F–F) modification.^{8,11}

(b) With C_{70} . With C_{70} and **6**, the 1:1 stoichiometry was established via mole ratio plots, and the K_{assoc} values for this system were 1110 ± 92 and 1060 ± 24 M^{-1} , determined in a manner similar to that used with C_{60} (Table 1, entries 3 and 4; and Supporting Information).

Complexation Studies of 4b with C_{60} and C_{70} :

(a) With C_{60} . The stoichiometry of the complexation between pentakis(propylthio)corannulene (**4b**) and C_{60} or C_{70} in both cases was found also to be 1:1. Their K_{assoc} values, however, were significantly lower than those observed with **6**: average values of only 62 ± 23 and 53 ± 6 M^{-1} (Table 1, Entries 5 and 6, and Figures 6a and 6b, respectively) were obtained from the double (B–H) and single reciprocal (F–F) treatments, respectively, for the C_{60} :**4b** complexation. Slightly higher values were obtained from the determinations conducted using the lower C_{60} :**4b** mole ratios (i.e., 0.70–3.51). As is well-known, the B–H treatment, gave the higher correlation coefficient and K_{assoc} values for the linear plot since it tends to overemphasize smaller chemical shift changes. With the higher C_{60} :**4b** mole ratios (i.e., 10.4–35.6), the agreement between the K_{assoc} values obtained from the B–H and F–F treatments was closer (45 ± 4 and 49 ± 4 M^{-1} , respectively), as compared with 69 ± 12 and 58 ± 9 M^{-1} , as obtained with the lower C_{60} :**4b** mole ratios.

(b) With C_{70} . The K_{assoc} values for the C_{70} :**4b** complexation determined by the B–H and F–F treatments gave smaller K_{assoc} average values of 90 ± 16 and 94 ± 19 M^{-1} (Table 1, entries 7 and 8). Slightly higher K_{assoc} values were obtained for the complexation between C_{70} and **4b** as compared with C_{60} , which is just the reverse of what was seen with **6**. Figures 7a and 7b show the chemical shift changes ($\Delta\delta$) of the protons of the **4b** host as functions of added C_{60} and C_{70} guests, respectively. The largest (absolute) $\Delta\delta$ changes are observed for the protons on the corannulene ring, followed by those on the propyl methylene group β to the sulfur atom, then by the protons on the propyl methyl group, and finally by the protons on the propyl methylene group α to the sulfur atom. All of the association constants reported herein were deter-

(9) Job, P. *Ann. Chim.* **1928**, *9*, 113–203.

(10) (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Tsukube, H.; Furuta, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. In *Comprehensive Supramolecular Chemistry*; Davies, J. E. D., Ripmeester, J. A., Eds.; Elsevier Science, Oxford, 1996; Vol. 8, pp 425–482.

(11) Foster, R.; Fyfe, C. A. *J. Chem. Soc., Chem. Commun.* **1965**, 642. For a discussion of the relative advantages of employing the Foster–Fyfe modification to the Benesi–Hildebrand treatment of complexation data obtained from ^1H NMR studies, see ref 8.

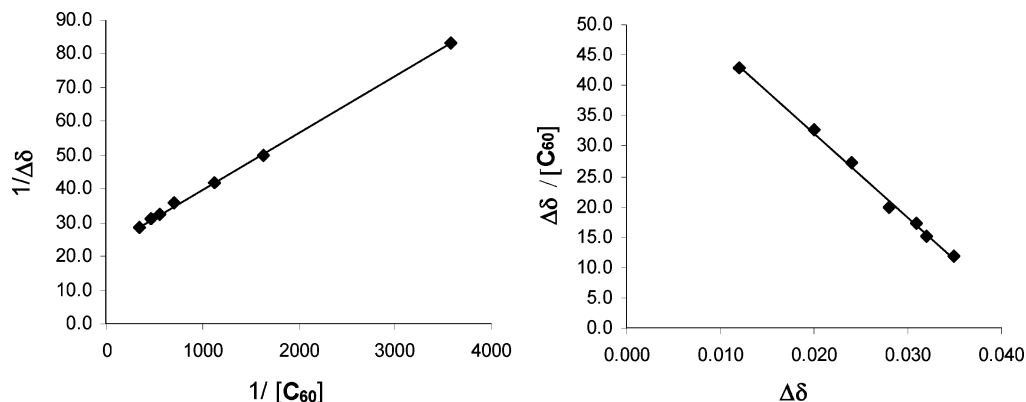


FIGURE 5. (a) Benesi–Hildebrand and (b) Foster–Fyfe plots for the complexation of C_{60} and **6** (Note: chemical shift changes are to higher fields).

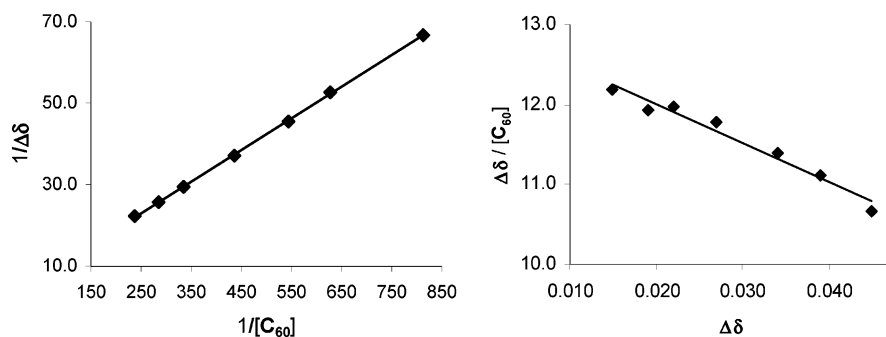


FIGURE 6. (a) Benesi–Hildebrand and (b) Foster–Fyfe plots for the complexation of C_{60} and **4b**. Note: chemical shift changes were to higher fields.

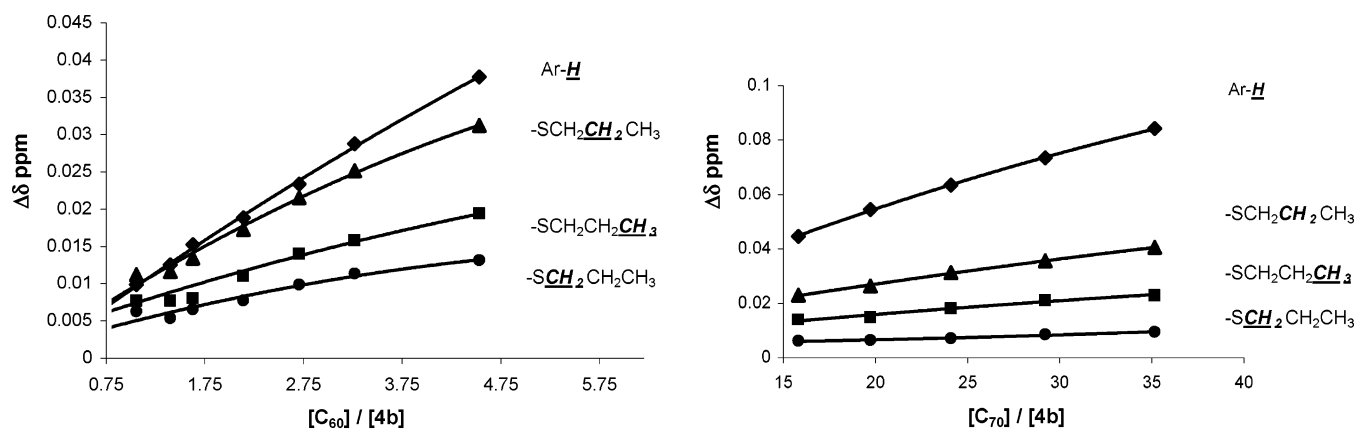


FIGURE 7. Plots showing absolute values of chemical shift changes ($\Delta\delta$) of the various protons on **4b** (a) as a function of added C_{60} (left) and (b) as a function of added C_{70} (right). (Note: the chemical shifts for the corannulene protons (Ar-H) in both cases were to higher fields, whereas all other shifts were to lower fields.)

mined using the values obtained from the largest chemical shift changes.

Complexation Studies of **1 and **5b** with C_{60} and C_{70} .** When similar complexation studies were conducted using C_{60} and C_{70} with unsubstituted corannulene (**1**) and with decakis(propylthio)corannulene (**5b**) in CS_2 , no indication for complexation could be seen in these cases.

Discussion of Results and Conclusions

Our earlier study of the complexation of substituted corannulenes **2a**, **2b**, and **3**, and of corannulene **1** itself, with C_{60} and C_{70} had been conducted in toluene- d_8 .³ It is well-known that the effect of the solvent used in com-

plexation studies may have a significant effect on the binding constants.¹² We therefore decided to conduct an additional complexation study of **2b** in CS_2 with C_{60} and C_{70} in order to make some comparisons with the earlier study. This compound is representative of the compounds previously reported since it had K_{assoc} values of approximately 360 M^{-1} for binding with C_{60} in toluene- d_8 .³ In the present study using CS_2 as the solvent, values of 320 ± 25 and $296 \pm 21\text{ M}^{-1}$ for the complexation of **2b** and C_{60} were obtained using the B–H and F–F methods, respectively (Table 1, entries 9 and 10). Within

(12) Mizyed, S.; Georghiou, P. E.; Ashram, M. *J. Chem. Soc., Perkin Trans. 2* **2000**, 277–280 and references therein.

TABLE 1. K_{assoc} (M^{-1}) for C_{60} and C_{70} Complexes with **4b**, **6**, and **2b** in CS_2 at 298 K^a

entry	complex	run 1		run 2		averages
		method ([G]/[H])	K_{assoc} (r^2)	method ([G]/[H])	K_{assoc} (r^2)	
1	C_{60} : 6	B–H (0.36–3.74)	1373 ± 17 (0.999)	B–H (9.90–29.8)	1462 ± 27 (0.991)	1420 ± 64
2	C_{60} : 6	F–F (0.36–3.74)	1384 ± 38 (0.996)	F–F (9.90–29.8)	1460 ± 94 (0.980)	1420 ± 54
3	C_{70} : 6	B–H (0.29–3.43)	1040 ± 48 (0.996)	B–H (0.37–3.29)	1170 ± 46 (0.998)	1110 ± 92
4	C_{70} : 6	F–F (0.29–3.43)	1042 ± 52 (0.990)	F–F (0.37–3.29)	1076 ± 60 (0.985)	1060 ± 24
5	C_{60} : 4b	B–H (0.70–3.51)	69 ± 12 (0.999)	B–H (10.4–35.6)	45 ± 4 (0.999)	62 ± 23
6	C_{60} : 4b	F–F (0.70–3.51)	58 ± 9 (0.901)	F–F (10.4–35.6)	49 ± 4 (0.968)	53 ± 6
7	C_{70} : 4b	B–H (0.53–3.96)	78 ± 5 (0.999)	B–H (10.7–37.1)	101 ± 6 (0.999)	90 ± 16
8	C_{70} : 4b	F–F (0.53–3.96)	80 ± 3 (0.991)	F–F (10.7–37.1)	107 ± 6 (0.986)	94 ± 19
9	C_{60} : 2b	B–H (0.35–3.13)	302 ± 13 (0.999)	B–H (0.34–3.90)	338 ± 19 (0.999)	320 ± 25
10	C_{60} : 2b	F–F (0.35–3.13)	281 ± 19 (0.993)	F–F (0.35–3.90)	311 ± 13 (0.976)	296 ± 21
11	C_{70} : 2b	B–H (0.71–3.91)	84 ± 9 (0.999)	B–H (1.07–4.71)	113 ± 12 (0.999)	99 ± 20
12	C_{70} : 2b	F–F (0.71–3.91)	89 ± 10 (0.956)	F–F (1.07–4.71)	105 ± 10 (0.971)	97 ± 11

^a For the concentrations of host and guest compounds employed, see Supporting Information.

experimental error, these values cannot be considered to be significantly different from those found in toluene- d_8 . The K_{assoc} values for **2b**: C_{70} in CS_2 are also listed in Table 1, but these had not previously been measured in toluene- d_8 .

For **4b**, the complexation-induced chemical shift changes for the protons on the corannulene ring were to higher (upfield) fields, as they also were for the corannulene protons on **2a**, **2b**, and **3**.³ A similar shielding effect by the respective fullerene on these protons upon complexation of **4b** with C_{60} and C_{70} could therefore also account for the observations made in the present study. This would indicate that an inclusion analogous to that depicted in Figure 2 for C_{60} with **2a** occurs with C_{60} (or C_{70}) with **4b**, in which the corannulene protons are those which have the closest contact with the fullerenes that have been embraced by the propylthio pendants.

The trends in chemical shift changes for the propylthio group protons in **4b** with either C_{60} or C_{70} were very similar, as can be seen in Figures 7a and 7b. It is somewhat puzzling, however, that with both C_{60} and C_{70} , it is the protons on the $-\text{CH}_2-$ groups that are β to the sulfur atoms that experience the largest downfield shifts. This could be due to two opposing effects: although it would be expected that the protons on the $-\text{CH}_2-$ groups α to the sulfur atoms would experience a deshielding effect due to an enhanced electron-withdrawing effect of the sulfur atoms interacting with the complexed electron-deficient fullerenes, there would be a corresponding opposing shielding effect due to the proximity of these protons to the same embedded or embraced fullerenes. The methyl groups are situated relatively more remotely and behave in a manner similar to what was previously observed in the cases of **2a** and **3**.

The higher average K_{assoc} values obtained for the 1:1 complexation of **4b** with C_{70} vs C_{60} in the present study (Table 1, entries 7 vs 5 and 8 vs 6) suggest that the

propylthio appendages can more effectively embrace the more cylindrically shaped C_{70} molecule than they are able to with C_{60} . The relatively larger chemical shift differences in the corannulene ring protons in the case of the C_{70} :**4b** complex versus those seen with the C_{60} :**4b** complex further support the contention that C_{70} forms the more deeply embedded complex of the two.

As indicated above, no evidence for complexation was found with either fullerene with unsubstituted corannulene (**1**) or with the decakis-propylthio compound **5b**. Apparently, the bare face of the parent hydrocarbon (**1**) without any sulfur atoms attached is not a strong enough π -donor to complex neutral fullerenes. In the case of decakis(propylthio)corannulene (**5b**), on the other hand, a doubling of the electron-rich sulfur atoms from 5 to 10 might have been expected to enhance the binding capability toward the electron-deficient C_{60} and C_{70} fullerenes. A binding enhancement toward C_{60} had been observed in our previous study³ with **2a**, which has five arylthio appendages, over **3**, which has only four. However, the long side chains on **5b** probably crowd the concave face in order to avoid each other and thereby block access of the fullerene (Figure 8). As well, a larger entropic cost would result from the greater number of degrees of freedom possible in the 10 propylthioether appendages. Both of these factors could inhibit complexation with the fullerenes used under the conditions examined. A similar entropic effect has been noted by Masci¹³ in his complexation studies with homooxacalixarenes and was also proposed by us with “Zorbarene”, a new naphthalene-ring-based receptor that we recently reported.¹⁴

The “fly trap” molecule **6**, on the other hand, shows much higher binding affinities than **4b** for both C_{60} and C_{70} . In contrast to **4b**, however, the larger K_{assoc} values

(13) Masci, B. *Tetrahedron* **2001**, *57*, 2841–2845.

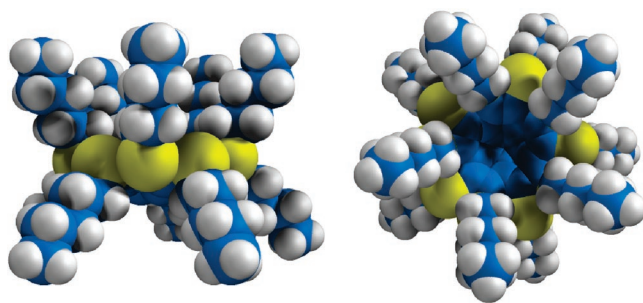


FIGURE 8. Side view (left) and top view/concave face (right) of a space-filling model.

were observed for the C_{60} complexation with **6** than with C_{70} . Possible explanations for both phenomena will be considered: First, a solvophobic effect¹⁵ due to the higher solubility of C_{70} vs C_{60} in CS_2 could account for the higher K_{assoc} values observed, in this case, for the complexation of **6** with C_{60} . Second, even though there are multiple sulfur atoms in both **4b** and **6**, the latter has twice as many and does not have its sulfur atoms encumbered with tetrahedral alkylthio carbon atoms. In the fly trap, the sulfur atoms are connected via orthophenylene rings, which are planar and thus reduce the steric impedance that occurs with the propylthio appendages. Since there are also fewer degrees of freedom of motion in these groups in **6**, there is a considerably smaller entropic cost to overcome in order to bring the sulfur atoms into contact with the surfaces of the respective fullerenes. Finally, the relatively electron-rich orthophenylene rings also can augment binding of the fullerenes within the corannulene bowl through favorable embracing π - π interactions with the surfaces of the fullerene guests. A crystal structure of a clathrate formed between two molecules of **6** embracing a single molecule of benzene⁶ shows the ability of the host to wrap three of the flaps around the entrapped benzene. In this paper, on the basis of both the X-ray data from the above clathrate and modeling studies, it was hypothesized that all five flaps could flex to accommodate a spherical guest. The results from the study reported here would appear to be consistent with this hypothesis.

Experimental Section

General Methods. Carbon disulfide (redistilled, industrial hygiene analysis grade) and buckminsterfullerenes C_{60} (99.5%) and C_{70} (>98%) were purchased and used without further purification. Unless otherwise indicated, 1H spectra were conducted in CS_2 with TMS as internal standard and a $DMSO-d_6$ external lock and recorded in pulse mode at 298 K at 500 MHz, using a 16 K data table for a 10.0 ppm sweep width having a digital resolution of 0.321 Hz. Chemical shifts in the 1H NMR spectra are reported relative to TMS shifts (0.000 ppm).

(14) Tran, A. H.; Miller, D. O.; Georghiou, P. E. *J. Org. Chem.* **2005**, *70*, 1115–1121.

(15) For a discussion of a solvophobic effect on the complexation on related systems with C_{60} see Mizyed, S.; Ashram, M.; Miller, D. O.; Georghiou, P. E. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1916–1919, and references therein.

The chemical shifts used for plotting and data analysis were the mean values of the multiplet signals that were observed. The $DMSO-d_6$ external lock was made by injecting a sample of $DMSO-d_6$ with 5% TMS into a closed-end capillary tube and sealing the open end. For each measurement, the same capillary tube containing the $DMSO-d_6$ was inserted into the NMR tube using a specially designed Teflon insert.

Determination of Stoichiometry. Job plot (method of continuous variation) determinations were conducted by varying the mole fractions of the host compound and C_{60} , using solutions which were approximately 7.86×10^{-4} M in CS_2 solution. After mixing, each of the respective solutions (total combined final volumes = 1.00 mL) in a series of nine NMR tubes was sonicated for approx 10 min and in some cases were then allowed to stand overnight. Job plots were produced by plotting the mole fractions of the host compound against the mole fractions of C_{60} , multiplied by the $\Delta\delta$ values determined for each set of chemical shifts present for both the host and guest molecules. With other samples for which quantities were limited, mole ratio plots of $\Delta\delta$ against [host]/[guest] ratios were determined and in all cases examined either confirmed or indicated the formation of 1:1 complexes.

Association Constant (K_{assoc}) Determinations. The association (stability) constants were determined by 1H NMR spectroscopy.⁸ Changes in the chemical shift ($1/\Delta\delta$) of the aromatic signal of the host as a function of $1/[C_{60}]$ or $1/[C_{70}]$ were determined, and K_{assoc} values were determined using the double reciprocal or Benesi–Hildebrand data treatment or by using the Scatchard–Foster–Fyfe treatment by plotting $\Delta\delta/[C_{60}]$ or $\Delta\delta/[C_{70}]$ versus $\Delta\delta$. In a typical experiment, aliquots of a stock solution of the host (for the C_{60} experiment, approximately 600 μL , 7.86×10^{-4} M; for C_{70} experiment, approximately 600 μL , 7.73×10^{-4} M) were added to NMR tubes; the $DMSO-d_6$ external lock was inserted into the sample, and the reference signals of pure host were recorded. The calculated amounts of solid C_{60} or C_{70} were then added in small portions to the host solutions in the NMR tubes. After each addition, the solutions were sonicated for approximately 10 min. 1H NMR measurements were recorded at 298 K at 500 MHz, as above. Data were analyzed by least-squares regression analyses using Excel and validated according to criteria described by Hirose¹⁶ and Fielding.⁸

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Supporting Information Available: Complexation data summarized in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) Hirose, K. *J. Inclusion Phenom.* **2001**, *39*, 193–209.