Host–Guest Systems

Supramolecular Dynamics of Cyclic [6]Paraphenyleneacetylene Complexes with [60]- and [70]Fullerene Derivatives: Electronic and Structural Effects on Complexation**

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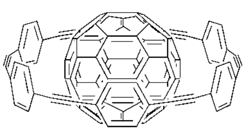
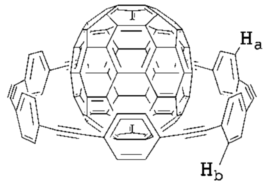
Although a variety of host molecules have been studied extensively to elucidate the inclusion phenomena of buckminsterfullerene C_{60}, the supramolecular properties of other fullerenes, including fullerene derivatives, are not yet well understood.[1–3] In contrast to I_h-symmetrical C_{60}, these other fullerenes are perturbed structurally and electronically. It has been known that the electronic properties of [60]fullerene derivatives correlate well with the electronegativity of the attached atoms.[4] For example, the attachment of electron-positive silicon atoms considerably increase the electron density of the π systems of [60]fullerene derivatives.[4,5] Recently we found that the carbon nanoring **1** (cyclic [6]paraphenyleneacetylene) forms stable inclusion complexes with the fullerenes C_{60}, C_{70}, and $C_{61}(COOEt)_2$ **2** in solution as well as in the solid state.[2b,6] Dynamic ^{1}H NMR spectra have revealed the interesting features of these complexes: 1) the Gibbs activation energies for dissociation ($\Delta G^{\neq}_{\text{dis}}$) provide a reliable measure for evaluating the stability of the fullerene complexes and 2) the center of each fullerene is not aligned with the center of **1**, and the activation energy for vibration of a C_{70} molecule around the center of the cavity is higher than the value for dissociation of the complex, while that of C_{60} is lower. These results can be attributed to the structural difference between C_{60} and C_{70}. The inclusion phenomena of C_{70} have been studied from the viewpoint of purification of fullerenes;[2] however, the difference in the supramolecular properties of C_{60} and C_{70} has not been studied in detail so far. To explore the nature of the curved conjugated systems, and to construct new supramolecular structures based on fullerene derivatives,[7] we have studied the dynamic behavior of the complexes of **1** with several fullerene derivatives (**3**–**10**) including the silylated fullerenes **6** and **7**.[5]



1·C_{60}



1·C_{70}

New methanofullerene derivatives **3**–**5**, **9**, and **10**[8] were prepared in moderate yields by treating the corresponding malonic esters with fullerenes under the conditions used by Camps and Hirsch.[9] The formation and regiochemistry of these new compounds were confirmed by transesterification into the known derivatives **2** and **8**.[10–12]

Fullerene derivatives **3**–**10** form stable inclusion complexes with **1** in CD_2Cl_2 solutions.[13] Figure 1 shows the spectral changes of **1**·**7** and **1**·**9** as typical examples. Similar to the ^{1}H NMR spectra of **1**·**2**,[6b] the spectrum of **1** shows two singlets of equal intensity at −100 °C in the presence of an equal amount of **3**–**7**, but only one singlet at 30 °C. However, one of the aromatic signals of **1** that appears as a singlet in the presence of an equal amount of **8**–**10** at 30 °C begins to broaden at about −20 °C, and two relatively small singlets of equal intensity first appear at about −50 °C. The major signal finally splits into two singlets of equal intensity at −80 °C (Figure 1 b). The spectral changes indicate that the methano[70]fullerene complexes should exist in an equilibrium mixture of two diastereomers (A and B) as shown in Scheme 1. The ratio of the isomers varies with the substituents and temperatures (A:B for **1**·**8** = ca. 9:1, **1**·**9** = ca. 3:1 and **1**·**10** = ca. 9:1 at −80 °C). The NOE experiments of **1**·**9** reveal that the major component is isomer A and the minor one is B. The chemical shifts of the inner protons (H_a and H_c) of both isomers resonate at about 0.4 ppm higher field than those of the outer protons (H_b and H_d) because of the anisotropy effect of the relatively flat midsection of C_{70}. Analysis of the NMR spectra provide one $\Delta G^{\neq}$ value for **1**·**3**–**7** and two $\Delta G^{\neq}$ values for **1**·**8**–**10** (Table 1).

The $\Delta G^{\neq}_{\text{dis}}$ values of C_{60} derivatives are in the order **1** > **2**–**5** > **6** > **7**; the silylated fullerenes **6** and **7** exhibit considerably small values. Fullerenes **6** and **7** have bulky substituents on the silicon atoms, but they have little effect on the complexation, as shown by the $\Delta G^{\neq}$ values of **2**–**5** being almost identical to each other. The results also suggest that the dissociation of the host and guest should occur from the opposite side to the attached group of the fullerene derivatives. Thus, the order of $\Delta G^{\neq}_{\text{dis.}}$ values would correspond to the electronic properties of fullerene π systems. It has been known that the silylated C_{60} derivatives are electron rich,[4,5]

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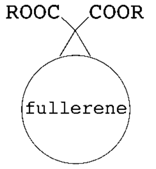
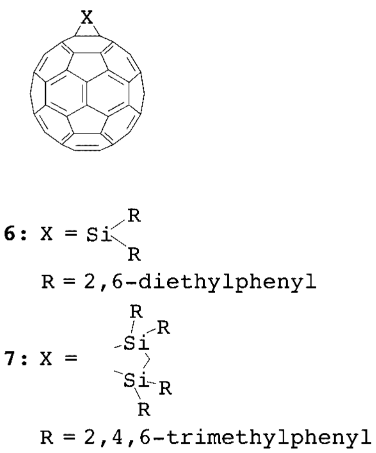


[60]fullerene
2: R = Et
3: R = CH_2(2,4,6-trimethylphenyl)
4: R = CH_2(4-t-butylphenyl)
5: R = CH_2[3,5-di(*t*-butyl)phenyl]

[70]fullerene
8: R = Et
9: R = CH_2(2,4,6-trimethylphenyl)
10: R = CH_2[3,5-di(*t*-butyl)phenyl]



and therefore an electronic repulsion between **1** and **6** (or **7**) may play an important role in weak binding between the host and guest. The results are in good agreement with our previous conclusion.[6b]

Table 1 also shows two $\Delta G^{\neq}$ values for the C_{70} complexes. The lower values are similar to each other and can be assigned to the $\Delta G^{\neq}$ value for dissociation from complex A. The higher values are in the order **8** < **9** ~ **10**. Construction of CPK models revealed that the sizable ester groups of **9** and **10** should act as stoppers for **1**; therefore, the interconversion between complex A and B should occur faster than the dissociation of complex B. Thus, the values of about 11.0 kcal mol^{-1} correspond to the activation energies for the vibration motion of the C_{70} molecule in the cavity of **1**. On the other hand, the smaller value for **1·8** would arise from the simple dissociation of complex B.

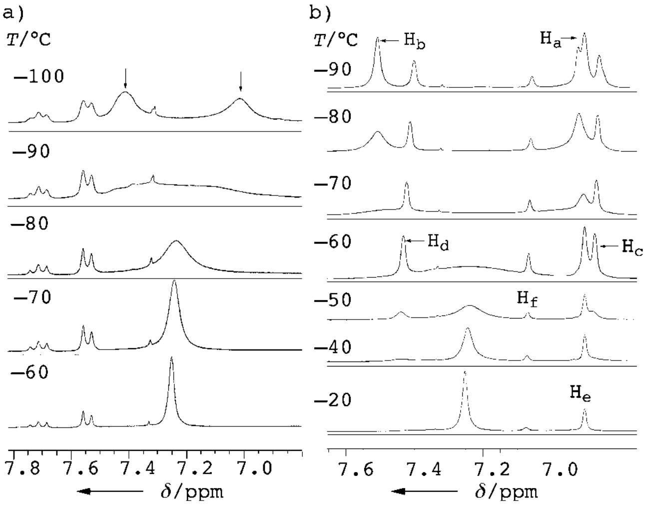


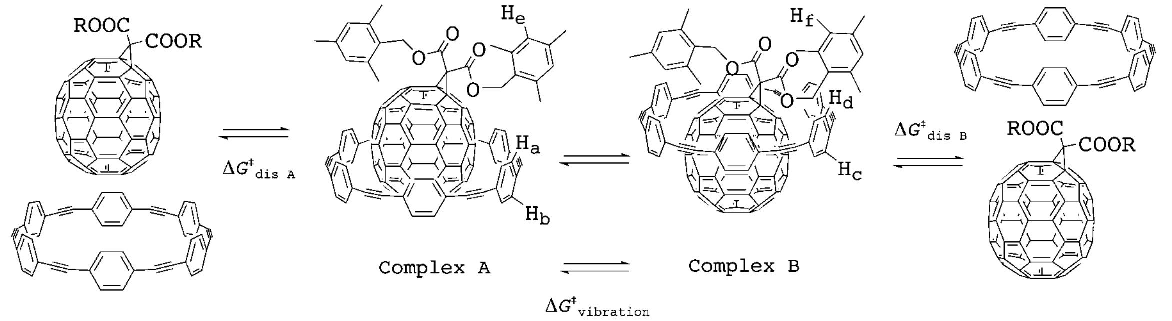
Figure 1. Temperature-variable NMR spectra of an equimolar solution of a) **1** and **7**, and b) **1** and **9**.

Table 1: $\Delta G^{\neq}$ values of complexes with **1**.[a]

Guest	$\Delta G^{\neq}$	Guest	$\Delta G^{\neq}$
C_{60}	9.9 ± 0.2	C_{70}	9.6 ± 0.2
2	9.4 ± 0.2	**8**	9.3 ± 0.1
3	9.2 ± 0.2		10.1 ± 0.1
4	9.3 ± 0.3	**9**	9.4 ± 0.1
5	9.3 ± 0.3		11.1 ± 0.2
6	8.8 ± 0.2	**10**	9.4 ± 0.1
7	8.5 ± 0.2		11.0 ± 0.2

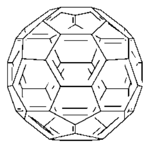
[a] These values were calculated from the observed coalescence temperatures and $\Delta\delta$ values of signals of **1** (kcal mol^{-1}).

The value for the vibration motion of C_{70} is at least 2.5 kcal mol^{-1} higher than that of C_{60} (< 9.0 kcal mol^{-1}). The diameter of the midsection of C_{70} seems identical to that of C_{60}. This fact means that there is some factor at work beyond just the "size" of the fullerene. This factor appears to be "friction" at the molecular level, since there is a greater surface area of contact between the nanoring and the fullerene in the transition state when the ring passes the equator of C_{70} than when it passes the equator of C_{60}. A similar phenomenon was recently reported by Rubin et al. for squeezing helium and dihydrogen into and out of a fullerene through a narrow hole.[14] The present discovery is thus a second example of "molecular friction" and is therefore particularly noteworthy. Moreover, the large barrier as well as

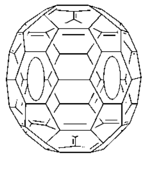


Scheme 1. Schematic representation of the complexation of **1** and methano[70]fullerene derivative, and the model structures of complexes A and B of **1·9**.

the relatively large anisotropy effect would also arise from the electronic properties of the relatively flat midsection of C_{70}. The structure of C_{70} can be illustrated as a combination of two corannulenes and [5]paraphenylene on the basis of the Kekulé resonance hybrid.[15] Thus, C_{70} can be regarded as the smallest member of capped arm-chair [5.5]single-walled carbon nanotubes. The results suggest that there are substantial differences in the electronic properties between C_{60} and carbon nanotubes, and the convex surface of C_{60} would be considerably electron deficient.



C_{60}



C_{70}
resonance hybrid

Furthermore, complexes B can be regarded as fullerene-based pseudorotaxanes. The current results will open the way to the future construction of new supramolecular structures with novel machine characteristics.

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[8] Selected physical and spectral data: **3**: m.p. >300 °C; MS (FAB): m/z 720 ($[C_{60}]^+$, 100); ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta =$ 2.28 (s, 6H), 2.33 (s, 12H), 5.51 (s, 4H), 6.86 ppm (s, 4H). **4**: m.p. 165–166 °C; MS (FAB): m/z 720 ($[C_{60}]^+$, 100); ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta = 1.31$ (s, 18H), 5.43 (s, 4H), 7.35 (AA′BB′, $J_{AB} = 8.3$ Hz, 4H), 7.39 ppm (AA′BB′, $J_{AB} = 8.3$ Hz, 4H). **5**: m.p. 160–161 °C; MS (FAB): m/z 720 ($[C_{60}]^+$, 100); ^{1}H NMR ($CDCl_3$, 270 MHz): $\delta = 1.24$ (s, 36H), 5.41 (s, 4H), 7.21 (d, $J =$ 1.8 Hz, 4H), 7.34 ppm (t, $J = 1.8$ Hz, 2H). **9**: black powder, m.p. 170–171 °C; MS (FAB): m/z 1207 ($[M+H]^+$, 43), 840 ($[C_{70}]^+$, 100); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.25$ (s, 6H), 2.33 (s, 12H), 5.43 (s, 4H), 6.78 ppm (s, 4H). **10**: black powder, m.p. 158–159 °C; MS (FAB): m/z 1347 ($[M+H]^+$, 30), 840 ($[C_{70}]^+$, 100); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (s, 36H), 5.42 (s, 4H), 7.27 (d, $J = 1.8$ Hz, 4H), 7.40 ppm (t, $J = 1.8$ Hz, 2H).

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