

EXTRAORDINARILY LARGE ASSOCIATION CONSTANTS OF AZULENES WITH FULLERENES

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Abstract

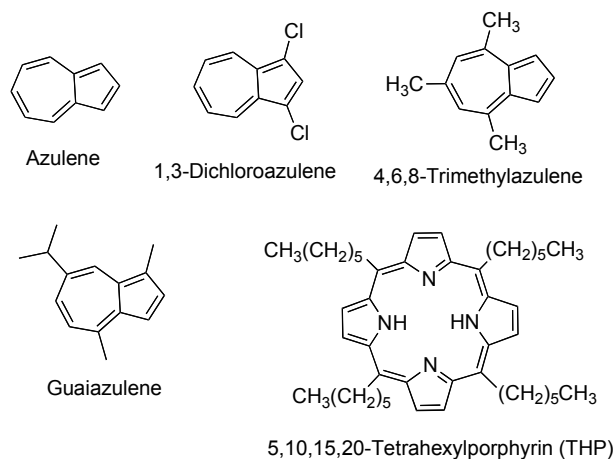
Azulenenes show very large association constants toward fullerenes (C_{60} and C_{70}) in the order of $10^4 - 10^5$, which is similar to and even larger than those of designed host molecules reported so far. They also exhibit almost no selectivity to both C_{60} and C_{70} , which may be attributed to end-on structure of the C_{70} / azulene complex.

Introduction

Fullerene-based supramolecular complexes have attracted much attention from the viewpoint of the separation of fullerenes¹⁻⁵ and the construction of photosynthetic systems and photonic devices.⁶ In light of stability of the complexes, host molecules with concave shape have been designed such as calixarene,^{7, 8} resorcarene,^{9, 10} cyclodextrin¹¹ and carbon nanoring.¹²⁻¹⁴ However, it has been recognized that concave-convex interaction is not always necessary¹⁵ to realize highly stabilized complex since the first finding of remarkably close approach between curved Δ -surface of fullerene and flat Δ -surface of porphyrin in 1997.¹⁶ Actually, porphyrin dimers,¹⁷⁻²² tetramer²³ and hexamer,²⁴ and even very simple monoporphyryns²⁵ show comparable or even larger association constants to fullerenes than the concave host molecules listed above. Such a nonclassical strong Δ - Δ interaction has been known only in the fullerene-porphyrin complexes so far. Here, we describe another example of the strong flat- Δ / curved- Δ interaction between fullerene and azulene having much smaller Δ -conjugate system than porphyrin.

Materials and Methods

Azulenenes²⁶⁻²⁸ and 5,10,15,20-tetrahexylporphyrin (THP)²⁹ shown in Scheme 1 were prepared according to the reported methods. Association constants between fullerenes and azulenes ($K_{C_{60}}$ and $K_{C_{70}}$) were determined by spectral changes on the fluorescence spectra upon the titration of fullerene solution to the azulene solution (Figure 1). The 1 : 1 stoichiometry of the azulene complexes with fullerenes is confirmed by continuous variation plots monitored by fluorescence (Figure 2).



Scheme 1. Structures of azulenes and porphyrin used for the determination of association constants with fullerenes.

Results and Discussion

Azulenes show extraordinarily large association constants ($10^4 - 10^5 \text{ dm}^3 \text{ mol}^{-1}$) and no or low selectivity to C_{60} and C_{70} (Runs 1 – 4 in Table 1). As compared with the host molecules reported so far, the association constants of azulenes are comparable to or larger than those of bridged calixarenes,^{30,31} azacalixpyridines,³² cyclotrimeratrylenes,^{33, 34} and di- and tetraporphyrins.^{17,23} However, they are smaller than the well-designed host molecules such as carbon nanorings,^{12,35} cyclic diporphyrins^{21,22} and hexaporphyrins.²⁴ Among flat Δ -conjugated molecules, azulenes exhibit the largest association constants; the association constants of azulenes (K_{C60} and K_{C70}) are larger than those of monoporphyrins, flat molecule with larger Δ -conjugated system (Run 5).³⁶ Noteworthy is that naphthalene, structural isomer of azulene, and other alternately conjugated aromatics were reported to show much less association constants towards fullerenes ($1 - 500 \text{ dm}^3/\text{mol}$).^{37, 38}

In order to gain insight into the complexation of azulenes with fullerenes, we calculated the energy-minimized structures of the complexes (Figure 3) and the enthalpy of the association (Table 2) by *ab initio* Hartree-Fock method using STO 3-21G* basis set. Surprisingly, end-on structure of C_{70} / azulene complex is more stable than its side-on structure (Run 1 in Table 2). This result is supported by the fact that azulene shows almost the same association constants to C_{60} and C_{70} (Run 1 in Table 1), because the structure in the polar region of C_{70} is the same as that of C_{60} as shown in Figures 3a and b. This complex structure of C_{70} / azulene

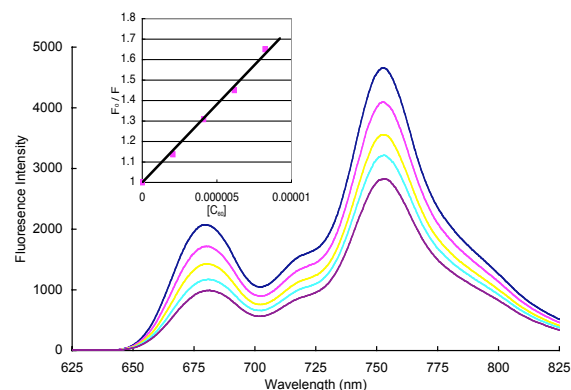


Figure 1. Fluorescence Spectra of azulene ($8.46 \times 10^{-5} \text{ mol/dm}^3$) in the presence of C_{60} ($0 - 8.23 \times 10^{-6} \text{ mol/dm}^3$) in toluene at 298K. Inset: Stern-Volmer plot (correlation coefficient: 0.995).

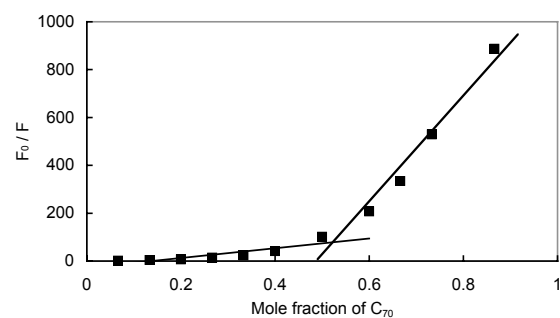


Figure 2. Job's plot of azulene ($1.16 \times 10^{-4} \text{ mol/dm}^3$) and C_{60} ($1.16 \times 10^{-4} \text{ mol/dm}^3$) in toluene on fluorescence ($\lambda_{\text{ex}} = 351 \text{ nm}$)

Table 1. Association constants of azulenes and porphyrins with C_{60} ($K_{C60} / \text{dm}^3 \text{ mol}^{-1}$) and C_{70} ($K_{C70} / \text{dm}^3 \text{ mol}^{-1}$) in toluene at 298 K, and their ratio (K_{C70} / K_{C60}).

Run	Donor	$K_{C60} (\text{dm}^3 \text{ mol}^{-1})$	$K_{C70} (\text{dm}^3 \text{ mol}^{-1})$	K_{C70} / K_{C60}
1	Azulene	7.6×10^4	7.9×10^4	1.0
2	1,3-Dichloroazulene	6.7×10^4	7.3×10^4	1.1
3	4,6,8-Trimethylazulene	1.7×10^5	1.5×10^5	0.88
4	Guaiazulene	5.4×10^3	8.3×10^4	1.5
5	THP	1.7×10^3	1.5×10^4	8.8
6	Naphthalene	0.67^a	11^a	16

^a Determined by UV-VIS spectra.^{37, 38}

is in marked contrast with that of C_{70} / porphyrins, where side-on structures are more stable (Run 2 in Table 2).^{17, 21, 25, 36, 39} The following two reasons are conceivable for the structural difference in the C_{70} complexes of azulene and porphyrin. Since the size of azulenes is much smaller than that of porphyrins, the difference in the contact areas of end-on and side-on complexes of azulenes (ex. azulene / C_{70} (end-on) and azulene / C_{70} (side-on)) is much smaller than that of porphyrins (ex. THP / C_{70} (end-on) and THP / C_{70} (side-on)). On the other hand, azulenes possess both electron donating and accepting character in the five and seven membered rings, respectively. Such an adjacent and opposite electronic character of the two rings is very much suitable for the electrostatic interaction with electron-rich 6 – 6 and electron-deficient 6 – 5 junctures of fullerenes,⁴⁰ giving extraordinarily large association constants. In both complex structures shown in Figures 1a and b, 6 – 6 and 6 – 5 junctures in C_{60} and the polar region of C_{70} face the electron-deficient seven-membered and electron-rich five-membered rings, respectively. However, azulene / C_{70} (side-on) does not form such electronically compensatory interactions so well, resulting in less stable complex than the end-on structure (Run 1 in Table 2).

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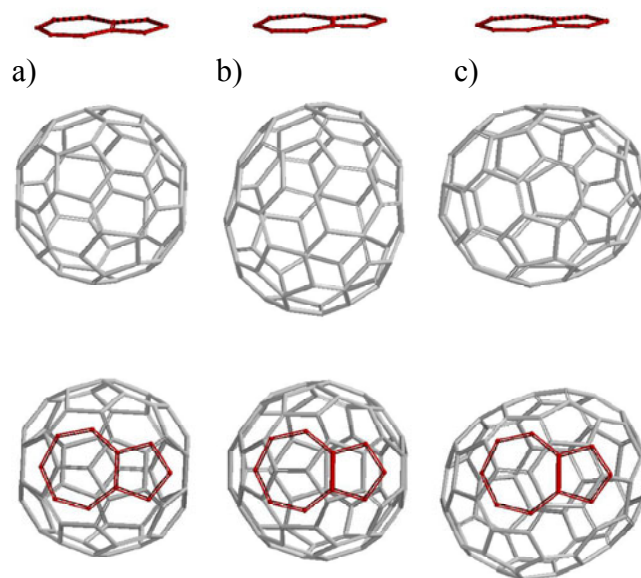


Figure 1. Side- and top-views of energy-minimized structures of azulene with a) C_{60} , b) C_{70} (end-on) and c) C_{70} (side-on). Hydrogen atoms are omitted for clarity.

Table 2. Enthalpy of association (ΔH^0) of azulene and THP with C_{60} and C_{70} (end-on and side-on structures).

Run	Donor	ΔH^0 (kcal/mol ¹)		
		C_{60}	C_{70} (end-on)	C_{70} (side-on)
1	Azulene	-0.148	0.0414	0.0719
2	THP	5.82	5.19	2.31

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