Pergamon

Tetrahedron Letters 43 (2002) 3277–3280

TETRAHEDRON
LETTERS

Creation of nanoscale oxaarenecyclynes and their C_{60} complexes

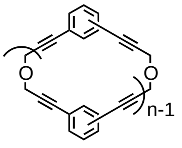
Yoshihiro Yamaguchi,[a] Shigeya Kobayashi,[a] Nobuhiro Amita,[a] Tateaki Wakamiya,[a]
Yoshio Matsubara,[a] Kunihisa Sugimoto[b] and Zen-ichi Yoshida[a,]*

[a]*Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, 577-8502, Japan*
[b]*X-Ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara, Akishima, Tokyo, 196-8666, Japan*

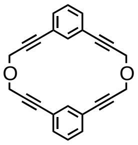
Received 15 February 2002; revised 11 March 2002; accepted 15 March 2002

Abstract—Novel nanoscale oxaarenecyclynes (**3** and **4**) consisting of diethynylbenzene and ether units were synthesized, which form supramolecular complexes with C_{60}. © 2002 Elsevier Science Ltd. All rights reserved.

Geometrically-controlled and shape-persistent macrocycles have attracted much attention. Among them, macrocycles having binding sites inside or outside the cavity are known.[1] However, those which contain binding sites as a macrocyclic ring member are novel and interesting, because they could be useful for examining the problem of recognition of a rigid spherical substrate (e.g. C_{60}) by rigid macrocycles. As such macrocycles, we have designed a novel family of cyclynes (**1**) consisting of diethynylbenzene and ether units, and reported the synthesis and novel Ag^+-induced cyclization of a simple member **2** (*m*-, $n=2$).[2]

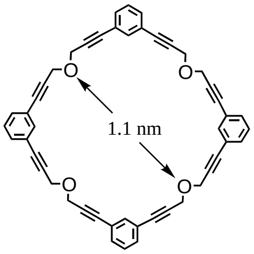


1

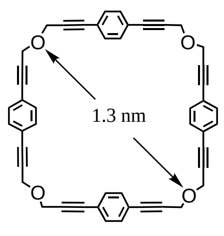


2

The nanoscale oxaarenecyclynes **3** (*m*-, $n=4$) and **4** (*p*-, $n=4$) having a large cavity of this family, in which four oxygen atoms (n-donor) and four benzene rings (π-donor) are alternately arranged, are expected to form supramolecular complexes with a large spherical molecule such as C_{60} based on Yoshida's concept, which regards C_{60} as a transition metal-like superatom,[3] and AM1 calculation. We report here synthesis of **3** and **4** and the formation of supramolecular complexes with C_{60}. Regarding complex formation of C_{60} with oxaarenecyclyne-related macrocycles, some investigations have been made.[4–6]



3



4

For the synthesis of **3** and **4**, we chose the strategy involving Sonogashira Pd coupling[7] as the key step, because employment of the Williamson synthesis in the final step of the synthetic route provided low product yield.[2]

Thus, iodoaniline (**5a**: *m*-, **5b**: *p*-) was converted to a triazene derivative **6**, which had a propargyl alcohol unit introduced by the Pd coupling. The obtained **6** by the reaction with propargyl bromide, led to **7** which is a key compound in this synthetic route. Protection of the terminal acetylene group by the TMS group, followed by conversion of the triazene group into an iodo-group[8] afforded **8**, which is another key compound in this synthetic route, in good yield. The Pd coupling reaction between **7** and **8** provided compound **9**, which was converted to **10** by alkaline hydrolysis on one hand, and to **11** by iodination of the triazene group on the other hand. Treatment of **10** and **11** in the same manner (Sonogashira Pd coupling, iodination and desilylation) as described above afforded the precursor compound **12**. The intramolecular cyclization of **12a** or

---

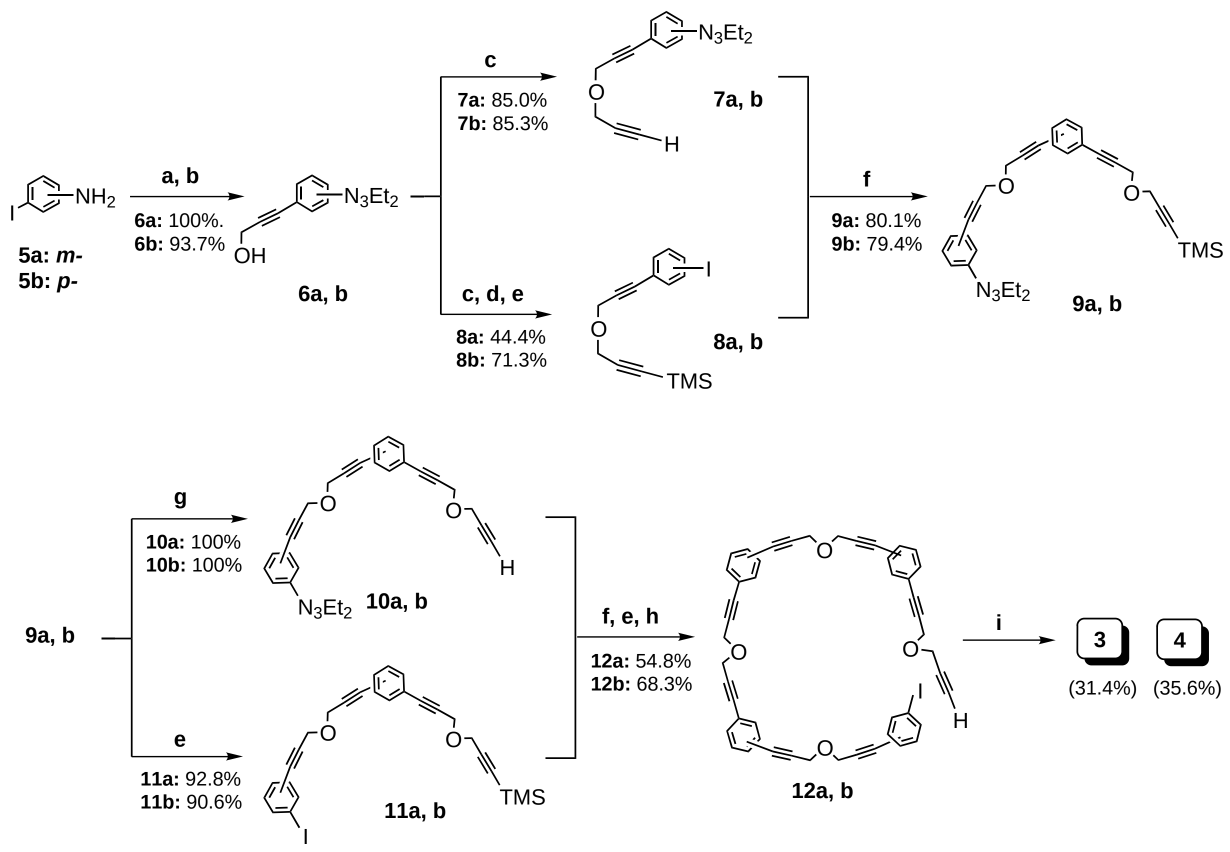
Keywords: coupling reaction; fullerenes; macrocycles; molecular recognition.

* Corresponding author. Tel.: +81-6-6721-2332 (ext. 4121); fax: +81-6-6723-2721; e-mail: yamaguch@chem.kindai.ac.jp

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)00539-7

12b under high-dilution reaction conditions provided the desired nano oxaarencyclyne **3** or **4** in medium yield (**3**; 31.4%, **4**; 35.6%) (Scheme 1).

The observed simple signals of ^{1}H and ^{13}C NMR spectra[9] for **3** and **4** support their symmetrical structure. The MS spectra[9] of the corresponding saturated derivative prepared by the catalytic hydrogenation of **3** and **4** showed a reasonable molecular ion peak. In this manner, the macrocyclic structure of **3** and **4** was confirmed by spectral data. Finally, the structure of **4** was determined by single-crystal X-ray analysis (Fig. 1).[10] As shown in Fig. 1, **4** is not coplanar and has a small bond angle strain at C–C≡C–C (175.2–179.1°)



Scheme 1. (a) i. 6 M HCl, $NaNO_2$, (ii) Et_2NH, K_2CO_3, $MeCN–H_2O$; (b) propargyl alcohol, $Pd(Ph_3P)_4$, CuI, pyrrolidine; (c) propargyl bromide, KOH, 18-crown-6, THF; (d) ^{n}BuLi, TMSCl, THF; (e) I_2, MeI; (f) $Pd(dba)_2$, Ph_3P, CuI, Et_3N; (g) 1 M KOH, MeOH; (h) 1 M KOH, $MeOH–CHCl_3$; (i) $Pd(dba)_2$, Ph_3P, CuI, Et_3N–THF.

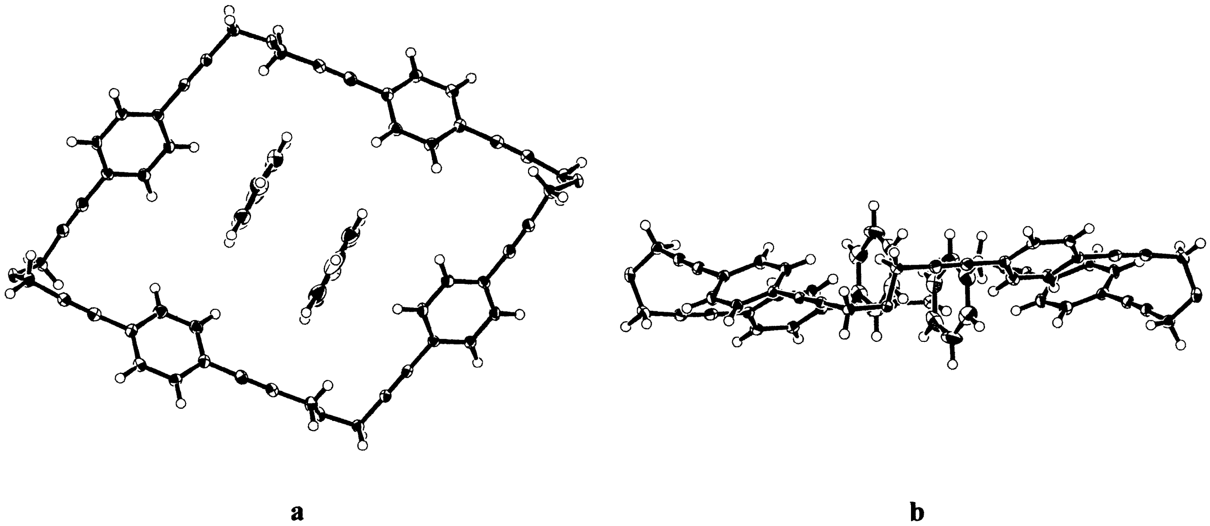


Figure 1. ORTEP drawing of **4** (a, front view; b, side view) including two benzene molecules (solvent). Ellipsoids are drawn at 50% probability.

and C–O–C (114.3 and 111.2°). Interestingly, **4** included two benzene (the solvent used for recrystallization) molecules in the cavity, suggesting that the cavity of oxaarenecyclyne is hydrophobic.[11]

The diagonal O–O distances of **4** obtained from its crystal structure incorporating two benzene molecules in the cavity are 13.4 and 20.3 Å, respectively. Taking the van der Waals radius of the oxygen atom (1.4 Å) into consideration, the cavity size of **4** is estimated as 10.6 and 17.5 Å, respectively (13.4 Å from MM-2 calculation). On the other hand, the cavity size of **3** obtained from its MM2-optimized structure is estimated as 11.5 Å. Therefore, **3** and **4** have sufficient cavity size for including C_{60} with almost 10 Å in van der Waals diameter. Furthermore, as mentioned above, both **3** and **4** have four n- or π-donor groups, respectively, which can interact well with four equatorial double bond carbons of C_{60}. Thus, nano oxaarenecyclynes **3** and **4**, despite their rigid framework, seem to incorporate C_{60} (rigid substrate) to form the supramolecular complexes, provided under appropriate conditions.

The formation of supramolecular complexes of C_{60} with **3** and **4** was confirmed by the following experiments: The color change from purple to reddish-brown was observed only upon refluxing the toluene solution of C_{60} and **3** (or **4**) (molar ratio; 1:1) for 45 min. The absorption spectra measurements were made for the solution after cooling to 298 K. As shown in Figs. 2 and 3, the intensity of the C_{60} absorption band in the 400–550 nm region increased with concentration of **3** (or **4**). This is ascribed to the formation of the oxaarenecyclyne (**3** or **4**)-C_{60} complex in solution.[12] The complex formation was not observed at ambient temperature. Job's plot[13] and isosbestic point (**3**: 607 nm, **4**: 608 nm) between C_{60} and the receptor (**3** or **4**), provided evidence for a 1:1 complex formation. The formation constant of the complexes at 298 K was determined by spectroscopic titration method (**3** for C_{60}: $3.41 \pm 1.51 \times 10^3$ dm^3 mol^{-1}, **4** for C_{60}: $5.43 \pm 0.37 \times 10^3$ dm^3 mol^{-1}) (Figs. 2 and 3).[14] Both constants for *m*- and *p*-cyclynes are of the same order, but the latter is slightly larger than the former. The AM1 heat of complex formation[15] is 2.23 kcal/mol for the **3**-C_{60} complex, and 0.59 kcal/mol for the **4**-C_{60} complex, reflecting the difference in distance between the receptor oxygen atoms and the C_{60} molecular surface in both complexes.

Therefore, the larger formation constant for the **4**-C_{60} complex could be ascribed to its larger entropy (freedom) effect. The MM2/AM1 structure for both complexes (see Figs. 2 and 3) supports this interpretation. LUMO coefficients at the apical position for Saturn-type C_{60} complexes with **3** and **4** become larger than those of C_{60}, suggesting the increase in reactivity of C_{60} of the Saturn-type C_{60} complexes. Investigation on novel functions emerging from the supramolecular complex of C_{60} with **3** and **4** is currently in progress. The result will be published in due course.

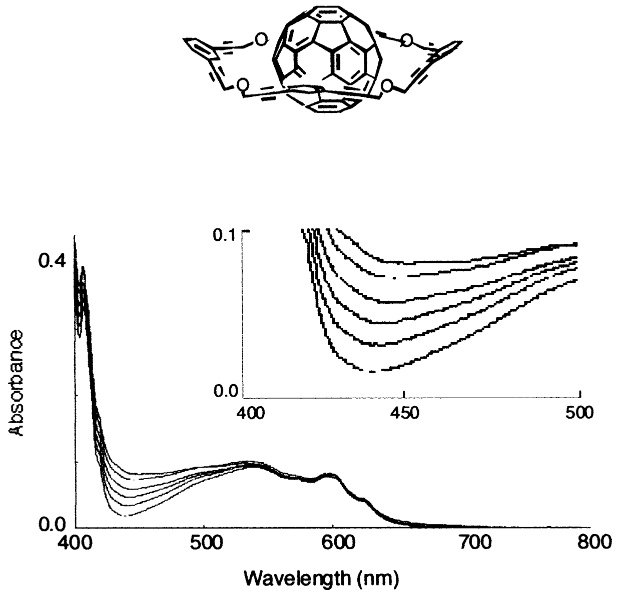


Figure 2. Absorption spectra of C_{60} (1.05×10^{-4} mol dm^{-3}) in the presence of oxaarenecyclyne **3** in toluene. Concentrations of **3**: 0.00, 0.21, 0.42, 0.63, 0.84, 1.05 ($\times 10^{-4}$ mol dm^{-3}) from the bottom. The inset shows the magnification of absorption spectra between 400 and 500 nm.

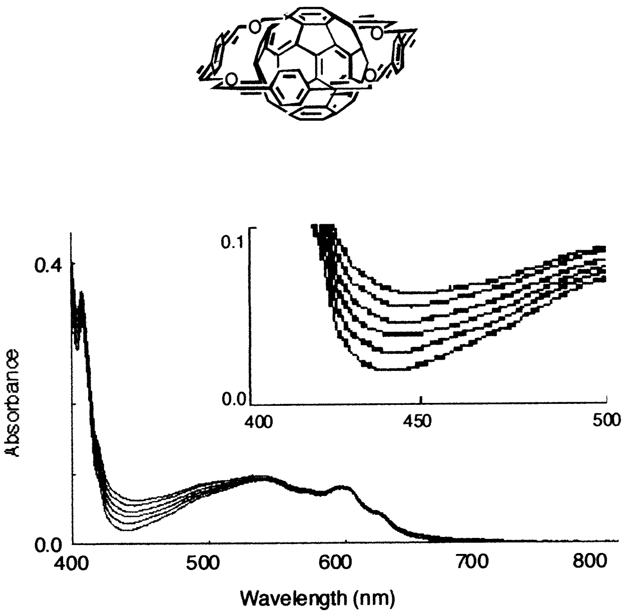


Figure 3. Absorption spectra of C_{60} (1.03×10^{-4} mol dm^{-3}) in the presence of oxaarenecyclyne **4** in toluene. Concentrations of **4**: 0.00, 0.21, 0.41, 0.62, 0.82, 1.03 ($\times 10^{-4}$ mol dm^{-3}) from the bottom. The inset shows the magnification of absorption spectra between 400 and 500 nm.

Acknowledgements

We are grateful to JSPS for financial support of this research (JSPS-RFTF 9711601).

References

1. (a) Morrison, D. L.; Höger, S. *J. Chem. Soc., Chem. Commun.* **1996**, 2313–2314; (b) Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1714–1715; (c) Mackeay, L. G.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 43–44; (d) Anderson, S.; Neidlein, U.; Gramlich, V.; Diedrich, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1596–1597.
2. Yamaguchi, Y.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *J. Am. Chem. Soc.* **2000**, *122*, 7404–7405.
3. Yoshida, Z. Presented at The IUPAC Third International Symposium on Functional Dyes, July 16–21, 1995, Santa Cruz, USA, Opening Lecture, and at Japan–Northern Baltic Symposium on Synthetic Chemistry, June 25–26, 1996, Helsinki, Finland, Abstracts PL18.
4. Fuji and co-workers have reported oxacalix[3]arenes to form a sitting the center-type complex with C$_{60}$: Tsubaki, K.; Tanaka, K.; Kinoshita, T.; Fuji, K. *J. Chem. Soc., Chem. Commun.* **1998**, 859–860.
5. We have also reported complexation of C$_{60}$ with nanoscale crown ether derivatives: Yoshida, Z.; Matsubara, Y.; Yamaguchi, Y. *Japan Society for the Promotion of Science 116 Committee Report* **1999**, *51*, 203–206.
6. Oda and co-workers have reported the synthesis of arenecyclynes (Kawase, T.; Ueda, N.; Tanaka, K.; Seirai, Y.; Oda, M. *Tetrahedron Lett.* **2001**, *42*, 5509–5511) and the formation of an inclusion complex with C$_{60}$ (private communication).
7. For a review, see: Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp. 521–549.
8. Wu, Z.; Moore, J. S. *Tetrahedron Lett.* **1994**, *35*, 5539–5542.
9. **3**: ^{1}H NMR (300 MHz, CDCl$_3$), δ 4.53 (s, 16H), 7.26 (t, J=7.6 Hz, 4H), 7.39 (d, J=7.6 Hz, 8H), 7.56 (bs, 4H); ^{13}C NMR (75.4 MHz, CDCl$_3$), δ 57.3, 85.0, 86.0, 122.8, 128.4, 131.7, 135.1; IR (KBr, cm^{-1}) 2921, 2852, 2233, 1477, 1355, 1203, 1074, 1035, 887, 794, 682, 557.

   4: ^{1}H NMR (300 MHz, CDCl$_3$), δ 4.54 (s, 16H), 7.33 (3, 16 H); ^{13}C NMR (75.4 MHz, CDCl$_3$), δ 58.1, 86.5, 86.6, 122.6, 131.6; IR (KBr, cm^{-1}) 2894, 2846, 2231, 1508, 1496, 1442, 1363, 1346, 1257, 1241, 1081, 1033, 1020, 970, 883, 835, 655, 545.

   The saturated derivative of **3**: ^{1}H NMR (300 MHz, CDCl$_3$), δ 1.89 (tt, J=6.6, 7.2 Hz, 8H), 2.67 (t, J=7.2 Hz, 8H), 3.39 (t, J=6.6 Hz, 8H), 6.98 (s, 2H), 7.00 (d, J=7.2 Hz, 4H), 7.18 (t, J=7.2 Hz, 2H); HRMS (EI, 70 eV) calcd 704.4805, found 704.4732.

   The saturated derivative of **4**: ^{1}H NMR (300 MHz, CDCl$_3$), δ 1.87 (tt, J=6.5, 7.5 Hz, 16H), 2.67 (t, J=7.5 Hz, 16H), 3.37 (t, J=6.5 Hz, 16H), 7.09 (s, 16H); ^{13}C NMR (75.4 MHz, CDCl$_3$), δ 31.2, 31.8, 69.6, 128.4, 139.3; HRMS (EI, 70 eV) calcd 704.4805, found 704.4750.
10. Crystal data for **4**·2C$_6$H$_6$: C$_{60}$H$_{44}$O$_4$, M=829.01, monoclinic, $P2_1/n$, a=15.343(4), b=5.8076(12), c=26.216(6) Å, β=104.925(5)°, V=2257.2(8) Å^3, Z=2, D_{calcd}=1.220 g/cm^3, R=0.048, R_{W}=0.074, Rigaku Mercury, 26018 measured reflections, Mo Kα, 5161 unique (R_{int}=0.060), 312 variables [I>−10.00$\sigma(I)$].

    The X-ray structures of **3**, **3**-C$_{60}$ complex and **4**-C$_{60}$ complex are not established yet, because of difficulty in obtaining single crystals for X-ray analysis.
11. Oxaarenecyclynes **3** and **4** did not show concentration dependence in the ^{1}H NMR spectra in CDCl$_3$ (10^{-2}–10^{-4} M), indicating that these did not tend to self-associate.
12. Significant shifts in ^{1}H and ^{13}C NMR spectra were not observed for the supramolecular complexes of C$_{60}$ with **3** or **4**.
13. (a) Rabie, U. M.; Patal, B. P.; Crabtree, R. H. *Inorg. Chem.* **1996**, *36*, 2236; (b) Zimmerman, S. C.; Wu, W.; Zeng, Z. *J. Am. Chem. Soc.* **1991**, *113*, 196.
14. The absorption spectra measurements for Job's plot and the determination of each complex formation constant were made for the solution after refluxing for 45 min followed by cooling to 298 K.
15. The AM1 heat of formation is adopted instead of the experimental one because the convergent experimental values are difficult to get owing to high complexation temperature.