A C_{60}-armed *p-tert*-Butylcalix[4]-aza-crown†

J. Chem. Research (S), 1998, 808–809†

Chuan-Feng Chen,* Ji-Sheng Li, Qi-Yu Zheng, Gai-Jiao Ji and Zhi-Tang Huang

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

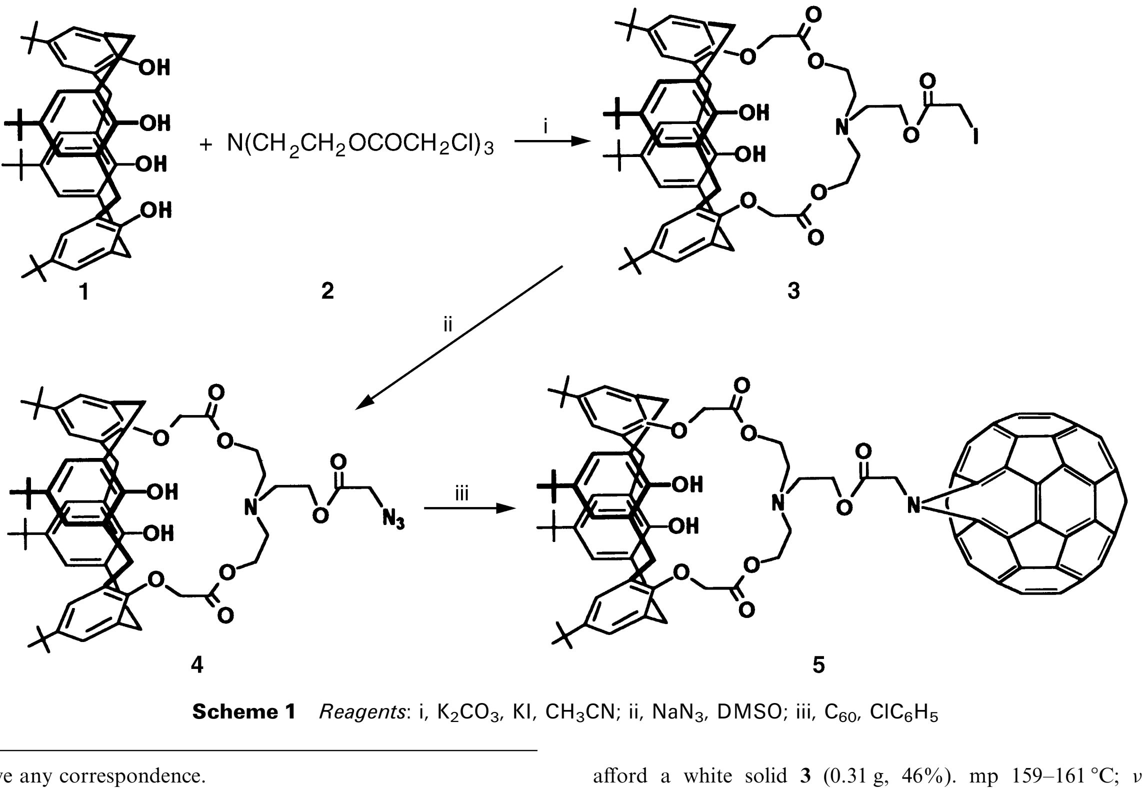
A C_{60}-armed *p-tert*-butylcalix[4]-aza-crown was synthesized and characterized using MALDI–TOF–MS, FT–IR, UV–VIS, ^1H and ^{13}C NMR spectra.

Following the development of calixcrowns, especially calix[4]crowns, in host–guest chemistry,[1,2] studies on calix-aza-crowns[3] have recently attracted increasing attention for their potential complexation properties towards transition metal ions. Although armed aza-crowns[4] are known as a class of specific synthetic carrier molecules for cations, to the best of our knowledge, no reports on armed calix-aza-crowns have been made so far. On the other hand, a large number of additions to C_{60} have been reported,[5] and new and interesting chemical transformations of C_{60} are still under active research.[6,7] Recently, the first C_{60} functionalized calixcrown was reported by Shinkai's group.[7] We here report the synthesis and spectroscopic properties of the first C_{60}-armed *p-tert*-butylcalix[4]-aza-crown. After a solution of chloroacetic chloride and triethanolamine in chloroform was refluxed overnight, triethanolamine tri(chloroacetate) **2** was obtained in 93% yield. The *p-tert*-butylcalix[4]-aza-crown **3** with cone conformation was synthesized by the reaction of *p-tert*-butylcalix[4]arene with **2** in acetonitrile in the presence of K_2CO_3 and KI. When the azide **4**, which was obtained by the treatment of **3** with NaN_3 in dimethyl sulfoxide, reacted with C_{60} in refluxing chlorobenzene, the monoadduct **5** was produced.

It is known that when an alkyl azide reacts with C_{60}, addition occurs at the junction of the five and six-membered rings to give an azafulleroid.[8] The ^{13}C NMR spectrum of **5** showed 40 peaks between 125 and 152 ppm for the aromatic carbons, in which 32 peaks were assignable to the carbons of the C_{60} core. Of the 32, 28 signals have a relative intensity of 2 and the others have a relative intensity of 1. These are consistent with the azafulleroid structure of **5** having a C_s symmetry. A pair of doublets at 3.35 and 4.22 ppm for the methylene protons between the aromatic rings were observed in the ^1H NMR spectrum of **5**, which shows that its calix[4]arene skeleton exists in the cone conformation.[2] Matrix-assisted laser desorption-ionization time of flight mass spectrometry (MALDI–TOF–MS) of **5** gave a (M + 2) ion peak ($m/z = 1654$), (calix[4]azacrown + 2)$^+$, and $C_{60}{}^+$ peaks ($m/z = 934$ and 720, respectively). The structure of **5** was also confirmed by the presence of hydroxy group absorption at 3447 cm^{-1} and ester-carbonyl group absorption at 1749 cm^{-1} in its FT–IR spectrum. In the UV–VIS spectrum of **5**, the absorptions in the visible region appear to be similar to those of other azafulleroid derivatives.[8b,c]

Experimental

Synthesis of p-tert-*Butylcalix*[4]-*aza-crown* **3**.—A mixture of *p-tert*-butylcalix[4]arene **1** (1 mmol), triethanolamine tri(chloroacetate) **2** (1.05 mmol), anhydrous K_2CO_3 (1 mmol) and KI (2 mmol) in acetonitrile (30 ml) was refluxed for 6 h under N_2. After the solvent was removed, the residue was separated by silica gel column chromatography with chloroform–ethyl acetate (20:1, v/v) as eluent to afford a white solid **3** (0.31 g, 46%). mp 159–161 °C; ν_{max}/cm^{-1} 3450, 1752. δ_H ($CDCl_3$) 1.03 (18 H, s), 1.20 (18 H, s), 2.99 (2 H, t), 3.09 (4 H, t), 3.32 (4 H, d, *J* 13.3 Hz), 3.65 (2 H, s), 4.29 (2 H, t), 4.35 (4 H, d, *J* 13.3 Hz), 4.44 (4 H, t), 4.76 (4 H, s), 6.84 (4 H, s),



Scheme 1 *Reagents*: i, K_2CO_3, KI, CH_3CN; ii, NaN_3, DMSO; iii, C_{60}, ClC_6H_5

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

6.95 (4 H, s), 7.09 (2 H, s, OH). δ_C ($CDCl_3$): 169.56, 168.80, 150.22, 149.74, 147.28, 141.71, 132,75, 127.83, 125.76, 125.02, 72.36, 63,79, 63.74, 53.71, 53.64, 51.86, 33.93, 33.78, 31.54, 31.41, 31.06. *m/z* (FAB): 1045 (M^+) (Found: C, 64.04; H, 7.10; N, 1.21. $C_{56}H_{72}INO_{10}$ requires C, 64.30; H, 6.94; N, 1.34%).

Synthesis of the Azide **4**.—To a solution of NaN_3 (0.22 mmol) in dimethyl sulfoxide (5 ml) compound **3** (0.1 mmol) was added. After the reaction mixture had been stirred for 1 h at room temperature, 10 ml of water was added and the mixture was extracted with ethyl acetate (3 × 10 ml). The extractant was washed with water (3 × 10 ml) and then dried with anhydrous Na_2SO_4. After the solvent had been removed, the product (152 mg, 79%) was obtained as a colorless oil. ν_{max}/cm^{-1} 3465, 2105, 1748.

Synthesis of C_{60}-armed p-tert-*Butyl calix*[4]*-aza-crown* **5**.—To a solution of C_{60} (0.1 mmol) in chlorobenzene (70 ml), the azide **4** (0.105 mmol) was added. The reaction mixture was refluxed for 8 h under N_2. After the solvent had been removed, the residue was separated by silica gel column chromatography with toluene–cyclohexane (1:1, v/v) as eluent to remove unreacted C_{60}, then with toluene–THF (15:1, v/v) as eluent to afford product **5** (71 mg, 65% based on the consumed C_{60}). mp > 300 °C. λ_{max}/nm (CH_2Cl_2): 242, 265, 328, 425, 540. δ_H (600 MHz, $CDCl_3$): 0.88 (18 H, s), 1.26 (18 H, s), 3.35 (4 H, d, *J* 13.2 Hz), 3.76 (4 H, t), 4.22 (4 H, d, *J* 13.2 Hz), 4.60 (6 H, m), 4.78 (2 H, t), 4.82 (2 H, s), 4.95 (4 H, s), 6.67 (4 H, s), 6.96 (4 H, s), 7.09 (2 H, s, OH). δ_C (150.9 MHz, $CDCl_3$): 169.14, 167.98, 151.91, 150.38, 148.28, 148.21, 145.44, 145.15, 145.06, 144.90, 144.78, 144.71, 144.56, 144.40, 144.30, 144.09, 144.00, 143.84, 143.59, 143.35, 143.32, 143.25, 143.13, 141.99, 141.31, 140.92, 139.82, 139.03, 138.76, 138.34, 138.15, 137.08. 136.83, 136.47, 136.27, 134.45, 132.29, 132.09, 128.66, 128.42, 126.27, 125.78, 73.38, 61.93, 61.52, 53.76, 53.70, 53.11, 34.26, 32.01, 31.61, 31.26, 30.76.

We are grateful for financial support from the National Natural Science Foundation of China.

Received, 16th June 1998; Accepted, 1st September 1998
Paper E/8/04563A

References

1 V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713.
2 Q. Y. Zheng, C. F. Chen and Z. T. Huang, *Tetrahedron*, 1997, **53**, 10345.
3 (*a*) V. Böhmer, G. Ferguson, J. F. Gallagher, A. J. Lough, M. A. McKervey, E. Madigan, M. B. Moran, J. Phillips and G. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1521; (*b*) P. Beer, D. Chen, A. J. Gouolden, A. Graydon, S. E. Stokes and T. Wear, *J. Chem. Soc., Chem. Commun.*, 1993, 1834; (*c*) I. Bitter, A. Grün, G. Toth, B. Balazs and L. Toke, *Tetrahedron*, 1997, **53**, 9799.
4 H. Tsukube, *J. Chem. Soc., Chem. Commun.*, 1984, 315.
5 A. Hirsch, *Synthesis*, 1995, 895.
6 (*a*) A. Ikeda, C. Fukuhara and S. Shinkai, *Chem. Lett.*, 1997, 407; (*b*) C.-F. Chen, J.-S. Li, G.-J. Ji, Q.-Y. Zheng and D.-B. Zhu, *Synth. Commun.*, 1998, **28**, 3097.
7 M. Kawaguchi, A. Ikeda and S. Shinkai, *J. Chem. Soc., Perkin Trans. 1*, 1998, 179.
8 See examples: (*a*) M. Prato, Q. C. Li, F. Wudl and V. Lucchini, *J. Am. Chem. Soc.*, 1993, **115**, 1148; (*b*) M. Takeshita, T. Suzuki and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1994, 2587; (*c*) N. X. Wang, J. S. Li and D. B. Zhu, *Chin. Sci. Bull.*, 1994, **39**, 2039; (*d*) G. X. Dong, J. S. Li and D. H. Chan, *J. Chem. Soc., Chem. Commun.*, 1995, 1725.