Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

The First Crown Ether-Bearing [60]Fullero-Pyrrolidine: Synthesis and Regulation of Absorption Spectrum by ions Binding

Zhixin Guo [a] , Yuliang Li [a] , Juhua Xu [a] , Zhong Mao [a] , Yi Wu [b] & Daoben Zhu [a]

[a] Institute of Chemistry, Chinese Academy of Sciences , Beijing, 100080, P. R. China

[b] Institute of Microchemistry , Beijing, 100091, P. R. China

To cite this article: Zhixin Guo , Yuliang Li , Juhua Xu , Zhong Mao , Yi Wu & Daoben Zhu (1998) The First Crown Ether-Bearing [60]Fullero-Pyrrolidine: Synthesis and Regulation of Absorption Spectrum by ions Binding, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:11, 1957-1962, DOI: 10.1080/00397919808007169

To link to this article: http://dx.doi.org/10.1080/00397919808007169

SYNTHETIC COMMUNICATIONS, 28(11), 1957-1962 (1998)

THE FIRST CROWN ETHER-BEARING [60]FULLERO-PYRROLIDINE: SYNTHESIS AND REGULATION OF ABSORPTION SPECTRUM BY IONS BINDING

Zhixin Guo Yuliang Li* Juhua Xu Zhong Mao Yi Wu† Daoben Zhu

Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, P. R. China
† Institute of Microchemistry, Beijing 100091, P. R. China

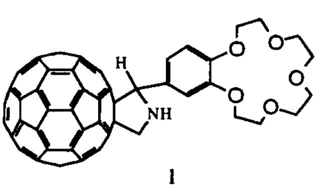
A monoadduct of [60]Fulleropyrrolidine having a 15-crown-5 structure has been prepared and characterised. It is found that the absorption spectrum of this crowned fullerene can be regulated hypsochromically by metal ions complexation.

A great deal of effort has been directed towards the chemical modification of [60]fullerene since fullerenes are available in preparative amounts[1-3]. Some functional [60]fullerene derivatives show potential usage in the biological and material areas[3-5]. Recently, several substituted [60]fulleropyrrodines processing acceptor-donor system were synthesized, which can lead to the development of advanced materials with new optical optomagnetic properties. Being a functional group possessing certain properties such as molecular recognition and molecular regulation [6-8], crown ether moieties play an important role both in biological and material sciences. Although several crowned fullerenes were synthesised[9-13], major is concerned about the formation of LB films as the crown ether moieties favoured

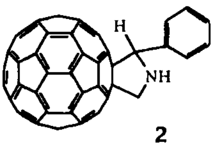
---

* To whom correspondence should be addressed

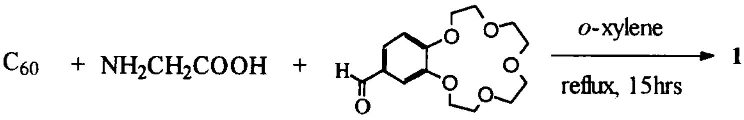
protic solvents while the fullerene moiety exhibits highly hydrophobic nature. Little attention is paid to the regulation of the ground/excited state properties through selective metal ions binding. We have recently described the reactions of azomethine ylides with [60]fullerenes through 1,3-dipolar cycloaddition[14] and we tried to combine crown ether moiety onto [60]fulleropyrrodine, which may be an acceptor-donor system. Here we report our results.



1



2



Refluxed in *m*-xylene, 4'-formyl-benzo-15-crown-5[15] reacted readily with glycine to form the conresponding azomethine ylide, which reacted with [60]fullerene by 1,3-dipolar cycloaddition to yield the monoadduct **1**. The crude product was primarily purified *via* column chromatography on silica gel. Pure product was obtained *via* HPLC and characterised by FD-MS, ^{1}HNMR, and ^{13}CNMR. The corresponding non-crowned [60]fulleropyrrolidine **2** was also obtained *via* refluxing benzaldehyde, glycine, and [60]fullerene in chlorobenzene for three hours. Anhydrous perchlorates of alkaline and alkaline-earth metals were employed so as to form complexes with the crowned [60]fulleropyrrolidine **1**.

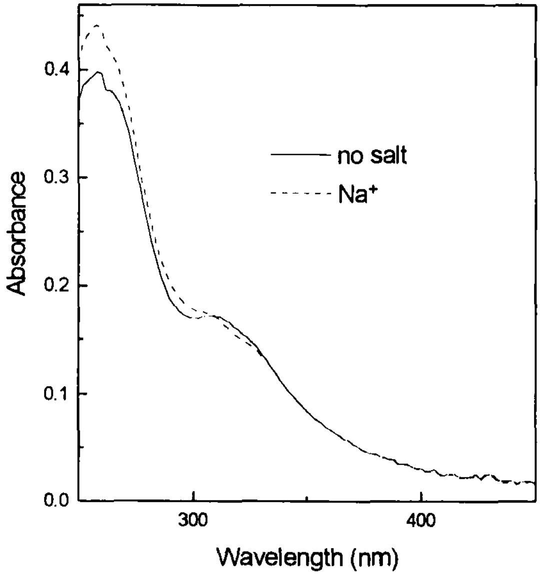


FIG. Absorption spectra of crowned [60]fulleropyrrolidine **1** with addition of anhydrous sodium perchlorate; ratio of **1**/salt = 1:50; concentration of **1**: 5.0 × 10^{-6} mol/l ; solvent: CH_2Cl_2/CH_3CN (1:1, v/v)

The absorption spectrum of crowned [60]fulleropyrrolidine **1** can be hypsochromically shifted by alkaline and alkaline-earth metals ions complexation. When $NaClO_4$ was added, the absorption peak of 308nm shifted to 304 nm(FIG). Other perchlorates of alkaline and alkaline-earth metals can also cause the similar shifts. In the case of uncrowned [60]fulleropyrrolidine **2**, little change can be observed after the same metal ions are added. Thus the formation of complexes can regulate the absorption spectrum of crowned [60]fulleropyrrolidine **1**. It is proposed that the presence of electron-donor (methyleneoxy groups) and electronacceptor ([60]fullerene moiety) in crowned [60]fulleropyrrolidine **1** lead to an intramolecular charge transfer upon excitation that results in an increase of the dipole moment. Complexation by a cation reduces the donor character of the oxygen atoms of the crown and results in a hypsochromic effect.

Experimental

N-hydrogen-2-[(benzo-15-crown-5)-4'-yl]-3,4-[60]fulleropyrrolidine

To a solution of [60]fullerene (216 mg, 3x10^{-4} mol) in o-xylene (100 cm^3), glycine (56 mg, 1.5x10^{-3} mol) and 4'-formyl-benzo-15-crown-5 (44mg, 1.5x10^{-4} mol) were added. The mixture was stirred and heated to reflux for 15 h. The brown solution was concentrated and chromatographed on silica-gel using benzene-methanol(4:1, v/v). Further purification was accomplished by HPLC on JAIGEL-(1,2)H column using chloroform as eluent. Evaporation of the eluent yield the crowned fulleropyrrolidine 68 mg (44%); m/z (FD) (MAT-90) (1030[M+1]$^+$, 100% and 720 ([M-$C_8H_{16}O_5$]$^+$, %); δ_H (200M Hz, Unity 200, solvent: $CDCl_3$) 3.6~4.2(m, 16H), 4.8~5.1(d, 2H), 5.7(s, 1H), 6.8~7.7(m, 3H); δ_C (400M Hz, Bruker ARX 400, solvent: $CDCl_3$) 154.51, 149.37, 149.24, 148.97, 147.18, 147.14, 146.36, 146.28, 146.21, 146.20, 146.16, 146.10, 146.03, 145.89, 145.75, 145.69, 145.59, 145.49, 145.41, 145.38, 145.31, 145.27, 145.24, 145.22, 1`45.16, 145.12, 144.60, 144.53, 144.32, 144.27, 143.90, 143.19, 143.17, 142.96, 142.67, 142.60, 142.54, 142.41, 142.24, 142.18, 142.17, 142.10, 142.02, 141.94, 141.90, 141.85, 141.68, 141.54, 141.15, 141.10, 139.86, 139.74, 138.91, 135.84, 135.77, 130.23, 126.84, 111.88, 86.04, 77.05, 71.04, 70.38, 70.32, 69.37, 69.28, 69.20, 68.73, 68.67.

Acknowledgements

This work was supported by the National Natural Science Foundation of China.

References

1. Hirsh, A. *The Chemistry of the Fullerenes*, Thieme, Stuttgard, 1994
2. Taylor, R. edited, *The Chemistry of Fullerenes*, World Scientific, Singapore, 1995
3. Diederich, F. and Thilgen, C. *Science*, 1996, **271**, 317
4. Jensen, A. W., Wilson, S. R., and Schuster, D. I. *Bioorg. & Med. Chem.*, 1996, **4(6)**, 767
5. Koruga, D., Matija, L. Misic, N., and Rakin, P. *Mater. Sci. Forum* 1996, **214**, 49
6. Hiraoka M. edited, *Crown Ethers and Analogous Compounds*, Elsevier, Amsterdam, 1992
7. Cacciapaglia, R. and Mandolini, L. *Chem. Soc. Rev.*, 1993, 221
8. Lehn, J.-M. *Supramolecular Chemistry*, VCH Verlagsgesellschaft, Weinheim, 1995

9. Wilson, S. R. and Wu, Y. *J. Chem. Soc., Chem. Commun.*, 1993, 784

10. a. Osterodt, J., Nieger, M., Windscheif, P.-M., and Vögtle, F. *Chem. Ber.*, 1993, **126**, 2331; b. Osterodt, J., Zett, A. and Vögtle, F. *Tetrahedron*, 1996, **52(14)**, 4949

11. a. Diederich, F., Jonas, U., Granlich, V., Herrmann, A., Ringsdorf, H., and Thilgen, C. *Helv. Chim. Acta.*, 1993, **76**, 2445; b. Jonas, U., Cardullo, F., Belik, P., Diederich, F., Gögel, A., Harth, E., Herrmann, A., Isaacs, L., Müllen, K., Ringsdorf, H., Thilgen, C., Uhlmann, P., Vasella, A., Waldraff, C. A. A. and Walter, M. *Chem. Eur. J.*, 1995, **1(4)**, 243

12. Davey, S. N., Leigh, D. A., Moody, A. E., Tetler, L. W., and Wade, F. A. *J. Chem. Soc. Chem. Commun.*, 1994, 397

13. Lamparth, I., Schick, G., and Hirsch, A. *Liebigs Ann./Recueil*, 1997, 253

14. a. Han, H., Li, Y., and Zhu, D. *Chin. Chem. Lett.*, 1995, **6(3)**, 201; b. Li, Y., Han, H., Yang, J., Bai, F., Li, Y., Xu, J., and Zhu, D. *Electrochem. Soc. Proc.*, 1995, **95(10)**, 1111; c. Zheng, D., Li, Y., Yang, J., and Zhu, D. *Fullerene Science & Technology* 1996, **4(5)**, 1067; d. Li, Y., Xu, J., Zheng, D., Yang, J., Pan, C., and Zhu, D. *Solid State Commun.*, 1996, **101(2)**, 123; e. Li, Y., Mao, Zh., Xu, J., Yang, J., Guo, Zh., and Zhu, D. *Chem. Phys. Lett.*, 1997, **265**, 361

15. Hsiue, G., Wen, J., and Hsu, Ch. *Makromol. Chem.*, 1991, **192**, 2243

(Received in Japan 8 September 1997)