

Synthesis of Calix[4]pyrroles: A Class of New Molecular Receptor

Shi Jun SHAO*, Xian Da YU, Shu Qin CAO

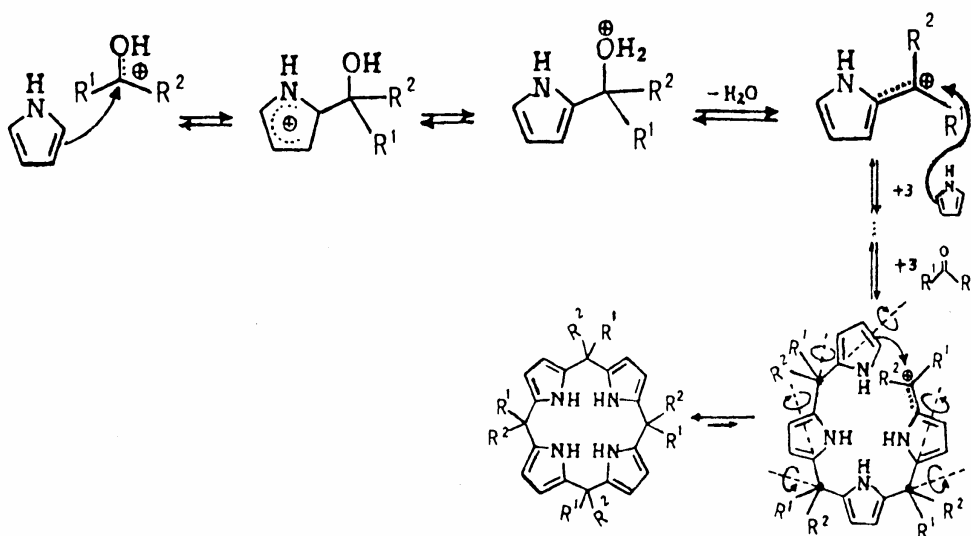
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
342 Tianshui Rd., Lanzhou 730000

Abstract: Calix[4]pyrroles, as a class of new molecular receptor in the area of supramolecular chemistry, have displayed interesting anion and neutral substrate binding properties. In this paper, several new calix[4]pyrrole macrocycles were synthesised and characterized.

Keywords: Calix[4]pyrroles; porphyrinogen; condensation; pyrrole; ketone; homologues.

Recently Sessler and co-workers discovered that the *meso*-octaalkylporphyrinogens showed interesting anion and neutral substrate binding properties and might serve as a class of new easy-to-make molecular receptor in the area of supramolecular chemistry¹. However, the *meso*-octaalkylporphyrinogens are not *bona fide* precursors of the porphyrins. Sessler *et al.* thought this class of macrocycle was perhaps mis-named and might better be referred to as calix[4]pyrroles². This renaming, which is supported by structural studies, helps establish an obvious analogy to the calixarenes.

Scheme 1.



R¹COR²: 1. Cyclopentanone; 2. CH₃COCH₂CH(CH₃)₂; 3. PhCOCH₃

The first such species, *meso*-octamethylcalix[4]pyrrole, was obtained over a century ago by Baeyer. Subsequently, this synthesis was refined by a number of research groups³⁻⁵. The macrocycle of calix[4]pyrroles is formed by electrophilic α -substitution of pyrrole by ketone, acid-catalyzed oligomerization, and spontaneous, non-template cyclization wherein four pyrrole units are combined⁶ (see **Scheme 1**).

The new compounds **1-3** were prepared according to the one-step method by the condensation of equimolar quantities of pyrrole and the relevant ketone in MeOH or EtOH, at room temperature, catalyzed by hydrochloric acid or 4-toluenesulfonic acid, followed by extraction and repeated crystallization from suitable solvents to give white crystals in 5~30% yields, and then dried *in vacuo* at 60°C. The product of pyrrole with methyl *iso*-butyl ketone consisted of two equipollent isomers (compd. **2a** and **2b**). Their structures have been characterized by IR, FAB-MS, and ¹H-NMR. The results of elemental analysis tally with the calculated data.

Table 1. IR, MS and ¹H-NMR data of compounds **1-3**

| Compd. | m.p.(°C) | FAB-MS(m/z) | IR(ν , cm ⁻¹) | ¹ H-NMR(CDCl ₃ , δ ppm) |
|-----------|----------|--|---|---|
| 1 | 231-232 | 532(M ⁺) | 3563,3497,3414,3213, 3107,2953,2868,1577, 1450,1415,1419,1226, 1041,764 | 7.01(broad, m, 4H, NH) 5.84(s, 8H, pyrrole CH) 2.00(t, 16H, CH ₂) 1.68(t, 16H, CH ₂) |
| 2a | 225-227 | 596(M ⁺),581, 539,481,425 | 3437,3109,2955,2866, 1575,1464,1413,1369, 1294,1200,1049,768 | 6.93(broad, m, 4H, NH) 5.88(s, 4H, pyrrole CH) 5.85(s, 4H, pyrrole CH) 1.78-1.39(m, 24H, CH ₃ , CH ₂ CH) 0.81-0.60(m, 24H, C(CH ₃) ₂) |
| 2b | 172-173 | 596(M ⁺),581, 539,481,425 | 3443,3111,2955,2868, 1576,1464,1415,1367, 1292,1201,1045,767 | 6.93(broad, m, 4H, NH) 5.88(s, 4H, pyrrole CH) 5.85(s, 4H, pyrrole CH) 1.78-1.39(m, 24H, CH ₃ , CH ₂ CH) 0.80-0.60(m, 24H, C(CH ₃) ₂) |
| 3 | 217-219 | 676(M ⁺) | 3452,3418,3329,2978, 1944,1877,1802,1752, (1703),1572,1489,1444, 1215,1026,772,698 | 7.19(broad, m, 24H, C ₆ H ₅ and NH) 5.87(d, 4H, pyrrole CH) 5.75(d, 4H, pyrrole CH) 1.89(s, 12H, CH ₃) |

Acknowledgment

This work was financially supported by the Director Foundation of Lanzhou Institute of Chemical Physics(96-07 and 98-06).

References

1. P. A. Gale, J. L. Sessler, and V. Kral, *J. Chem. Soc., Chem. Commun.*, **1998**, (1), 1.
2. P. A. Gale, J. L. Sessler, V. Kral, and V. Lynch, *J. Am. Chem. Soc.*, **1996**, *118*, 5140.
3. P. Rothmund, C. L. Gage, *J. Am. Chem. Soc.*, **1955**, *77*, 3340.
4. W. H. Brown, B. J. Hutchinson, and M. H. MacKinnon, *Can. J. Chem.*, **1971**, *49*, 4017.
5. D. Jacoby, C. Floriani, A. Chiesi-villa, and C. Rizzoli, *J. Am. Chem. Soc.*, **1993**, *115*, 3595.
6. J. Fuhrhop, G. Penzlin, "Organic Synthesis---Concepts, Methods, Starting Materials", Verlag Chemie, Weinheim, 1983, p.226.

Received 6 October 1998