Synthesis and Carbon-13 NMR Longitudinal Relaxation Time Studies of Porphyrin Dimers Possessing Conformational Fluctuation

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Abstract: The synthesis and carbon-13 NMR longitudinal relaxation times (T_1) studies on the calixarene-substituted porphyrin dimers possessing conformational fluctuation were carried out for the first time. The T_1 values were measured under proton-noise-decoupling conditions by the inversion-recovery technique. The T_1 values for a calix[4]arene bridged porphyrin dimer **1** decrease with the increase in the solvent polarity. This implies that the T_1 values reflect the diffusion rate. As to a motion of the phenol unit, there are two different motions for phenol units in **1** and **2**: a seesaw motion around a C-2 to C-2' axis (A) and a rotational motion around a C-1 to C-4 axis (B). The T_1 values indicate that in **1** motion (B) is predominant over motion (A). This shows that motion (A) is specifically suppressed because of the hydrogen-bonding interactions in **1**.

Key words: relaxation times (T_1), ^{13}C NMR, calix[4]arene, porphyrin dimer, conformation, hydrogen bond, conformational fluctuation, solvent polarity, electron transfer

1 Introduction

Recently, porphyrins (**1**) and calixarenes (**2**) have been receiving increasing attention in the field of supramolecular chemistry. To combine the advantages of calixarene and porphyrin, calixarene-porphyrin systems have been synthesized as photoinduced electron transfer models (3-6) as for photosynthetic reaction centers (7). These included coupled diporphyrins, the study of which should clarify the role of the special pair acting as primary electron donor in the reaction center. From a stereochemical viewpoint, the calix[4]arene moiety has conformational fluctuation in solution (**2**), therefore, it is of great significance to assess the conformational properties characteristic of calixarene cavities possessing two porphyrins. So, one of the central issues is how porphyrin-porphyrin interactions influence the

electric properties of the dimer in calixarene. Among NMR spectroscopic methods, dynamic NMR studies (8) and NMR relaxation time studies (9-11) can provide useful information about the conformational properties. Herein, we describe the synthesis and ^{13}C NMR relaxation time (T_1) studies on the calixarene-substituted porphyrin derivatives **1**, **2**, and an acyclic analog **3** for the first time. The main purpose of this study is to understand how the molecular motion of the calix[4]arene changes with or without the intramolecular hydrogen-bonding interaction.

2 Experimental

Melting points were determined with a Yanagimoto melting point apparatus. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer operated at

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Fig. 1 Calixarene Derivatives and the Numbering System for their Carbons.

300 MHz at room temperature (25°C) in the Fourier transform mode. Chloroform- d_1 was used as a solvent and tetramethylsilane was used as an internal reference for ^1H NMR measurement. FAB mass spectra were recorded on JEOL-DX 303. Dichloromethane was freshly distilled over calcium hydride.

Zn(II)porphyrin-substituted 25, 26, 27, 28-tetrapropoxycalix[4]arene 2: To a stirred and refluxing solution of 250 mg (0.13 mmol) of **1**, 430 mg (1.4 mmol) of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, and 380 mg (2.5 mmol) of BaO in 50 mL of dry DMF was added dropwise 1.0 g (8.2 mmol) of 1-bromopropane in 50 mL of dry THF over a period of 0.5 h. After the reaction mixture was refluxed for 12 h, then cooled, treated with 1 N HCl, and extracted several times with CH_2Cl_2 . The combined organic layers were finally washed with water, dried over sodium sulfate, and the solvent was removed under reduced pressure. The purification by silica gel column chromatography down with ethyl acetate-hexane gave 200 mg (75 %) of 25, 26, 27, 28-tetrapropoxycalix[4]-arene derivative **2**.

Compound 2 purple powder; mp > 300°C; ^1H NMR (300 MHz, CDCl_3) δ 1.54 (36H, s, $\text{C}(\text{CH}_3)_3$), 1.60 (12H, t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.72-1.88 (24H, m, pyrrole β - CH_2CH_3), 2.00, 2.48, 2.49, 2.77 (each 6H, s, pyrrole β - CH_3), 2.23-2.40 (8H, m, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.69, 4.80 (each 4H, d, $J = 14$ Hz, ArCH_2Ar), 4.00-4.24 (24H, m, $\text{OCH}_2\text{CH}_2\text{CH}_3$, pyrrole β - CH_2CH_3), 6.90 (2H, t, ArH), 7.19 (4H, d, $J = 7.5$ Hz, ArH), 7.83 (2H, t, $J = 1.5$ Hz, *meso*- ArH), 7.92 (4H, s, ArH), 7.99 (8H, d, $J = 1.5$ Hz,

meso- ArH), 10.26, 10.29 (each 2H, s, *meso*- H); FAB/MS m/z 2046 (M^+) (Found: C, 73.64; H, 7.23; N, 5.20. $\text{C}_{132}\text{H}_{156}\text{N}_8\text{O}_4\text{Zn}_2 \cdot \text{CHCl}_3$ requires C, 73.65; H, 7.30; N, 5.17 %).

T_1 Measurements. NMR samples consisted of 0.5 ml of solution in 5-mm o.d. tubes which were sealed under vacuum after degassing by 5 freeze-pump-thaw cycles. All glassware was washed with 0.01 M EDTA solution to remove paramagnetic impurities. ^{13}C NMR measurements were performed at a Varian Gemini-300 spectrometer operated at 300 MHz at room temperature (25°C). Relaxation times (T_1) were measured under proton-noise-decoupling conditions by the inversion-recovery technique. A waiting time (t_w) of at least five times the longest relaxation time was used in each case. Three kinds of pulse sequence were used to determine T_1 for different carbon atoms. All spectra were recorded at 25°C, and each run took 8-14h. T_1 values were determined by a linear least-squares, two-parameter fit of the experimental data directly performed by the spectrometer computer. At least ten points were included for each T_1 calculation (correlation coefficient $\gamma > 0.98$).

3 Results and Discussion

Zn(II) porphyrin di-substituted 25, 27-dipropoxy-26, 28-dihydroxycalix[4]arene **1** was prepared in 6 steps according to the literature (12). The preparation of 25, 26, 27, 28-tetrapropoxycalix[4]arene **2** is shown in

Scheme 1 Synthetic Route for **2**.

Scheme 1. **2** was synthesized by the reaction of 1-bromopropane and **1** in DMF in the presence of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and BaO . The ^1H NMR spectra revealed that the structure of **1** and **2** were fixed in a cone-conformation (**2**), thus, they gave a pair of doublets for the ArCH_2Ar protons. They also showed that two hydroxyl groups of **1** formed intramolecular hydrogen bonds.

The chemical shifts (δ) of ^{13}C NMR spectra are summarized in **Table 1**. The assignment of each carbon was reasonably effected by COSY (^1H - ^{13}C) NMR technique.

The T_1 values are summarized in **Table 2**. The T_1 values thus obtained agreed usually to less than 8% from the mean. A lot of interesting viewpoints can be raised about the data in **Table 2**. First, the T_1 values for **1** decrease with the increase in the solvent polarity. This implies that the T_1 values in **Table 2** reflect the diffusion rate. Secondly, it is known that the framework of the “cone” conformation in **1** is firmly maintained through strong intramolecular hydrogen-bonding interactions (**2**). As for **2**, the interactions are absent. As seen in **Table 2**, the T_1 values for **2** are generally greater than those for **1**: in CDCl_3 , $\Delta T_1 = 7.50$ s for C-2, 1.15 s for C-3, 1.46 s for C-4, and 0.45 s for C-5. This substantiates that the ring of **2** are fluctuated because of the absence of hydrogen-bonding interactions.

The third point is related to a motion of the phenol unit. In **1**, the T_1 values for C-3 are always greater than those for C-4. In **2**, on the other hand, the difference between C-3 and C-4 is slight. We can suggest two different motions for phenol units in **1** and **2**: a seesaw motion around a C-2 to C-2' axis (A) and a rotational motion around a C-1 to C-4 axis (B). The data indicate that in **1** motion (B) is predominant over motion (A).

This indicates that motion (A) is specifically suppressed because of the hydrogen-bonding interactions in **1**. In other words, the most remarkable conformational feature without the hydrogen-bonding interaction is that, though the two porphyrin rings are bridged by the *para*-position of the calix[4]arene **2**, they might tend to closely come together or overlap.

In conclusion, the present paper demonstrated that (i) relaxation times of calix[4]arene-bridged porphyrin dimer were estimated with ^{13}C NMR for the first time

Table 1 Chemical Shifts (δ) of Carbons in **1**, **2**, and **3**.

Substrate	δ / ppm				
	C-1	C-2	C-3	C-4	C-5
1	151.15	118.73	135.92	139.20	31.40
2	157.49	125.72	135.42	140.70	29.85
3	153.60	113.80	135.52	137.40	—

a) 25°C , CDCl_3 , internal standard TMS, substrate concentration: 0.10 mol dm^{-3} .

Table 2 Relaxation Time (T_1) of Carbons in **1**, **2**, and **3**.

Substrate	Solvent	T_1 / s				
		C-1	C-2	C-3	C-4	C-5
1	CDCl_3	11.50	9.42	1.15	0.82	0.60
1	$\text{C}_5\text{D}_5\text{N}$	a)	a)	0.70	0.55	0.45
1	$(\text{CD}_3)_2\text{SO}$	3.44	2.70	0.42	0.15	0.19
2	CDCl_3	b)	16.92	2.30	2.28	1.05
3	CDCl_3	22.10	b)	2.10	2.20	—

a) The peak could not be assigned because of the overlap with the solvent peaks.

b) The accurate T_1 could not be determined because of the weak intensity.

Fig. 2 Two Different Motions for Phenol Units.

and (ii) T_1 values provided new insights into molecular motion in calix[4]arene. Further examination on the conformational motions and the electrostatic interactions between the two porphyrin rings in calix[4]arene is now under investigation.

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