Conformational Change of C$_{30}$DME, *α,ω*-13,16-Dimethyloctacosanedioate Dimethylester, at Various Temperatures

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Previously, C$_{30}$DME, *α,ω*-13,16-dimethyloctacosanedioate dimethylester, was prepared from a structural fatty acyl component of the membrane lipids in a strict anaerobic thermophilic bacterium.[1,2] This molecules has two polar heads linked covalently by a saturated hydrocarbone as in Figure 1.

At the air/water interface C$_{30}$DME has transitions from linear to reverse U-shaped conformation, in which the long hydrocarbons are bent and the polar heads are anchored on the water surface.[3-5] This bending conformation was speculated to be due to the unique structure of the molecule; two alkyl chains in the middle and an ester linkage on both ends. However, there is a lack of information about the conformational change of this new bola-form long chain diester molecule. In this paper, we present our findings on the motion of C$_{30}$DME by DSC (differential scanning calorimeter, Rheometric Scientific Ltd.) and solid-state ^{13}C NMR at various temperatures, and verification of the thermally driven conformational change of the molecule. We obtained a reproducible DSC thermogram by repeating the thermal history. Figure 2 shows the DSC thermogram of C$_{30}$DME after 3 scans from -30 to 80 °C by the heating and cooling processes with a heating rate of 5 °C/min and cooling of 10 °C/min. Whenever we repeat the heating and cooling processes, we obtained the same thermogram as in Figure 2. There are two distinct transitions by heating process at 8 °C and 40 °C. The first larger melting peak at 8 °C is attributed to the melting of the extended chain, which could be observed by the melting point apparatus. The second, smaller endotherm (circled in Figure 2), ΔH = 1.02 kcal/mol, which is in the temperature range we are concerned with in this paper, could be involved in the conformational transition of C$_{30}$DME. In between the two transitions, the equilibrium state can be considered as a conformationally disordered 3D structure.[6]

To verify the conformation-dependent displacements of the molecule we have obtained the solid-state ^{13}C NMR

Figure 2. DSC thermogram of C$_{30}$DME. Arrows indicate the direction of the heating and cooling processes.

spectra of C$_{30}$DME at the Korea Basic Science Institute, Daejeon, Korea on a Bruker DSX400 (9.4 Tesla). The high power proton decoupling and magic angle spinning (MAS) but cross polarization (CP) were employed to determine the chemical shift variations of all carbons in the molecule versus temperature.[7] The ^{13}C chemical shift was referenced to external tetramethyl silane (TMS). The continuous wave proton decoupling strength was 50 kHz. The sample was spun in a 5 mm zirconia rotor at 5 kHz and at temperatures from 25 to 80 °C. The 36° pulse length of 2 *μ*s for ^{13}C and 10 sec repetition delay were used. Typically, 200 acquisitions were performed to get a spectrum. Numerical ordering of each carbon atom is indicated in the thermodynamically stable conformations shown in Figure 3. Figure 3a indicates the linear shape and 3b is the bent U-shape conformation having R-S stereochemistry.

Since molecules like C$_{30}$DME have mobility, the cross polarization (CP) technique is not appropriate. Therefore, the ^{13}C MAS NMR experiments without CP were performed. All resonance peaks were clearly assigned and confirmed *via* ACD/CNMR (Advanced Chemistry Development Inc.), because the ^{13}C NMR spectrum in solid-state at room temperature was similar to that in the solution. A peak originating from the Teflon spacer was observed at 111.25 ppm with a broadened linewidth. Figure 4 shows the chemical shifts

Figure 1. Chemical structure of C$_{30}$DME.

(a)

(b)
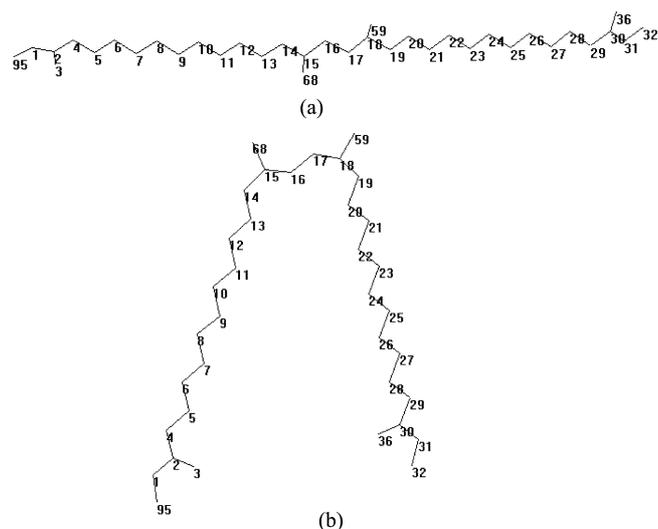
Figure 3. Numerical ordering of (a) linear and (b) bent U-shape C$_{30}$DME.

(CS) of C$_{30}$DME at various temperatures.

The CS of C$_{30}$DME shows three different patterns. The first is a monotonically decreased upfield (shielding) shift as in Figure 4(a) for many carbon atoms including C95(symmetry with C32), C2(C30), C6-C12(C21-C27), C13(C20), C14(C19), and C5(C28) sites. Second is an abrupt drop of upfield shift for C15(C18) and C16(C17) carbons in Figure 4(b). Third is a downfield shift of C4(C29) and C68(C59) carbons as in Figure 4(c). The CS on NMR is a useful probe for the conformational change of the molecule. Simply, the upfield shift represents the shielding of the external magnetic field by the electrons surrounding the nucleus.[8]

The ^{13}C chemical shift of carbon sites for C$_{30}$DME have been noticeably changed depending on the sample temperature, while the methyl carbons (C68, C59) in the middle of the chain and carbonyl carbons (C95, C32) in the end kept CS analogous. In the center of the molecule, the CS's of two carbon sites (C15, C16) abruptly shifted to the higher field at 40 °C and negligibly changed at higher temperature as shown in Figure 4b. Since the *gauche* conformation produces more electron shielding than *trans*, the molecule is shifted to the higher field of CS. This well-known *γ-gauche* effect accounts for the conformational dependent ^{13}C chemical shifts in bulk polymers.[9] The reliably changed chemical shift shows the conformational transformation in the center of the molecule between 30 and 40 °C, and that the molecular orientation is arranged from *trans* to *gauche* form.[10] The conformation of the molecule is transformed by that the skew angle between γ sites, which is step wisely decreased with increasing sample temperature. The CS of methene carbons (C4, C29) in the end of the chain is gradually shifted to a lower field with increasing sample temperature. This is possible by the cross-bending of intra-molecular interaction, which makes a downfield shift of CS. The rest of the carbon sites have gradually shifted to a higher field of CS with increasing temperature, which is due to the increasing free motion as the sample temperature increases. To verify the confor-
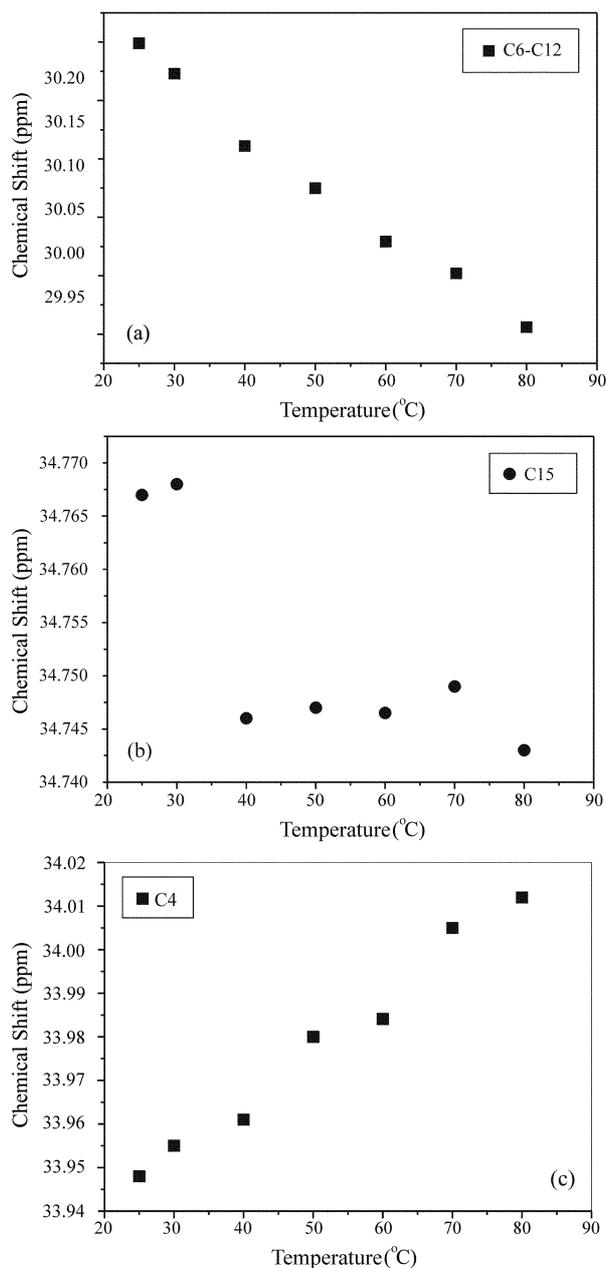
Figure 4. Chemical shifts of C$_{30}$DME at various temperatures; (a) monotonic upfield shift of C6-C12 carbons, (b) abrupt upfield shift of C15 carbon, and (c) monotonical downfield shift of C14 carbons.

mational change of the molecule, geometical optimizations and NMR chemical shifts were calculated by semi-emperical AM1 and HF methods in the Gaussian 94. The 3-21G* base sets were used for the HF method and parameters are R$_1$ = 19.0 and R$_2$ = 15.7, where R$_1$ represents the height and R$_2$ is the distance between two ester carbons, respectively. Table 1 lists the calculated CS for central carbon atoms for the linear (trans) and bent (gauche) conformations, where the methyl carbons (C59, C68) in the middle of the conformation show increased CS and the other carbons (C14-19) exhibit decreased CS. Other carbon atoms also show the same trends as the ^{13}C NMR. Such quantitative agreements

Table 1. The calculated CS for the several carbon atoms in $C_{30}DME$ in linear (trans) and bending (gauche) conformations

	Chemical Shift (HF/3-21G*//AM1)		Chemical Shift (HF/3-21G*//HF/3-21G*)	
	Linear	Bending	Linear	Bending
C14	35.65	34.24	32.49	32.08
C15	28.58	27.84	28.23	27.63
C16	34.35	33.70	30.84	29.30
C17	34.35	33.31	30.84	29.40
C18	28.59	26.98	28.23	26.91
C19	35.66	36.60	32.49	33.54
C59	18.80	25.09	15.90	22.30
C68	18.80	21.83	15.90	18.82

between the ^{13}C NMR experiment and calculation have confirmed that the main chain structure of $C_{30}DME$ came from the linear to bending conformation by rotating on the C(16)-C(17) axis. Also, the AM1 calculated energy difference between the linear and the bending conformational is 0.78 kcal/mol.

In this study, the conformational change of a bola-form long chain diester, $C_{30}DME$, has been investigated on the solid-state ^{13}C NMR at various temperatures. Theoretical calculations coupled with experimental observations show a conformational change from linear to an U-shape at around 40 °C. In this case, two hydrocarbons at the middle of the chains perform the key role in rotating the long alkyl chain.

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