

Chemisorption of CO₂ by Chitosan Oligosaccharide/DMSO: Organic Carbamato-Carbonato Bond Formation

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Electronic Supporting Information (ESI)

Figure S1. Partial ¹H NMR spectrum of CS•HCl dissolved in D₂O and its proposed chemical structure. The degree of deacetylation (DDA) was determined using the integration of the acetyl protons (**H-Ac**) and the sum of the protons attached to **C-2**, till **C-6** according to the following equation¹: $DDA = (1 - [(H-Ac/3)/(H-((C-2)-(C-6))/6)]) \times 100\% \approx 94.8\%$

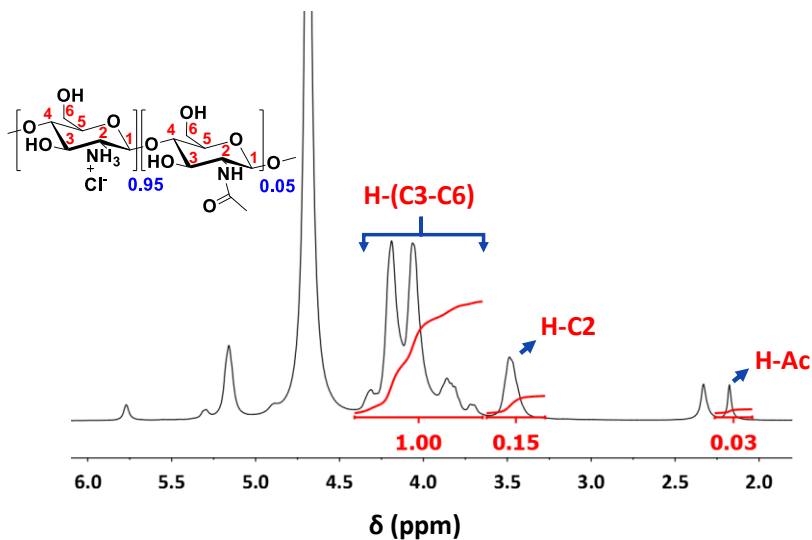


Table S1. CHN results of CS•HCl obtained from EA. DDA was calculated from the weight ratio between carbon and nitrogen ($W_{C/N}$) according to the following equation²:

$$DDA = (4 - (0.583 \times W_{C/N})) \times 100\%$$

C %	H%	N%	$W_{C/N} = 5.228$	$DDA = 95.2\%$
35.60	6.24	6.81		

Figure S2. NMR spectra of Gln•HCl/NaOH/DMSO- d_6 before (red) and after (black) bubbling CO₂. **A.** ¹³C NMR, **B.** ¹H NMR, **C.** & **D.** ¹H-¹⁵N HSQC spectra.

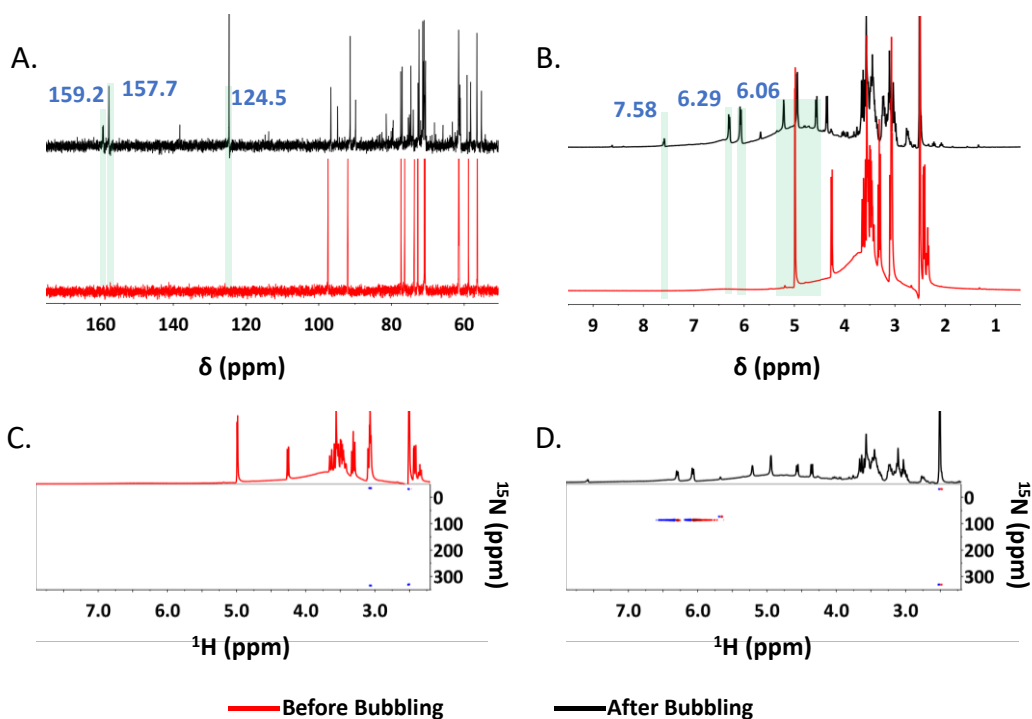


Figure S3. Partial ^{13}C NMR spectra of glucose/NaOH pellet/in $\text{DMSO-}d_6$ obtained before (red) and after bubbling of CO_2 (black). The peak emerged at 167.5 ppm corresponds to inorganic bicarbonate as a result of the side reaction of the NaOH with CO_2 .

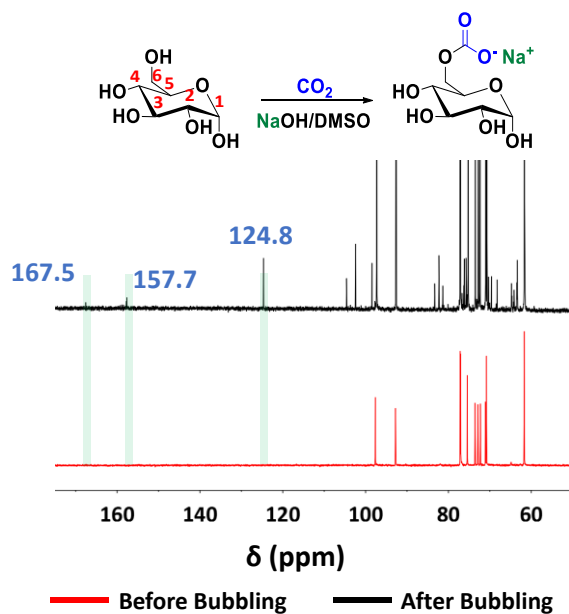
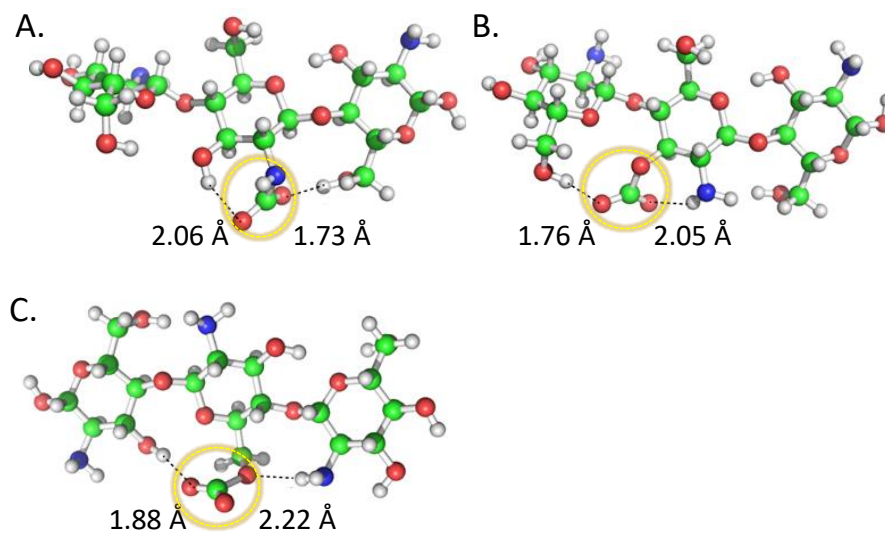


Figure S4. DFT optimized structures of hypothetically-formed single CO_2 species at the central glucosamine unit: **A.** Carbamate. **B.** Ionic organic alkylcarbonate at **C-3**. **C.** Ionic organic alkylcarbonate at **C-6**.



In an earlier report, we displayed that the interaction between a CO₂ molecule and the amino group using a glucoseamine trimer was more favorable compared to the interaction with the hydroxyl group at **C-6** by ~2 kcal mol⁻¹.³ In terms of stability, the obtained energy values (Table S2) showed that the formed ionic organic alkylcarbonate product is thermodynamically more favorable. For all cases, the optimized structures (Figure S4) indicated that the organic carbonate/carbamate anion is stabilized through hydrogen bonding with the adjacent hydroxyl and amino groups, in agreement with our previous finding for the carbonate formation in chitin-acetate/DMSO binary system.^{2,3} The calculated relative energy values for the three possible structures showed that the formation of organic carbonate at **C-6** is more favorable over **C-3** by ~ 3 kcal mol⁻¹, which support the reactivity of the alkoxide ions toward CO₂ as anticipated from the proton affinity data (*vide supra*).

Table S1. Relative stability (kcal mol⁻¹) of carbonate and carbamate at the central unit of the glucoseamine trimer. The more negative value, the higher stability.

	ΔE	ΔH	ΔG
Carbamate	0.00	0.00	0.00
Carbonate (C-3)	0.03	-0.82	0.09
Carbonate (C-6)	-3.93	-4.07	-2.97

References:

- 1 A. Hirai, H. Odani and A. Nakajima, *Polym. Bull.*, 1991, **26**, 87–94.
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- 3 A. F. Eftaiha, F. Alsoubani, K. I. Assaf, C. Troll, B. Rieger, A. H. Khaled and A. K. Qaroush, *Carbohydr. Polym.*, 2016, **152**, 163–169.