

# Chemisorption of CO<sub>2</sub> by Chitosan Oligosaccharide/DMSO: Organic Carbamato-Carbonato Bond Formation

Abdussalam K. Qaroush<sup>a\*</sup> Khaleel I. Assaf,<sup>b</sup> Sanaa K. Bardaweel,<sup>c</sup> Ala'a Al-Khateeb,<sup>d</sup> Fatima Alsubani,<sup>d</sup> Esraa Al-Ramahi,<sup>d</sup> Mahmoud Masri,<sup>e</sup> Thomas Brück,<sup>e</sup> Carsten Troll,<sup>f</sup> Bernhard Rieger,<sup>f</sup> Ala'a F. Eftaiha,<sup>d\*</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, The University of Jordan, Amman 11942, Jordan.

<sup>b</sup>Department of Life Sciences and Chemistry, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany.

<sup>c</sup>Department of Pharmaceutical Sciences, Faculty of Pharmacy, The University of Jordan, Amman 11942, Jordan.

<sup>d</sup>Department of Chemistry, the Hashemite University, P.O. Box 150459, Zarqa 13115, Jordan.

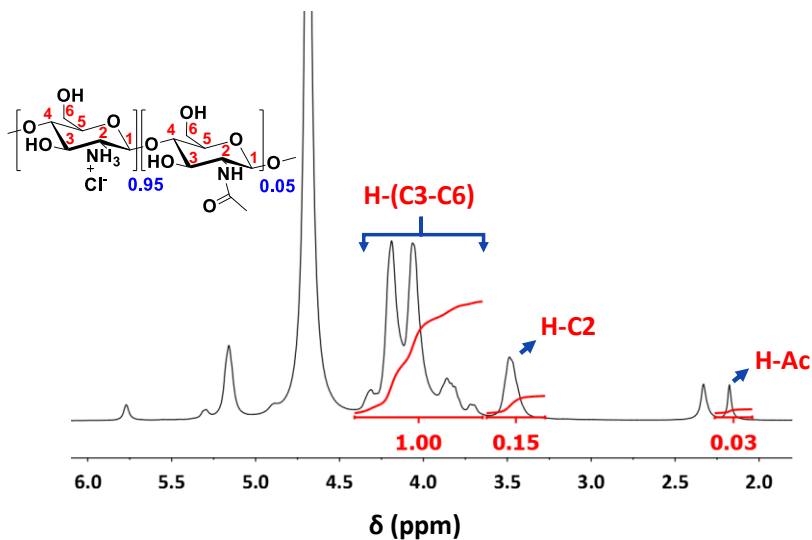
<sup>e</sup>Division of Industrial Biocatalysis, Department of Chemistry, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany.

<sup>f</sup>WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching bei München, Germany.

\* Corresponding Authors: a.qaroush@ju.edu.jo (AKQ)  
alaa.eftaiha@hu.edu.jo (AFE)

## Electronic Supporting Information (ESI)

**Figure S1.** Partial <sup>1</sup>H NMR spectrum of CS•HCl dissolved in D<sub>2</sub>O 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 equation<sup>1</sup>:  $DDA = (1 - [(H-Ac/3)/(H-((C-2)-(C-6))/6)]) \times 100\% \approx 94.8\%$

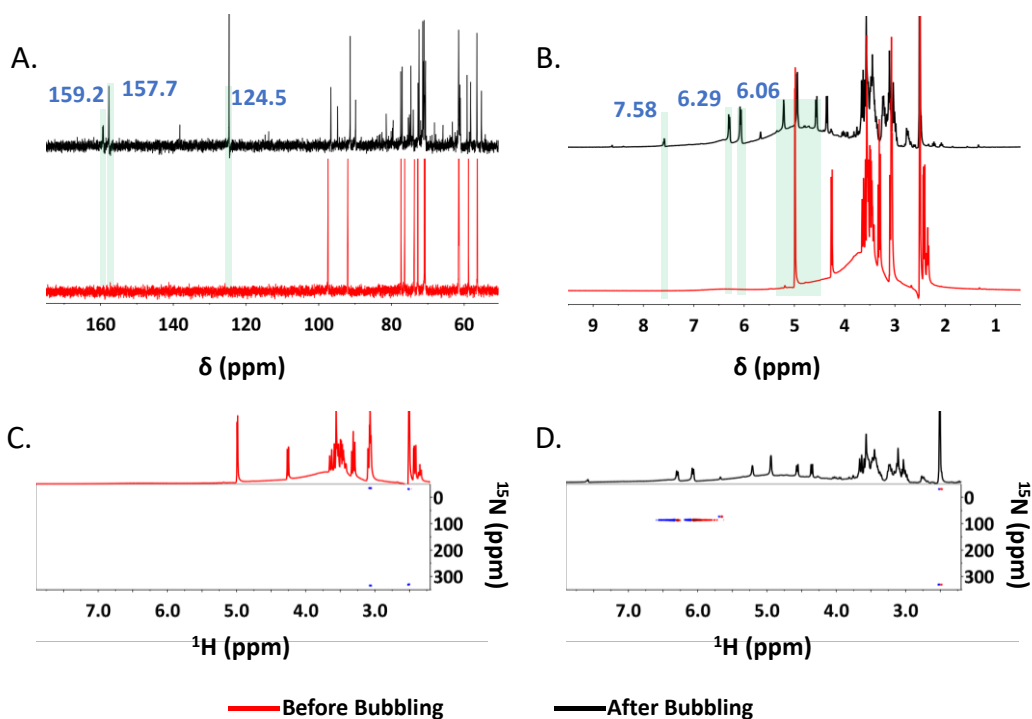


**Table S1.** CHN results of CS•HCl obtained from EA. DDA was calculated from the weight ratio between carbon and nitrogen ( $W_{C/N}$ ) according to the following equation<sup>2</sup>:

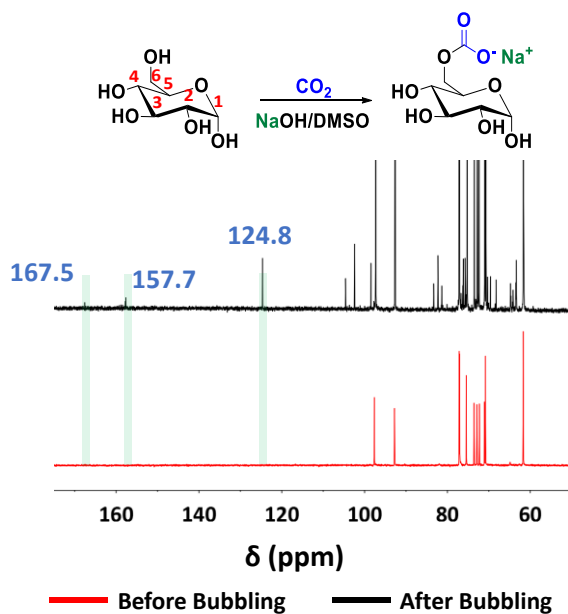
$$DDA = (4 - (0.583 \times W_{C/N})) \times 100\%$$

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

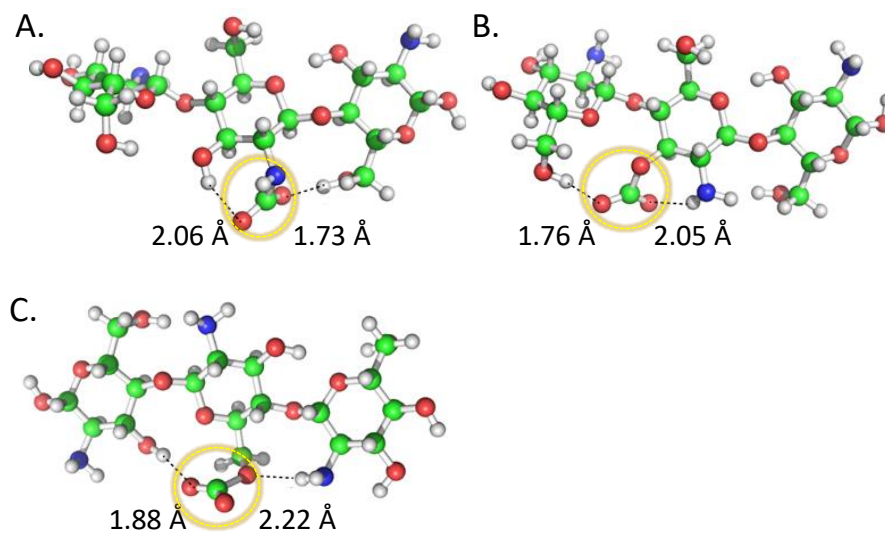
**Figure S2.** NMR spectra of Gln•HCl/NaOH/DMSO- $d_6$  before (red) and after (black) bubbling  $CO_2$ . **A.**  $^{13}C$  NMR, **B.**  $^1H$  NMR, **C.** & **D.**  $^1H$ - $^{15}N$  HSQC spectra.



**Figure S3.** Partial  $^{13}\text{C}$  NMR spectra of glucose/NaOH pellet/in  $\text{DMSO-}d_6$  obtained before (red) and after bubbling of  $\text{CO}_2$  (black). The peak emerged at 167.5 ppm corresponds to inorganic bicarbonate as a result of the side reaction of the NaOH with  $\text{CO}_2$ .



**Figure S4.** DFT optimized structures of hypothetically-formed single  $\text{CO}_2$  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 CO<sub>2</sub> 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<sup>-1</sup>.<sup>3</sup> 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.<sup>2,3</sup> 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<sup>-1</sup>, which support the reactivity of the alkoxide ions toward CO<sub>2</sub> as anticipated from the proton affinity data (*vide supra*).

**Table S1.** Relative stability (kcal mol<sup>-1</sup>) of carbonate and carbamate at the central unit of the glucoseamine trimer. The more negative value, the higher stability.

	$\Delta E$	$\Delta H$	$\Delta G$
Carbamate	0.00	0.00	0.00
Carbonate ( <b>C-3</b> )	0.03	-0.82	0.09
Carbonate ( <b>C-6</b> )	-3.93	-4.07	-2.97

## References:

- 1 A. Hirai, H. Odani and A. Nakajima, *Polym. Bull.*, 1991, **26**, 87–94.
- 2 Z. M. dos Santos, A. L. P. F. Caroni, M. R. Pereira, D. R. da Silva and J. L. C. Fonseca, *Carbohydr. Res.*, 2009, **344**, 2591–2595.
- 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.