ACS Sustainable Chemistry & Engineering

pubs.acs.org/journal/ascecg

Letter

Mechanochemical vs Wet Approach for Directing CO_2 Capture toward Various Carbonate and Bicarbonate Networks

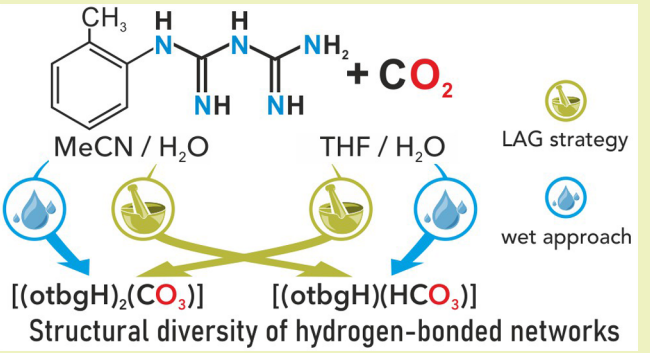
Michał K. Leszczyński, Dawid Kornacki, Michał Terlecki, Iwona Justyniak, Goran I. Miletić, Ivan Halasz, Piotr Bernatowicz, Vadim Szejko, and Janusz Lewiński*

Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 4374−4380

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The distinct research areas related to CO_2 capture and mechanochemistry are both highly attractive in the context of green chemistry. However, merger of these two areas, *i.e.*, mechanochemical CO_2 capture, is still in an early stage of development. Here, the application of biguanidine as an active species for CO_2 capture is investigated using both solution-based and liquid-assisted mechanochemical approaches, which lead to a variety of biguanidinium carbonate and bicarbonate hydrogen-bonded networks. We demonstrate that in solution, the formation of the carbonate vs bicarbonate networks can be directed by the organic solvent, while, remarkably, in the liquid-assisted mechanochemical synthesis employing the same solvents as additives, the selectivity in network formation is inversed. In general, our findings support the view of mechanochemistry not only as a sustainable alternative but rather as a complementary strategy to solution-based synthesis.



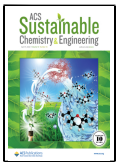
KEYWORDS: *Mechanochemistry, Liquid-assisted grinding, CO_2 capture, Biguanide, Carbonate, Bicarbonate, Hydrogen-bonded networks*

INTRODUCTION

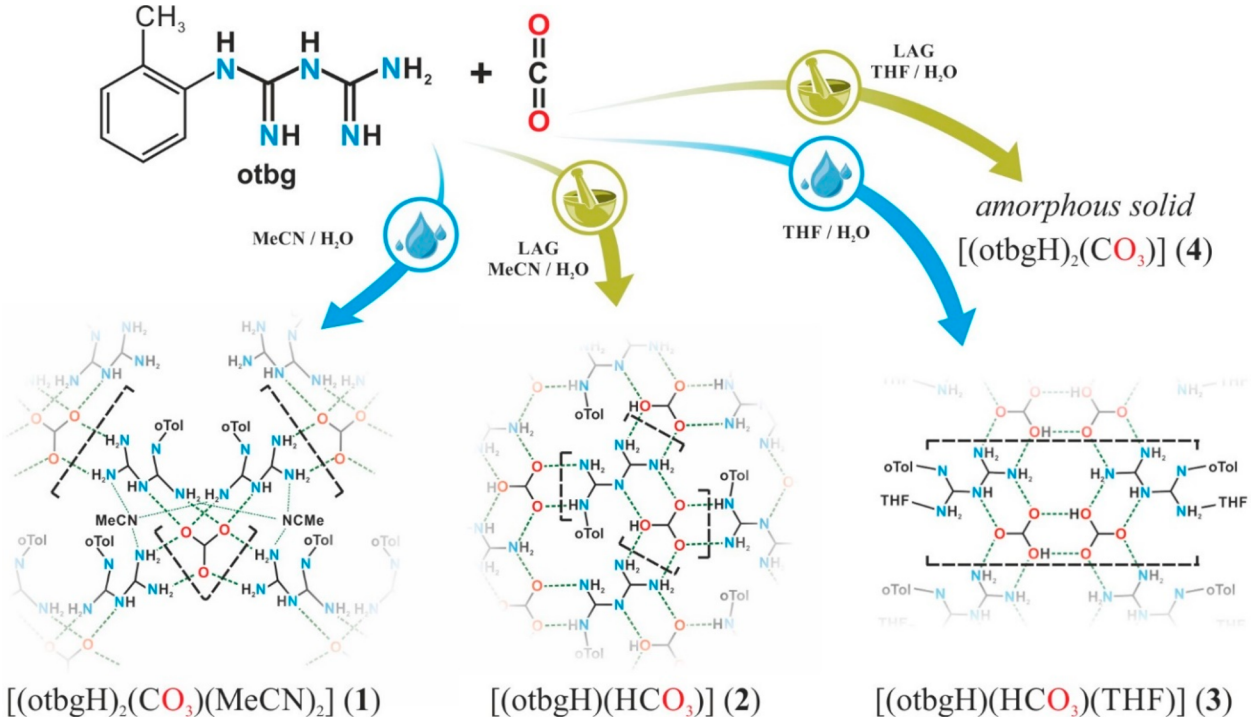
Continuously increasing environmental awareness in the recent decades has encouraged the development of many sustainability-driven initiatives, defined within the Twelve Principles of Green Chemistry, aiming at enhanced efficiency and environmental safety of chemical processes.[1,2] In this notion, the mechanically induced solid state chemical transformations have been elevated from mere curiosity to a dynamically growing research field providing highly efficient alternatives to the classic solution-based synthetic methods[3,4] Within this recent advent of mechanochemistry, a broad range of remarkable developments have been demonstrated in synthetic organic[5−8] and inorganic chemistry,[9−11] as well as materials science.[12−18] One of the emerging research fields in this area concerns mechanically induced chemical reactions at the gas−solid interface.[19] With regard to the principles of green chemistry development of gas−solid-state small-molecule ball-milling processes involving CO_2 would be highly desirable, but this research field is still at its infancy with only a handful of reports in the past decade. For example, Pinhas and co-workers used gaseous CO_2 in the solvent-free and catalyst-free conversion of an aziridine to an oxazolidinone,[20] and Métro and co-workers developed facile formation of L-lysine ammonium carbamate upon grinding of L-lysine in a CO_2 atmosphere.[21] Another interesting contribution concerned the graphite functionalization and exfoliation by ball milling in the presence of dry ice[22,23] and probing the reactivity of a ZIF material toward gaseous CO_2.[24]

Following the pioneering studies concerning CO_2 fixation and conversion using nitrogen-rich organic bases,[25,26] the metal-free approach aimed at CO_2 conversion has evolved into one of the most promising green sources of C1 synthons over the past decade.[27−29] In these mostly solution-based investigations, the initial reaction step involves formation of carbamate-type zwitterionic species, which can be hydrolyzed toward carbonates or bicarbonates. However, in-depth understanding of the mechanism of carbamate hydrolysis appears as a nontrivial task due to a number of possible reaction pathways including cooperative interactions of multiple molecules.[30] In this regard, apart from the strongly basic amidine or guanidine derivatives, one of the most commonly studied CO_2 absorption systems involves polymeric species functionalized with amine moieties.[31,32] Therefore, a promising development appears to be the use of biguanide derivatives, which combine both high basicity and capabilities of internal proton transfer, but this

Received: December 13, 2021
Revised: March 24, 2022
Published: April 1, 2022



Scheme 1. Reaction Pathways Leading to 1−4 Representing CO_2 Fixation by otbg Using MeCN and THF in Solution-Based and LAG Strategies



research area appears to be surprisingly underdeveloped, with only a handful of reports related to the study of CO_2 sensing platforms based on the polyhexamethylene biguanide (PHMB) polymer.[33,34] As part of our systematic studies on both designing of various reaction systems in wet and solid state reaction environments[35−37] as well as the use of CO_2 as a substrate in the preparation of functional materials,[38−41] herein we confront the mechanochemical vs solution approach to CO_2 fixation by a model biguanide. Our investigations reveal that a variety of carbonate and bicarbonate products differing in molecular structures and supramolecular architectures can be formed in the studied reaction system depending on both the solvent (MeCN vs THF) and the methodology (solution vs liquid-assisted grinding (LAG)) used (Scheme 1). In particular, we found that the selectivity of carbonate vs bicarbonate formation in the solution-based method is related to the type of used solvent. Remarkably, if the same solvent was used for a LAG process, the reaction selectivity toward carbonate vs bicarbonate was reversed and accompanied by an extraordinary difference in the resulting supramolecular architecture of the hydrogen-bonded network, in comparison to the wet approach. Finally, the process of CO_2 release form the developed biguanidinium networks was studied, revealing low decomposition temperatures, which is desirable for the application as controlled CO_2 capture-and-release systems.

RESULTS AND DISCUSSION

Initially, the CO_2 capture process was studied in a MeCN/H_2O solution environment. Exposing the MeCN/H_2O (40:1 by volume) solution of 1-(o-tolyl)biguanide (otbg) to gaseous CO_2 resulted in an immediate deposition of white precipitate, which was identified as a solvate $[(otbgH)_2(CO_3)(MeCN)_2]$ (**1**) using a variety of techniques (see below). High quality single crystals ($C222_1$ space group) of **1** were prepared by slow diffusion of CO_2 into a MeCN/H_2O (40:1 vol) solution of otbg at room temperature after ca. 2 days. Single crystal X-ray diffraction studies (SCXRD) revealed that the crystal structure **1** consists of $[otbgH]^+$ cations and carbonate dianions interconnected by hydrogen bonds, which results in the formation of a 2D supramolecular hydrogen-bonded network layers (Figure 1a; Figures S1 and S2) forming a 3D stacked structure (Figure 1b). Moreover, the crystal structure of **1** includes MeCN molecules, and each MeCN molecule bridges three independent biguanidinium moieties by hydrogen-bonded interactions (Scheme 1, bottom left corner) (N−N distances: 3.105(4), 3.154(3), and 3.169(4) Å). Significantly, **1** could also be easily prepared as a crystalline precipitate in good yield by direct air capture (DAC) of atmospherical CO_2 upon exposure of a MeCN/H_2O (40:1 vol) otbg solution to open air at −24 °C for 1 day. The identity and phase-purity of the prepared materials were confirmed using elemental analysis, PXRD (Figure S8), FTIR, and NMR spectroscopies. The FTIR spectrum of **1** (Figure S29) was rather complex but involved a signal at 1371 cm^{-1}, related to the stretching mode of the carbonate anion. Moreover, the ^{13}C CPMAS NMR spectrum (Figure 2; Figure S11) appeared very informative due to a characteristic sharp signal at 169 ppm, typical for carbonate ions. Purity of **1** was additionally confirmed using ^1H and ^{13}C NMR spectroscopies in D_2O solution (Figures S15 and S16). Noteworthy, the materials capable of absorbing CO_2 directly from air (at ca. 400 ppm concentration), such as iminoguanidinate-based systems,[42−45] are highly desirable with regard to their use toward achieving the "negative CO_2 emission" goal.

Encouraged by the observation of extended hydrogen-bonded networks in **1**, we wondered if applying the mechanochemical approach could influence the reaction pathway and lead to formation of different products. Therefore, we conducted a mechanochemical reaction by grinding otbg with a stoichiometric amount of H_2O (1:1) as

https://doi.org/10.1021/acssuschemeng.1c08402
ACS Sustainable Chem. Eng. 2022, 10, 4374−4380

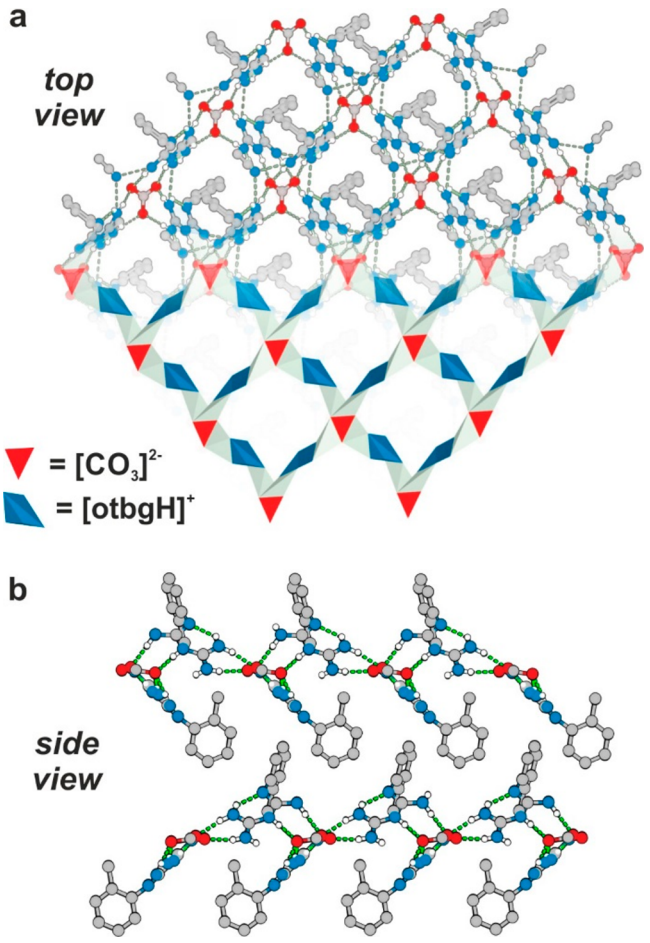


Figure 1. Crystal structure of **1**: (a) 2D supramolecular hydrogen-bonded network (o-tolyl groups have been omitted in picture for clarity). (b) Stacking of the 2D layers. C = gray, N = blue, O = red, H = white.

well as a small amount (20 μL for 200 mg of the reaction mixture) of acetonitrile as an additive in a CO_2-rich atmosphere, afforded by introduction of an excess of solid CO_2 into the reaction vessel prior to grinding. As a result of the LAG process (15 min, 30 Hz), a white powder of a bicarbonate [(otbgH)(HCO_3)] (**2**) was formed in almost quantitative yield. Numerous attempts at recrystallization of **2** were unsuccessful, but the crystal structure was solved by simulated annealing using PXRD data (Figure 3c; Figures S5 and S6). The PXRD data analysis revealed that the crystal structure of **2** is composed of biguanidinium cations and bicarbonate anions interconnected into an extended hydrogen-bonded network (Figure 3a and b; Figures S6 and S7). The exact location of protons in the biguanidinium moiety was additionally confirmed using DFT calculations (see Supporting Information for more details). Interestingly, the bicarbonate anions in **2** did not assemble into the characteristic dimeric moieties[46,47] but formed monomers stabilized by seven hydrogen bonds (one donating and six accepting) formed with the surrounding four biguanidinium cations. The extended hydrogen-bonded network formed double-layered 2D sheets with 86% of the hydrogen bonds located within each layer and 14% devoted to linking the separate layers into the double-layered assembly, which, as a whole, formed a stacked 3D crystal structure (Figure 3b). Additionally, elemental analysis confirmed that **2** was prepared as a phase-pure solid (see Supporting Information for details), while both the FTIR spectrum with a signal at 1346 cm^{-1} (Figure S30) and the ^{13}C CPMAS NMR spectrum with a signal at 161 ppm (Figure 2; Figure S12) well substantiated the presence of the bicarbonate ion. Additionally, ^{1}H and ^{13}C NMR spectra in D_2O solution confirmed the purity of the product **2** (Figures S17 and S18).

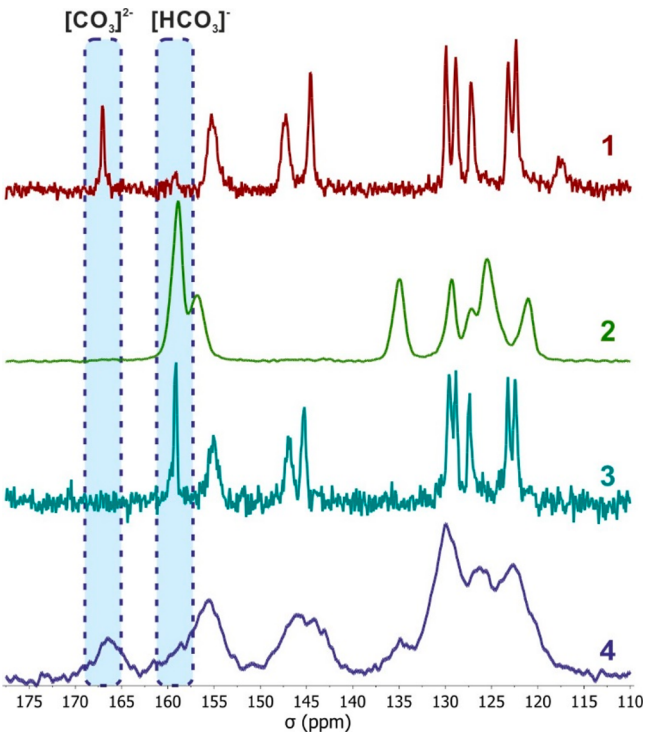


Figure 2. ^{13}C CP-MAS NMR spectra of **1**, **2**, **3**, and **4** (110−180 ppm range).

Having observed the acetonitrile molecules bridging the three independent biguanidinium moieties by hydrogen bonds in **1**, we wondered if using a different donor solvent could affect the structure of the formed network. Therefore, in next experiment, we used THF for the study of CO_2 capture by otbg. Absorption of gaseous CO_2 by a THF/H_2O solution (50:1 by volume) of otbg resulted in precipitation of a solvated bicarbonate [(otbgH)(HCO_3)(THF)] (**3**) in almost quantitative yield. Single crystals of **3** were prepared by slow diffusion of CO_2 into a THF/H_2O solution (50:1 by volume) of otbg. The identity and purity of **3** was confirmed using a variety of analytical techniques (see below). Analysis of the SCXRD data revealed that the crystal structure of **3** consists of bicarbonate dimers interconnected by biguanidinium cations (Figure 4a; Figures S3 and S4), which self-organized into an extended hydrogen-bonded network of a rosette-ribbon structure (Figure 4). The crystal structure of **3** does involve also THF solvent molecules coordinated by the N−H···O hydrogen bond to the biguanidinium moiety backbone (N−O distance of 2.827(3) Å) (Figure 4). The PXRD study (Figure S9) and elemental analysis confirmed that **3** was a phase-pure compound, and both the FTIR spectrum featuring a signal at 1343 cm^{-1} (Figure S31) and the ^{13}C CPMAS NMR spectrum exhibiting a sharp signal at 161 ppm (Figure 2; Figure S13), as well as ^{1}H and ^{13}C NMR spectra in D_2O solution (Figures S19 and S20), substantiated the presence of the bicarbonate species.

https://doi.org/10.1021/acssuschemeng.1c08402
ACS Sustainable Chem. Eng. 2022, 10, 4374−4380

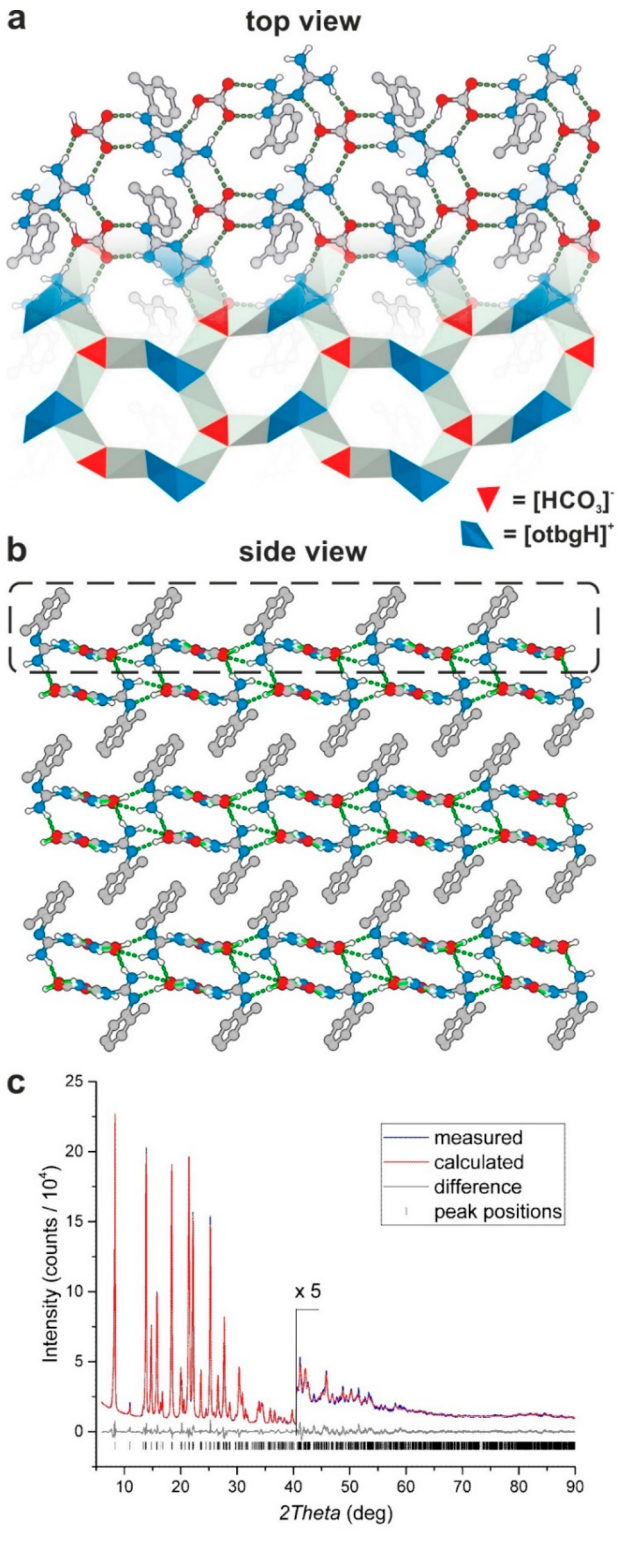


Figure 3. Crystal structure of **2**: (a) 2D supramolecular hydrogen-bonded network (half-layer), (b) stacking of the 2D layers (half-layer marked in rectangle), (c) PXRD diffractogram of **2** including experimental and fitted data. C = gray, N = blue, O = red, H = white.

Additionally, the LAG procedure was involved to investigate the mechanochemical CO_2 capture by otbg in the presence of THF and water. As a result, $[(otbgH)_2(CO_3)]$ (**4**) was prepared as a white amorphous powder, as evidenced by a PXRD study (Figure S10), which hindered our attempts to

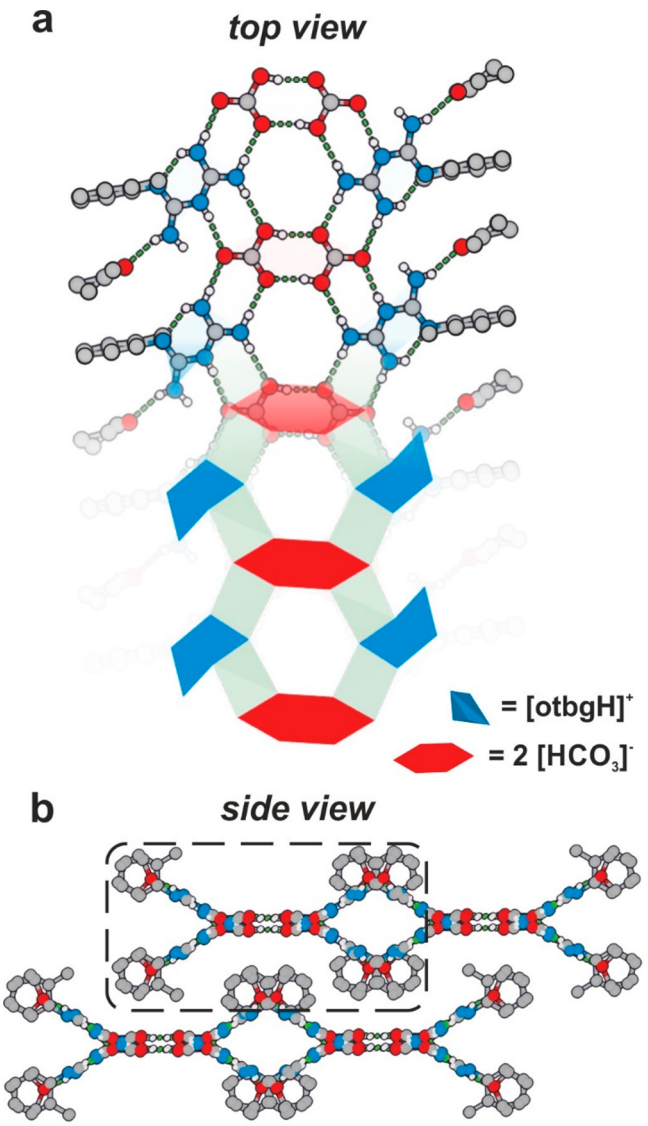


Figure 4. Crystal structure of **3**: (a) 1D supramolecular hydrogen-bonded ribbon, (b) stacking of the 1D ribbons in **3** (single ribbon marked in rectangle). C = gray, N = blue, O = red, H = white.

investigate its internal structure. Despite our unsuccessful attempts to crystallize **4**, its chemical composition was studied using ^{13}C CPMAS NMR (Figure 2; Figure S14), which revealed a broad signal at 168 ppm, characteristic for the CO_3^{2-} species. The composition of **4** was additionally studied using FTIR spectroscopy, revealing a signal at 1367 cm^{-1} related to carbonate ions (Figure S32) and elemental analysis (see Supporting Information for details), which unequivocally confirmed the formula $[(otbgH)_2(CO_3)]$. Purity of **4** was additionally confirmed by analysis of the ^1H and ^{13}C NMR spectra in D_2O solution (Figures S21 and S22).

As demonstrated, otbg appears as a promising molecule for CO_2 capture applications. Despite the fact that absorption of CO_2 using the typical amine-based systems (e.g., polyethylenimine) usually leads to formation of carbamate or carbamic acid derivatives,[48,49] neither of these species were detected as products in conducted reactions involving otbg. Instead, all of the products were identified as pure carbonates or bicarbonates, which was confirmed by both solid state ^{13}C CPMAS NMR (Figures 2; Figures S11−S14) and ^1H and ^{13}C

https://doi.org/10.1021/acssuschemeng.1c08402
ACS Sustainable Chem. Eng. 2022, 10, 4374−4380

NMR studies in D_2O solutions of **1**, **2**, **3**, and **4** (Figures S15–S22), as well as elemental analysis. Thus, the observed results of CO_2 absorption using otbg solutions are consistent with the literature reports concerning similar transformations involving guanidines, amidines, and urea, which form carbonates or bicarbonates upon exposure to CO_2 in the presence of water.[25,26,50] Nevertheless, the most desired properties of potential CO_2 scrubbing systems concern not only capture but also easy and on-demand release of CO_2. In this regard, we investigated the thermal decomposition of **1**, **2**, **3**, and **4** using thermogravimetric analysis (TGA), which revealed that in all of the studied cases CO_2 can be released at low temperatures (Figures S24–S27). The thermal decomposition of all of the studied materials resulted in formation of otbg, as evidenced by the observed weight loss values corresponding to the release of CO_2, H_2O, and (optionally) organic solvent. The decomposition step leading to the formation of otbg was observed at relatively low temperatures: 89, 110, 93, and 115 °C for **1**, **2**, **3**, and **4**, respectively. Further thermal decomposition of the studied samples closely matched the decomposition pathway of the pure otbg sample, which additionally confirmed the proposed formation of the otbg phase in the initial decomposition step (Figure S28). Finally, we have studied the possibility for recovery of the otbg base by thermal decomposition (at 100 °C) of **1** and **3** followed by ^{1}H NMR spectroscopic analysis (Figure S23). As a result, we found that **1** could be readily decomposed to obtg with essentially no signs of biguanide degradation even after five cycles of a CO_2 absorption–thermal decomposition process (final yield of the collected otbg was 85% with respect to the starting material used in the initial cycle). In the case of **3**, the initial decomposition also allowed for recovery of the otbg, but extended repetition of this procedure resulted in partial degradation of otbg (Figure S23).

CONCLUSIONS

In conclusion, we demonstrated that the CO_2 capture process using the studied biguanide system in the presence of water and organic solvents leads to various hydrogen-bonded structures depending on the solvent type and application of solution-based or mechanochemical strategy. In particular, we found that the controlled formation of carbonate vs bicarbonate networks could be achieved by selection of the organic solvent. Remarkably, the reaction selectivity toward carbonate/bicarbonate is inversed if the mechanochemical approach is used instead, which was also accompanied by a substantial change in the supramolecular architecture of the resulting hydrogen-bonded networks. Moreover, thermal CO_2 release from the studied materials was investigated, revealing low temperatures of thermal decomposition, which is desirable for controlled CO_2 capture-and-release applications. In general, our findings support the view of mechanochemistry not only as a sustainable alternative but also as a complementary strategy to solution synthesis, which might lead to products unavailable using the traditional wet-chemistry procedures. Further investigations in this research area, including application of a range of other organic derivatives and various CO_2 capture conditions, are currently underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c08402.

Experimental procedures, supporting figures and tables concerning single crystal X-ray diffraction, powder X-ray diffraction, NMR spectroscopy, TGA, and IR spectroscopy (PDF)

Crystallographic data for product **1** (CCDC 2099296) based on the single crystal X-ray diffraction study (CIF)

Crystallographic data for product **2** (CCDC 2093967) based on the powder diffraction study (CIF)

Crystallographic data for product **3** (CCDC 2099297) based on the single crystal X-ray diffraction study (CIF)

AUTHOR INFORMATION

Corresponding Author

Janusz Lewiński – *Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland; Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland;* orcid.org/0000-0002-3407-0395; Email: lewin@ch.pw.edu.pl

Authors

Michał K. Leszczyński – *Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland; Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland;* orcid.org/0000-0001-9339-101X

Dawid Kornacki – *Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland*

Michał Terlecki – *Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland*

Iwona Justyniak – *Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland*

Goran I. Miletić – *Ruđer Bošković Institute, 10000 Zagreb, Croatia*

Ivan Halasz – *Ruđer Bošković Institute, 10000 Zagreb, Croatia;* orcid.org/0000-0002-5248-4217

Piotr Bernatowicz – *Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland;* orcid.org/0000-0001-8891-0380

Vadim Szejko – *Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland;* orcid.org/0000-0002-7787-7084

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.1c08402

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the National Science Centre, Poland, Grant OPUS 2017/25/B/ST5/02484, for financial support. Moreover, this work was realized in the framework of the COST Action CA18112 "Mechanochemistry for Sustainable Industry".

REFERENCES

(1) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press, 1998.

(2) Erythropel, H. C.; Zimmerman, J. B.; de Winter, T. M.; Petitjean, L.; Melnikov, F.; Lam, C. H.; Lounsbury, A. W.; Mellor, K.

E.; Janković, N. Z.; Tu, Q.; et al. The Green ChemisTREE: 20 Years after Taking Root with the 12 Principles. *Green Chem.* **2018**, *20*, 1929−1961.
(3) Ardila-Fierro, K. J.; Hernández, J. G. Sustainability Assessment of Mechanochemistry by Using the Twelve Principles of Green Chemistry. *ChemSusChem* **2021**, *14*, 2145−2162.
(4) Do, J.-L.; Friščić, T. Mechanochemistry: A Force of Synthesis. *ACS Cent. Sci.* **2017**, *3*, 13−19.
(5) Wang, G.-W. Mechanochemical Organic Synthesis. *Chem. Soc. Rev.* **2013**, *42*, 7668−7700.
(6) Leonardi, M.; Villacampa, M.; Menéndez, J. C. Multicomponent Mechanochemical Synthesis. *Chem. Sci.* **2018**, *9*, 2042−2064.
(7) Tan, D.; Friščić, T. Mechanochemistry for Organic Chemists: An Update. *Eur. J. Org. Chem.* **2018**, *2018*, 18−33.
(8) Kubota, K.; Pang, Y.; Miura, A.; Ito, H. Redox Reactions of Small Organic Molecules Using Ball Milling and Piezoelectric Materials. *Science* **2019**, *366*, 1500−1504.
(9) Boldyreva, E. Mechanochemistry of Inorganic and Organic Systems: What Is Similar, What Is Different? *Chem. Soc. Rev.* **2013**, *42*, 7719.
(10) Tan, D.; García, F. Main Group Mechanochemistry: From Curiosity to Established Protocols. *Chem. Soc. Rev.* **2019**, *48*, 2274−2292.
(11) Fiss, B. G.; Richard, A. J.; Douglas, G.; Kojic, M.; Friščić, T.; Moores, A. Mechanochemical Methods for the Transfer of Electrons and Exchange of Ions: Inorganic Reactivity from Nanoparticles to Organometallics. *Chem. Soc. Rev.* **2021**, *50*, 8279−8318.
(12) Kumar, S.; Jain, S.; Nehra, M.; Dilbaghi, N.; Marrazza, G.; Kim, K.-H. Green Synthesis of Metal−Organic Frameworks: A State-of-the-Art Review of Potential Environmental and Medical Applications. *Coord. Chem. Rev.* **2020**, *420*, 213407.
(13) Stolar, T.; Užarević, K. Mechanochemistry: An Efficient and Versatile Toolbox for Synthesis, Transformation, and Functionalization of Porous Metal−Organic Frameworks. *CrystEngComm* **2020**, *22*, 4511−4525.
(14) Prochowicz, D.; Saski, M.; Yadav, P.; Grätzel, M.; Lewiński, J. Mechanoperovskites for Photovoltaic Applications: Preparation, Characterization, and Device Fabrication. *Acc. Chem. Res.* **2019**, *52*, 3233−3243.
(15) de Oliveira, P. F. M.; Torresi, R. M.; Emmerling, F.; Camargo, P. H. C. Challenges and Opportunities in the Bottom-up Mechanochemical Synthesis of Noble Metal Nanoparticles. *J. Mater. Chem. A* **2020**, *8*, 16114−16141.
(16) Friščić, T.; Mottillo, C.; Titi, H. M. Mechanochemistry for Synthesis. *Angew. Chem., Int. Ed.* **2020**, *59*, 1018−1029.
(17) Szczęśniak, B.; Borysiuk, S.; Choma, J.; Jaroniec, M. Mechanochemical Synthesis of Highly Porous Materials. *Mater. Horizons* **2020**, *7*, 1457−1473.
(18) Julien, P. A.; Mottillo, C.; Friščić, T. Metal−Organic Frameworks Meet Scalable and Sustainable Synthesis. *Green Chem.* **2017**, *19*, 2729−2747.
(19) Bolm, C.; Hernández, J. G. Mechanochemistry of Gaseous Reactants. *Angew. Chem., Int. Ed.* **2019**, *58*, 3285−3299.
(20) Phung, C.; Ulrich, R. M.; Ibrahim, M.; Tighe, N. T. G.; Lieberman, D. L.; Pinhas, A. R. The Solvent-Free and Catalyst-Free Conversion of an Aziridine to an Oxazolidinone Using Only Carbon Dioxide. *Green Chem.* **2011**, *13*, 3224−3229.
(21) Al-Terkawi, A.-A.; Lamaty, F.; Métro, T.-X. Efficient CO_2 Sequestration by a Solid−Gas Reaction Enabled by Mechanochemistry: The Case of l -Lysine. *ACS Sustain. Chem. Eng.* **2020**, *8*, 13159−13166.
(22) Jeon, I.-Y.; Shin, Y.-R.; Sohn, G.-J.; Choi, H.-J.; Bae, S.-Y.; Mahmood, J.; Jung, S.-M.; Seo, J.-M.; Kim, M.-J.; Wook Chang, D.; Dai, L.; Baek, J.-B. Edge-Carboxylated Graphene Nanosheets via Ball Milling. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 5588−5593.
(23) Idris Abdu, H.; Eid, K.; Abdullah, A. M.; Sliem, M. H.; Elzatahry, A.; Lu, X. Dry Ice-Mediated Rational Synthesis of Edge-Carboxylated Crumpled Graphene Nanosheets for Selective and Prompt Hydrolysis of Cellulose and Eucalyptus Lignocellulose under Ambient Reaction Conditions. *Green Chem.* **2020**, *22*, 5437−5446.
(24) Brekalo, I.; Yuan, W.; Mottillo, C.; Lu, Y.; Zhang, Y.; Casaban, J.; Holman, K. T.; James, S. L.; Duarte, F.; Williams, P. A.; et al. Manometric Real-Time Studies of the Mechanochemical Synthesis of Zeolitic Imidazolate Frameworks. *Chem. Sci.* **2020**, *11*, 2141−2147.
(25) Villiers, C.; Dognon, J. P.; Pollet, R.; Thuéry, P.; Ephritikhine, M. An Isolated CO_2 Adduct of a Nitrogen Base: Crystal and Electronic Structures. *Angew. Chem., Int. Ed.* **2010**, *49*, 3465−3468.
(26) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuéry, P.; Ephritikhine, M.; Cantat, T. A Diagonal Approach to Chemical Recycling of Carbon Dioxide: Organocatalytic Transformation for the Reductive Functionalization of CO_2. *Angew. Chem., Int. Ed.* **2012**, *51*, 187−190.
(27) Zhang, S.; He, L.-N. Capture and Fixation of CO2 Promoted by Guanidine Derivatives. *Aust. J. Chem.* **2014**, *67*, 980.
(28) Xiong, T.-K.; Li, X.-J.; Zhang, M.; Liang, Y. Organic Synthesis of Fixed CO 2 Using Nitrogen as a Nucleophilic Center. *Org. Biomol. Chem.* **2020**, *18*, 7774−7788.
(29) P, S.; Mandal, S. K. From CO_2 Activation to Catalytic Reduction: A Metal-Free Approach. *Chem. Sci.* **2020**, *11*, 10571−10593.
(30) Said, R. B.; Kolle, J. M.; Essalah, K.; Tangour, B.; Sayari, A. A Unified Approach to CO_2-Amine Reaction Mechanisms. *ACS Omega* **2020**, *5*, 26125−26133.
(31) Li, Y. N.; He, L. N.; Liu, A. H.; Lang, X. D.; Yang, Z. Z.; Yu, B.; Luan, C. R. In Situ Hydrogenation of Captured CO_2 to Formate with Polyethyleneimine and Rh/Monophosphine System. *Green Chem.* **2013**, *15*, 2825−2829.
(32) Varghese, A. M.; Karanikolos, G. N. CO_2 Capture Adsorbents Functionalized by Amine − Bearing Polymers: A Review. *Int. J. Greenh. Gas Control* **2020**, *96*, 103005.
(33) Ma, W.; Xing, J.; Wang, R.; Rong, Q.; Zhang, W.; Li, Y.; Zhang, J.; Qiao, X. Optical Fiber Fabry−Perot Interferometric CO_2 Gas Sensor Using Guanidine Derivative Polymer Functionalized Layer. *IEEE Sens. J.* **2018**, *18*, 1924−1929.
(34) Kazanskiy, N. L.; Butt, M. A.; Khonina, S. N. Carbon Dioxide Gas Sensor Based on Polyhexamethylene Biguanide Polymer Deposited on Silicon Nano-Cylinders Metasurface. *Sensors* **2021**, *21*, 378.
(35) Kubisiak, M.; Zelga, K.; Bury, W.; Justyniak, I.; Budny-Godlewski, K.; Ochal, Z.; Lewiński, J. Development of Zinc Alkyl/Air Systems as Radical Initiators for Organic Reactions. *Chem. Sci.* **2015**, *6*, 3102−3108.
(36) Budny-Godlewski, K.; Justyniak, I.; Leszczyński, M. K.; Lewiński, J. Mechanochemical and Slow-Chemistry Radical Transformations: A Case of Diorganozinc Compounds and TEMPO. *Chem. Sci.* **2019**, *10*, 7149−7155.
(37) Budny-Godlewski, K.; Leszczyński, M. K.; Tulewicz, A.; Justyniak, I.; Pinkowicz, D.; Sieklucka, B.; Kruczała, K.; Sojka, Z.; Lewinski, J. A Case Study on the Desired Selectivity in the Solid-state Mechano- and Slow-chemistry, Melt, and Solution Methodologies. *ChemSusChem* **2021**, *14*, 3887.
(38) Sokołowski, K.; Bury, W.; Justyniak, I.; Fairen-Jimenez, D.; Sołtys, K.; Prochowicz, D.; Yang, S.; Schröder, M.; Lewiński, J. Permanent Porosity Derived from the Self-Assembly of Highly Luminescent Molecular Zinc Carbonate Nanoclusters. *Angew. Chem., Int. Ed.* **2013**, *52*, 13414−13418.
(39) Sokołowski, K.; Bury, W.; Justyniak, I.; Cieślak, A. M.; Wolska, M.; Sołtys, K.; Dzięcielewski, I.; Lewiński, J. Activation of CO_2 by *t*BuZnOH Species: Efficient Routes to Novel Nanomaterials Based on Zinc Carbonates. *Chem. Commun.* **2013**, *49*, 5271−5273.
(40) Sokołowski, K.; Bury, W.; Tulewicz, A.; Cieślak, A. M.; Justyniak, I.; Kubicki, D.; Krajewska, E.; Milet, A.; Moszyński, R.; Lewiński, J. Experimental and Computational Insights into Carbon Dioxide Fixation by RZnOH Species. *Chem.—Eur. J.* **2015**, *21*, 5496−5503.

https://doi.org/10.1021/acssuschemeng.1c08402
ACS Sustainable Chem. Eng. 2022, 10, 4374−4380

(41) Sołtys-Brzostek, K.; Terlecki, M.; Sokołowski, K.; Lewiński, J. Chemical Fixation and Conversion of CO_2 into Cyclic and Cage-Type Metal Carbonates. *Coord. Chem. Rev.* **2017**, *334*, 199−231.
(42) Custelcean, R. Iminoguanidines: From Anion Recognition and Separation to Carbon Capture. *Chem. Commun.* **2020**, *56*, 10272−10280.
(43) Seipp, C. A.; Williams, N. J.; Kidder, M. K.; Custelcean, R. CO_2 Capture from Ambient Air by Crystallization with a Guanidine Sorbent. *Angew. Chem., Int. Ed.* **2017**, *56*, 1042−1045.
(44) Williams, N. J.; Seipp, C. A.; Brethomé, F. M.; Ma, Y.-Z.; Ivanov, A. S.; Bryantsev, V. S.; Kidder, M. K.; Martin, H. J.; Holguin, E.; Garrabrant, K. A.; et al. CO_2 Capture via Crystalline Hydrogen-Bonded Bicarbonate Dimers. *Chem.* **2019**, *5*, 719−730.
(45) Custelcean, R.; Williams, N. J.; Wang, X.; Garrabrant, K. A.; Martin, H. J.; Kidder, M. K.; Ivanov, A. S.; Bryantsev, V. S. Dialing in Direct Air Capture of CO_2 by Crystal Engineering of Bisiminoguanidines. *ChemSusChem* **2020**, *13*, 6381−6390.
(46) White, N. G. Antielectrostatically Hydrogen Bonded Anion Dimers: Counter-Intuitive, Common and Consistent. *CrystEngComm* **2019**, *21*, 4855−4858.
(47) Zhao, W.; Flood, A. H.; White, N. G. Recognition and Applications of Anion−Anion Dimers Based on Anti-Electrostatic Hydrogen Bonds (AEHBs). *Chem. Soc. Rev.* **2020**, *49*, 7893−7906.
(48) Shen, X.; Du, H.; Mullins, R. H.; Kommalapati, R. R. Polyethylenimine Applications in Carbon Dioxide Capture and Separation: From Theoretical Study to Experimental Work. *Energy Technol.* **2017**, *5*, 822−833.
(49) Zhao, Q.; Wang, Q.; Zhang, C.; Du, Z.; Tian, M.; Mi, J. Effect of Chain Topology of Polyethylenimine on Physisorption and Chemisorption of Carbon Dioxide. *ChemPhysChem* **2015**, *16*, 1480−1490.
(50) Manna, U.; Das, G. An Overview of CO_3^{2-} /HCO_3^- Binding by Aerial CO_2 Fixation within the Self-Assemblies of Hydrogen-Bond Donor Scaffolds. *CrystEngComm* **2021**, *23*, 512−527.

https://doi.org/10.1021/acssuschemeng.1c08402
ACS Sustainable Chem. Eng. 2022, 10, 4374−4380