Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information for

What's New with CO_2? Recent Advances in Polycarbonate Production

Donald J. Darensbourg and Stephanie Wilson

Name	cyclopentene carbonate[i]	1,2,3,4-tetra-hydronaphthalene carbonate[ii]	indene carbonate[iii,a]		styrene carbonate[iv]	cyclohexene carbonate[4,b]	ethylene carbonate[4]	ethylene carbonate[c]	cyclohexene carbonate[v],[b]
Empirical Formula	$C_6H_8O_3$	$C_{11}H_{10}O_3$	$C_{10}H_8O_3$		$C_9H_8O_3$	$C_7H_{10}O_3$	$C_3H_4O_3$	$C_3H_4O_3$	$C_7H_{10}O_3$
Molecular Weight, g/mol	128.12	190.19	176.16		164.15	142.15	88.06	88.06	142.15
Geometric Isomer	*cis-*	*cis-*	*cis-*		-	*trans-*	-	-	*trans-*
Crystal System	*orthorhombic*	*monoclinic*	*monoclinic*		*orthorhombic*	*orthorhombic*	*monoclinic*	*monoclinic*	*orthorhombic*
Space Group	$P2_12_12_1$	$P2_1/n$	$P12_1/c1$		$Pna2_1$	$P2_12_12_1$	C2/c	C2/c	$P2_12_12_1$
Cell Volume, Å^3	591.90(16)	887.4(5)	1628.8(14)		776.1(5)	700.5(4)	366.80(11)	380.34	694.914
Density, Mg/m^3	1.438	1.424	1.437		1.405	1.348	1.595	1.538	1.359
Goodness of Fit	1.320	1.155	1.032		1.085	0.479	1.081	*NA*	*NA*
R1, %	4.27	4.85	3.69		2.95	3.30	3.05	25.01	3.52
C=O, Å	1.197(3)	1.203(2)	1.1974(18)	1.1959(18)	1.1963(14)	1.200(2)	1.1967(19)	1.150	1.193
C-C, Å	1.542(3)	1.550(3)	1.543(2)	1.535(2)	1.5308(18)	1.486(12)	1.513(2)	1.516	1.501
O-C-C-O, deg.	0.348	2.005	8.252	14.187	21.667	23.947	24.287	28.326	29.717

Table S1. X-ray crystallographic data for various 5-membered cyclic carbonates. Data obtained from appropriate .cif files from WebCSD[vi] and, when necessary, through modeling using CrystalMaker. [vii] *(a)* Two distinct yet similar polymorphs of

indene carbonate exist within the unit cell. *(b)* Disorder exists in the cyclohexane ring due to ring-flipping. *(c)* Data collected at room temperature.

WebCSD Family Name	O-C-C-O, deg.	C=O, Å	C-C, Å	R1, %
RUJXOJ[viii]	2.278	1.112	1.542	3.78
VECHUH[ix]	3.543	1.158	1.404	5.86
HOBHUB[x,a]	5.240	1.205	1.465	8.33
SEYLIR[xi,b]	5.473	1.221	1.460	6.67
RUJXOJ[8]	19.951	1.212	1.366	3.78
NIDCUY[xii]	20.218	1.185	1.387	4.87
ITECUG[xiii]	22.995	1.191	1.477	5.52
WEZLIW[xiv]	25.351	1.179	1.600	10.9
SUDMEJ[xv]	28.870	1.209	1.533	6.9
YEFRUW[xvi,c]	30.510	1.247	1.239	5.6

Table S2. X-ray crystallographic data for propylene carbonates. .Cif files obtained from WebCSD,[6] and data obtained using CrystalMaker.[7] *(a)* PC bound to zinc through carbonyl oxygen. *(b)* PC bound to cadmium through carbonyl oxygen. *(c)* According to WebCSD, disorder was observed in the propylene carbonate, but this was not apparent from the .cif file.

[i] D.J. Darensbourg, S.J. Wilson, "Coupling Reactions of CO_2 and Unexplored Epoxides: Polycarbonate *vs.* Cyclic Carbonate Formation." Poster presented at the 11th International Conference on Carbon Dioxide Utilization, Dijon, France; June 27-30, 2011. The structure of CPC has also been recently published in K.M. Tomczyk, P.A. Guńka, P.G. Parzuchowski, J. Zachara, G. Rokicki, *Green Chem.* 2012, **14**, 1749-1758, though no .cif file was available.

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[iii] D.J. Darensbourg, S.J. Wilson, *J. Am. Chem. Soc.* 2011, **133**, 18610-18613.

[iv] D.J. Darensbourg, S.H. Wei, unpublished results.

[v] D.J. Darensbourg, S.L. Lewis, J.L. Rodgers, J.C. Yarbrough, *Inorg. Chem.*, 2003, **42**, 581-589.

[vi] We wish to acknowledge the use of the EPSRC funded Chemical Database Service at Daresbury. "The United Kingdom Chemical Database Service", Fletcher, D.A., McMeeking, R.F., Parkin, D., J. Chem. Inf. Comput. Sci. 1996, **36**, 746-749.

[vii] Crystallographic images generated using CrystalMaker®: a crystal and molecular structures program for Mac and Windows. CrystalMaker Software Ltd, Oxford, England (www.crystalmaker.com)

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[xiii] Y. Hasegawa, K. Takahashi, S. Kume, H. Nishihara, *Chem. Commun.*, 2011, **47**, 6846.

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[xv] N. Perchenek, A. Simon, *Z. Anorg. Allg. Chem.*, 1993, **619**, 98.

[xvi] K.-I. Okamoto, J.R. Kirchoff, W.R. Heineman, E. Deutsch, M.J. Heeg, *Polyhedron*, 1993, **12**, 749.