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One-Step Synthesis and Structure of an Oligo(spiro-orthocarbonate)

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The synthesis of crystalline covalent solids from molecular building blocks generally yields amorphous products due to the difficulty in attaining the appropriate kinetic reversibility, which is needed for crystallization as demonstrated for solids held together by hydrogen and coordinate bonds.[1,2] Cognizant of the tremendous technological implications of developing synthetic routes for covalently linked organic networks, we have recently embarked on a program aimed at initially building up large organic molecules using simple one-step reactions. As a first object of this study we chose the spiro-orthocarbonate (SOC) building block for its importance as an expanding monomer in polymer chemistry, and for the lack of crystal structures of any oligomers or polymers based on this unit.[3,4] Here we report a simple one-step synthesis and the first crystal structure of an oligomer based on SOC (termed oligo-SOC).

The reaction of pentaerythritol (0.20 g, 1.47 mmol), **1**, and tetraethylorthocarbonate (0.25 mL, 1.20 mmol), **2**, according to Scheme 1 at 260 °C for 12 h in a sealed Pyrex tube (o.d. × i.d. = 11 × 9 mm^2) gave a white crystalline solid. The solid was washed with boiling water (3 × 30 mL) and diethyl ether (3 × 10 mL) to give 0.13 g (45% yield) of oligo-SOC. It is insoluble in refluxing water, dichloromethane, chloroform, acetonitrile, methanol, ethanol, *N*,*N*′-dimethylformamide, pyridine, nitrobenzene, hexane, and benzene. It is unaffected by concentrated ammonium hydroxide or sulfuric acid at room temperature. Chemical elemental analysis of the solid gave an empirical formula of $C_6H_8O_4$ corresponding to the expected repeat unit, and FT-IR showed characteristically strong υ_{C-O} stretch bands at 1183 and 1005 cm^{-1} corresponding to C−O bonds in (CO_4) and (CH_2−O), respectively.[5,6]

To further confirm the connectivity within the solid, the ^{13}C CPMAS NMR spectrum of the material was measured and found to give four major resonance peaks at δ 114.6, 65.0, 38.5, 30.2 ppm (Figure 1a). The first two peaks labeled A and C were respectively assigned to the carbon atoms in ***C***O_4 and ***C***H_2−O, which is in agreement with those resonance peaks recorded for the solution ^{13}C NMR spectrum (δ 114.5 and 65.4 ppm) for model compound 3,3,9,9-tetramethyl-1,5,7,11-tetraoxaspiro[5.5]undecane, **3**.[7]

Additionally, an interrupted decoupling experiment, in which carbon atoms bound to protons are expected to show no resonance, reveal the expected disappearance of the C peaks (Figure 1b). The remaining peaks labeled B′ and B are known to be in the region for quaternary carbon atoms: indeed the chemical shift of B (30.2 ppm) is coincident with that found for **3** (29.1 ppm) for ***C***$(-CH_2)_4$, and the fact that B′ is shifted to lower field indicates that it is bound to an electronegative group, an aspect that has led us to assign B′ (38.5 ppm) to ***C***$(-CH_2)_2(-CH_2OH)_2$ end groups. It is worth noting that the difference of +8.5 ppm in chemical shift between fully reacted and half reacted pentaerythritol in this compound has also been observed to a similar extent (+7.9 ppm) in the analogous molecular compounds.[3] Furthermore, the end groups have also been detected in the FT-IR spectrum where υ_{O-H} appears at 3041 cm^{-1}.

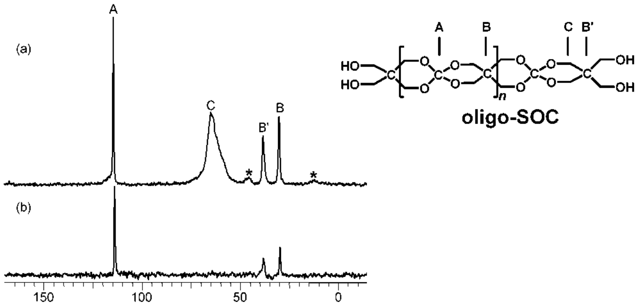
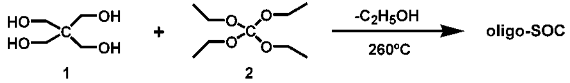


Figure 1. ^{13}C CPMAS NMR (at 75.45 MHz) spectra for oligo-SOC (a) coupled and (b) decoupled. Spectra were obtained using $^1H-^{13}C$ cross-polarization for signal enhancement (ca. 1 ms contact time) and high-power proton decoupling (ca. 90 kHz). The natural abundance ^{13}C spectra shown are the result of 2048 signal averages, with a 5 s delay between scans. Spinning sidebands are denoted by an asterisk (*).

Scheme 1 The Synthesis of Oligo-SOC



To further confirm the formation of the spiro-motif, we successfully prepared compound **3** from 2,2-dimethyl-1,3-propanediol and tetraethyl orthocarbonate under the same conditions as in Scheme 1. At this point it became clear to us that the compound is likely to be an oligomer of the spiro-orthocarbonate building block.

Attempts to obtain crystals of sufficient size for single-crystal X-ray diffraction studies were unsuccessful; however, due to the high crystallinity of oligo-SOC, it was possible to examine the small crystals by electron and X-ray powder diffraction techniques (Figure 2), which were consistent with a monoclinic cell with symmetry *I*2 and with $a = 9.167$ Å, $b = 5.681$ Å, $c = 5.880$ Å, $\beta = 90.0°$.

The unit cell volume admits only two tetrahedral units (one CO_4 and one CC_4) in the primitive repeat unit. We conclude that there are only three possible periodic (crystalline) structures: the two 3-dimensional corner-sharing network structures named for $CdSO_4$ and cristobalite (diamond topology) exemplified by BPO_4, and the rodlike edge sharing structure of, e.g., BPS_4.[8]

Due to the extreme sensitivity to radiation damage, quantitative electron diffraction data could only be obtained for one orientation

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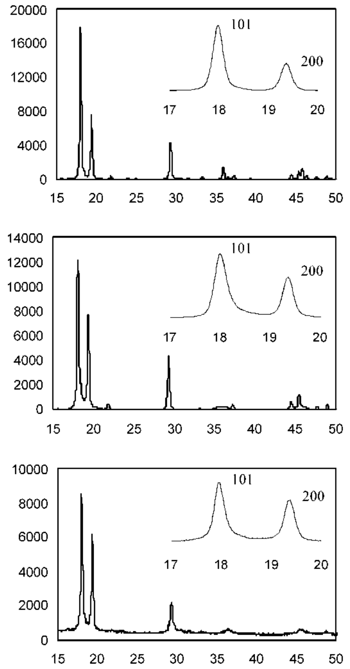

Figure 2. Calculated and experimental powder diffraction patterns. Top: Calculated for the final model without stacking disorder. Middle: Calculated for the same model but with 20% stacking faults. Bottom; Experimental. Note the asymmetry on the high angle side of the 101 line, and the agreement of the relative intensities of 101 and 200 in the second and third cases.

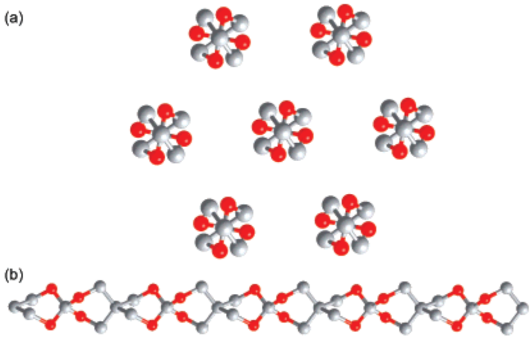

Figure 3. The crystal structure of oligo-SOC shown (a) down **b** and (b) along **b**. Hydrogen atoms are not shown (C, gray; O, red).

(010); however, the projection of the structure determined[9] using these data clearly indicated an approximately hexagonal arrangement of rodlike molecules formed by edge sharing of the two types of tetrahedra very close to our final model (Figure 3). Thus the BPS$_4$ topology is the only possibility and we note that BPS$_4$ itself has very similar unit cell dimensions.

Three strong diffraction lines (101, 200, 211) dominate the X-ray powder diffraction pattern of oligo-SOC (Figure 2). However, the 101 line showed an asymmetric profile on the high-angle side suggesting the presence of stacking disorder in the structure along **b**.[10] The presence of a narrow *hkl* line (211), with *k* different from zero, excludes a random planar disorder but suggests instead stacking faults with a shift between adjacent layers by *a*/2. In this model, the *hkl* lines with *h* even are not broadened by the planar faults, as observed experimentally in the powder pattern for lines 200 and 211. In addition, in contrast to the 101 line, no line asymmetry is observed for the 200 line in agreement with the above solution.

A Rietveld refinement with GSAS using soft bond length and angle constraints gave a structure consistent with the electron diffraction results but due to the proposed stacking disorder a large *R* factor (ca. 30%).[11] The program DIFFaX was used to estimate the probability of faults in the sample.[12] The structure was cut into layers perpendicular to the *b* direction with thickness the dimension of the *b* axis. Two types of layers are present in the model differing by a shift *a*/2. Random stacking sequences of the two layers were generated. The main effect of the presence of stacking faults on the powder pattern is the decrease of the intensity of the 101 line and the appearance of profile asymmetry at high angles. The best agreement with the experimental data is obtained for a 20 ± 5% faulting probability, corresponding to an average of one fault every fifth layer or an average length of 28 Å per oligo-SOC chain, which corresponds to an average of pentameric chains (Figure 3).[15]

It is worth noting that the hexagonal packing of spiro-chains and the conformation of the six-membered rings (Figure 3b) in oligo-SOC (Figure 3a) are respectively coincident to those observed in BPS$_4$ and molecular oxygen spiro compounds,[14,15] lending further support to the structure derived for oligo-SOC.

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Supporting Information Available: Observed and calculated structure factors and a typical [010] electron diffraction pattern for oligo-SOC (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Feldman, K. S.; Campbell, R. F.; Saunders, J. C.; Chuljin, A.; Masters, K. M. *J. Org. Chem.* **1997**, *62*, 2(25), 8814.

(2) Hydrogen-bonded frameworks: Russell, V. A.; Evans, C. C.; Li, W. J.; Ward, M. D. *Science* **1997**, *276*, 575. Desiraju, G. R. *Chem. Commun.* **1997**, 1475. Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696. Inorganic frameworks: Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807. Metal-organic frameworks: Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319.

(3) *Expanding Monomers*; Sadhir, R. K., Luck, R. M., Eds.; CRC Press: Boca Raton, FL, 1992.

(4) A search of the Cambridge Crystallographic Data Base revealed no crystalline oligomers or polymers based on SOC.

(5) Calcd. elemental microanalysis for oligo-SOC, $C_6H_8O_4$: C, 50.00; H, 5.56; N, 0.00. Found: C, 50.03 H, 6.81; N, 0.00.

(6) FT-IR spectrum for oligo-SOC (KBr, 3500−400 cm^{-1}): 3401 (s, br), 2958 (w), 2932 (w), 2889 (m), 1481 (w), 1464 (s), 1371 (s), 1230 (vs), 1183 (vs), 1107 (vs), 1021 (vs), 1006 (vs), 565 (s).

(7) Sakai, S.; Kiyohara, Y.; Itoh, K.; Ishi, Y. *J. Org. Chem.* **1970**, *35*, 2347.

(8) We have a very extensive collection of periodic 4-connected nets, and we have reason to believe that we know all simple possibilities. See e.g.: O'Keeffe, M.; Brese, N. E. *Acta Crystallogr. A* **1992**, *48*, 663−669. O'Keeffe, M.; Hyde, B. G. *Crystal Structures I: Patterns and Symmetry*; Mineral. Soc. Am.: Washington, DC, 1996.

(9) A total of 40 independent *h*0*l* intensities, corrected for excitation error, were used to refine the four independent *x* and *z* coordinates, thickness, and a common thermal parameter using a purpose-written Metropolis algorithm. The thickness (20 Å) justified treating the data as kinematic. A typical diffraction pattern and observed and calculated structure factors are deposited.

(10) Guinier, A. *X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies*; Freeman: San Francisco, 1963; Chapter 7. Wilson, A. J. C. *X-ray Optics*; Methuen: London, 1962; Chapter 6.

(11) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System (GSAS)*; Los Alamos National Laboratory Report LAUR 86-748, 1994.

(12) Treacy, M. M. J.; Newsam, J. M.; Deem, M. W. *Proc. R. Soc. London* **1991**, *A433*, 499.

(13) Approximate coordinates: C1 0.0000, 0.0000, 0.0000; C2 0.0000, 0.5000, 0.0000; C3 0.0741, 0.1577, 0.1684; C4 −0.1077, 0.8446, 0.1170; O1 0.1203, 0.3594, 0.0384; O2 −0.0259, 0.6417, 0.1877; H1 0.1600, 0.0500, 0.1900; H2 0.0300, 0.2000, 0.3150; H3 −0.1300, 0.9000, 0.2750; H4 −0.2100, 0.8500, 0.0050.

(14) Weiss, A.; Schaefer, H. *Z. Naturforsch.* **1963**, *18b*, 81.

(15) Bromley, M. K.; Looney, M. G.; Solomon, D. H.; Gable, R. W.; Helliwell, M.; Hodge, P. *Acta Crystallogr.* **1998**, *C54*, 1019.

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