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Carbon Dioxide Solubility Enhancement through Silicone Functionalization: "CO_2-philic" Oligo(dimethylsiloxane)-substituted Diphosphonates*

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Abstract: Carbon dioxide has received significant attention as a potential environmentally benign medium to replace hazardous organic compounds, but is a relatively poor solvent. The addition of siloxane substituents provides an attractive and inexpensive means to solubilize a wide variety of compounds in CO_2. By synthesizing and testing a family of *gem*-diphosphonate ligands that have been rendered CO_2-philic by incorporation of a number of related, discrete dimethylsiloxane oligomers, we show that small variations in substituents have a significant effect on the CO_2-philicity of the ligand. To our knowledge, this is the first systematic study of the effect of siloxane substituent size, branching, and

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position on the affinity of a ligand for CO_2. In addition, we present a general approach to the preparation of novel *gem*-diphosphonate ligands.

Keywords: supercritical carbon dioxide, solubility, silicone functionalization

INTRODUCTION

In recent years, carbon dioxide has gained increasing prominence as an environmentally benign solvent in a number of practical applications (1–4). Unlike many conventional solvents, it is inexpensive and essentially non-toxic, and does not contribute to either photochemical smog or ozone destruction. In its supercritical state (SC-CO_2, which is readily accessible at a critical point of 73 bar and 31°C), its low viscosity and high diffusivity make it a promising medium for extraction processes (5–7). Liquid CO_2 is also of interest as an extraction medium because the lower pressures required for its use confer lower hazards and equipment costs. Moreover, many of the favorable properties of SC-CO_2 are shared by sub-critical CO_2 (8–10).

Few substances of interest, however, are soluble in CO_2. As a result, "CO_2-philic" functional groups are often added to compounds to make them soluble (11). Most commonly, fluorocarbons are the CO_2-philes of choice, although dimethylsiloxane (methyl silicone) polymers have also been investigated (12–15). Silicone polymers are less expensive than fluorocarbons, but they are difficult to characterize. They are typically synthesized as polydisperse mixtures, making precise structure-property relations impossible to evaluate. Silicone-solubilized compounds in which a functional group of interest is attached to a siloxane polymer (16,17) are probably the most useful for practical applications. The resulting heterogeneous materials cannot, however, be employed directly to determine the amount or nature of siloxane material necessary to solubilize a particular functional group, or to understand the interactions between functional groups in the supercritical medium. For such fundamental studies, a family of compounds with different, well-defined substituents is required.

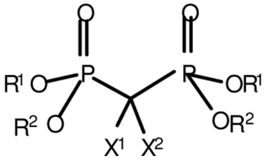
We have long had an interest in metal ion complexants bearing a phosphoryl ($P = O$) group, especially chelating ligands containing two such groups (18–25). Based on their extensive use as chelating agents, these diphosphonates are a logical choice for use as extractants in CO_2. Although other investigators have described the use of phosphoryl-containing ligands in SC-CO_2 (26–28), these reports have not involved compounds incorporating multiple phosphoryl groups. In a pair of previous papers (29,30), we detailed the preparation of several silyl-substituted alkylenediphosphonic acids and our initial evaluation of their solubility in SC-CO_2. In this study, we extend our investigations of the influence of silicon-containing substituents on the CO_2-compatibility of diphosphonates by synthesizing a series of tetraalkyl *gem*-diphosphonates bearing well-defined oligo(dimethylsiloxane) substituents and examining their phase behavior with CO_2, thus providing the first systematic study of the effect of siloxane substituent size, branching and position on the affinity of a ligand for CO_2.

EXPERIMENTAL

Reagents

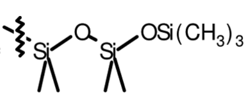
1, 1, 1, 3, 3, 5, 5-heptamethyltrisiloxane was purchased from Gelest (Tullytown, PA). All other reagents, including compound 8 (Table 1),

Table 1. Oligo (dimethylsiloxane)-substituted *gem*-diphosphates



Cmpd	R^1	R^2	X^1	X^2
1	Et	Et	$(CH_2)_3$ S1^1	H
2	Et	Et	$(CH_2)_3$ S1^1	$(CH_2)_3$ S1^1
3	Et	Et	$(CH_2)_3$ S1^2	H
4	Et	Et	$(CH_2)_3$ S1^2	$(CH_2)_3$ S1^2
5	Me	$(CH_2)_3$ S1^1	H	H
6	Me	$(CH_2)_3$ S1^1	H	H
7	Me	Eh	$(CH_2)_3$ S1^2	$(CH_2)_3$ S1^2
8	Et	Et	H	H
9	Me	Eh	H	H

SI^1 =



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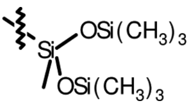

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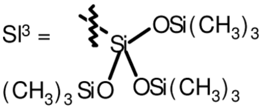
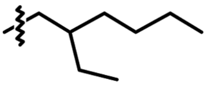


Eh =



were obtained from Aldrich Chemical Company (Milwaukee, WI) and used without further purification. The preparation of compound 9 (Table 1) has been described elsewhere (31).

Characterization Methods

^1H and ^{31}P NMR spectra were recorded on a 300 MHz General Electric Omega 300 spectrometer. All NMR spectra were recorded in $CDCl_3$ and are reported in δ (ppm). ^1H chemical shifts were measured relative to residual $CHCl_3$ at δ_H 7.26. *J* values are given in Hz. Chemical shifts for all proton-decoupled ^{31}P NMR spectra were determined relative to external 85% H_3PO_4. Gas chromatography was performed on a Hewlett-Packard 5890 A gas chromatograph using a DB-5 (0.25 μm) capillary column. Silica gel (230–400 mesh) purchased from Aldrich Chemical Company (Milwaukee, WI) was used for column chromatography. Plates pre-coated with silica gel 60 F_{254} (EM Science; Gibbstown, NJ) were utilized for thin-layer chromatography (TLC). Catalytic hydrogenolysis was performed using a Parr hydrogenation apparatus. Elemental analyses of the siloxane-containing compounds described in this work were not reproducible. Thus, their identity was confirmed by high-resolution mass spectrometry and purity established by ^1H and ^{31}P NMR. Elemental analyses of final products were conducted by Galbraith Laboratories (Knoxville, TN). Mass spectrometry for final products was provided by the Washington University Mass Spectrometry Resource (St. Louis, MO).

Synthetic Procedures

General Description

A geminal diphosphonate may be functionalized at either of two positions: the methylene bridge or the ester groups. Bridge substitution is possible by virtue of the electron-withdrawing phosphonate groups. Like the carbonyl groups of a malonate ester, the phosphoryl groups of a *gem*-diphosphonate activate the methylene hydrogens toward alkylation. Similarly, esters of phosphonic acids may be formed by many of the routes used to make esters of carboxylic acids. As shown in Fig. 1, both of these strategies were employed in the syntheses of 1–7.

Specifically, bridge-substituted diphosphonates 1–4 and 7 were produced by deprotonation of the appropriate tetraester with potassium *t*-butoxide followed by alkylation with allyl iodide. The resulting allylic compounds 10–12 were hydrosilylated with the appropriate

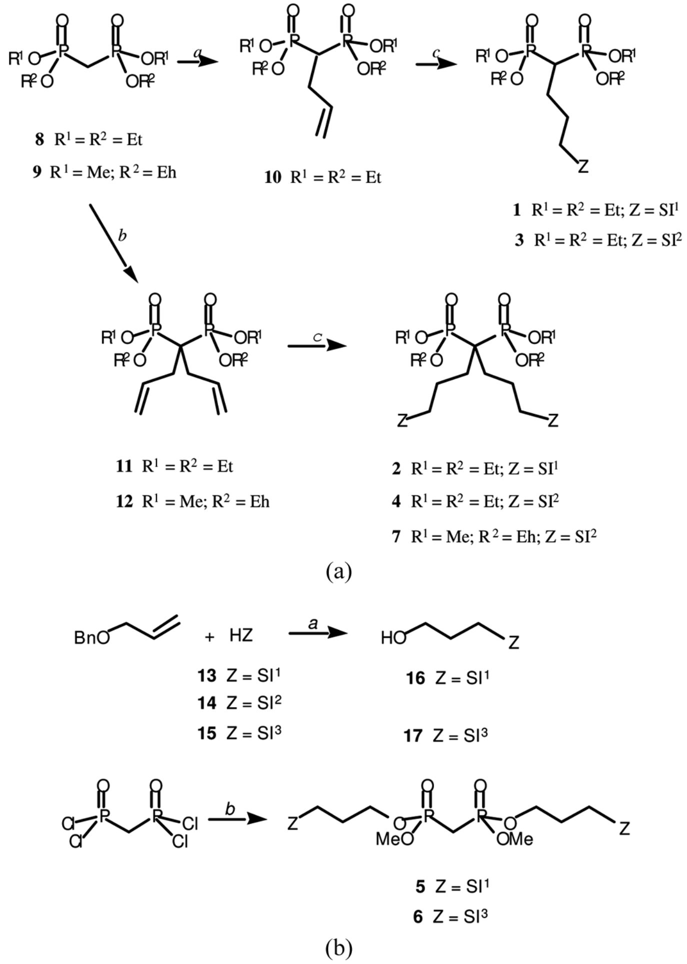


Figure 1. (a) Preparation of bridge-substituted tetraalkyl *gem*-diphosphonates. a *i*. KOt-Bu (1 eq), benzene, 18 h; *ii*. Allyl iodide (1 eq), 18 h; b *i*. KOt-Bu (3 eq), benzene, 18 h; *ii*. Allyl iodide (3 eq), 18 h; c HSI¹, HSI², or HSI³ (1.5 eq/allyl), H_2PtCl_6 (5×10^{-5} eq), 100°C,; 2–6 h; (b) Preparation of methylenebis-(siloxypropylmethylphosphonate) esters. a *i*. H_2PtCl_6 (5×10^{-5} eq), 100°C, 2–24 h; ii. H_2, 50 psig, 24 h ; b *i*. 16 or 17 (2 eq), benzene, tetrazole (0.1 eq), NPr^i_2Et (4 eq), 18 h, RT; *ii*. MeOH (excess), 4 h, RT.

oligo(dimethylsiloxy)silane to generate novel siloxane-containing compounds in yields ranging from 37% to 96%.

For compounds substituted at the ester groups, siloxane-containing benzyl ethers were first synthesized by hydrosilylating allyl benzyl ether with the appropriate hydrosiloxane. The benzyl protecting groups were then removed *via* catalytic hydrogenolysis. The benzyl ethers were then purified by vacuum distillation. The resulting alcohols 16 and 17 were condensed with methylenebis(phosphonic dichloride) in the presence of tetrazole (32,33). Undesired mixed esters such as monomethyl tri-[3-(1,1,3,3,5,5,5-heptamethyltrisiloxy)-1-propylene] methylenediphosphonate, which were obtained as by-products in small amounts, were separated from the desired products by column chromatography. The resulting methylenebis(siloxypropyl methyl phosphonate) esters, containing chiral phosphorus centers, were obtained as mixtures of *meso* and *d,l* diastereomers. A more detailed description of the synthesis of the individual compounds follows.

Preparation of Bridge-substituted Methylenebis(phosphonate)s

Synthesis of Allylated Diphosphonates

In a typical preparation, an unsubstituted diphosphonate was weighed into a round bottom flask, and dissolved in benzene (100 mL). Potassium *t*-butoxide (1 mole eq.) was added and the reaction was stirred at room temperature under a nitrogen atmosphere for 18 h. During this time, the potassium *t*-butoxide was consumed. Allyl iodide (1 mole eq.) was added and the reaction was stirred for another 18 h. For the synthesis of dialkylated species, the amounts of potassium *t*-butoxide and allyl iodide were doubled. Potassium iodide that precipitated during the course of the reaction was removed by filtration. Benzene and excess allyl iodide were removed on a rotary evaporator. The crude product was purified *via* column chromatography on silica.

- *Tetraethyl 3-butene-1, 1-diphosphonate 10*. Tetraethyl methylenediphosphonate 8 (5.0 g, 17.3 mmol) was treated with KO*t*-Bu (4.3 g, 17.3 mmol) and allyl iodide (2.9 g, 17.3 mmol). Purification by column chromatography (25% acetone/hexane: 50% acetone/hexane: 75% acetone/hexane; second band) yielded the *allylic tetraethyl diphosphonate* (2.25 g, 40%) as a colorless liquid. δ_H 1.34 (12 H, t, J 7.1 Hz, CH_3), 2.38 (1 H, tt, J 6.3, $J_{P,H}$ 23.7, PCHP), 2.69 (2 H, m, $PC(CH_2)P$), 4.19 (8 H, apparent quintet, J 7.4, OCH_2), 5.13 (1H, br dq, J 1.5, 17.1), 5.05 (1H, br dd, J 1.4, 9.8), 5.96 (1 H, m, =CH); δ_P 23.74 (s).
- *Tetraethyl 1,6-heptadiene-4,4-diphosphonate 11*. Tetraethyl methylenediphosphonate 8 (5.0 g, 17.3 mmol) was treated with KO*t*-Bu (4.3 g, 38.1 mmol) and allyl iodide (6.4 g, 38.1 mmol). Purification by column chromatography (25% acetone/hexane: 50% acetone/hexane: 75%

acetone/hexane; first band) yielded the *diallylic tetraethyl diphosphonate* (5.77 g, 93%) as a colorless liquid. δ_H 1.33 (12 H, t, *J* 7.1, CH_3), 2.64 (4 H, dt, *J* 15.6, *J* 7.6 , PC(CH_2)$_2$P), 4.18 (8 H, apparent quintet, *J* 7.3, OCH_2), 5.08 (2 H, br, =CH), 5.11 (2 H, br d, *J* 9, =CH),6.00 (2 H, m, =CH). δ_P 26.13 (s).

- *P,P′-Dimethyl P,P′-di-(2-ethylhexyl) 1,6-heptadiene-4,4-diphosphonate 12*. Methylenebis(2-ethylhexyl methyl phosphonate) 9 (0.5 g, 1.2 mmol) was treated with KO*t*-Bu (0.3 g, 2.4 mmol) and allyl iodide (0.4 g, 2.6 mmol). Purification by column chromatography (25% acetone/hexane: 50% acetone/hexane: 75% acetone/hexane; first band) yielded the *diallylic mixed diphosphonate* (0.58 g, 95%) as a colorless liquid. δ_H 0.90 (12 H, m, CH_3), 1.29 (12H, m), 1.40 (4H, m),1.55 (2 H, m, CH), 2.66 (4 H, m, PC(CH_2)P), 3.80 (d, *J* 10.7), 3.83 (d, *J* 10.7), 4.00 (br d, *J* 7.3, OCH_2), 4.04 (2 H, br d, *J* 7.3, OCH_2), 5.13 (2 H, m, =CH), 5.08 (2 H, br d, *J* 1.0, =CH), 5.98 (m, 2 H, =CH). δ_P 27.29 (s), 27.38 (s).

Hydrosilylation of Allylated Diphosphonates

For the subsequent hydrosilylation of these allylated diphosphonates, the diphosphonate was weighed in a round bottom flask and the appropriate amount of the oligo(dimethylsiloxy)silane (1.1 mole eq.) was added with stirring. A 0.1 M solution of chloroplatinic acid in isopropyl alcohol (Speier's catalyst (34); 5×10^{-5} equiv./allyl) was then added *via* syringe and the reaction mixture stirred under nitrogen at 100°C. The progress of hydrosilylation was monitored by disappearance of the allylic protons in the ^{1}H NMR spectrum.

The addition of 1,1,1,3,3,5,5-heptamethyltrisiloxane 13 to the bridge-substituted allyl diphosphonates 10–12 is quite rapid in the presence of Speier's catalyst at 100°C, with most additions being complete after one hour. The rate decreases with increasing substitution at the Si-H group. Hydrosilylation of 10 with 14 requires 18 h to reach completion. Also, diphosphonate 10, bearing only one allyl group, reacts somewhat faster than 11 and 12, with two.

- *Tetraethyl 4-(1,1,3,3,5,5,5-heptamethyltrisiloxy)butane-1, 1-diphosphonate 1*. Allylic diphosphonate 10 (1.5 g, 4.6 mmol) was treated with hydrosiloxane 13 (1.5 g, 6.9 mmol) and Speier's catalyst at 100°C for 18 h and purified by column chromatography (5% MeOH/CH_2Cl_2: 10% MeOH/CH_2Cl_2; second band) to obtain the *siloxy diphosphonate* (2.2 g, 87%) as a colorless liquid. δ_H 0.01 (6 H, s, CSi(CH_3)$_2$O), 0.07 (6 H, s, OSi(CH_3)$_2$O), 0.08 (9 H, s, OSiCH_3), 0.54 (2 H, m, SiCH_2), 1.33 (12 H, t, *J* 7.1, CH_3), 1.57 (2 H, m, CH_2CSi), 1.92 (2 H, m, $PC(CH_2)P$), 2.28 (1H, tt, *J* 6.0, *J* 24.2, PCHP), 4.17 (4H, apparent quintet, *J* 7.2, OCH_2), 4.18 (4H, apparent quintet, *J* 7.2, OCH_2); δ_P 24.81 (s). *m*/*z* (HRMS-FAB): 557.2293 $[M + Li]^+$. Calc. for $C_{19}H_{48}O_8P_2Si_3Li$: 557.2292).

- *Tetraethyl 1,7-bis-(1,1,3,3,5,5,5-heptamethyltrisiloxy)heptane-4, 4-diphosphonate 2*. Di-allylic diphosphonate 11 (0.5 g, 1.4 mmol) was treated with hydrosiloxane 13 (0.9 g, 4.1 mmol) and Speier's catalyst at 100°C for 1 h. Unreacted 13 was removed by vacuum distillation to obtain the *bis(siloxy)diphosphonate* as a colorless liquid (1.06 g, 96%). δ_H 0.02 (12 H, s, $CSi(CH_3)_2O$), 0.07 (12 H, s, $OSi(CH_3)_2O$), 0.08 (18 H, s, $OSiCH_3$), 0.52 (4 H, m, $SiCH_2$), 1.31 (12 H, t, *J* 7.1, CH_3), 1.52 (4H, m, CH_2CSi), 1.90 (4H, m, $PC(CH_2)_2P$), 4.16 (8 H, apparent quintet, *J* 7.3, OCH_2). δ_P 27.66 (s). *m*/*z* (HRMS-FAB): 813.346 ($[M + H]^+$. Calc. for $C_{29}H_{74}O_{10}P_2Si_6$: 813.345).
- *Tetraethyl 4-(1,1,1,3,5,5,5-heptamethyltrisiloxy)butane-1, 1-diphosphonate 3*. Allylic diphosphonate 10 (1.0 g, 3.1 mmol) was treated with hydrosiloxane 14 (1.0 g, 4.6 mmol) and Speier's catalyst at 100°C for 3 days and purified by column chromatography (50% acetone/hexane; second band) to obtain the *siloxy diphosphonate* (0.62 g, 37%) as a colorless liquid. δ_H 0.00 (3 H, s, $SiCH_3$), 0.08 (18 H, s, $OSi(CH_3)_3$), 0.46 (2 H, m, $SiCH_2$), 1.33 (12 H, t, *J* 7.3, CH_3), 1.56 (2 H, m, CH_2CSi), 1.90 (2 H, m, $PC(CH_2)P$), 2.28 (1 H, tt, *J* 5.9, *J* 24.1, PCHP), 4.16 (4H, apparent quintet, *J* 7.2, OCH_2), 4.17 (4H, apparent quintet, *J* 7.2, OCH_2); δ_P 24.80 (s); *m*/*z* (HRMS-FAB): 557.2284 ($[M + Li]^+$. Calc. for $C_{19}H_{48}O_8P_2Si_3Li$: 557.2292).
- *Tetraethyl 1,7-bis-(1,1,1,3,5,5,5-heptamethyltrisiloxy)-heptane-4,4-diphosphonate 4*. Di-allylic diphosphonate 11 (0.5 g, 1.4 mmol) was treated with hydrosiloxane 14 (0.9 g, 4.1 mmol) and Speier's catalyst at 100°C for 18 h and purified by column chromatography (50% acetone/hexane; second band) to obtain the *bis-siloxy diphosphonate* (0.58 g, 52%) as a colorless liquid. δ_H 0.00 (6 H, s, $SiCH_3$), 0.09 (36 H, s, $OSi(CH_3)_3$), 0.43 (4 H, m, $SiCH_2$), 1.31 (12 H, t, *J* 7.1, CH_3), 1.51 (4 H, m, CH_2CSi), 1.88 (4 H, m, $PC(CH_2)_2P$), 4.18 (8 H, apparent quintet, *J* 7.2, OCH_2); ^{31}P NMR: δ_P 27.70 (s). *m*/*z* (HRMS-FAB): 819.3526 ($[M + Li]^+$. Calc. for $C_{29}H_{74}O_{10}P_2Si_6Li$: 819.3533).
- *P,P′-Dimethyl P,P′-di-(2-ethylhexyl) 1,7-bis(1,1,3,3,5,5,5-heptamethyl trisiloxy)heptane-4, 4-diphosphonate 7*. Di-allylic diphosphonate 12 (0.2 g, 0.39 mmol) was treated with hydrosiloxane 14 (0.3 g, 1.2 mmol) and Speier's catalyst at 100°C for 4 h and purified by column chromatography (5% MeOH/CH_2Cl_2; second band) to obtain the *bis-siloxy diphosphonate* (0.25 g, 89%) as a colorless liquid. δ_H 0.02 (12 H, s, CSi-$(CH_3)_2O$), 0.07 (12 H, s, $OSi(CH_3)O$), 0.08 (18 H, s, $OSiCH_3$), 0.52

(4 H, m, $SiCH_2$), 0.89 (6 H, t, *J* 6.8, CH_3), 0.90 (6 H, t, *J* 7.3, CH_3), 1.29 (12 H, m, CH_2), 1.39 (4 H, m, CH_2), 1.52 (4 H, m, CH_2CSi), 1.88 (4H, m, $PC(CH_2)_2P$), 3.78 (3H, d, *J* 10.7, OCH3), 3.81 (3H, d, *J* 10.6, OCH3), 4.00 (4 H, m, OCH_2); δ_P 28.98 (s), 29.08 (s). *m*/z (HRMS-FAB): 959.5077 ($[M+Li]^+$. Calc. for $C_{39}H_{94}O_{10}P_2Si_6Li$: 959.5098).

Preparation of Gem-diphosphonates Functionalized at the Ester Group

Synthesis of 3-[Oligo(dimethylsiloxy)]-1-Propyl Alcohols

As a first step in the synthesis of *gem*-diphosphonates functionalized at the ester group, 3-[oligo(dimethylsiloxy)]-1-propyl alcohols were prepared. In a typical procedure, allyl benzyl ether (41 mmol) was weighed into a round-bottom flask and the appropriate mass of oligo(dimethylsiloxy)silane was added (41 mmol). A 0.1 M solution of chloroplatinic acid in isopropyl alcohol was added *via* syringe. The reaction mixture was stirred under nitrogen at 100°C. TLC (5% EtOAc/pet. ether, ammonium molybdate development) was used to establish the completion of hydrosilylation. The resulting 3-[oligo(dimethylsiloxy)]-1-propyl benzyl ether was purified by vacuum distillation. Its purity was determined by GC (50°C for 2 min, 10°C/min to 200°C, 200°C for 15 min). The benzyl protecting group was then removed by catalytic hydrogenation. Specifically, the siloxypropyl benzyl ether was placed in a hydrogenation bottle followed by 5% Pd/C catalyst and methanol (*Caution! Adding catalyst after methanol may ignite the solvent vapors.*) The apparatus was filled with hydrogen (50 psig) and vented thrice, then filled a fourth time, sealed, and shaken. After ~24 h, hydrogen consumption was no longer apparent. The catalyst was removed by filtration with Celite and the methanol was removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 and successively washed with 10% $NaHCO_3$ and H_2O. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure.

- *3-(1, 1, 3, 3, 5, 5, 5-heptamethyltrisiloxy)-1-propanol 16*. Allyl benzyl ether (6.07 g, 41.0 mmol), hydrosiloxane 13 (9.01 g, 40.5 mmol), and Speier's catalyst (20 μL, 2 μmol) were heated to 100°C for 1 h and vacuum distilled to obtain *3-(1, 1, 3, 3, 5, 5, 5-hetamethyltrisiloxy)propyl benzyl ether* (11.23 g, 75%) as a colorless liquid. bp 94°C/15 mTorr – 100°C/10 mTorr; δ_H 0.02 (6 H, s, $CSi(CH_3)_2O$), 0.076 (6 H, s, $OSi(CH_3)_2O$), 0.084 (9 H, s, $OSi(CH_3)_3$), 0.56 (2 H, m, $SiCH_2$), 1.66 (2 H, m, CH_2CSi), 3.44 (2 H, t, *J* 7.1, OCH_2), 4.51 (2 H, s, CH_2Ph), 7.29 (1 H, apparent quintet, *J* 4.5, Ph), 7.35 (4 H, d, *J* 4.5, Ph). This material (11.23 g, 30.3 mmol) was hydrogenated using Pd/C (0.84 g) and MeOH (80 mL) to obtain the *siloxypropanol* as a colorless liquid (7.19 g, 85%). δ_H 0.02 (6 H, s, CSi(CH_3)$_2$O), 0.08 (9 H, s, OSi(CH_3)$_2$), 0.09 (6 H, s, OSi(CH_3)$_3$), 0.54 (2 H, m, SiCH_2), 1.60 (3 H, m, CH_2CSi + OH), 3.60 (2 H, t, *J* 6.7, OCH_2). *m/z* (HRMS-FAB): 287.1513 ($[M + Li]^+$. Calc. for $C_{10}H_{28}O_3Si_3Li$: 287.1506).

- *3-[tris(trimethylsiloxy)]-1-propanol 17.* Allyl benzyl ether (7.65 g, 51.6 mmol), hydrosiloxane 15 (15.29 g, 51.5 mmol), and Speier's catalyst (30 μL, 3 μmol) were heated to 100°C for 112 h and vacuum distilled to obtain *3-[tris(trimethylsiloxy)silyl]propyl benzyl ether* (11.17 g, 48%) as a colorless liquid. bp 100–125°C/10 mTorr; δ_H 0.09 (27 H, s, OSi(CH_3)$_3$), 0.46 (2 H, m, SiCH_2), 1.65 (2 H, m, CH_2CSi), 3.43 (2 H, t, *J* 7.1, OCH_2), 4.51 (2 H, s, CH_2Ph), 7.30 (1 H, apparent quintet, *J* 4.4, Ph), 7.36 (4 H, d, *J* 4.4, Ph). This material (11.17 g, 25.1 mmol) was hydrogenated using Pd/C (0.8 g) and MeOH (80 mL) to obtain the *siloxypropanol* as a colorless liquid (7.83 g, 88%). δ_H 0.10 (s, 27H, OSi(CH_3)$_3$), 0.47 (m, 2H, SiCH_2), 1.61 (m, 3H, CH_2CSi + OH), 3.60 (t, 2H, *J* 6.6, OCH_2). *m/z* (HRMS-FAB): 361.1681 ($[M + Li]^+$. Calc. for $C_{12}H_{34}O_4Si_4Li$: 361.1694).

Synthesis of P,P′-dimethyl P,P′-di-[3-oligo(dimethylsiloxy)-1-Propylene] methylenediphosphonates

The preparation of P,P′-dimethyl P,P′-di-[3-oligo(dimethylsiloxy)-1-propylene] methylenediphosphonates was accomplished by the procedure of Zhao and Landry (32). Methylenebis(phosphonic dichloride) (4 mmol), 1*H*-tetrazole (0.1 mole eq.), diisopropylethylamine (4 mole eq.), and 3-[oligo(dimethylsiloxy)]-1-propanol (2 mole eq.) were dissolved in benzene cooled in an ice bath. The mixture was stirred for 18 h under nitrogen at room temperature. An excess of methanol was used to quench the reaction and stirring was continued for ~4 h. The benzene was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with 1 M $KHSO_4$ and brine, successively. The organic layer was dried over anhydrous Na_2SO_4 and the CH_2Cl_2 was removed on the rotary evaporator. Column chromatography was used to remove unreacted alcohol remaining in the organic layer with the product. The ^1H and ^{31}P NMR spectra of the products reflect the presence of both *dl* and *meso* isomers.

- *P,P′-Dimethyl P,P′-di-[3-(1,1,1,3,3,5,5-heptamethyltrisiloxy)-1-propyl]-methylenediphosphonate 5.* Methylenebis(phosphonic dichloride) (0.6 g, 4.0 mmol), 16 (2.2 g, 8.0 mmol), tetrazole (0.03 g, 0.4 mmol), and NPr^i_2Et (2.1 g, 16.0 mmol) in benzene (25 mL) were reacted as described and purified by column chromatography (EtOAc; third band) to obtain the *mixed tetraester* (1.14 g, 39%) as a colorless liquid. δ_H 0.02 (12 H, s, $Si(CH_3)_2$, 0.078 (12 H, s, $Si(CH_3)_2$), 0.082 (18 H, s, $OSi(CH_3)_3$), 0.54 (4 H, m, $SiCH_2$), 1.70 (4 H, m, CH_2CSi), 2.45 (2 H, t, $J_{P,H}$21.0, PCH_2P), 3.80 (3 H, d, $J_{P,H}$ 11.2, OCH_3), 3.82 (3 H, d, $J_{P,H}$ 11.2, OCH_3), 4.05 (2 H, apparent q, J 7.2, OCH_2), 4.06 (2 H, apparent q, J 7.2, OCH_2); δ_P 21.29 (s), 21.32 (s). m/z (HRMS-FAB): 735.2610 ($[M+Li]^+$. Calc. for $C_{23}H_{62}O_{10}P_2Si_6Li$: 735.2594).

- *P,P′-Dimethyl P,P′-di-[3-tris(trimethylsiloxy)silyl-1-propyl] methylene-diphosphonate 6*. Methylenebis(phosphonic dichloride) (0.6 g, 2.5 mmol), 17 (1.8 g, 5.0 mmol), tetrazole (0.035 g, 0.5 mmol), and $NPr^i{}_2Et$ (0.71 g, 5.5 mmol) in benzene (16 mL) were reacted as described and purified by column chromatography (EtOAc, second band) to obtain the *mixed tetraester* (0.75 g, 34%) as a colorless liquid. δ_H 0.09 (54H, s, $OSi(CH_3)_3$), 0.45 (4H, m, $SiCH_2$), 1.70 (4H, m, CH_2CSi), 2.45 (2H, t, $J_{P,H}$ 21.3, PCH_2P), 3.80 (3H, d, $J_{P,H}$ 11.2, OCH_3), 3.82 (3H, d, $J_{P,H}$ 11.2, OCH_3), 4.04 (4H, m, OCH_2); δ_P 21.31(s), 21.35 (s); m/z (HRMS-FAB): 883.2951 ($[M+Li]^+$. Calc. for $C_{27}H_{74}O_{12}P_2Si_8Li$: 883.2970).

Vapor-liquid Equilibrium Measurements

Samples were dried under vacuum at 50°C for 24 h and stored in a desiccator prior to use. The experimental apparatus and procedure has been described in a previous report (35).

RESULTS AND DISCUSSION

In a pair of earlier reports (29,30), we demonstrated that the attachment of a well-defined silicon-containing moiety to an alkylenediphosphonic acid, in particular, the preparation of a di-[3-(trimethylsilyl)-1-propyl] (TMSP) ester of the acid, results in a significant increase in its CO_2-solubility vis-à-vis a conventional, alkyl-substituted analog. Because the emphasis in this earlier work was on the influence of the structure of the parent alkylenediphosphonic acid (e.g., methylene- *vs*. propylene-diphosphonic acid) on the solubility of the TMSP esters in CO_2, these studies provided no insight into the effect of either the characteristics of the silicon-bearing substituent itself or its position in the molecule on this solubility. In this work, we have addressed these issues by the preparation and characterization of a series of carefully chosen,

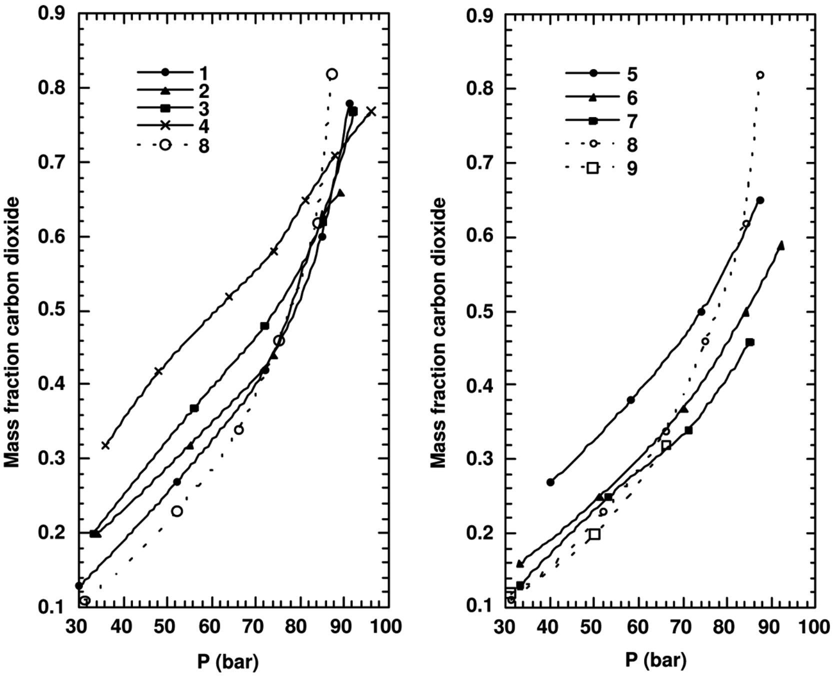


Figure 2. Pressure dependence of the mass fraction of carbon dioxide in the ligand-rich phase for siloxane-functionalized *gem*-diphosphonates in equilibrium with CO_2 (T = 40°C). (Solid lines are intended solely as a guide to the eye.)

siloxane-functionalized *gem*-diphosphonates, the structures of which are provided in Table 1.

Without exception, the product compounds were liquids under ambient conditions, thereby precluding the facile application of the dynamic extraction approach to measuring solubility employed in our studies of TMSP esters (30). Instead, the affinity of each of the compounds for CO_2 was evaluated by measuring the amount of CO_2 that partitions into each at pressures from 30 to 90 bar at a constant temperature (40°C) (35). Figure 2 shows the amounts of CO_2 incorporated into the ligand-rich phase in each case, a direct reflection of the compatibility of the ligands with CO_2. Mass fractions instead of mole fractions are shown to account for the wide range of molecular masses of the various compounds. More CO_2 molecules will be required to surround a large molecule to the same extent as a small molecule. Thus, high molecular weight compounds will absorb higher mole fractions of CO_2 even without enhanced CO_2 affinity. Mass fractions are less sensitive to variations in molecular size.

Although these data were obtained at lower pressures than those likely to be used in an extraction, they nonetheless indicate the relative CO_2-philicities of the different compounds. Widely used equations of state, such as Peng-Robinson, employ a single interaction parameter between CO_2 and the solute to predict the entire binary phase diagram. Although an interaction parameter obtained from data gathered in one region of temperature and pressure may not quantitatively predict behavior at far different pressures and temperatures (6), the relative trends of interaction parameters for different analytes should be consistent in the different regions. Thus, compounds that absorb a large fraction of CO_2 at low pressures are expected to be the most soluble in the supercritical fluid phase at higher pressures. Moreover, as we have already noted, the solubility of materials in liquid CO_2, not just SC-CO_2, is of increasing interest in the context of the applications of CO_2 as an extraction solvent.

The observed incorporation of CO_2 into the diphosphonate-rich phases depends upon the number and nature of the substituent groups, as is clearly illustrated by the results presented in Fig. 3. In general, below about 75 bar, the parent 8, with no siloxane functionality, absorbs less CO_2 than 1, which bears one linear trisiloxane substituent at the diphosphonate α -carbon. Compound 2, bearing two such trisiloxane groups, in turn absorbs more CO_2 than 1. The specific structure of the siloxane substituents obviously also plays an important role. Compounds 3 and 4, with trisiloxane substituents attached by their central silicon atoms, absorb substantially more CO_2 than their respective straight-chain isomers 1 and 2, a result reminiscent of recent studies reporting differences in the CO_2-philicity of compounds bearing isomeric alkyl substituents (36,37).

Siloxane substitution of the phosphonate alkyl ester group also enhances the uptake of CO_2. Compounds 5 and 6 both absorb more CO_2 at low pressures than 8. Interestingly, 5 absorbs more CO_2 than 6, even though 6 contains more methyl silicone functionality. Siloxane substitution also enhances the CO_2 affinity of diphosphonates bearing larger alkyl ester groups. Compound 7, bearing two 2-ethylhexyl esters in addition to its siloxypropyl groups, absorbs slightly more CO_2 than its siloxane-free analogue 9 at all pressures studied.

The higher CO_2 uptake by the siloxane-substituted diphosphonates is not due solely to their larger sizes or increased alkyl functionality. Compound 9, with much larger alkyl ester substituents than 8, absorbs no more CO_2 at low pressures. (Instrument breakage prevented measuring the uptake by 9 at higher pressures.) Similarly, 7 absorbs even less CO_2 than 2, despite 7's much larger alkyl esters. The trends described here are also apparent when the data are plotted as mole fraction (not shown) rather than mass fraction.

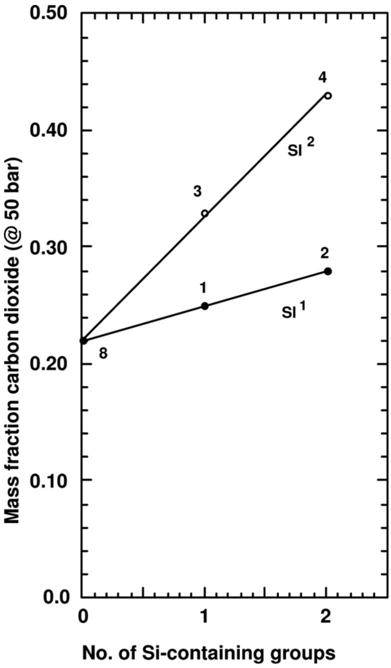


Figure 3. Dependence of the mass fraction of CO_2 in the ligand-rich phase ($P = 50$ bar; $T = 40°C$) on the number of silicon-bearing functional groups appended for several siloxane-functionalized *gem*-diphosphonates.

The CO_2 uptake of the unsubstituted tetraethyl ester 8 increases with increasing pressure much faster than that of the derivatives 1–7. This suggests that the $8/CO_2$ mixture critical pressure is somewhat lower than the mixture critical pressures of the substituted compounds with CO_2, a probable consequence of the higher volatility of the unsubstituted 8. The increased CO_2-philicity conferred by the siloxane groups is thus no longer apparent as the mixture critical point is approached. Less volatile compounds, such as metal complexes of these ligands, are expected to derive more benefit from siloxane substitution.

The ligand-rich phases of all these compounds consist primarily of CO_2 even at 90 bar. Extrapolating the mole fraction trends to higher pressures suggests that the mixture critical points of all these compounds with CO_2 are at pressures of about 100–130 bar at 40°C. Above the critical pressure, each CO_2/diphosphonate mixture would be a single phase at all compositions.

CONCLUSIONS

Siloxane substituents enhance the affinity of *gem*-diphosphonates for CO_2, with the extent of enhancement depending on both the structure of the siloxane substituents and the total amount of siloxane functionality present. Taken together with our earlier results for silyl-substituted diphosphonic acids (29,30), this work clearly demonstrates that the use of structurally well-defined, silicon-based substituents represent a viable alternative to the use of silicon-based polymers or ligand fluorination as a route to the improvement of the solubility of extractants in carbon dioxide. The generality and potential applications of this enhancement are under investigation.

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