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Aggregation Patterns in α,α′-Stabilized Carbanions: Assembly of a Sodium Cage Polymer by Slip-Stacking of Dimers

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The α,α′-stabilized carbanion complexes [$PhSO_2CHCNNa\cdot THF$], **3**, [t-$BuSO_2CHCNNa$], **4**, [$PhSO_2CHCNK$], **5**, [t-$BuSO_2CHCNK$], **6**, and [$MeSO_2CHCNLi\cdot TMEDA$], **7**, have been synthesized via the metalation of the parent (organo)sulfonylacetonitriles by BuLi, BuNa, or BnK in THF solution (or THF/TMEDA in the case of **7**). In addition, complexes **3** and **7** have been characterized by single-crystal X-ray analyses and have been found to adopt related structures in the solid state. Complex **7** is a molecular dimer containing a central 12-membered $(OSCCNLi)_2$ ring core, with each metal rendered tetracoordinate by binding to a chelating TMEDA molecule. As found in related complexes, no direct carbanion to lithium contacts are present in the structure of **7**. Complex **3** forms a polymeric cage structure composed of associated “dimeric” $(OSCCNNa)_2$ rings, similar to those found in **7**. The larger sodium cations, and the presence of only one THF molecule/metal, allow additional contacts with the anions, leading to hexacoordination at the metal centers. These contacts include long-range transannular Na–N interactions (2.8042(14) Å) across the central dimeric ring and “interdimer” Na–C connections (2.8718(15) Å). Dissolution of complexes **3**–**6** and their lithiated derivatives [$PhSO_2CHCNLi\cdot TMEDA$], **1**, and [t-$BuSO_2CHCNLi\cdot THF$], **2**, in DMSO-d_6 results in almost identical chemical shifts for each type of ligand. This suggests that charge-separated complexes of the form $[RSO_2CHCN]^-[M(DMSO\text{-}d_6)_n]^+$ are formed in highly polar solution.

Introduction

α-Stabilized carbanions play a central role in modern chemistry as intermediates in numerous carbon−carbon bond-forming reactions.[1] The utility of these species in synthesis[2,3] has also led to considerable interest in their structure and bonding patterns.[4] We have recently become attracted to a specialized class of these compounds, α,α′-stabilized carbanions, where a methylene group bridges between a pair of stabilizing units, such as sulfonyls, nitriles, or phosphonates.[5] In the course of our studies into the use of these ligands to form geminated bimetallic complexes, R_2CM_2,[6] we have found that the intermediate monolithiated complexes may break with the traditional structural patterns established for their α-stabilized derivatives.[7−9] For example,

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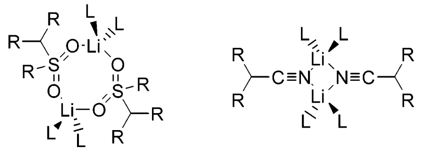

Figure 1. Dimeric aggregation of lithiated sulfones and nitriles, where L = Lewis base.

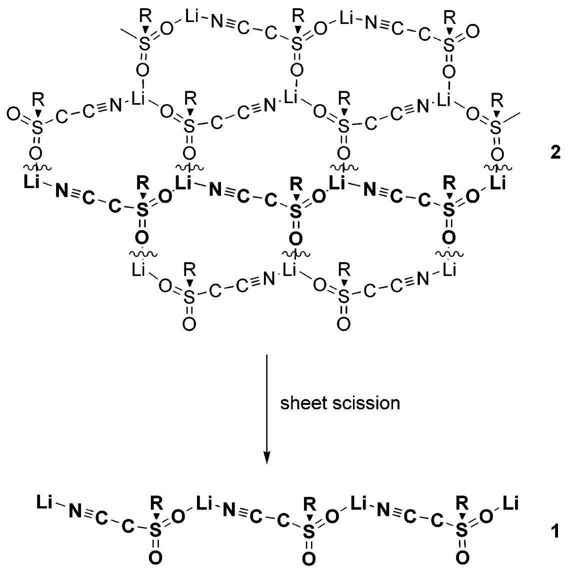

Figure 2. Simplified schematic view of the relationship between the structures of complexes **1**, R = Ph, and **2**, R = *t*-Bu. (The donor solvents and carbanionic hydrogen have been removed for clarity.)

in general monolithiated sulfones form eight-membered $(SO_2Li)_2$ ring dimers, and monolithiated nitriles form four-membered Li_2N_2 ring dimers in the solid state (Figure 1).[10,11]

However, in the complexes [PhSO$_2$CHCNLi·TMEDA], **1**, and [*t*-BuSO$_2$CHCNLi·THF], **2**, where the carbanion is directly connected to both a sulfonyl and a nitrile, neither ring dimer is retained in the solid state. Instead, **1** is a helical chain polymer and **2** forms a two-dimensional honeycomb sheet network (Figure 2). The common feature in the two structures is the "head-to-tail" linking of the ligands by the lithium centers, i.e. the metals bridge between an oxygen of the sulfonyl from one ligand and the nitrogen of the nitrile from a second ligand. The sheet structure of complex **2** can therefore be considered to be composed of chains of **1** linked together.

In this study we report the synthesis and characterization of the sodium and potassium analogues of **1** and **2**, [PhSO$_2$CHCNNa·THF], **3**, [*t*-BuSO$_2$CHCNNa], **4**, [PhSO$_2$CHCNK], **5**, and [*t*-BuSO$_2$CHCNK], **6**. In particular, the remarkable polymeric cage structure of **3** will be outlined and its relationship with the previously characterized lithium complexes **1** and **2**, as well as new molecular lithium complex [MeSO$_2$CHCNLi·TMEDA], **7**, will be discussed.

Experimental Section

All manipulations were carried out under a protective argon atmosphere using standard Schlenk techniques.[12] All glassware was flame-dried under vacuum before use. All solvents were distilled form sodium benzophenone ketyl, degassed, and stored over 4 Å molecular sieves. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was distilled from CaH_2 and stored over 4 Å molecular sieves. $MeSO_2CH_2CN$, $PhSO_2CH_2CN$, and *t*-BuSO$_2$CH$_2$CN were purchased from Lancaster and recrystallized from either hexane or toluene. *n*-Butyllithium (BuLi) was purchased from Aldrich as a 1.6 M solution in hexane and was standardized by titration with salicylaldehyde phenylhydrazone directly before use.[13] Butylsodium (BuNa) and benzylpotassium (BnK) were prepared according to modified literature procedures and stored in an argon-filled glovebox.[14] Deuterated solvents for the NMR studies were stored over 4 Å molecular sieves under an argon atmosphere. The NMR spectra were recorded on a Bruker AMX 400 spectrometer at 25 °C and were calibrated with respect to the deuterated solvent. All ^{13}C assignments were determined using HMQC experiments. The IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrophotometer as Nujol mulls, and elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer.

Synthesis of [PhSO$_2$CHCNNa·THF], 3. $PhSO_2CH_2CN$ (2 mmol, 0.36 g) was dissolved in THF (20 mL) and cooled to −78 °C. A 1 equiv amount of BuNa (2 mmol, 0.16 g) was added to the stirred solution via a solid additions tube. The resulting solution was allowed to stand and warm slowly to ambient temperature. A white microcrystalline solid formed after 12 h. Complete dissolution of the solid was achieved by strong heating of the mixture. X-ray-quality crystals were obtained on slow cooling of the hot solution in a water bath. The product was isolated via filtration, dried in vacuo, and transferred to a glovebox for analysis. The product was found to lose THF under vacuum; hence, the elemental analyses and the yield are based upon the relative integrals of the anion and THF in the ^1H NMR spectrum, 1:0.86 in this instance. Yield: 0.31 g, 63.5%. (Anal. Found: C, 51.64; H, 4.83; N, 5.22. Calcd for $C_{11.44}H_{14.88}NO_{2.86}S$: C, 51.84; H, 4.86; N, 2.28.) ν_{max}/cm^{-1} (C≡N): 2169 (Nujol). ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.67 (d, 2H, *o*-H, Ph), 7.38 (m, 3H, *m*-, *p*-H, Ph), 3.60 (m, 3.4H, O−CH$_2$, THF) 2.57 (s, 1H, SO$_2$–CH), 1.76 (m, 3.4H, CH$_2$, THF).^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 151.49 (*i*-C, Ph), 128.91 (*p*-C, Ph*)*, 128.10, (*m*-C, Ph), 126.33 (CN), 124.21 (*o*-C, Ph), 67.00 (O−CH$_2$, THF), 37.46 (SO$_2$–CH), 25.10 (CH$_2$, THF).

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Synthesis of [*t*-BuSO$_2$CHCNNa], 4. *t*-BuSO$_2$CH$_2$CN (1 mmol, 0.16 g) was dissolved in THF (30 mL) and cooled to −78 °C. A 1 equiv amount of BuNa (1 mmol, 0.08 g) was added to the stirred solution via a solid additions tube. The resulting mixture was then allowed to stand and warm slowly to ambient temperature. A white microcrystalline solid formed after 2 h. The product was isolated by filtration, dried under vacuum, and transferred to a glovebox for analysis. Yield: 0.12 g, 65.6%. (Anal. Found: C, 37.26; H, 5.21; N, 7.07. Calcd for $C_6H_{10}NaNO_2S$: C, 39.33; H, 5.50; N, 7.65.) ν_{max}/cm^{-1} (C≡N): 2160 (Nujol). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 2.02 (s, 1H, SO$_2$–CH), 1.17 (s, 9H, CH$_3$, *t*-Bu). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 128.01 (CN), 58.57 (C, *t*-Bu), 26.37 (SO$_2$–C), 24.34 (CH$_3$, *t*-Bu).

Synthesis of [PhSO$_2$CHCNK], 5. PhSO$_2$CH$_2$CN (2 mmol, 0.36 g) in THF (5 mL) was added dropwise to a mixture of BnK (2 mmol, 0.26 g) in THF (10 mL), resulting in the formation of an off-white precipitate. The solid was isolated via filtration, dried under vacuum, and transferred to a glovebox for analysis. Yield: 0.30 g, 68.5%. (Anal. Found: C, 42.80; H, 2.65; N, 6.39. Calcd for $C_8H_6KNO_2S$: C, 43.81; H, 2.76; N, 6.39). ν_{max}/cm^{-1} (C≡N): 2157 (Nujol). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.67 (d, 2H, *o*-H, Ph), 7.39 (m, 3H, *m*-, *p*-H, Ph), 2.55 (s, 1H, SO$_2$–CH). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 151.45 (*i*-C, Ph), 128.92 (*p*-C, Ph), 128.11 (*m*-C, Ph), 126.29 (CN), 124.20 (*o*-C, Ph), 37.45 (SO$_2$–CH).

Synthesis of [*t*-BuSO$_2$CHCNK], 6. *t*-BuSO$_2$CH$_2$CN (1 mmol, 0.16 g) in THF (5 mL) was added dropwise to a solution of BnK (1 mmol, 0.13 g) in THF (20 mL). An insoluble white precipitate rapidly formed. The product was isolated via filtration, dried under vacuum, and transferred to a glovebox for analysis. Yield: 0.15 g, 75.4%. (Anal. Found: C, 36.32; H, 5.03; N, 6.74. Calcd for $C_6H_{10}KNO_2S$: C, 36.16; H, 5.06; N, 7.03.) ν_{max}/cm^{-1} (C≡N): 2150 (Nujol). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 2.02 (s, 1H, SO$_2$–CH), 1.17 (CH$_3$, *t*-Bu). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 128.01 (CN), 58.57 (C, *t*-Bu), 26.35 (SO$_2$–C), 24.33 (CH$_3$, *t*-Bu).

Synthesis of [MeSO$_2$CHCNLi·TMEDA], 7. MeSO$_2$CH$_2$CN (1 mmol, 0.12 g) was dissolved in TMEDA (5 mL) and treated with a 1 equiv amount of BuLi (1 mmol of a 1.6 M solution in hexane) causing the formation of an oil. Complete dissolution was achieved on vigorous heating and the addition of THF (2 mL). Storage at −20 °C produced X-ray-quality crystals. (The crystals are readily soluble and will redissolve at room temperature.) Yield: 0.09 g, 37.3%. Mp: 76 °C. (Anal. Found: C, 44.81; H, 8.66; N, 17.01. Calcd for $C_9H_{20}LiN_3O_2S$: C, 44.76; H, 8.35; N, 17.42.) ν_{max}/cm^{-1} (C≡N): 2146 (Nujol). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 2.68 (s, 3H, Me), 2.37 (s, 1H, SO$_2$–CH), 2.26 (s, 4H, CH$_2$, TMEDA), 2.10 (s, 6H, CH$_3$, TMEDA). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 127.02 (CN), 57.25 (CH$_2$, TMEDA), 47.554 (CH$_3$, SO$_2$–Me), 45.57 (CH$_3$, TMEDA), 37.13 (SO$_2$–C).

Computational Details. The Gaussian 98 series of programs were used for the calculations.[15] No symmetry constraints were imposed, and the molecules were allowed to freely optimize initially at the HF/6-31G* level and then reoptimized at the higher B3LYP/6-31++G** level of theory.[16−18] Frequency analysis using both levels of theory was used to ensure that true minima were located.

X-ray Crystallography. Single-crystal diffraction data were recorded on a Nonius Kappa CCD diffractometer at 123 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All non-H atoms were refined anisotropically. The H atoms of **7** were refined isotropically as was H1 (the H atom of the C(H)CN group) of compound **3**. The structures were refined by full-matrix least squares and against F^2 to convergence using the SHELXL-97 program.[19] Specific crystallographic data and refinement parameters are given in Table 1.

Table 1. Crystallographic Parameters for **3** and **7**

param	**3**	**7**
chem formula	$C_{12}H_{14}NNaO_3S$	$C_9H_{20}LiN_3O_2S$
fw	275.29	241.28
cryst size (mm)	0.70 × 0.20 × 0.20	0.35 × 0.20 × 0.10
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	5.8700(1)	8.3970(4)
b (Å)	21.7690(5)	8.7020(4)
c (Å)	10.1300(2)	11.0240(6)
α (deg)	90	85.483(2)
β (deg)	90.949(1)	69.939(2)
γ (deg)	90	64.124(3)
V (Å^3)	1294.27(4)	678.39(6)
Z	4	2
no. of reflcns collcd	5498	5562
no. of indepndt reflcns	2916	3064
R_{int}	0.0141	0.0507
D_{calc} (g cm^{-3})	1.413	1.181
μ (mm^{-1})	0.282	0.228
R^a	0.0307	0.0508
R_w ^{b}	0.0799	0.1172

^{a} Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for “observed” reflections having $F_o^2 > 2\sigma(F_o^2)$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

Results and Discussion

Solid-State Studies. All of the sodium and potassium complexes prepared were found to have very limited solubility in organic solvents, resulting in their characterization by single-crystal X-ray diffraction being rather problematic. Nevertheless, in the case of complex **3** suitable crystals were successfully prepared and its structure was subsequently determined. As shown in Figure 3, complex **3** forms a polymeric cage structure. Each sodium bridges between four separate anions by binding to a pair of sulfonyl and nitrile groups, one carbanionic carbon, and a single THF molecule, giving a distorted octahedral geometry at the metal centers.

A detailed examination of the structure of **3** proves useful in understanding its formation and rationalizing its highly unusual structure. The core of the polymer cage can conveniently be broken down into “dimeric” (OSCCNNa)$_2$ 12-membered ring building blocks. Formation of the polymer

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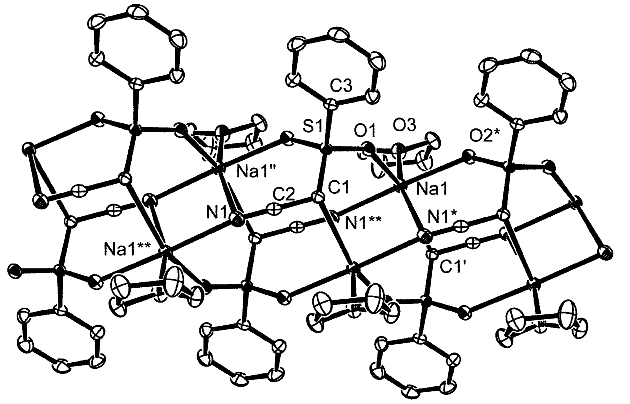

Figure 3. Section of the polymeric structure (50% probability ORTEP) of **3** with the hydrogen atoms omitted for clarity.

Scheme 1. Assembly of **3** through Slip-Stacking of Dimeric Fragments (THF Solvation Omitted for Clarity)

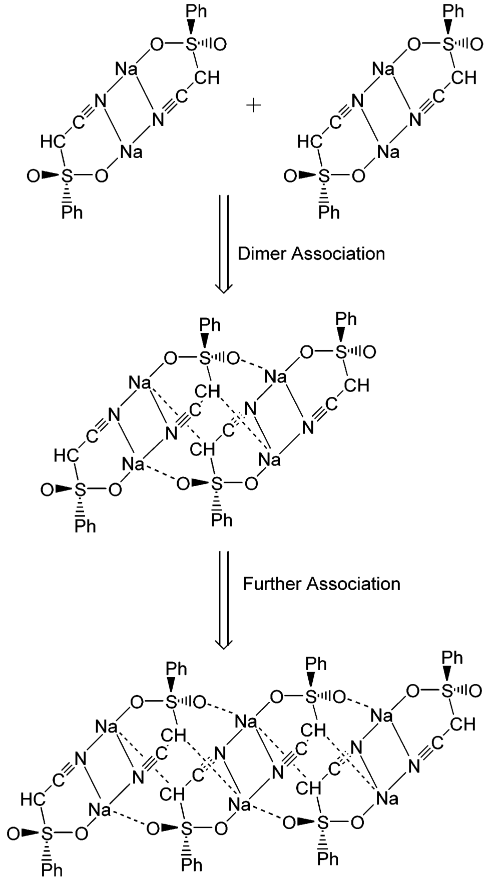

Table 2. Key Bond Lengths (Å) and Angles (deg) for **3** and **7**[a]

Compound **3**

Na(1)−O(3)	2.3236(11)	Na(1)−N(1)**	2.4532(13)
Na(1)−O(1)	2.3449(11)	Na(1)−N(1)*	2.8042(14)
Na(1)−O(2)*	2.3513(11)	Na(1)−C(1)′	2.8718(15)
O(1)−S(1)	1.4545(10)	C(1)−S(1)	1.6832(14)
O(2)−S(1)	1.4549(10)	C(3)−S(1)	1.7800(13)
N(1)−C(2)	1.1598(18)	C(1)−C(2)	1.3958(19)

O(3)−Na(1)−O(1)	115.11(4)	O(3)−Na(1)−O(2)*	85.22(4)
O(1)−Na(1)−O(2)*	97.58(4)	O(3)−Na(1)−N(1)**	91.32(4)
O(1)−Na(1)−N(1)**	87.38(4)	O(2)−Na(1)−N(1)**	174.73(4)
O(3)−Na(1)−N(1)*	164.95(4)	O(1)−Na(1)−N(1)*	77.11(4)
O(2)−Na(1)−N(1)*	84.37(4)	N(1)*−Na(1)−N(1)**	98.24(4)
O(3)−Na(1)−C(1)′	85.79(4)	O(1)−Na(1)−C(1)′	157.76(4)
O(2)*−Na(1)−C(1)′	91.28(4)	N(1)*−Na(1)−C(1)′	84.49(4)
N(1)*−Na(1)−C(1)′	83.61(4)	C(2)−N(1)−Na(1)″	88.92(9)
C(2)−N(1)−Na(1)**	158.20(11)	N(1)−C(2)−C(1)	176.46(14)
Na(1)**−N(1)−Na(1)″	81.76(4)	C(2)−C(1)−H(1)	121.1(12)
C(2)−C(1)−S(1)	116.42(10)	O(1)−S(1)−O(2)	118.13(6)
S(1)−C(1)−H(1)	117.3(12)	O(2)−S(1)−C(1)	108.99(6)
O(1)−S(1)−C(1)	109.51(6)	O(2)−S(1)−C(3)	105.48(6)
O(1)−S(1)−C(3)	104.26(6)	C(2)−N(1)−Na(1)″	88.92(9)
C(1)−S(1)−C(3)	110.17(6)		

Compound **7**

Li(1)−O(1)	1.893(4)	Li(1)−N(1)#	2.001(4)
Li(1)−N(2)	2.118(4)	Li(1)−N(3)	2.106(4)
O(1)−S(1)	1.4547(17)	C(1)−S(1)	1.660(3)
O(2)−S(1)	1.4377(16)	C(3)−S(1)	1.769(2)
C(1)−C(2)	1.384(3)	N(1)−C(2)	1.155(3)

O(1)−Li(1)−N(1)#	118.91(19)	N(2)−Li(1)−N(3)	87.70(15)
C(2)−N(1)−Li(1)#	158.4(2)	C(2)−C(1)−S(1)	120.72(19)
N(1)−C(2)−C(1)	178.4(3)	C(1)−S(1)−C(3)	110.33(13)
S(1)−C(1)−H(11)	117.3(16)	O(2)−S(1)−O(1)	117.56(11)
O(2)−S(1)−C(1)	110.07(12)	O(1)−S(1)−C(1)	108.95(11)
O(2)−S(1)−C(3)	105.57(12)	O(1)−S(1)−C(3)	104.04(12)

[a] Symmetry operations: (*) 1 + *x*, *y*, *z*; (**) 1 − *x*, −*y*, 1 − *z*; (′) 2 − *x*, −*y*, 1 − *z*; (″) *x* − 1, *y*, *z*; (#) 1 − *x*, 1 − *y*, 2 − *z*.

can then be considered to occur by the stacking (face-to-face) association of the dimeric units through Na−C and Na−O bonding (Scheme 1). A valid alternative description of **3** is a stepladder polymer.[20]

The notion of stacking dimers in the assembly of larger oligomers or polymers has clear precedent from the ring-laddering and ring-stacking principles developed by Snaith and co-workers.[21] These structural principles have found use in numerous areas of main group chemistry, and they have been extensively reviewed and elaborated upon.[22,23] In **3**, the association is unique and merits comment. In the classical examples of stacked structures, such as the hexamer $[(t\text{-Bu}(\text{Ph})\text{C}{=}\text{NLi})_6]$[21a] and the dodecamer $[(t\text{-BuC}{\equiv}\text{CLi})_{12}\cdot 4\text{THF}]$,[24] the stacked rings are eclipsed and rotated with respect to one another (by 60 and 90°, respectively, for the above compounds) to maximize the metal to anion interactions. In contrast, although the dimeric $(\text{OSCCNNa})_2$ rings in **3** are approximately parallel, they are not eclipsed or rotated with respect to each other; rather they are slipped or off-set. This mode of aggregation allows the formation of two strong sodium to oxygen contacts (Na(1)−O(1) 2.3449(11) Å) and two weaker secondary sodium to carbon contacts (Na(1)−C(1)′ 2.8718(15) Å) between a pair of neighboring dimers; see Table 2 for a list of key bond lengths and angles. This

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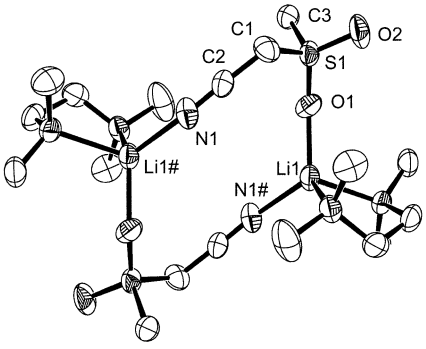

Figure 4. Molecular structure (50% probability ORTEP) of **7** with the hydrogens removed for clarity.

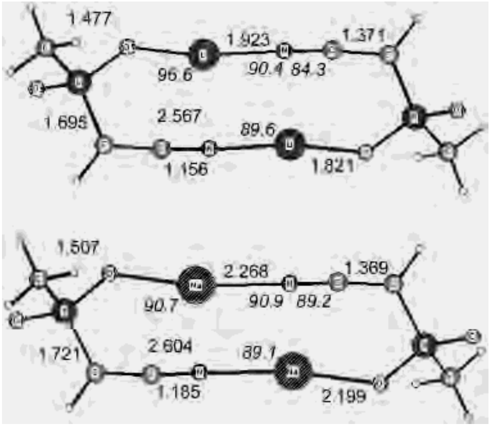

Figure 5. Geometry-optimized (B3LYP/6-31++G**) structures for the lithiated and sodiated $(OSCCNM)_2$ ring dimers. Key bond lengths (Å) and angles (deg, in italics) are shown.

association takes place on both faces of each dimer leading to the polymeric structure observed. Furthermore, the formation of **3** through the association of $(OSCCNNa)_2$ ring dimers is given substantial credence by the structural characterization of the dimeric complex [$MeSO_2CHCNLi{\cdot}TMEDA$], **7** (Figure 4). A more detailed discussion of the structure of **7** will follow this section.

An analysis of the bond lengths within **3** indicates that there are four strong bonding interactions to each metal: two sulfonyl oxygens; a nitrogen from a nitrile; and an oxygen from a THF molecule. The bond lengths between the metals and these groups are within the expected ranges for such interactions (see Table 1).[7] The coordination sphere of the metals is completed by two relatively long interactions, the transannular Na(1)−N(1)* at 2.8042(14) Å and the sodium to carbanion interaction, Na(1)−C(1)′, at 2.8718(15) Å. First, the long Na(1)−N(1)* interactions are consistent with our previous calculations (B3LYP/6-31++G**) on the related Li_2N_2 ring dimer [$\{MeSO_2CHCNLi\}_2$], which on optimization displayed long transannular Li−N distances (2.567 Å, compared with 1.923 Å for the remaining Li−N bond). A similar calculation on [$\{MeSO_2CHCNNa\}_2$] gave the structure shown in Figure 5, again with long transannular Na−N distances (2.604 Å). In both cases it appears that strong chelation of the metal is precluded due to the limited flexibility of the anion. Nevertheless, the larger size of the sodium cation does result in the difference between the transannular and "linear" Na−N distances being much closer than in the lithium complex (with the difference between the distances being 0.336 and 0.644 Å, respectively). Hence, the Na(1)−N(1)* interaction is retained in **3** but no such interaction is found in the solvated lithium complex **7**, where the distance is >3.5 Å.

In a similar vein, although the Na(1)−C(1)′ distances of 2.8718(15) Å in **3** are significantly longer than those normally found for direct sodium to carbon contacts (approximately 2.6 Å), they appear to contribute to the stabilization of the structure.[25] In particular, the carbanionic carbons protrude out of the mean plane of the $(OSCCNLi)_2$ rings and they are also distinctly pyramidalized. This can be seen from the sum of the angles around C(1) being only 354.8°, the pyramidalization angle χ_1 (which is defined for this purpose as the difference between the improper torsion angle S(1)−C(1)−C(2)···H(1) and 180°) being 26.1°, and finally the deviation Δ_1 of C(1) from the S(1)−C(2)−H(1) plane being 0.162 Å.[26] In addition, the C(1)−S(1) and C(1)−C(2) bonds are noticeably longer in **3**, at 1.6832(14) and 1.3958(19) Å, respectively, than in the lithiated complexes **1**, **2**, and **7**, at 1.664 Å (mean) and 1.384 Å (mean), respectively, consistent with the additional bonding interaction with the sodium.

Moving on to consider complex **7**, this compound was prepared as a direct analogue to the previously reported chain polymer **1**; however, in this instance a molecular dimer composed of a 12-membered $(OSCCNLi)_2$ ring was produced (Figure 4).[27] In fact, the structures of **1** and **7** are closely related. Both complexes display head-to-tail linking of the ligands by bridging lithium centers. Moreover, the helix in **1** utilizes two monomeric units per turn and scission of the extending Li−O bonds at these points, and rotation of the appropriate groups would result in a dimer akin to **7**. The similarity between **1** and **7** is also seen in bond lengths in the two complexes; for example, Li(1)−N(1)$^{\#}$ is 1.976(6) and 2.001(4) Å and Li(1)−O(1) is 1.889(6) and 1.893(4) Å, respectively. The main differences are the more acute angles at the nitrile nitrogen and the bridging oxygen of the sulfonyl group in **1** to accommodate the twisting of the helix, where C(2)−N(1)−Li(1)$^{\#}$ is 152.2(2) and 158.4 (2)° and Li(1)−O(1)−S(1) is 136.7(2) and 148.84(16)°, respectively, for **1** and **7** (whereas the N(1)−Li(1)−O(1) angles remain similar at 118.9(3) and 118.90(19)°, respectively). Hence, considering the relatively small structural changes required to transform between a dimer and a polymer the energetic difference between the two is probably very small in these instances.

In contrast to the pyramidalized carbanions in **3**, the geometry about C(1) in **7** is close to planarity, with the sum of the angles being 359.24°, χ_1 being 10.3°, and Δ_1 being 0.060 Å. Nonetheless, the overall geometries of the anionic ligands in **3** and **7** are similar and are also consistent with those previously characterized for **1** and **2**.[7] In particular,

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(26) The χ value for a perfectly planar carbanion would be 0°, whereas a χ value of 60° would be found for a perfectly tetrahedral center.

(27) For a related dimeric structure see: Boche, G.; Langlotz, I.; Marsch, M.; Harms, K. *Chem. Ber.* **1994**, *127*, 2059.

Table 3. ^{1}H NMR Data (δ_H, ppm) for Compounds **1**−**6** in DMSO-d_6 at 25 °C

	1	**2**	**3**	**4**	**5**	**6**
S−CH	2.57	2.02	2.57	2.02	2.55	2.02
o-H	7.68		7.67		7.67	
m-H	7.38		7.38		7.39	
p-H	7.38		7.38		7.39	
CH_3		1.16		1.17		1.17

Table 4. ^{13}C NMR Data (δ_C, ppm) for Compounds **1**−**6** in DMSO-d_6 at 25 °C

	1	**2**	**3**	**4**	**5**	**6**
C≡N	126.47	128.13	126.33	128.01	126.29	128.01
S−CH	37.57	26.44	37.46	26.37	37.45	26.35
S−C, *t*-Bu		58.63		58.57		58.57
CH_3, *t*-Bu		24.37		24.34		24.33
i-C, Ph	151.53		151.49		151.45	
o-C, Ph	124.29		124.21		124.20	
m-C, Ph	128.17		128.10		128.11	
p-C, Ph	129.00		128.91		128.92	

all of the metalated complexes have the “lone pair” of the carbanion gauche with respect to the pair of sulfonyl oxygens, and the nitrile unit lies antiperiplanar to the organic unit attached to the sulfonyl (with the torsion angle |C(3)−S(1)−C(1)−C(2)| in the narrow range between 83.0(3) and 91.3(2)° for the four complexes).

Spectroscopic Analyses. Although we have been unable to grow suitable single crystals of complexes **4**−**6** for X-ray analysis, their identities have been established by NMR spectroscopy. Tables 3 and 4 detail the ^{1}H and ^{13}C NMR spectroscopic data for metalated compounds **1**−**6**. Rather surprisingly, although all the complexes were prepared in THF solution, only **3** was found to contain significant quantities of the Lewis base. However, trace quantities (<5%) of THF were discernible in their ^{1}H NMR spectra, suggesting that the donor is present initially but is easily lost under vacuum for the powdered (noncrystalline) samples.

We have previously detailed the bonding information obtained from the NMR data of **1** and **2**.[7] Of particular interest here is the similarity of the chemical shifts for each type of metalated ligand, i.e., independent of the cation present. Since significant differences in the electronic structure of the compounds would be expected on changing the cation, it is likely that dissolution in the highly polar solvent DMSO-d_6 leads to formation of charge separated species of the type $[RSO_2CHCN]^-[M{\cdot}n\text{DMSO-}d_6]^+$ (where R = Ph or *t*-Bu and M = Li, Na, or K).[28]

Conclusions

Although the macromolecular structures of the complexes **1**, **2**, **3**, and **7** are substantially different from one another (molecular dimer **7**, chain polymer **1**, cage polymer **3**, and sheet polymer **2**), they possess common features. The two main similarities are the strong directional head-to-tail linking of the anionic ligands by the group 1 metals and the fixed localized geometry of the anions. Increasing the size of the cation from lithium to sodium allows further coordination contacts to be made with the ligands, and in the case of **3**, this results in the aggregation of dimeric units, similar to those of **7**, to furnish the cage polymer. The presence of sodium to carbon contacts in **3** is notable since these are not normally present for lithiated α-stabilized carbanions.[10,11,29]

We are now beginning to understand and rationalize the novel structural and bonding patterns emerging from this class of α,α′-stabilized carbanions. However, we are still at an early stage of our ultimate goal of being able to predict their solid-state structures on the basis of the nature of ligand, the metal present, and the solvent system used.

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Supporting Information Available: Crystallographic information in CIF format for **3** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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