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Solid-State and Theoretical Model Structures of Monolithiated (Organosulfonyl)acetonitriles and the Characterization and Reactivity of Their Geminated Dilithio Derivatives

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Two monolithiated (organosulfonyl)acetonitriles [$PhSO_2CHCNLi\cdot TMEDA$], **1**, and [*t*-$BuSO_2CHCNLi\cdot THF$], **2**, have been synthesized and, in turn, characterized in the solid state by X-ray crystallography. The complexes form novel chain and sheet polymeric structures in preference to the more common $(SO_2Li)_2$ or Li_2N_2 ring dimers associated with lithiated sulfones or nitriles. The X-ray crystal structures of the parent ligands RSO_2CH_2CN, where R = Ph **5** or *t*-Bu **6**, were also elucidated to allow a direct evaluation of the effects of metalation on the bonding within the complexes. Ab initio calculations at the HF/6-31G* level of theory support the view that the simple dimers are not formed due to the inflexibility of the ligand backbone, precluding chelation and consequently destabilizing these structures. In contrast, polymer formation allows the metal to bridge between separate ligands, eliminating the need for internal chelation. Both **1** and **2** contain “naked” anions where there is no direct bond between the anionic C atoms and the metal centers. The anionic C atom in **2** is essentially planar, whereas in **1** this center is distinctly pyramidylized. Crystal structure and solution ^1H and ^{13}C NMR data, in combination with ab initio (HF/6-31G*) and density functional (B3LYP/6-31++G**) calculations on model systems, indicate that both the sulfonyl and the nitrile units of the ligands participate in delocalizing the charge of the anions throughout the $S{\cdots}C{\cdots}C{\equiv}N$ linkage. In addition, the dilithiated salts [$PhSO_2CCNLi_2\cdot THF$], **3**, and [*t*-$BuSO_2CCNLi_2\cdot 0.75THF$], **4**, have been prepared by the reaction of 2 equiv of MeLi with **5** or **6** in THF solution. Both complexes have been characterized by ^1H and ^{13}C NMR spectroscopy and found to be authentic geminal organodimetallic species, with the methylene group being doubly deprotonated. Complexes **3** and **4** react cleanly with excess MeI to form the dialkylated products $PhSO_2CMe_2CN$, **7**, and *t*-$BuSO_2CMe_2CN$, **8**, respectively, in a single step.

Introduction

The use of α-stabilized carbanions as intermediates in organic synthesis has a prestigious history reaching back over 100 years, and interest in the reactions of these species continues unabated.[1] In this regard, sulfonyl (RSO_2) and nitrile ($C{\equiv}N$) groups are widely utilized due to their powerful carbanion-stabilizing properties, coupled with their potential for removal or derivatization.[2] The countercation in these intermediates is most commonly an electropositive metal, with lithium being the metal of choice due to the availability and ease of use of alkyllithium reagents.[3] In turn, this has led to lithiated sulfones and nitriles being extensively studied in their own right, both theoretically[4,5] and experimentally.[6−9] Indeed, the investigations on these stabilized carbanionic species have been a central pillar in our modern understanding of the aggregation and bonding within organolithium chemistry.[2,10] Seminal studies by Gais[6] and Boche[7] established that in the solid state sulfones generally form eight-membered

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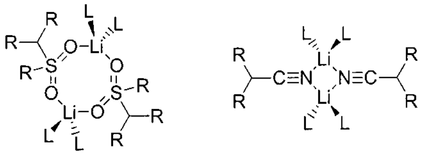

Figure 1. General structural types for lithiated sulfones and nitriles, where L = Lewis base.

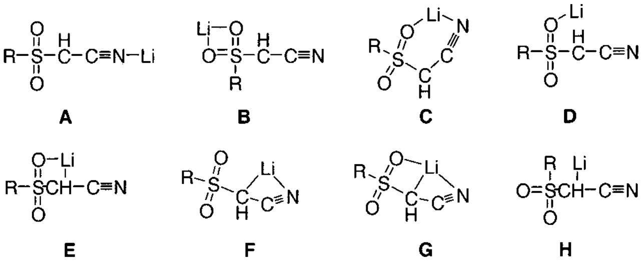

Figure 2. A variety of possible localized bonding modes for monolithiated (organosulfonyl)acetonitriles (aggregation and solvation are ignored for simplicity).

$(SO_2Li)_2$ ring dimers, whereas nitriles generally form four-membered Li_2N_2 ring dimers (Figure 1). A particularly unusual feature of both classes of these complexes is the lack of a direct bond between the (naked) carbanion and the metal. Instead, the metals bind to the highly electronegative oxygen or nitrogen atoms of the ligands.[11]

Developments in this area have now reached the point where the structures of lithiated sulfones and nitriles are seemingly largely predictable. We were interested in posing the question: which α-stabilizing unit will dominate the structural and bonding arrangement when both a sulfonyl and a nitrile unit are present within the parent ligand (Figure 2)? Herein, we report the syntheses, solution NMR, and solid-state structural characterizations of two monolithiated (organosulfonyl)acetonitriles, $[PhSO_2CHCNLi{\cdot}TMEDA]$, **1**, and $[t\text{-}BuSO_2CHCNLi{\cdot}THF]$, **2**, that aggregate into novel polymeric assemblies, marking a departure from the classical architectures of either lithiated sulfones or nitriles.[12]

Furthermore, since the methylene group of the parent ligands binds to two α-stabilizing groups, the possibility of doubly deprotonating this unit to form geminated organodimetallic species (R_2CM_2) was investigated.[13] In this regard, the syntheses, characterizations, and reactivities of the complexes $[PhSO_2CCNLi_2{\cdot}THF]$, **3**, and $[t\text{-}BuSO_2CCNLi_2{\cdot}0.75THF]$, **4**, are detailed. Finally, a combined ab initio and density functional computational study of model neutral ligands, their anions, and their lithiated salts is used to rationalize the unusual aggregation and bonding patterns adopted for these species.

Experimental Section

All manipulations were carried out under a protective argon atmosphere using standard Schlenk techniques.[14] All solvents were distilled over sodium/benzophenone until blue, degassed, and stored over 4 Å molecular sieves prior to use. Compounds **5** and **6** were purchased from Lancaster, recrystallized from hexane, dried under vacuum, and stored in a desiccator over KOH before use. All glassware was flame-dried under vacuum before use. MeLi was purchased from Aldrich as a 1 M solution in Et_2O, and *n*-BuLi was purchased from Aldrich as a 1.6 M solution in hexane. Both MeLi and *n*-BuLi were standardized by titration with salicylaldehyde phenylhydrazone directly before use.[15] MeI was distilled directly before use. Deuterated solvents for 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. All ^{13}C assignments were determined using HMQC experiments. The IR spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer as Nujol mulls, and elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer.

Synthesis of $[PhSO_2CHCNLi{\cdot}TMEDA]$, 1. (Phenyl)sulfonylacetonitrile (0.36 g, 2 mmol) was dissolved in a solution of THF (10 mL) and TMEDA (0.30 mL, 2 mmol). *n*-Butyllithium (2 mmol of a 1.6 M solution in hexanes) was added dropwise to the mixture, and the reaction was allowed to stir at ambient temperature for 1 h. All solvent was removed under vacuum to give a clear oil. Hexane (20 mL) was added and the mixture placed in an ultrasonic bath for 1 h, yielding a pale yellow solid. The solid was isolated by filtration, dried in vacuo, and subsequently used for analysis. High-quality crystals of **1** were obtained by recrystallizing the solid from a neat THF solution over 2 days at −28 °C. Yield: 370 mg, 57%. Mp: 124−126 °C (Found: C, 55.67; H, 7.41; N, 12.98. $C_{14}H_{22}LiN_3O_2S$ requires C, 55.43; H, 7.31; N, 13.85). ν_{max}/cm^{-1} (C≡N): 2151s (Nujol). ^1H NMR (400 MHz, $[D_6]$-DMSO, 25 °C): δ 7.66 (d, 2H; *o*-H, Ph), 7.37 (m, 3H; *m*- and *p*-H, Ph), 2.56 (s, 1H; SO_2-CH), 2.15 (s, 4H; CH_2, TMEDA), 2.04 (s, 12H; CH_3, TMEDA). ^{13}C NMR (100 MHz, $[D_6]$-DMSO, 25 °C): δ 151.92 (*i*-C, Ph), 129.47 (*p*-C, Ph), 128.65 (*m*-C, Ph), 124.71 (*o*-C, Ph), 126.93 (C≡N), 57.70 (CH_2, TMEDA), 46.04 (CH_3, TMEDA), 38.04 (SO_2-CH).

Synthesis of $[t\text{-}BuSO_2CHCNLi{\cdot}THF]$, 2. (*tert*-Butyl)sulfonylacetonitrile (0.32 g, 2 mmol) was dissolved in THF (15

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mL), and *n*-butyllithium (2 mmol, of a 1.6 M solution hexanes) was added dropwise to this solution at ambient temperature. A white precipitate was instantly produced, and the mixture was stirred at ambient temperature for 1 h. The mixture was then heated until complete dissolution was evident. High-quality crystals of **2** were obtained on cooling the remaining solute slowly over 24 h to ambient temperature. The crystals were isolated by filtration, dried in vacuo, and subsequently used for analysis. Yield: 190 mg, 40%. Decomposed above 250 °C (Found: C, 49.08; H, 7.30; N, 5.29. $C_{10}H_{18}LiNO_3S$ requires C, 50.20; H, 7.58; N, 5.85). ν_{max}/cm^{-1} ($C\equiv N$): 2156s (Nujol). ^1H NMR (400 MHz, [D_6]-DMSO, 25 °C): δ 3.60 (m, 4H; O-CH_2, THF), 2.02 (s, 1H; SO_2-CH), 1.76 (m, 4H; CH_2, THF), 1.17 (s, 9H; CH_3, *t*-Bu). ^{13}C NMR (100 MHz, [D_6]-DMSO, 25 °C): δ 128.46 ($C\equiv N$), 67.41 (O-CH_2, THF), 58.99 (SO_2-C, *t*-Bu), 26.81 (SO_2-CH), 25.52 (CH_2, THF), 24.76 (CH_3, *t*-Bu).

Synthesis of [$PhSO_2CCNLi_2\cdot THF$], 3. (Phenyl)sulfonylacetonitrile (0.18 g, 1 mmol) was dissolved in THF (20 mL), and methyllithium (2 mmol, of a 1 M solution in Et_2O) was added dropwise to this solution at ambient temperature. An off-white precipitate was instantly produced, and the mixture was stirred at ambient temperature for 3 h. The precipitate was separated by filtration and dried in vacuo before transferal to a glovebox. Yield: 230 mg, 92%. Decomposed above 200 °C (Found: C, 53.18; H, 5.00; N, 5.32. $C_{12}H_{13}Li_2NO_3S$ requires C, 54.35; H, 4.94; N, 5.28). ν_{max}/cm^{-1} ($C\equiv N$): broad peak at 2046 with shoulders at 2095 and 2177 (Nujol). ^1H NMR (400 MHz, [D_6]-DMSO, 25 °C): δ 7.66 (m, 2H; *o*-H, Ph), 7.37 (m, 3H; *m*- and *p*-H, Ph), 3.59 (m, 4H; O-CH_2, THF), 1.75 (m, 4H; CH_2, THF). ^{13}C NMR (100 MHz, [D_6]-DMSO, 25 °C): δ 151.94 (*i*-C, Ph), 129.40 (*p*-C, Ph), 128.60 (*m*-C, Ph), 124.68 (*o*-C, Ph) 126.86 ($C\equiv N$), 67.48 (O-CH_2, THF), 25.58 (CH_2, THF). No signal for the anionic C atom was located even on extended acquisition times.

Synthesis of [*t*-$BuSO_2CCNLi_2\cdot 0.75THF$], 4. (*tert*-Butylsulfonyl)acetonitrile (0.16 g, 1 mmol) was dissolved in THF (20 mL), and methyllithium (2 mmol, of a 1 M solution in Et_2O) was added dropwise to this solution at ambient temperature. A brown precipitate was instantly produced, and the mixture was stirred at ambient temperature for 3 h. The precipitate was separated by filtration and dried in vacuo before transferal to a glovebox. Yield: 180 mg, 84%. Decomposed above 170 °C (analyses based on 0.75 equiv of THF present from integration of the ^1H NMR spectrum; this stoichiometry proved reproducible on the preparation of several batches of the complex. Found: C, 45.95; H, 6.66; N, 5.44. $C_9H_{15}Li_2NO_{2.75}S$ requires C, 47.59; H, 6.66; N, 6.17). ν_{max}/cm^{-1} ($C\equiv N$): broad peak at 2022 with shoulders at 2059, 2096, and 2149 (Nujol). ^1H NMR (400 MHz, [D_6]-DMSO, 25 °C): δ 3.59 (m, 3H; O-CH_2, THF), 1.74 (m, 3H; CH_2, THF), 1.16 (s, 9H; CH_3, *t*-Bu). ^{13}C NMR (100 MHz, [D_6]-DMSO, 25 °C): δ 128.53 ($C\equiv N$), 67.44 (O-CH_2, THF), 59.02 (SO_2-C, *t*-Bu), 25.55 (CH_2, THF), 24.77 (CH_3, *t*-Bu), 22.30 (SO_2-C, α-C).

Synthesis of $PhSO_2CMe_2CN$, 7. (Phenyl)sulfonylacetonitrile (0.18 g, 1 mmol) was dissolved in THF (25 mL), and methyllithium (2 mmol, of a 1 M solution in Et_2O) was added dropwise to this solution at ambient temperature. An off-white precipitate was instantly produced, and the mixture was stirred at ambient temperature for 3 h. Methyl iodide (1 mL, 7 mmol) was added dropwise, resulting in a clear brown solution. The mixture was stirred for 0.5 h, and the solvent was removed in vacuo and replaced by water (15 mL), and the organics were extracted into EtOAc (3 × 20 mL). The organic layer was then dried over $MgSO_4$, all solvents were removed in vacuo, and the solid was recrystallized from EtOAc and hexane (3:7). Yield: 154 mg, 74% (first crystalline batch). Mp: 103−104 °C (Found: C, 57.55; H, 5.16; N, 6.69. $C_{10}H_{11}NO_2S$ requires C, 57.40; H, 5.30; N, 6.69). ν_{max}/cm^{-1} ($C\equiv N$): 2241s (Nujol). ^1H NMR (400 MHz, [D_6]-DMSO, 25 °C): δ 7.97 (d, 2H; *o*-H, Ph), 7.92 (t, 2H; *p*-H, Ph), 7.78 (t, 1H; *m*-H, Ph), 1.65 (s, 6H; CH_3); ^{13}C NMR (100 MHz, [D_6]-DMSO, 25 °C): δ 136.08 (*p*-C, Ph), 133.16 (*i*-C, Ph), 130.82 (*o*-C, Ph), 130.17 (*m*-C, Ph), 118.63 ($C\equiv N$), 58.12 (C, CMe_2), 20.71 (CH_3).

Synthesis of *t*-$BuSO_2CMe_2CN$, 8. The procedure was the same as for **7** with the exception of replacing (phenyl)sulfonylacetonitrile by (*tert*-butyl)sulfonylacetonitrile (0.16 g, 1 mmol) and that the product was recrystallized from neat hexane. Yield: 147 mg, 77% (first crystalline batch). Mp: 82 °C (Found: C, 51.15; H, 8.22; N, 7.28. $C_8H_{15}NO_2S$ requires C, 50.77; H, 7.99; N, 7.40). ν_{max}/cm^{-1} ($C\equiv N$): 2239s (Nujol). ^1H NMR (400 MHz, [D_6]-DMSO, 25 °C): δ 1.76 (s, 6H; CH_3, CMe_2), 1.53 (s, 9H; CH_3, *t*-Bu). ^{13}C NMR (100 MHz, [D_6]-DMSO, 25 °C): δ 119.86 ($C\equiv N$), 67.24 (SO_2-C, *t*-Bu), 56.78 (C, CMe_2), 25.26 (CH_3, *t*-Bu), 22.70 (CH_3, CMe_2).

X-ray Crystallography. Single-crystal diffraction data were recorded by a Nonius Kappa CCD diffractometer at 150 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All non-H atoms were refined anisotropically except for those of the chelate ligand of compound **1**. This was modeled isotropically as disordered over two sites whose occupancies refined as 63(1):37(1). All H atoms of the compounds **5** and **6** refined isotropically, as were the atoms H(1) of compounds **1** and **2** (i.e., the H bonded to the anionic C atom). All other H atoms in compounds **1** and **2** were placed in calculated positions and in riding modes. The structures were refined by full-matrix least-squares and against F^2 to convergence using the SHELXL-97 program.[16] For **5** the absolute structure is indicated by a refined Flack parameter value of 0.06(15).[17] Specific crystallographic data and refinement parameters are given in Table 1. CCDC reference numbers are 177256−177259.

Computational Details. The Gaussian 94 program (revision E.2), run on a Silicon Graphics Origin 200 workstation, was used for the calculations.[18] No symmetry constraints were imposed, and all molecules were allowed to freely optimize. Structures **I**−**VIII** were geometry optimized at both the standard HF/6-31G* and the higher B3LYP/6-31++G** levels of theory.[19−21] Due to the size of the calculations the dimeric structures **IX**−**XII** were geometry optimized only at the HF/6-31G* level. Frequency analysis using both levels of theory was used for calculations **I**−**VIII** to determine if the true minima were located. The cited IR frequencies were calculated at the B3LYP/6-31G*//B3LYP/6-31G* level and scaled by a factor of 0.9614.[22] Absolute energies and atomic coordinates for the calculated molecules can be supplied on request from the author.

Results and Discussion

Solid-State Studies of the Monolithiated Complexes. Complexes **1** and **2** were prepared by the monodeprotonation of the ligands $PhSO_2CH_2CN$, **5**, and *t*-$BuSO_2CH_2CN$, **6**, respectively, by 1 molar equiv of *n*-BuLi in the appropriate solvent mixture. Single

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Table 1. Crystallographic Parameters for 1, 2, 5, and 6

	1	**2**	**5**	**6**
chem formula	$C_{14}H_{22}LiN_3O_2S$	$C_{10}H_{18}LiNO_3S$	$C_8H_7NO_2S$	$C_6H_{11}NO_2S$
fw	303.35	239.25	181.21	161.22
cryst size (mm)	0.30 × 0.25 × 0.15	0.30 × 0.30 × 0.05	0.25 × 0.25 × 0.25	0.35 × 0.15 × 0.15
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$P2_1/a$	$Pmn2_1$	$Pnma$
a (Å)	8.7582(4)	10.2227(4)	8.8415(8)	17.3947(5)
b (Å)	9.5126(5)	6.4498(2)	10.0748(10)	8.5665(2)
c (Å)	20.4591(12)	19.7438(8)	4.7850(4)	5.47070(10)
β (deg)	91.471(3)	94.117(2)	90	90
V (Å^3)	1703.95(16)	1298.44(8)	426.23(7)	815.20(3)
Z	4	4	2	4
no. reflns collected	5898	4813	7566	1939
no. ind reflns	3260	2545	521	1121
R_{int}	0.0700	0.0551	0.067	0.0221
D_{calc} (g cm^{-3})	1.182	1.224	1.412	1.314
μ (cm^{-1})	0.196	0.240	0.335	0.340
R	0.0673	0.0470	0.0326	0.0300
R_w	0.1821	0.1093	0.0749	0.0753

crystals suitable for X-ray analysis of both the metalated complexes and the parent ligands were prepared and their structures elucidated. The analysis of **1** revealed a one-dimensional polymeric chain structure, in which each metal is coordinated to one oxygen of a sulfonyl, a cyano nitrogen, and two nitrogens from a TMEDA donor solvent molecule (Figure 3). Each metal bridges two separate ligands that are twisted with respect to each other, giving an overall assembly of a helical polymer with two monomer units per turn.

The individual polymeric chains of **1** are chiral since each sulfur bonds to four different groups: a phenyl ring, an anionic-C atom, an oxygen bonded to lithium, and also to a nonligating oxygen. All the sulfur atoms in a given chain adopt the same chirality (i.e., all *R* or all *S*), resulting in the formation of the helical structure. However, the bulk crystal is rendered racemic since adjacent chains in the lattice alternate between right- and left-handed helices.[23] Previously, there has been significant interest in preparing optically stable chiral sulfones, and this has been achieved at sulfur by isotopical labeling of the attached oxygens (^{16}O and ^{18}O).[24] Of more practical relevance, chiral sulfoximines have recently proved to be versatile reagents in asymmetric synthesis.[25]

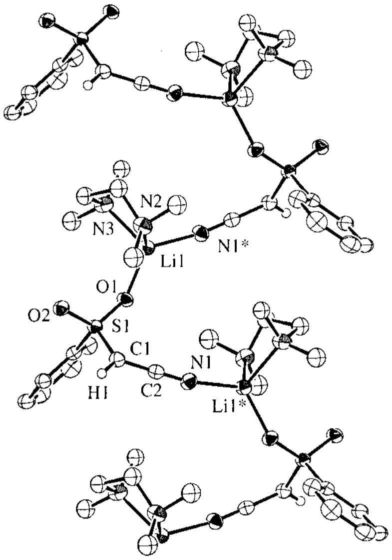

Figure 3. Section of the molecular structure of **1**.

To date, very few metal complexes containing an anionic C atom connected to both a sulfonyl and a nitrile have been structurally characterized.[26,27] However, a structure that bears some resemblance to **1** is the lithium thiocyanate complex [{LiSCN·TMEDA}$_\infty$], where the metals bridge between a sulfur and a nitrogen from two different anions (in addition to the didentate TMEDA molecule) to form a chain polymer.[28] In this instance zigzag chains are formed rather than helices, and the chains align in the crystal to produce pseudosheets. Another complex related to **1** is the lithiated *tert*-butyl cyanoacetate [{*t*-BuOC(O)=C(H)CNLi·TMEDA}$_2$].[29] In this instance a discrete dimer containing a central $(LiOCCCN)_2$ 12-membered ring is formed, where the metals bridge the anionic oxygen and the cyano nitrogen of two separate ligands.

To determine the effect of altering the denticity of the donor ligand, TMEDA was replaced by THF, and using ligand **6**, the *t*-Bu variant of **5**, high-quality crystals of **2** were successfully prepared. Single-crystal X-ray analysis of **2** revealed that a complex two-dimensional honeycomb sheet is created by the fusion of 16-membered rings (Figure 4). Each ring is trimeric, containing three metal centers and three ligands, and interconnects with six other rings within the sheet. Each trimeric ring contains two distinct types of edges: (i) four S−O−Li linkages, and (ii) two S−C−C−N−Li linkages.

The formation of such large rings involving lithium is rare, where the norm is four-, six-, or occasionally eight-membered rings.[10,30] Interestingly, our recent report on the structures of the related lithiated α-

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[23] For another example of a helical lithium compound see: Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1991**, *113*, 8187.

[24] (a) Stirling, C. J. M. *J. Chem. Soc.* **1963**, 5741. (b) Sabol, M. A.; Andersen, K. K. *J. Am. Chem. Soc.* **1969**, *91*, 3603. (c) Annunziata, R.; Cinquini, M.; Colona, S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2057.

[25] (a) Reggelin, M.; Zur, C. *Synthesis* **2000**, 1. (b) Mikolajczk, M.; Drabowicz, J.; Kielbasinski, P. *Chiral Sulfur Reagents*; CRC Press: New York, 1997. (c) Pyne S. G. *Sulfur Rep.* **1992**, *12*, 57.

[26] (a) Naota, T.; Tannna A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **2000**, *122*, 2960. (b) Yagupolskii, Y. L.; Pavlenko, N. V.; Lork, E. *Heteroat. Chem.* **1998**, *9*, 565.

[27] Iorga, B.; Ricard, L.; Savignac, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3311.

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[29] Boche, G.; Langlotz, I.; Marsch, M.; Harms, K. *Chem. Ber.* **1994**, *127*, 2059.

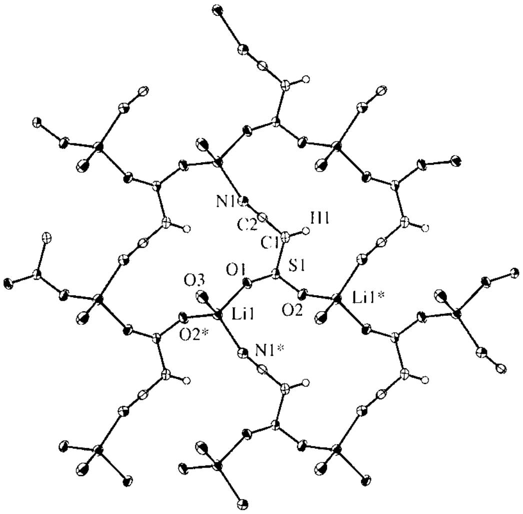

Figure 4. Section of the molecular structure of **2** with the hydrogens (except that of the anionic C atom) and the carbons of the *t*-Bu and THF groups omitted for clarity.

cyanophosphonates [$(RO)_2P(O)CHCNLi·THF$], where R = Et or *i*-Pr, revealed the formation of rings with 24 atoms, which each contain four metal centers.[31] However, the expected Li_2O_2 dimeric ring motif associated with lithiated phosphonates is retained in these instances, and the extended aggregation is a result of interdimer ligation of the nitrile unit.[32] In contrast, the expected dimeric motif, either $(SO_2Li)_2$ or Li_2N_2, seen for lithiated sulfones and nitriles is absent in **1** and **2**.

As in **1**, each lithium in **2** is tetracoordinate; however, the metals now bridge between three separate ligands by binding to two sulfonyl oxygens and one cyano nitrogen, in addition to a single THF molecule. Rather unexpectedly, all of the THF molecules bind on the same face of the sheet layer, with the *t*-Bu groups of the sulfonyl on the opposite face; that is, the polymer is regioselectively solvated (Figure 5).[33] This *anti* arrangement is most likely preferred due to a minimization of the steric interactions between adjacent THF molecules and *t*-Bu groups.

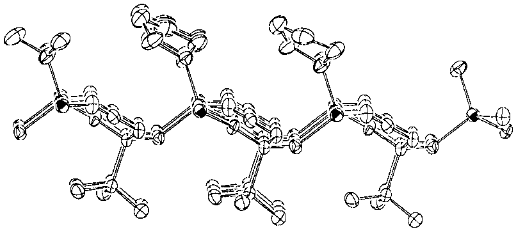

Figure 5. View of **2** through the edge of a sheet showing the THF molecules and *t*-Bu groups on opposite faces.

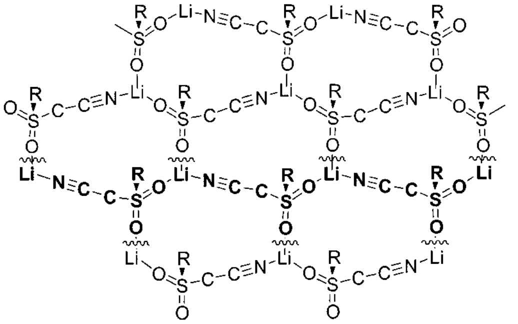

Figure 6. Idealized representation of the sheet structure of **2** showing its relationship with **1** in bold (THF molecules and hydrogens are removed for clarity).

Following the analysis of the aggregated nature of the (organosulfonyl)acetonitrile species, it is intriguing to speculate on the assembly of complexes **1** and **2**. First, the sheet structure of **2** can be derived by the fusion of individual polymeric chains of **1**; that is, the chains associate via bonding through the initially nonligating oxygen atoms to a vacant coordination site on each metal (created on going from bidentate TMEDA to monodentate THF). An alternative view is to consider that homochiral chains of **1** can be formed by selective Li−O bond cleavage in **2**. Breaking the Li−O bonds of the short Li−O−S links at the opposite ends of each trimeric ring in **2** results in the formation of a homochiral, one-dimensional, polymer akin to **1**, as shown in Figure 6 In contrast, alternative cleavage routes across the sheet result in heterochiral polymers, which contain both *R* and *S* chiral sulfur centers. Therefore, the solid-state structures of **1** and **2** appear to be closely related, with the "linear", relatively inflexible, (LiNCCSO) linkages being the common motif and the driving force for the formation of the polymers in preference to simple dimers.

Looking in detail at the geometric parameters within **1** and **2**, it can be seen that the anions exhibit significant delocalization of the charge over the ligands. Specifically, the C(1)−C(2) distances are 1.384(4) and 1.385(4) Å, the C(2)−N(1) distances are 1.155(4) and 1.160(3) Å, and the S(1)−C(1) distances are 1.668(3) and 1.665(3) Å, for **1** and **2**, respectively (Table 2). Overall, the bond lengths within the S(1)−C(1)−C(2)−N(1) linkages of **1** and **2** are intermediate between the relevant single, double, and triple bonds (single C−C, 1.54 Å; double C═C, 1.33 Å; single S−C, 1.81 Å; double S═C, 1.61 Å; double C═N, 1.24; triple C≡N, 1.14).[34] Moreover, the effects of metalation can clearly be seen by using the crystal structures of neutral ligands **5** and **6** for comparison (Figures 7 and 8).[35]

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(33) For another example of a regioselectively solvated polymer see: Kennedy, A. R.; Mulvey, R. E.; Robertson, A. *Chem. Commun.* **1998**, 89.

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(35) For related structures see: (a) Sammes, M. P.; Harlow, R. L.; Simonsen, S. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1126. (b) Harlow, R. L.; Simonsen, S. H.; Sammes, M. P. *Acta Crystallogr., Sect. B* **1976**, *32*, 2690. (c) Loghry, R. A.; Simonsen, S. H. *Acta Crystallogr., Sect. B* **1976**, *32*, 1505 (d) Harlow, R. L.; Sammes, M. P.; Simonsen, S. H. *Acta Crystallogr., Sect. B* **1974**, *32*, 2903.

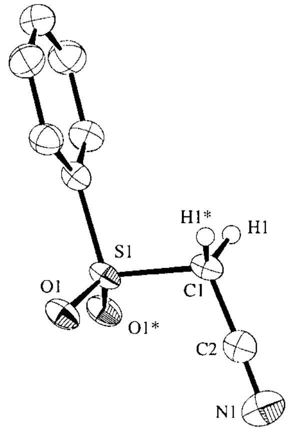

Figure 7. Molecular structure of **5**.

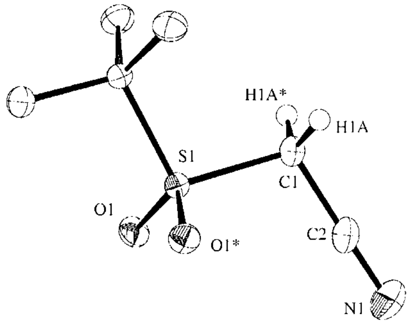

Figure 8. Molecular structure of **6**.

Table 2. Key Bond Lengths (Å) and Angles (deg) for 5 and 6 and for the Anionic Ligand Portions of 1 and 2

	1	**2**	**5**	**6**
S(1)−O(1)	1.462(2)	1.4556(17)	1.4411(17)	1.4424(9)
S(1)−O(2)	1.448(2)	1.4594(17)		
S(1)−C(1)	1.668(3)	1.665(3)	1.801(4)	1.8077(17)
S(1)−C(3)	1.780(3)	1.821(2)	1.755(4)	1.8118(17)
C(1)−C(2)	1.384(4)	1.385(4)	1.467(5)	1.459(3)
N(1)−C(2)	1.155(4)	1.160(3)	1.139(5)	1.140(3)
C(1)−C(2)−N(1)	177.9(3)	178.9(3)	177.8(5)	179.5(2)
S(1)−C(1)−C(2)	118.7(2)	118.8(2)	108.6(3)	108.97(12)
S(1)−C(1)−H(1)	115(2)	119.0(16)	104.6(16)	107.5(10)
C(2)−C(1)−H(1)	122(2)	122.2(16)	115.1(17)	119.0(11)
O(1)−S(1)−O(1*)			118.72(15)	116.73(7)
O(1)−S(1)−O(2)	117.43(13)	117.67(11)		
O(1)−S(1)−C(1)	109.15(15)	108.84(12)	107.47(9)	107.84(5)
C(1)−S(1)−C(3)	110.22(15)	111.98(13)	102.08(18)	110.22(15)
O(1)−S(1)−C(3)	105.36(14)	104.45(10)	109.82(5)	109.82(5)
O(2)−S(1)−C(1)	109.62(14)	109.40(11)		
O(2)−S(1)−C(3)	105.36(14)	104.38(11)		

Lithiation results in significantly shortening the C(1)−C(2) and S(1)−C(1) bonds (by 0.078 Å mean and 0.138 Å mean, respectively). In addition, the C−N bonds lengthen by a small degree on metalation (by 0.018 Å mean), indicating that the C≡N triple bond is slightly perturbed by lithiation. This bonding situation is similar to that found in related lithiated nitriles, where ketene iminate structures are commonly found, as shown by **I** in Figure 9.[7] A better representation of the bonding present in **1** and **2** is shown as **J** in Figure 9, where the charge is delocalized over the $S\cdots C\cdots C\equiv N$ framework.

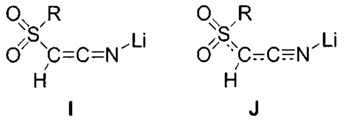

Figure 9. Idealized representation of ketene iminate (**I**) and extended $S\cdots C\cdots C\equiv N$ delocalization (**J**).

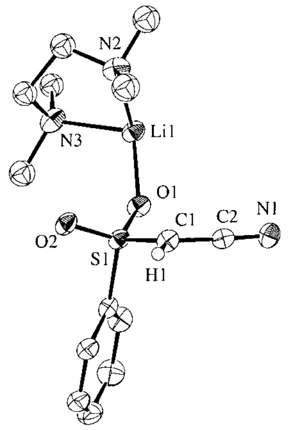

Figure 10. Asymmetric unit of **1** with the hydrogens (except that of the anionic C atom) omitted for clarity.

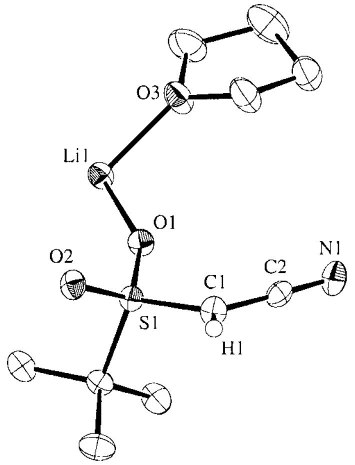

Figure 11. Asymmetric unit of **2** with the hydrogens (except that of the anionic C atom) omitted for clarity.

The S−O bond distances also lengthens slightly (0.018 Å mean) on metalation, but from the data it is unclear if this is a consequence of anion formation or rather due to ligation to a metal in the solid state.[10] This can be seen in **1**, where the S−O distance for the nonligating oxygen O(2) changes by only 0.007 Å compared with that in "metal-free" **5**.

The localized geometric features of **1** and **2** can best been seen by viewing the asymmetric units of the crystal structures shown in Figures 10 and 11.

Anion formation and lithium complexation do not greatly alter the almost linear N(1)−C(2)−C(1) angles (<1° change) or the O(1)−S(1)−O(2) angles (<1.5° change). However, a distinct outcome of metalation is the change in hybridization at the anionic carbon C(1). The planarity of the anionic C atoms in **1** and **2** can be assessed in terms of (i) the sum of the angles at C(1) (356.5° and 360.0°), (ii) the deviation (Δ_1) of C(1) from the S(1)−H(1)−C(2) plane (0.13 and 0.05 Å), and (iii) the pyramidalization angle (χ_1, which is defined for this purpose as 180°, the improper torsion angle S(1)−C(1)−C(2)$\cdots$H(1)) for the C(1) atom (22.3° and 1.0°, respectively, for **1** and **2**).[36] Clearly, from these values the

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[36] For a completely planar carbanion the χ value would be 0°, and for a tetrahedral atom the χ value would be 60°. For comparison, the χ values for C(1) in the ligands **5** and **6** are 63.2° and 63.0°, respectively.

anionic C atom in **2** is essentially planar, whereas that in **1** is much more pyramidylized, and can be considered to be intermediate between sp^2 and sp^3 hybridized. Previously, there has been much discussion regarding the nature of the geometry at the anionic carbon in related systems.[6,32] Structural and theoretical data indicate that the arrangement adopted at the anionic carbon is determined by the minimization of torsional strain around this center.

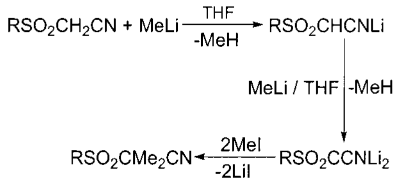
It is also worth noting that in both metalated complexes the "lone pair" of the anion is gauche with respect to the two oxygen atoms of the adjacent sulfonyl and antiperiplanar to the Ph or *t*-Bu group of the same unit. This represents a conformational change from the parent ligands, where the |C(3)−S(1)−C(1)−C(2)| torsion angles are 180.0° for **5** and **6** and 83.0(3)° and 91.3(2)° for **1** and **2**. Again, this is in agreement with the situation commonly found in other lithiated sulfones.[6] Overall, although the aggregated assemblies of **1** and **2** are completely novel, the localized geometries of the individual ligands are remarkably similar to the lithiated sulfone and nitrile homologues.

Characterization and Reactivity of the Dilithiated Complexes. Recently, there has been increasing interest in the preparation and utility of geminated organodimetallic complexes, since these have proven to have differing reactivities and selectivities compared with their monometallic derivatives.[13,37] The dimetalation of **5** and **6** to form complexes **3** and **4** proceeded readily on the addition of 2 molar equiv of MeLi to THF solutions of the ligands. These reactions resulted in the instantaneous precipitation of complexes **3** and **4**, which were subsequently isolated by filtration. Presently, all attempts to grow X-ray quality crystals of **3** and **4** have been unsuccessful due to their poor solubility in common solvent systems.

The absence of a methylene signal in the ^{1}H NMR spectra of **3** and **4** (run as solutions in D$_6$-DMSO) confirmed the formation of the geminated organodimetallic complexes. The authentication of doubly lithiated complexes is in fact not a trivial matter. Previously, Boche discovered the formation of quasi-dianion complexes (QADACs), which are co-complexes between a monolithiated species and a lithium base reagent but which react as expected for a dianion.[38] It is therefore critical that such dianionic complexes are fully characterized if their reactivity and selectivity properties are to be understood.

The presumed dilithiated derivatives of (organosulfonyl)acetonitriles have been utilized previously to prepare olefins and substituted cyclopropanes in good yield and, in addition, with excellent stereocontrol.[39] Complexes **3** and **4** were reacted with excess MeI to determine if they behaved as expected for dianions, by forming two new C−C bonds in a single step. These reactions cleanly afforded the dialkylated products **7** and **8** in good yields (Scheme 1).

Scheme 1



Where R = Ph or *t*-Bu. Isolated yields >70%

Computational Studies

To further rationalize the bonding patterns and aggregation adopted by **1** and **2**, a theoretical investigation of some model ligands, their anions, and their lithiated compounds was carried out. First, to determine the role of the sulfonyl and the nitrile units in stabilizing the charge, the model ligands MeCH$_2$CN, **I**, MeSO$_2$CH$_2$Me, **II**, and MeSO$_2$CH$_2$CN, **III**, and their anions [MeCHCN]$^-$, **IV**, [MeSO$_2$CHMe]$^-$, **V** and [MeSO$_2$CHCN]$^-$, **VI**, were geometry optimized at both the standard HF/6-31G* and the higher B3LYP/6-31++G** levels of theory (Figure 12).[19−21] Comparison of the bond lengths and angles obtained using the two computational methods showed some variations. Nevertheless, for each method the magnitude of the geometric changes for the calculations is similar, and therefore for simplicity, only the HF/6-31G* values will be discussed in detail.

The bonding patterns previously found for nitriles, sulfones, and their anions are reproduced in the calculations of **I**−**IV**.[4] For the nitrile, formation of the free anion results in lengthening the C−N bond and shortening the adjacent C−C bond (by 0.026 and 0.081 Å, respectively) to give a ketene iminate localized structure. Similarly, formation of the free anion for the sulfone results in significantly shortening the S−C(anion) bond and a slight lengthening of the S−C(methyl) and the S−O bonds (by 0.126, 0.036, and 0.022 Å, respectively). The dramatic shortening of the S−C(anion) bond in sulfones has been determined to be caused by a combination of Coulombic, hyperconjugative, and polarization effects. Also, the free anionic C atoms in **II** and **IV** are distinctly pyramidalized, with χ_1 values of 37.9° and 41.5°, respectively (Table 4).

Moving on to consider the (methylsulfonyl)acetonitrile calculations, the bond lengths and angles within the calculated structure **V** are in close agreement with those observed within the relevant sections of compounds **I** and **III** and are also very similar to those observed experimentally for **5** and **6** (with the differences in bond lengths and angles mostly being <0.05 Å and <3° between the calculated and experimentally determined values). In contrast, although the bond lengths are similar, the bond angles within the anion **VI** vary significantly from those in **II** and **IV**. In particular, the anionic C atom in **VI** is much closer to planarity, with a χ_1 value of 14.3° (Table 4). Also, an examination of the variation in the bond lengths on going from **V** to **VI** indicates that both the nitrile and the sulfonyl groups participate in stabilizing the charge on the anion.

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(37) (a) Müller, J. F. K.; Batra, R. *J. Organomet. Chem.* **1999**, *584*, 27. (b) Andrews, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 779. (c) Andrews, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1997**, 1183. (d) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, *122*, 1307. (e) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 696. (f) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 610.

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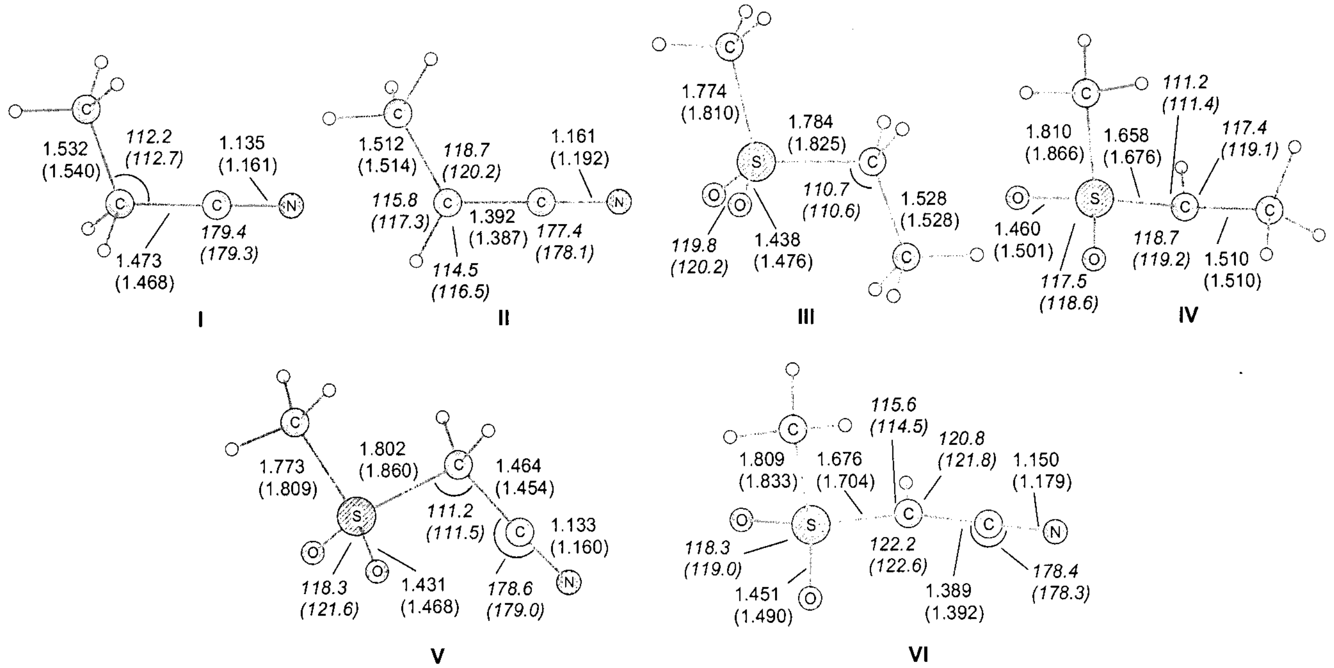

Figure 12. Geometry optimized (HF/6-31G*) structures for the neutral ligands and their anions **I**−**VI**. Key bond lengths (Å) and angles (deg, in italics) are shown, with the values in parentheses being those obtained from calculations at the B3LYP/6-31++G** level.

Table 3. Key Bond Lengths (Å) and Angles (deg) Involving the Metal Centers in 1 and 2

	For **1**		
Li(1)−O(1)	1.889(6)	Li(1)−N(1*)	1.976(6)
Li(1)−N(2)	2.115(6)	Li(1)−N(3)	2.089(6)
N(2)−Li(1)−N(3)	88.6(2)	O(1)−Li(1)−N(1*)	118.9(3)
O(1)−Li(1)−N(2)	118.8(3)	O(1)−Li(1)−N(3)	107.6(3)
N(2)−Li(1)−N(1*)	107.3(3)	N(3)−Li(1)−N(1*)	111.5(3)
Li(1*)−N(1)−C(2)	165.1(3)	Li(1)−O(1)−S(1)	136.7(2)
	For **2**		
Li(1)−O(1)	1.908(4)	Li(1)−O(2*)	1.930(4)
Li(1)−O(3)	1.952(4)	Li(1)−N(1*)	2.001(5)
O(1)−Li(1)−O(3)	101.8(2)	O(1)−Li(1)−O(2*)	112.1(2)
O(1)−Li(1)−N(1*)	102.08(19)	O(3)−Li(1)−O(2*)	110.2(2)
O(3)−Li(1)−N(1*)	118.8(2)	O(2*)−Li(1)−N(1*)	111.1(2)
Li(1*)−N(1)−C(2)	152.2(2)	Li(1)−O(1)−S(1)	151.21(17)
Li(1*)−O(2)−S(1)	135.66(17)		

Table 4. Degree of Pyramidalization of the Anionic Carbons in 1 and 2 from the X-ray Data and in II and IV−XII from the HF/6-31G* Calculations

	ΣC(1)/deg	Δ_1/Å	$\chi_1{}^a$/deg
1	356.5	0.13	22.3
2	360.0	0.05	1.0
II	349.0	0.25	37.9[b]
IV	348.3	0.29	41.5
VI	358.6	0.09	14.3
VII	357.8	0.11	17.6
VIII	357.5	0.12	18.3
IX	358.7	0.09	13.4
X	356.7	0.14	21.0
XI	355.4	0.16	24.6
XII	359.0	0.07	11.2

[a] $\chi_1 = 180 - |$S−C(anion)−C(nitrile)···H(anion)$|$. [b] $\chi_1 = 180 - |$C(nitrile)−C(anion)−C(methyl)−H(anion)$|$ for **II**.

Specifically, the S−C(anion) bond shortens by 0.126 Å, which is exactly the same value as was found on going from **III** to **IV**, and the C−N bond lengthens by 0.017 Å, which is a smaller change than was found on going from **I** to **II**. This pattern suggests that the sulfonyl group is more dominant than the nitrile in stabilizing the charge.[4a]

From these results it can be concluded that both the nitrile and the sulfonyl units act as α-stabilizing groups in (organosulfonyl) acetonitrile anions. It also appears that for the free anions the anionic C atom of these species is more planar than in the corresponding nitriles or sulfones, which is consistent with an increase in the sp^2 character at the anionic carbon. In a similar fashion, the doubly stabilized lithiomalonitrile salts, [LiCH(CN)$_2$], and bis(organosulfonyl)methane anions, [(RSO$_2$)$_2$CH]$^-$, generally possess planar anionic C atom centers.[40,41]

Next, the monomeric lithiated compounds were considered. Two minima were located, one where the lithium bridges both oxygens of the SO$_2$ group **VII**, and a second where the metal binds to a single oxygen of the sulfonyl and the nitrogen of the nitrile to form a six-membered $\overline{\text{LiOSCCN}}$ ring **VIII**, as shown in Figure 13. No minimum was located for a structure with a direct bond between the lithium and the anionic carbon or where metal binds simultaneously to both oxygen atoms of the sulfonyl and the nitrogen of the nitrile (geometry optimization of these structures reverted to isomer **VII** or **VIII**).

The N/O chelate **VIII** is 12.30 kcal mol^{-1} more stable than O/O chelate **VII**, and this difference is most likely

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(40) (a) Hiller, W.; Frey, S.; Strähle, J.; Boche, G.; Zarges, W.; Harms, K.; Marsch, M.; Wollert, R.; Dehnicke, K. *Chem. Ber.* **1992**, *125*, 87. (b) Lambert, C.; Schleyer, P. v. R.; Pieper, U.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 77. (c) Jens, K.; Kopf, J.; Lorenzen, N. P.; Weiss, E. *Chem. Ber.* **1988**, *121*, 1201.

(41) (a) Zhu, S.-Z. *J. Fluorine Chem.* **1993**, *62*, 31. (b) Zhu, S.-Z. *J. Fluorine Chem.* **1993**, *64*, 47. (c) Siedle, A. R.; Gleason, W. B.; Newmark, R. A.; Skarjune, R. P.; Lyon, P. A.; Markell, C. G.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1990**, *29*, 1667. (d) Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle P. D. *Inorg. Chem.* **1988**, *27*, 1593. (e) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 1345.

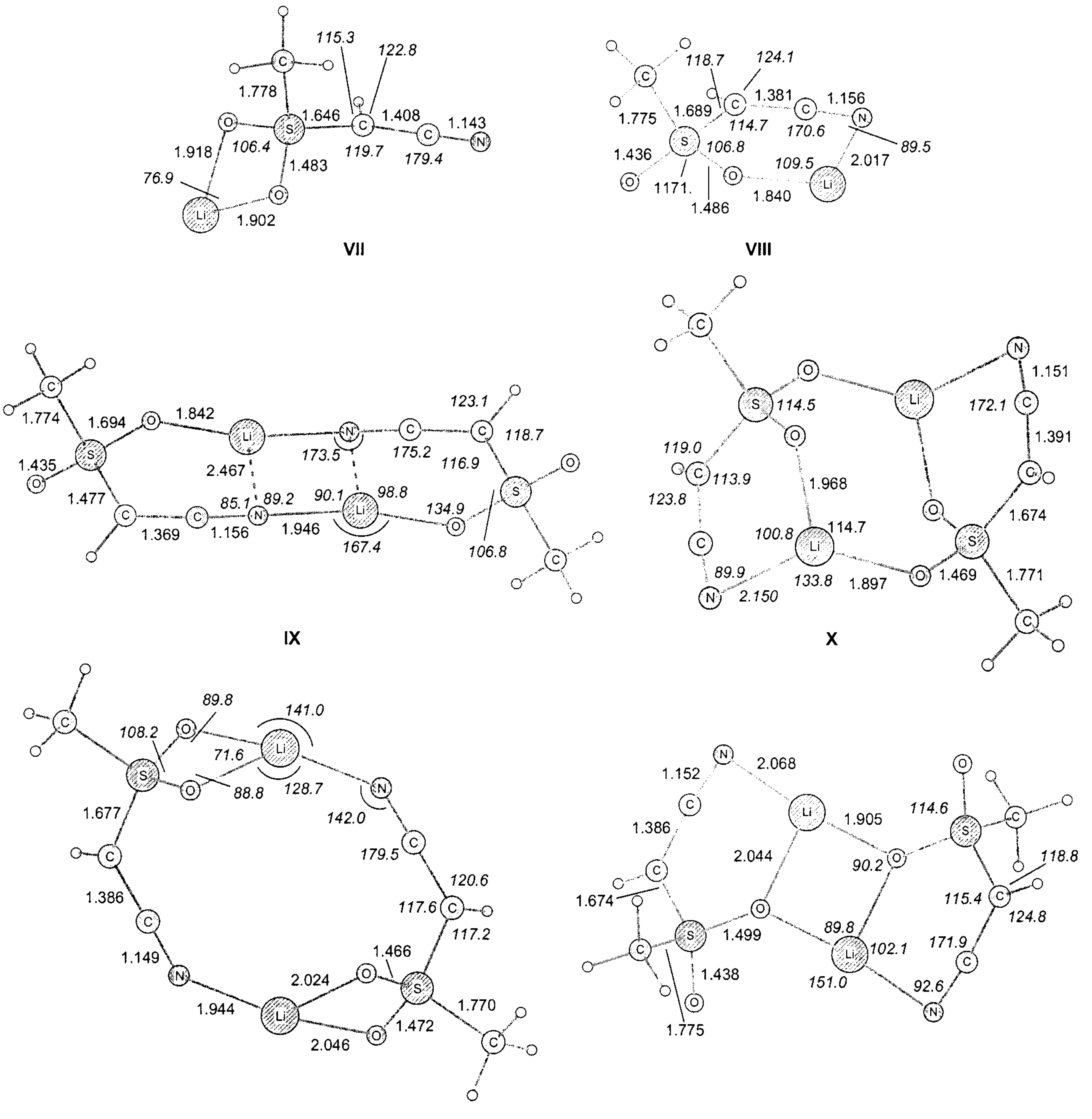

Figure 13. Geometry optimized (HF/6-31G*) structures for the lithiated monomeric and dimeric complexes **VII**–**XII**. Key bond lengths (Å) and angles (deg, in italics) are shown.

due to a more isotropic spread of charge at the lithium in **VIII**, in combination with a relief of ring strain in the SO_2Li ring of **VII**.[42] Recalculating these structures at the higher B3LYP/6-31++G**//B3LYP/6-31++G** level resulted in an almost identical difference in energy of 12.36 kcal mol^{-1} between the two isomers. The bond lengths within complexes **VII** and **VIII** are similar to those in the free anion **VI**, with all differences being <0.04 Å, and again the anionic C atoms are slightly pyramidalized (Table 4). The most pronounced effects of lithiation on the bond lengths are associated with the S–O bonds which bind to the metal. These bonds lengthen by 0.032 Å (mean) in **VII** and by 0.035 Å in **VIII**, with the remaining, noncoordinating, S–O bond in **VII** actually shortening by 0.015 Å. Such asymmetric S–O bond lengths were also found in the experimentally determined structure of **1**, although the difference between the two was only 0.014 Å, compared with 0.050 Å in **VIII**.

Finally, a series of calculations were carried out on some of the theoretically possible dimeric lithiated complexes, with a view to rationalizing the formation of the unusual polymeric structures observed for **1** and **2**. Four possible structural types were geometry optimized: (i) a Li_2N_2 ring dimer chelated by the sulfonyl units **IX**, (ii) a $(SO_2Li)_2$ ring dimer chelated by the nitrile units **X**, (iii) a pair of SO_2Li ring monomers joined

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[42] (a) Armstrong, D. R.; Carstairs, A.; Henderson, K. W. *Organometallics* **1999**, *18*, 3589. (b) Henderson, K. W.; Williard, P. G. *Organometallics* **1999**, *18*, 5620.

through nitrile bridges **XI**, and (iv) a Li_2O_2 ring dimer chelated by the nitrile units **XII** (Figure 13). The stability of the complexes was determined to be in the order **X** > **IX** > **XI** > **XII**, with relative energies of 0, 4.02, 7.47, and 9.16 kcal mol^{-1}, respectively. It is unsurprising that the two most unfavored isomers are **XI** and **XII** since no solid-state structures based on either SO_2Li or Li_2O_2 four-membered ring motifs have been characterized for lithiated sulfones.[43] The two isomers that most closely resemble the structures adopted by simple lithiated nitriles and sulfones are **IX** and **X**. Both **IX** and **X** could, at first glance, be considered to be composed of a pair of monomers based on the N/O chelate structure **VIII**, with dimerization being facilitated through the nitrogen in **IX** and the "free" oxygen in **X**. However, a close inspection of the bond lengths within **IX** and **X** reveals that both structures contain at least one long interaction to the metal. In **IX** the "chelating" Li−N bond length is 2.467 Å, which is much longer than would be expected for such an interaction (2.017 Å in **VIII**). In fact, structure **IX** is best described as a 12-membered $(NCCSOLi)_2$ ring with weak transannular Li···N interactions. In **X** the Li−N bond length is 2.150 Å, and the Li−O bond length associated with formation of the chelate is 1.968 Å (compared with 2.017 and 1.840 Å, respectively, in **VIII**). Similar trends in the bond lengths are also seen in complexes **XI** and **XII**, indicating that the ligands in all of these species are under considerable strain in order to achieve tricoordination at the metal centers.

From these results it can be deduced that the polymeric chain structure of **1** and the sheet structure of **2** are indeed formed as a consequence of the relative inflexibility of the ligands. Moreover, the "linear" (LiNCCSO) linkages alluded to earlier appear to be the basic building block of both **1** and **2**, with one- and two-dimensional polymerization able to occur without significant distortions in the ligand framework, while maintaining close contacts with the metal present.

Spectroscopic Analyses. All NMR spectroscopic data for complexes **1**−**4** were collected as solutions in D_6-DMSO due to their relatively poor solubility in other solvents. The use of strong donor media is most likely a necessity in order to disassemble the polymers into smaller aggregates. It is therefore important to note that the bonding modes determined in the solid state may differ significantly from those of the solvated complexes in solution. Nevertheless, analyses of the NMR and IR spectroscopic properties of the complexes are valuable in assessing the nature of the bonding present within the ligands.

Complexes **1**−**4** display only one set of resonances for their ^1H and ^{13}C spectra, and the chemical shift values for the important signals are listed in Tables 5 and 6, respectively, along with those for compounds **5**−**8**. It is recognized that formation of "naked" anions results in two opposing effects on the chemical shift positions in the ^1H and ^{13}C spectra: (i) a decrease in frequency due to the increase in charge, and (ii) an increase in frequency associated with the change in hybridization at the anionic carbon (a move to a more planar geometry).

Table 5. ^1H NMR Data (δ_H, ppm) for Compounds 1−8 in D_6-DMSO at 25 °C

	1	2	3	4	5	6	7	8
S−CH	2.56	2.02			5.26	4.96		
o-H	7.66		7.66		8.00		7.97	
m-H	7.37		7.37		7.86		7.78	
p-H	7.37		7.37		7.75		7.92	
CH_3		1.17		1.16		1.38		1.53

The variations in the chemical shift positions outlined in Tables 5 and 6 give some insight into the charge distribution within the anions. The most significant changes on lithiation are associated with the anionic C atom and the nitrile, where (i) the ^1H signal for the α-CH decreases in frequency (>2.5 ppm), (ii) the ^{13}C signal for the α-C(anion) decreases in frequency (>7 ppm), and (iii) the ^{13}C signal for the nitrile increases in frequency (>14 pm). Overall these shifts in frequency are consistent with the charge on the anion being localized in the S(1)−C(1)−C(2) moiety, which supports the X-ray and theoretical data collected for these species.

It is also pertinent to note that there are only minor changes in the ^1H and ^{13}C chemical shift values between the mono- and dilithiated complexes. In particular, the ^{13}C signal for the α-C(anion) lowers in frequency by only 4.51 ppm on going from **2** to **4**. These relatively small changes may indicate the formation of direct Li−C contacts in the dilithiated salts, which would be consistent with the known structures of related compounds.[3,44] No ^{13}C signal for the α-C(anion) could be located for **3** even on extended acquisition times, and again this is indicative of broadening caused by coupling of the quaternary carbon to Li.[45]

From the IR spectra it can be seen that the nitrile stretch decreases by >100 cm^{-1} for each successive lithiation of both **5** and **6** (Table 7). This trend is a result of a weakening of the nitrile triple bond and is compounded by ligation to one or more metal centers. The approximately 100 cm^{-1} decrease for the nitrile stretch on monolithiation is similar to that observed for the related cyanophosphonates.[31] Both dilithiated complexes **3** and **4** gave very broad IR bands in the region 2000−2200 cm^{-1}. Each spectrum has at least three distinct peaks in this area, which suggests that there are several different bonding environments in the solid-state structure of the complexes. These may occur from different aggregation states of the complex or alternatively by the formation of an aggregate that contains different ligand environments.[7a] Interestingly, the dilithiated trimethylsilylacetonitrile complex $[\{Me_3SiC(Li)_2CN\}_{12}\cdot 6OEt_2\cdot C_6H_{14}]$ is a cluster, with three different types of anionic ligand that all contain direct Li−C bonds.

Table 7 also contains the calculated (B3LYP/6-31G*) nitrile frequencies for the model structures **I**, **II**, and **V**−**VIII** (all frequencies have been scaled by a factor of 0.9614).[22] From these values it can be seen that there is a reasonable correlation between the experimentally

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(43) A Li_2O_2 ring is however found in a lithium sulfinyl complex: Marsch, M.; Massa, W.; Harms, K.; Baum, G.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1011.

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Table 6. ^{13}C NMR Data (δ_C, ppm) for Compounds 1−8 in D$_6$-DMSO at 25 °C

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
C≡N	126.93	128.46	126.86	128.53	112.66	113.10	118.63	119.86
S-αC	38.04	26.81	*a*	22.30	45.08	37.58	58.12	56.78
S−C, *t*-Bu		58.99		59.02		62.02		67.24
CH$_3$, *t*-Bu		24.76		24.77		23.04		25.26
i-C, Ph	151.92		151.94		137.65		133.16	
o-C, Ph	124.71		124.68		128.66		130.82	
m-C, Ph	128.65		128.60		130.15		130.17	
p-C, Ph	129.47		129.40		135.56		136.08	

[a] No signal located.

Table 7. IR Nitrile Stretching Frequencies for Compounds 1−8 (Nujol mull) and for the Optimized Structures I, II, and V−VIII (B3LYP/6-31G*)

	ν(C≡N)		ν(C≡N)
1	2151	**I**	2278
2	2151	**II**	2092
3	2046[a]	**V**	2287
4	2022[a]	**VI**	2159
5	2254	**VII**	2204
6	2256	**VIII**	2111
7	2241		
8	2239		

[a] Strongest absorbance in this area but others are present; see the Experimental Section (also see ref 8a for discussion of a similar effect).

and theoretically determined nitrile stretching frequencies for the neutral ligands **5** and **6** and the model ligands **I** and **V**. Although the theoretically produced nitrile stretching frequency for **VIII** is close to the experimentally determined values for **1** and **2**, it should be noted that the localized bonding modes between the metal and the nitrile vary significantly. In particular, the Li(1)−N(1)−C(2) bond angles in **1** and **2** are more linear than in **VIII** (165.1(3)°, 152.2(2)°, and 89.5°, respectively), and this will effect the nature of the Li−N interaction.

Conclusions

Complex **1** is a one-dimensional chain structure in the solid state, whereas complex **2** is a two-dimensional sheet, composed of interlocking 16-membered rings. The unusual polymeric aggregation of **1** and **2** is a consequence of the relatively poor flexibility of the (organosulfonyl)acetonitrile anionic ligands. These structures are in fact closely related, where the sheet structure of **2** can be formed by the fusion of chains similar to **1**. In this instance it appears that the replacement of the bidentate donor solvent ligand TMEDA for monodentate THF creates a free coordination site on the metal, leading to ligation to the remaining “free” oxygen of the sulfonyl unit and formation of the sheet structure of **2**.

Anion formation in **1** and **2**, where there are no Li−C contacts, results in an extended delocalized S⋯C⋯C≡N system. Both the sulfonyl and the nitrile units aid in this delocalization, although the sulfonyl appears to be the stronger α-stabilizing group. The anionic C atom in the (organosulfonyl)acetonitrile anions contains no Li−C contacts and is essentially planar in **2** and is distinctly pyramidylized in **1**. This difference is most likely a consequence of greater torsional strain around the anionic C atom in the chain polymer structure of **1**.

Finally, the ligands **5** and **6** can readily be doubly deprotonated to form the geminated dilithio derivatives **3** and **4**. These complexes again are mostly likely to be polymeric or at least highly aggregated in the solid state, but presently their identity remains elusive.

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Supporting Information Available: Listings giving crystallographic data for **1**, **2**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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