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On the Structure of Sulfur-Stabilized Allyllithium Compounds in Solution

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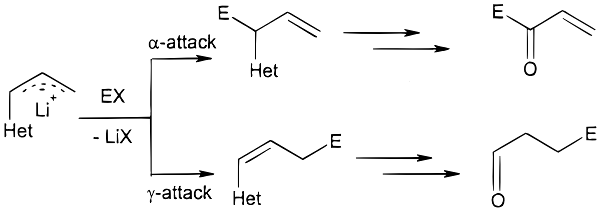
A combination of density functional calculations (B3LYP/6-31+G(d) level of theory) and experimental investigations (NMR and cryoscopic measurements) lead to structural assignments *in solution* for a series of three sulfur stabilized allyllithium compounds **1**−**3**. All three lithium species are monomers in THF under the experimental conditions studied here and exist exclusively in an endo conformation. Increasing the oxidation state of sulfur (thiol → sulfoxide → sulfone) causes a change in the solution state structure of the allyllithium compounds. In the case of 1-thiophenylallyllithium **1**, a fast equilibrium between two η^1-species is present with the equilibrium favoring the η^1 C_α−Li contact ion pair. The preference for this conformation can be attributed to the charge stabilizing properties of the sulfur substituent. For the lithiated sulfoxide **2**, this equilibrium is frozen on the NMR time scale and two different lithium species (a η^1 C_α−Li and a η^1 C_γ−Li contact ion pair), each possessing an intramolecular Li−O contact, coexist in d_8-THF. In the case of the lithiated sulfone **3**, several solvated conformations are in rapid equilibrium with each other on the NMR time scale in solution. The presence of two chelating oxygen atoms allows the lithium to form a OLiO scissor-like contact ion pair that competes with the η^1 C_α−Li and the η^1 C_γ−Li contact ion pairs also calculated for compound **3**.

Introduction

Heterosubstituted allyllithium compounds, being highly nucleophilic, find widespread use in synthetic organic chemistry.[1−3] They react readily with alkylating reagents, carbonyl compounds, heterocumulenes[4] as well as with many other electrophiles. Of especial interest is the ability of these compounds to serve either as a homoenolate equivalent (electrophilic attack at the γ-carbon; see Scheme 1) or as an acyl anion equivalent (attack at the α-carbon).

Scheme 1



As a consequence of the ambident nature of heterosubstituted allyllithium compounds, the question of the regioselectivity of addition as well as its ultimate control must be addressed. Fundamental to the understanding and control of the regioselectivity is a knowledge of the structure of the allyllithium compound in solution. Structural studies are, however, difficult to perform due to the tendency of these compounds to form complex fluxional aggregates in solution as well as due to their intrinsic instability (allyllithium compounds are generally thermally unstable, extremely air and moisture sensitive and cannot usually be isolated as solids). A recent study on 1-amino heterosubstituted allyl alkali compounds[5] could show that structural assignments *in solution* can be performed when one combines ab initio calculations with experimental NMR and cryoscopic investigations. Although there have been NMR studies[6,7] as well as ab inito calculations[7−9] reported for sulfur stabilized allyllithium compounds in the past, there has been, to the best of our knowledge, no structural study that has combined all available means of investigation to arrive at a structural assignment in solution for sulfur substituted allyllithium compounds. Furthermore, the ability of sulfur to exist in various oxidation states, i.e., thioethers (SR), sulfoxides (SOR) or sulfones (SO_2R), poses a very interesting question. How does the structure and electronic properties of the heterosubstituted allyllithium compound depend on the oxidation state of the sulfur? In order to directly address this question, we

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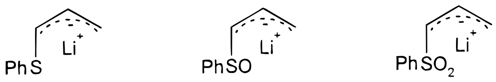

1 2 3

Figure 1. Sulfur-substituted allyllithium compounds selected for study.

Table 1. Degree of Aggregation (*n*) of the Heterosubstituted Allyllithium Compounds 1−3[a]

SPh (**1**)		SOPh (**2**)		SO_2Ph (**3**)	
c[a]	$n \pm \sigma$	c[a]	$n \pm \sigma$	c[a]	$n \pm \sigma$
97.97	1.10 ± 0.12	103.23	1.08 ± 0.08	99.18	1.11 ± 0.07
185.23	1.08 ± 0.09	206.50	1.11 ± 0.15	218.73	1.06 ± 0.07
205.47	1.07 ± 0.10	226.50	1.15 ± 0.08	220.02	1.11 ± 0.09

[a] Measured at −108 °C in THF. [b] Molal concentration (mmol/kg).

selected 1-thiophenylallyllithium **1** and its sulfoxide **2** and sulfone **3** analogues for study (Figure 1).

Results and Discussion

Aggregation. Using the cryoscopic method of Bauer and Seebach,[10] we determined the molecular weight of all three lithiated compounds. The values given in Table 1 are the average of several measurements performed under the same experimental conditions. All three compounds do not show, within experimental error, any tendency to form oligomers in THF at low temperatures (−108 °C). In addition, the concentration seems to have little influence upon the degree of aggregation.[26]

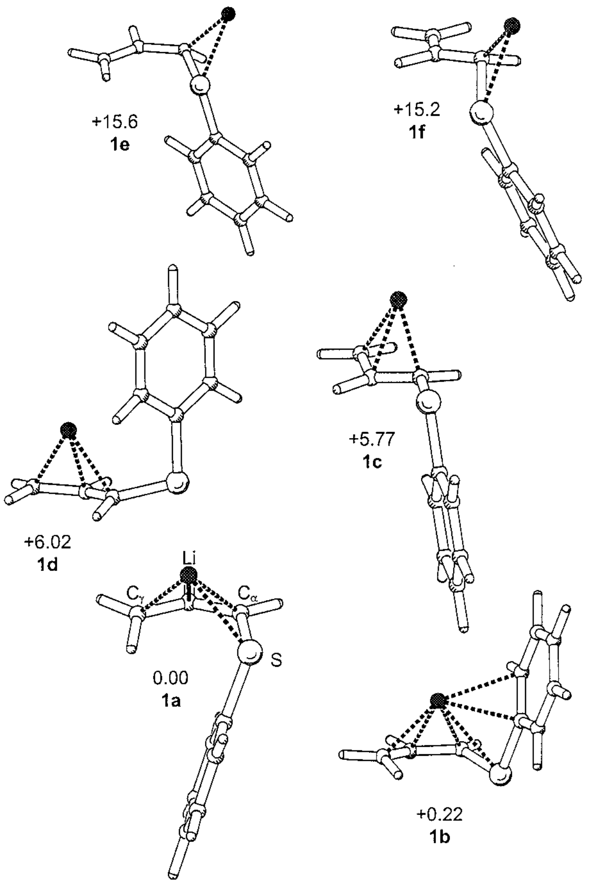

Figure 2. Energetically stable conformations found for 1-thiophenylallyllithium **1** at the B3LYP/6-31+G(d) level of theory. Relative energies are given in kcal/mol.

1-Thiophenylallyl Lithium 1. A conformational search for **1**, as described in the computational details section, lead to six different, energetically stable conformers at the B3LYP/6-31+G(d) level of theory (Figure 2). As has been discussed elsewhere,[5] the stability of the different conformers of heterosubstituted allyllithium compounds correlates directly with the number of electrostatic contacts between the lithium and the anionic substrate with three different structural patterns emerging from the conformational search. The two most unstable conformers (**1e**, **1f**) exhibit a η^2 bonding pattern and are typical for α-heteroatom stabilized carbanions.[11] The allyl system is decoupled, a $C_\beta{=}C_\gamma$ double bond is present and the lithium is more or less localized in the neighborhood of the α-carbon. Somewhat more stable are two conformers that exhibit an *exo* configuration about the C_α-C_β bond (**1c**, **1d**). These structures possess the typical η^3 bridging pattern of allyl alkali compounds[12] and differ only in the position of the phenyl group relative to the lithium. The two most stable conformers found (**1a**, **1b**) possess an endo configuration and are ca. 6 kcal/mol more stable than the η^3-*exo* conformers. Due to the favorable endo geometry, an additional electrostatic contact between the lithium and the heterotaom is possible for these two conformers and is the main reason for their enhanced stability as compared to the exo conformers.[5]

An ^1H NMR spectrum of **1** (the spectral data are to be found in the Experimental Section) shows the presence of only one lithiated species in d_8-THF. Interestingly enough, the ^1H NMR spectrum of **1** does not change in the slightest in the temperature range from ca. −100 °C

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Table 2. Influence of Specific Solvation upon the Structure and Electronic Properties of the Allylic Backbone of the Most Stable Conformer (1a) of 1-Thiophenylallyllithium 1[a]

	unsolvated **1a**	**1a**· one THF	**1a**· two THF	**1a**· three THF
ΔE_{solv}[b]	0.00	−18.56	−26.16	−37.87[c]
	geometrical parameters[d]			
C_α−Li	2.129	2.179	2.261	2.195
C_β−Li	2.089	2.123	2.160	2.886
C_γ−Li	2.144	2.194	2.319	3.878
H_α−Li	3.029	3.064	3.066	2.654
H_β−Li	2.870	2.876	2.797	3.307
$H_{\gamma\ \mathrm{in}}$−Li	2.384	2.422	2.606	4.186
C_α−C_β	1.412	1.413	1.419	1.451
C_β−C_γ	1.393	1.389	1.382	1.360
$\angle C_\alpha C_\beta C_\gamma$	128.7	129.1	130.4	131.6
	Wiberg bond orders			
C_α−C_β	1.414	1.396	1.364	1.331
C_β−C_γ	1.557	1.574	1.620	1.744
C_α−S	1.091	1.096	1.094	1.097
	natural (NPA) charges[e]			
qC_α	−0.772	−0.773	−0.794	−0.831
qC_β	−0.304	−0.298	−0.299	−0.300
qC_γ	−0.812	−0.786	−0.745	−0.711
qS	+0.201	+0.211	+0.234	+242
	hyperconjugative interactions[f]			
$\pi_{C\beta-C\gamma}\rightarrow p_{C\alpha}$	12.9	12.1	24.2	31.4
$p_{C\alpha}\rightarrow\pi^*_{C\beta-C\gamma}$	96.9	93.2	84.9	71.6
$p_{C\alpha}\rightarrow\sigma^*_{S-Ci}$	10.6	11.4	12.3	14.2
$n_S\rightarrow\sigma^*_{Ci-Co}$	12.4	13.9	16.8	19.7

[a] Calculated at the B3LYP/6-31+G(d) level of theory. [b] The energy of solvation was calculated according to: $\Delta E_{\mathrm{solv}} = E(\text{monomer}\cdot n\ \text{THF}) - n\,E(\text{THF}) - E(\text{monomer})$ and given in kcal/mol. [c] A frequency calculation for the triply solvated species was not technically possible at the B3LYP/6-31+G(d) level. In this case, the scaled HF/6-31+G(d) value for the zero point energy of **1a**·3 THF was employed in the calculation of ΔE_{solv}. [d] All geometrical parameters are given in angstroms and degrees. [e] NPA charges in electrons. [f] kcal/mol.

(when the THF becomes too viscuous for further measurements) to room temperature, thus indicating that a temperature dependent equilibrium between oligiomers is most probably not present for this compound.

Based on the magnitude of the $^3J_{\alpha,\beta}$ coupling constant of 7.9 Hz, an endo configuration could be unambiguously assigned to the lithium species present in solution. NMR investigations on a closely related compound, 1-thiophenyl, 3-methyl allyllithium, also concluded that the endo conformation is thermodynamically more stabil than the exo.[6] This phenomen, known as the “cis-effect”,[13] is observed both experimentally and theoretically for all lithiated compounds studied here.

Of the three endo conformers calculated, the most unstable one (**1e**) could immediately be ruled out on the basis of a [^{6}Li,^{1}H]-HOESY experiment. Two strong cross-peaks were found to H_α and the inner γ-proton ($H_{\gamma\ \mathrm{in}}$). A third, somewhat weaker cross-peak to H_β was also observed, thus providing direct experimental proof of a η^3 contact of the lithium to the allyl backbone. No cross-peaks were observed to any of the protons in the phenyl group.

Although two nearly isoenergetic endo conformers, each with a η^3 contact of the lithium to the allyl system, were found at the B3LYP/6-31+G(d) level of theory (**1a** and **1b**), **1b** is not present in solution (a cross-peak to the ortho proton in the phenyl group would otherwise be observed in the [^{6}Li,^{1}H]-HOESY spectrum). THF, being a much better donor ligand than a weakly coordinating aromatic ring, shoves the phenyl group out of the first coordination sphere of the lithium cation. Indeed, binding one THF to **1b** and reoptimizing the structure at the HF/6-31+G(d) level of theory causes the Li-phenyl contact to be immediately given up, even though there is enough space in the coordination sphere of the lithium for both the phenyl group and the THF.

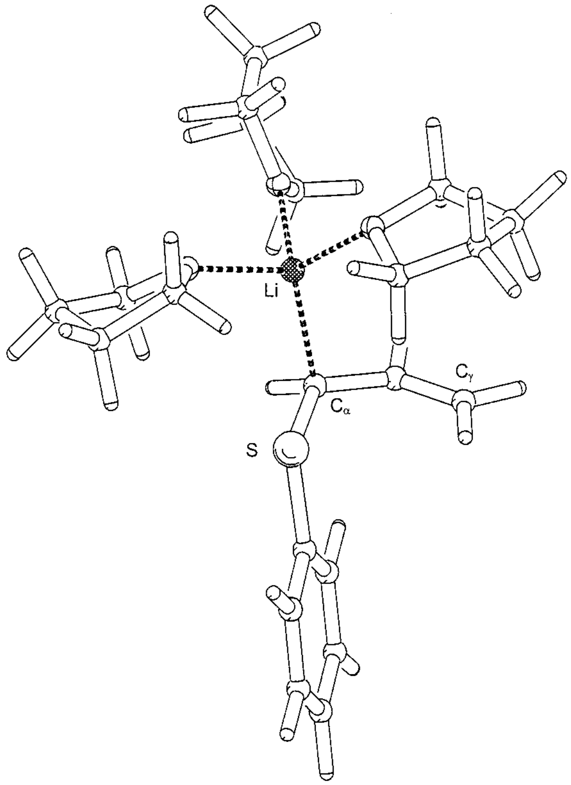

Figure 3. The structure of compound **1** in THF. Calculated at the B3LYP/6-31+G(d) level of theory.

Successive coordination of THF molecules to lithium and reoptimization at the B3LYP/6-31+G(d) level of theory shows that specific solvation has quite some influence upon the structure and electronic properties of the anionic substrate. Increasing the solvation causes the C_γ-Li contact to be gradually given up (Table 2) whereas the electrostatic contact of the lithium to the α-carbon is maintained. Ab initio calculations of solvated complexes of **1a** indicate that three THF molecules are present in the first solvation sphere of the lithium cation (Figure 3). The stabilization due to the introduction of a third THF is, with 12 kcal/mol, even higher than that calculated for the second THF (8 kcal/mol). It is unlikely that more than three THF are present in the first coordination sphere of the lithium cation. Computational limitations prevented us from directly investigating this. Lithium is, however, known to prefer the coordination number four in solution.[14] In addition, a theoretical study on a related compound (1-dimethylaminoallyllithium) showed that a fourth THF cannot be introduced into the first coordination sphere of the lithium.[5] An estimation of the solvation number in the solid state[15] of **1** was performed by generation of the lithiated species in normal THF, evaporation to dryness, solution in d_8-THF and integration of the resulting ^{1}H NMR spectrum. Two THF molecules per lithium are most probably present in the solid state. We did not succeed in obtaining crystals suitable for an X-ray analysis.

Table 3. Influence of Specific Solvation on the ^{13}C NMR Chemical Shifts of the Allylic Backbone of the Most Stable Conformer (1a) of 1-ThiophenylallylLithium 1[a]

	exptl[b]	unsolvated **1a**	**1a**· one THF	**1a**· two THF	**1a**· three THF
δC_α	36.7	63.6	60.8	59.7	49.4
δC_β	147.9	148.3	146.4	148.9	148.8
δC_γ	75.7	63.9	64.6	68.5	83.8
δC_i	150.2	145.7	149.0	155.1	155.7
δC_o	124.1	129.3	129.7	128.6	128.7
δC_m	126.6	132.7	131.9	131.7	131.3
δC_p	120.7	128.8	127.4	125.8	125.0
$\Sigma\|\Delta\delta\|/n^c$		**9.0**	**6.2**	**5.7**	**4.5**

[a] Calculated at the B3LYP/6-31+G(d) level of theory. [b] All values are given in ppm relative to TMS. [c] Average error per carbon atom.

Specific solvation enhances the α-carbanion character of **1**. This fact can clearly be seen in the calculated structural data and electronic properties of the solvated complexes (Table 2). Increasing the degree of specific solvation causes a lengthening of the $C_\alpha-C_\beta$ and a shortening of the $C_\beta-C_\gamma$ bond with corresponding changes in their bond orders. In addition, there is an increasing polarization in the NPA[16,17] charges calculated for the allylic substrate in favor of an α-carbanion.

According to current understanding, coulomb interactions, hyperconjugation and polarization (in this order) are the mechanisms in which a sulfur substituent stabilizes a neighboring negative charge.[18-20] In the case of compound **1**, coulomb interactions and polarization effects can be roughly estimated by the calculated NPA charges. The most important hyperconjugative interactions involving the sulfur atom are summarized in Table 2. Both the calculated charges and the hyperconjugation energies clearly show that specific solvation increases the ability of the sulfur group to localize and stabilize the negative charge on the α-carbon. These results indicate that specific solvation plays a larger role in determining the extent of α-heteroatom stabilization than has been previously suspected.

Although the computational results indicate that a $C_\alpha-$Li contact is preferred, the [^{6}Li,^{1}H]-HOESY spectrum of **1** shows that either a η^3 bridged species is present or a fast equilibrium exists between two η^1-species. Since the strongest intensity was observed for the cross-peak to H_α, thus indicating that the lithium cation is, on average, closest to C_α, we believe that an equilibrium is present. This behavior is consistent with the well-known fact that a sulfur group is capable of stabilizing a developing negative charge on a carbon atom.[19] In addition, similar equilibria between η^1-species have been observed for 1-*tert*-butylthioallyllithium[21] as well as for several silyl substituted allyllithium compounds.[22] Interestingly enough, a crystal structure of 1-*tert*-butylthioallyllithium showed, in contrast to solution, the presence of a η^3 species.[9] We did not succeed in locating a stationary point for a solvated η^1 $C_\gamma-$Li species on either the HF or the B3LYP level of theory. This could, however, be due to the computational neglection of the dielectric field present in solution.

Determination of the ^{13}C NMR shifts at the GIAO-B3LYP/6-31+G(d) level of theory and comparison with experiment (Table 3) shows that increasing the specific solvation causes an increasingly better match between the experimental and theoretical shifts. Indeed, the average error found for the complex solvated with three THF (±4.5 ppm/C atom) lies within the error bars expected for the theoretical method,[23] thus allowing the solvated structure illustrated in Figure 3 to be assigned to compound **1** in solution. There is, however, a rather large discrepancy between the calculated and experimental ^{13}C shifts for C_α and C_γ (12.7 and 8.1 ppm, respectively). This is not to be attributed to neglection of electronic correlation effects as can be seen from the excellent match between theory and experiment in the case of the sulfoxide **2** (see below) but instead supports the assumption of a fast equilibrium between two η^1-species. A significant amount of a η^1 $C_\gamma-$Li species present in solution would lead to conformational averaging of the experimental values, especially for C_α and C_γ.

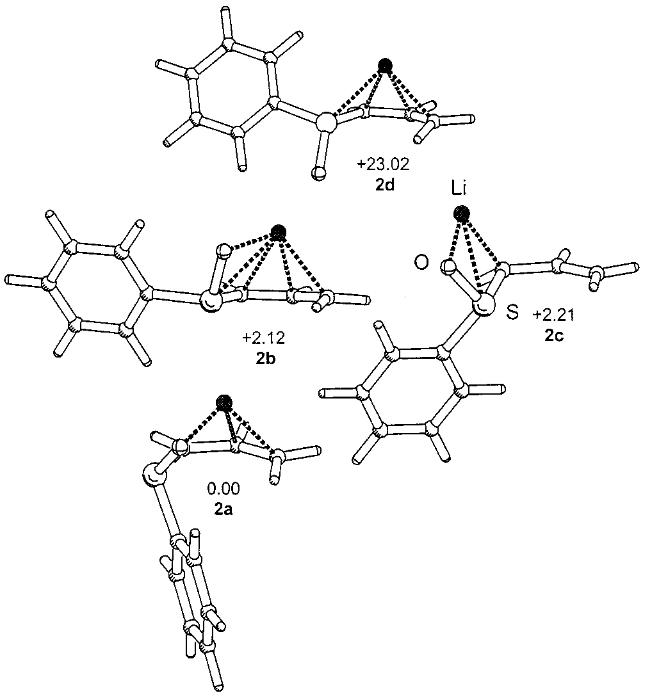

Figure 4. Energetically stable endo conformers found for compound **2** at the B3LYP/6-31+G(d) level of theory. Relative energies are given in kcal/mol.

Additional support for structural assignments in solution based on comparison of calculated with experimental parameters (in this case HOSEY Li/H distance data with calculated structural data) is provided by a recent article which reports on the solution-state structure of a chiral lihium amide.[24] The solution structure of 1-thiophenylallyllithium **1** contrasts sharply with the structure reported for 1-aminoallyllithium compounds in solution.[5] The electron donating property of an amino group destabilizes a η^1 C_α-species. A η^1 $C_\gamma-$Li species is instead formed that, in addition, tends to dimerize.[5,25]

1-(Phenyl)sulfoxoallyllithium 2. Since all lithiated compounds investigated in this article exhibit an *endo* conformation about the C_α-C_β bond,[26] we restricted our conformational search on compound **2** to endo conformers in order to save computational resources. The four energetical minima thus found are illustrated in Figure 4. Three of the conformers possess the typical η^3 allyllithium bonding pattern. Of these three structures, two have an additional intramolecular Li−O contact (**2a** and **2b**). Due to this additional electrostatic interaction, **2a** and **2b** are considerably (>20 kcal/mol) more stable than the third η^3 conformer **2d** in which a Li−O contact is not

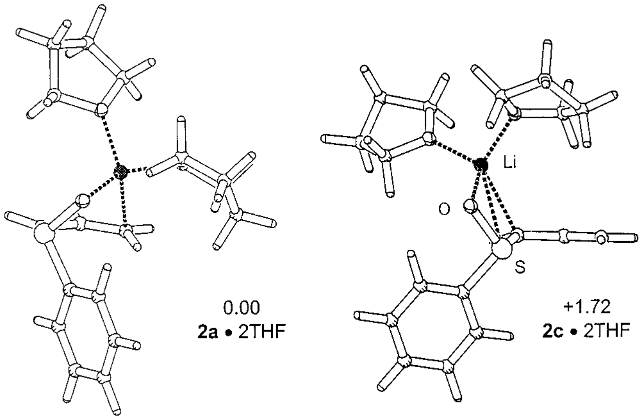

Figure 5. Energetically stable solvated conformers found for compound **2** at the B3LYP/6-31+G(d) level of theory. Relative energies are given in kcal/mol.

possible. The fourth conformer **2c** is a η^2 structure in which the allyl system is decoupled. The lithium is localized at the α-carbon. Due to the presence of the Li−O contact, **2c** is surprisingly stable and lies only 2.2 kcal/mol above the global minimum.

A conformational search for solvated species was then performed using the semiempirical method PM3. The conformers thus found were reoptimized at the HF/6-31+G(d) level of theory. All semiempirical stationary points converged at the HF level to give two different, energetically stable, solvated conformers for **2** which were then reoptimized at the B3LYP/6-31+G(d) level of theory (Figure 5). The two solvated structures found closely resemble the unsolvated conformers **2a** and **2c**. Solvated structures of conformer **2b** are not energetically stable, probably due to steric interactions between the phenyl group and the solvate molecules. The computational results indicate that the presence of an intramolecular Li−O contact in **2** reduces the number of THF molecules bound to lithium as compared to the thiophenyl compound **1**. Attempts to introduce a third THF into the coordination sphere of lithium functioned only at the semiempirical PM3 level. As soon as an optimization was attempted at the HF level of theory, one of the THF molecules left the first coordination sphere of the cation. An experimental estimation of the solvation number[15] of **2** indicates that two THF molecules per allyllithium unit are present in the solid state.

Interestingly enough, conformer **2c**·2THF in which the cation is decoupled from the allyl system is only 1.7 kcal/mol more unstable than **2a**·2THF. Calculation of the energy of solvation shows that specific solvation stabilizes conformer **2c** more than **2a**. The calculated solvation energies (Table 4) indicate that conformer **2a** is only 0.5 kcal/mol more stable than **2c**. Both conformers are thus expected to be present in solution. Indeed, ^1H and ^{13}C NMR spectra showed the presence of (exactly) two sets of signals and a ^6Li NMR spectra yielded two peaks thus conforming the presence of two different lithiated species in d_8-THF for 1-(phenyl)sulfoxoallyllithium **2** in approximately equal concentrations. A [^6Li,^1H]-HOESY spectrum of **2** shows cross-peaks for both species to either H_α and/or H_γ. Due to the large experimental line width and partial signal overlap, it was not possible to differentiate between H_α and H_γ contacts. In addition, a cross-peak to the ortho-proton of the phenyl group was observed for both species. Warming the solution of **2** caused a slight broadening of the signals observed in the ^1H and ^{13}C NMR spectra; the solution decomposes, however, before coalescence is observed. A conformational equilibrium between **2a**·2THF and **2c**·2THF is therefore not present on the NMR time scale. Due to computational limitations, we did not calculate the path of interconversion between **2a**·2THF and **2c**·2THF.

Table 4. Influence of Specific Solvation upon the Structure and Electronic Properties of Two Conformers (2a and 2c) of 1-(Phenyl)sulfoxoallyllithium 2[a]

	unsolvated **2a**	**2a**· two THF	unsolvated **2c**	**2c**· two THF
ΔE_{solv}[b]		−24.6		−25.1
		geometrical parameters[c]		
C_α−Li	2.396	3.000	2.141	2.325
C_β−Li	2.256	2.697	3.194	3.323
C_γ−Li	2.211	2.388	3.973	4.095
H_α−Li	3.205	3.783	2.679	2.772
H_β−Li	3.028	3.449	3.768	3.881
$H_{\gamma\,in}$−Li	2.309	2.357	4.032	4.163
H_o−Li	3.816	3.874	3.731	3.917
C_α−C_β	1.421	1.419	1.471	1.454
C_β−C_γ	1.381	1.376	1.334	1.341
$\angle C_\alpha C_\beta C_\gamma$	130.8	130.7	131.3	131.9
		Wiberg bond order		
C_α−C_β	1.334	1.316	1.381	1.193
C_β−C_γ	1.644	1.669	1.597	1.812
C_α−S	1.110	1.143	1.057	1.079
		natural (NPA) charges[d]		
qC_α[e]	−0.825	−0.792	−0.802	−0.906
qC_β	−0.271	−0.229	−0.275	−0.233
qC_γ	−0.749	−0.726	−0.788	−0.587
qS	+1.217	+1.271	+1.219	+1.264

[a] Calculated at the B3LYP/6-31+G(d) level of theory. [a] The energy of solvation was calculated according to: ΔE_{solv} = E(monomer·*n* THF) − *n E*(THF) − *E*(monomer) and given in kcal/mol. [b] All geometrical parameters are given in angstroms and degrees. [c] NPA charges in electrons.

Table 5. A Comparison of Theoretical and Experimental ^{13}C Chemical Shifts of the Two Different Conformers of 1-(Phenyl)sulfoxoallyllithium 2[a]

	exptl (species A)	**2a**· 2 THF	exptl (species B)	**2c**· 2 THF
δC_α	72.3	72.2	73.0	74.0
δC_β	141.6	146.5	141.3	144.7
δC_γ	81.5	76.7	82.4	82.1
δC_i	151.6	159.7	150.8	161.4
δC_o	126.8	131.8	126.8	130.8
δC_m	128.0	131.8	128.0	131.1
δC_p	127.1	130.9	127.1	131.2
$\Sigma\lvert\Delta\delta\rvert/n$[b]		3.3		1.6
$\Sigma\lvert\Delta\delta\rvert/n$[c]		4.4		3.7

[a] Calculated at the B3LYP/6-31+G(d) level of theory. [b] Average error per carbon atom in the allyl system. [c] Average error per carbon atom for all carbons.

As expected, inclusion of specific solvation in the calculation loosens the contact of the cation to the anionic substrate slightly. As can be seen from the geometrical parameters and bond orders in Table 4, solvation polarizes the allyl system in the direction of a C_α=C_β double bond for conformer **2a** and an decoupled allyl system for **2c**.

Calculation of the ^{13}C NMR shifts of both solvated conformers found at the B3LYP/6-31+G(d) level of theory and comparison with the experimental data (Table 5) shows that it is difficult to decide which set of experimental ^{13}C shifts corresponds to which calculated conformation since the difference in the measured shifts lies within the accuracy of the computational method employed. The best assignment is to be found in Table 5. Due to the excellent match between experimental and theoretical shifts, there is little doubt that both of the calculated conformers are present in solution.

1-(Phenyl)sulfonylallyllithium 3. X-ray structural analyses for several lithiated norbornyl allyl sulfones[7] have been reported as well as for the *exo* configuration of compound **3**.[27] All of these lithiated species crystallize in dimeric units in which the lithium cations are coordinated to the oxygen atoms. There is no direct electrostatic contact between the lithium cation and the allylic substrate in the solid state structures of these compounds. The presence of two chelating oxygen atoms in these compounds enables the lithium to form a very stable intramolecular OLiO scissor contact ion pair that is, at least in the solid state, obviously quite capable of competing with the allyl anion−lithium cation interaction. This is in direct contrast to the solid state structures of other heteroatom substituted allyllithium compounds, in all of which the lithium is bound not only to the heteroatom but also to the allylic backbone.[7,25,27,28] Recent structural investigations on lithiated allylic norbornyl sulfones showed that the situation is much more complicated in THF solution than in the solid state. Not only is there an exo/endo equilibrium present that prefers the *endo* form but also a monomer−dimer aggregational equilibrium, both of which occur rapidly on the NMR time scale. The resulting conformational and aggregational averaging of the chemical shifts leads to deceptively simple NMR spectra for these sulfones.[7]

Cryoscopic investigations performed on 1-(phenyl)-sulfonyl allyllithium **3** (Table 1) show that, in contrast to the lithiated norbornyl sulfones,[7] a monomer is the preferred aggregational state of **3** in THF at low temperatures. Furthermore, ^{1}H NMR spectral data for **3** indicates the presence of an endo conformation (${}^{3}J_{H\beta H\gamma in}$ = 10.9 Hz) which could be confirmed with NOESY experiments.[26] We did not succeed in obtaining an X-ray structure analysis for *endo*-**3**.

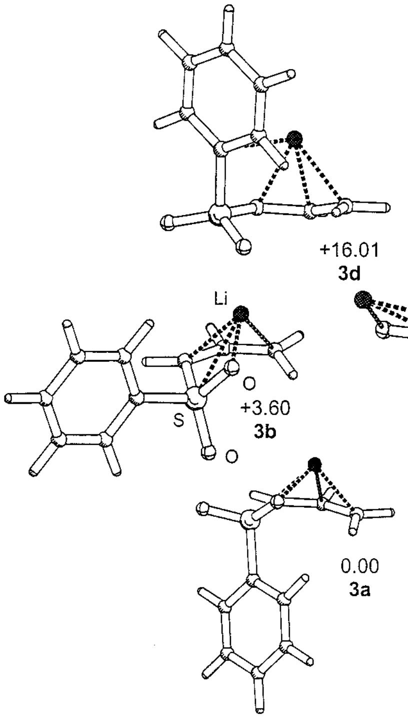

Figure 6. Energetically stable endo conformers found for compound **3** at the B3LYP/6-31+G(d) level of theory. Relative energies are given in kcal/mol.

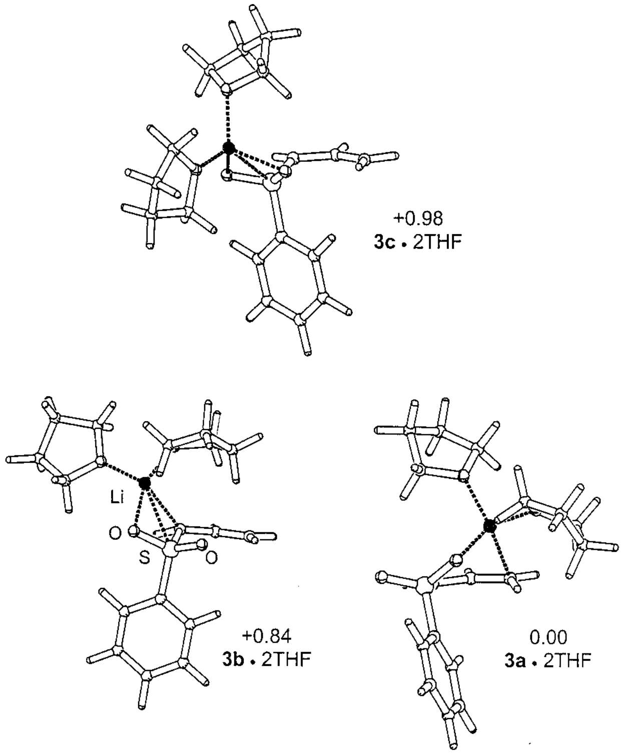

Figure 7. Energetically stable solvated conformers found for compound **3** at the B3LYP/6-31+G(d) level of theory. Relative energies are given in kcal/mol.

A conformational search for endo conformers of **3** lead, in addition to structures analogous to those reported for the lithiated thioether **1** and the sulfoxide **2**, to an additional scissor contact ion pair **3c** in which there is no direct electrostatic contact between the lithium cation and the allylic anion (Figure 6). In spite of the "naked" allyl anion, this conformer is relatively stable and lies 6 kcal/mol above the global minimum (**3a**). Assuming that the lithium cation has a coordination number of four in solution, we added the requisite number of THF molecules to the first coordination sphere of the energetically stable unsolvated conformers and performed a conformational search for solvated species at the PM3 level of theory. In contrast to compounds **1** and **2** which resulted in only a handful of solvated conformers, approximately thirty different nearly isoenergetical structures were found for **3** at the semiempirical level of theory. Due to computational (time) limitations, it was not feasible to reoptimize all these conformations at a higher level of theory. The conformers were sorted into structural classes and three examples were optimized at a level of theory high enough to accurately determine the ^{13}C NMR chemical shifts (B3LYP/6-31+G(d) level of theory). The relative stabilities of the solvated complexes all lie within 1 kcal/mol of each other and it is to be expected that all of the structures illustrated in Figure 7 as well as several others that have not yet been calculated are present in

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solution. Assuming that the conformational equilibrium between the different conformers is fast on the NMR time scale (as could be demonstrated for the related lithiated norbornyl sulfone) and that all conformers are present in solution, the experimental ^{13}C NMR shifts must be conformationally averaged since only one lithiated species is to be seen in the NMR spectra. A comparison of calculated with experimental shifts shows that this is most probably the case. None of the theoretical shifts calculated for any single solvated complex satisfactorily matches the experimental values.

Conclusions

This study shows that, if the solution state structure is correctly modeled computationally at a sufficient level of theory (B3LYP/6-31+G(d) in this case), calculated ^{13}C NMR shifts are accurate enough to unambiguously allow a structural assignment in solution. Due to the fluctional nature of such solvated complexes, it needs to be explicitly stated that the assignment made is not an absolute assignment in the sense of an X-ray structural analysis in which a particular conformation is frozen, for example, but is instead to be understood as being an “average” structure that, upon random sampling of the solution, is to be found most if not almost all of the time. Even for cases in which a fast equilibrium between several practically isoenergetical conformers is present in which no single conformation prevails on the NMR time scale, a comparison of theoretical with experimental shifts yields invaluable insights into the complex equilibria that can and do occur in solution.

The knowledge of the solution structure of these three lithiated compounds enabled us to develop a trustworthy model system for calculations on the mechanism of heterocumulene fixation.[4] Further computational investigations on this theme are underway and will be reported on in forthcomming articles.

Computational Details

Full conformational searches were performed for the sulfur substituted allyllithium compounds at the semiempirical PM3[29] level using the SPARTAN[30] program package. The semiempirical conformers thus found were reoptimized at the HF/6-31+G(d) level of theory. All ab initio calculations were performed using either Gaussian94[31] or Gaussian98.[32] Optimal HF structures then served as starting geometries for optimizations at the B3LYP/6-31+G(d) level. All stationary points found were characterized as energy maxima or minima by calculating their vibrational frequencies. All relative stabilities and energies of solvation reported in this article contain a correction for the zero point energy which was not scaled for the B3LYP results. Zero point energies calculated at the HF level were scaled by 0.91.[33] Absolute energies and (unscaled) zero point energies of all species calculated here are to be found in Table 8. Atomic charges, hyperconjugative interactions and bond orders were obtained using the natural bond orbital (NBO) analysis of Reed et al.[34] as implemented in Gaussian98. Energies of solvation (ΔE_{solv}) were calculated according to the equation: $E(Y{\cdot}n\text{THF}) - E(\text{X}) - nE(\text{THF})$ where X is the most

Table 6. Structural and Electronic Properties of Several Solvated Conformers of 1-(Phenyl)sulfonylallyllithium 3[a]

	3a· two THF	**3b·** two THF	**3c·** two THF
ΔE_{solv}[b]	−27.09	−35.97	−36.04
	geometrical parameters[c]		
C_α−Li	2.978	2.329	3.684
C_β−Li	2.667	3.535	4.727
C_γ−Li	2.346	4.432	5.060
H_α−Li	3.896	2.521	4.170
H_β−Li	3.437	4.056	5.649
$H_{\gamma in}$−Li	2.309	4.509	4.541
C_α−C_β	1.418	1.457	1.444
C_β−C_γ	1.377	1.353	1.356
$\angle C_\alpha C_\beta C_\gamma$	132.8	131.8	131.5
	Wiberg bond order		
C_α-C_β	1.321	1.167	1.198
C_β-C_γ	1.661	1.837	1.806
C_α-S	1.042	1.037	1.121
	natural (NPA) charges[d]		
qC_α[e]	−0.840	−0.925	−0.839
qC_β	−0.225	−0.249	−0.247
qC_γ	−0.742	−0.544	−0.557
qS	+2.155	+2.133	+2.124

[a] Calculated at the B3LYP/6-31+G(d) level of theory. [b] The energy of solvation was calculated according to: $\Delta E_{solv} = E(\text{monomer}{\cdot}n\ \text{THF}) - n\ E(\text{THF}) - E(\text{monomer})$ and given in kcal/mol. [c] All geometrical parameters are given in angstroms and degrees. [d] NPA charges in electrons.

Table 7. A Comparison of Experimental with Theoretical ^{13}C Chemical Shifts of the Solvated Conformers of 1-(Phenyl)sulfonylallyllithium 3[a]

	exptl	**3a·** 2 THF	**3b·** 2 THF	**3c·** 2 THF
δC_α	60.6	77.1	76.1	73.9
δC_β	127.6	138.8	147.0	134.4
δC_γ	85.1	95.3	70.7	91.3
δC_i	152.6	158.6	160.5	157.9
δC_o	127.4	129.2	128.5	128.9
δC_m	124.6	130.0	132.5	128.5
δC_p	135.4	131.8	132.7	131.3
$\Sigma\|\Delta\delta\|/n$[b]		12.6	16.4	8.7
$\Sigma\|\Delta\delta\|/n$[c]		6.1	9.8	4.6

[a] Calculated at the B3LYP/6-31+G(d) level of theory. [b] Average error per carbon atom in the allyl system. [c] Average error per carbon atom for all carbons.

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Table 8. Energies (Hartree) and Unscaled Zero Point Energies (ZPE) Calculated for the Different Conformers of 1−3 at the HF/6-31+G(d) and B3LYP/6-31+G(d) Levels of Theory

	E_{HF}	ZPE_{HF}	E_{B3LYP}	ZPE_{B3LYP}
THF	−230.981445	0.125674	−232.459380	0.117014
1a	−750.997104	0.162864	−754.094013	0.152287
1b	−750.995536	0.162583	−754.093292	0.151920
1c	−750.989687	0.162173	−754.084086	0.151554
1d	−750.987793	0.161812	−754.083320	0.151181
1e	−750.977477	0.162001	−754.067835	0.150966
1f	−750.978156	0.161962	−754.068426	0.150870
1a·1 THF	−982.011111	0.289936	−986.584527	0.270849
1a·2 THF	−1213.007999	0.416922	−1219.058007	0.389257
1a·3 THF	−1443.999424	0.543916	−1451.524135	
2a	−825.839381	0.167445	−829.302456	0.155992
2b	−825.834225	0.166838	−829.298705	0.155625
2c	−825.832204	0.167253	−829.298575	0.155635
2d	−825.796353	0.167356	−829.265789	0.156014
2a·2 THF	−1287.845718	0.421312	−1294.263378	0.393010
2c·2 THF	−1287.844485	0.421175	−1294.260441	0.392821
3a	−900.686709	0.173651	−904.510788	0.161530
3b	−900.678594	0.172478	−904.504648	0.161134
3c	−900.672912	0.173012	−904.494799	0.161420
3d	−900.650862	0.172778	−904.468271	0.161224
3a·2 THF			−1369.475509	0.398721
3b·2 THF			−1369.474156	0.398522
3c·2 THF			−1369.473905	0.398614

stable *unsolvated* conformer and $Y \cdot n$ THF is the most stable *solvated* conformer of compound **1**, **2**, or **3**, respectively. Optimal B3LYP/6-31+G(d) structures were used to calculate the chemical shielding using the GIAO−B3LYP[35] method as implemented in Gaussian98. The calculated ^{13}C NMR shielding values were referenced to $SiMe_4$ that had been calculated at the same level of theory.

Experimental Section

General Procedures. Chemical shifts for all lithium species were obtained in d_8-THF. All NMR spectra were obtained at 400 MHz (^1H), 100 MHz (^{13}C) and 66 MHz (^6Li). All spectral acquisition temperatures stated have an estimated error of ±0.5 °C. All organolithium compounds were handled under a protective argon atmosphere (99.99%, Messer-Griesheim) that had been dried and scrubbed clean from CO_2 by P_2O_5 and KOH. Commercial THF was stored several days over KOH, decanted, distilled over fresh KOH, refluxed over Na/benzophenone and distilled before being stored in a brown bottle over Na-wire. Absolute THF intended for cryoscopic measurements was distilled over CaH prior to use. Deuterated THF was distilled and stored over Na/Pb prior to use. ^{6}Lithium marked *n*-butyllithium was prepared as reported in the literature.[36]

Synthesis of the Allylic Precursors 4−6. *Allylphenylsulfide **4*** was prepared using a modified literature procdure.[37a,38] ^1H NMR: 7.17−7.36, 5.87, 5.09, 3.54. ^{13}C NMR: 135.9, 133.6, 129.8, 128.7, 126.2, 117.6, 37.1. *Allylphenylsulfoxide **5*** was synthesized according to Carlson et al.[39] ^1H NMR: 7.29, 5.86, 5.09, 3.54. ^{13}C NMR: 142.9, 131.0, 128.9, 125.2, 124.2, 123.7, 60.8. *Allylphenyl sulfone **6*** was derived from a procedure reported in the literaure.[37b,40] ^1H NMR: 7.84, 7.48−7.64, 5.75, 5.29, 5.10, 3.77. ^{13}C NMR: 138.3 133.7, 129.0, 128.5, 124.7, 124.6, 60.8.

Preparation of the Organolithium Compounds 1−3. All three allyllithium compounds were prepared from the corresponding heterosubstituted allylsulfide **4**, allylsulfoxide **5** or allyl sulfone **6** by direct deprotonation with *n*-butyllithium in tetrahydrofurane (THF) at low temperatures. All experimental structural investigations on the allyllithium compounds reported in this article were performed in THF.

Cryoscopic Measurements. The preparation of the allyllithium compounds was achieved by dissolving an exactly determined amount (2−5 mmol, weighed to three decimal units of precision) of the allyl precursor in 5−7 mL of THF in a dry cryoscopic flask containing an Ar atmosphere. The solution was then cooled to −78 °C and exactly one equivalent (determined to 0.01 mL) of a 1.6 M solution of *n*-butyllithium was added. The precise concentration of the *n*-butyllithium was determined immediately prior to use by titration (syringe accurate to 0.01 mL) with diphenyl acetic acid.[41] The yellowish solution thus obtained was stirred at −78 °C for 1 h followed by slow evaporation of the THF under vacuum. 1-Thiophenylallyllithium **1** could be dried at room temperature. 1-(Phenyl)sulfoxoallyllithium **2** and 1-(phenyl)sulfonylallyllithium **3** had to be kept at −25 °C until the pressure fell below 10^{-1} mbar. The flask was then flushed with argon and weighed. The allyllithium compound was then dissolved in 20−30 mL of THF and the flask again weighed. The amount of THF added was obtained from the difference in weight. The measurements themselves have been described elsewhere.[10] The results are to be found in Table 1.

NMR Measurements. The NMR probes were prepared by placing 0.4 mmol of the allyl precursor and ca. 0.4 mL of dry d_8-THF in a dry NMR tube sitting in a Schlenk flask filled with argon. The Schlenk flask was cooled to −78 °C and one equivalent of *n*-Bu^6Li was added to the NMR tube. (The concentration of the *n*-Bu^6Li solution should be higher than 1.6 M since larger amounts of hexane reduce the solubility of the organolithium compound). The NMR tube was sealed with a screw lock. All three lithiated compounds are mechanically quite unstable. Although they can be stored at low temperatures for a (few) hours before decomposing, they rapidly degenerate when subjected to the high mechanical stress of being spun in a NMR spool. Time-consuming measurement techniques (especially HOESY-experiments) thus proved quite difficult. It was not possible to extract Li−H distance information from HOESY spectra. We could, however, succeed in determining whether H/Li contact was present or not present. The following parameters were used for the HOESY-experiments: 90° Pulse length of 7.8 μs (^6Li) and 8.7 μs (^1H). Mixing time 2s; relaxation time 5s. Spectral width: 1460 Hz (f_2) and 3880 Hz (f_1). Phase sensitive (TPPI) t_1 increments were performed with 16 scans with calculation of the FID in t_1 containing 256 points and zerofilling to 1 kB.

Full spectral data for all three allyllithium compounds are provided below. The peak assignments reported below were determined via DEPT spectra, two-dimensional CH-correlation experiments, NOESY spectra and, where necessary, extensive simulation of the ^1H NMR coupling patterns observed. Readers interesting in obtaining photocopies of the original spectra of these lithited compounds should contact the authors.

*1-Thiophenylallyllithium **1*** (all NMR experiments on **1** were performed at room temperature): ^1H NMR: 7.15 (d, $2H_o$, $^3J_{H,H} = 7.9$ Hz) 6.96 (t, $2H_m$ $^3J_{H,H} = 7.5$ Hz) 6.71 (t, H_p $^3J_{H,H} = 7.3$ Hz), 6.33 (6.29−6.37) (m_c, H_β), 3.62 (dd, $H_{\gamma in}$ $^3J_{H\beta,H\gamma in} = 15.9$ Hz; $^2J_{H\gamma in,H\gamma out} = 2.8$ Hz), 3.16 (dd $H_{\gamma out}$ $^3J_{H\beta,H\gamma out} = 9.8$ Hz), 2.79 (d H_α $^3J_{H\alpha,H\beta} = 7.9$). ^{13}C NMR: 150.2 (C_i), 147.9 (C_β), 126.6 (C_m), 124.1 (C_o), 120.7 (C_p), 75.7 (C_γ), 36.7 (C_α). ^6Li NMR: 0.14. [^6Li, ^1H]-HOESY cross-peaks to $H_{\gamma in}$, H_β and H_α.

*1-(Phenyl)sulfoxoylallyllithium **2*** (All NMR experiments on **2** were performed at −50 °C): **Species A** ^1H NMR: 7.60 ($2H_o$ signal overlap with species B), 7.17 (H_p overlaps B) 7.15 ($2H_m$ overlaps B), 6.17 (m H_β overlaps species B), 3.63 (d H_α $^3J_{H\alpha,H\beta}$

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≈ 11 Hz, overlaps species B), 3.55 (d $H_{\gamma\mathrm{in}}$ $^3J_{H\beta,H\gamma\mathrm{in}}$ ≈ 15 Hz, overlaps species B) 3.26 ($H_{\gamma\mathrm{out}}$ $^3J_{H\beta,H\gamma\mathrm{out}} = 9.9$). ^{13}C NMR: 151.6 C_i, 141.6 C_β, 128.0 (C_m) 127.1 (C_p), 126.8 (C_o); all phenyl group signals overlap species B, 81.5 (C_γ), 72.3 (C_α). ^{6}Li NMR: two signals, one at −0.44 and one at-0.28; assignment as to which signal belongs to Species A and which to Species B is not possible. **Species B:** 7.60 (2H_o signal overlap with species A), 7.17 (H_p overlaps A) 7.15 (2H_m overlaps A), 6.17 m H_β (overlaps A), 3.63 (d H_α $^3J_{H\alpha,H\beta}$ ≈ 11 Hz, signal overlap with species A), 3.55 (d $H_{\gamma\mathrm{in}}$ $^3J_{H\beta,H\gamma\mathrm{in}}$ ≈15 Hz, signal overlap with species A), 3.36 (and to $H_{\gamma\mathrm{out}}$ $^3J_{H\beta,H\gamma\mathrm{out}} = 11.4$). ^{13}C NMR: 150.8 C_i, 141.3 C_β, 128.0 (C_m) 127.1 (C_p), 126.8 (C_o); all phenyl group signals overlap species A, 82.4 C_γ, 73.0 C_α. ^{6}Li NMR: two signals, one at −0.44 and one at-0.28; assignment as to which signal belongs to Species A and which to Species B is not possible. ^{1}H,^{6}Li HOESY contacts to the *ortho*-phenyl protons and to H_α and/or $H_{\gamma\mathrm{in}}$ were observed for both species. Due to the experimental line width, it was not possible to differentiate between H_α and $H_{\gamma\mathrm{in}}$ contacts in the HOESY spectrum.

1-(Phenyl)sulfonylallyllithium ***3*** (all NMR experiments on **3** were performed at −25 °C): ^{1}H NMR: 7.78 (d, 2H_o $J_{H,H}$ = 7.2 Hz), 7.16−7.25 (m, 3H), 6.26 (td H_β), 3.88 (dd, $H_{\gamma\mathrm{in}}$ $^3J_{H\beta,H\gamma\mathrm{in}} = 16.6$ Hz, $^2J_{H\gamma,H\gamma} = 2.7$ Hz), 3.54 (dd, H_γ $^3J_{H\beta,H\gamma\mathrm{out}} = 10.6$ Hz), 3.49 (d, H_α $^3J_{H\alpha,H\beta} = 10.9$ Hz. ^{13}C NMR: 153.7 (C_i), 136.5 (C_β), 128.7 (C_m), 128.4 (C_o), 125.7 (C_p), 86.2 (C_γ), 61.7 (C_α). ^{6}Li NMR: 0.91. [^{6}Li, ^{1}H]-HOESY cross-peaks to $H_{\gamma\mathrm{in}}$ and H_o.

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