

# A Density Functional Study of 2-Lithio-1,3-dithiane and 2-Lithio-2-phenyl-1,3-dithiane: Conformational Preference of the C–Li Bond and Structural Analysis

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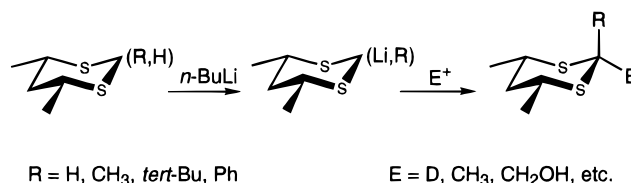
**Abstract:** The energetics and structural properties of 1,3-dithiane (**1**), 2-phenyl-1,3-dithiane (**2**), and their corresponding axial and equatorial 2-lithio derivatives have been probed by using density functional theory (DFT) at the Becke3LYP/6-31G(*d,p*) level. In agreement with the experimental observations, a very high preference for the equatorial orientation of the C–Li bond is calculated, the calculated energy difference between **1**-Li-ax and **1**-Li-eq being 14.2 kcal·mol<sup>-1</sup> and the calculated energy difference between **2**-Li-ax and **2**-Li-eq being 4.10 kcal·mol<sup>-1</sup>. Population analysis indicates high positive charge at lithium and small C–Li Wiberg bond indexes in these 1,3-dithianyllithiums, suggesting an ionic rather than covalent nature for the C–Li bond. The collected structural data are in line with the expectation that  $n_C \rightarrow \sigma^*_{S-C}$  hyperconjugation stabilizes the equatorial isomers, whereas  $n_C/n_S$  repulsive orbital interactions destabilize the axial isomers. Nevertheless, coordination of equatorial lithium by the ring sulfurs is apparent in the computed contact ion pairs for **1**-Li-eq and **2**-Li-eq. An interesting structure was predicted for the axial form of 2-lithio-2-phenyl-1,3-dithiane wherein the lithium is bonded to C(2), C<sub>ipso</sub>, C<sub>ortho</sub>, and one of the ring sulfurs, in a highly delocalized system in the case of the minimum energy isomer.

## Introduction

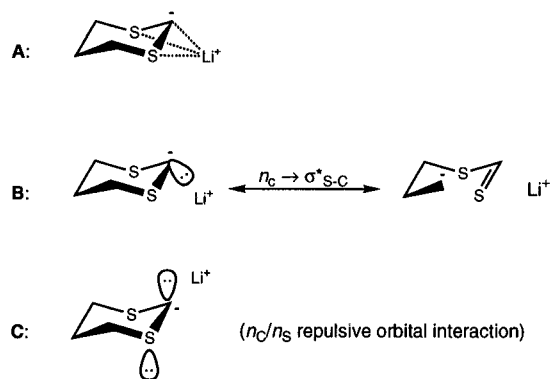
An important development in the area of carbanion chemistry and stereoselective carbon–carbon bond formation originated from Eliel's laboratory in the mid-1970's. Eliel and co-workers<sup>1</sup> discovered that anancomeric 1,3-dithianyllithiums react with electrophiles in a highly stereoselective manner, resulting in equatorial substitution as shown in Scheme 1. Consideration of the steric requirements for equatorial to axial isomerization when the R group is *tert*-butyl provided an estimate of >6 kcal/mol for the equatorial preference of lithium in the intermediate 2-lithio-1,3-dithianes,<sup>1</sup> and this interesting thermodynamic phenomenon was subsequently exploited in asymmetric synthesis.<sup>2</sup>

Interpretation of the above observations was initially advanced in terms of intramolecular chelation of equatorial lithium, in a contact ion pair, by one of the unshared electron pairs of each of the two sulfur atoms (**A** in Chart 1).<sup>1</sup> Nevertheless, theoretical studies by Lehn and Wipff<sup>3</sup> suggested that stereo-electronic effects stabilize equatorial lithium. In particular  $n_C \rightarrow \sigma^*_{S-C}$  is a two-orbital/two-electron interaction that stabilizes the equatorial C–Li<sup>+</sup> orientation (**B** in Chart 1), whereas  $n_C \leftrightarrow n_S$  is a two orbital/four electron repulsive interaction when lithium is axial (**C**, in Chart 1). Indeed, additional studies by

## Scheme 1



## Chart 1



Eliel showed that neither S–Li nor C–Li ion pairing is required for the high stereoselectivity observed in the substitution reaction depicted in Scheme 1.<sup>5</sup>

On the other hand, relevant X-ray crystallographic studies by Dunitz, Seebach, *et al.* demonstrated the equatorial orientation of the C–Li bond in 2-lithio-2-methyl-1,3-dithiane<sup>6</sup> and 2-lithio-2-phenyl-1,3-dithiane.<sup>7</sup> Interestingly, the former species exists in the crystal as a dimer, with lithium interacting equally

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(6) Amstutz, R.; Seebach, D.; Seiler, P.; Schweizer, B.; Dunitz, J. D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 53.

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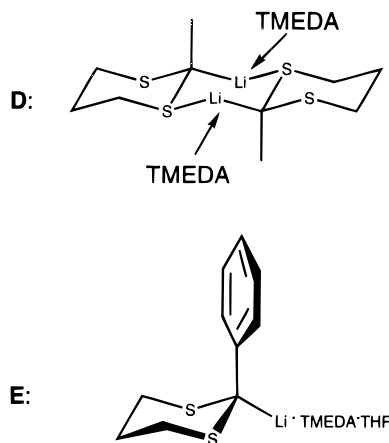
(1) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1087.

(2) Eliel, E. L.; Koskimies, J. K.; Lohri, B.; Frazee, W. J.; Morris-Natschke, S.; Lynch, J. E.; Soai K. In *Asymmetric Reactions and Processes*; Eliel, E. L., Otsuka, S., Eds.; American Chemical Society: Washington, DC, 1982.

(3) Lehn, J.-M.; Wipff G. *J. Am. Chem. Soc.* **1976**, *98*, 7498.

(4) Should a covalent C–Li bond be involved, the appropriate terminology would be  $\sigma_{C-Li} \rightarrow \sigma^*_{S-C}$ . See, for example: Juaristi, E.; Cuevas G. *The Anomeric Effect*; CRC Press: Boca Raton, FL, 1995.

Chart 2



strongly with C(2) and one sulfur atom of the second 1,3-dithiane ring in the dimer (**D** in Chart 2), whereas the phenylated derivative is monomeric (**E** in Chart 2). The lithium ion coordination sphere is completed by tetramethylethylenediamine (TMEDA) or tetrahydrofuran (THF) in these crystal structures.<sup>6,7</sup> Electron-density difference maps calculated for **D** and **E** did not provide reliable data regarding the ionic versus covalent character of the C–Li bonds in 2-lithio-1,3-dithianes.<sup>8</sup>

The present study was undertaken with three main goals in mind: (1) to explore the ability of density functional theory (DFT)<sup>9</sup> to probe the energetic and electronic properties of organolithiums, in particular 1,3-dithianyllithiums;<sup>10</sup> (2) to reinvestigate the molecular structure of 1,3-dithianyllithiums and to compare the results with the earlier *ab initio* study of model fragments of the same molecules by Lehn and Wipff<sup>3</sup> since DFT has proved to predict the molecular conformational features and the energetics more accurately than the Hartree–Fock methods;<sup>11</sup> and (3) to obtain an insight into the factors responsible for the high preference of equatorial lithium in 2-lithio-1,3-dithianes.

### Computational Methods.

Complete geometry optimization (without symmetry constraints) was performed on the complete structures of **1** and **2** (Figure 1) at the *ab initio* level and within the frame of DFT at the Becke3LYP/6-31G(*d,p*) level with the Gaussian 92 program (G92).<sup>12</sup> The Becke3LYP hybrid functional defines the exchange functional as a linear combination of Hartree–Fock, local, and gradient-corrected exchange terms.<sup>13</sup> The exchange functional is combined with a local and gradient-corrected correlation functional.

The correlation functional used is actually  $CE_C^{LYP} + (1 - C)E_C^{VWN}$ , where LYP is the correlation functional of Lee, Yang, and Parr,<sup>14</sup> which

(7) Amstutz, R.; Dunitz, J. D.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 465.

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(11) Foresman, J. B.; Frisch, M. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996; pp 146–150.

(12) Gaussian 92/DFT, Revision G.2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1993.

(13) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372, 5648.

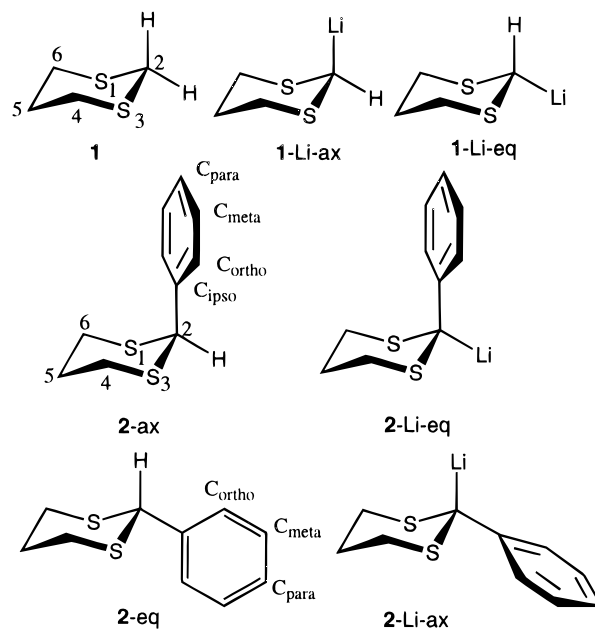


Figure 1.

includes both local and nonlocal terms, and VWN is the Vosko, Wilk, and Nusair 1980 correlation functional fitting the RPA solution to the uniform gas, often referred to as local spin density (LSD) correlation.<sup>15</sup> VWN is used to provide the excess local correlation required, since LYP contains a local term essentially equivalent to VWN.<sup>13</sup>

The orbital basis set used was 6-31G(*d,p*), which adds polarization functions to heavy atoms and hydrogens. Natural bond orbital analyses (NBO) were carried out with version 4.0, which is included in G92.<sup>16</sup>

### Results and Discussion

**A. 1,3-Dithiane (1) and 2-Lithio-1,3-dithiane (1-Li-ax and 1-Li-eq).** Table 1 lists the energetic and structural results for the parent 1,3-dithiane and its lithium derivative. The calculated energy difference between 1-Li-ax and 1-Li-eq (Figure 1) is 14.2 kcal/mol, the equatorial 2-lithio derivative being more stable. This result is in agreement with the experimental value derived by Eliel *et al.*,<sup>1</sup> who reported a thermodynamical preference of >6 kcal/mol for equatorial lithium in 2-lithio-1,3-dithianes.<sup>17</sup>

The calculated energy difference obtained in this study from DFT is also in fair agreement with the STO-3G results obtained by Lehn and Wipff<sup>3</sup> on model fragments **F** and **G** (Chart 3). Indeed, assuming a covalent nature for the C–Li bond, Lehn and Wipff estimated that equatorial organolithium **F** is 3.5 kcal mol<sup>-1</sup> lower in energy than axial **G**. This energy difference favoring equatorial **F** increased to 9.0 kcal mol<sup>-1</sup> in ionic species.<sup>18</sup>

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785–789. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

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(17) Of course, solvation may be particularly important for studying the real organolithium species. For example, the  $\Delta S$  of solvated lithio derivatives of 2-phenyl-1,3-dithiane for the axial  $\rightleftharpoons$  equatorial equilibrium should not be zero. Conformations favoring intramolecular chelation would also require the displacement of one or two solvent molecules by the sulfur atoms and is expected to be entropically favorable.

(18) Nevertheless, Hartree–Fock minimal basis set calculations consistently estimate the barriers either too high or low. Part of the success of the DFT can be attributed to correlational effects.

**Table 1.** Calculated Relative Energies and Structural Data for 1,3-Dithiane (**1**) and Its Axial (1-Li-ax) and Equatorial (1-Li-eq) 2-Lithio Derivatives (Figure 1)<sup>a</sup>

	<b>1</b>	1-Li-ax	1-Li-eq	exptl <sup>8</sup> 1-Li-eq
relative energy <sup>b</sup>		14.2	0.0	
S(1)–C(2) <sup>c</sup>	1.83	1.84	1.80	1.78
S(3)–C(4) <sup>c</sup>	1.83	1.83	1.86	1.83
C(4)–C(5) <sup>c</sup>	1.53	1.54	1.53	1.53
C(2)–H <sup>c</sup>	1.09	1.10	1.09	
C(2)–Li <sup>c</sup>		1.99	1.98	2.19
S(3)–Li <sup>c</sup>		3.17	2.36	2.52
S–C–S <sup>d</sup>	115.5	111.7	113.5	109.4
C–S–C <sup>d</sup>	98.4	97.7	107.3	105.4
S–C–C <sup>d</sup>	114.4	114.2	114.1	113.0
H–C(2)–Li <sup>d</sup>		112.3	158.3	
C–Li–S <sup>d</sup>		35.8	48.0	47.3
S–C–S–C <sup>e</sup>	59.6	64.6	45.2	
C–S–C–C <sup>e</sup>	57.8	60.2	52.5	
C–C–C–S <sup>e</sup>	65.8	64.1	63.5	
Li–S–C–C <sup>e</sup>		91.4	6.4	

<sup>a</sup> Total Energies in hartrees are given in Table 3, Supporting Information. <sup>b</sup> Energy in kcal mol<sup>-1</sup>. <sup>c</sup> Bond lengths in angstroms. <sup>d</sup> Bond angles in degrees. <sup>e</sup> Torsional angles in degrees.

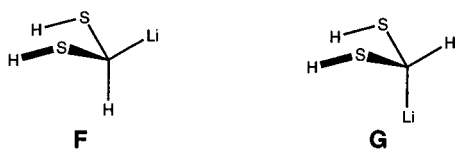
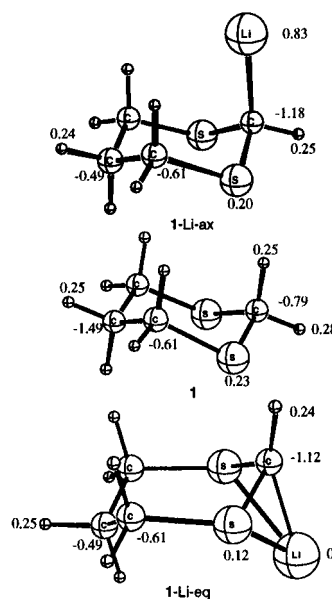
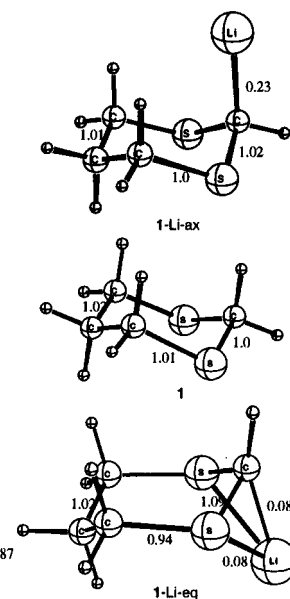
**Chart 3**

Figure 2 shows the calculated atomic charges and Wiberg bond indexes in **1**, 1-Li-ax, and 1-Li-eq. Several relevant observations deserve mention: (1) The substantial positive charge centered on lithium (+0.83 when axial, +0.87 when equatorial) indicates a nearly complete transfer of an electron to carbon; that is, the C(2)–Li bond is highly ionic.<sup>19</sup> Furthermore, covalent bonding should manifest in large overlap populations between atoms; nevertheless, the estimated Wiberg bond indexes for the C(2)–Li bond are quite small, 0.23 in 1-Li-ax and only 0.08 in 1-Li-eq. These observations argue again for the ionic nature of the bond.<sup>20</sup>

(2) Significant bonding is observed in 1-Li-eq between lithium and the ring sulfurs, the corresponding bond indexes being 0.08 (Figure 2). This finding provides some support for the original rationalization, see model **A** (Chart 1).<sup>1</sup> Nevertheless, comparison of bond lengths and bond indexes for C(2)–S and S–C(4,6) in the parent dithiane **1** and in 1-Li-eq supports the stereoelectronic stabilizing interaction depicted in **B**. Indeed, substitution of the equatorial H(2) by lithium, **1** → 1-Li-eq, results in a shortening of the C(2)–S bonds (1.83 Å → 1.80 Å) and a lengthening of the S–C(4,6) bonds (1.83 Å → 1.86 Å). Concomitantly, the C(2)–S bond index increases (1.0 → 1.09), whereas the S–C(4,6) bond index diminishes (1.01 → 0.94). These observations are of course in line with the expectation based on  $n_{C(2)} \rightarrow \sigma^*_{S-C(4,6)}$  orbital interactions.<sup>3,4</sup> (3) The substantial flattening of the ring around C(2) in going from **1** to 1-Li-eq (for example, the C–S–C bond angle changes from 98.4° to 107.3°, and the S–C–S–C torsional angle decreases from 59.6° to 45.2°) is also indicative of electronic transfer from carbon toward sulfur, with concomitant sp<sup>3</sup> to sp<sup>2</sup> hybridization change.

**B. Conformational Preference of 2-Phenyl-1,3-dithiane (2-ax ⇌ 2-eq).** Table 2 summarizes the energetic and structural

**Natural Charges:****Wiberg Bond Indexes:****Figure 2.** NBO population analysis of calculated 1,3-dithiane (**1**) and its lithiated derivatives at the Becke3LYP/6-31G(*d,p*) level.**Table 2.** Calculated Relative Energies and Structural Data for Axial (2-ax) and Equatorial 2-Phenyl-1,3-dithiane (2-eq) and Their Axial (2-Li-ax) and Equatorial (2-Li-eq) 2-Lithio Derivatives (Figure 1)<sup>a</sup>

	2-ax	2-eq	2-Li-ax	2-Li-eq
relative energy <sup>b</sup>	2.86	0.0	4.10	0.0
S(1)–C(2) <sup>c</sup>	1.85	1.85	1.83, 1.78	1.80
S(3)–C(4) <sup>c</sup>	1.84	1.84	1.85, 1.83	1.86
C(4)–C(5) <sup>c</sup>	1.53	1.53	1.53, 1.53	1.53
C(2)–Li <sup>c</sup>			2.04	2.05
S(1)–Li <sup>c</sup>			2.42	2.32
S(3)–Li <sup>c</sup>			3.67	2.32
C(2)–C <sub>ipso</sub> <sup>c</sup>	1.54	1.51	1.45	1.48
C <sub>ipso</sub> –C <sub>ortho</sub> <sup>c</sup>	1.40	1.40	1.44	1.41
C <sub>ortho</sub> –C <sub>meta</sub> <sup>c</sup>	1.40	1.40	1.41, 1.38	1.39
C <sub>meta</sub> –C <sub>para</sub> <sup>c</sup>	1.40	1.40	1.39, 1.41	1.40
S–C–S <sup>d</sup>	99.7	99.5	99.6	106.2
S–C–C <sup>d</sup>	114.2	114.6	113.0, 114.5	113.9
S–C–C <sub>ipso</sub> <sup>d</sup>	115.0	109.5	117.4, 119.6	118.9
C–C <sub>ipso</sub> –C <sub>ortho</sub> <sup>d</sup>	120.9	120.0	122.3, 121.7	121.7
S–C–S–C <sup>e</sup>	61.1	58.4	59.5, 61.3	50.4
C–S–C–C <sup>e</sup>	59.9	58.4	59.7, 56.5	55.1
C–C–C–S <sup>e</sup>	64.8	65.0	64.9, 65.8	62.9

<sup>a</sup> Total energies in hartrees are given in Table 3, Supporting Information. <sup>b</sup> Energy in kcal mol<sup>-1</sup>. <sup>c</sup> Bond lengths in angstroms. <sup>d</sup> Bond angles in degrees. <sup>e</sup> Torsional angles in degrees.

data calculated for **2** and its 2-lithio derivatives, 2-Li-ax and 2-Li-eq (Figure 1). The phenyl group in **2** can adopt either the axial or equatorial conformation, and the calculated energy difference,  $\Delta H^\circ = -2.86$  kcal/mol in favor of 2-eq, is fairly similar to the experimental conformational free energy difference reported by Kleinpeter *et al.*,<sup>21,22</sup>  $\Delta G^\circ_{300K} = -2.34$  kcal/mol. (It is known that  $\Delta S^\circ \cong 0$  for the axial ⇌ equatorial equilibrium in phenylcyclohexane.<sup>23</sup>)

The calculated minimum energy conformations for 2-ax and 2-eq show the phenyl ring perpendicular to the plane that bisects the 1,3-dithiane ring in the axial isomer, but aligned in the

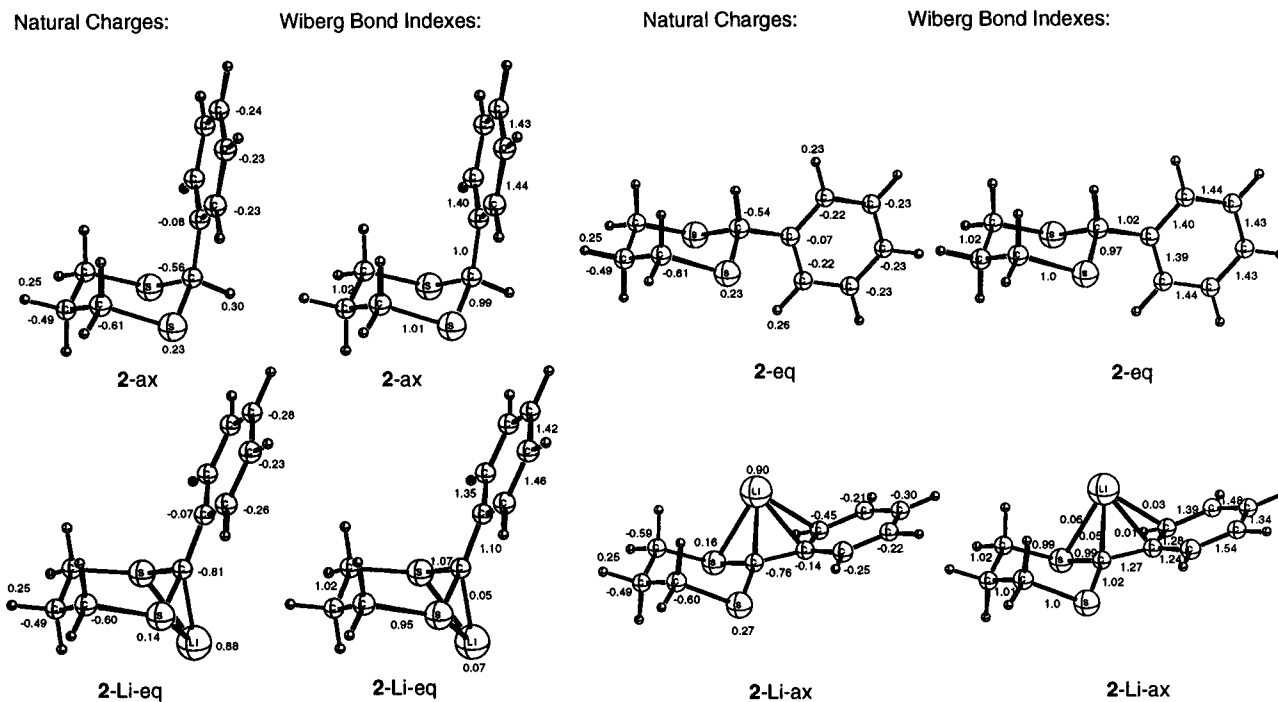
(21) Köhler, H.; Tschierske, C.; Zschacke, H.; Kleinpeter, E. *Tetrahedron* **1990**, *46*, 4241.

(22) See, also: Kleinpeter, E. In *Conformational Behavior of Six-Membered Rings. Analysis, Dynamics, and Stereoelectronic Effects*; Juaristi, E., Ed.; VCH Publishers: New York, 1995; Chapter 6.

(23) See, for example: Juaristi, E. *Introduction to Stereochemistry and Conformational Analysis*; Wiley: New York, 1991; p 265.

(19) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.

(20) Streitwieser, A.; Bachrach, S. M.; Dorigo, A.; Schleyer, P. v. R. In *Lithium Chemistry*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; Chapter 1.



**Figure 3.** NBO population analysis of 2-phenyl-1,3-dithiane (**2**) and its lithiated derivatives at the Becke3LYP/6-31G(*d,p*) level.

bisecting plane in **2-eq** (Figure 3). This result is also in agreement with previous conformational studies in analogous systems.<sup>24</sup>

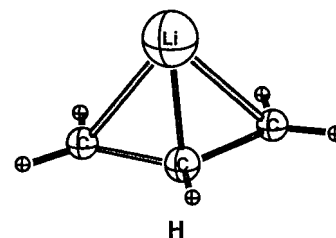
### C. 2-Lithio-2-phenyl-1,3-dithiane (**2-Li-ax** and **2-Li-eq**).

The calculated energy difference between **2-Li-ax** and **2-Li-eq** is 4.10 kcal/mol, the equatorial lithio derivative being more stable. Comparison with **1-Li-ax/1-Li-eq**, where the equatorial preference of lithium is 14.2 kcal/mol (see section A) indicates that introduction of the phenyl ring reduces the energetic difference by approximately 10 kcal/mol. This is quite a strong effect, arising probably from the ability of the phenyl ring to delocalize the electronic density at C(2), and thereby to minimize the manifestation of stereoelectronic effects. In addition, sterically, phenyl competes with lithium for the equatorial orientation. On the question of the potential participation of stereoelectronic interactions in **2-Li**, Figure 3 shows the calculated atomic charges and Wiberg bond indexes in **2-ax**, **2-eq**, **2-Li-ax**, and **2-Li-eq**. The following observations seem most relevant: (1) As in the case of **1-Li**, the large positive charge centered on the lithium atom (+0.88 in **2-Li-eq** and +0.90 in **2-Li-ax**) is indicative of a nearly complete transfer of one electron to carbon, and suggests a highly ionic C(2)–Li bond.<sup>19</sup> This conclusion is supported by the very small values for the C(2)–Li Wiberg bond indexes in both **2-Li-ax** and **2-Li-eq**, 0.05. This observation may also be interpreted in terms of a highly ionic bond.<sup>20</sup>

(2) The structural pattern for C(2)–S (shortening of the bond through metalation, **2-ax** → **2-Li-eq**, 1.85 Å → 1.80 Å) and S–C(4,6) (bond lengthening in the conversion of **2-eq** to **2-Li-ax**, 1.84 Å → 1.86 Å) is again in line with the expectation when  $n_{C(2)} \rightarrow \sigma^*_{S-C(4,6)}$  hyperconjugation is operative.

(3) The calculated structure for **2-Li-eq** (Figure 3) shows, as was the case with **1-Li-eq**, bonding interactions between lithium and the ring sulfurs. The calculated S–Li bond indexes are 0.07, actually larger than the corresponding value for C(2)–Li, 0.05.

### Chart 4



(4) A most interesting observation is the computed structure of **2-Li-ax** (Figure 3). Axial lithium is bonded to C(2), S(1), and the aromatic ring in a bridged structure that resembles allyllithium (**H**, Chart 4).<sup>20,25</sup> As a consequence of this bridging, the phenyl ring in **2-Li-ax** adopts a conformation perpendicular to the bisecting plane (torsion angle S–C(2)–C<sub>ipso</sub>–C<sub>ortho</sub> = 13.8°). Delocalization of electron density from C(2) to the aromatic ring is apparently more important in **2-Li-ax** than in **2-Li-eq** since it helps to minimize  $n_{C(2)}/n_S$  two-orbital/four electron repulsive interactions.

### Conclusions

DFT is able to reproduce the very high preference of the C–Li bond to occupy the equatorial position in 1,3-dithianyl- (14.2 kcal/mol) and 2-phenyl-1,3-dithianyllithium (4.1 kcal/mol). NBO analysis of the global minima in these organolithiums indicates an ionic nature for the C–Li bond, and provides support for the stereoelectronic rationalization<sup>3</sup> of the equatorial carbanion. In particular, the computed structural data are in line with stabilizing  $n_C \rightarrow \sigma^*_{S-C}$  orbital interactions in the equatorial isomers. Nevertheless, evidence for intramolecular S–Li coordination<sup>1</sup> in **1-Li-eq** and **2-Li-eq** is also obtained. On the other hand, repulsive  $n_C/n_S$  orbital interactions in the axial dithianyllithiums is apparently responsible for the very high energy of axial 2-lithio-1,3-dithiane, and for the extensive coordination of lithium with the phenyl ring in axial 2-lithio-2-phenyl-1,3-dithiane.

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**Supporting Information Available:** A listing of total energies for dithianes **1** and **2** and their lithium derivatives (in hartrees) at the Becke3LYP/6-31G(*d,p*) level of theory (1 page). See any current masthead page for ordering and Internet access instructions.

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