1,5-Dilithiated Arenes: Double Metal Bridging Verified by Three X-ray Structures and MNDO Calculations

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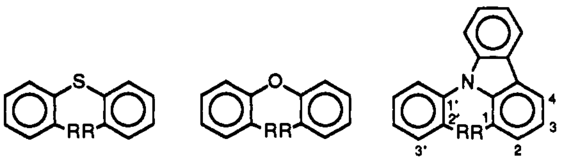
Abstract: The crystal structures of three 1,5-doubly lithium bridged heteroatom-linked diaryl systems with sulfur (**4**), oxygen (**5**), and nitrogen (**6**) as flexible centers have been determined. All are monomers in the crystals. Each lithium bridges both deprotonated ortho carbons symmetrically. The coordination sphere of the metal is completed by the bidentate ligand tetramethylethylenediamine (TMEDA). The π-system is coplanar in *o,o'*-bis(lithio•TMEDA)diphenyl thioether (**4b**), but the rings are tilted markedly in *o,o'*-bis(lithio•TMEDA)diphenyl ether (**5b**) and in 1,2'-bis(lithio•TMEDA)-*N*-phenylcarbazole (**6b**). The distance between the metalated carbons is responsible for the degree of twisting of the phenyl rings. The structural features of **4b** and **6b** are reproduced well by MNDO calculations (with ethylenediamine (EDA) (**4a**–**6a**) as a model for TMEDA), but less so for the oxygen derivative **5b**. MNDO emphasizes the thermodynamic preference for double lithium bridging in *o,o'*-dilithiated diphenyl systems. The MNDO relative energies of **4a**–**6a** agree well with ab initio results with regard to the stabilization effects of each of the three heteroatoms ortho to a negative charge. Gilman's claim that *N*-phenylcarbazole gave the *o,o'*-dilithiated-*N*-phenyl product could not be confirmed; instead, one of the adjacent sites on the carbazole ring is metalated. The principle of symmetrical doubly lithium bridging has been evaluated computationally (MNDO) for two aromatic systems dilithiated in the 1,4-positions. The symmetrically doubly bridged rotamer of *o,o'*-bis(lithio•EDA)biphenyl (**9a'**) (with perfectly coplanar π-systems) is 8.8 kcal/mol more stable than the isomer with perpendicular phenyl rings (**9a''**). Steric proximity of $H_8/H_{8'}$ in doubly bridged 2,2'-bis(lithio•EDA)-1,1'-binaphthyl (**10a'**) prevents coplanarity of the naphthyl moieties. A slight preference (0.7 kcal/mol) for the perpendicular conformation (**10a''**) results. While the π-systems are not coplanar in **10a'**, this is compensated by the tilting of the naphthyl moieties. Thus, the distance between both anionic centers in **10a'** is still appropriate for lithium double bridging. X-ray structures of **5b** and **6b** and the MNDO geometry of **10a** emphasize the preference for symmetrical double lithium bridging, even if the π-systems are twisted.

Introduction

Heteroatoms facilitate the metalation of aromatic rings[4–6] to such an extent that two phenyl rings connected via a heteroatom can be metalated during the same process. These reactions were discovered independently in the 1930's by Gilman[7–9] and Wittig,[10] who pioneered the field of aromatic lithiation. While doubly metalated diphenyl ether (**2**) was used synthetically a long time ago,[11] repetition of Gilman's hydrogen–lithium exchange reactions of diphenyl thioether[12] (**1**) only gave the "dianion" in traces.[13] Indeed, the detailed structures of these dimetalated compounds (**4**–**6**) have not been established. The positions of metalations were only deduced by inference in the early work, e.g. by determining the structures of the products obtained by subsequent reactions. In at least one case, such assignments are questionable. Gilman claimed that the dilithiation of *N*-phenylcarbazole (**3**) led to the *o,o'*-dilithio-*N*-phenyl derivative (this was based on melting point comparisons of the carboxylated product).[14] Based on analogy with **1** and **2**, dilithiation of **3** to give **6** seems more likely.



R = H	**1**	**2**	**3**
R = Li	**4**	**5**	**6**
R = Li•EDA	**4a**	**5a**	**6a**
R = Li•TMEDA	**4b**	**5b**	**6b**

Our goal was to isolate **4**–**6** and to investigate their structures directly. The synthetic utility of such compounds,[15] e.g. for the preparation of six-membered heterocycles by reaction with bifunctional electrophiles,[16] has been amply demonstrated.

The high degree of ionic character of the lithium–carbon bond[17,18] leads to aggregation of organolithium compounds, both in solution[19] and in the solid state.[20,21] However, crystalline

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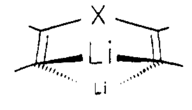
monomers are found if extensive π-delocalization,[22] polydentate ligands,[23] or steric hindrance[24] is present. Dilithio compounds can avoid intermolecular aggregation through what has been described as "intramolecular dimerization" (bridging).[25] Nonclassical double lithium bridging was originally proposed as an explanation for the ready racemization of 2,2′- and 4,4′-dilithio-3,3′-bithienyl derivatives.[26] On the basis of semiempirical[27] and ab initio[28] calculations, our group predicted the symmetrical doubly lithium bridged structure as the most stable conformation of 1,4-dilithium derivatives (**7**), e.g. of butadiene and of biphenyl.

7 

1,4 - double bridging

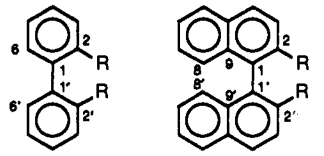
 8

1,5 - double bridging

The X-ray analysis[29] of the latter confirmed this proposal and provided the first experimental proof for this kind of nonclassical lithium bonding. Other 1,4-doubly lithium bridged structures have been demonstrated subsequently.[30,31] Although a simple electrostatic model[32] can account for much of the bonding characteristics of these kinds of lithium compounds,[33] consideration of the carbanion orbital orientations and the effects of charge distribution[34] yield a more detailed understanding of the structural features of lithium-bridged dianions.

An early idea, that "Möbius–Hückel" aromaticity might contribute to the stability of **7**,[28] probably is insignificant. Nevertheless, systems of type **8** were first examined to test this concept, as the heteroatoms would provide two more electrons to the π-system. The X-ray structure of **5b** has been mentioned briefly in two review articles[20a,b] and in a conference contribution.[35] We now provide full information.

Despite the accumulated evidence for double lithium bridging, its generality and energetic importance has been questioned by Murdoch et al.[36] on the basis of strong experimental evidence.[37] They prepared optically active 2,2′-dilithio-1,1′-binaphthyl (**10**) but found no evidence for racemization at temperatures between −131 and −45 °C. This sets a lower limit of 18.4 kcal/mol to the barrier, and establishes that the C_{2v} structure (found to be best for *o,o*′-dilithiobiphenyl (**9**)) is not readily accessible energetically for **10**.



R = Li	**9**	**10**
R = Li•EDA	**9a**	**10a**
R = Li•TMEDA	**9b**	**10b**

This paper reexamines and extends the principle of double lithium bridging. We address the following questions: (1) What are the X-ray structures of **4**, **5**, and **6**? Are all of these similar 1,5-dilithio derivatives, or is **6** exceptional, as proposed by Gilman in 1943? (2) Do 1,5-dilithiated aromatic systems prefer doubly bridged structures (**8**)? Must the aromatic moieties be coplanar in such arrangements? (3) How can Murdoch's observation requiring nonplanarity in 2,2′-dilithio-1,1′-binaphthyl (**10**) be reconciled with the known planar, C_{2v} preference of *o,o*′-dilithiobiphenyl (**9**)? What do MNDO calculations reveal about the structure and potential energy surface of **10**? What is the solvation effect on the energetic preferences for conformations of **9** and **10**?

Preparation

The title compounds were prepared by adding 2 equivs of *n*-butyllithium to a mixture of the substrate and 2 equivs of TMEDA in hexane. Subsequent cooling afforded pale-yellow *o,o*′-bis(lithio•TMEDA)diphenyl thioether[38,39] (**4b**), white *o,o*′-bis(lithio•TMEDA)diphenyl ether[40] (**5b**), and pale-yellow 1,2′-bis(lithio•TMEDA)-*N*-phenylcarbazole[41] (**6b**) crystals.

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[38] Complete crystal structure data for **4b** and **6b** structure determinations are available as supplementary material (see note at the end of the paper).

[39] *Crystal structure data* for **4b**: $C_{24}H_{40}Li_2N_4S$, M = 344.4, monoclinic system, space group $P2_1/c$, $a = 11.832(11)$, $b = 11.982(3)$, $c = 19.181(5)$ Å, $\beta = 92.76(2)°$, $V = 2716.2(13)$ Å^3, $Z = 4$, $D_c = 1.053$ g/cm^3, $F(000) = 936$, $\lambda = 0.71073$ Å (Mo Kα), $T = 200 \pm 1$ K, graphite monochromator. Data were collected on a Nicolet R3m/V diffractometer using a crystal of dimensions 0.3 × 0.4 × 0.6 mm^3 by the ω-scan method ($3.0 > 2\theta < 53.0°$). Three standard reflections were measured every 100 reflections. From 5447 unique measured data, 1504 reflections with $F > 6.0\sigma(F)$ were used for structure solution (direct methods) and subsequent full-matrix least-squares refinement (SHELXTL Plus). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in fixed positions using the riding model and were refined isotropically: 281 refined parameters; final $R = 9.39\%$, final w$R = 6.7\%$.

[40] *Crystal structure data* for **5b** ($C_{24}H_{40}Li_2N_4O$) has been deposited on the occasion of a conference contribution (see ref 35) at the Cambridge Crystallographic Data Centre (REFC = CODWOH).

[41] *Crystal structure data* for **6b**: $C_{30}H_{43}N_5Li_2$, $M_r = 487.59$, orthorhombic system, space group $P2_12_12_1$ (No. 19), $a = 11.598(2)$, $b = 14.570(2)$, $c = 17.369(2)$ Å, $V = 2935.1$ Å^3, $Z = 4$, $D_c = 1.103$ g/cm^3, μ(Mo Kα) = 0.6 cm^{-1}, $F(000) = 1056$, $T = -35$ °C. Data were collected on a crystal specimen of dimensions 0.4 × 0.5 × 0.6 mm^3 on a Syntex-P2$_1$ diffractometer (Mo Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator, ω-scans, $\Delta\omega = 1.0°$, scan speed 0.9–29.3 deg/min, $(\sin \theta/\lambda)_{max} = 0.550$ Å^{-1}, *hkl* range +12,±16,+19). Lp corrections were applied, corrections for absorption and crystal instabilities were not necessary. Of the 4503 measured intensities, 4061 were unique ($R_{int} = 0.02$) and 3591 "observed" with $F_o \geq 4.0\sigma(F_o)$. The structure was solved by direct methods (SHELXS 86) and completed by difference syntheses. Twenty H atoms could be located; 19 were calculated at idealized geometrical positions. Those at the disordered methylene C atoms (see below) were neglected. Refinement of 332 parameters converged at $R = wR = 0.056$, $w = 1/\sigma^2(F_o)$ (anisotropic, disordered methylene C atoms isotropic in two alternatives with $^1/_2$ occupancy, H atoms constant with $U_{iso} = 0.05$ Å^2 for phenyl H atoms and 0.08 Å^2 for all others; SHELX 76). Refinement of the inverse structure did not result in significant differences. $\Delta\rho_{fin}$(max/min) = 0.63/−0.43 e/Å^3. The methylene groups of the TMEDA molecule at Li$_2$ were disordered. The disorder results also in relatively large displacement parameters of the *N*-methyl groups which could not be split up, however. As a result, the distance C_{53}–C_{511} is artificially shortened (2.0 Å).

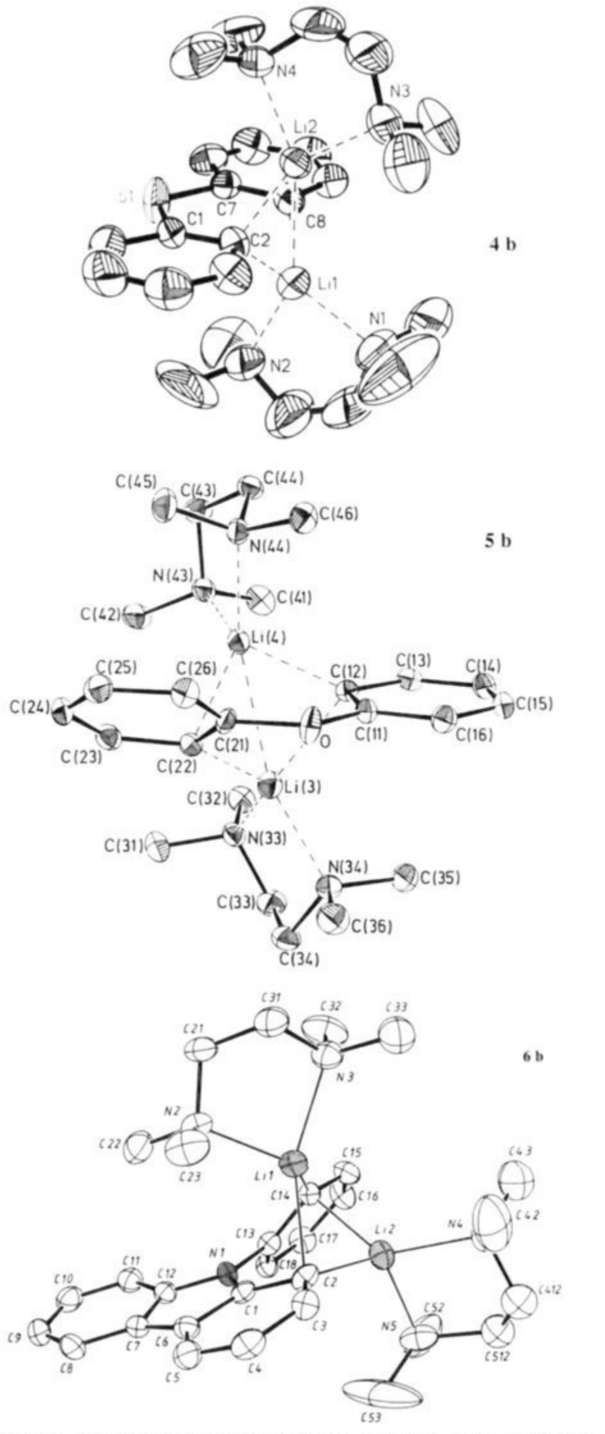

Figure 1. Molecular structures of **4b**, **5b**, and **6b** in the crystal and crystallographic numbering scheme used (ORTEP, displacement ellipsoids at the 50% level, H atoms omitted for clarity).

X-ray Crystal Structures

ORTEP diagrams of **4b**–**6b** are shown in Figure 1; Table I summarizes the characteristic features of **4b**–**6b** and of some reference compounds. The deviation of the two phenyl rings in **5b** and **6b** from coplanarity is most striking. Although each dianion exhibits the expected 1,5-double lithium bridging of the anionic carbons, it does not necessarily force the rings to be coplanar as in the biphenyl moiety of *o,o'*-bis(lithio·TMEDA)-biphenyl[29] (**9b**) (Figure 2).

The distance between the two metalated carbons is longest in **4b** (3.21 Å), resulting in the least twisting (5.2°). Similar but slightly shorter C–C distances in **5b** (3.05 Å) and **6b** (3.09 Å) can only be accommodated by larger twisting angles (34.8° and 40.4°, respectively). The difference between **4b** on the one hand and **5b** and **6b** on the other is even more obvious if the phenyl rings are hypothetically forced to be coplanar. The metalated carbons would approach to 2.85 Å in **5b** and **6b** compared to 3.19 Å in **4b** (Table I). Nonmetalated ortho carbons in such an arrangement can approach to 2.9 Å, as demonstrated in the X-ray structure of [Li(12-crown-4)$_2$][CHPh$_2$].[42] The distance between metalated carbons in **9b** is comparably short (2.87 Å), but the angle between the two sp^2 hybrid orbital axes (Table I) is different from those in **4b**–**6b** because of the missing heteroatom between the phenyl rings. If hydrogen atoms were bonded to the metalated carbons in **5b**, their distance in the hypothetically coplanar conformation would be 1.23 Å compared to 1.79 Å in **9b**. Thus, steric hindrance of the metalated sp^2 hybrid orbitals accounts for the deviation of coplanarity of **5b** and **6b**.

The noncoplanarity of the phenyl rings in **5b** and **6b** is associated with an interesting feature of lithium binding. Each lithium in these isomers approximately lies in plane with one phenyl ring but out of the plane of the other. Two different types of bonding result. The equatorial position gives rise to a σ-interaction of lithium with the sp^2 lone pair of the anionic carbon whereas the π-orbitals of the second phenyl ring enable a π-interaction with the same lithium. The resulting average bond length differences of Li to each carbon atom are 0.10 and 0.17 Å for **5b** and **6b**, respectively, compared to only 0.06 Å in **4b** and 0.03 Å in **9b**. The first evidence for this type of bonding was found for the Li–N interaction in the dimer *N*-lithiocarbazole·2THF[43] with a Li–N bond length difference of 0.14 Å.

The objections against symmetrical doubly lithium bridging raised by Brown and Murdoch[36] (vide supra) appear to be founded in the interpretation of the term "symmetrical". They inferred erroneously that "symmetrical double bridging" in **10** requires a planar organic moiety as in **9b** (Table I, Figure 2). The three structures presented here show that symmetrical lithium double bridging in a twisted organic "dianion" system can exist even for C–Li bond length differences larger than those in **9b**. A similar doubly bridged, twisted arrangement should also be possible for the binaphthyl, dianion, whose organic moiety obviously cannot adopt a planar conformation (vide infra). However, in a footnote, Brown and Murdoch consider a twisted structure of dilithiobinaphthyl with each lithium "spanning the 2,2'-positions in unsymmetrical fashion"[44] as a possible ground-state conformation. Extensive semiempirical calculations covering this aspect and its implications will be discussed in the following section.

There are many structural similarities among the title compounds (Figure 1, Table I). In addition to the C–Li contacts in each isomer, two nitrogens of the TMEDA coligand complete the distorted tetrahedral coordination of the metal. There is no contact between lithium and the heteroatoms of the anionic moieties. C–Li bond lengths are within the range of distances of aryl carbon atoms bonded to bridging lithium atoms,[20] as are Li–Li distances (Table I). We note the widening of the Li–Li distances with increasing twist angles between the phenyl rings. This twisting also causes an increase in the differences in C–Li distances within each isomer. The systematic deviation of the bond angles from 120° within the aromatic rings is typical for lithium and heteroatom substitution at a phenyl ring.[45]

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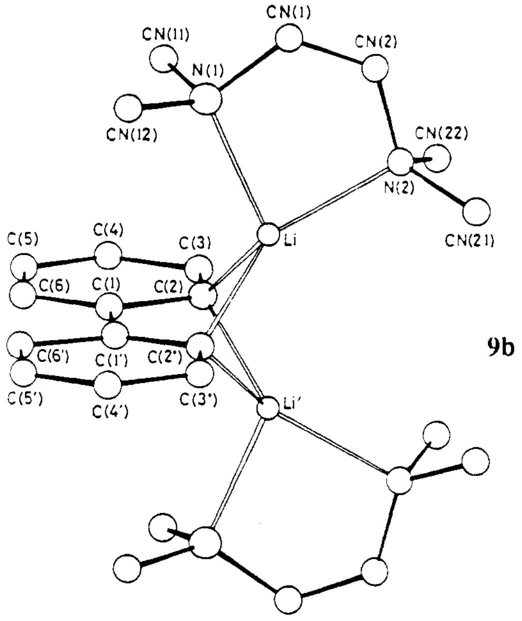
Table I. Selected Bond Lengths (Å) and Bond Angles (deg) of Lithiated Compounds from X-ray Analyses[a]

	Li–phenyldimer[b]	*o,o'*-Li_2-biphenyl[c] (**9b**)	*o,o'*-Li_2-diphenylthioether (**4b**)			*o,o'*-Li_2-diphenylether (**5b**)			1,2'-Li_2-*N*-phenylcarbazole (**6b**)		
	Li	Li[d]	Li_1		Li_2[d]	Li_3		Li_4[d]	Li_2		Li_{14}[d]
Li···Li (Å)	2.49	2.55		2.56			2.62			2.67	
C_2–Li (Å)	2.21	2.12	2.18		2.14	2.21		2.13	2.32		2.13
C_8–Li (Å)	2.28	2.15	2.13		2.20	2.11		2.23	2.12		2.26
N–Li[e] (Å)	2.19	2.12	2.16		2.12	2.16		2.11	2.21		2.14
C–Li–C (deg)	105.6	84.3	96.1		95.5	89.7		89.0	88.2		89.2
Li–C_2–Li (deg)	67.4	74.1		72.7			74.1			73.7	
Li–C_8–Li (deg)	67.4	72.8		72.3			74.1			75.1	
C–C_{Li}–C (deg)	111.8	115.0 115.3	113.3		113.4	112.4		112.0	112.0		110.7
Ph/Ph[f] (deg)		0.0		5.2			34.8			40.4	
$C_2 \cdots C_8$ (Å)	3.57	2.87		3.21			3.05			3.09	
$\{C_2 \cdots C_8\}$[g] (Å)	3.57	2.87		3.19			2.85			2.85	
$sp^2 \cdot\cdot sp^2$[h] (deg)		57.9		105.5			98.0			99.5	

[a] The atom numbering C_2 and C_8 refers to the crystallographic numbering of **4b**. The corresponding atoms in **5b**, **6b**, and **9b** are C_{12}/C_{22}, C_2/C_{14}, and $C_2/C_{2'}$, respectively (see Figures 1 and 2). C_2 in **6b** is part of the carbazole ring system; C_{14} belongs to the *N*-phenyl ring. Complete tables of bond distances and angles with esd's for **4b**, **5b**, and **6b** are available as supplementary material. [b] Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3157. [c] Reference 29. [d] The atom numbering of the lithiums refers to the crystallographic numbering in Figure 1. [e] Average Li–$N_{(TMEDA)}$ distance. [f] Twist angle between RMS plane of phenyl rings. [g] With hypothetically planarized phenyl rings (see text). [h] Angle between sp^2 hybrid orbital axes of hypothetically planarized phenyl rings.



9b

Figure 2. ORTEP diagram of **9b** (atoms with arbitrary radii).

Semiempirical Calculations

X-ray geometries provide tests of the reliability of calculated structures. The MNDO (Modified Neglect of Diatomic Overlap) method[46] describes lithium compounds of considerable size satisfactorily,[31,47] despite its known deficiencies of overestimated Li–C and Li–H bond strengths and of underestimated conjugation of π-systems.[48] The three monomeric species investigated allow assessment of the method's performance on intramolecular aggregates. When lithium ions are solvated, the theoretical (gas-phase) results should approach solution behavior. For computer time reasons the TMEDA ligand was simplified by replacing the four methyl groups by hydrogens. Ethylenediamine (EDA) should be very similar to TMEDA as a complexing ligand. Two different starting geometries were chosen for each isomer: the doubly bridged form and a conformer with classical Li–C bonding. Each geometry was confirmed to be a local minimum by calculating the force constant matrices.[49] (The conformers with fixed dihedral angles are exceptions.)

Table II. Selected MNDO Bond Lengths (Å) and Bond Angles (deg) of **4a**–**6a**[a]

	4a (X = S)		**5a** (X = O)		**6a** (X = N)	
	Li_1	Li_2	Li_3	Li_4	Li_2	Li_{14}
Li···Li (Å)	2.43		2.43		2.46	
C_2–Li (Å)	2.09	2.09	2.09	2.09	2.05	2.15
C_8–Li (Å)	2.09	2.09	2.09	2.09	2.15	2.06
N–Li[b] (Å)	2.31	2.31	2.30	2.30	2.31	2.31
C–C_{Li}–C (deg)	116.9	116.9	116.0	116.0	114.0	116.4
dihedral Ph/Ph[c] (deg)	0.0		2.4		41.6	
$C_2 \cdots C_8$ (Å)	3.17		3.02		3.08	
X···Li (Å)	3.18	3.18	3.07	3.05	3.16	2.88

[a] The atom numbering corresponds to the one in Table I. [b] Average Li–$N_{(TMEDA)}$ distance. [c] Twist angle between RMS plane of phenyl rings.

Important features of the calculated structures are summarized in Table II; these are represented in Figure 3. The twist angle of the phenyl groups is reproduced strikingly well for the sulfur (**4a**) and for the nitrogen (**6a**) derivatives. However, this is not the case for the oxygen derivative (**5a**), which shows a deviation of 32.4° in the dihedral angle between calculated and experimental structures. The geometry around the heteroatoms in each isomer (Figure 4) does not explain this discrepancy. The potential energy surface for the twisting of the phenyl rings is very flat, as can be seen from the low deformation energy of **5a** (Scheme I; 1.5 kcal/mol) to the experimental phenyl ring twist angle (34.8°). MNDO tends to favor planar ring systems in doubly bridged *o,o'*-dilithiated compounds.[50] Steric repulsion due to the ortho aromatic hydrogens prevents a planarized carbon skeleton in **6a** (Scheme I). The strong overestimation of the Li–C interaction by MNDO,[18] which also leads to somewhat shorter calculated Li–C bond lengths than in the crystals, could be responsible for the planarization of **5a**. The shorter C–Li bonds cause closer Li–Li contacts, while at the same time widening distances between the ligands and lithium. Between **6a** and **6b**, there is remarkable agreement in structural details (Figure 4).

Gilman inferred[14] that *N*-phenylcarbazole is metalated in both ortho positions of the phenyl substituent. MNDO heats of formation of this isomer and the one with metalation positions as found in the crystal were compared without additional lithium ligands.[51] The doubly bridged isomer is 38.2 kcal/mol lower in

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(46) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Li parametrization: Thiel, W.; Clark, T. *QCPE* **1982**, *2* (No. 438), 63.

(47) (a) Sygula, A.; Lipkowitz, K.; Rabideau, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 6602. (b) Thiel, W. *Tetrahedron* **1988**, *44*, 7393. (c) Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 7191. (d) Suñer, G. A.; Deyá, P. M.; Saá, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 1467.

(48) Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985.

(49) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

(50) Kranz, M.; Clark, T. Unpublished results.

(51) Hacker, R. Ph.D. Thesis, Universität Erlangen-Nürnberg, Erlangen, Germany, 1988.

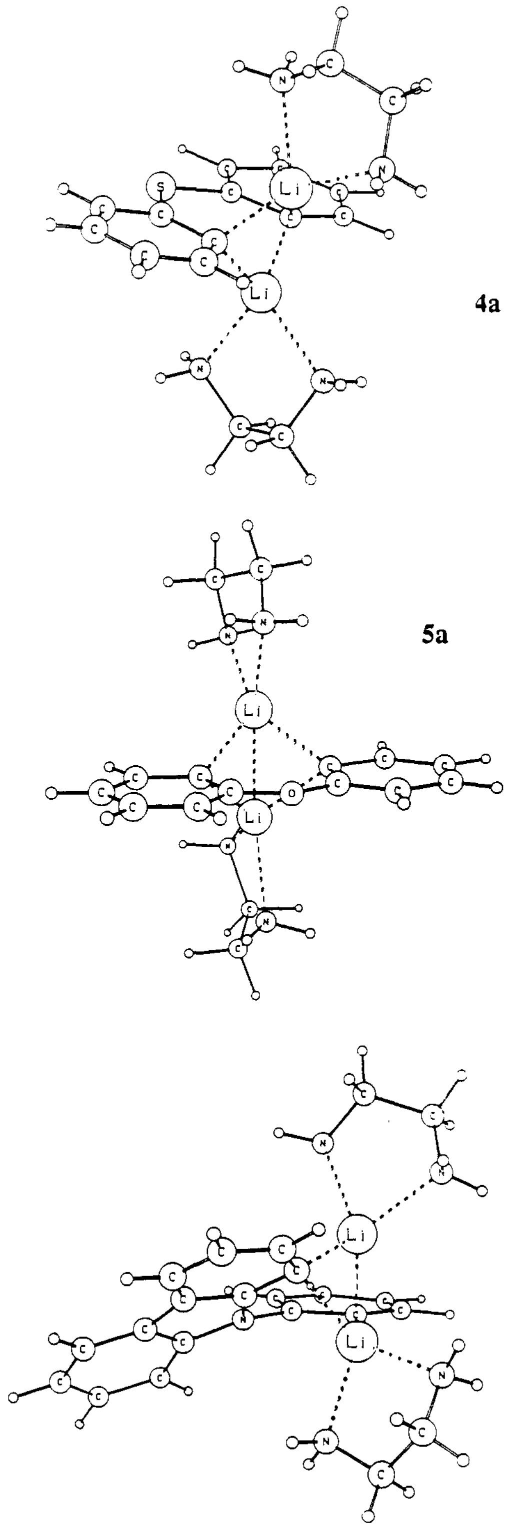


Figure 3. MNDO geometries of **4a**–**6a**.

energy. This value emphasizes the extra stabilization through intramolecular association although it is expected to decrease upon solvation.

In order to estimate the hypothetical gain in energy through double lithium bridging in the title systems, we have located the nonbridged local minima for **4a**–**6a** (Scheme I). **4a** and **5a** exhibit a considerable stabilization upon bridging (−17.7 and −14.1 kcal/mol, respectively). The small gain in energy upon bridging for **6a** (−5.0 kcal/mol) can be attributed to unfavorable steric congestion in the bridged arrangement and favorable interaction of the 2′-lithium with the π-system of the carbazole moiety in the twisted form of **6a**. This is not possible in **4a** and **5a**.

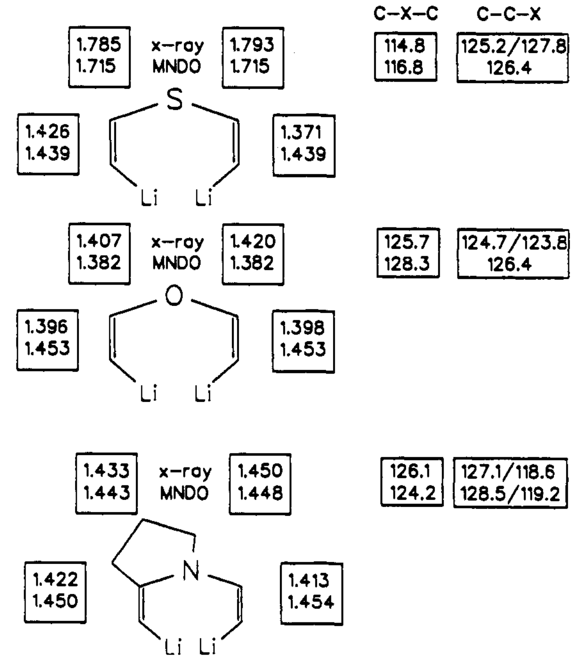
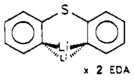
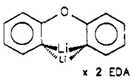
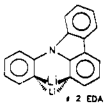
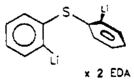
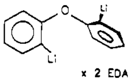
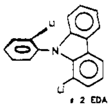
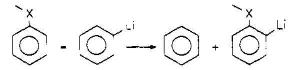
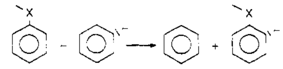


Figure 4. Experimental and calculated bond lengths (Å) and angles (deg) in the vicinity of the heteroatoms of **4**–**6**.

Scheme I. MNDO Heats of Formation (kcal/mol) and MNDO and ab Initio (3-21G//3-21G)[a] Relative Energies (kcal/mol) of Metalation Reactions of **4a**–**6a**

	4a X = S	5a X = O	6a X = N
			
ΔH_f° [kcal/mol]	-60.08	-82.86 (-81.41)[b]	-8.41 (-3.45)[c]
rel. energy [kcal/mol]	0.0	0.0	0.0
			
ΔH_f° [kcal/mol]	-42.43	-68.76	- 3.40
rel. energy [kcal/mol]	+17.7	+14.1	+ 5.0
Equation 1: MNDO $Ph_2X + (MeLi \cdot EDA)_2 \dashrightarrow Ph_2X(Li \cdot EDA)_2 + 2\,CH_4$			
$\Delta(\Delta H_f^\circ)$ [kcal/mol]	-13.6	- 4.5	- 2.7
Equation 2: RHF 3-21G//3-21G[a] 			
rel. energy [kcal/mol]	- 9.1	-23.6	-25.4
Equation 3: RHF 3-21G//3-21G[a] 			
rel. energy [kcal/mol]	-13.2	- 2.4	+ 3.0

[a] Reference 53. [b] With dihedral angle of phenyl rings fixed at experimental value. [c] With phenyl rings fixed to be coplanar.

Henry Gilman established a ranking of the ortho-directing ability of some heteroatoms (O > S > N) by means of competitive metalations of dibenzo-fused five-membered heterocycles.[52] The MNDO heats of metalation of **4a**–**6a** (eq 1 in Scheme I) give a heteroatom ranking (S ≫ O > N) which does not agree with

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(52) (a) Gilman, H.; VanEss, M. W.; Willis, H. B.; Stuckwisch, C. G. *J. Am. Chem. Soc.* **1940**, *62*, 2606. (b) Gilman, H.; Stuckwisch, C. G. *J. Am. Chem. Soc.* **1945**, *67*, 877.

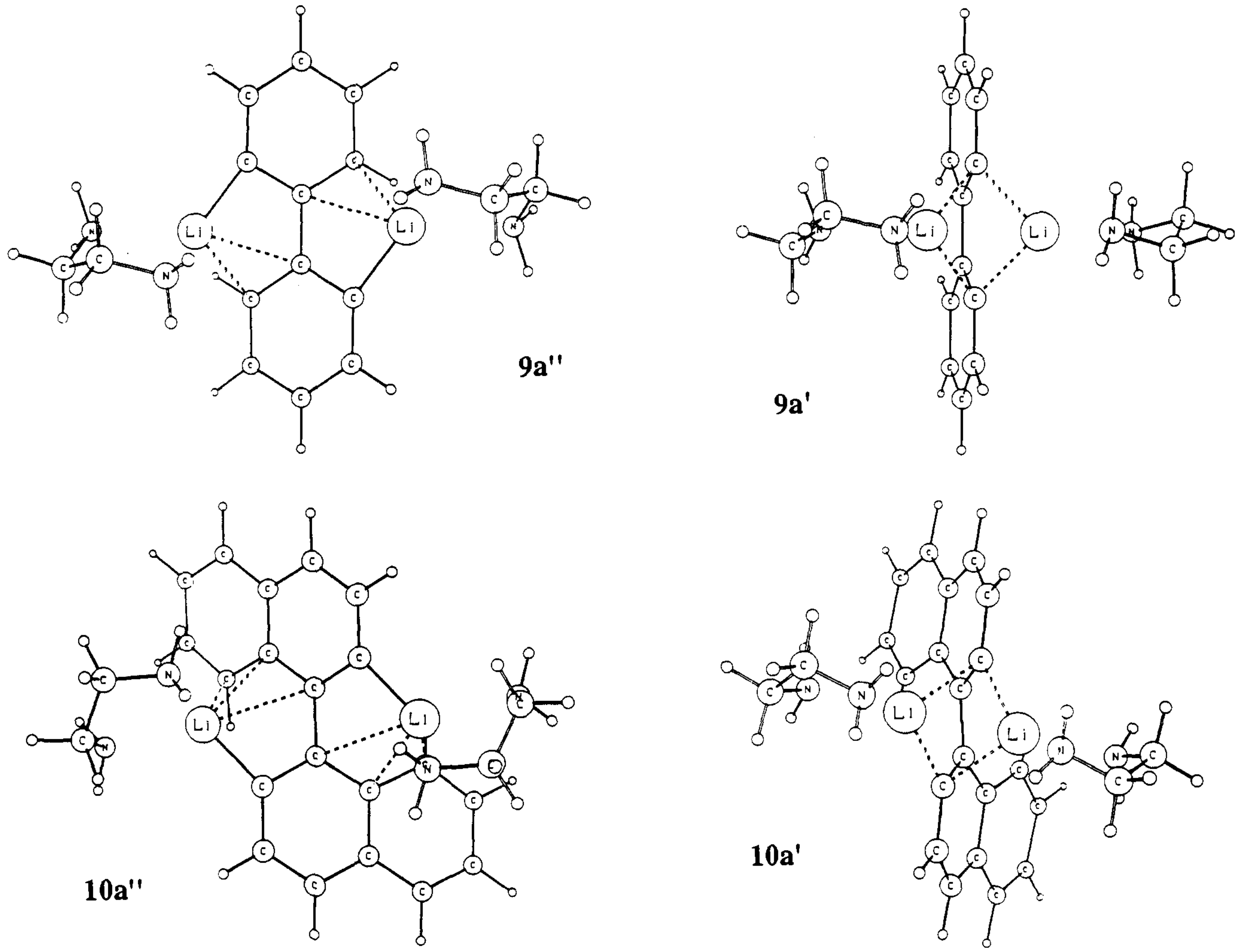

Figure 5. MNDO geometries of bridged and perpendicular **9a** and **10a**.

Table III. MNDO Heats of Formation (kcal/mol), Twist Angles (C_2–C_1–$C_{1'}$–$C_{2'}$) (deg), and Selected Bond Lengths (Å) of Bridged and Perpendicular **9a** and **10a** Isomers

	9a′ (bridged)	**9a″** (perp)	**10a′** (bridged)	**10a″** (perp)
ΔH_f (kcal/mol)	−52.15	−43.39	−5.10	−5.80
rel energy (kcal/mol)	0.0	+8.8	+0.7	0.0
symmetry	C_2	C_2	C_2	C_2
twist angle (deg)	0.1	127.0	42.5	122.0
Li–Li (Å)	2.48	4.50	2.57	4.85
C_2–Li (Å)	2.07	1.92	2.02	1.92
$C_{2'}$–Li (Å)	2.07	3.67	2.21	3.81
$C_{1'}$–Li (Å)	2.54	2.52	2.43	2.66
$C_{6'}$–Li (Å)	3.82	2.34		
$C_{9'}$–Li (Å)			3.48	2.44
$C_{8'}$–Li (Å)			4.33	2.36
C_{Li}–$C_{Li'}$ (Å)	2.93	3.68	2.93	3.58
C_6–$C_{6'}$ (Å)	3.07	3.72		
C_9–$C_{9'}$ (Å)			3.31	3.80
C_1–$C_{1'}$ (Å)	1.523	1.519	1.528	1.520

these experimental deductions. This may be due to differences between the experimental probes and our systems. The ability of various heteroatoms to stabilize a negative charge at the ortho position of a phenyl ring has been investigated by ab initio calculations (RHF 3-21G//3-21G)[53] of thiophenol, phenol, and aniline (Scheme I). When a gegenion (Li) is present, first-row substituents are favored through direct metal–heteroatom contact (eq 2 in Scheme I). On the other hand, a negative charge is stabilized best by sulfur (eq 3 in Scheme I). Distances around 3 Å between lithiums and the heteroatoms in the MNDO structures of **4a**–**6a** (Table II) preclude a direct interaction and vindicate the correlation between eqs 3 and 1 of Scheme I.

2,2′-Dilithio-1,1′-binaphthyl (10). In order to investigate the behavior of the binaphthyl system upon dilithiation, 2,2′-dilithio-1,1′-binaphthyl (**10**) and *o,o′*-dilithiobiphenyl (**9**) have been calculated with MNDO including EDA as ligand for lithium. Heats of formation and structural data are given in Table III, geometries are shown in Figure 5.

MNDO rotational isomers of unsolvated **9** were calculated earlier.[27] Solvation is known to play an important role for lithium structures,[20] but computational facilities restricted the size of the molecules that could then be calculated. Including solvation of **9** with EDA (**9a**) reduces the energy difference between the perpendicular (**9a″**) and the doubly bridged isomer (**9a′**) (+8.8 kcal/mol) by half compared to the unsolvated species (+16.8 kcal/mol). Even so, weak interactions of the lithiums with the π-system of the phenyl rings (cf. $C_{6'}$–Li, Table III) in the perpendicular conformation do not compensate for the loss of a second contact to an anionic carbon atom in the double bridged geometry.

Two almost equally stable rotamers are calculated for **10a** (Table III). The unbridged isomer (**10a″**), which has a C_2–C_1–$C_{1'}$–$C_{2'}$ dihedral angle of 122°, is even slightly more stable than the doubly bridged species (**10a″**; twist angle 43°). In the former, the coordination sphere of each lithium is completed by the adjacent phenyl system, similarly to **9a″**. There is one more C–Li contact ($C_{8'}$···Li, $C_{9'}$···Li) in perpendicular **10a″** than in the

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(53) (a) Harder, S. Ph.D. Thesis, State University of Utrecht, Utrecht, The Netherlands, 1990. (b) Harder, S.; Brandsma, L.; Kanters, J. A.; Duisenberg, A.; van Lenthe, J. H. *J. Organomet. Chem.* **1991**, *420*, 143.

corresponding **9a″** isomer ($C_{6'}\cdots Li$) (Table III). The π-system of **10a** should be more readily available for stabilization of positive charge than that in **9a**. Steric interaction of $H_8\cdots H_{8'}$ prevents a facile planarization of the binaphthyl moiety,[54] in contrast to the biphenyl system.[55] Despite the large twist angle of 43°, **10a′** exhibits exactly the same distance between metalated carbon atoms (2.93 Å) as planar **9a′**. A marked bending of the C_2–C_1–$C_{1'}$ (and $C_{2'}$–$C_{1'}$–C_1) angle (115.8°) in the binaphthyl system is responsible for the equal $C_{Li}\cdots C_{Li'}$ distances in **9a′** and **10a′** (cf. $C_6\cdots C_{6'}$ and $C_9\cdots C_{9'}$ distances in **9a′** and **10a′**, respectively). Thus, steric hindrance to planarization of **10a′** does not lead to puckering of the naphthyl rings but rather to tilting of the naphthyl rings in order to help ensure a favorable distance for lithium double bridging between the carbanion centers. Reversal of the order of stability between the rotamers of **9a** and **10a** can be attributed to the distortion of **10a′** and to the better complexation of the lithiums in **10a″** compared to those in **9a″**. Therefore, MNDO suggests an equilibrium between the bridged and the twisted conformation of **10a** as its ground-state geometry.

It has been argued[56] that the energy difference of 16.8 kcal/mol[27] between unsolvated coplanar and perpendicular **9** calculated with MNDO "suggests that the lowest minimum-energy path of racemization of binaphthyl proceeds through a transition state resembling the coplanar bridged dilithiobiphenyl, and implies that the barrier to racemization of 2,2′-dilithio-1,1′-binaphthyl is comparable to or less than the barrier to racemization of 1,1′-binaphthyl." We have demonstrated that the value of 16.8 kcal/mol is much too high because solvation was not taken into account and that relative stabilities of dilithiated aromatics are not transferable from one molecule to another (Table III). The calculated geometries of solvated **10a** clearly show (Figure 5) that the symmetrically doubly bridged isomer is far from a transition structure for racemization. The ring systems of binaphthyl and biphenyl are much too different to be able to relate their properties to one another. Their experimental barriers to rotation are 17 kcal/mol apart,[54,55] and it is not obvious how this obstacle can be overcome by double lithiation. Rotational barriers will be discussed in detail elsewhere.[57]

Conclusions

The crystal structures (**4b**–**6b**) of dilithiated biphenyl ether (**2**), diphenyl thioether (**1**), and *N*-phenylcarbazole (**3**) all show symmetrical double lithium bridging involving the metalated ortho positions of the phenyl rings. Such "intramolecular aggregation" and the presence of the bidentate ligand TMEDA at each lithium results in monomeric units in the crystals. MNDO calculations reproduce almost all the structural characteristics of **4b**–**6b**, except for the twist angle of the phenyl rings in **5b**. Ab initio calculations on a model system (phenyl anions with ortho heteroatom substituents) reveal a stronger stabilization by sulphur (−13.2 kcal/mol) than for oxygen (−2.4 kcal/mol); nitrogen is destabilizing (+3.0 kcal/mol). MNDO heats of metalation, leading from **1**–**3** to **4a**–**6a**, respectively, support this ranking.

The extent of extra stabilization through double bridging compared to the nonbridged isomers has been determined computationally for **4a**–**6a** and for two 1,4-dilithiated compounds (*o,o′*-dilithiobiphenyl·2EDA (**9a**) and 2,2′-dilithio-1,1′-binaphthyl·2EDA (**10a**)). The stabilization of **4a** and of **5a** is considerable (−17.7 and −14.1 kcal/mol, respectively). The **6a** and **9a** stabilizations (−5.0 and −8.8 kcal/mol, respectively) are smaller due to lithium complexation by the contiguous π-system in the perpendicular conformations. Rotamers of **10a** have almost the same energy because the approach of the anionic carbons in the doubly bridged arrangement is hindered sterically by repulsion in the rest of the molecule, e.g. $H_8\cdots H_{8'}$.

The experimental behavior of **10** led Murdoch et al.[36] to challenge the effectiveness of symmetrical lithium double bridging in general. We have now clarified the situation. The inclusion of solvation in **9a** does decrease the computed stabilization energy due to lithium double bridging from 16.8 to 8.8 kcal/mol. Twisting, e.g. of the naphthyl moieties in **10a**, does not prevent lithium double bridging.

Our experimental and computational results corroborate that symmetrical doubly lithium bridged arrangements can be expected generally for organic "dianions" as long as the distances between the anionic centers are appropriate.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, and the Convex Computer Corp.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and anisotropic displacement parameters for **4b** and **6b** and archive entries of MNDO calculations of **4a**–**6a**, **9a′**, **9a″**, **10a′**, and **10a″** (30 pages); observed and calculated structure factors of **4b** and **6b** (40 pages). Ordering information is given on any current masthead page.

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[54] (a) Cooke, A. S.; Harris, M. M. *J. Chem. Soc.* **1963**, 2365. (b) Carter, R. E.; Dahlgren, L. *Acta Chem. Scand.* **1969**, *23*, 504.

[55] Kurland, R. J.; Wise, W. B. *J. Am. Chem. Soc.* **1964**, *86*, 1877.

[56] Reference 36: footnote 7.

[57] Kranz, M.; Clark, T.; Schleyer, P. v. R. *J. Org. Chem.*, in press.