REMARKABLE STRUCTURES OF LITHIUM COMPOUNDS

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Abstract - The geometries of lithium compounds do not follow classical structural considerations. Lithium bonds have a high degree of ionic character, but also engage in multicenter covalent bonding. Replacement of a hydrogen in a molecule by lithium almost always results in some fundamental change in geometry or electronic structure. Triplet ground states and anti van't Hoff forms may be favored. Lithium also can participate in stoichiometries which violate the octet rule, e.g., CLi_5 and CLi_6. The extra electrons in these hypermetallated species are not associated with the central atom, but contribute to metal-metal bonding. Lithium often prefers bridging positions; symmetrical multiple bridging is also quite common. Association energies of lithium compounds are quite large and double bridging within a molecule can be considered to be the intramolecular equivalent of association. X-ray determinations and theoretical calculations provide the best information concerning structural details. Results from both these areas will be described and compared. Formerly, bits and pieces of information were available. These are now fitting together so that patterns and regularities are becoming apparent.

INTRODUCTION

Lithium, the first of over 80 metals in the periodic table, should exhibit many of the chemical and structural properties common to this group of elements. Many very familiar lithium compounds are widely employed as synthetic intermediates: they are more useful than other alkali metal and even magnesium compounds for this purpose (1). Despite the obvious importance structural studies of lithium molecules have lagged far behind other interests until relatively recently. Deplorably, synthetic chemists often are concerned only with their starting materials and products and tend to ignore the structures of reagents or reactive intermediates. Thus, organic textbooks describe organolithium compounds only as "carbanions" or as monomers, both are grossly inaccurate oversimplifications for these associated, polar organometallic species (2,3). Observed behavior depends on the degree of aggregation and the nature of the solvation. However, the currently fashionable concern with stereospecific synthesis emphasizes the need to consider intermediates as three dimensional entities which control reaction orientations. Even here, oversimplified models often are employed. We hope to help alleviate the lack of knowledge in this area, but lithium structures are interesting in their own right. Chemists cannot claim to command their science without a basic appreciation for the bonding rules governing this seemingly simple first row main group element.

Lithium compounds are generally strongly associated in the solid, in solution, and in the gas phase; interaction with donor atoms in solvents or ligands also contributes to the complications which have discouraged more widespread physical investigations (2). Although increasingly valuable general knowledge is being obtained from spectroscopic studies (4), the best sources of detailed information concerning the geometries of lithium compounds are X-ray structures and theoretical calculations. This paper reports related findings in both these areas. At the present time, there were about 175 lithium entries in the Cambridge Crystallographic Database(5). However, many of these involve lithium cations surrounded only by solvent molecules, etc., and are of little interest in the present context. Only about 60 of the structures are "organometallic", in the sense that the lithium is associated with one or more carbon atoms or is present in an "organic" molecule (5).

The first lithium X-ray structure, of ethyllithium tetramer, was reported by H. Dietrich in 1963 (6). He has remained an active contributor to this area and has kindly examined most of our compounds described in the present report (7). In 1964, E. Weiss began his dedicated exploration of the structures of alkali metal compounds by reporting the studies of methyllithium tetramer (8). Two of our lithium X-ray results were determined in his laboratory (9). Stucky's contributions to this area (1970-1978) (10) have also been particularly significant in showing how lithium cations associate with π electrons in a variety of olefinic and aromatic molecules. Quite recently, there has been a burst of activity, numerous structures have been determined by the Sussex (Lappert, Eaborn) (11), ETH Zürich (Dunitz, Seebach) (12), Amsterdam (van Koten) (13),

Klumpp (14), and other groups (15). Most of the reported X-ray structures have associated sol-
vent molecules or multidentate ligands like TMEDA. Hence, it appears likely that these forms
in the crystal also may represent the structures of solvated species present in solution rea-
sonably well.

Theoretical calculations afford many advantages. The geometries of relatively small lithium
compounds can be calculated routinely (16) at such high ab initio levels that accuracy can be
taken for granted. Even relatively small split-valence basis sets which are more practical for
widespread use give good results. The 3-21G basis set, for example, provides many more func-
tions on lithium than the number of electrons. This leads to good mathematical approximations.
In addition, electron correlation corrections tend to be unimportant in systems with high
ionic character.

Since experimental thermochemical data on lithium compounds are extremely sparce, theoretical
calculations afford the best source of energetic information. A full calculational study on a
given species involves an extensive search of the potential energy surface and the location of
as many fixed points (e.g., minima, transition states for intromolecular interconversions, re-
actions, etc.) as possible. Energy differences between structural alternatives reveal the de-
gree to which an observed form is favored over other possibilities. Lithium structures do not
follow classical rules: replacement of an H by Li in a molecule almost always leads to a major
change in geometry, electronic state, or both. The computertime-efficient MNDO method (17),
parameterized for lithium by Thiel and Clark (18), facilitates such searches, which are then
followed by ab initio calculations at the highest levels practicable. In addion, Li-O and Li-N
association energies are given well by MNDO, this permits calculational studies of solvation
on the relatively large systems which typically are found in crystal structures and are of
interest experimentally.

Much of our theoretical work on lithium compounds is part of a continuing collaborative effort
with John A. Pople, Carnegie-Mellon University. In addition, Professor Pople's group has de-
veloped Gaussian series of the ab initio programs, basis sets, and correlation methods we
have employed (16).

Figure 1 presents some of the unusual structures of lithium compounds we have discovered cal-
culationally (19-37). Many of these not only have remarkable geometries but are peculiar in
having triplet ground states. Small aggregates also have been examined (30,38), as closer
models of species likely to be present under more typical experimental conditions. A number of
features of lithium structures are illustrated, e.g., propensities for anti-van't Hoff geome-
tries (molecules with planar tetracoordinate carbons (19,20), etc.) ability to bridge two or
more atoms in vicinal (26,28,30,31), 1,3- (27,29), or 1,4-arrangements (29), multiple bridging
involving two or more lithiums (30,31), stabilization of strained structures (33) and reactive
intermediates (34-36), and participation in hypermetallated octet rule-violating stoichiome-
tries (37). The original literature provides details.

METHYLLITHIUM, ITS OLIGOMERS, AND RELATIONSHIP TO INTRAMOLECULAR BRIDGING

The organolithium prototype, methyllithium, has been the subject of many theoretical studies
(39), but these have left several important questions unanswered. In collaboration with Krishnan
Raghavachari, Bell Laboratories, we have carried out an investigation at ab initio levels high
enough to be definitive. CH_3Li monomer, for which only general information is available exper-
imentally from an early matrix isolation study (41), is characterized by a C-Li bond length
of 2.00 Å and an unusually widened HCLi angle of 115°. Electropositive substituents cause this
σ effect, which is general for simple alkyl metal compounds. Thus, the LiCC angle in ethyl-
lithium is 116°. The C-Li bonds are longer in the oligomers; 3-21G values are 2.16 Å (dimer),
2.13 Å (trimer), and 2.25 Å in the staggered tetramer. The last agrees well with experiment
(2.27 Å). Our best association energies of methyllithium are: dimerization, -42, trimerization,
-82; and tetramerization, -128 kcal/mol. These energies are much too large to be overcome by
solvation; dissociation is not expected to occur in any of the commonly employed solvents.
Even TMEDA is shown by an X-ray study (8) not to dissociate the tetramer, but to coordinate
with lithium in a monodentate fashion.

Methyllithium dimer and trimer are found calculationally to have four- and six-membered ring
structures with freely rotating methyl groups. The analogous planar, eight-membered ring struc-
ture for the tetramer (C_{4h} symmetry) is only 12.4 kcal/mol above the tetrahedral arrangement
in energy. Since the latter has only one but the former two coordination sites per lithium,
the energy difference might even be smaller in solution. This helps explain dynamic processes
which have been observed for alkyllithium aggregates (42). In particular, primary alkyllithium
compounds with prochiral CH_2 groups attached to lithium undergo stereomutation. We suggested a
few years ago (43) that such processes might occur via pentacoordinate structures involving
planar organolithium ring intermediates. This has now been supported by further calculations.
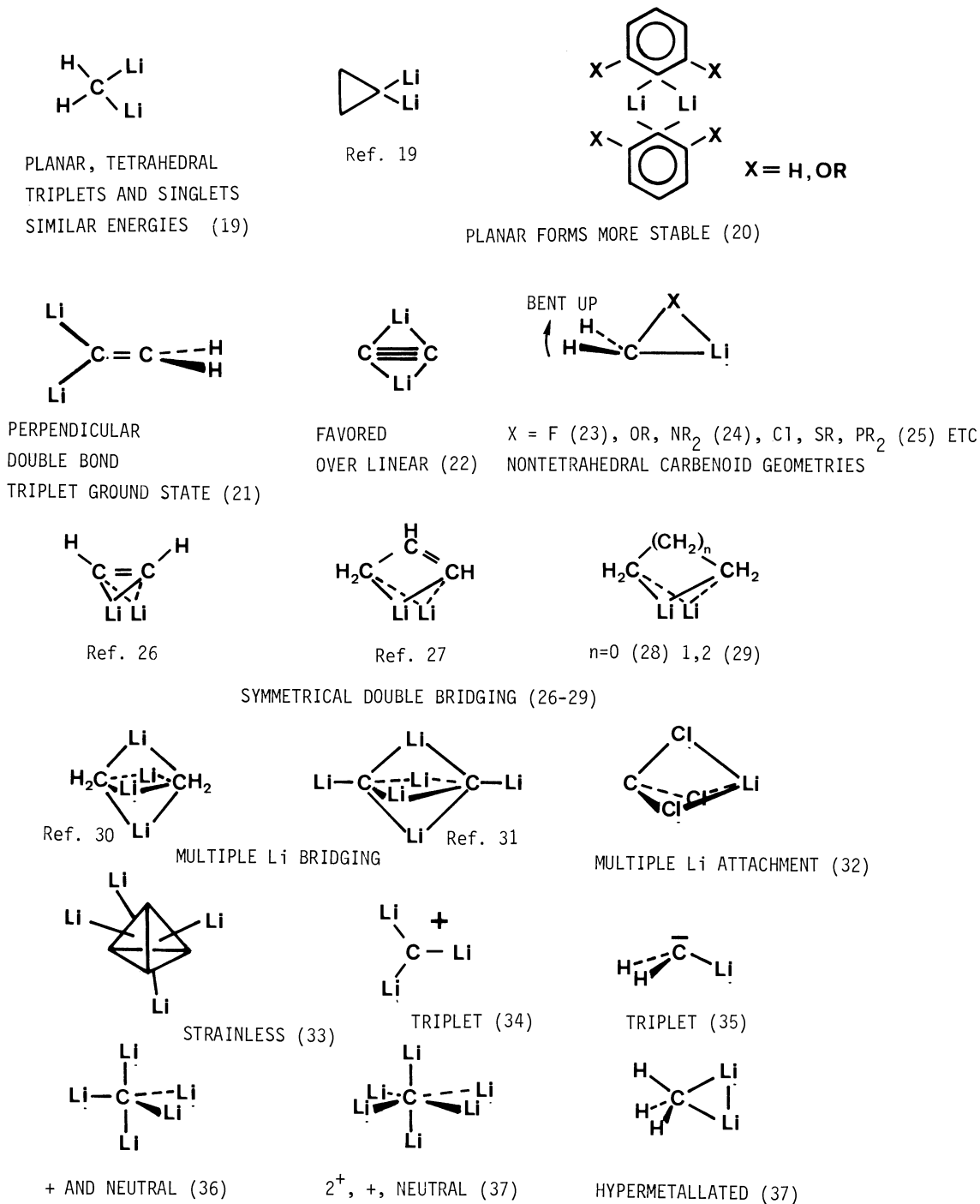The cyclic tetramer, examined with two planar CH_3 groups for computational simplicity, lies

PLANAR, TETRAHEDRAL
TRIPLETS AND SINGLETS
SIMILAR ENERGIES (19)

Ref. 19

PLANAR FORMS MORE STABLE (20)

X = H, OR

PERPENDICULAR
DOUBLE BOND
TRIPLET GROUND STATE (21)

FAVORED
OVER LINEAR (22)

BENT UP

X = F (23), OR, NR_2 (24), Cl, SR, PR_2 (25) ETC
NONTETRAHEDRAL CARBENOID GEOMETRIES

Ref. 26

Ref. 27

n=0 (28) 1,2 (29)

SYMMETRICAL DOUBLE BRIDGING (26-29)

Ref. 30

Ref. 31

MULTIPLE Li BRIDGING

MULTIPLE Li ATTACHMENT (32)

STRAINLESS (33)

TRIPLET (34)

TRIPLET (35)

+ AND NEUTRAL (36)

2^+, +, NEUTRAL (37)

HYPERMETALLATED (37)

FIGURE 1.   SOME PUBLISHED RULE-VIOLATING LITHIUM STRUCTURES
DISCOVERED CALCULATIONALLY

only 28.6 kcal/mol above the global minimum in energy. Roughly 20 kcal/mol should be required for the planarization of a single methyl or, in the systems studied experimentally, by a -CH₂R* group with the R* oriented on the outside. This agrees quite well with the experimental values around 15 kcal/mol (42).

All calculational studies (39,40) of the tetrahedral tetramer find eclipsed arrangements of each methyl group above a Li₃ face to be preferred over the staggered conformations found in the three crystal structures of methyllithium tetramer as well as that of (CH₃Na)₄ (8). At our best calculational level, the eclipsed form is favored by 6.9 kcal/mol (or 1.7 kcal/mol per methyl group). This indicates that other effects are operating in the crystal structures, where each lithium exhibits further assoiation with a donor solvent or a second tetrameric aggregate. The favored staggered arrangement of the isolated tetramer is due to attractive H...Li inter-actions; this general effect also characterizes other lithium structures (44).


ECLIPSED CH₃'S 0.0

STAGGERED CH₃'S 6.9
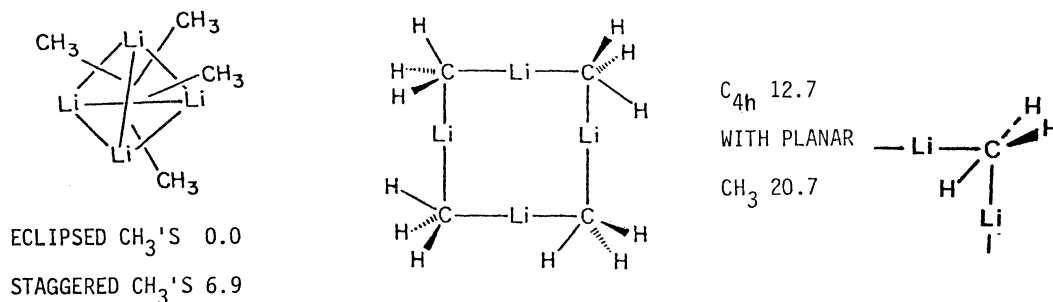
A number of X-ray structures of dimers, tetramers, and hexamers are available (5-15). The most recent work involves substituted lithioacetylenes; either dimers or tetrahedral tetramers are favored depending upon the ligand. X-ray (9b) and nmr (45) results agree. E. Kaufmann's Masters Thesis reports a comprehensive theoretical examination of many organolithium oligomers (38b).

We have emphasized (46), as has Streitwieser (47), that multiple metal bridging should be an extremely common feature of "polyanion" systems. The electrostatic advantages of alternating plus and minus charges in square or, even better, in rhomboid arrangements are quite large. Double lithium bridging is the intramolecular equivalent of dimerization. The 3-21G//3-21G data shown provide a comparison. The cyclization energies, $\underline{1} \rightarrow \underline{2}$, converting extended 1,3-di-lithiopropane and 1,4-dilithiobutane (29), into doubly bridged ($\underline{2}$) conformations, approach the dimerization energy of methyllithium as the methylene chain between the two lithium atoms be-comes longer.
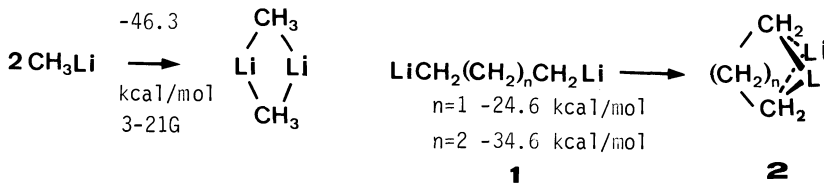

Doubly bridged dilithium compounds (like $\underline{2}$) are known as solvent- or chelate-stabilized forms in several instances discussed below and a great number of unrecognized possibilities have been described in the literature (46). Alternatively, dimerization to give tetrahedral aggre-gates might occur. Our calculated (MNDO) structure of $\underline{2}$ (n=1), shown in $\underline{3}$, is like (CH₃Li)₄ but has opened tetrahedral edges (29).


3
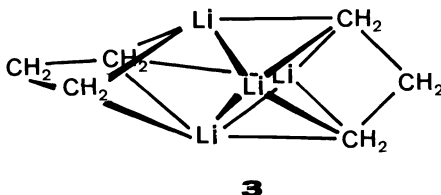
ALLYLLITHIUM AND ALLENYLLITHIUM

As the calculated lithium structures (e.g., Figure 1) refer to hypothetical motion-free mon-omers, some experimentalists have questioned the relevance of these results to the struc-tures of lithium compounds in solution and other condensed phases (48). Such monomer calcu-lations do appear to have considerable general significance. Several specific examples may now be cited. The first of these is allenyllithium; the fully optimized 4-31G structure (4) published in 1979 (49) shows a bent carbon skeleton (<CCC = 161.4°), an HC_1C_2 angle of 130°, and C-C bond lengths of 1.28 and 1.34 A. Dietrich has now determined the first two crystal structures of allenyllithium derivatives on compounds with t-butyl and -C≡C-t-Bu side chains, differently arranged (7b). Both dimeric structures also have attached solvent mole-cules, but the key geometrical features, even including the CCR angle, are remarkably close to our calculated values. See 4 for some comparisons. The C-Li distances are' longer in the crystal than calculated for the monomer, but this is due to the effect of association men-tioned earlier.

The geometry-optimzed allyllithium structure, first calculated in 1978 (50), shows a symmet-rically bridging lithium and a remarkable deviation of the hydrogens from the carbon plane. These features, the bending of the middle H towards and the two inner H's away from the metal, are supported by higher level 3-21G calculations (5) and by analogous X-ray structures of π-allylnickels (51) and of dilithiohexatrene, a "bis-allyl anion" system (52). An experimental group's attribution of the unusually small $^{13}C_2$-H coupling constant to even more pronounced hydrogen bending (48) has now been shown to be incorrect; the widening of the CCC angle characteristic of allyl anion systems is responsible instead (50, 53). The only available X-ray structure of allyllithium is that of a polymer (54), but we can expect further results shortly. Both allyllithium and allenyllithium represent simple examples of 1,3-bridging involving π systems Benzyllithium and fluorenyl lithium, studied by Stucky (10), both favor 1,3-bridging over alternative multiple association. Both types of bridging are typical for lithium compounds in π systems.

4

6

7
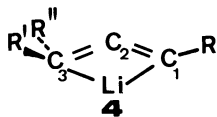
| PARAMETER	BASIS SET		X-RAY (7b)	
	4-31G (49)	6-31G*	A	B
C_1C_2	1.277	1.269	1.29	1.281
C_2C_3	1.341	1.344	1.33	1.365
$<C_1C_2C_3$	161.4°	160.9°	166°	165.6°
$<RC_1C_2$	130.0°	127.9°	131°	129.2°

5
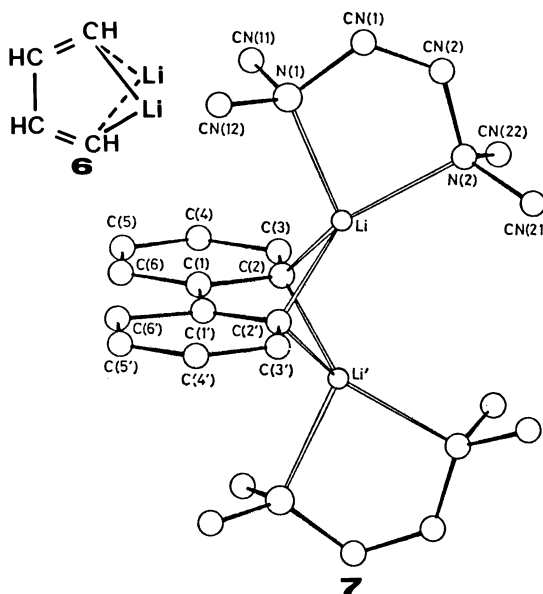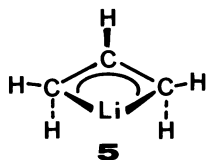
o,o'-DILITHIOBIPHENYL

A number of systems related to cis,cis-1,4-dilithiobutadiene are known experimentally. Our calculational study indicated the symmetrically doubly bridged structure (6) should be much more stable than any alternative geometry (55). "Möbius-Hückel" aromaticity contributes, but the electrostatic interactions discussed above are of comparable if not greater importance. Based on these considerations, we predicted (55, 56) that o,o'-dilithiobiphenyl should also favor symmetrical doubly bridging. This was fully confirmed by Schubert's X-ray structure (7); both rings are perfectly co-planar (57).

The extra stabilization due to double bridging is considerable and provides thermo-chemical driving force for special chemical reactivity. The presence of a lithium atom in a molecule often leads to the "activation" of another hydrogen in an adjacent position. Thus, we have shown that biphenyl can be dilithiated directly with TMEDA-activated n-BuLi to give 7 (56). The first ortho lithiation has many precedents. In this instance, we suggest that association of a butyllithium aggregate with the π face of one of the phenyl rings may activate the ad-

jacent ortho position of the second phenyl ring in a twisted conformation. In a separate experiment, o-lithiobiphenyl undergoes a second lithiation in the o'-position. The MNDO calculated structure of o-lithiobiphenyl (8) indicates a special activation of the hydrogen adjacent to lithium: This C-H bond is lengthened, the positive charge on hydrogen is enhanced and the LUMO coefficient is largest. These indices, found in a number of other structures we have calculated, have lead without failure to the prediction of the experimental second lithiation sites.

However, the mechanism of the actual second lithiation probably involves incorporation of the substrate into a mixed aggregate with butyllithium. This brings the lithiating moiety into the proximity of the activated hydrogen and facilitates reaction To gain more experimental information, Dietrich (7a) determined the structure of o-lithiobiphenyl (9). Like the related structure of phenyllithium (58), 9 is a dimer with TMEDA solvation. In general agreement with our mechanistic postulates, the biphenyl units in 9, in contrast to 7 are twisted. The lithium distance to the o'-CH group is moderately large in the crystal, but further association of butyllithium in the aggregate undergoing H/Li exchange explains the observed result. We note that new aryllithium X-ray structures are tetrameric or involve incorporation into mixed tetrameric aggregates (13, 15e).
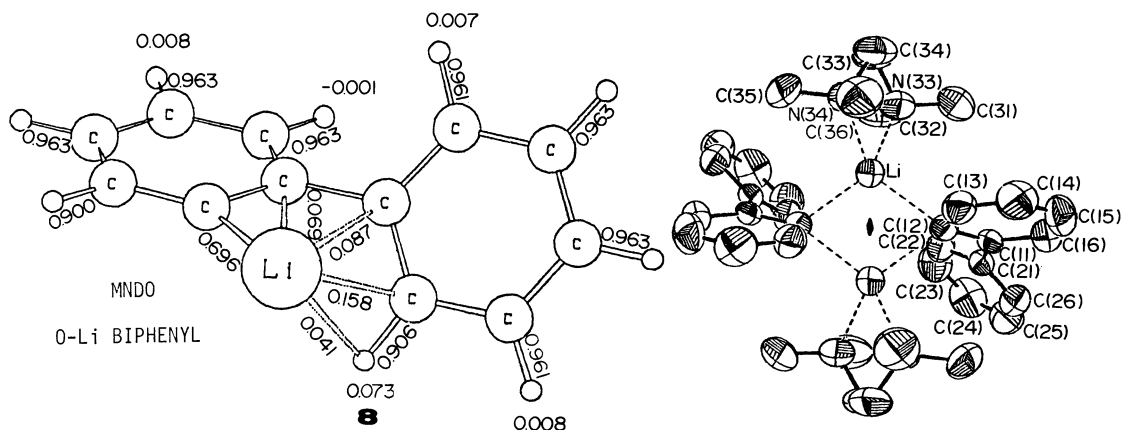

DOUBLE LITHIUM BRIDGING

Double lithium bridging is expected to be an extremely common feature of the structures of polylithium compounds (46, 47). We have reported numerous 1,2-, 1,3-, and 1,4-examples in calculational studies (Figure 1). In particular, we predicted that 1,4-dilithio-cis-2-butene, 10 (this compound is known (59) but no X-ray determination is available), should have a symmetrically doubly bridged structure (46). While these calculations were in progress, an X-ray structure showing the expected features was published on a related system (11) by Lappert's group (11a). Dietrich (7e) has now obtained a very similar structure on a simpler derivative, dilithiated 1,4-diphenyl-cis-2-butene (12). The crystal structure is disordered since the cis-2-butene moiety lies on different sides in different molecules. The X-ray determination thus indicates a quasi-central six-membered ring, as indicated by the dotted lines in 12. This quasi-ring, as well as the two phenyl groups, all lie in a perfect plane. Both lithiums do not adopt the highest possible symmetry, (C_{2v}), but tilt in opposite directions (roughly, a C_2 point group). This feature is reproduced by MNDO calculations, which also indicate the cis butene arrangement (12) to be favored over the trans for the dilithium complex, but not for the dianion (7e).
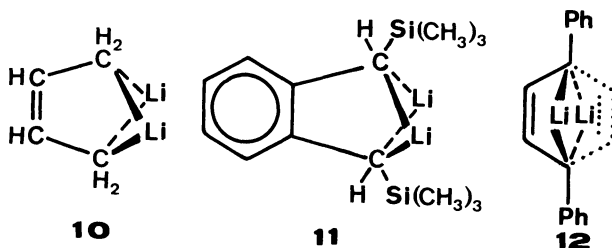
0,0'-DILITHIODIPHENYLETHER

A further example of double bridging is provided by Dietrich's (7d) crystal structure of o,o'-dilithiodiphenyl ether 13, a compound also prepared by Neugebauer by direct dilithiation of diphenylether. Activation of an ortho position by an adjacent oxygen function is well precedented (1-3); the second lithiation is analogous to the situation discussed for biphenyl (56). The twisting of both phenyl rings in the crystal structure is again reproduced well by MNDO calculations. Such twisting is also indicated calculationally on simpler models. In some of these, the oxygen has been replaced by a CH_2 group. Hence, there is little indication that six π electron aromaticity contributes significantly to the structure of 11; electrostatic considerations provide an adequate explanation. Actually the first suggestion of such double bridging arrangements between two attached aromatic rings was proposed as an explanation for the ready racemization of 2,2'- and 4,4'-dilithium-3,3'-bithienyl derivatives (60). While no X-ray structures are available, Kos's MNDO calculations agree completely.
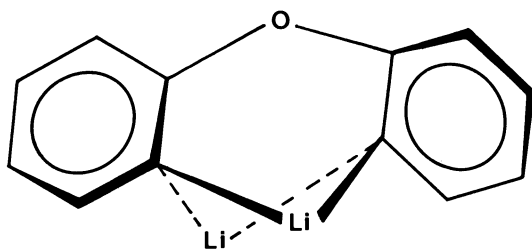
13
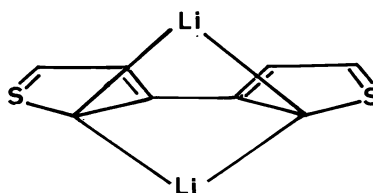
C_3Li_4 AND C_3Li_6

In a classic investigation, West showed that perlithiated propyne with excess butyllithium to give one of the most stable lithiocarbons, C_3Li_4 (61, 62). Although there is still no detailed experimental information available, our calculations indicate a remarkable structure with a W-shaped LiCCCLi backbone and two symmetrical bridging lithiums (63). The geometry, now optimized at 3-21G, is shown in 14. The structure actually is easy to understand since the parent C_3^{4-} anion is isoelectronic with CO_2. In C_3Li_4 two lithiums are associated with the terminal acetylene-like carbons, $LiCCCLi^{2-}$. As in allenyllithium (4) or in allyllithium (5), the remaining lithiums are bridged in a 1,3-manner. However, the bridging involves two sets of cumulene orbitals orthogonally arranged. The angle between the middle carbon and the two bridging Li's is only slightly widened from the idealized 90° value.

C_3Li_4 - 3-21G STRUCTURE
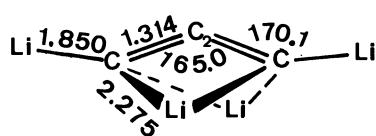
<LiC$_2$Li 102.5°, C$_2$Li = 1.968
14

C_3Li_6 - MNDO STRUCTURE
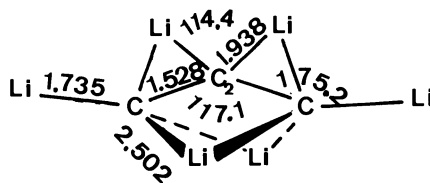
<LiC$_2$Li = 72.4°, C$_2$Li = 2.144
15

The "bare" carbon atom, C-2 in C_3Li_4 (14), is remarkable. All nearest neighbours are arranged in a roughly pyramidal, C_{2v} manner extending in one direction away from this carbon. Further association at the vacant site should be favorable; e.g., $(C_3Li_4)_n$ oligomers, which have been observed mass spectroscopically, may involve association in some head-to-tail manner. In addition, the best MNDO structure (15) we have been able to find for C_3Li_6, another lithiocarbon stoichiometry observed by Lagow (64), is not based on cyclopropane but on C_3Li_4 with an additional Li_2 molecule attached to the bare carbon (65). The structure shown has a planar tetracoordinate carbon, but is indicated to be much more stable than the "tetrahedral" alternative! While all lithiocarbons are expected to be associated in condensed phases, dimer or oligomer structures will also be unusual, and one awaits the results of experimental studies with interest. Because of the large number of possibilities, it is not easy to make structural predictions calculationally on larger systems at theoretical levels high enough to afford some certainty.

C_5Li_4

These reservations notwithstanding, we have examined possible geometries for C_5Li_4, a compound also obtained by West and by Klein experimentally by perlithiation of penta-1,3-diyne (66). There are a great number of possible ways in which four lithium atoms can be arranged around a C_5 nucleus. A thorough calculational study would require all these possibilities to be tested, but it is also possible to make accidental discoveries calculationally. Thus, Kos (65) began an MNDO investigation with the various classical structures, e.g., 16, but did not impose any symmetry restrictions. Under such circumstances, geometry optimization can often lead to very different structures provided no energy barriers need to be overcome. Indeed, 16, optimized to 17, a really beautiful structure electronically as well as aesthetically! The $LiCCCCLi^{2-}$ system with two terminal acetylenic lithiums, suggested as a possibility (66), is present, but it is strongly bent. Two orthogonal 6 π electron systems accommodate each of the two anions, an example of "double aromaticity in two orthogonal planes" (67). One 6 π system is perpendicular to the plane and, if the orbital on lithium is at all effective, describes an aromatic ring system. The other 6 π system lies in the ring plane and interacts with the in-plane s and p orbitals of the enclosed lithium atom. The remaining lithium at C-3 adopts a classical geometry, but affords a good opportunity for association with other molecules.

PERPENDICULAR   IN PLANE
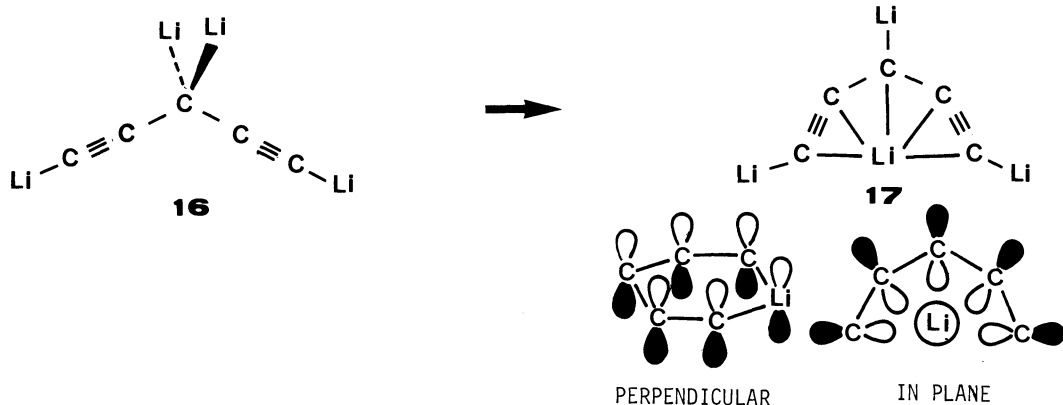
As is apparent from 17, only two of the lithiums are essential to the electronic structure, this was shown calculationally by replacing both terminal lithiums by hydrogen, and experimentally by doing the same with t-butyl. This was also suggested by the prior remarkable experimental observation that hexa-2,4-diyne was metallated to the trilithio derivative, but all the hydrogens were replaced on a single carbon (66). Structure 17, with one terminal Li substituted by CH_3, rationalizes this nicely. Indeed, the starting material which Dr. Neugebauer chose, terminally substituted by two t-butyl groups, was lithiated smoothly in a stepwise manner. The monolithio derivative was crystalline, but unstable, and rearranged readily into the allenyllithium, t-BuC≡C-C=C=CHtBuLi(18), whose structure has already been discussed. To preclude this rearrangement, a methyl group was attached to C_3; the crystal structure (7b) of the resulting monolithium compound (see 4) did not resemble our idealized calculated structure, 19, but favored the unsymmetrical allenyllithium geometry already discussed. In solution, the ^{13}C nmr signals of 19 are symmetrical, but rapid equilibration is indicated by the identity of the observed chemical shifts with average values of allenyllithium and uncomplexed acetylene models.

18
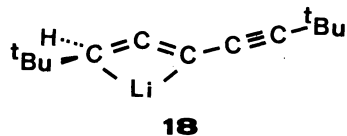
Me$_3$Si groups are known to stabilize carbanions well (25). Replacement of methyl by this group leads to a monolithium derivative whose ^{13}C chemical shifts are indicative of a symmetrical rather than time-average structure (68). Dietrich's X-ray analysis (7c) agrees with this conclusion; the structure is that of an unsolvated dimer, 20. Although we had not considered the dimers calculationally, the relationship of 20 to 19 is clear.

19

20
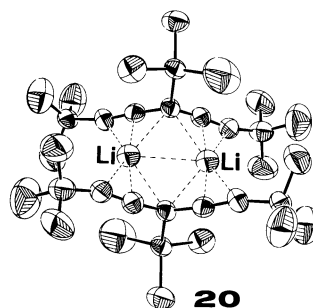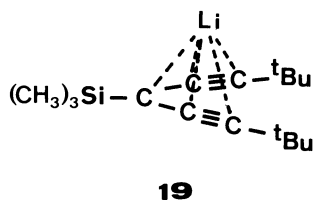
Finally, Professor E. Weiss was able after considerable effort to solve the structure of the dilithium compound, (tBuC≡C)$_2$CLi$_2$, a tetramer with one ether solvent molecule per monomer (9a). While the structure, 21, has symmetry, individual molecules have different environments. However, the similarity between the pentadiyne moiety shown in the lower front (and upper rear) with the centrally located lithium coordinating with both triple bonds is in striking agreement with the structural prediction of 17. The two other penta-diyne moieties interact differently with lithium atoms.
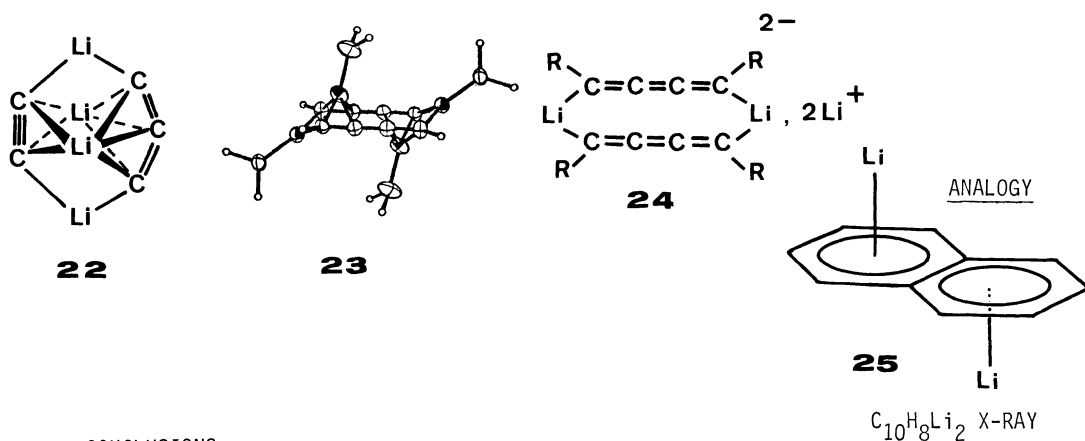
[(tBuC≡C)$_2$CLi$_2$·THF]$_4$

21
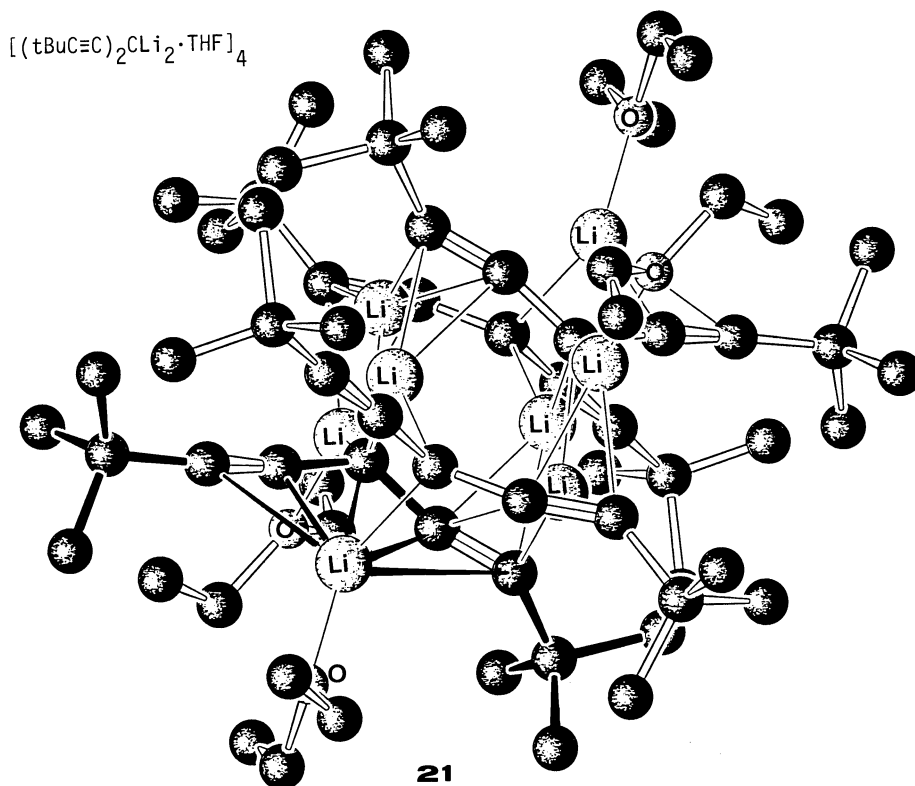
Using MNDO, Kos examined a large number of C$_5$Li$_4$ alternatives but none, with one exception was significantly better than 17. The exception, 22, is some 37 kcal/mol more stable, but appears at first glance to be absurd: two of the C-C bonds are broken. However, quantum mechanical programs often understand chemical bonding better than chemists. Semi-empirical programs may err, but even "wrong" answers make some sense. Closer inspection of structure 22 reveals that it is comprised of C$_2$Li$_2$ and C$_3$Li$_4$ units sharing two lithiums in common. Lagow has shown that pyrolysis of lithiocarbons leads first to C$_3$Li$_4$ and then to C$_2$Li$_2$ (62), the only stable binary combination in the phase diagram of carbon and lithium. This means that pyrolysis of lithium compounds will lead to cleavage of C-C bonds by insertion of lithium atoms, just as implied by 22.

A DILITHIO BUTATRIENE

The last report concerns a particularly pleasing structure, also a cumulene derivative. A substituted 1,4-butatriene "dianion" was prepared by Dr. Neugebauer by adding lithium metal to 1,4-di-t-butyldiacetylene. Quenching reactions gave cis and trans 1,4-substituted buta-triene products. However, Dr. John Stezowski's (68) crystal structure $\underline{23}$ shows clearly that the dilithiated intermediate has a cis configuration. Inversion (which should be rapid in any butatrienyl monoanion intermediate) occurred during the quench reactions.

Structure $\underline{23}$ is our chief concern here. The dimeric character and the nearly parallel ar-rangement of the cumulene units are apparent. The four lithiums bridge between these linear units in a symmetrical (C_{2h} point group) but peculiar way. Two of the lithiums coordinate to only two carbons while the two other lithiums bind simultaneously on opposite sides to four carbons. Each lithium is THF solvated. We did not try to predict this structure calculation-ally, but quite different starting geometries, tested subsequently with MNDO, rearranged upon optimization into $\underline{23}$. Obviously, we are dealing with a favorable bonding arrangement. The basic electronic structure, a cis, planar 1,4-butatriene dianion, has two orthogonal π units containing four and six electrons. Two lithium cations will bind two of these units together by bridging to give the planar moiety, $\underline{24}$. As in the experimental structure of di-lithionaphthalene, $\underline{25}$,(10), the two additional lithiums in $\underline{23}$ bridge opposite faces by in-teracting with as many carbons as possible and avoiding competition. The two lithiums in $\underline{24}$ are also bent out of the plane in $\underline{23}$ as a consequence.

22   **23**

$$\begin{array}{c} {}^{2-} \\ \begin{array}{c} R \\ \end{array} C{=}C{=}C{=}C \begin{array}{c} R \\ \end{array} \\ Li \qquad\qquad Li \;,\; 2\,Li^{+} \\ \begin{array}{c} R \\ \end{array} C{=}C{=}C{=}C \begin{array}{c} R \\ \end{array} \end{array}$$

24

<u>ANALOGY</u>

25

$C_{10}H_8Li_2$ X-RAY

CONCLUSIONS

The structures of lithium compounds are very different from their hydrogen counterparts and are characterized by polar character, electrostatic interactions, and multicenter covalent bonding. Unlike the directed and strongly covalent bonds involving hydrogen, lithium prefers to interact with many atoms similtaneously. Fluxional systems with rather flat potential energy surfaces are common. Bridged structures are the rule, not the exception, and multiple bridging is a characteristic feature of polylithium compounds. Neither the coordination number nor the geometrical arrangement of ligands around lithium is of dominating importance. Tetrahedral tetracoordination is common, but lower and especially higher lithium coordination are often found especially with π systems and polydentate ligands. As with electron deficient species in general, the weakness of any given interaction or bond is made up by the larger number of such contacts.

Theoretical calculations have proven their worth as exploratory tools in this area, and are especially important when detailed experimental information is not easily achieved or when energies are required.

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