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How Advantageous is the Intramolecular Aggregation of 1,4-Organodilithio Compounds ?

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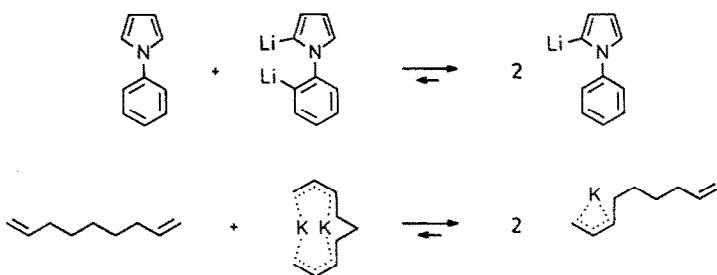
Abstract: 1,11-Dilithio-5,5,7,7-tetramethyl-5,7-dihydrodibenz[*c,e*]joxepin (3) is a conformationally confined analogue of *o,o'*-dilithiobiphenyl (1). A temperature variable nmr study of this model compound, monitoring the coalescence of its diastereotopic methyl groups, has revealed a barrier of about 12 kcal/mol to planarization, just 2 kcal/mol less than that found with the metal-free heterocycle. Thus, the energetic benefit of intramolecular aggregation of *o,o'*-dilithiobisaryls is found to be significantly smaller than predicted by *ab initio* calculations.

Organodimetal compounds are a widespread class of reactive intermediates ¹. Several of them can be conveniently generated by the addition of alkali or alkali-earth metals to acetylene, diene or styrene type hydrocarbons. More frequently, permutational processes are employed such as two-fold halogen/metal, metalloid/metal or hydrogen/metal exchange reactions. Under such circumstances the second metal is generally found to be incorporated more slowly than the first one. There are, however, several mechanistically intriguing exceptions to this rule. In particular, in media of low polarity, a first hydrogen/metal interconversion ("metalation") reaction may be followed by a second, much faster one. For example, diphenyl ether gives bis(2-lithiophenyl) ether ², thiophene gives 2,5-dilithiothiophene ³ and *N*-methylpyrrole gives a mixture of 2,4- and 2,5-dilithio-*N*-methylpyrrole ³. In all these cases, little if any monometalated products are detected besides the preponderant dimetalated ones even when only stoichiometric amounts of reagent are used. The relative acceleration of the second metalation step is reminiscent of the E2cb mode where rapid β -elimination occurs only after preceding α -deprotonation ⁴. In addition, preferential or exclusive formation of dimetalated products must not always be a result of two consecutive metalation processes. The introduction of the first metal, the slow step, may also be accomplished as a halogen/metal exchange ⁵ or a nucleophilic addition ^{6,7} reaction instead.

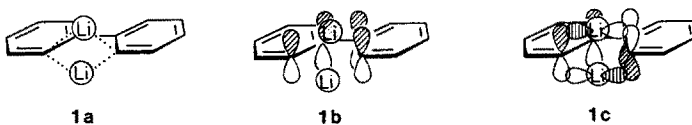
We have rationalized the spontaneous generation of organodimetal species by assuming initial mixed aggregate formation ⁸. If this concept is correct, the second step would be brought about under quasi-intramolecular conditions and energetic expenses for activation entropy would hence be avoided. More recently, however, this kinetic view of the problem was progressively replaced by static considerations, emphasizing the advantage of the intramolecular aggregation of suitably tailored dilithio compounds through two symmetrical carbon-metal-carbon bridges ^{9,10}. In this way, the ground state of the dimetalated species would be entropically favored and this would provide a significant extra driving force for its formation ⁹.



Intramolecular aggregation requires the substrate to be able to adopt appropriate shapes that facilitate a coiling of the dimetal-bearing structural segment. For example, any direct interaction between the two organometallic centers of 2,5-dilithiothiophene is geometrically precluded. However, even in the absence of such constraints, intramolecular aggregation does not appear to be energetically attractive. As we have been able to demonstrate by transmetalation experiments, α -lithio-*N*-phenylpyrrole is thermodynamically more stable than an equimolar mixture of *N*-phenylpyrrole and α,o -dilithio-*N*-phenylpyrrole (although the dimetalated species is obtained almost exclusively when an excess of *N*-phenylpyrrole is treated with *N,N,N',N'*-tetramethylethylenediamine-complexed butyllithium in a solvent mixture of diethyl ether and hexane, irrespective of the stoichiometric substrate-reagent ratio) ¹¹. Similarly, (*Z,Z*)-2,7-nonadienylenedipotassium, selectively prepared in hexane suspension, equilibrates with 1,8-nonadiene in tetrahydrofuran solution to give mainly the monometalated (*Z,Z*)-2,7-nonadienylpotassium ¹².

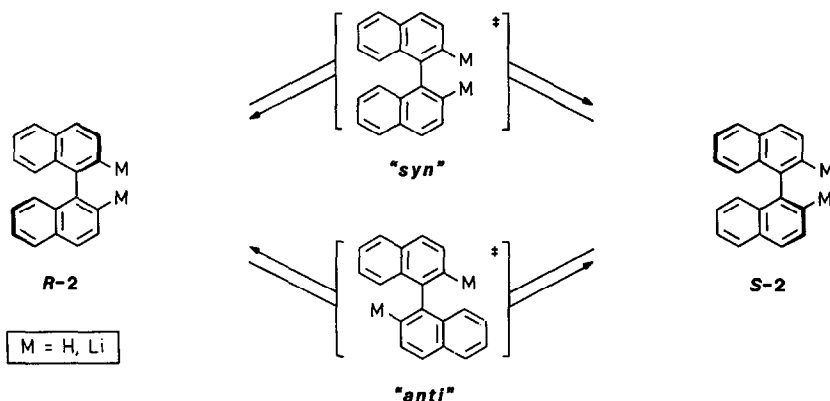


The equilibration-by-transmetalation approach fails with arene type substrates due to their low acidity. On the other hand, *o,o'*-dilithiobiphenyl (**1**) has become a reference standard. According to extensive theoretical investigations, an extraordinarily large stabilization was predicted to result from intramolecular aggregation (**1a**) and, in addition, from orbital symmetry matched "Möbius-Hückel aromaticity" (**1b** + **1c**) ¹³. The two symmetrical carbon-lithium-carbon bonds were calculated to be strong enough to make the coplanar, doubly bridged structure, if solvent-free, 17 kcal/mol ¹⁰ more favorable than the propeller-like twisted conformation. If the dilithio species **1** is complexed with two molecules of ethylenediamine (EDA), this value was estimated to decrease to 9 kcal/mol ¹⁴. Biphenyl itself is known to adopt approximate coplanarity in the crystalline state ^{15, 16}, whereas its rings display a dihedral angle of about 40° in the gas phase or in solution ¹⁷.

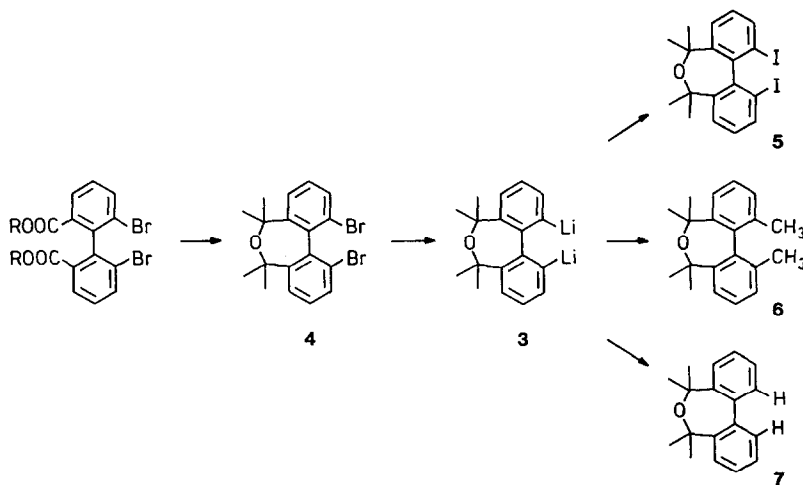


If the computed numbers were reliable, one would have to assume an intermediate value of some 12 kcal/mol for ether solvated *o,o'*-dilithiobiphenyl. Such a huge aggregation energy would inevitably be reflected in a drastic change in the reactivity of the bridged species **1** when compared with ordinary aryllithium compounds which are known to be only loosely aggregated ^{18 - 21}. However, the beautiful preparative work accomplished by Wittig ²² and Hellwinkel ^{23, 24} with *o,o'*-dilithiobiphenyl does not reveal any unusual chemical behavior associated with this key reagent. Under these circumstances it seemed desirable to determine the efficiency of intramolecular 1,4-aggregation *experimentally*. Related work had been

already carried out by Murdoch²⁵ who found 2,2'-dilithio-1,1'-binaphthyl (**2**) to retain its atropisomerism in ethereal solution at temperatures up to -45 °C. Unfortunately, the significance of these findings was compromised by an ambiguity about the transition state of the racemization process. A comparison of the racemization barriers between the hydrocarbon and its *o,o'*-dimetalated derivative would be meaningful only if the lowest energy path involves a coplanar species with the two lithium atoms facing each other ("*syn*"), rather than each of them facing an axis-remote ring ("*anti*").

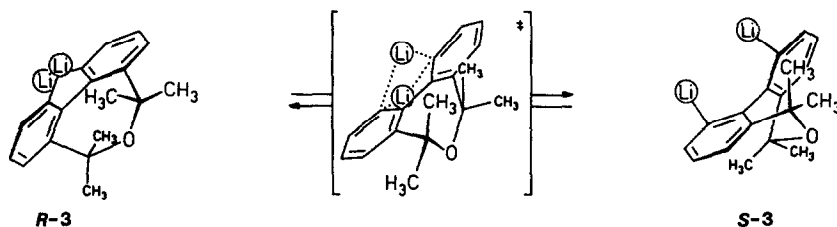


Therefore, we have selected the rotationally restricted 1,11-dilithio-5,5,7,7-tetramethyl-5,7-dihydrodibenz[*c,e*]oxepin (**3**) as a model compound. The dilithio species **3** was easily generated from the corresponding dibromide **4** by halogen/metal exchange with *tert*-butyllithium and was trapped with iodine to afford the diiodo compound **5** (51%) and with dimethyl sulfate to afford the hexamethyl substituted compound **6** (94%), while the unsubstituted parent ring system **7**²⁶ was produced upon protonolysis (81%). The dibrominated precursor **4** was prepared from dimethyl 5,6-dibromodiphenoate²⁷ in a two-step sequence (35%).



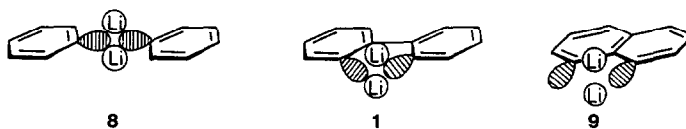
The conformational mobility of the metal-free dibenzoxepin derivative **7** had already been studied previously and a torsional barrier of 13 kcal/mol had been derived from variable temperature nmr

measurements²⁸. The same motion of the dilithio species **3** should encounter a barrier lowered precisely by the amount of energy gained by intramolecular aggregation, the aryl-aryl coplanarity at the transition state allowing optimum carbon-lithium-carbon bridging whereas at the twisted ground state (*R*-**3** and *S*-**3**) the lithium atoms are too far away from the neighboring ring *ortho*-position (estimated C-Li' distance 3.2 - 3.3 Å) to make the interaction attractive. The torsional barrier of our dilithio species **3** was found to fall in the range of 12.0 - 12.5 kcal/mol while our reinvestigation of dibenzoxepin parent compound **7** resulted in a slight increase of the literature value, the barrier amounting now to 14.0 - 14.5 kcal/mol. Thus, we have to conclude that the intramolecular aggregation of *o,o'*-dilithiated biaryls provides an energy gain of hardly more than 2 kcal/mol.



Then why do *ab initio* calculations produce such misleading data? We suspect two factors to be simultaneously responsible.

Current quantum mechanical methods tend to overestimate the ionicity of carbon-lithium bonds²⁹ while all physical and chemical evidence points to a significant amount of covalent character³⁰. If electrostatic attraction between carbanions and metal cations was the only important contributor to stability, geometry would play a minor role. The spatial arrangements of *o,o'*-dilithiobiphenyl (**1**) and the orientationally extreme cases phenyllithium-dimer (**8**) and 1,8-dilithionaphthalene (**9**; or 5,6-dilithioacenaphthene)³¹ would be qualitatively equivalent. Consequently, the entropy-economic *intramolecular* aggregation would inevitably have to outperform the analogous intermolecular process. However, if one conceives the organometallic bond as a directional, partially covalent interaction, only the dimer **8** can offer an optimized structure. Shapes **1** and, worse, **9** oblige the lithium atoms to occupy an eccentric position with respect to the orbital expansion. The resulting loss in aggregation enthalpy is apparently big enough to compensate for the gain in entropy due to intramolecularity.



The computational treatment¹⁴ makes a second misjudgment when comparing the EDA complexes of both the doubly bridged, coplanar and the non-aggregated, twisted structure of *o,o'*-dilithiobiphenyl. The pronounced tendency of lithium to achieve tetracoordination^{30, 32} is satisfied only in the former case. In the twisted form, however, each lithium is surrounded by only three ligands. The empty binding sites would likely be occupied by additional solvent molecules, thus increasing the stability of the non-aggregated species.

One last question remains to be addressed. Does the conclusiveness of our study not suffer from the presence of lithium bromide in the organometallic solution? Soluble salts are inevitably formed as by-products when the halogen/metal exchange is carried out with *tert*-butyllithium. If lithium bromide would get associated with the ground state, but not the coplanar transition state, the torsional barrier would be artificially raised. In our opinion, this complication can be ruled out, since aryllithiums, when dissolved in neat tetrahydrofuran, exhibit little tendency to form mixed aggregates with lithium salts³³. Nevertheless, we shall attempt to generate salt-free *o,o'*-dilithiobiphenyl (3) and to repeat our temperature variable nmr work with such samples.

EXPERIMENTAL

1. Generalities

The standard equipment and methods used throughout this work have been described in a previous related article¹¹. - *Nuclear magnetic resonance spectra* of hydrogen nuclei were recorded at 400 MHz with a Bruker ARX 400 spectrometer. Deuteriochloroform was used as the solvent for the routine experiments. The chemical shifts given refer to the signal of the internal standard tetramethylsilane (δ 0.00). The kinetic studies at variable temperatures were performed in perdeuterated tetrahydrofuran, chemical shifts referring to the residual signal of the non-deuterated tetrahydrofuran (δ 3.58). The absolute values of the temperatures were determined by means of a methanol probe³⁴. Coupling constants (*J*) are measured in Hz. Coupling patterns are described by these abbreviations: s (singlet), d (doublet), t (triplet), q (quadruplet), td (triplet of doublets) and m (multiplet).

2. Procedures and Products

6,6'-Dibromobiphenyl-2,2'-di(1-methylethanol) : Dimethyl 6,6'-dibromobiphenyl-2,2'-dicarboxylate²⁷ (10 g, 23 mmol) was added to a solution of methylmagnesium chloride (0.19 mol) in tetrahydrofuran (62 mL) at 25 °C. After 3 h of heating to reflux, the cold reaction mixture was poured into a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with ether (3 x 50 mL) and the combined organic layers were washed with brine (0.10 L). After evaporation of the solvent, 9.9 g (100%) of crude product was collected; mp 122 - 127 °C (after trituration in hexane and sublimation). - ¹H-NMR : δ 7.59 (2 H, dd, *J* 7.5, 1.0), 7.39 (2 H, dd, *J* 7.5, 1.1), 7.21 (2 H, t, *J* 7.5), 2.69 (2 H, s), 1.65 (6 H, s), 1.50 (6 H, s). - MS : 431 (0.5%, *M*⁺[⁸¹Br₂] + 1), 395 (3%), 82 (100%). - Analysis : calc. for C₁₈H₂₀Br₂O₂ (428.16) C 50.49, H 4.71; found C 50.59, H 4.66%.

1,11-Dibromo-5,5,7,7-tetramethyl-5,7-dihydrodibenz[*c,e*]oxepin (4) : A suspension of the crude diol obtained above (9.9 g, 0.02 mol) in 2 M sulfuric acid (0.30 L) was heated to reflux for 3 h. The mixture was extracted with ether (4 x 50 mL). The combined organic layers were washed with a saturated aqueous solution (0.20 L) of sodium carbonate and brine (0.10 L). After evaporation of the solvent, 7.9 g of a yellow oil were obtained. Elution with 1 : 30 (v/v) mixture of diethyl ether and pentane from silica (250 g) gave 3.4 g of white crystals; 35% (with respect to the diester starting material); mp 116 - 118 °C (after evaporation of the solvent); mp 107 - 109 °C (after sublimation). - ¹H-NMR : δ 7.66 (2 H, dd, *J* 7.9, 1.1), 7.45 (2 H, dd, *J* 7.9, 1.1), 7.24 (2 H, t, *J* 7.8), 1.59 (6 H, s), 0.93 (6 H, s). - MS : 412 (6%, *M*⁺[⁸¹Br₂]), 394 (100%). - Analysis : calc. for C₁₈H₁₈Br₂O (410.15) C 52.71, H 4.42; found C 53.02, H 4.43%.

1,11-Diiodo-5,5,7,7-tetramethyl-5,7-dihydrodibenz[*c,e*]oxepin (5) : Precooled (-75 °C) tetrahydrofuran (45 mL) and the dibromo compound 4 (3.0 g, 7.3 mmol) were consecutively added to *tert*-butyllithium (29 mmol), from which the original solvent (pentane) had been stripped off. After about 15 min of stirring at -50 °C, iodine (3.7 g, 15 mmol) was added. At 25 °C, unconsumed iodine was destroyed by adding a 10% aqueous

solution (40 mL) of sodium thiosulfate. The aqueous layer was extracted with hexane (3 x 40 mL) and the combined organic layers were washed with brine (0.10 L). Elution with pentane from basic alumina (40 g) gave 1.8 g (51%) of white crystals; mp 193 - 196 °C (after sublimation). - $^1\text{H-NMR}$: δ 7.95 (2 H, dd, J 7.7, 1.1), 7.50 (2 H, dd, J 7.6, 1.0), 7.07 (2 H, t, J 7.5), 1.58 (6 H, s), 0.92 (6 H, s). - MS: 504 (12%, M^+), 489 (74%), 377 (20%), 235 (100%). - Analysis: calc. for $\text{C}_{18}\text{H}_{18}\text{I}_2\text{O}$ (504.14) C 42.88, H 3.60; found C 42.59, H 3.36%.

1,5,5,7,7,11-Hexamethyl-5,7-dihydrodibenz[*c,e*]oxepin (6): Precooled (-75 °C) tetrahydrofuran (25 mL) and the dibromo compound **4** (1.6 g, 3.9 mmol) were consecutively added to neat *tert*-butyllithium (16 mmol). At -50 °C, dimethylsulfate (0.76 mL, 1.00 g, 8.0 mmol) was added. At 25 °C, unconsumed dimethyl sulfate was destroyed with a 20% aqueous solution (25 mL) of ammonium hydroxide. The aqueous layer was extracted with hexane (3 x 10 mL) and the combined organic layers were washed with brine (50 mL). The solvents were evaporated to afford 1.0 g (94%) of white crystals; mp 80.5 - 82.0 °C (after recrystallization from ethanol). - $^1\text{H-NMR}$: δ 7.3 (2 H, m), 7.2 (4 H, m), 2.11 (6 H, s), 1.59 (6 H, s), 0.87 (6 H, s). - MS: 280 (4%, M^+), 265 (100%). - Analysis: calc. for $\text{C}_{20}\text{H}_{24}\text{O}$ (280.41) C 85.67, H 8.63; found C 85.58, H 8.52%.

5,5,7,7-Tetramethyl-5,7-dihydrodibenz[*c,e*]oxepin (7): Precooled (-75 °C) tetrahydrofuran (12 mL) and the dibromo compound **4** (2.0 g, 4.9 mmol) were consecutively added to neat *tert*-butyllithium (20 mmol). At -50 °C, an ethereal solution (7.7 mL) of hydrogen chloride (10 mmol) was added. The material was absorbed on silica (40 g). Elution with pentane gave 1.0 g (81%) of white crystals; mp 85 - 86 °C (after recrystallization from methanol and sublimation; lit.²⁶: mp 92 - 93 °C "with a slight softening at 87 °C"). - $^1\text{H-NMR}$ (-50 °C): δ 7.51 (2 H, d, J 7.6), 7.5 (4 H, m), 7.4 (2 H, m), 1.59 (6 H, s), 0.96 (6 H, s). - $^1\text{H-NMR}$ (39 °C; coalescence temperature): δ 7.47 (2 H, dd, J 7.6, 1.0), 7.40 (2 H, dd, J 7.7, 1.8), 7.36 (2 H, td, J 7.2, 1.1), 7.29 (2 H, td, J 7.2, 1.6), 1.3 (12 H, m, broad).

3. NMR Studies

a) *Sample preparation*: The dibromide **4** (0.30 g, 0.73 mmol) was added to *tert*-butyllithium (2.9 mmol) dissolved in precooled (-75 °C) perdeuterated tetrahydrofuran (5 mL). At -50 °C, the sample was concentrated (to approximately 2 mL) by evaporation of more than half of the solvent (together with the isobutane and isobutene formed) under reduced pressure (0.01 mmHg). At -75 °C, the organometallic solution was diluted by the addition of fresh perdeuterated tetrahydrofuran (2.0 mL). By means of a precooled pipet, an aliquot (1.0 mL) was transferred into a nitrogen purged 5 mm NMR tube, which was plunged into liquid nitrogen before being sealed under vacuum. - $^1\text{H-NMR}$ (-100 °C) of **1,11-dilithio-5,5,7,7-tetramethyl-5,7-dihydrodibenz[*c,e*]oxepin (3)**: δ 7.8 (2 H, m), 6.9 (2 H, m), 6.7 (2 H, m), 1.43 (6 H, s), 0.91 (6 H, s). - $^1\text{H-NMR}$ (-7 °C, coalescence temperature): δ 7.8 (2 H, s broad), 7.0 (2 H, m), 6.8 (2 H, m), 1.2 (12 H, broad).

b) *Kinetic evaluation of the temperature effect on the spectra*: On the basis of the observed coalescence temperatures, free energies of activation of 14.4 and 12.3 kcal/mol (at 312 and 266 K) were calculated³⁴ to be associated with the torsional process of the parent compound **7** and its *o,o'*-dilithio derivative **3**, respectively. In parallel, a line-shape analysis³⁵ of the two high-field signals was carried out. Using Eyring's formalism³⁶ of the absolute transition state, ΔG_{298}^\ddagger values of 14.0 and 12.5 kcal/mol were obtained for the parent compound **7** and the dilithio derivative **3**. The latter approach, however, was found to be impaired by practical problems and thus should not be considered as highly accurate. Upon solvent evaporation (see preceding paragraph) some decomposition of the *o,o'*-dilithiated species had occurred. The signals of the by-products, although of minor intensity, obscure the critical spectral range between δ 1.8 and 0.7 to some extent. More importantly, the low field methyl peaks of the dilithio species **3** (and, if much less pronouncedly, of the parent compound **7**) are broadened at low temperatures. This phenomenon may reflect restricted rotation of the two methyl groups lying closely above or below the planes of the aromatic rings and, on the other hand, an interaction of methyl hydrogens with the strong quadrupolar moment of the near-by ^7Li nuclei.

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