

## Symmetrical Double Lithium Bridging in 2,2'-Di(lithium-tmeda)biphenyl (tmeda = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>): Experimental Confirmation of Theoretical Predictions

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In accordance with predictions based on molecular orbital calculations, the crystal structure of 2,2'-dilithiobiphenyl consists of monomeric units containing a planar biphenyl unit symmetrically bridged by two tmeda-complexed lithium atoms (tmeda = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>).

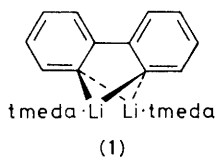
Both *ab initio* and semi-empirical MNDO calculations reveal that 1,4-dilithiobutadiene systems should strongly prefer structures in which each lithium bridges two carbons.<sup>1,2</sup> Such geometries [*e.g.* (1) for 2,2'-dilithiobiphenyl] maximise favourable electrostatic (ion aggregate)<sup>2,3</sup> and orbital ('Möbius-Hückel aromaticity')<sup>1</sup> interactions. As we have pointed out,<sup>2</sup> structures like (1) are the intramolecular equivalent of the intermolecular association commonly observed for lithium compounds.<sup>4</sup> Indeed, symmetrical lithium double bridging is indicated by our theoretical investigations to be a similarly general geometrical feature of polyolithiated compounds.<sup>1,2,5</sup> We have also demonstrated the *kinetic* preferences for the formation of such structures experimentally: direct metallation of biphenyl, by means of the 1:1 *n*-butyl-lithium-tetramethylethylenediamine (tmeda) complex, proceeds regiospecifically to yield 2,2'-dilithiobiphenyl.<sup>2</sup> The theoretical predictions<sup>1,2</sup> are now confirmed by *X*-ray crystallography: this compound does indeed have structure (1).

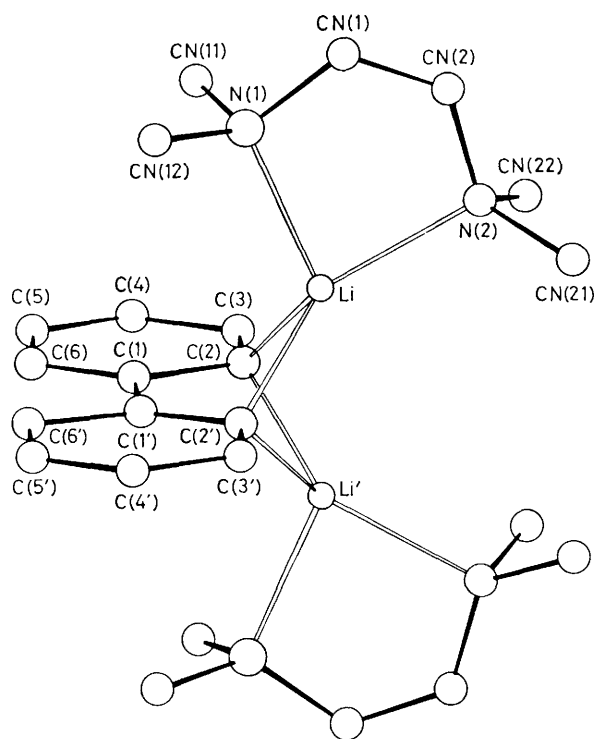
Crystals of (1) were recrystallized from diethyl ether and the tmeda content was determined by <sup>1</sup>H-n.m.r. integration of a sample after reaction with methanol. The *X*-ray structure of (1) (Figure 1) comprises a perfectly planar biphenyl moiety lying in the crystallographic mirror plane. Each lithium,

co-ordinated by tmeda, interacts with C(2) and C(2') on opposite sides of this plane. The average C-Li distance, 2.13 Å, and the Li-Li separation, 2.55 Å, compare well with the values (2.074 and 2.435 Å, respectively) calculated with the 4-31G basis set for the similar structure of 1,4-dilithiobutadiene (without the tmeda ligands).<sup>1</sup> The crystal structure of the phenyl-lithium-tmeda dimer<sup>6</sup> affords another comparison: C-Li (av.) = 2.24, N-Li (av.) = 2.19, and Li-Li = 2.49 Å. Unfortunately, the tmeda ligands in (1) are disordered. While the locations of the nitrogen atoms are fixed, all the carbon atoms assume two different positions separated by *ca.* 1 Å for the methyl and somewhat less for the methylene carbons. Refinement is difficult; the *R*-factor was only 11.9%. (Similar problems have been encountered with the structures of other tmeda complexes of lithium compounds.)<sup>7</sup> The main features of the structure of (1) are secure, however.

Along with Dietrich<sup>8</sup> and Weiss,<sup>5,9</sup> Stucky was a pioneer in the study of the structures of organolithium compounds by *X*-ray methods and interpreted the results with the aid of CNDO and INDO calculations.<sup>7,10</sup> Our findings underscore the power of molecular orbital calculations as an initial means of exploring the rule-breaking structure of lithium compounds.<sup>1-3,5</sup>

*Crystal data:* C<sub>24</sub>H<sub>40</sub>N<sub>2</sub>Li<sub>2</sub>, *M* = 398.5, orthorhombic, space group *Pnma*, *a* = 19.626(6), *b* = 12.556(4), *c* = 10.575(4) Å, *U* = 2606 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.016 g/cm<sup>3</sup> (-15 °C), graphite-monochromated Mo-*K<sub>α</sub>* radiation, λ = 0.710 69 Å. The specimen, under nitrogen, was mounted in a capillary; 2412 independent reflections (2° ≤ 2θ ≤ 48°) (-15 °C) were measured. The structure was solved by direct methods (MULTAN 80) and refined by full-matrix least-squares with anisotropic thermal parameters for some atoms.





**Figure 1.** The crystal structure of 2,2'-di(lithium-tmda)biphenyl. Some important distances (Å) and angles (°) are (e.s.d's in parentheses): C(2)-Li, 2.12(1); C(2')-Li, 2.15(1); Li-Li', 2.55(1); N(1)-Li, 2.13(1); N(2)-Li, 2.11(1); C(2)LiC(2'), 84.3(4); C(2)-LiN(1), 111.2(5); C(2)LiN(1), 110.7(5); C(2)LiN(2), 132.2(6); C(2)LiN(2), 133.2(6); N(1)LiN(2), 85.0(5); Li'LiC(2), 53.0(3); Li'LiC(2'), 53.6(3); Li'LiN(1), 155.1(5); Li'LiN(2), 119.9(5); LiC(2)Li', 74.1(4); LiC(2')Li', 72.8(4).

Final  $R = 0.119$ ,  $R_w = 0.155$  for  $1257 F_o \geq 4.5\sigma(F_o)$ .†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.