X-Ray Crystal Structure of [$\{o\text{-}C_6H_4(CHPh)_2\}\{Li(tmeda)\}_2$] (tmeda=$Me_2NCH_2CH_2NMe_2$). Unsymmetrical Lithium Bridging and (*E,E*)-Conformation of the Phenyl Groups

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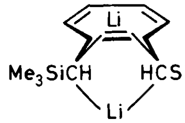
The lithium atoms in the title compound are shown by *X*-ray analysis to prefer quite different locations, in contrast to the symmetrical double bridging exhibited by other 1,4-dilithium compounds, but in agreement with model MNDO calculations; furthermore, the (*E,E*) conformation of the two phenyl groups differs from the (*E,Z*) conformation reported in methyltetrahydrofuran solution.

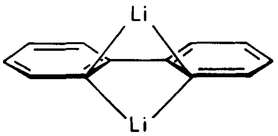
Recent investigations of the structures of dilithio organometallic compounds, *e.g.*, [$\{o\text{-}C_6H_4(CHSiMe_3)_2\}\{Li(tmeda)\}_2$] (tmeda = $Me_2NCH_2CH_2NMe_2$) (**1**)[1] and 2,2′-di(lithium-tmeda)biphenyl (**2**),[2] have confirmed the preference for symmetrical 1,4-double lithium bridging predicted theoretically.[3—5] 1,4-Di(lithium-tmeda)-1,4-diphenyl-*cis*-but-2-ene (**3**) shows only a slightly different structure; the lithium atoms occupy 'twisted' doubly bridging positions.[6]

We report the *X*-ray structure of [$\{o\text{-}C_6H_4(CHPh)_2\}\{Li(tmeda)\}_2$] (**4**)-2(Li-tmeda) which is of interest because (i) the positions of the lithium atoms are different from those in (**1**)—(**3**), and (ii) the phenyl groups occupy the (*E*,*E*) conformation, whereas (**4**)-2Li in methyltetrahydrofuran solution at room temperature is reported to be more stable in the (*E*,*Z*) conformation.[7]

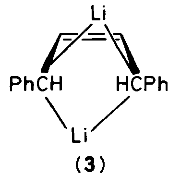
Dark red crystals of (**4**)-2(Li-tmeda) were prepared from *o*-dibenzylbenzene with 2.5 mol. equiv. n-butyl-lithium in hexane–tmeda (12 h at room temperature). The *X*-ray structure† (Figure 1) reveals two tmeda-complexed lithium atoms, one on each side of the *o*-xylylidene ring. The lithium atom Li(3) is co-ordinated to four carbon atoms {C(17) [2.23(1)], C(1) [2.36(1)], C(2) [2.43(1)], and C(27) [2.40(1) Å]} and has a location similar to that of both lithium atoms in (**1**). In contrast, Li(4) occupies a benzyl-lithium-like[8] site, and co-ordinates essentially to only three‡ carbon atoms {C(3) [2.59(1)], C(2) [2.22(1)], and C(27) [2.19(1) Å]}. Of these, only two [C(2) and C(27)] are in common with Li(3). Both phenyl rings bend in the same direction as a consequence. Other precedents for the type of multicentre bonding exhi-



(**1**)



(**2**)



(**3**)

[$o\text{-}C_6H_4(CHPh)_2$]
(**4**)

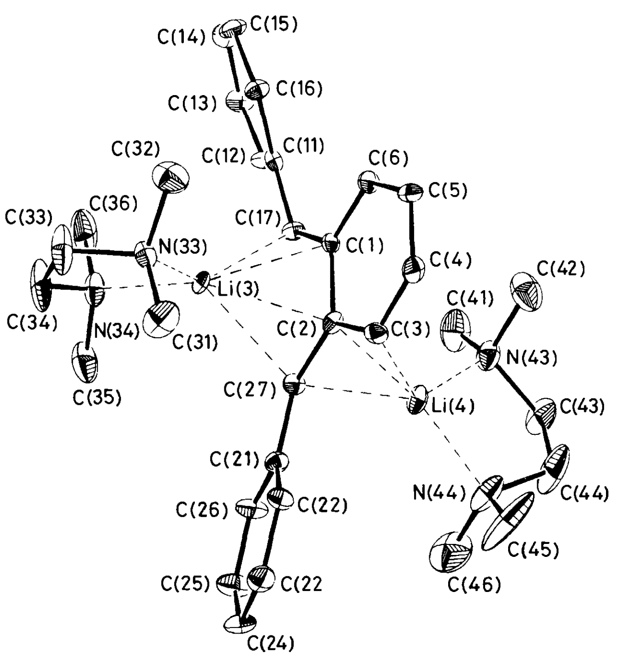


Figure 1. *X*-Ray structure (ORTEP drawing, 10% probability ellipsoids) of [$\{o\text{-}C_6H_4(CHPh)_2\}\{Li(tmeda)\}_2$], (**4**)-2(Li-tmeda). Some additional important distances (Å) and angles (°) are (e.s.d's in parentheses): Li(3)–N(33), 2.04(1); Li(3)–N(34), 2.06(1); Li(4)–N(43), 2.03(2); Li(4)–N(44), 2.04(2); C(17)–Li(3)–C(27), 76.9(4); C(1)–Li(3)–C(2), 35.2(3); C(3)–Li(4)–C(21), 72.7(4); C(2)–Li(4)–C(27), 38.0(3); plane C(1)—C(6) *versus* plane Li(3),N(33),N(34), 88.62; plane C(1)—C(6) *versus* plane C(11)—C(16), 34.99; plane C(1)—C(6) *versus* plane C(21)—C(26), 20.12; plane C(1)—C(6) *versus* plane Li(4),N(43),N(44), 87.13. That the lack of symmetry of the complex is not simply a consequence of the molecular packing in the crystal has been proved by the *X*-ray structure determination of the low temperature phase at 113 K which is triclinic ($P\bar{1}$) with two independent molecules in the asymmetric unit.

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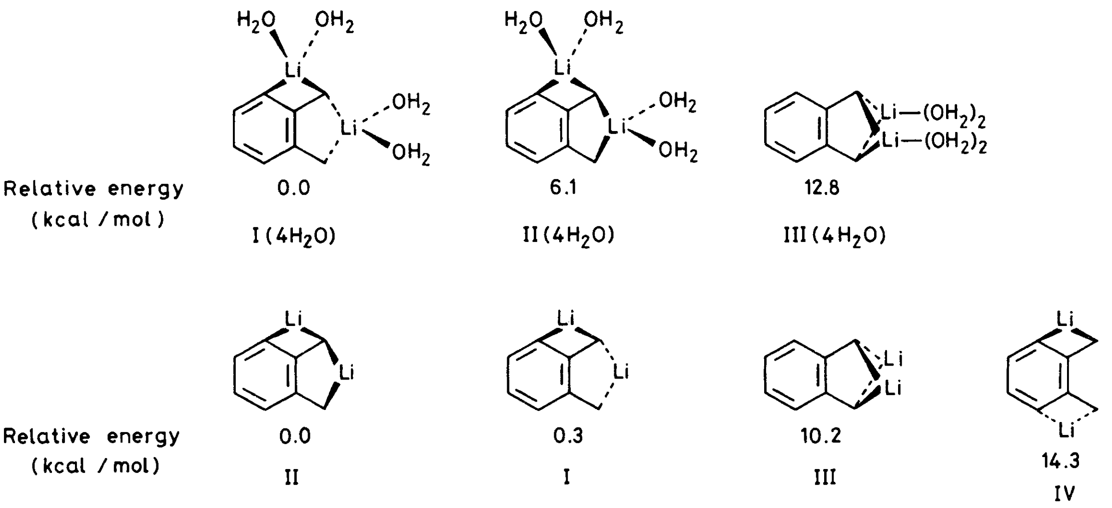
† *Crystal data:* $C_{32}H_{48}N_4Li_2$, M = 502.642, monoclinic, space group $P2_1/c$, a = 10.663(4), b = 21.188(9), c = 14.549(5) Å, β = 96.99(4)°, U = 3262 Å^3, Z = 4, D_c = 1.023 g/cm^3 at 291 K. Graphite monochromated Mo-K_α radiation, λ = 0.71069 Å. The specimen, under argon, was mounted in a capillary, and 3031 independent reflections (1350 >2σ) were measured at 291 K. The structure was solved by direct methods (Multan 76)[15] and at first refined by Fourier methods[16] with anisotropic temperature parameters followed by least square methods (X-RAY 76[17]) using weights $1/\sigma^2(F_O^2)$. Final $R(F^2)$ = 0.077, $R_w(F^2)$ = 0.059 for 1350 $F_O^2 > 2\sigma$. The atomic co-ordinates for this work (and also for the structure determination at 113 K) 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.

‡ The distance of Li(4) to C(21) is rather large: 2.77(1) Å.



MNDO Calculations

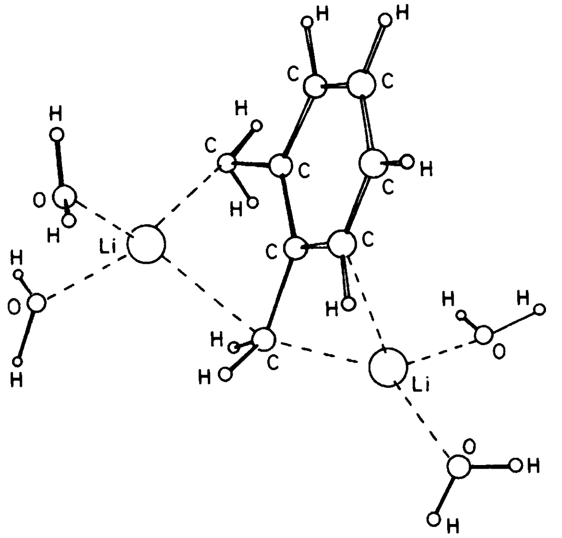


Figure 2. The most stable configuration of $[\{o\text{-}C_6H_4(CH_2)_2\}\{Li(H_2O)_2\}_2]$, I($4H_2O$), as calculated by MNDO.

bited by Li(3) are found in triphenylmethyl-lithium–tmeda,[9] fluorenyl-lithium–bisquinuclidene,[10] and in the predicted structure of allyl-lithium.[11]

The inherent preference for *unsymmetrical* lithium locations in dilithio-*o*-xylenes is supported nicely by MNDO model calculations.[12] Both unsolvated and solvated symmetrically doubly bridged forms (III) are considerably less stable than their experimentally related counterparts I, in which both lithium atoms have quite different co-ordination sites. These results indicate again that solvation effects can be significant in calculating lowest energy structures of organolithium compounds.[11b,13] Thus, I($4H_2O$) (Figure 2) is clearly more stable than II ($4H_2O$) and the symmetrically bridged III ($4H_2O$). In the unsolvated series I—IV, II is slightly more stable than I.[14]

The conformation of the two phenyl groups in (**4**)-2(Li-tmeda) is *E,E* (Figure 1), as is the arrangement of the two Me_3Si groups in (**1**). This is especially noteworthy because the conformation of the phenyl substituents of (**4**)-2Li, prepared similarly in methyltetrahydrofuran solution at room temperature, has been reported to be *E,Z*.[7] Our results do not support the suggestion that the *E,Z* isomer should be more stable thermodynamically than the sterically less congested *E,E* isomer because of a better interaction of the lithium cations with the negative charge delocalized into the phenyl rings.[7] The matter is being re-examined.

The reasons for the preference of (**4**)-2(Li-tmeda) for a strongly unsymmetrical geometry in contrast to the structures of (**1**), (**2**), and (**3**) are discussed in the following paper.[14]

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