Amination Reactions of Alkoxyamidolithium Compounds: an *Ab Initio* S.C.F. M.O. Model involving an (N–O)-Lithium-bridged Intermediate

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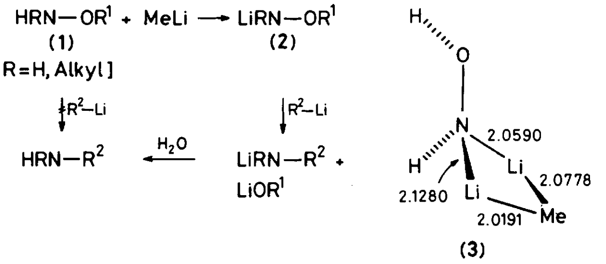
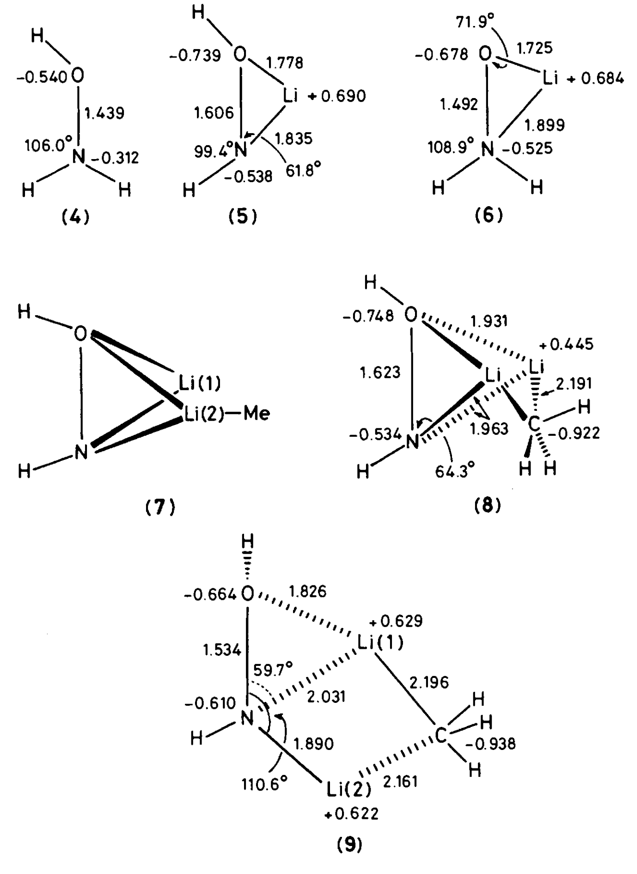
Ab initio S.C.F. M.O. calculations indicate that the reaction of alkoxyamidolithium $LiRN–OR^1$ with an organolithium R^2Li to give $LiOR^1$ and $LiRNR^2$ proceeds *via* an intermediate in which the N–O bond is lithium-bridged and hence is longer than in the precursor alkoxyamine; such a structure is thereby 'primed' for $LiOR^1$ elimination and $N–R^2$ bond formation, and accordingly seems more apt than a recently proposed one obtained from MNDO calculations in which both Li atoms are terminally attached to the nitrogen.

Recent synthetic work[1] has shown that alkoxyamines (**1**) are 'activated' [through conversion into alkoxyamidolithiums (**2**)] by methyl-lithium towards supposedly nucleophilic displacement by a further organolithium (R^2Li) thus giving, after hydrolysis, useful yields of amines R^2NRH (Scheme 1). M.O. calculations have subsequently[2] examined the mechanism of these reactions using hydroxylamine as the model alkoxyamine. Initial lithiation yielded LiNHOH, the *ab initio* geometry optimisation calculations showing that the Li, although formally placed on N, bridges the N–O bond. This bond is then significantly longer (1.609 Å) and more polarised (charges on N and O, −0.604 and −0.807 respectively) than in H_2NOH itself (1.437 Å; charges −0.493 and −0.610 respectively). However, further MNDO calculations (used owing to



Scheme 1



Optimised geometries: distances in Å.

convergence problems with the *ab initio* calculations) on the intermediate formed by the addition of MeLi to LiNHOH give a structure (**3**) in which Li-bridging does not occur, suggesting to us that the aforementioned N–O bond lengthening would be lost in structure (**3**). A further unsatisfactory aspect of (**3**) is that the O atom, 3-co-ordinate in LiNHOH, has reverted to being 2-co-ordinate as in hydroxylamine itself, while, for the N atom, many stable complexes containing RR′N ligands (R=H, R′=OH here) bridging two Li atoms are known[3] and the two N–Li bonds are of comparable length. Overall, structure (**3**) hardly seems 'primed' to reorganise to the final products. Indeed, the loss of Li-to-N–O bridging not only removes the *cause* of N–O bond lengthening but with it, in distancing *both* Li atoms from the O atom, an easily visualised rationale of LiOH elimination. We now report a successful *ab initio* S.C.F. M.O. optimisation of the intermediate, whose structure, in retaining an Li to N–O bridge, removes many of the unsatisfactory features noted above for (**3**).

In another context, we too had optimised, at the 6–31G level, the structures of hydroxylamine (**4**), and of its *N*- and *O*-monolithiated derivatives (**5**) and (**6**), respectively. Boche and Wagner[2] noted the main difference between their versions of (**4**) and (**5**) as the much longer N–O bond in the latter, but did not specify that it is precisely the Li-bridging which further polarises and lengthens the N–O bond. Intuitively, given the N and O atomic charges in (**4**), an entering Li atom is unlikely to ignore the O atom in sole favour of the N one, and this is borne out by our findings, firstly, that in optimising (**5**), a Li atom placed terminally on N moves to adopt the bridged structure with the O–Li bond shorter than the N–Li one, and, secondly, that the formally *O*-lithio derivative (**6**) is more stable than the isoelectronic (**5**) by 17.7 kcal/mol (1 cal = 4.184 J).[4] Stressing these points, recent *ab initio* calculations[5] (6–31G**) on lithiations of ammonia *N*-oxide, $H_3N{\rightarrow}O$, showed that successive Li substitution of N-attached hydrogens gave Li-bridged N–O bonds, with increasingly polar and longer N–O bonds, *e.g.*, for $H_3N{\rightarrow}O$, 1.374 Å; for $Li_3N{\rightarrow}O$, 1.713 Å. The key feature of such structures is thus the clear preference of lithium for forming a bridged structure and, inherent in this, for forming a bond to oxygen; such bridging, symmetric and otherwise, is already recognised as a common occurrence in 1,4-dilithiated organic compounds.[6]

Given the above findings it seemed likely that any structure formed from LiNHOH (**5**), and MeLi should retain, or indeed increase, the Li-bridging found in (**5**). Accordingly, geometry optimisation calculations (6–31G) were performed on the following likely models: (a) a structure with two terminal Li atoms, thus based on the MNDO structure (**3**) of Boche and Wagner,[2] (b) a structure (**7**) with the MeLi moiety positioned perpendicular to the N–O bond of (**5**) thus giving new Li–O and Li–N bridge bonds of lengths different from those already present in (**5**), and (c) a structure (**8**) with a mirror plane of symmetry coinciding with the HNOH framework and with a CH bond of the bridging methyl group, thus producing equivalent lithium-bridge bonds to N, to O, and to the methyl C. The results of these calculations show (i) that the terminal structure (**3**) does not represent a minimum, both Li atoms initially moving upwards towards the N–O bond, and (ii) that structure (**8**) possessing equivalent sets of bridge-bonds is less stable than structure (**7**) in which they are inequivalent. In the geometry optimisation of the latter, the MeLi(2) moves so that Li(2) bridges the N and the methyl C atoms and, at the same time, the methyl group bridges both lithium atoms, structure (**9**). Stressing that (**9**) is the global minimum, release of (**8**) [which is 4 kcal/mol less stable than (**9**)] from imposed C_s symmetry gives (**9**), as does full geometry optimisation of (**3**).

The key feature of intermediate (**9**) is retention from (**5**) of the Li(1) bridging of the N–O bond, with a 0.1 Å lengthening of this bond compared with the value in H_2NOH (**4**). Moreover, while the O–Li(1) bond remains short, the N–Li(1) bond is significantly longer than that found in LiNHOH (**5**), particularly when viewed in conjunction with the very short N–Li(2) bond. Thus the N bridges the two lithium atoms very asymmetrically so that formation of the intermediate (**9**) can be visualised *via* the largely electrostatic complexation of $^{\delta-}$MeLi$^{\delta+}$ by the polar $^{\delta+}$Li(1)–N$^{\delta-}$ bond of (**5**). Now the effect of this is crucially to weaken the existing N–Li(1) bridge bond of (**5**), so that Li(1) becomes more closely associated with the O atom. Therefore elimination of Li(1)OH can be conceived by rupture of the relatively long N–O, N–Li(1), and C–Li(1) bonds. Rearrangement of the HNLi(2)CH_3 fragment might then occur concertedly to give $CH_3NHLi(2)$, or stepwise by total cleavage of C–Li(2) to give $^{+}$NHLi(2) (whose relatively high stability has been noted[2]) and $^{-}$CH$_3$. Either way it is clear that the intermediate in this reaction must have an Li-bridged N–O bond.

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