Hydrazido-, Diazenido-, and Amido-derivatives of Lithium: A Theoretical Study related to Nitrogen Fixation Reactions †

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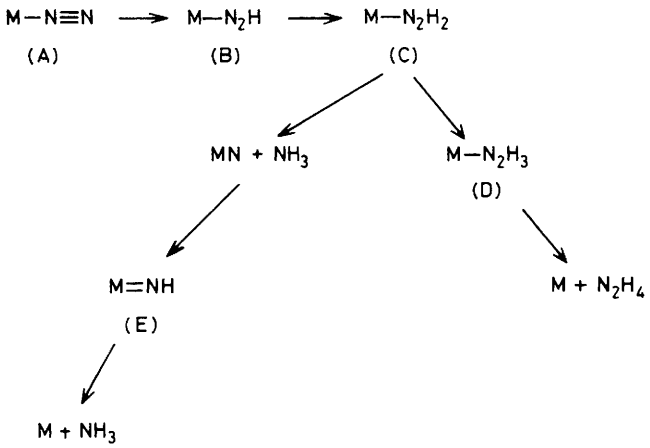
Ab-initio calculations on model compounds, principally lithium derivatives, which represent supposed intermediates in the protonation of N_2 bound to transition metals have been carried out. It is shown that there are stable configurations of the model compounds which have not been detected experimentally and which may be significant in real processes. It is also shown that coulombic forces are at least as significant as π bonding in determining the structures of the model systems. The results are compared with approximate calculations on real systems.

The protonation of co-ordinated N_2 is a stepwise process, in which some of the intermediate species have been identified with a considerable degree of certainty. However, other steps are far from clear and speculation about the identity and structure of species is considerable.[1] The purpose of this paper is to investigate by means of model calculations the structures of a number of identified or reputed intermediates in the protonation process, and to relate them to empirical data.

For this purpose the following reaction Scheme is postulated, although it is not intended to suggest that intermediates other than those represented here are unlikely or impossible. The Scheme encompasses all those stages discussed herein and there is considerable experimental evidence for all the intermediates postulated. The intermediates (A)—(E) are discussed in turn.



Scheme.

The real systems of interest have transition metals and heavy ligands which would be prohibitively expensive for *ab-initio* calculations, particularly if geometry variations are to be examined. Two strategies are available: either to deal with real systems and simple model Hamiltonians (*e.g.* at the Hückel level) or to take model systems with real Hamiltonians. We prefer the latter because the results are independent of assumptions for the Hamiltonian and simple model molecules can reveal factors that should be present in more complicated systems. The systems we studied were mainly those with Li as the metal atom. This is the simplest metal atom which bonds primarily through its σ electrons yet possesses vacant π orbitals. A few calculations have been made replacing Li by B, N, and F, in which these π orbitals are progressively filled, and by P in which the possibility of *d*-orbital participation in the bonding is introduced.

† *Non-S.I. unit employed*: 1 Hartree (E_H) = 4.36×10^{-18} J.

Experimental

Computational Methods.—All calculations were carried out using the GAUSSIAN 70 series of programs, except in the case of the molecule $[P{-}N{=}NH_2]^+$ where the GAUSSIAN 76 was used.[2] All molecules were considered in a singlet ground state and as closed-shell systems. The minimal STO-3G basis supplied by the programs was used, containing *s* and *p* functions only, except in the case of P, where a set of *d* functions was employed.

For all the molecules, the NH bond length was fixed at 1.05 Å and the NNH and HNH bond angles constrained to 120°. The N–N and N–X bond lengths and the NNX angles were optimized.

Results and Discussion

Dinitrogen Complexes (A).—Dinitrogen complexes are known to display end-on co-ordination of N_2, both terminal and bridging.[1] There is currently one example of side-on N_2 in a simple complex, although this has not been proven unequivocally.[3] Certainly in model studies it would seem advisable to concentrate upon reactions of terminal end-on N_2, which is known to protonate rapidly and cleanly. We have previously carried out detailed calculations on such species.[4] The principal consequence of complexing N_2 in this fashion is its polarisation leading to charge distribution in the sense $M{-}N^{\delta+}{-}N^{\delta-}$.[5] The consequent enhanced base character of the N_2 should lead to protonation on the terminal nitrogen.

Diazenido-complexes (B).—Complexes of diazenide, $-N_2H$, have been implicated in the protonation of co-ordinated N_2, either as short-lived intermediates between N_2 and N_2H_2,[1] or because materials such as $[WF(N_2H)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) can be obtained by deprotonation of a hydrazido(2−) species.[6] The structure of the diazenido-ligand is probably best represented as $M{-}N{=}N\diagdown_H$, although it has also been suggested that there is an alternative hydrido-dinitrogen form (see below) in equilibrium with it under cer-

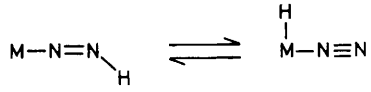
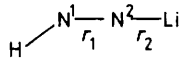
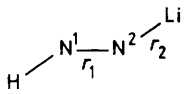
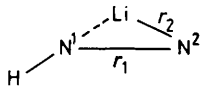


Table 1. Geometries and charges for three configurations of Li(NNH)

	θ/°	r_1/Å	r_2/Å	Charges (electronic units) on atoms H	N^1	N^2	Li
	180	1.22	1.64	0.303	0.004	−0.235	−0.072
	120	1.28	1.74	0.091	−0.249	−2.209	0.366
	65	1.28	1.74	0.171	−0.126	−0.243	0.198

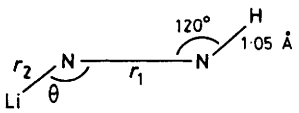
* The minimum energy for Li(NNH), which is found with this configuration, is at −115.3707 E_H. The second Li–N separation is 1.67 Å.

tain circumstances.[7] There is no doubt that organodiazenido-compounds generally function as though the diazenide were a three-electron donor and take up a singly bent configuration, unless the electronic requirements of the metal are such that the diazenide can donate only one electron. The ligand then adopts the *trans* doubly bent configuration characteristic of diazene itself.[8] The possibility of an overall linear form has also been discussed. The only exception to these generalisations is the product derived from the nucleophilic attack of carbanions R^- on N_2 in $[Mn(C_6H_5)(CO)_2(N_2)]$ where the ligand has been claimed, on somewhat dubious grounds, to be

in the configuration M–N=N.[9] There is no precedent for this, and quite a lot of evidence to contradict it.

The first series of calculations were made on Li(NNH). By constraining the angles LiNN and HNN to 120° and allowing the dihedral angle between the two planes to vary, we showed that the molecule Li(NNH) prefers a *trans*-planar configuration. This is consistent with the known structure of HNNH.

The energy as a function of θ = LiNN (shown below) was then examined and the most stable position for the Li was found to be bridging the N–N bond. The energy of this struc-



ture was minimized with respect to r_1 and r_2, but maintaining NNH = 120° and N–H = 1.05 Å, and keeping these parameters fixed, the energy of the system was calculated as a function of θ as shown in Figure 1.

The empty *p* orbitals on Li are extensively involved in the bonding, appearing with substantial weight in several of the highest occupied molecular orbitals (h.o.m.o.). This leads to the dramatic difference between N_2H_2 and Li(NNH). At the angles LiNN of 120 and 240° there are now energy maxima rather than minima as for diazene. The position of the absolute minimum (θ = 65°) represents a novel geometry and ground state in which the LiNN bonding is best considered as three-centred.

The compound Li(NNMe) shows a similar energy profile,

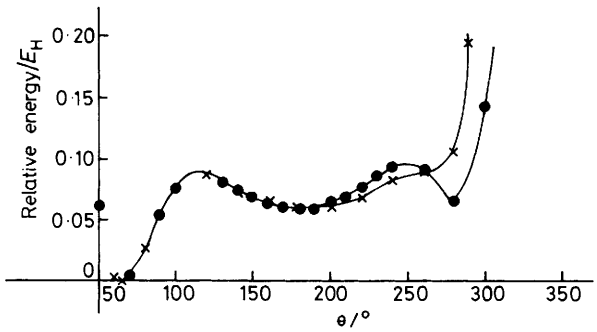


Figure 1. Energy profiles for Li(NNMe) (×) and Li(NNH) (●) as a function of θ. The zero of energy is the deepest minimum in each case

except that as θ rises above 240°, steric repulsion becomes significant and the energy rises rapidly (Figure 1).

Table 1 shows the detailed geometries, energies, and charges for Li(NNH) when θ = 65, 120, or 180°. All three structures have $r_1 \simeq 1.25$ Å, which approximates to an N=N double bond and all three have $r_2 \simeq 1.70$ Å, which is a reasonable value for a Li–N covalent single bond. The situation in which Li–N is shortest is the one in which π bonding of a conventional sort is maximised (LiNN = 180°). This indicates that the stablest configuration is the one containing two Li–N σ links, and that the stabilisation due to π bonding in the linear form, which leads to the highest negative charge on the lithium, is less than that arising from a Li–N σ bond.

The orbital sequences are shown in Figure 2. They are very approximate representations in an attempt to correlate molecular orbital (m.o.) and traditional structural representations. They make clear that the minimum-energy configuration has a bonding base of two three-centre σ bonds constituted from p_x and p_z, then a π bond (p_y), and the h.o.m.o. is actually anti-bonding for N–N. For θ = 120° (Figure 2) this picture still holds essentially, but for θ = 180°, the bonds from p_x and p_y seem to involve relatively little of the Li orbitals, and the Li–N bonding is essentially σ, with a contribution from the N–N anti-bonding π orbital. Note the absence of *s*-orbital participation in the valence shells.

We conclude that, for lithium, side-on bonding to the diazenido-ligand is a preferred configuration and that π bonding does not determine the structure. The suggestion [10] that Sellmann's reactions [9] involve side-on N_2R becomes more

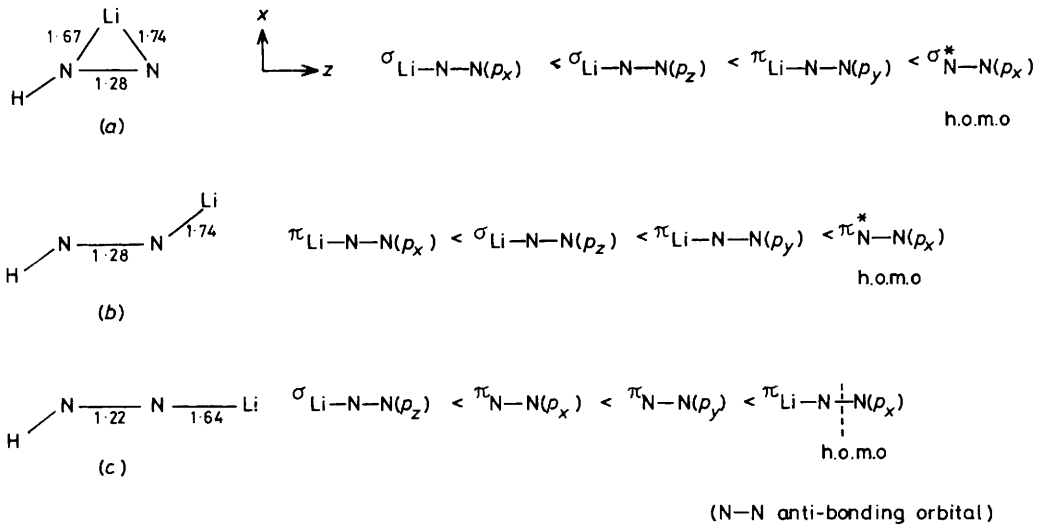


Figure 2. Orbital sequences for various geometries of Li(NNH)

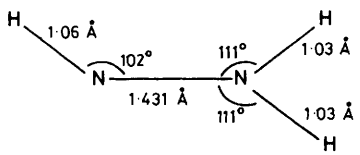
plausible, and the search for other side-on species becomes worthwhile. There are no unequivocal examples in the literature, although Li is known to bond side-on in certain complicated dinitrogen complexes of, for example, nickel.[1]

Hydrazido(2−) *Complexes* (C).—Although there was initially some indecision concerning whether the ligand designated formally as NNH_2^{2-} binds to a metal end-on, or whether it rearranges to diazene, and binds side-on (see below), this has now been settled in favour of the end-on structure.[11] There is,

however, evidence for at least two forms of the end-on structure in which the group can be considered either as a four-electron [12] donor or as a two-electron donor.[13] These formulations are based upon bond length considerations; in both structures M–N–N is linear. No bent hydrazido(2−) complexes with θ = 120° are known, although values considerably less than 180° have been reported.[14]

Although NNH_2 is not known to bridge between metals,[15] HN=NH can,[16] and diazene has been postulated as bonding side-on in some mononuclear molybdenum complexes,[17] but no unequivocal evidence for this is available.

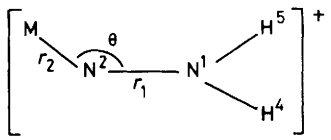
Calculation and chemistry [14] suggest that $\bar{N}=\overset{+}{N}H_2$ (*iso*-diazene) is less stable than either *cis*- or *trans*-N_2H_2. The structure of N_2H_3 has been shown to have a minimum energy in the form shown below. It is not planar.[18]



The ground state of NNH_2 is a triplet with the singlet, as represented by $\bar{N}=\overset{+}{N}H_2$, *ca.* 20 kJ mol^{-1} higher. The ground state is also probably planar.[18]

We chose to investigate the structure of a series of molecules $[M{-}N{=}NH_2]^+$, all having singlet ground states, for M = H, Li, B, N, F, or P. In all cases we found NNH_2 was planar, consistent with all the available *X*-ray data on hydrazido(2−) complexes, and previous calculations on $N_2H_3^+$. In all the cases examined, we were able to show that a planar arrangement of the five atoms is favoured, unlike the neutral radical discussed above.

We first minimised energies for the planar arrangement and the relevant data are shown in Table 2. For M = H and



F, minimum energies were achieved with θ = *ca.* 109°. This is perhaps unexpected, since 120° might, at first sight, seem more reasonable, but for M = H the calculations agree with those of Pople and co-workers [18] both in bond length and angle. Table 2 shows the energy differences $\Delta E = E^{180°} - E^{min}$ for the five molecules. For M = Li or N, θ(opt) = 180° (opt = optimised) and for M = B, θ(opt) = 120°. We thus have evidence for three forms of co-ordinated NNH_2, but only one of these, with θ = 180°, corresponds to a geometry found by experiment. We found no evidence for a second minimum when varying bond lengths, corresponding to the other experimental structure; nor, in contrast to Li(NNH), was more than one minimum for a given M found as θ was varied.

Figure 3 shows the order of energy levels for the linear forms of all the molecules. Comparison shows that all the h.o.m.o.s have anti-bonding character. However, since three-centre and five-centre systems are being dealt with, these designations are simplifications and can be misleading. It is also apparent that, in any non-linear molecule, designations such as σ and π quickly lose their significance and an orbital may be σ with respect to one pair of atoms and π with respect to another.

(*a*) M = H or F. The geometry of both $[MNNH_2]^+$ for

Table 2. Minimum energy geometries, energies, and atomic charges for $[M(NNH_2)]^+$

M	r_1/Å	r_2/Å	θ/°	ΔE/kJ mol^{-1}	E/E_H
H	1.28	1.08	109.4	180	−108.9196
Li	1.26	1.77	180.0	0.00	−115.7809
B	1.28	1.71	120.5	34	−132.6012
N	1.34	1.15	180.0	0.00	−162.0458
F	1.30	1.33	109.5	330	−206.3523

	Charges (electronic units) on atoms				
	M^2 = H	M^2 = Li	M^2 = B	M^2 = N	M^2 = F
N^1	−0.1499	−0.1887	−0.1755	−0.2113	−0.1741
N^2	0.1178	−0.0494	−0.0020	0.1877	0.3314
M^2	0.3165	0.6569	0.5247	0.3180	0.1056
H^4	0.3717	0.2906	0.3430	0.3528	0.3813
H^5	0.3440	0.2906	0.3098	0.3528	0.3558

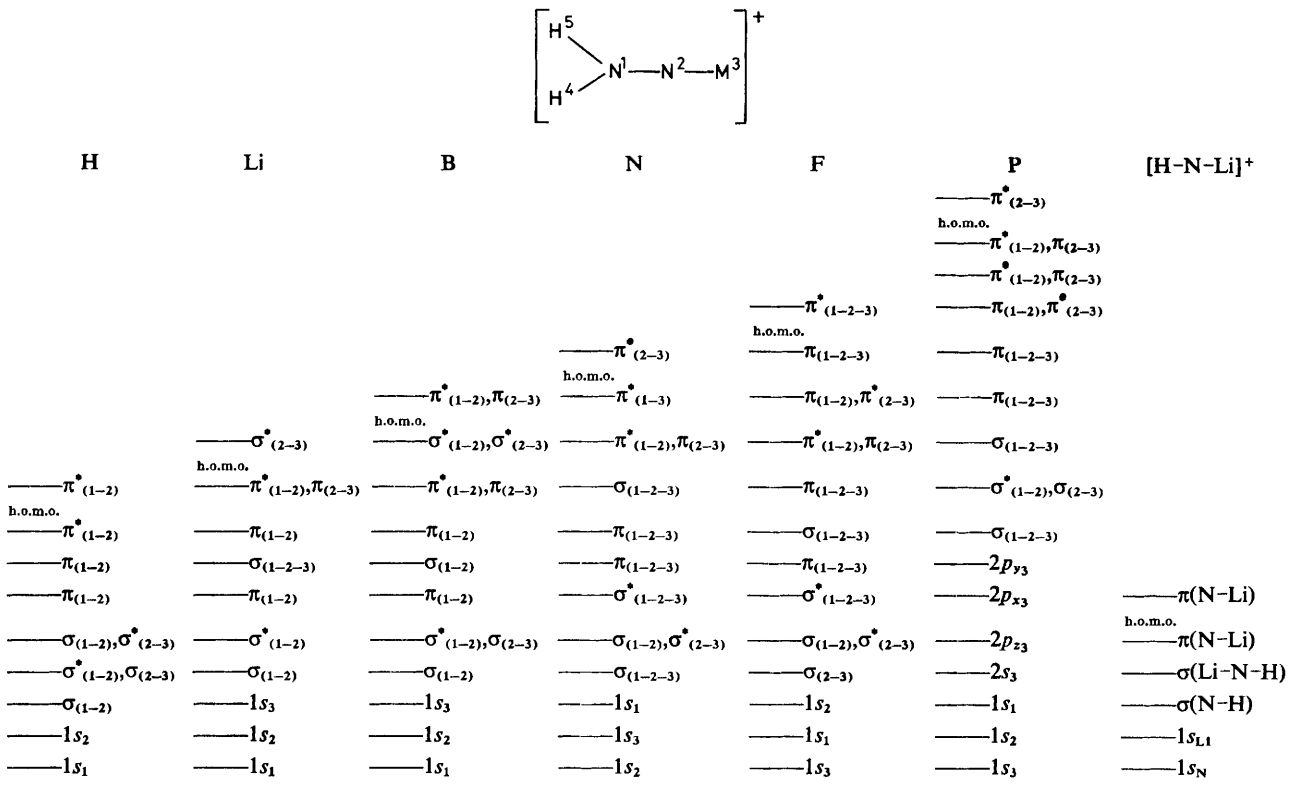
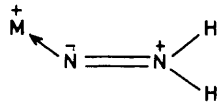


Figure 3. Relative positions of orbitals for the linear forms of $[M(NNH_2)]^+$ and $[Li(NH)]^+$

M = H or F in the ground state has θ = *ca.* 109°. This suggests sp^3 hybridisation about the nitrogen atom. Yet we do not have sufficient electrons on the nitrogen for tetrahedrally disposed electron pairs. Neither H^+ nor F^+ have empty *p* orbitals with which to accommodate π electron density from the nitrogens and the bond lengths H–N and F–N are those to be expected of single bonds. The N–N separations (see Table 2) are midway between the values expected for single (1.40 Å) and double (1.20 Å) bonds.

Despite this, there cannot be tetrahedral hybridisation about N_2 if the *iso*-diazene fragment is represented in valence bond terms as below, and an MNN angle of 120° would seem more appropriate. The energy difference between the 109° and 120° configurations (Figure 4) is *ca.* 0.01 E_H (or 26 kJ mol^{-1}), which is really too small to insist on the significance of one



angle or the other as belonging to the ground state, and in the case of B^+ and Li^+ it could be argued that the differences between 109, 120, and 180° are indicative only of preference rather than being solidly predictive.

The positive charge on complexed H^+ is higher than on complexed F^+, but the amido-hydrogens in both cases carry rather similar charges. In both systems, N^1 has a negative charge and N^2 is positive, but the positive charge is greater for M = F^+. This accords with electronegativity expectations. Examination of the orbitals involved in bonding shows that

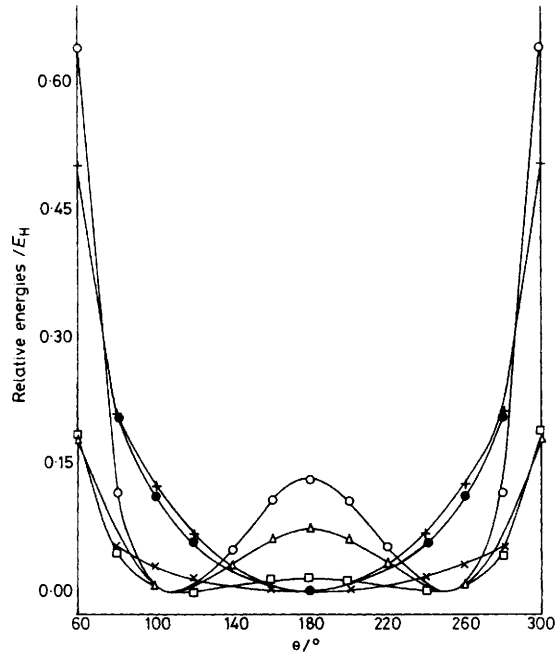
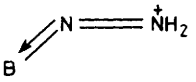


Figure 4. Energies of the systems $[M(NNH_2)]^+$ as a function of the angle θ: M = F (○), P (+), B (□), H (△), N (●), and Li (×)

the N–F bond has extensive π character even though it is a single bond.

(*b*) M = B. In the case of M = B, the boron has vacant *p* orbitals which are nominally available to receive nitrogen π electron density. This does not, however, lead to a greater reduction of charge than expected solely on electronegativity grounds (see Table 2 and Figures 3 and 4). A valence bond structure such as shown below is consistent with BNN = 120°. Whereas the N–N separation is of the usual magnitude, B–N

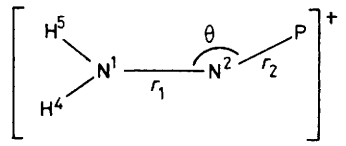


is clearly rather long because a value of less than *ca.* 1.6 Å might have been expected. The charges on N^1 and on the amido-hydrogens are not very different from the cases considered above (M = H^+ or F^+), but N^2 is also negative, which again suggests that formal π bonding is not important. The orbital populations confirm that N ⟶ B π bonding is not important. If anything, π bonding is in the sense B ⟶ N.

(*c*) M = Li or N. The molecules with M = Li and N both show minima at MNN = 180° (see Figure 4), although the minimum for M = N is much the more pronounced. Moreover, the lengths of the bonds r_1 and r_2 suggest that both molecules cannot be represented by the same formal valence bond structure.

The N^1–N^2 bond is shorter for M = Li than for M = N and M–N is very long for Li and exceedingly short (approaching N–N triple bond length) for N. Of the two, N is considerably less positive than Li and the amido-hydrogens are less positive for Li than for N. This is consistent with a flow of charge along the molecule to the central nitrogen upon replacing Li by N, and suggests that electronegativity differences are as important in forcing multiple bonding as the availability of empty orbitals. However, if such arguments were extended to transition elements, it would be necessary to replace the concept of electronegativity of the element with electronegativity of the element and its attached ligands (which has been referred to as 'electron-poorness'). Electronegativities do not vary significantly along a transition series for a given oxidation state, although they change with oxidation state for a given element.

Table 3. Minimum energy, geometry, and atomic charge for $[PN{=}NH_2]^+$



r_1/Å	r_2/Å	θ/°	ΔE/kJ mol^{-1}	E/E_H
1.35	1.45	180.0	0.00	−445.3831

Charges (electronic units) on atoms: N^1 −0.27, N^2 −0.10, P 0.80, H^4 0.29, H^5 0.29.

Examination of the orbital populations shows N($2p_y$) and N($2p_z$) extensively involved in π bonding. In contrast, Li($2p_y$) and Li($2p_z$) and even Li(2*s*) and Li($2p_x$) are not heavily populated, which is at least consistent with the bond length data.

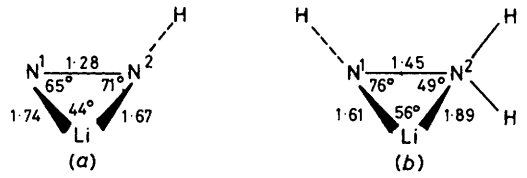
(*d*) M = P. We carried out calculations with M = P in order to discover whether the presence of *d* orbitals on the phosphorus would change the situation described above. Clearly it does to some degree. The N–N separation changes little, and N–P, at 1.45 Å, is as long as the predicted P≡N (1.45 Å). There is considerable N–P multiple bonding, but the charge on P is almost 0.5 units more positive than that on N^1, and N^2 is negative, rather than positive. In fact, in terms of charge distribution, $[Li(NNH_2)]^+$ is rather similar to $[P(NNH_2)]^+$. In terms of Pauling electronegativity, P (2.1) falls midway between N (3.0) and Li (1.0), so that the availability of electrons in *p* orbitals on P must enhance P ⟶ N π bonding (Li cannot π bond in this sense) even if N ⟶ N π bonding is inhibited by electronegativity. Finally, *d* orbitals are minimally involved in bonding (Table 3).

In summary, we infer that NNH_2 may bind in at least three ways, depending upon the metal, but not side-on. The energy barrier between different forms for a given M may be very small but seems greater towards the right-hand side of the period, and this may be paralleled by increased M–N multiple bonding. The mere availability of empty orbitals potentially suited for π bonding in the sense N ⟶ M does not mean that this necessarily happens. The energies of those orbitals are just as important as their availability in determining whether π bonding occurs.

Hydrazido(1−) *Complexes* (D).—There are very few of these known. They are generally reactive, and in at least one case, $[W(\eta\text{-}C_5H_5)_2(NHNHPh)]^+$, rearrange above 0 °C to yield a hydrazido(2−) species, $[W(\eta\text{-}C_5H_5)_2H(NNHPh)]^+$.[19] The conversion of a hydrazido(2−) species to a hydrazido(1−) species, as demanded by the initial Scheme, has yet to be observed, although the converse certainly has.[20] The significance of the stage represented by such complexes in protonation processes has yet to be completely evaluated.

Calculation shows that the species $Li(NHNH_2)$ prefers the configuration adopted by hydrazine itself, with the substituents at each nitrogen atom, together with that nitrogen, in a plane at right angles to the plane containing the second N and its substituents. However, LiNN is very far from 120°.

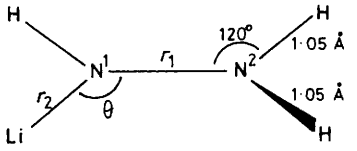
Variation of r_1, r_2, and θ lead to the optimum values: r_1 =



Charges (electrons)

	(a)	(b)
Li	+0.20	+0.18
N^2	−0.24	−0.34
N^1	−0.13	−0.32
$H(N^2)$	+0.17	+0.18
$H(N^2)$		+0.18
$H(N^1)$		+0.12

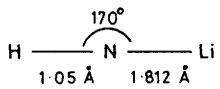
Figure 5. Comparison of Li(NNH) (*a*) with $Li(NHNH_2)$ (*b*) (bond distances in Å)



1.447 Å (N–N single bond), r_2 = 1.610 Å, which is shorter by more than 0.1 Å than the corresponding bond in Li(NNH), and θ = 76°. As in Li(NNH), the lithium can be considered as bonding to both nitrogen atoms with Li–N bond lengths corresponding approximately to single bonds. Side-on bonding of hydrazide(1−) to transition metals in complexes is an increasingly common occurrence.[21] Comparison of bond lengths and charges (Figure 5) shows that the hydrazido-complex is slightly expanded in its skeleton as compared to the diazenido-complex, and the difference in charge produced by adding two positive hydrogen atoms is accounted for almost entirely by the nitrogens becoming more negative. In both structures the population of Li(2*s*) is unexpectedly low, and Li($2p_x$) has a negligibly small population. Thus, these systems have large ionic character.

The tendency of Li to form bonds with as many adjacent atoms as possible is not without theoretical precedent. For example, allenyl-lithium has been predicted to have a side-on structure.[22] What we observe here seems to fit into the general pattern of lithium chemistry. Calculation shows that Li(NMeNMe$_2$) should also have a side-on configuration (Figure 6). We are attempting to confirm this prediction experimentally.

Amido-complexes (E).—Many transition-metal alkylimido-complexes are known and these generally have a linear M–N–C(alkyl) skeleton. Unfortunately less information is available concerning structures of complexes containing the parent imido-group. Our calculations were made on the model $[Li{=}NH]^+$ in order to determine whether linearity and bonding are necessarily related. The minimum-energy configuration is as shown (see Table 4).



The system contains only six electrons. Assuming that two are involved in N–H bonding, then the remaining four could

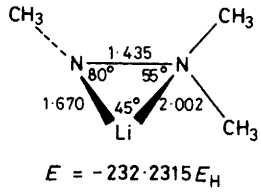
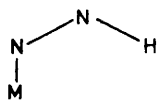


Figure 6. Equilibrium geometry for Li(NMeNMe$_2$) (bond distances in Å)

form one σ and one π linkage between lithium and nitrogen, with a valence representation $[H{-}N{\rightleftarrows}Li]^+$. Apparently, this is not the case. Most of the positive charge is on Li (0.74 e) and the Li–N bond is very long, longer than a predicted single bond. There is very little involvement of any orbital of Li in bonding and the h.o.m.o., designated π(Li–N), is primarily N($2p_y$). The inference is that the interaction is primarily electrostatic, and that the linearity is simply an expression of the repulsion between the positive Li and the positive H and has little to do with π bonding. Deformations from linearity can still require considerable energy, in this case *ca.* 80 kJ mol^{-1} is required to bend LiNH to 120°. This molecule is probably an extreme case in which covalent bonding might not be favoured. The nitrogen is electron deficient and electronegative. Consequently any donation of electrons by it is likely to be discouraged.

Extrapolations from Li to transition-element compounds might be considered foolhardy. Our own *ab-initio* calculations on transition-metal N_2 complexes [4] make clear that orbitals other than those in the conventional valence shell are very important in the bonding, and consequently approximate discussions such as those of the extended-Hückel type are bound to be in error in detail.

One of the most detailed of such discussions of protonation is due to Dubois and Hoffmann.[23] They consider the N_2H group in a variety of environments, both six- and five-co-ordinate. However, the discussion does not consider all the possible orientations of N_2H with respect to the metal uncovered by us. They do note that if bending occurs at the metal-bound nitrogen, then a *cis* configuration of doubly bent N_2H is favoured in octahedral six-co-ordinate complexes (see below), and that singly bent systems have a lower electron

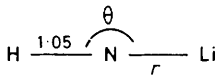


density on the metal-bound nitrogen than on the other. This charge distribution is in accord with our calculations.

Subsequently, Dubois and Hoffmann considered NNH_2, NNH_3, and nitrido-species and comparison with our findings is difficult. However, they do note the increase in metal–nitrogen interactions which occurs on passing from a dinitrogen complex to the protonated species. This, of course, is quite consistent with the empirical data, but our work shows that this is reflected more by bond lengths than by geometrical rearrangements of atoms.

After completion of our manuscript, a paper by Yamabe *et al.*[24] on the electron structure of the 16-electron complex $[Cr(PH_3)_4N_2]$ and its mono- and di-protonated derivatives has appeared. The calculations were *ab-initio* SCF m.o. using a minimal basis (STO-3G) for all the atoms except Cr, for which a [5*s*3*p*2*d*] basis was used. The Cr–N and N–N bond lengths were optimised for the neutral species

Table 4. Data for equilibrium geometry of $[Li{=}NH]^+$



			$\Delta E = E^{170°} - E^{120°}$ /	Charges (electronic units) on atoms		
r/Å	θ/°	E/E_H	kJ mol^{-1}	N	Li	H
1.812	170	−61.3514	86.6	−0.01	+0.74	+0.27

(with an assumed square pyramidal geometry having N_2 at the apex and CrNN = 180°) and the lengths and geometry were retained unchanged for the calculations on the protonated species.

On the basis of bond orders, Yamabe *et al.* [24] deduced that Cr–N shortens upon protonation and that N–N lengthens, and from charge densities the protons were found to carry a relatively small charge (0.14 in the mono-, +0.30 in the di-protonated species). They attributed the high proton affinity of these molecules to this small charge which is consequent upon electron transfer from a d_π orbital of the metal. As no investigation of geometry changes upon protonation was made, there is no overlap with our work.

Conclusions

The main object of our study was to suggest factors which should be considered in discussing the protonation of co-ordinated N_2. These are as follows. (*i*) The geometries of co-ordinated ligands should be construed carefully as indicating σ and π bonding in a valence bond sense. The results of our calculations show that in compounds of Li, the charge distribution and resulting electrostatic forces can force geometries consistent with certain valence bond structures, without, however, those structures being involved. (*ii*) The energies between different geometric forms (of NNH_2) may often be very small. This is shown in Figure 4. Consequently, extrapolating from an observed structure to an inferred charge distribution may be dangerous. (*iii*) Sideways bonding may be preferable for species such as N_2H and $NHNH_2$. Consequently, if these form from bound dinitrogen during protonation, considerable rearrangement or loss of other ligands may be necessary in order to accommodate them on the metal. The impossibility of adequate changes could prevent their formation. However, we cannot exclude such species being generated from dinitrogen or hydrazide(2−) species even if a preferred co-ordination mode cannot be readily envisaged.

Clearly, in that our *ab-initio* approach, the approximate *ab-initio* treatment of Yamabe *et al.*,[24] and the extended-Hückel approach are approximations to real systems, none can reproduce observed behaviour exactly. They can give different, complementary, and sometimes overlapping information about real systems.

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