Electronic Structure of Nitrenes. LiN, the Simplest Ionic Species[1a]

Clifford E. Dykstra,[1b] Peter K. Pearson,[1c] and Henry F. Schaefer III*[1d]

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received August 21, 1974*

Abstract: From qualitative molecular orbital arguments, it is predicted that the $^3\Sigma^-$–$^3\Pi$ separation in the ionic LiN molecule should be significantly less than the 3.69 eV found spectroscopically for the analogous covalent molecule NH. To test this prediction, an ab initio theoretical study of the electronic structure of LiN has been carried out. A Slater basis set was employed, of size Li(4s 2p), N(4s 3p 1d). Both self-consistent-field and configuration interaction (CI) methods were used. For both $^3\Sigma^-$ (335 configurations) and $^3\Pi$ (546 configurations) states, the CI included all interacting single and double excitations with respect to the two-configuration wave functions required to ensure dissociation to Hartree-Fock atomic wave functions. Consistent with the ionic model, the two states are predicted to be very close in energy, the $^3\Sigma^-$ state being the lower by 0.30 eV. An important aspect of the study is the prediction of electronic transition probabilities. It is shown that the use of natural orbitals greatly facilitates the calculation of transition moments, and the "length" form is seen to be less sensitive to details of the correlated wave function than is the "velocity" form. The $^3\Sigma^-$–$^3\Pi$ oscillator strength, consistent with the ionic model, increases rapidly as a function of bond distance.

The diatomic molecule NH and its derivatives R-N are usually referred to as nitrenes. Nitrenes are reactive intermediates of increasing importance in both organic and inorganic chemistry.[2-6] This interest has in part been motivated by certain similarities between nitrenes and another class of free radicals, the carbenes.[7] Both nitrenes and carbenes usually have small energy separations between their lowest singlet and triplet electronic states. In addition, both classes of molecules seem to conform to the idea of Skell[8] that singlet states should insert into double bonds in a stereospecific manner, while triplets insert nonstereospecifically.

The simplest nitrene, NH, is perhaps the most thoroughly studied, both from an experimental and theoretical point of view. The X $^3\Sigma^-$ state has long been known to be the ground state, but the precise position of the first excited a $^1\Delta$ state has only been determined[9] during the past year to be 12,580 cm^{-1} or 1.56 eV. The b $^1\Sigma^+$ state lies at 21,230 cm^{-1} = 2.63 eV,[10] and all three of these states arise from the electron configuration

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi^2 \qquad (1)$$

The next two states of NH arise from the excited electron configuration

$$1\sigma^2\ 2\sigma^2\ 3\sigma\ 1\pi^3 \qquad (2)$$

Of these the $^3\Pi$ is found[10] at 29,780 cm^{-1} = 3.69 eV and the $^1\Pi$ at 43,340 cm^{-1} = 5.37 eV. Several theoretical studies[11-13] of the excited electronic states of NH have yielded satisfactory agreement with experiment. Particularly impressive were the essentially correct predictions, prior to experimental determination,[9] of the (X $^3\Sigma^-$ − a $^1\Delta$) singlet-triplet separation. More recently, ab initio calculations[14] have been reported for CH_3N, the simplest alkylnitrene. The positions of the electronic state of CH_3N are quite analogous to those of NH and the bonding is basically of the same covalent type. However, it should be noted that the dipole moments of CH_3N (~2.2 D) are somewhat larger than those of NH (~1.6 D).

The present theoretical study is directed toward the simplest nitrene after NH, namely LiN. To our knowledge, this molecule has not been the subject of previous experimental or theoretical investigations. Our interest in LiN arises from the anticipation that its electronic structure should be qualitatively different from either NH or the alkylnitrenes. That is, one expects a highly ionic Li^+N^- bond. Although one expects the electron configurations analogous to (1) and (2) to be the two lowest, the relative positions of the electronic states may change. Qualitatively, this may be seen by taking the ionic model to the extreme, Li^+N^-. Since Li^+ is a closed-shell ion, in the ionic limit one would expect the open-shell structure of LiN to be the same as that of the N^- ion. The lowest electron configuration for N^- is $1s^2\ 2s^2\ 2p^4$ and hence the electronic ground state will be of ^3P symmetry. Under $C_{\infty v}$ symmetry, this ^3P state has degenerate $^3\Pi$ and $^3\Sigma^-$ components. Thus our naiive ionic model predicts the $^3\Pi$ and $^3\Sigma^-$ states of LiN to be degenerate. Recall that the $^3\Sigma^-$–$^3\Pi$ separation in the covalent NH radical is a full 3.69 eV.[10] Although we are by no means suggesting that the ionic picture be taken at face value, we would expect the $^3\Sigma$–$^3\Pi$ separation to be significantly less in LiN than in NH. This same qualitative prediction should hold for other ionic nitrenes R^+N^- as well.

Theoretical Approach

The basis set of Slater functions used in the present research is seen in Table I. The double ζ s basis sets for both atoms are those of Huzinaga and Arnau.[15] The two sets of p functions on lithium were roughly extrapolated from the double ζ results of Huzinaga and Arnau for B, C, and N. The nitrogen p functions are from the "nominal" basis set of Bagus, Gilbert, and Roothaan.[16] The N atom d function orbital exponent was chosen on the basis of previous experience.[17] To summarize, this basis set is derived from standard sources and for the separated atoms is of near Hartree-Fock caliber, i.e., yielding self-consistent-field (SCF) energies within 0.001 hartree of the exact ground state Hartree-Fock energies for the Li and N atoms. For the LiN molecule the basis is expected to be less adequate, and near r_e may yield SCF energies as much as 0.020 hartrees ≈0.5 eV above the molecular Hartree-Fock limit. Molecular integrals were evaluated as described in an earlier paper.[18]

It is easy to show from group theoretical considerations[19] that the $^3\Sigma^-$ state of LiN dissociates adiabatically to ground state atoms, ^2S_g Li + ^4S_u N. However, at large internuclear separations the $^3\Sigma^-$ SCF configuration

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^2 \qquad (3)$$

cannot describe the ground state atomic Hartree-Fock wave functions. To do this a two-configuration wave function is required[20]

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 5\sigma^2\ 1\pi^2 \qquad (4)$$

Table I. Basis Set of Slater Functions for LiN

Li		N	
Function type	Orbital exponent ξ	Function type	Orbital exponent ξ
1s	4.687	1s	8.528
1s	2.482	1s	5.999
2s	1.976	2s	2.252
2s	0.6716	2s	1.415
2p	1.3	2p	5.573
2p	0.6	2p	2.555
		2p	1.352
		3d	2.0

Table II. SCF and CI Total Energies in Hartrees for LiN[a]

	$^3\Sigma^-$		$^3\Pi$	
R	SCF	CI	SCF	CI
2.8	−61.7875	−61.8412	−61.7961	−61.8505
3.0	−61.8083	−61.8626	−61.8069	−61.8622
3.2	−61.8184	−61.8735	−61.8096	−61.8656
3.4	−61.8216	−61.8777	−61.8070	−61.8638
3.6	−61.8204	−61.8778	−61.8012	−61.8588
3.8	−61.8165	−61.8756	−61.7936	−61.8520
4.0	−61.8109	−61.8722	−61.7850	−61.8442
5.0	−61.7767	−61.8560	−61.7504	−61.8043
10.0	NA	−61.8470	NA	−61.7810

[a] Bond distances are given in bohr radii. As discussed in the text, a single configuration description of these states is not appropriate (NA) at large *R*.

Table III. Predicted Spectroscopic Constants for LiN[a]

	$^3\Sigma^-$	$^3\Pi$
E, hartrees	−61.8781	−61.8656
r_e, Å	1.85	1.70
D_e, eV	0.85	2.30
T_e, eV	0.00	0.34
T_0, eV	0.00	0.35
B_e, cm^{-1}	1.049	1.245
ω_e, cm^{-1}	657	833
α_e, cm^{-1}	0.0167	0.0150
$\omega_e x_e$, cm^{-1}	13.97	7.99

[a] These results were obtained from the configuration interaction calculations.

Therefore, in our CI calculations, all configurations differing by one or two orbitals from either (3) or (4) have been included. Note, however, that the inner six electrons are always held frozen in the $1\sigma^2\ 2\sigma^2\ 3\sigma^2$ core. In addition, for double excitations, those angular momentum couplings having identically zero matrix elements[21-24] with both (3) and (4) were deleted. In this case, this problem is solved readily by including only those double excitations which retain the $^3\Sigma^-$ coupling of the outer two electrons in (3) and (4). The final wave functions for the $^3\Sigma^-$ state each include 335 configurations.

For the $^3\Pi$ state the conventional SCF configuration is

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma\ 1\pi^3 \qquad (5)$$

However, this configuration cannot properly describe dissociation to ^2P_u Li + ^4S_u N, as demanded by the Wigner-Witmer rules.[18] The second configuration

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma\ 1\pi^2\ 2\pi \qquad (6)$$

is required for this purpose. However, there are four linearly dependent $^3\Pi$ eigenfunctions which result from electron configuration 6. Using appropriate Clebsch-Gordan coefficients one finds that the angular momentum coupling which describes the atomic Hartree-Fock wave functions for ^2P_u Li + ^4S_u N is (deleting the $1\sigma^2\ 2\sigma^2\ 3\sigma^2$ core)

$$\begin{aligned}\frac{1}{2\sqrt{3}}\{ &+ 3(4\sigma\alpha\ 1\pi_-\alpha\ 1\pi_+\alpha\ 2\pi_+\beta)\\ &- 1(4\sigma\alpha\ 1\pi_-\alpha\ 1\pi_+\beta\ 2\pi_+\alpha)\\ &- 1(4\sigma\alpha\ 1\pi_-\beta\ 1\pi_+\alpha\ 2\pi_+\alpha)\\ &- 1(4\sigma\beta\ 1\pi_-\alpha\ 1\pi_+\alpha\ 2\pi_+\alpha)\} \qquad (7)\end{aligned}$$

A shorthand notation for this coupling would be

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ (4\sigma\ 1\pi^2\ {}^4\Sigma^-)(2\pi\ {}^2\Pi) \quad {}^3\Pi \qquad (8)$$

where the recoupling of the 3-electron $^4\Sigma^-$ and 1-electron $^2\Pi$ eigenfunctions to yield an overall $^3\Pi$ state is implicit.

A theoretical description of the $^3\Pi$ state will be equivalent to that described earlier for the $^3\Sigma^-$ state by including all single excitations with respect to (6) and (7), plus all double excitations with nonvanishing Hamiltonian matrix elements with either (6) or (7). To isolate the minimum number of angular momentum couplings having nonzero matrix elements with (7) is a problem somewhat more difficult than those discussed in previous work along these lines.[21-24] And in fact we have not carried out the complete reduction. However, if one includes all *interacting* single and double excitations with respect to (6) and *all* single and double (regardless of coupling type) excitations with respect to (7), a total of 1138 $^3\Pi$ configurations are found. In the present work, we have reduced this total to 546 by eliminating most of the doubly excited couplings having zero matrix elements with (7). As the primary example of how this is done, consider the double excitation $4\sigma\ 1\pi \rightarrow 6\sigma\ 3\pi$, or

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 6\sigma\ 1\pi\ 2\pi\ 3\pi \qquad (9)$$

There are nine linearly independent $^3\Pi$ eigenfunctions which arise from this electron configuration.[25] However, if one of the nine couplings is of the form

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ (6\sigma\ 1\pi\ 3\pi\ {}^4\Sigma^-)(2\pi\ {}^2\Pi) \quad {}^3\Pi \qquad (10)$$

then the eight remaining couplings, chosen in any manner, except that they must be othogonal to (10), will have identically zero H matrix elements with (8). Since there are $(10\sigma)(4\pi) = 40$ electron configurations of type (9), we were able to delete $40 \times 8 = 320$ configurations in this manner.

To obtain a nearly optimal set of molecular orbitals, the iterative natural orbital method of Bender and Davidson[26] was adopted. Since the present calculations represent a nearly full valence CI, only a small energy lowering was obtained. However, the CI expansion is much more compact and the resulting natural orbitals can be interpreted in chemical terms.

Potential Curves and Spectroscopic Constants

Table II gives the calculated total energies as a function of internuclear separation. From these the CI potential curves seen in Figure 1 were constructed. Near the minimum for each state, the CI energies were treated as an empirical function of internuclear distance by fitting the five points nearest the minimum of each curve to a fourth order polynomial. Following standard methods,[27] vibrational and rotational spectroscopic constants were then calculated and are given in Table III.

It is clear that the relationship between the $^3\Sigma^-$ and $^3\Pi$ states of LiN is indeed very different from that seen in the covalent nitrenes NH and CH_3N. In fact the $^3\Sigma^-$-$^3\Pi$ separation is predicted to be 0.30 eV, or less that one-tenth of the experimental separation (3.69 eV[10]) in NH. This result certainly appears to confirm qualitatively the merit of the ionic model discussed in the introductory section.

Another significant difference relative to NH concerns the bond distances. For NH, the r_e values are essentially identical: 1.045 Å for $^3\Sigma^-$ and 1.046 Å for $^3\Pi$. However, for LiN, there is a full 0.15 Å difference in bond distances. Note also that the R-N bond distance in LiN is much longer than in NH and significantly longer than in CH_3N, where $^{14}r_e$(C-N) ~ 1.47 Å.

The dissociation energies of both electronic states are rather small, the $D_e = 0.85$ eV for the $^3\Sigma^-$ state being particularly conspicuous. As mentioned in our discussion of basis sets, these predicted dissociation energies may be as much as 0.5 eV less than the exact (unknown) values. The small ground state D_e tends to limit the number of ways in which LiN might be observed experimentally. One possibility, however, is a crossed molecular beam study[28] of the reaction

$$\mathrm{N} + \mathrm{Li}_2 \longrightarrow \mathrm{LiN} + \mathrm{Li} \qquad (11)$$

Due to the low (1.1 eV) dissociation energy of Li_2, reaction 11 should be roughly thermoneutral or perhaps slightly exothermic, and the reaction might well proceed at thermal energies.

Although the LiN dissociation energy has not been determined experimentally, at least two predictions of its value have been made in the literature. In the earlier of these, due to Margrave and Sthapitanonda,[29] D_0(LiN) was predicted to be 118-178 kcal/mol. More recently, Herm and Herschbach[30] have predicted a much smaller value of 48 kcal/mol. Our estimate of $D_0(^3\Sigma^-$ LiN) ≤ 30 kcal/mol is clearly much closer to that of Herm and Herschbach. Finally we note that the Herm-Herschbach result was based on an assumed bond distance ~0.15 Å shorter than that found here. An appropriate adjustment to their ionic model would clearly result in a dissociation energy even closer to ours.

An interesting point seen in Figure 1 is that the $^3\Sigma^-$ and $^3\Pi$ potential curves cross at $R = 2.98$ bohrs = 1.58 Å. Thus, the $^3\Pi$ state is predicted to be the ground state for internuclear separations less than 1.58 Å. The crossing occurs just below the $v = 5$ vibrational level of the $^3\Sigma^-$ ground state, and about midway between the $v = 0$ and $v = 1$ levels of the excited $^3\Pi$ state. Thus, if the calculated potential curves are to be taken literally, the LiN electronic spectrum, occurring in the infrared, will be complicated. However, the relative positions of our calculated $^3\Sigma^-$ and $^3\Pi$ potential curves are uncertain by at least 0.1 eV, so a literal interpretation would be unwise. Since the shape of the curves is unlikely to change in a more complete theoretical treatment, the primary concern is that they may be shifted with respect to each other.

Electronic Transition Probabilities

Two expressions for the oscillator strength for an electronic transition from state a to state b are the "length" form

$$f_{ab}^{\,l} = \tfrac{2}{3}(E_b - E_a)|\langle\psi_a|\sum_i \mathbf{r}_i|\psi_b\rangle|^2 \qquad (12)$$

and the "velocity" form

$$f_{ab}^{\,v} = \tfrac{2}{3}(E_b - E_a)^{-1}|\langle\psi_a|-i\sum_i \nabla_i|\psi_b\rangle|^2 \qquad (13)$$

where E_a and E_b are the energies of the wave functions ψ_a and ψ_b, and the summation index i ranges over all electrons. Although expressions 12 and 13 are equivalent for exact energy eigengunction, this equality does not hold for approximate wave functions. The equality of (12) and (13) follows from the commutation property of H and $\mathbf{r}$, which can be used to derive still other equivalent expressions,[31] perhaps the most obvious of which is the geometric mean[32]

$$f_{ab}^{\,m} = \tfrac{2}{3}|\langle\psi_a|\sum_i \mathbf{r}_i|\psi_b\rangle|\cdot|\langle\psi_a|-i\sum_i \nabla_i|\psi_b\rangle| \qquad (14)$$

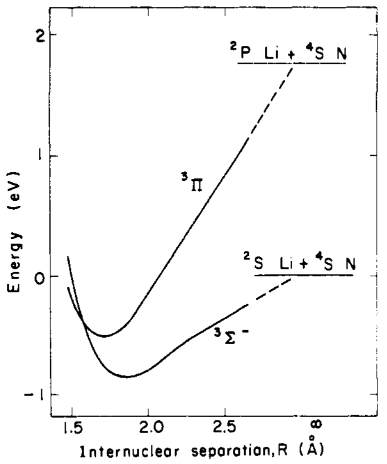

Figure 1. Theoretical potential energy curves for the *LiN* molecule.

It is a common practice[17] to evaluate both length and velocity forms and use the agreement between the resulting f_{ab} values as a crude indication of the reliability of the predictions. For LiN, where the energy separation $(E_b - E_a)$ is subject to a large percentage uncertainty, the use of the geometric mean (which does not involve ΔE) is particularly appealing.

Since Hartree-Fock transition probabilities typically differ from experiment by a factor of 3,[33] the use of correlated wave functions (such as those reported here) is highly advisable. Unfortunately, the calculation of transition moments from large CI wave functions is a notoriously difficult problem.[34] Since each of the wave functions calculated here is expressed in terms of its own natural orbitals, the orbitals used in ψ_a will have no convenient orthogonality relationships with the orbitals used in ψ_b. The computational difficulty resulting from this "nonorthogonality problem" is best illustrated by noting that if ψ_a and ψ_b are antisymmetrized products of n orbitals, loss of orthogonality between the sets of orbitals increases the number of contributions to the transition moment from n to $n!$. In the present calculations, ψ_a and ψ_b are of course sums of large numbers of such antisymmetrized products, increasing the computational difficulties by orders of magnitude. However, one of us (P.K.P.) has developed a new method (for the calculation of transition moments), which exploits the spin and spatial symmetry of CI wave functions to such a degree that such calculations have become quite feasible. For details of the method, the reader is referred elsewhere.[35]

Since our wave functions are obtained in terms of natural orbitals, one would hope that the transition moments might be accurately calculated using less than the entire 335 and 546 configuration wave functions for the $^3\Sigma^-$ and $^3\Pi$ states. To test this idea, the configurations in each wave function were ordered by coefficient, and only the n most important configurations from each wave function were used to compute the transition moments. These results are summarized in Table IV. There we see first that the use of natural orbitals does allow a greatly simplified, yet accurate, calculation of the transition moments. That is, by approximating each CI wave function as a linear combination of the first 200 configurations, one performs only (200 × 200)/(335 × 546) → 22% of the labor required using the complete CI expansions. Since the results are for our purposes identical, the former procedure is distinctly preferable. In addition Table IV indicates that the "length" transition moment is much less sensitive to the details of the wave function than is the "velocity" transition moment. For example, at R = 3.4 bohrs, $\langle\psi_a|\Sigma_i\mathbf{r}_i|\psi_b\rangle$ changes by 0.3% when 100 instead

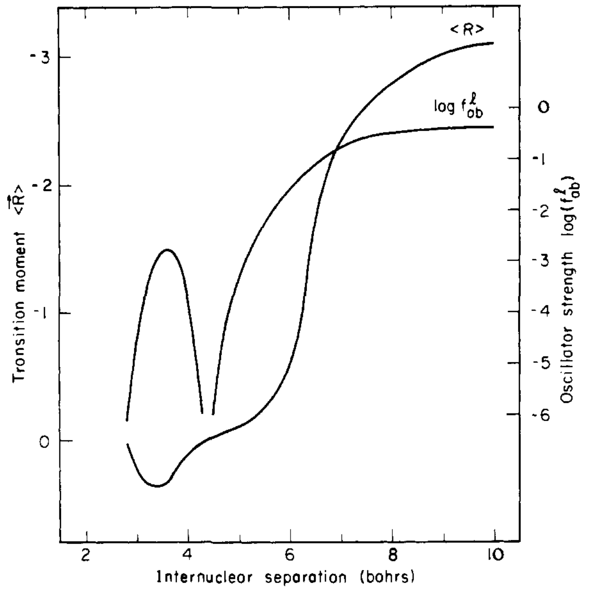

Figure 2. Transition moment and oscillator strength for the $^3\Pi \leftarrow {}^3\Sigma^-$ transition of LiN as a function of internuclear separation.

Table IV. Transition Moments Obtained Using the *n* Most Important (Ranked by Coefficient) Configurations in Each CI Wave Function[a]

No. of configurations *n*	$R = 3.4$: $\langle\psi_a|\sum_i r_i|\psi_b\rangle$	$R = 3.4$: $\langle\psi_a|-i\sum_i\nabla_i|\psi_b\rangle$	$R = 10.0$: $\langle\psi_a|\sum_i r_i|\psi_b\rangle$	$R = 10.0$: $\langle\psi_a|-i\sum_i\nabla_i|\psi_b\rangle$
1	−0.00949	+0.02366	−1.64497	−0.11587
12	−0.25746	−0.00126	−2.81764	−0.19369
27	−0.30251	−0.01063	−2.81861	−0.19318
60	−0.30056	−0.01676	−2.81870	−0.19448
100	−0.29611	−0.01197	−2.81857	−0.19468
160	−0.29667	−0.01261	−2.81858	−0.19473
200	−0.29673	−0.01245		
260	−0.29671	−0.01246		

[a] The use of natural orbitals provides a basis for the expected convergence with respect to *n*. The direction of the transition moments is perpendicular to the internuclear axis.

of 60 configurations are used. However, the same change in method of calculation produces a change of 5.0% in $\langle\psi_a|-i\Sigma_i\nabla_i|\psi_b\rangle$.

Table IV also shows that electron correlation plays a very important role in determining the transition moments at $R = 3.4$. In fact, the magnitude of the CI length moment is a factor of 3 greater than the SCF value. For the velocity moment, note that even the signs of the SCF and final CI results are different. At $R = 10.0$, it should be pointed out that the most important $^3\Pi$ configuration is not (5), as at $R = 3.4$, but rather (7). There the problem with the one configuration results is due primarily to the lack of the second configuration 4 in the $^3\Sigma^-$ wave function.

Using the 260 most important configurations, oscillator strengths were calculated at R = 2.8, 3.4, 4.0, 5.0, 7.5, and 10.0 bohrs. These results are summarized in Table V. Some idea of the reliability of these predictions may be obtained by comparing the $R = 10.0$ result with the experimental ^2S_g-^2P_u oscillator strength[36] of the Li atom. The length, velocity, and mixed forms of the oscillator strength are respectively 73, 80, and 76% of the Li atom oscillator strength. However, it is clearly seen in Table V that the oscillator strength is a strong function of R, and may not have reached its limiting value at $R = 10.0$. To check this point, the Li atom oscillator strength was computed with our basis set and found to be 101% (length) and 104% (velocity) of experiment.

As mentioned earlier, the percentage uncertainty in our calculated $^3\Sigma^-$-$^3\Pi$ separation near the R_e values of the two potential curves tends to make the length and velocity forms of the oscillator strength unreliable. However, one is hopeful that the mixed form would be more useful. In any case, the oscillator strength is relatively small at $R = 3.4$ bohrs. This can be qualitatively understood in terms of our ionic model Li^+N^-, in which the $^3\Sigma^-$-$^3\Pi$ transition connects two states of the N^- ion. Since the two states arise from the $1s^2\ 2s^2\ 2p^4$ configuration, they are both of g parity and hence the transition is electric-dipole forbidden.

The transition moment and oscillator strength derived from the more reliable length form are plotted as a function of bond distance in Figure 2. There we see that the somewhat unusual behavior demonstrated in Table V is due to change in the sign of $\langle\mathbf{R}\rangle = \langle\psi(^3\Pi)|\Sigma_i\mathbf{r}_i|\psi(^3\Sigma^-)\rangle$ at an internuclear separation near 4.4 bohrs. This sign change is emphasized by the discontinuity at 4.4 bohrs in the logarithm of the oscillator strength.

To understand this behavior, let us examine the detailed nature of the $^3\Pi$ CI wave function. Note first that the 2π orbital in electron configuration 7 is essentially the Li 2p atomic orbital, especially at large bond distances. As the molecule dissociates (internuclear separation increases), the importance of the $4\sigma\ 1\pi^2\ 2\pi$ configuration increases monotonically. Thus the quantity $\langle 4\sigma\ 1\pi^2\ 2\pi|\mathbf{R}|\psi(^3\Sigma^-)\rangle$, which is positive, makes an increasingly important contribution to the transition moment as the internuclear separation increases. This quantity, of course, becomes the Li atom transition moment at infinite separation.

The other principal contributor to the transition moment is the quantity $\langle 4\sigma\ 1\pi^3|\mathbf{R}|\psi(^3\Sigma^-)\rangle$. This matrix element is *opposite* in sign to that of the $4\sigma\ 1\pi^3\ 2\pi$ configuration and generally much smaller. However, near r_e, the CI coefficient of the $4\sigma\ 1\pi^3$ configuration is so much larger than that of $4\sigma\ 1\pi^2\ 2\pi$ that the two contributions to the oscillator strength are of the same magnitude but opposite sign. As the bond distance increases, the 1π orbital becomes increasingly a pure nitrogen 2p orbital and the $4\sigma\ 1\pi^3$ configuration describes the $2p^4$ electron configuration of N^- Since transitions among the states of N^- arising from $2p^4$ are par-

Table V. Transition Moment Matrix Elements and Oscillator Strengths for the $^3\Sigma^- \rightarrow {}^3\Pi$ Transition of LiN[a]

R, bohrs	$|\langle\psi_a|\sum_i r_i|\psi_b\rangle|^2$	$|\langle\psi_a|-i\sum_i\nabla_i|\psi_b\rangle|^2$	$f_{ab}{}^l$	$f_{ab}{}^v$	$f_{ab}{}^m$
2.8	0.000114	0.001140	-7.90×10^{-7}	−0.0731	-2.40×10^{-4}
3.4	0.1341	0.001168	1.11×10^{-3}	0.0627	0.00834
4.0	0.01123	0.004307	1.97×10^{-4}	0.109	0.00464
5.0	0.01221	0.00547	4.00×10^{-4}	0.0743	0.00545
7.5	6.73	0.0353	0.294	0.359	0.325
10.0	9.61	0.0272	0.422	0.275	0.341
∞	10.7	0.0505	0.484	0.497	0.490
∞ (Experiment[b])			0.48 ± 0.2	0.48 ± 0.2	0.48 ± 0.2

[a] The three different forms of the oscillator strength are given in eq 12–14. The twofold spatial degeneracy of the $^3\pi$ state has been incorporated in the tabulated moments. [b] Reference 33.

Table VI. Natural Orbital Occupation Numbers for LiN

	$^3\Sigma^-$ (R = 3.4 bohrs)	$^3\Pi$ (R = 3.2 bohrs)
1σ	2.000	2.000
2σ	2.000	2.000
3σ	2.000	2.000
4σ	1.961	0.992
5σ	0.024	0.006
6σ	0.005	0.002
7σ	0.003	0.001
8σ	0.001	0.0001
1π	1.982	2.931
2π	0.016	0.058
3π	0.006	0.006
4π	0.001	0.004

ity forbidden, the matrix element $\langle 4\sigma\ 1\pi^3|\mathbf{R}|\psi(^3\Sigma^-)\rangle$ decreases with increasing internuclear separation.

To summarize, the contributions to $\langle\mathbf{R}\rangle$ from the two most important configurations in the $^3\Pi$ wave function are of opposite sign. Further, the magnitude of the contribution from the $4\sigma\ 1\pi^2\ 2\pi$ configuration increases with r(Li-N), while that from $4\sigma\ 1\pi^3$ decreases with r(Li-N). These observations explain the unusual behavior seen in Table V and Figure 2.

Electronic Structure

The simplest indicators of the nature of complex CI wave function are the natural orbital occupation numbers, seen in Table VI for the $^3\Sigma^-$ and $^3\Pi$ states. We see first that the occupation numbers are qualitatively very similar to those predicted by the molecular orbital approximation, configurations 3 and 5. For the $^3\Sigma^-$ state the 5σ orbital is the most important after the Hartree-Fock occupied orbitals. For the $^3\Pi$ state, the σ virtual orbitals are quite unimportant, but the 2π orbital has a relatively large occupation number.

These occupation numbers may be understood qualitatively in terms of the most important configurations of each wave function. These are seen in Table VII for $^3\Sigma^-$ and $^3\Pi$ near their respective equilibrium geometries. The magnitude of the 5σ occupation number is understood in terms of configurations 2, 3, and 4 of the $^3\Sigma^-$ wave function. The even greater importance of the 2π orbital in the $^3\Pi$ wave function is seen from the importance of the $1\pi \rightarrow 2\pi$ and $1\pi^2 \rightarrow 2\pi^2$ configurations. Note that all four $^3\Pi$ configurations arising from orbital occupancy 6 are included in the $^3\Pi$ wave function. The properly dissociating coupling 7 is the most important, with coefficient 0.126. The value 0.163 given in Table VI reflects the importance of all four configurations,[37] being $(c_1{}^2 + c_2{}^2 + c_3{}^2 + c_4{}^2)^{1/2}$, where the c's are the coefficients of the four different couplings in the CI wave function.

Table VII. Important Configurations for the $^3\Sigma^-$ and $^3\Pi$ States of LiN Near Their Respective Minima

Configuration	Couplings Included	Coefficient
$^3\Sigma^-$ (R = 3.4 bohrs)		
1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^2$	1	0.984
2. $4\sigma 1\pi \rightarrow 5\sigma 2\pi$	2	0.100
3. $4\sigma^2 \rightarrow 5\sigma^2$	1	0.069
4. $4\sigma \rightarrow 5\sigma$	2	0.060
5. $4\sigma 1\pi \rightarrow 6\sigma 3\pi$	2	0.045
6. $1\pi^2 \rightarrow 2\pi^2$	1	0.044
$^3\Pi$ (R = 3.2 bohrs)		
1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^3$	1	0.970
2. $1\pi \rightarrow 2\pi$	4	0.163
3. $1\pi^2 \rightarrow 2\pi^2$	4	0.133
4. $4\sigma 1\pi \rightarrow 5\sigma 2\pi$	4	0.069

Finally, the electric dipole moments of the two electronic states have been calculated, using SCF wave functions and a comparable Gaussian basis set. For the $^3\Sigma^-$ state at R = 3.2 bohrs, the electronic and nuclear contributions with respect to the Li atom are 63.97 and 56.94 D. The electronic contribution is of $\mathrm{Li^+N^-}$ polarity, while the nuclear contribution is of opposite sign. Thus the dipole moment is 7.0 D. Similarly, the $^3\Pi$ state dipole moment at R = 3.2 bohrs is predicted to be 6.2 D. For comparison, the dipole moment of LiF is 6.33 D.[38] The same dipole moments were obtained using the wave functions described in this paper: $\mu(^3\Pi)$ = 5.27 D; $\mu(^3\Sigma^-)$ = 6.17 D at R = 3.4. Thus it is reasonable to conclude, on this ground as well, that LiN is distinctly ionic. Although this conclusion might appear to be an obvious one, it should be pointed out that the nitrogen atom is much less electronegative than fluorine. The most obvious evidence of this is the fact that $\mathrm{N^-}$ in its ground state is unstable[39] relative to N + e, while the electron affinity of F is a hefty 3.40 eV.[40]

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References and Notes

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(2) (a) W. I. Lwowski, Ed., "Nitrenes", Interscience, New York, N.Y., 1970; (b) Y. Hayashi and D. Swern, *J. Am. Chem. Soc.*, **95**, 5205 (1973).

(3) P. F. Alewood, P. M. Kazmaier, and A. Rauk, *J. Am. Chem. Soc.*, **95**, 5466 (1973).

(4) H. D. Gafney, J. L. Reed, and F. Basolo, *J. Am. Chem. Soc.*, **95**, 7998 (1973).

(5) P. A. Lehman and R. S. Berry, *J. Am. Chem. Soc.*, **95**, 8614 (1973).

(6) J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *Chem. Phys. Lett.*, **25**, 321 (1974).

(7) W. Kirmse, Ed., "Carbene Chemistry", Academic Press, New York, N.Y., 1971.

(8) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).

(9) A. Gilles, J. Masanet, and C. Vermeil, *Chem. Phys. Lett.*, **25**, 346 (1974).

(10) B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, Oxford, 1970.

(11) P. E. Cade, *Can. J. Phys.*, **46**, 1989 (1968).

(12) W. M. Huo, *J. Chem. Phys.*, **49**, 1482 (1968).

(13) S. V. O'Neil and H. F. Schaefer, *J. Chem. Phys.*, **55**, 394 (1971).

(14) D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **98**, 3754 (1974).

(15) S. Huzinaga and C. Arnau, *J. Chem. Phys.*, **53**, 451 (1970).

(16) P. S. Bagus, T. L. Gilbert, and C. C. J. Roothaan, *J. Chem. Phys.*, **56**, 5195 (1972).

(17) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.

(18) H. F. Schaefer, *J. Chem. Phys.*, **52**, 6241 (1970).

(19) E. Wigner and E. E. Witmer, *Z. Phys.*, **51**, 859 (1928).

(20) G. Das and A. C. Wahl, *J. Chem. Phys.*, **44**, 87 (1966).

(21) A. Bunge, *J. Chem. Phys.*, **53**, 20 (1970).

(22) C. F. Bender and H. F. Schaefer, *J. Chem. Phys.*, **55**, 4798 (1971).

(23) A. D. McLean and B. Liu, *J. Chem. Phys.*, **58**, 1066 (1973).

(24) E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 83 (1974).

(25) H. F. Schaefer, *J. Comput. Phys.*, **6**, 142 (1970).

(26) C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966).

(27) G. W. King, "Spectroscopy and Molecular Structure", Holt, Rinehart and Winston, New York, N.Y., 1964.

(28) J. L. Kinsey, "MPT International Review of Science", J. C. Polanyi, Ed., Butterworths, London, 1972, Physical Chemistry Series One, Vol. 9.

(29) J. L. Margrave and P. Sthapitanonda, *J. Phys. Chem.*, **59**, 1239 (1955).

(30) R. R. Herm and D. R. Herschbach, *J. Chem. Phys.*, **52**, 5783 (1970).

(31) H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms", Springer-Verlag, Berlin, 1957, 251.

(32) A. E. Hansen, *Mol. Phys.*, **13**, 425 (1967).

(33) H. E. Popkie and W. H. Henneker, *J. Chem. Phys.*, **55**, 617 (1971).

(34) H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, and R. G. Parr, *J. Chem. Phys.*, **47**, 1936 (1967).

(35) P. K. Pearson, Ph.D. Thesis, University of California, Berkeley, Calif., 1974.

(36) G. Stephenson, *Nature (London)*, **167**, 156 (1951).

(37) H. F. Schaefer, Ph.D. Thesis, Stanford University, 1969. See the discussion of "Compacting the Wave Function", pp 104–106.

(38) L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, *J. Chem. Phys.*, **38**, 1203 (1963).

(39) H. F. Schaefer and F. E. Harris, *Phys. Rev. Lett.*, **23**, 1561 (1968).

(40) R. Milstein and R. S. Berry, *J. Chem. Phys.*, **55**, 4146 (1971).