

Theoretical Approaches to the Problem of the "Size" of the Lone Pair on Nitrogen¹⁻³

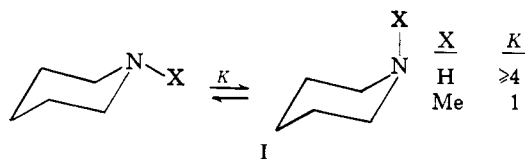
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The relative energies of a system composed of an ammonia molecule and a helium atom have been calculated as functions of the nitrogen-helium internuclear distance for the two extreme cases where the helium atom approaches the nitrogen atom either along an N-H bond or along the threefold axis of the ammonia molecule from the side away from the hydrogens. A van der Waals' calculation employing the method of Hill shows that, for a given energy, the helium can approach more closely to the nitrogen by the latter path for distances where the repulsion outweighs the attractive (London) forces. Detailed quantum mechanical calculations indicate that the total repulsion between the ammonia molecule and the helium atom is much greater for all internuclear distances when the helium approaches the nitrogen along the N-H axis.

Introduction

While the cyclohexane ring has been very carefully studied by the methods of conformational analysis,⁴ the piperidine ring has received very little attention.⁵ Aroney and LeFèvre⁶ made use of molecular Kerr constants⁷ to study the conformations of piperidine (I, X = H), and N-methylpiperidine (I, X = Me).



They concluded that the equilibria between the equatorially and axially orientated groups were as shown. From our knowledge of the behavior of atoms in molecules, as shown for example by the accuracy of the van der Waals type calculation,⁸⁻¹⁰ it seemed to us

(1) This research was supported by Grants GP-1174 and G-19981 from the National Science Foundation.

(2) A summary of this paper was presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963.

(3) This paper is VIII in the series "Organic Quantum Chemistry" (Paper VII: N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **86**, 2811 (1964)) and paper XLI in the series "Conformational Analysis" (paper XL: N. L. Allinger and C. D. Liang, *Tetrahedron*, in press).

(4) E. L. Eliel, N. L. Allinger, S. A. Angyal, and G. B. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p. 36.

(5) Ref. 4, p. 244.

(6) M. Aroney and R. J. W. LeFèvre, *J. Chem. Soc.*, 3002 (1958).

(7) C. G. LeFèvre and R. J. W. LeFèvre, *Rev. Pure Appl. Chem.*, **5**, 261 (1955).

(8) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

(9) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(10) N. L. Allinger, J. Allinger, and M. A. DaRooge, *ibid.*, **86**, 4061 (1964).

unlikely that *K* could be as large as one when X was equal to methyl. An axial methyl on a cyclohexane ring is unfavorable,¹¹ mainly because of the repulsion between it and the methylene groups at C-3 and C-5. The slightly different bond lengths of the C-N and N-H bonds compared to the C-C and C-H bonds would change somewhat the repulsion between the axial methyl on nitrogen and these methylenes, but it would seem qualitatively that the same sort of result would be expected, contrary to the conclusions of Aroney and LeFèvre. For the piperidine case, the hydrogen on nitrogen is located at such a distance as to be attracted to the methylenes at C-3 and C-5, and it does not appear possible to predict *a priori* whether the hydrogen would prefer to be axial or equatorial, but it does appear that the energy difference between the two positions should be quite small, again contrary to Aroney and LeFèvre. These latter conclusions depend on the accuracy to which the Kerr constants can be calculated for the different conformations of the molecules concerned. Such calculations involve the use of the transverse and longitudinal polarizabilities of the various bonds in the system and require that all of the bond angles in the system be known. For the systems at hand, unfortunately, the angles are not accurately known from experiment, and the assumption of tetrahedral values will introduce some error. There appears to be a lack of agreement as to the values of the bond polarizabilities, and the accuracy to which they are known is not completely clear.¹² Just how these different errors might affect the final calculated Kerr constants is uncertain but has led us to question the conclusions drawn from them.

Discussion and Results

Since information on the preferred conformations of these systems is of potential importance, it seemed worthwhile to study the problem in much more detail. This paper is concerned with the theoretical studies which have been carried out, in which the goal was to try to define the "size" of the lone pair on nitrogen. The following paper¹³ will discuss various experimental approaches to the problem.

We are primarily interested in the general case of a tricovalently bound nitrogen interacting with a closed shell species. For purposes of calculation we have

(11) (a) Ref. 4, p. 439; (b) J. B. Hendrickson, *J. Am. Chem. Soc.*, **84**, 3355 (1962).

(12) R. F. Zürcher, *J. Chem. Phys.*, **37**, 2421 (1962).

(13) N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *J. Am. Chem. Soc.*, **87**, 1232 (1965).

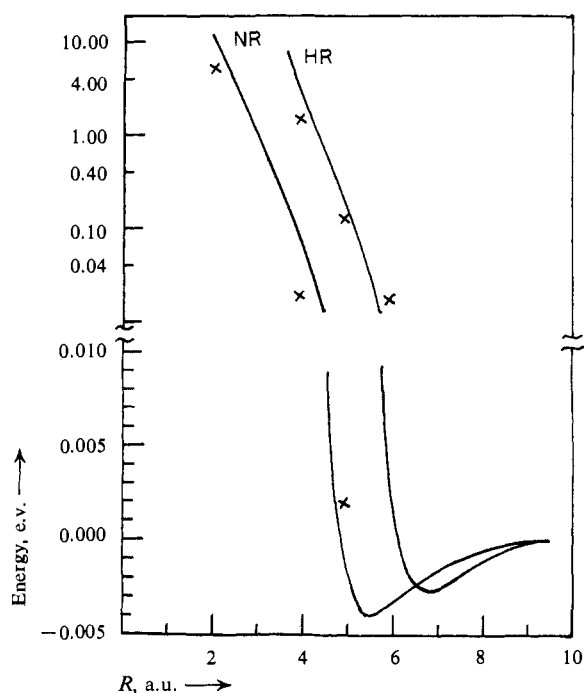


Figure 1. The total energy of the system ($\text{He} + \text{NH}_3$) as a function of R , the distance between nitrogen and helium. The curves HR and NR refer to approach of the helium atom to the nitrogen along an H-N bond and along the three-fold ammonia axis from the side away from the hydrogens, respectively, obtained by the Hill method. The crosses represent the same quantities obtained by quantum mechanical calculation.

taken the ammonia molecule and the helium atom, respectively, as simple representative members of these classes of compounds. Since tricovalently bound nitrogen in most cases has very nearly tetrahedral bond angles between its substituents¹⁴ we have chosen to use this geometry for the present case, even though it is not quite correct for ammonia itself. The bond length of the N-H bond has been taken to be 1.01 Å. or 1.909 a.u. throughout.

van der Waals' Calculations

Hill has shown how the van der Waals' energy of two closed-shell species can be calculated in terms of two experimentally determined parameters.⁸ This method has been applied extensively and successfully to a number of systems.^{8,10,15} The method considers only closed shells, so that a lone pair would not enter the calculation explicitly at all. For an interaction between a helium atom and an ammonia molecule, one would consider four separate interactions, that of the helium with each other atom separately. This type of van der Waals' calculation has been carried out for two cases, first where the helium approaches the nitrogen along an N-H bond axis, and second where the helium approaches the nitrogen along the threefold axis of ammonia from the side away from the hydrogens. The latter case will be referred to as the NR system, and the former as HR, where R is the distance between the nitrogen and helium nuclei in atomic units. The necessary numerical quantities are given in Table I.

(14) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication Number 11, The Chemical Society, London, 1958.

(15) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 4601 (1962).

Table I. van der Waals' Data

Atom	van der Waals' radius, Å.	Interaction	ϵ , cal./mole
N	1.50	N He	46
He	1.48	H He	22
H	1.20		

In Figure 1 are shown graphs of the van der Waals energies of the systems as functions of the nitrogen-helium distance. The van der Waals curves cross one another at a nitrogen-helium distance of about 3.4 Å., and which arrangement has the lower energy therefore depends on the distance. When the helium atom approaches the nitrogen to within 3 Å. or less, the force between the helium and nitrogen is still attractive if the helium is approaching along an N-H axis, but the hydrogen closest to the helium exerts a considerable repulsion on the latter, and this repulsion dominates the energetics of the situation. Thus, for distances from nitrogen of less than about 3 Å. we would say the hydrogen is "bigger" than the lone pair, but this would not be true at large distances.

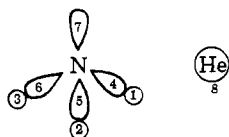
Quantum Mechanical Calculations

Because of the nature of the above van der Waals calculations, it was a foregone conclusion that the qualitative results would be obtained as they were. The conclusions of Aroney and LeFèvre, if correct, would appear to indicate some sort of unexpected interaction between the lone pair on the nitrogen and other parts of the system. If this is indeed the case, such a van der Waals calculation as given above, which does not explicitly include the lone pair, would necessarily lead to an erroneous conclusion. It therefore seemed to us that a proper detailed quantum mechanical calculation should be carried out to give a sounder theoretical basis from which to draw conclusions.

A semiempirical method has been used in the present work which is an extension of Pariser and Parr's molecular orbital method for π -electronic systems,¹⁶ in which the σ -electrons and nonbonding electrons are all considered explicitly. The ammonia molecule was assumed to have a tetrahedral structure with the N atom at the center of the tetrahedron and the four sp^3 orbitals pointing toward the vertices (the consequences of this assumption will be discussed later). Each hydrogen is located on the axis of a tetrahedral nitrogen orbital. The nitrogen nucleus plus its two 1s electrons, the three hydrogen nuclei, and the helium nucleus constitute the core, while all of the other electrons constitute the electronic system and are treated explicitly. The problem then concerns a five-center-eight-orbital-ten-electron system. The atomic orbitals which enter into the problem were numbered as shown below.

Molecular Orbitals (MO). These orbitals were obtained by diagonalizing Hückel matrices constructed in the following way. The core integrals α_x were

(16) (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953); (b) R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).



obtained by using McWeeny and Peacock's formula¹⁷

$$\delta\alpha_x = \{(A_x - A_c) + \frac{1}{2}[Z_x(I_x - A_x) - (I_c - A_c)]\} / (-4.79) \quad (1)$$

where the subscripts x and c refer to the atom x under consideration and the carbon atom (as reference), respectively, and I and A are the valence state ionization potential and electron affinity, respectively, and Z_x is the number of electrons contributed by the orbital centering on x . We note that $\delta\alpha_x$ is in units of β_0 , the Hückel β for benzene, which was taken to be -2.39 e.v.

The resonance integrals over two neighboring orbitals i and j were calculated according to Mulliken's formula¹⁸

$$\beta_{ij} = \frac{\frac{1}{2}(I_i + I_j)A_{ij}S_{ij}/(1 + S_{ij})}{I_o A_o S_o/(1 + S_o)} \beta_0, \quad (2)$$

where I_i and I_j are ionization potentials for atoms i and j , respectively, and S_{ij} is the overlap integral over orbitals i and j , and A_{ij} equals 0.773 for σ -type overlap and 1 for π -type overlap. Subscript o refers to similar quantities for the C-2p π orbitals in benzene. In the Hückel matrices, β_{ij} values are expressed in units of β_0 . Only β_{14} , β_{25} , and β_{36} were considered for all systems. For systems NR or HR, β_{78} or β_{18} , respectively, were also considered.

In Table II are presented the values of the ionization potentials and the electron affinities used. The calculated α - and β -values are shown in Table III. Slater

Table II. Values of Atomic Ionization Potential (I) and Electron Affinity (A), e.v.

Atom	I	A
C	11.16 ^a	0.03 ^a
H	13.595 ^b	0.7157 ^b
N	18.93 ^a	4.15 ^a
He	24.581 ^b	

^a Values given for carbon with electronic configuration $sp^2 sp^2 sp^2 \pi$, and for nitrogen with electronic configuration $(sp^2)^2 sp^3 sp^3 sp^3$, by J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962).
^b G. Herzberg, "Atomic Spectra and Atomic Structure," Dover, New York, N. Y., 1944, pp. 200, 219.

type AO's were used with effective nuclear charges of 3.90, 1.7, and 1.0 for nitrogen, helium, and hydrogen, respectively.

Electronic Repulsion Integrals. In the evaluation of electronic repulsion integrals, we employed features characterizing the Pariser and Parr method, namely the formal neglect of differential overlap between AO's and the adjustment of some theoretical quantities by semiempirical methods. Integrals of the form $(45|11)$ or $(45|45)$ have been neglected since the former type have extremely small values as compared with those

(17) R. McWeeny and T. E. Peacock, *Proc. Phys. Soc. (London)*, **A70**, 41 (1957).

(18) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

Table III. Core and Resonance Integrals for the Hückel Matrix^a

$\alpha_1 = -0.33619 = \alpha_2 = \alpha_3$			
$\alpha_4 = -1.25160 = \alpha_5 = \alpha_6$			
$\alpha_7 = -2.78600$			
$\alpha_8 = -3.97411$			
R	β_{18}	β_{78}	β_{14}^b
H 5.909	0.49302	0.00000	2.10780
H 4.909	1.04049	0.00000	2.10780
H 3.909	1.82294	0.00000	2.10780
N 5.909	0.00000	0.04532	2.10780
N 4.909	0.00000	0.16960	2.10780
N 3.909	0.00000	0.55467	2.10780
N 3	0.00000	1.33871	2.10780
N 2	0.00000	2.57300	2.10780
N ∞	0.00000	0.00000	2.10780

^a All values in units of β_0 . ^b $\beta_{14} = \beta_{25} = \beta_{36}$.

of other integrals, and justification for neglecting integrals of the latter type was found in a crude calculation on their significance in affecting the ground-state energies. The calculation showed that inclusion of these integrals would alter the ground-state energies of the systems NR and HR by nearly equal amounts. Since we are only interested in the relative energies, the error produced by neglecting these integrals should not be serious.

The semiempirical adjustment of some theoretical quantities includes the determination of valence-state ionization potentials, the evaluation of one-center repulsion integrals from atomic spectral data, and the extrapolation of two-center integrals from their theoretical values at fairly large distances to the empirical values at zero internuclear distance. For the ionization potentials the values given in Table II were used.

One-Center Integrals. Four kinds of one-center integrals enter into this problem; they are

$$(HH|HH) = (11|11) = (22|22) = (33|33)$$

$$(HeHe|HeHe) = (88|88)$$

$$(NN|NN) = (44|44) = (55|55) = (66|66) = (77|77)$$

$$(NN|N'N') = (44|55) = (44|66) = (44|77) = (55|66) = (55|77) = (66|77)$$

The integral $(HH|HH)$ was taken to be the difference between the ionization potential and the electron affinity of the hydrogen atom, following the approximation proposed by Pariser.¹⁹ By similar reasoning, the integral $(HeHe|HeHe)$ was obtained as the difference between the second and the first ionization potentials of the helium atom.

The orbitals centering on the nitrogen atom are considered to be sp^3 hybrids. Therefore we can write

$$X_N = \frac{1}{2}[(S_N) + \sqrt{3}(2\sigma_N)] \quad (3)$$

and

$$X_{N'} = \frac{1}{2}[(S_N) + \sqrt{3} \cos \theta(2\sigma_N) + \sqrt{3} \sin \theta(2\pi_N)] \quad (4)$$

where X_N and $X_{N'}$ are two different orbitals centering on the nitrogen nucleus and S_N , π_N , and σ_N are the nitrogen 2s, 2p π , and 2p σ orbitals, respectively, and $\bar{\pi}$ is the 2p orbital perpendicular to 2p σ and to 2p π , and θ is the tetrahedral angle.

(19) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

Using eq. 3 and 4, one can show that (NN|NN) and (NN|N'N') can be expressed in terms of the integrals of the following form.

$$\begin{aligned}(\sigma_N \sigma_N | \sigma_N \sigma_N) &= (\pi_N \pi_N | \pi_N \pi_N) \\(S_N S_N | S_N S_N) &= (S_N S_N | \pi_N \pi_N) = (S_N S_N | \sigma_N \sigma_N) \\(\sigma_N \sigma_N | \pi_N \pi_N) &= (\pi_N \pi_N | \bar{\pi}_N \bar{\pi}_N) \\(S_N \sigma_N | S_N \sigma_N) &= (S_N \pi_N | S_N \pi_N)\end{aligned}$$

The values of these one-center integrals were obtained by considering the following processes

$$2N(s^2 \pi \bar{\pi} \sigma, V_3) \rightarrow N^+(s^2 \bar{\pi} \sigma, V_2) + N^-(s^2 \pi^2 \bar{\pi} \sigma, V_2) \quad (5)$$

$$2N(s \pi^2 \pi \sigma, V_3) \rightarrow N^+(s \bar{\pi}^2 \sigma, V_2) + N^-(s \pi^2 \bar{\pi}^2 \sigma, V_2) \quad (6)$$

$$2N(s \pi^2 \bar{\pi} \sigma, V_3) \rightarrow N^+(\pi^2 \bar{\pi} \sigma, V_2) + N^-(s^2 \pi^2 \bar{\pi} \sigma, V_2) \quad (7)$$

The calculated energy changes corresponding to eq. 5-7, respectively, are²⁰

$$\Delta E = (\pi_N \pi_N | \pi_N \pi_N) = 12.98 \text{ e.v.} \quad (8)$$

$$\Delta E = (\pi_N \pi_N | \pi_N \pi_N) = 12.76 \text{ e.v.} \quad (9)$$

and

$$\Delta E = (S_N S_N | S_N S_N) = 13.60 \text{ e.v.} \quad (10)$$

Since the electron configuration of the nitrogen atom is considered to be sp^3 , which is the average of one part of $s^2 p^3$ and three parts of sp^4 , we derived the value of $(\pi_N \pi_N | \pi_N \pi_N)$ as the weighted mean of values corresponding to eq. 8 and 9 as follows.

$$(\pi_N \pi_N | \pi_N \pi_N) = 1/4 (12.98 + 3 \times 12.76) = 12.82 \text{ e.v.}$$

The value of $(S_N S_N | S_N S_N)$ was taken from eq. 10 to be 13.60 e.v. For the other two integrals, $(\pi_N \pi_N | \bar{\pi}_N \bar{\pi}_N)$ and $(S_N \sigma_N | S_N \sigma_N)$, we used the values 11.3123 and 2.8949 e.v., respectively. These values were derived for the electronic configuration $s^{1/2} p^{11/3}$ by Anno from spectroscopic data.²⁰ Using eq. 3 and 4, we obtained (NN|NN) = 12.332 and (NN|N'N') = 14.472 e.v. upon incorporation of the values of the one-center integrals over the unhybridized orbitals.

Two-Center Integrals. The following two-center repulsion integrals enter the problem.

$$(HH|H'H') = (11|22) = (11|33) = (22|33)$$

$$\begin{aligned}(NN|HH) &= (11|44) = (11|55) = (11|66) = \\ &(11|77) = (22|44) = (22|55) = (22|66) \\ &= (22|77) = (33|44) = (33|55) = (33|66) \\ &= (33|77)\end{aligned}$$

$$(NN|\text{HeHe}) = (44|88) = (55|88) = (66|88) = (77|88)$$

$$(HH|\text{HeHe}) = (11|88) = (22|88) = (33|88).$$

Of these, the integrals (NN|HH) and (NN|HeHe) are expressed in terms of the following integrals,

(20) T. Anno, *J. Chem. Phys.*, **29**, 1161 (1958).

$$\begin{aligned}(S_N S_N | S_H S_H), (S_N S_N | S_{He} S_{He}), (\sigma_N \sigma_N | S_H S_H), \\ (\sigma_N \sigma_N | S_{He} S_{He}), (\pi_N \pi_N | S_H S_H), (\pi_N \pi_N | S_{He} S_{He}), \\ (S_N \sigma_N | S_H S_H), \text{ and } (S_N \sigma_N | S_{He} S_{He}),\end{aligned}$$

where S_H and S_{He} are the 1s orbitals of H and He, respectively.

The extrapolation formulas for these integrals were obtained by a procedure similar to that used by Pariser and Parr for $(\pi_C \pi_C | \pi_C \pi_C)$. We use the extrapolation formula

$$(aa|bb) = 1/2 [(aa|aa) + (bb|bb)] + mR + nR^2 \quad (11)$$

where R is the internuclear distance between atoms a and b, and m and n are constants to be determined by using theoretical values of $(aa|bb)$ at two fairly large distances, r and r' , and empirical values of $(aa|aa)$ and $(bb|bb)$. The values of r and r' were chosen such that the resulting empirical curve of $(aa|bb)$ vs. distance merges smoothly to the theoretical curve.

During the process of evaluating the extrapolation formulas for various integrals, we found that it was only necessary to obtain those for $(S_H S_H | S_H S_H)$, $(S_N S_N | S_H S_H)$, $(\sigma_N \sigma_N | S_H S_H)$, $(\pi_N \pi_N | S_H S_H)$, $(S_N S_N | S_{He} S_{He})$, and $(\sigma_N \sigma_N | S_{He} S_{He})$. The rest have their theoretical and empirical values so close at zero internuclear distance that they become identical at all practical distances.

The extrapolation formulas thus obtained are

$$(S_H S_H | S_H S_H) = 12.879 - 2.009R + 0.103R^2 \quad \text{for } R < 6 \text{ a.u.} \quad (12)$$

$$(S_N S_N | S_H S_H) = 13.240 - 2.2867R + 0.11478R^2 \quad \text{for } R < 5.4 \text{ a.u.} \quad (13)$$

$$(\sigma_N \sigma_N | S_H S_H) = 12.850 - 1.9281R + 0.09362R^2 \quad \text{for } R < 5.4 \text{ a.u.} \quad (14)$$

$$(\pi_N \pi_N | S_H S_H) = 12.850 - 2.0509R + 0.1095R^2 \quad \text{for } R < 5.4 \text{ a.u.} \quad (15)$$

$$(S_N S_N | S_{He} S_{He}) = 21.72 - 5.76006R + 0.50702R^2 \quad \text{for } R < 3.2 \text{ a.u.} \quad (16)$$

$$(\sigma_N \sigma_N | S_{He} S_{He}) = 21.322 - 5.03087R + 0.37416R^2 \quad \text{for } R < 3.2 \text{ a.u.} \quad (17)$$

Values of all of the integrals used are given in Table IV.

Core Parameters. According to the argument of Goeppert-Mayer and Sklar,²¹ the core Hamiltonian for electron i can be written

$$\mathcal{H}_{\text{core}(i)} = T(i) + U_p(i) + \sum_{q \neq p} U_q(i) + \sum_r U_r^*(i) \quad (18)$$

where T is the kinetic energy operator, and U_p , U_q , and U_r^* are, respectively, potential energy operators in the field of the charged atoms p , q , and uncharged atoms r , which constitute the core.

Therefore the core integral α_p can be written as

$$\alpha_p = (X_p | \mathcal{H}_{\text{core}} | X_p) = -I_p - \sum_{q \neq p} n_q(q|pp) - \sum_r (r:pp) \quad (19)$$

where $(q|pp)$ is the nuclear attraction potential, namely the attraction of an electron in the AO p by a univalent

(21) M. Goeppert-Mayer and A. L. Sklar, *ibid.*, **6**, 645 (1938).

Table IV. Values of Electron Repulsion Integrals and Nuclear Attraction Integrals (e.v.)

	(11 11) = (22 22) = (33 33) = 12.879					
	(44 44) = (55 55) = (66 66) = (77 77) = 15.332					
	(88 88) = 29.824					
	(11 22) = (11 33) = (22 33) = 7.618					
(11 44) =	(22 55) = (33 66) = 12.09517					
	(11 55) = (11 66) = (11 77) = (22 44) = (22 66) = (22 77) =					
(33 44) =	(33 55) = (33 77) = 8.45883					
	(44 55) = (44 66) = (44 77) = (55 66) = (55 77) = (66 77) = 14.572					
<i>R</i>	(11 88)	(22 88) =(33 88)	(44 88)	(55 88) =(66 88)	(77 88)	(4 88)
N ∞	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
H 5.909	6.77984	4.01063	5.18256	4.41142	4.41142	23.01911
H 4.909	8.91297	4.66580	6.40101	5.25527	5.25527	27.70835
H 3.909	12.43716	5.53400	8.35825	6.48903	6.48903	34.79635
N 5.909	4.01063	4.01063	4.41142	4.41142	5.18256	23.01911
N 4.909	4.66580	4.66580	5.25527	5.25527	6.40101	27.70835
N 3.909	5.53400	5.53400	6.48903	6.48903	8.35825	34.79635
N 3	7.45642	7.45642	9.42075	9.42075	11.32258	45.09867
N 2	9.22195	9.22195	13.35714	13.35714	16.06071	65.84883

Table V. Values of Core Integrals (e.v.)

System	α_1	$\alpha_2 = \alpha_3$	α_4	$\alpha_5 = \alpha_6$	α_7	α_8
H 5.909	-88.32117	-82.78275	-116.59595	-115.05367	-112.17733	-92.22521
H 4.909	-92.58743	-84.09309	-119.03285	-116.74137	-113.86503	-100.35772
H 3.909	-99.63581	-85.82949	-122.94813	-119.20889	-116.33255	-112.70651
N 5.909	-82.78275	-82.78275	-115.05367	-115.05367	-113.71961	-89.45600
N 4.909	-84.09309	-84.09309	-116.74137	-116.74137	-116.15651	-96.11075
N 3.909	-85.82949	-85.82949	-119.20889	-119.20889	-120.07179	-105.80335
N 3	-89.67433	-89.67433	-125.08493	-125.08493	-125.99965	-121.87293
N 2	-93.20540	-93.20540	-132.94511	-132.94511	-135.47591	-148.02042
N ∞	-74.76149	-74.76149	-106.23083	-106.23083	-103.35449	-54.40500

positively charged atom q , and n_q is the charge on q , and $(r:pp)$ is the penetration integral between the AO p and neutral atom r .

Using eq. 19, we obtain the expressions for the core integrals as,

$$\begin{aligned} \alpha_1 &= -I_H - 2(2|11) - (4|11) - 4(5|11) - 2(8|11) \\ \alpha_2 &= -I_H - 2(1|22) - (5|22) - 4(4|22) - 2(8|22) \\ &= \alpha_3 \\ \alpha_4 &= -I_N - 4(44|55) - (1|44) - 2(2|44) - 2(8|44) \\ \alpha_5 &= -I_N - 4(44|55) - (2|55) - 2(1|55) - 2(8|55) \\ &= \alpha_6 \\ \alpha_7 &= -I_N - (77|77) - 3(44|55) - 3(1|77) - 2(8|77) \\ \alpha_8 &= -I_{He} - (1|88) - 2(2|88) - 5(4|88) \end{aligned}$$

It was found that at the distances under consideration, the following identities exist.

$$\begin{aligned} (2|11) &= (1|22) = (11|22) \\ (4|11) &= (1|44) = (5|22) = (2|55) = (22|55) \\ (5|11) &= (1|55) = (4|22) = (2|44) = (1|77) = (11|55) \\ (8|11) &= (1|88) = (11|88) \\ (8|22) &= (2|88) = (22|88) \\ (8|44) &= (44|88) \\ (8|55) &= (55|88) \\ (8|77) &= (77|88) \end{aligned}$$

Therefore all the nuclear attraction integrals except (4|88) were replaced by their corresponding repulsion integrals. In cases where extrapolated values of (44|88) were used, the theoretical values of (4|88) were scaled down accordingly. Otherwise, theoretical values were used.

The values of (4|88) at various distances are presented in Table IV. The core integrals calculated for all the systems are presented in Table V.

The off-diagonal elements (β -values) used here are the same as those in the Hückel matrices except that they are multiplied by a factor of -2.39 to convert to values in electron volts.

Electronic Energies. The diagonalization of matrices, the computation of the integrals over the MO's, and the calculation of the electronic energies were carried on an IBM 7070 electronic computer. The series of programs available³ will calculate and print out the diagonalized matrices, the integrals I , J , and K , the configuration energies, and the configurational interaction matrix elements among the ground and all the singly excited configurations, using as input the Hückel matrix, the Γ -matrix which has the electron repulsion integrals over the AO's as its elements, and the core matrix.

A preliminary run showed little effect on the ground-state energies by inclusion of configuration interaction with the singly excited configurations. Therefore the results reported here do not include configuration interaction. The computed electronic energies are shown in the third column of Table VI. The last column shows the relative total energies of the systems.

Table VI. Calculated Energies of the Systems HR and NR (e.v.)

R	Nuclear energy	Electronic energy	Total energy	Relative energy
N ∞	239.939	-549.836	-309.897	0.000
H 5.909	315.621	-625.502	-309.880	0.017
N 5.909	310.041	-619.938	-309.897	0.000
H 4.909	332.156	-641.921	-309.764	0.133
N 4.909	323.353	-633.247	-309.895	0.002
H 3.909	358.885	-667.297	-308.413	1.484
N 3.909	342.745	-652.633	-309.878	0.019
N 3.000	375.375	-685.046	-309.429	0.469
N 2.000	432.579	-740.633	-304.360	5.537

The adoption of the sp^3 hybridization for the nitrogen orbitals may appear at first quite unsuitable, as the bond orbitals have been estimated to contain much more p-character.²² However, during the course of the calculations it was noticed that repulsion integrals evaluated in different ways, thus having different values, still lead to the same relative energies for different systems. This is not surprising since in this problem the relevant repulsion integrals enter into the molecular integrals J , K , and I in such a manner that they largely cancel out in the expression for total electronic energy. Since a change in the degree of hybridization merely leads to a change in the values of all the repulsion

(22) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960; (b) A. B. F. Duncan, *J. Chem. Phys.*, **27**, 423 (1957).

integrals, we believe that the same relative energy would result from different hybridizations. As a check, when only 5% of s-character was assigned to the N-bond orbitals, the calculated repulsion integrals between He and the nitrogen orbitals did not differ appreciably from the ones calculated using nitrogen sp^3 orbitals. This indicates that even the absolute values of the calculated energies are not very sensitive to the degree of hybridization.

The agreement between the quantum mechanical calculation and the van der Waals calculation is extremely good for both systems HR and NR, as can be seen in Figure 1. It is concluded that, to the approximation used here, there is no basis for suspecting any anomalous behavior of the lone pair on nitrogen, and serious doubt is cast upon the conclusions drawn by Aroney and LeFèvre concerning the methyl group on the piperidine ring. Experimental work to be described in the following paper supports the conclusion drawn here, namely, that the methyl group is much "bigger" than the lone pair on nitrogen. The accuracy of the van der Waals calculation, the method, and the parameters used are all fully supported by the quantum mechanical calculation over the repulsive portion of the curve. Since correlation effects were not included in the quantum mechanical calculations, no information was obtained from that calculation concerning the attractive portion of the curve, but there appears to be no reason to question it.

Conformational Analysis. XLII. Experimental Approaches to the Problem of the Size of the Lone Pair on Nitrogen^{1,2}

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From the dipole moments of a number of piperidine and piperazine derivatives, the energetic preferences for a methyl group and for a hydrogen atom on nitrogen to assume the equatorial vs. the axial position in N-methylpiperidine and in piperidine have been determined. The methyl group was found to prefer the equatorial position by 1.7 kcal./mole, and the hydrogen atom by 0.4 kcal./mole, in benzene solution.

In 1958 Aroney and LeFèvre published a paper discussing the equatorial vs. axial preference for the hydrogen on nitrogen in piperidine (I), and for the methyl in N-methylpiperidine (II).³ They concluded that the hydrogen atom in I showed a pronounced

preference for the axial position, while the methyl in II was of equal energy in the axial or equatorial position. Our preceding paper¹ discussed a theoretical study of the situation which led us to conclude that the methyl group would strongly prefer to be equatorial in the N-methyl compound, and that the hydrogen on nitrogen in piperidine might preferentially be either axial or equatorial, since the energy difference between the two arrangements should not be very large. The present paper describes our experimental approaches to this problem. Recently other workers have studied the problem experimentally by qualitative methods,⁴⁻⁶ and to that extent we are in complete agreement with them.

(1) Paper XLI: N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 1227 (1965).

(2) This research was supported by Grant GP-1174 from the National Science Foundation. Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963. A preliminary communication appeared in *Tetrahedron Letters*, 3345 (1964).

(3) M. Aroney and R. J. W. LeFèvre, *J. Chem. Soc.*, 3002 (1958).

(4) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

(5) (a) T. M. Moynehan, K. Schofield, R. A. Y. Jones, and A. R. Katritzky, *J. Chem. Soc.*, 2637 (1962); (b) N. W. J. Pumphrey and M. J. T. Robinson, *Chem. Ind.* (London), 1903 (1963).

(6) A somewhat different aspect of the problem considered here is the conformational enthalpy of the amino group, which was recently studied by J. Sicher, J. Jonáš, and M. Tichý, *Tetrahedron Letters*, 825 (1963), and by E. L. Eliel, E. W. Della, and T. H. Williams, *ibid.*, 831 (1963).