

Stability and Aromaticity of Nitrogen Rings. N_3^+ , N_4 , and N_6

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Abstract: An *ab initio* calculation is performed for the structures N_3^+ , N_4 , and N_6 using single- ζ and double- ζ basis sets of STO's. A secondary minimum exists for N_3^+ in its cyclic form which lies above the energy of the linear symmetric and linear asymmetric geometries. N_4 in square planar, rectangular, and tetrahedral geometries is found to lie far above the energy of two nitrogen molecules. N_6 is somewhat stabilized relative to N_4 . The energies and structures are discussed in the context of aromaticity. Single- ζ and double- ζ results differ significantly, with the single- ζ calculations apparently overemphasizing the stability of small rings.

Because the triple bond in molecular nitrogen is so stable relative to molecules containing nitrogen-nitrogen double and single bonds, molecules containing catenated nitrogen atoms tend to be unstable toward decomposition to molecular N_2 .¹ Much of the chemistry of nitrogen can be understood on this basis. This is in striking contrast to carbon chemistry, where carbon-carbon bond energies follow a more regular progression from single to triple bonds, as shown in the comparison between carbon and nitrogen in Table I.

Table I. Bond Energies in Carbon and Nitrogen Compounds

Bond	Bond energy ^a		Ref
	kcal/mol	au	
C—C	88	0.140	b
C=C	173	0.276	c
C≡C	230	0.366	b
N—N	38	0.061	1
N=N	99	0.158	1
N≡N	226	0.360	1

^a 1 au = 27.2097 eV = 627.71 kcal/mol. ^b J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). ^c Based on data of W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968).

The result is that catenated forms of carbon become energetically competitive with acetylene, which leads to some rather well-known consequences. The *reason* for the weakness of the nitrogen-nitrogen double and single bonds relative to the triple bond presents an interesting theoretical problem. Possible explanations include lone-pair repulsions on adjacent nitrogens,¹⁻³ perhaps enhanced by hybridization effects.^{4,5}

From another point of view, the N atom is iso-electronic with a CH group and it might be expected that nitrogen systems having the same symmetry as their hydrocarbon analogues would show comparable electronic structures. Thus one is led to predict that the cyclic rings N_3^+ and N_6 ,⁶ containing two- and six-electron π systems, respectively, would show aromatic properties comparable to cyclopropenyl cation and

benzene, whereas N_4 is antiaromatic like its hydrocarbon analog, cyclobutadiene. The electronic basis for this prediction is shown in Figure 1. It is clear that the nitrogen lone pairs are equivalent to C-H bonds (assuming sp^2 -hybridized orbitals) and that the π -systems are also equivalent. In fact, the electronic similarity between C_4H_4 and N_4 had previously been pointed out by Shusturovich and co-workers,⁷⁻¹⁰ who studied the possible stabilization of a metal- N_4 complex analogous to the well-known system cyclobutadieneiron tricarbonyl.

In this paper we explore the question of the stability of extended nitrogen systems by studying the energy of the (hypothetical) rings N_3^+ , N_4 , and N_6 . Some alternative structures are also examined for purposes of comparison; these include linear equidistant N_3^+ and tetrahedral and rectangular N_4 . Questions of aromaticity are discussed in the course of making energy comparisons. All molecules are studied by use of *ab initio* SCF MO techniques, using both minimum and double- ζ sets of Slater-type orbitals where possible.

Method of Calculation

The molecular orbital program used was obtained from Dr. Stevens of Harvard University and has been discussed in recent publications.^{11,12} In closed shell applications, the Roothan SCF-MO equations are solved using a basis set of Slater-type exponential orbitals. Molecular integrals are evaluated exactly by the Gaussian transform procedure.¹³ Molecular symmetry is made use of to reduce the number of integrals computed, and in addition a set of parameters in the integral evaluation procedure allow one to strike an optimum balance between computation time and precision of the final energy. When open shell configurations are encountered, as in the case of linear equidistant N_3^+ and square planar N_4 , we use two techniques: Nesbet's method of symmetry and equivalence restrictions¹⁴ in an open shell calculation, and a closed shell calculation with configuration interaction with the low-lying vacant orbitals. For neutral mole-

(1) W. L. Jolly, "The Inorganic Chemistry of Nitrogen," W. A. Benjamin, New York, N. Y., 1964.

(2) W. E. Dasent, "Nonexistent Compounds," Marcel Dekker, New York, N. Y., 1965.

(3) R. T. Sanderson "Chemical Bonds and Bond Energy," Academic Press, New York, N. Y., 1971, p 61.

(4) L. Pauling, *Tetrahedron*, **17**, 229 (1962).

(5) M. Green in "Developments in Inorganic Nitrogen Chemistry," Vol. 1, C. B. Colbourn, Ed., Elsevier, New York, N. Y., 1966.

(6) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1971.

(7) E. M. Shusturovich, *Zh. Strukt. Khim.*, **10**, 947 (1969).

(8) E. M. Shusturovich, *Zh. Strukt. Khim.*, **10**, 159 (1969).

(9) E. M. Shusturovich, G. I. Kagan, and G. M. Kagan, *Zh. Strukt. Khim.*, **10**, 696 (1969).

(10) E. M. Shusturovich, G. I. Kagan, and G. M. Kagan, *Zh. Strukt. Khim.*, **11**, 108 (1970).

(11) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(12) E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, **15**, 5229 (1969).

(13) I. Shavitt and M. Karplus, *J. Chem. Phys.*, **43**, 398 (1965).

(14) R. K. Nesbet, *Rev. Mod. Phys.*, **32**, 272 (1960).

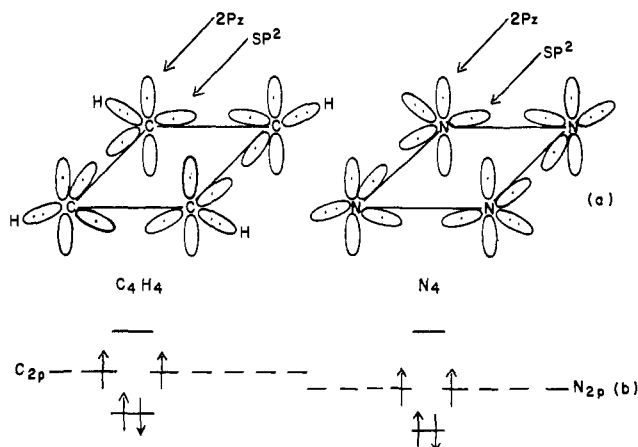


Figure 1. Electronic equivalence of square planar C₄H₄ and square planar N₄. The orbital energy pattern for the π electrons is shown.

cules we use Clementi's¹⁵ best atom exponents for the minimum basis set nitrogen orbitals and Huzinaga's¹⁶ reoptimized exponents for the double-ζ basis set. Some departure from these exponents is made for N₃⁺, where there will be an orbital contraction due to the positive charge.

N₂ Molecule, Basis Sets

There have been many prior *ab initio* SCF-MO calculations on the nitrogen molecule, at the minimum basis set level,¹⁷ double-ζ,¹⁸ Hartree-Fock limit,¹⁹ and beyond.²⁰ For our purposes, we are interested in comparing single-ζ to double-ζ bases with respect to optimum energy and internuclear distance and to test the integral accuracy controls in the program.

For the minimum basis set, Clementi's best atom exponents¹⁵ are $1s_N = 6.6631$, $2s_N = 1.9237$, and $2p_N = 1.9165$. The double-ζ basis calculations use¹⁶ $1s_N = 5.9990$, $1s_N' = 8.5276$, $2s_N = 1.4148$, $2s_N' = 2.2523$, $2p_N = 1.4961$, and $2p_N' = 3.2390$. Calculations in each basis set were done at three internuclear distances to find the optimum internuclear distance and energy, using both normal precision integral control parameters (5.0, 8.0, and 1.67 for *u*, *v*, and *w* in the Gaussian transform procedure) which give a precision in the total energy of about 0.0001 au and low-accuracy parameters (4.0, 6.0, and 1.50 for *u*, *v*, and *w*) which give a precision of about 0.001 au.

Results of these calculations are given in Table II. Comparing the single-ζ energies at normal and low precision shows agreement in the energy to within 0.001 au for each distance. A check on the double-ζ result at 2.0675 au also shows agreement to within this tolerance. Fitting a parabola through the single-ζ results at normal precision (NP) gave the optimum $R = 2.178$ au, $E = -108.5694$ au; low-precision (LP) parameters gave $R = 2.178$ au and $E = -108.5687$ au. The optimized results at NP and LP thus agree to

(15) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963); E. Clementi, D. L. Raimondi, and W. P. Reinhardt, *J. Chem. Phys.*, **47**, 1300 (1967).

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

(17) C. W. Scherr, *J. Chem. Phys.*, **23**, 569 (1955).

(18) J. W. Richardson, *J. Chem. Phys.*, **35**, 1829 (1961).

(19) P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.*, **44**, 1973 (1966).

(20) F. Grimaldi, *J. Chem. Phys.*, **43**, 559 (1965).

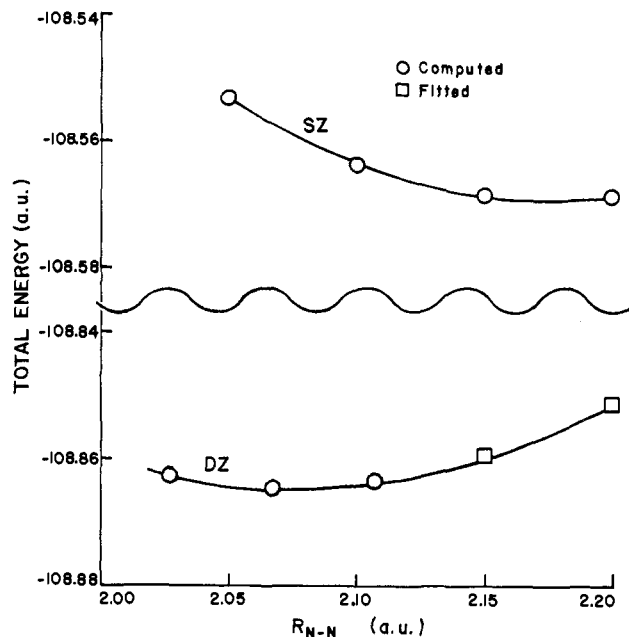


Figure 2. SCF energies for N₂, as a function of distance, at the SZ and DZ levels.

Table II. Test of Integral Transform Controls on N₂

Distance, au ^a	Basis set ^b	Integral precision ^c	Energy, au	Calculation time, min ^d
2.10	Single	Low	-108.5628	
2.15	Single	Low	-108.5679	
2.20	Single	Low	-108.5682	
2.10	Single	Normal	-108.5638	0.95
2.15	Single	Normal	-108.5687	
2.20	Single	Normal	-108.5690	
2.0275	Double	Low	-108.8626	
2.0675	Double	Low	-108.8644	9.0
2.1075	Double	Low	-108.8363	
2.0675	Double	Normal	-108.8643	13.1

^a Distance conversion factor: 1 au = 0.52917 Å. ^b Clementi exponents¹⁵ for single-ζ, Huzinaga exponents¹⁶ for double-ζ. ^c Low precision = 4.0, 6.0, 1.50; normal precision = 5.0, 8.0, 1.67. ^d On an IBM 360/65 computer.

within 0.001 au in distance (0.0005 Å) and 0.001 au in energy. Occasional checks on larger rings have verified this result. Since the saving in computer time when using LP is appreciable (Table II), and since a precision in the energy of 0.001 au is sufficient for the purposes of energy comparisons between N₂ and the higher rings, *all* results quoted will be at LP, unless otherwise noted.

A comparison between the computed single-ζ and double-ζ results (LP) is shown in Figure 2. The experimental distance in N₂ is 2.0675 au.²¹ Although minimum basis set calculations have been widely used for the prediction of molecular geometry,²²⁻²⁴ we observe in Figure 2 that the single-ζ (hereafter referred to as SZ) energy minimum occurs at an appreciably larger distance, 2.178 au, than the double-ζ (DZ) energy minimum, which lies at 2.0752 au, much closer to the

(21) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand-Reinhold, New York, N. Y., 1950.

(22) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(23) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(24) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261, 2276 (1967).

experimental distance. It was originally intended to optimize distances on larger molecules using SZ basis sets and then to compute DZ energies at the optimized SZ distance. Figure 2 shows that this procedure, *i.e.*, computation of the DZ energy at 2.178 au, would introduce an error of about 0.009 au (5.6 kcal/mol) in the reported DZ result. Since this is a significant error, whenever possible we include three-point geometry optimization in the DZ basis. For completeness and for comparison, SZ results are also reported.

Some of the *ab initio* calculations which have been done on N_2 using different basis sets and techniques are collected in Table III. The STO-3G energy lies well

Table III. *Ab Initio* Calculations on N_2

Distance, au	Basis set	Energy, au	Ref
2.068	STO-3G	-107.4682	44
2.068	Single- ζ		
	(Clementi exponents)	-108.5581	This work
2.068	Double- ζ		
	(Clementi exponents)	-108.8617	This work
2.068	Double- ζ		
	(Huzinaga exponents)	-108.8644	This work
2.070	(9s, 5p)		
	(contracted GTO)	-108.8438	25a
2.07	Hartree-Fock	-108.9928	19
2.068	Experimental	-109.618	53
2.178	SZ, optimum R	-108.5694	This work
2.075	DZ, optimum R	-108.8644	This work

outside the range of the rest of the calculations. The SZ calculations lie about 0.3 au above the DZ results. The DZ calculations using either Clementi's DZ exponents (giving $E = -108.8617$ au) or Huzinaga's DZ exponents (giving $E = -108.8644$ au) lie 0.02 au *below* a comparable Gaussian calculation,^{25a} although the reverse has been incorrectly quoted in the literature.²⁵ The DZ results are within about 0.1 au of the Hartree-Fock limit (-108.9956 au), lending support to the idea that double- ζ basis sets give an accurate simulation of Hartree-Fock results.²⁶ The unreliability of Hartree-Fock calculations in predicting *dissociation energies* is well known, *e.g.*, for $N_2 \rightarrow 2N$ (but see ref 27), but considerably more optimism is possible for the results of a calculation like $N_6 \rightarrow 3N_2$.

Results and Discussion

(A) N_3^+ Ion. The N_3^+ ion has been observed in mass spectrometric studies.²⁸⁻³¹ Although no structural data

(25) (a) T. W. Archibald and J. R. Sabin *J. Chem. Phys.*, **55**, 1821 (1971); (b) these authors compared the GTO energy of N_2 to the STO energy of $N + N$.

(26) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules," Addison-Wesley, Reading, Mass., 1972.

(27) As noted in ref 25a, to obtain an estimate of the binding energy in $N_2(^1\Sigma_g) \rightarrow 2N(^4S)$, one should correct for the fact that the calculation for $N(^4S)$ is much closer to the Hartree-Fock limit than is N_2 . Their DZ results show N_2 is 0.152 au below the HF limit, while $N(^4S)$ is 0.015 au below, a difference of 0.137 au. Combining our data with theirs gives an estimate of the "corrected binding energy" $BE = 108.8644 - 2(54.3861) + 2(0.137) = 0.3662$ au or 229.8 kcal/mol, in very good agreement with the experimental value of 226.8: D. C. Frost and C. A. McDowell, *Proc. Roy. Soc., Ser. A*, **236**, 278 (1956).

(28) J. L. Franklin, V. H. Dibeler, R. M. Reese, and M. Krauss, *J. Amer. Chem. Soc.*, **80**, 298 (1958).

(29) M. Saporoschenko, *Phys. Rev.*, **111**, 1550 (1958).

(30) W. Kaul and R. Fuchs, *Z. Naturforsch. A*, **15**, 326 (1960).

(31) R. K. Curran, *J. Chem. Phys.*, **38**, 2974 (1963).

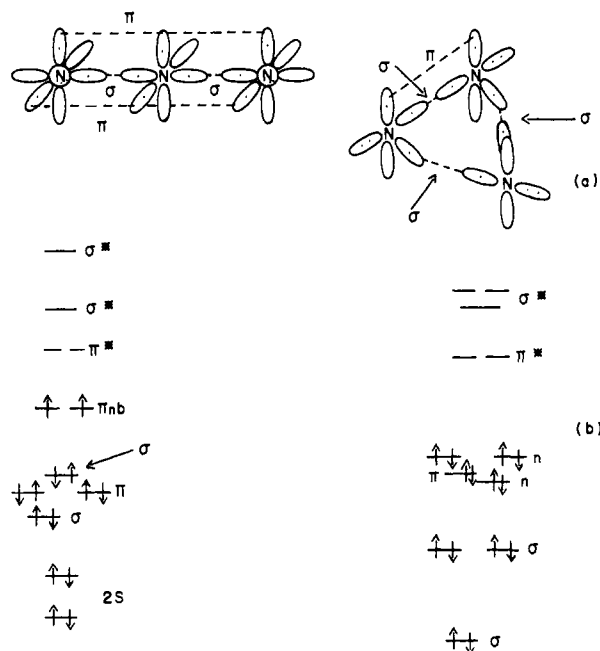


Figure 3. An orbital energy diagram for linear and cyclic N_3^+ , based on the minimum basis SCF results.

have been obtained, it has been assumed²⁸ to have a linear structure as do the N_3 radical and N_3^- ion.³² If this were correct the N_3^+ ion would be a ground state triplet, having two electrons in a degenerate nonbonding π orbital. However, a closed shell configuration can be achieved by bending to the cyclic triangular structure. An orbital energy diagram for cyclic and linear N_3^+ , based on the minimum basis SCF results to follow, is shown in Figure 3. From the diagram it appears that the cyclic structure is clearly preferred, since no electrons occupy nonbonding orbitals. However, the results of Peyerimhoff and Buenker³³ on the variation of total energy *vs.* orbital energy sums for ozone and azide ion (N_3^-) show that the orbital energy sums give a misleading prediction that the cyclic molecule is preferred. This is due largely to the fact that the sum of orbital energies does not include nuclear repulsion, which is larger in the cyclic than in the linear structure.

An *ab initio* study of the geometry of the N_3^+ ion has been reported by Archibald and Sabin,^{25a} using a Gaussian basis set approximately equivalent to the DZ set (see Table III.) Their rigorous calculations were restricted by the limitations of Roothaan's open-shell SCF method³⁴ to a study of the linear symmetric and linear asymmetric geometries, although approximate results (*via* Koopman's theorem and the N_3 molecule) were obtained for the bending of symmetric N_3^+ . They found the state of lowest energy to be linear and asymmetric ($^3\Sigma$), with $R_{12} = 3.105$ au, $R_{23} = 2.070$ au, and $E = -162.762$ au. The linear symmetric geometry of lowest energy ($^3\Sigma$) had $R = 2.24$ au and $E = -162.692$ au, or 0.07 au above the asymmetric geometry. A potential curve for bending of the linear symmetric N_3^+ showed the energy to be a steeply rising function of deviation from linearity, until at 120° the

(32) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(33) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **47**, 1953 (1967).

(34) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

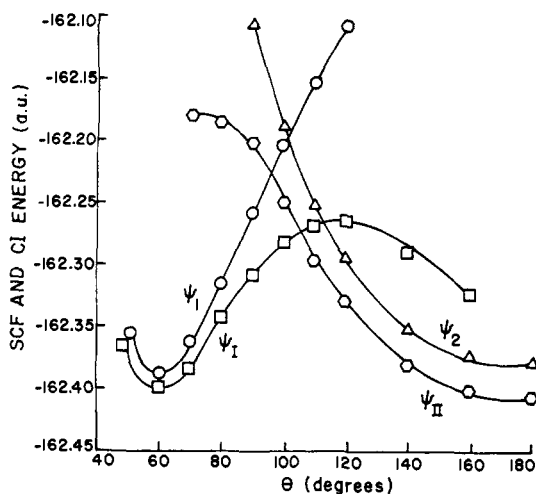


Figure 4. Variation of single-configuration and CI energies with θ , the bending angle in N_3^+ . The double minimum potential is clearly shown.

energy had increased by about 0.12 au, at which point the calculation was stopped.

However, if cyclic N_3^+ forms an aromatic system as suggested in the introductory section, we may see a considerable stabilization as bending is continued. To test this hypothesis, the calculations of Archibald and Sabin were extended as follows. (1) The bending of symmetric N_3^+ ($R_{12} = R_{23}$) was followed from 180 to 60° using a minimum basis set. The unique internuclear distance was optimized at each angle. (2) Geometry optimized DZ calculations were done at 180° (linear, symmetric) and 60° (cyclic).

The treatment of the bending of the linear molecule is similar to that previously described for ozone.³⁵ Defining the angle θ = the NNN angle, the system goes from $D_{\infty h}$ symmetry ($\theta = 180^\circ$) through C_{2v} symmetry ($60^\circ < \theta < 180^\circ$) to D_{3h} symmetry ($\theta = 60^\circ$). The symmetry change can be handled by assuming C_{2v} symmetry throughout, since C_{2v} is a subgroup of $D_{\infty h}$ and D_{3h} . The molecule is oriented such that it lies in the y - z plane with z for the C_2 axis, and local axes on each nitrogen are parallel to the global xyz axes. This serves to define the symmetry orbitals as identical with those used by Archibald and Sabin,^{25a} except for an interchange in the p_y orbitals: $a_1 = y_1 - y_3$, $b_2 = y_1 + y_3$. At $\theta = 180^\circ$ the electron configuration is $\dots (5a_1)^2(1b_1)^2(3b_2)^2(1a_2)^1(4b_2)^1$, where $(1a_2)$ and $(4b_2)$ are the degenerate components of a nonbonding π orbital, and the system is an open-shell triplet. At $\theta = 60^\circ$ the configuration is $\dots (6a_1)^2(1a_2)^0(1b_1)^2(3b_2)^2$, a closed shell. Furthermore, there is an orbital crossing at an intermediate angle near 100° with a pseudo-open-shell situation resulting.

These features of the change in electronic structure were dealt with by using a limited configuration interaction. Labeling the configurations in terms of the occupancy of a_1 , a_2 , b_1 , and b_2 orbitals, respectively, let $\psi_1 = 06\ 00\ 01\ 03$, $\psi_2 = 05\ 00\ 01\ 04$, and $\psi_3 = 05\ 01\ 01\ 03$. At the end point $\theta = 180^\circ$, the singlet energy may be obtained from a 2×2 CI mixing ψ_2 and ψ_3 . Over the rest of the potential surface, the relevant transition is $4b_2 \rightarrow 6a_1$ or $6a_1 \rightarrow 4b_2$, with ψ_1 being the lower energy single configuration near 60° and ψ_2 being the lower

near 180°. Thus a 2×2 CI calculation of the lowest singlet energy was carried out for angles θ from 50 to 180°. Denoting ψ_I = the CI state built from ψ_1 and ψ_{II} = the CI state built from ψ_2 , the results for the energy variation are shown in Figure 4. The CI energy minimum occurs for ψ_{II} at $\theta = 180^\circ$ (the energy of the singlet state is shown). Decreasing θ causes the system to pass through a transition state near $\theta = 105^\circ$ (the actual crossing of ψ_I and ψ_{II} is avoided, but a larger CI would be needed to show this) until a very stable secondary minimum is reached for ψ_I at $\theta = 60^\circ$. It is tempting to attribute this stabilization to the aromatic character of the cyclic N_3^+ ion; it contains a π -electron system with two electrons in a ring. However, the reliability of minimum basis set geometry calculations for small rings is brought into question by results on ozone,³⁵ where the cyclic molecule is incorrectly predicted to be more stable than the experimentally observed bent structure.³⁶ It was found by Siu and Hayes³⁷ that a DZ type calculation *does* predict a more stable bent form of ozone, in agreement with experiment. We thus turn to DZ calculations at points of interest on the bending curve.

Using Huzinaga's¹⁶ DZ exponents, a closed shell calculation of ψ_1 at $\theta = 60^\circ$ gave, upon geometry optimization, $E = -152.597$ au at $r = 2.655$ au. At $\theta = 180^\circ$ an open-shell calculation for the triplet state using Nesbet's method¹⁴ gave $E = -162.724$ au at the optimum $r = 2.249$ au. This energy is slightly lower than that of Archibald and Sabin,^{25a} who obtained $E = -162.692$ at $r = 2.24$ au for the linear symmetric N_3^+ triplet, with the asymmetric triplet lying 0.07 au below. An intermediate point in the region of the transition state where $r = 2.50$ au (assumed) and $\theta = 105^\circ$ gave for ψ_I an energy of -162.550 and for ψ_{II} an energy of -162.541 . Since the two energies are comparable, $r = 2.50$ au was a good choice, and this geometry must be close to that of the true transition state.

The results of all calculations on N_3^+ are collected in Table IV. Inspection of the table reveals several interesting facts. First, in a minimum basis set, exponent optimization causes a significant energy lowering relative to the best atom exponents. This is to be expected due to differences between a molecule and a positive ion, but this effect should largely disappear in a DZ basis. Second, in going from a SZ to a DZ basis, the cyclic structure loses in stability relative to the linear triplet by a significant amount: 0.02 au for SZ and 0.13 au for DZ. The SZ calculation thus overemphasizes the stability of the ring. Third, optimized geometries vary noticeably on doubling the size of the basis set. Finally, since the DZ results are seen to parallel those of Archibald and Sabin but lie slightly lower, the energy difference between linear symmetric and linear asymmetric forms must also be about 0.07 au. The probable relative order of energies, based on the data in Table IV, is: (SZ) lin asym (0.00), lin sym (0.07), trans st (0.14), ring (0.09); (DZ) lin asym (0.00), lin sym (0.07), trans st (0.24), ring (0.20).

What do these results indicate about the aromaticity of the N_3^+ ring? A linear version of N_3^+ is clearly preferred to the cyclic form, in spite of any stabilization coming from the cyclic π system. Part of this may be

(36) R. Huggins, *J. Chem. Phys.*, **24**, 131 (1956).

(37) A. K. Q. Siu and E. F. Hayes, *Chem. Phys. Lett.*, **21**, 573 (1973).

(35) J. S. Wright, *Can. J. Chem.*, **51**, 139 (1973).

Table IV. *Ab Initio* Calculations on N_3^+

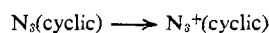
Geometry	Optimized distance, au	Basis set	Energy, au	Comments	Ref
Cyclic ($\theta = 60^\circ$)	2.688	SZ	-162.328	Clementi exponents	This work
Cyclic ($\theta = 60^\circ$)	2.580	SZ	-162.389	Ion optimized ^a	This work
Cyclic ($\theta = 60^\circ$)	2.58	SZ, 2×2 CI	-162.398	Ion optimized ^a	This work
Cyclic ($\theta = 60^\circ$)	2.655	DZ	-162.597	Huzinaga exponents	This work
Bent ($\theta = 105^\circ$)	2.53	SZ, 2×2 CI	-162.275	ψ_1	This work
Bent ($\theta = 105^\circ$)	2.50	DZ, 2×2 CI	-162.550	ψ_1	This work
Linear ($\theta = 180^\circ$)	2.20	SZ	-162.367	{ Open shell singlet	This work
			-162.410	{ Open shell triplet	This work
Linear ($\theta = 180^\circ$)	2.328	SZ, 2×2 CI	-162.383	Singlet	This work
Linear ($\theta = 180^\circ$)	2.249	DZ	-162.688	{ Open shell singlet	This work
			-162.724	{ Open shell triplet	
Linear symmetric	2.24	Gaussian	-162.692	Triplet	25a
Linear asymmetric	3.105	Gaussian	-162.762	Triplet	25a
	2.070				

^a 1s = 6.66, 2s = 2p = 2.00.

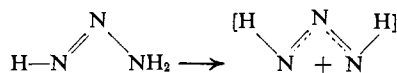
due to increased nuclear repulsion in the ring and part to "strain energy," *i.e.*, nonoptimum orientation of the hybrid orbitals in cyclic N_3^+ . However, the comparison between linear and cyclic N_3^+ is not in the spirit of the usual discussion of aromaticity, where one compares the stability of related π systems. For hydrocarbons, one compares the stability of the cyclopropenyl cation not to the propynyl cation (below), with a different σ system, but rather to the allyl cation, where the σ system of the carbon atom is comparable to that in cyclopropenyl⁺ (below), *i.e.*, sp^2 hybridized. Breslow³⁸ has shown by a variety of techniques that the ionization reaction cyclopropene \rightarrow cyclopropenyl⁺ requires less energy than that of the open chain reference compound propene \rightarrow allyl⁺. It therefore satisfies his definition of aromaticity, which is "aromatic compounds are thermodynamically more stable, that is, they contain less energy than related nonaromatic reference compounds."³⁸

In other words, the ease of ionization of cyclopropene is attributed to the stability of the cyclopropenyl⁺ ion which forms.

To make a similar case for N_3^+ is unfortunately rather difficult. We would need to compare



and



But since the first two are not the low-energy forms and the second two are unknown, this is not possible experimentally.

Many other criteria of aromaticity have been proposed, and several symposia have been concerned with arriving at a satisfactory theoretical definition.^{39,40} It has often been assumed that the presence of a planar cyclic system containing $4n + 2$ π electrons is sufficient in itself to guarantee aromaticity,⁴¹ because of the symmetry-determined pattern of the orbital energies.^{42,43} This essentially equates aromaticity with the

presence of such a π system. Cyclic N_3^+ possesses such a π system, and its molecular orbitals show the characteristic pattern of one bonding MO and a degenerate antibonding pair. Other criteria of aromaticity cannot easily be applied to N_3^+ . An interesting observation is that although the concept of aromaticity is elusive, it led to the search for cyclic N_3^+ , which was then shown to exist as a secondary minimum.

(B) N_4 Molecule. Since P_4 is a stable molecule with a tetrahedral structure, a previous calculation by Hillier and Saunders⁴⁴ on N_4 assumed a tetrahedral geometry. The STO-3G basis used gives an energy for N_2 which is more than 1.0 au above the minimum basis STO result (Table III), but the STO-3G basis is seeing increasing use for energy comparisons between closed shell molecules.⁴⁵ Hillier and Saunders⁴⁴ found an energy for tetrahedral N_4 ($r = 1.47$ Å) of -214.7359 au, which lies 0.201 au above the energy of two N_2 molecules in the same basis. In a CNDO/2 study, Archibald and Perkins⁴⁶ found the energy of tetrahedral N_4 to be above that of two N_2 's, while tetrahedral P_4 was below the energy of two P_2 's, in qualitative agreement with experiment. They attributed the decreased stability in N_4 to increased nuclear repulsions at the relatively short N-N single-bond distance. At a still lower level approximation, different geometries of N_4 were studied by Shusturovich and coworkers⁷⁻¹⁰ using an extended Hückel method and a rough grid of internuclear distances. These authors pointed out the similarity in electronic structure between N_4 and cyclobutadiene.

In this paper we do a geometry search at the STO minimum basis (SZ) level and supplement this with DZ calculations at selected points. Geometries studied include square planar (D_{4h}), rectangular (D_{2h}), and tetrahedral (T_d). All calculations were carried out in D_2 symmetry, a subgroup of D_{4h} , D_{2h} , and T_d . The system of global and local coordinate axes used to define the symmetry orbitals is shown in Figure 5.

For the square planar structure, the electron configuration in D_2 symmetry is $\dots(4a)^2(3b_1)^2(3b_2)^2(3b_3)^2$

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(41) E. Huckel, *Z. Phys.*, **70**, 204 (1931).

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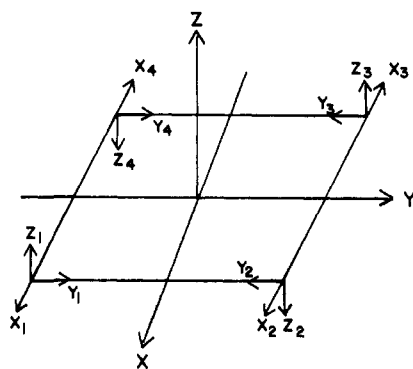
(44) I. H. Hillier and V. R. Saunders, *Chem. Commun.*, 1233 (1970).

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(46) R. M. Archibald and P. G. Perkins, *Chem. Commun.*, 569 (1970).

Table V. *Ab Initio* Calculations on N_4

Geometry	Distance, au	Basis set	Energy, au	Comments	Ref
Tetrahedral	2.778	STO-3G	-214.7359		44
Tetrahedral	2.882	SZ	-216.9205	Optimum r	This work
Tetrahedral	2.778	DZ	-217.292		This work
Square	2.714	SZ	-216.925	$^3A_{2g}$ (open shell)	This work
Square	2.714	SZ	-216.922	$^1B_{1g}$ (open shell)	This work
Square	2.700	SZ + CI	-216.926		This work
Square	2.700	DZ	-217.240	$^3A_{2g}$ (open shell)	This work
Rectangular	$r_1 = 2.500$ $r_2 = 2.900$	SZ	-216.935		This work

Figure 5. Global and local coordinate axes used to define the D_2 symmetry orbitals for the N_4 molecule.

$(4b_2)^1(4b_3)^1$, where the orbital occupancy and the ordering of levels is as indicated. Of particular interest are the symmetry orbitals of the π system, shown in Figure 6. Since the nonbonding $4b_2$ and $4b_3$ orbitals are the highest occupied MO's and are degenerate and each contain one electron, the square planar N_4 should be an open-shell triplet. From the results of Buenker and Peyerimhoff on cyclobutadiene⁴⁷ there should be a singlet state close in energy to the triplet state. To find the energy of these states three calculations were done: (1) an open shell calculation using Nesbet's method, a SZ basis, and optimizing the geometry; (2) a closed shell calculation with SZ basis, 2×2 CI, allowing the transition $\dots(4b_2)^2(4b_3)^0 \rightarrow (4b_2)^0(4b_3)^2$ and optimizing the geometry; and (3) an open-shell DZ calculation at $r = 2.70$ au.

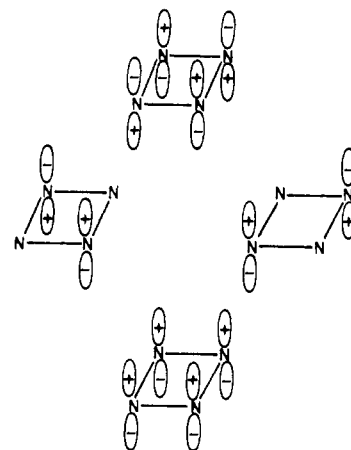
The results of these calculations appear in Table V. Using the notation correct for D_{4h} symmetry means that the configuration $\dots(4b_2)^1(4b_3)^1$ is actually $\dots(e_u)^2$, so states of symmetry A_{1g} , A_{2g} , B_{1g} , and B_{2g} arise. The open-shell calculation gives the most stable state as $^3A_{2g}$, with energy $E = -216.925$ au at $r = 2.714$ au. The $^1B_{1g}$ state is of almost the same energy at -216.922 au. The closed shell + CI calculation showed good agreement, with $E(^3A_{2g}) = -216.926$ au at $r = 2.70$ au. A single point at $r = 2.70$ au in the double- ζ basis using an open-shell calculation gave $E(^3A_{2g}) = -217.240$ au. Comparing to the N_2 energy in the appropriate basis (Table III) gives

$$\Delta E(\text{SZ}) = E_{N_4} - 2E_{N_2} = -216.925 - 2(-108.570) = 0.215 \text{ au}$$

$$\Delta E(\text{DZ}) = -217.240 - 2(-108.864) = 0.488 \text{ au}$$

The difference between the SZ and DZ results is re-

(47) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

Figure 6. Symmetry orbitals for the π system in square planar N_4 .

markable. The SZ calculation appears to drastically overemphasize the stability of N_4 . The discrepancy between SZ and DZ results cannot be due to the lack of geometry optimization in the DZ basis, since inspection of the SZ data showed a rather flat potential curve for ring expansion. We conclude that the N_4 ring, in a calculation (DZ) near the Hartree-Fock limit, is strongly destabilized relative to two molecules of N_2 . Also, the credibility of SZ calculations for energy comparisons is seriously weakened.

One possible way to stabilize N_4 is by distortion along a rectangular path. A search for the optimum rectangle (assumed to be a singlet state) was done by using a 2×2 CI calculation and searching a rough grid of r_1 and r_2 values (the sides of the rectangle). The results are presented in Figure 7 in the form of a contour map. This map was constructed from 20 values of (r_1, r_2) , and clear minima may be seen near $r_1 = 2.9$ and $r_2 = 2.5$ (or equivalently $r_1 = 2.5$ and $r_2 = 2.9$) where $E(\text{singlet}) = -216.935$ au. This point, while slightly more stable than the lowest triplet, still lies 0.205 au above the energy of two N_2 's. The configuration in D_2 symmetry, in order of increasing energy, is $(1a)^2(1b_1)^2(1b_2)^2(1b_3)^2 - (2a)^2(2b_3)^2(2b_2)^2(3a)^2(2b_1)^2(4a)^2(3b_1)^2(3b_3)^2(4b_3)^2(3b_2)^2, (4b_2)^0(5a)^0 \dots$

A low-lying transition can occur between the highest occupied π orbital ($4b_3$ at -0.416 au) and lowest vacant π orbital ($4b_2$ at $+0.015$ au), formerly the degenerate pair in the square planar N_4 . The CI thus includes the transition between these orbitals.

The energy of tetrahedral N_4 is useful as a standard with which to compare square and rectangular N_4 . The molecule has a closed shell with configuration (T_d symmetry): $(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(3a_1)^2(3t_2)^6(1e)^4$,

$(1t_1)^0(4t_2)^0$. Optimization of the unique internuclear distance gave, in the SZ basis, $E = -216.9205$ au at $r = 2.882$ au. A single DZ calculation at the same distance used by Hillier and Saunders, 2.778 au, gave $E = -217.292$ au. Comparing to two N_2 's gives calculated energy differences of

$$\Delta E(\text{SZ}) = -216.921 - 2(-108.570) = 0.219 \text{ au}$$

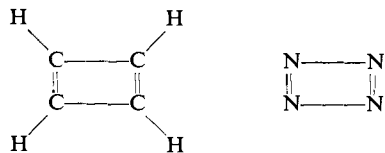
$$\Delta E(\text{DZ}) = -217.292 - 2(-108.864) = 0.436 \text{ au}$$

Although the DZ result has not been optimized, it is likely to be within 0.02 au of optimum energy and so we note again an *enormous* stabilization for the SZ energy of N_4 relative to the more reliable DZ value. Since the bond energy of N_2 is only 0.361 au, the energy of tetrahedral N_4 is greater than the energy of $N_2 + 2N$.²⁷ The strong destabilization in tetrahedral N_4 must certainly be due to the nuclear repulsions in the tetrahedral array and the unfavorable bond angles. Addition of d orbitals to the basis set would allow the formation of more favorable hybrid orbitals for bonding, but it is unlikely to have a significant effect on the relative energies.

All the calculations on N_4 are collected in Table V. We may summarize by giving the relative order of energies obtained, in atomic units, for the various geometries. These are shown in Table VI. Using a combination of SZ and DZ results, the probable order of stability is: $2N_2 > N_2 + 2N > \text{tetrahedral} > \text{rectangular} > \text{square}$.

The results of Buenker and Peyerimhoff⁴⁷ on cyclobutadiene have a direct relationship to these results. Their lowest level calculation, which is approximately at the DZ level with minimal CI, shows an energy for square triplet C_4H_4 about 0.03 au above that of two acetylene's. At a comparable level, our DZ calculation of square triplet N_4 lies 0.488 au above that of two N_2 's. In both cases the rectangular singlet lies only slightly lower than the square triplet. Why is cyclobutadiene roughly comparable to two C_2H_2 's, when N_4 lies so far above two N_2 's?

First, consider the following thermochemical argument. Assign cyclobutadiene and N_4 the rectangular geometry (below).



Using the bond energies from Table I, we obtain



These figures agree qualitatively with the DZ SCF results. In their discussion of the relationship of C_4H_4 to other systems, Buenker and Peyerimhoff⁴⁷ attribute a good deal of the stability of cyclobutadiene to the presence of C-H bonds, "... mainly because it aids in decreasing the resistance of certain molecular orbitals to cyclic structures by lessening their CC antibonding character." These authors predict that the N_4 ring would be unstable, because there are no such bonds to hydrogen. They thus place considerable emphasis in the discussion of ring stability on the σ bonds.

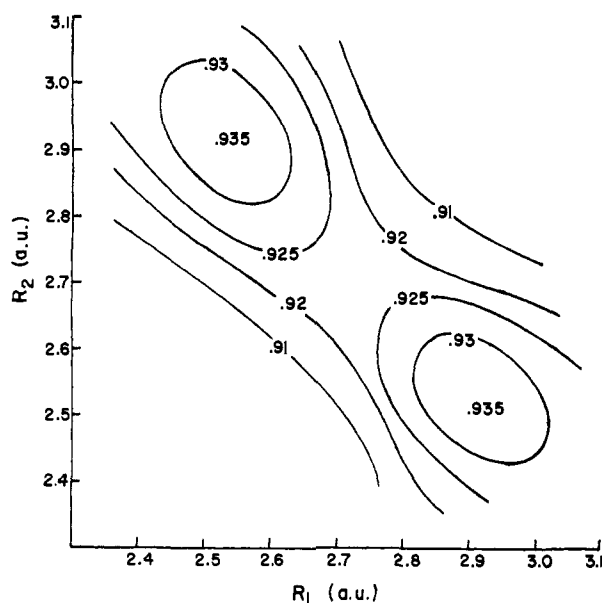


Figure 7. Contour map of the CI energy for the rectangular distortion of N_4 . The minima occur at -216.935 au.

Table VI. Relative Energies for N_4 (au)

Basic set	Geometry	Energy, au
SZ	$2N_2$	0.0
	Square	+0.215
	Rectangular	+0.205
	Tetrahedral	+0.219
DZ	$2N_2$	0.00
	Square	+0.488
	Rectangular	Not done
	Tetrahedral	+0.436

The usual interpretation given to the instability of cyclobutadiene has been that, in the square planar form, a doubly degenerate π nonbonding orbital contains two electrons. It is therefore a ring system containing $4n$ π electrons and termed antiaromatic.³⁸ The destabilization due to antiaromaticity has been estimated by Breslow⁴⁸ to be ~ 20 kcal/mol (0.03 au). Because N_4 is isoelectronic (same number of electrons) and isosymmetric (same symmetry group) with C_4H_4 , its molecular orbitals show exactly the same pattern. In particular, the π system for the square planar triplet shows one bonding, two nonbonding, and one antibonding orbital and contains 4 electrons. This pattern follows directly from the D_{3h} symmetry of the ring. Thus if the $4n + 2$ rule is a criterion of aromaticity, this system is antiaromatic.

Another criterion of antiaromaticity which has been used is that of double-bond localization in a cyclic system.⁴⁹ In N_4 , the energy of the singlet state obtained on rectangular distortion was below that of the square triplet. The SZ bond distances of 2.9 and 2.5 au are close to the experimental single-bond distance of 2.78 and 2.48 au observed in nitrogen systems (ref 32). The ring is not stabilized by delocalization.

A third measure of aromaticity would require a comparison on energetic grounds. For C_4H_4 , one compares the π energy of cyclobutadiene and 1,3-butadiene (the

(48) R. Breslow, *Accounts Chem. Res.*, **6**, 393 (1973).

(49) G. Binsch, "Double Bond Fixation, Ring Currents, and Aromaticity," ref 40, p 25.

open-chain reference compound) to the π energy of two isolated ethylene molecules and labels this difference the resonance energy, leading to the statement that the cyclobutadiene possesses no resonance energy while the butadiene molecule possesses a considerable amount.⁴² However, Buenker and Peyerimhof⁴⁷ have pointed out the difficulties of this approach in a full quantum mechanical calculation. First, there is no way to isolate the energy due to the π electrons of the system, since all electrons interact with each other. Second, the decomposition product of C_4H_4 is C_2H_2 , not ethylene, so a meaningful energy comparison must be with respect to the acetylene molecule. Finally, the CH bond system in C_4H_4 apparently plays a role in stabilizing the cyclobutadiene ring. Applied to N_4 , the same difficulties present themselves. We have demonstrated that the rectangular singlet lies below the square triplet, but we cannot draw any conclusions about the aromaticity of N_4 by reference to N_2 . In a quantum mechanical calculation, the concept "aromaticity" remains elusive. In any case, the "antiaromatic" π system in N_4 could account for only a minor part of the calculated destabilization.

Following the prediction by Longuet-Higgins and Orgel⁵⁰ of the possible stabilization of cyclobutadiene by interaction with a metal atom, and the subsequent synthesis of cyclobutadieneiron tricarbonyl,⁵¹ Shusturovich and coworkers considered the possible stabilization of an N_4 -metal complex. This seems reasonable on the grounds that N_4 has essentially the same electronic structure as C_4H_4 and should experience a comparable stabilization. The proposed N_4 -Fe complex was considered as a possible intermediate in the fixation of molecular nitrogen.¹⁰ However, the calculations in this paper essentially rule out that possibility; the energy of N_4 simply lies too far above that of N_2 .

(C) **N_6 Molecule.** The most obvious case of an aromatically stabilized nitrogen ring is N_6 , whose hydrocarbon analog is benzene. Assuming N_6 to be hexagonal (D_{6h} symmetry), it was pointed out by Roberts⁶ that the pattern of π orbital energies is identical with that in benzene. By the standard calculation of resonance energy, the N_6 ring should therefore be stabilized with respect to three isolated $N=N$ double bonds.

A previous *ab initio* calculation on N_6 showed no binding relative to six atoms of nitrogen.⁵² This surprising

result is probably due to deficiencies in the basis set employed, perhaps exaggerated by differences in closeness of approach to the Hartree-Fock limit for N and N_6 ,²⁷ as well as correlation energy problems. Here we compare the calculated energy of N_6 to that of three molecules of N_2 , presumably a safer procedure. Calculations are performed at the SZ level; due to the size of the molecule, no DZ calculation was done (this would require about 4 hr on the 360/65). The unique distance was varied to obtain the optimum energy; an energy $E = -325.468$ au was obtained at $r = 2.606$ au. This energy lies 0.242 au above that of three molecules of N_2 in the same basis. Formation of the ring thus leads to a destabilization of $0.242/3 = 0.080$ au per N_2 monomer, compared to the SZ calculation for N_4 which yields $0.215/2 = 0.108$ au per N_2 monomer. On this basis, the N_6 ring is seen to be favored relative to the N_4 ring. Use of the isolated single- and double-bond energies in Table I leads to a ΔH of -0.42 au for $N_6 \rightarrow 3N_2$ and -0.28 au for $N_4 \rightarrow 2N_2$. The SZ calculated values, however, give -0.242 and -0.215 au (for ΔE), respectively. Thus, it seems likely that we are observing a genuine stabilizing effect in the N_6 ring. Since the lone-pair repulsions in N_6 are even more severe than in N_4 due to the larger overlap, this stabilization may reasonably be attributed to delocalization in the π system, *i.e.*, aromaticity in the usual sense. However, the extent to which this conclusion would be supported by a DZ calculation is uncertain.

Summary

The use of simple ideas of aromaticity coupled with an *ab initio* investigation has led to the following results: (1) a secondary minimum exists for the N_3^+ ion in its cyclic form; (2) the N_4 molecule, either in square, rectangular, or tetrahedral geometry, has an energy far above that of two N_2 's; (3) the N_6 molecule appears to possess a certain stability relative to the N_4 molecule. In addition, comparison between single- ζ and double- ζ calculations show the energy predictions to be significantly different.

Acknowledgment. The author would like to thank the National Research Council of Canada (Grant No. A-6580) for financial support for this research.

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(53) The "experimental" molecular energy is calculated from the spectroscopic dissociation energy, and atomic energies are taken from C. E. Moore, *Nat. Bur. Stand. (U.S.) Circ.*, No. **467** (1949).

(50) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

(51) R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Commun.*, 1208 (1967); J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3254 (1965).