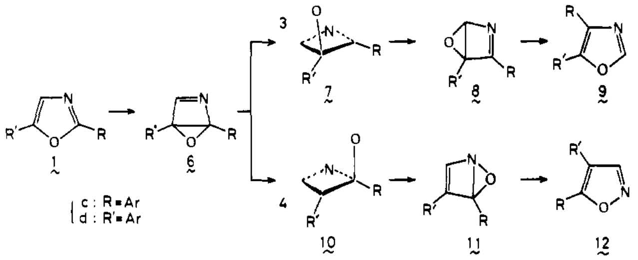
energy to go over the barrier of ring opening (17 kcal mol^{-1}). It is noteworthy to see that in the ground state **10a** is not a transition state in the conversion **6a** → **11a**. This is a result obtained by including singly and doubly excited configurations.

Let us discuss the influence of the substituent upon the reaction courses of paths 3 and 4. When an aromatic substituent is on the C_2 or C_5 atom, the amplitudes of p_π AO's of LUMO on these atoms increase. Therefore, the bicyclic intermediate formation is favorable in the $\pi \rightarrow \pi^*$ state of 2-aryloxazole (**1c**) or 5-aryloxazole (**1d**). In addition, the stabilization due to the conjugation effect with a substituent might play an important role in the determination of the reaction course. **7c** (or **10d**) is conjugated between an aromatic substituent and the C_2–N_3–C_4 (or N_3–C_4–C_5) part, whereas **7d** (or **10c**) is not. That is, one can expect that the transition state is stabilized considerably due to the conjugation and the energy barrier is lowered. Therefore, the 2,4 transposition is favorable in **1c** (path 3) and the 3,5 transposition in **1d** (path 4).



Concluding Remarks

In this paper the reaction mechanisms of photoisomerization of oxazoles are discussed on the basis of the results of ab initio MO-CI calculations. Four possible reaction paths are proposed and summarized pictorially in Figure 11. One of factors that controls the reaction course is the position of an aromatic substituent. The stabilization due to the conjugation with an aromatic substituent lowers the energy barrier to make the reaction favorable.

Though the basis set and the configuration selection employed in this work might not be sufficient to predict the reaction course quantitatively, the present calculation could describe the important features of the reaction mechanisms.

Acknowledgment. We thank the Computer Center of the Institute for Molecular Science for the use of the HITAC M-200H computer and the Library Program IMSPAC written by Prof. K. Morokuma and co-workers (IMS). We also express our gratitude to the Data Processing Center of Kyoto University for the use of the FACOM M-200 computer. This study was partly supported by a Scientific Research Grant (56540282) from the Ministry of Education of Japan.

Registry No. **1a**, 288-42-6; **2a**, 68289-74-7; **4a**, 84648-81-7; **6a**, 84648-82-8; **7a**, 84648-83-9; **10a**, 84648-84-0; **11a**, 84648-85-1.

Cyclic D_{6h} Hexaazabenzene—A Relative Minimum on the N_6 Potential Energy Hypersurface?

Paul Saxe and Henry F. Schaefer III*

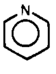
Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received July 12, 1982*

Abstract: Vogler has recently reported laboratory evidence for the formation of hexaazabenzene from photochemical elimination in *cis*-diazidobis(triphenylphosphorane)platinum(II). Previous theoretical studies have suggested that the D_{6h} benzene-like structure is not a minimum on the N_6 potential energy hypersurface. Here the N_6 problem has been addressed at the self-consistent-field (SCF) level of theory using double-ζ (DZ) and double-ζ plus polarization (DZ+P) basis sets. The smaller basis set yields the prediction that the D_{6h} structure is a transition state connecting two equivalent bond alternant N_6 equilibrium geometries. A second transition state for dissociation to three nitrogen molecules (which are energetically much lower than N_6) was also located. Contrary to previous theoretical work, hexaazabenzene is found to be a minimum at the highest completely consistent level of theory. The equilibrium geometry occurs for r_e(N–N) = 1.288 Å, a bond distance suggesting that N_6 is a classic aromatic molecule. The transition state to $3N_2$ lies 10.3 kcal higher and has the planar, bond alternant structure, r_1 (N–N) = 1.178 Å, r_2(N–N) = 1.551 Å. Harmonic vibrational frequencies for hexaazabenzene are predicted with both theoretical methods and demonstrate that the energy surface is very flat with respect to bond alternating B_{2u} displacements. The inclusion of correlation effects lowers the barrier to N_6 dissociation when geometrical structures obtained at the SCF level of theory are assumed.

Introduction

The N_6 molecule hexazine or hexaazabenzene is the final member of the series of aromatic and potentially aromatic molecules **1–7**. In this series of 13 unsubstituted compounds, 7 are well known and at least reasonably stable:[1,2] benzene (**1**), pyridine (**2**), pyridazine (**3a**), pyrimidine (**3b**), pyrazine (**3c**), *s*-triazine (**4c**), and *s*-tetrazine (**5c**). The eighth and last known compound of the series, 1,2,4-triazine (**4b**), was synthesized in 1966,[3] and an improved synthesis was reported in 1974,[4] but **4b** is apparently not well known, since a recent review[1] states that "the parent of this class has never been prepared".


1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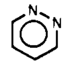
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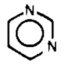
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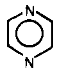
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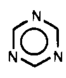
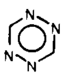

4c


5a


5b


5c


6


7

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(1) A. E. A. Porter, "Comprehensive Organic Chemistry", Vol. 4, D. Barton and W. D. Ollis, Eds., Pergamon Press, Oxford, 1979, pp 145–154.

(2) H. Neunhoeffer and P. F. Wiley, "Chemistry of 1,2,3-Triazines, 1,2,4-Triazines, Tetrazines, and Pentazines", Wiley, New York, 1978.

(3) W. W. Paudler and J. M. Barton, *J. Org. Chem.*, **31**, 1720 (1966).

(4) D. Krass and W. W. Paudler, *Synthesis*, **6**, 351 (1974).

Substituted examples of only one of the remaining five classes of compounds **1**–**7** have been prepared. The first 1,2,3-triazine (**4a**) prepared was the 4,5,6-triphenyl species reported by Chandross and Smolinsky[5] in 1960, and 17 additional 1,2,3-triazenes are noted in Neunhoeffer's 1978 review.[2] Based on the stability of the 4,5,6-trimethyl-1,2,3-triazine, reported by Closs and Harrison[6] in 1972, it has been suggested[2] that the parent **4a** should eventually prove (when synthesized) to be a relatively stable compound. However, there are no known examples of 1,2,3,4-tetrazines (parent **5a**), 1,2,3,5-tetrazines (parent **5b**), or pentazines (parent **6**).

With this experimental background in mind, it is not at all surprising that no report of the synthesis of hexazine was reported prior to 1980. In a certain sense, of course, hexazine is the most intriguing of all the azabenzenes, since at least in principle it could share benzene's D_{6h} structure, all six CH fragments having been replaced by nitrogen atoms. For these reasons, the report by Vogler, Wright, and Kunkely[7] of evidence for the formation of hexaazabenzene was a startling one. These authors studied the low-temperature photolysis of the azide complex *cis*-$[Pt(N_3)_2(PPh_3)_2]$ and analyzed the photoproducts in glasses of organic solvents (ethanol or methyltetrahydrofuran) at 77 K. A yellow coloration rapidly occurred (absorption maximum at λ 380 nm) which on warming the matrix immediately disappeared with simultaneous evolution of N_2.[7] Vogler, Wright, and Kunkely (VWK) concluded that the N_6 molecule is formed as the azide ligands are cleaved, i.e.,

$$cis\text{-}[Pt(N_3)_2(PPh_3)_2] \rightarrow Pt(PPh_3)_2 + N_6 \qquad (1)$$

At room temperature, flash photolysis of the same platinum azide in the same solvents gave a similar UV absorption at λ 380 nm.

Prior to the VWK experiment,[7] there had already been at least six theoretical investigations[8–13] of hexazabenzene. As early as 1962, Roberts[8] noted that Hückel calculations of the electronic states of hexazabenzene would be the same as those for benzene, "provided the extra unshared electron pairs are regarded as being strictly localized". However, among quantitative theoretical studies, there is no compelling evidence that D_{6h} hexazine is a relative minimum on the N_6 potential energy hypersurface. VWK appear to have been misled in this regard by certain statements in Wright's papers.[11,12] VWK state that Wright's calculations "lead to the conclusion that N_6 is slightly stabilized", whereas in fact Wright only suggested[12] that D_{6h} lies somewhat below N_2 plus the highly energetic N_4 species. Although N_6 certainly does have "stability" in the sense attributed by Wright, such "stability" may have little bearing on whether N_6 could be prepared in the laboratory. Since only D_{6h} geometries were considered in his work, Wright did not attempt to examine whether hexaazabenzene was a relative minimum on the N_6 potential surface.

In this light it may be noted that Dewar's MINDO/3 and MNDDO/1 studies[13] of the dissociation process

$$D_{6h}\, N_6 \rightarrow N_2 + N_2 + N_2 \qquad (2)$$

represent the earliest attempt to ascertain whether N_6 might be an observable species in the gas phase. MINDO/3 predicts N_6 to be a relative minimum, while MNDDO/1 (stated to generally provide more satisfactory results) predicts that reaction 2 proceeds without an activation barrier. A more recent, and in some respects the most useful, study of the N_6 problem is that of Ha, Cimiraglia, and Nguyen.[14] Using a 4-31G basis set[15] (of nearly double-zeta (ζ) quality[16]) they conclude (in concurrence with Dewar[13]) from self-consistent-field (SCF) and configuration interaction (CI) studies that, even within D_{3h} symmetry, hexazine falls apart in the gas phase to $3N_2$ without a barrier. This result notwithstanding, Ha[14] predicted an $n \rightarrow \pi^*$ electronic transition at 391 nm, in reasonable agreement with VWK's observed[7] λ_{max} 380 nm. Ha concluded that harmony with the VWK experiment might be reached if hexazine were stabilized by the ethanol matrix at 77 K.

As this manuscript was in the final stages of preparation, a semipopular review of theoretical aspects of the N_6 problem appeared.[17] This review focused our attention on the 1982 N_6 publication of Huber,[18] who applied the SCF method with a small double-ζ basis including polarization by floating orbitals. Huber demonstrated via normal coordinate analysis that the D_{6h} form of N_6 is not a minimum but a transition state at this level of theory. Huber states that "based on experience with calculations of this level, the result should not differ substantially by extending the basis." The present research indicates, among other things, that this suggestion by Huber is incorrect. That is, application of higher levels of theory to N_6 does bring about qualitative changes in the potential energy hypersurface.

Theoretical Perspective and Details

The best theoretical calculations to date concur that hexaazabenzene is *not* a minimum on the N_6 potential energy hypersurface. Although Ha[14] suggests the possibility that cyclic N_6 would be matrix-stabilized, no information concerning the flatness or shape of the N_6 energy surface near the optimum D_{6h} structure is provided. The present study picks up the N_6 problem at this point and pursues it at a higher level of theory. Specifically, it may be mentioned that the existence of a minimum on the D_{6h} potential curve is of limited value. Since D_{6h} N_6 has only one adjustable geometrical parameter, a minimum will necessarily exist as long as energies below that of six infinitely separated nitrogen atoms are found. Given the great strength of the N≡N bond in N_2, it is no surprise that all properly carried out theoretical studies to date agree that D_{6h} N_6 lies well below 6N. The goal of the present research was, then, to consider all the other vibrational degrees of freedom in the vicinity of the presumed hexaazabenzene structure in order to determine (a) whether the D_{6h} structure becomes a minimum at higher levels of theory and/or (b) whether the N_6 energy hypersurface is sufficiently flat near the D_{6h} structure that stabilization by a matrix is plausible.

Two basis sets of contracted Gaussian functions[16] were used in the present research. The first was the standard N(9s5p/4s2p) double-ζ (DZ) basis of Huzinaga[19] and Dunning.[20] In the second basis, a set of six Cartēsian d-like functions (polarization functions) with orbital exponent $\alpha = 0.8$ were added to each nitrogen atom. This double-ζ plus polarization (DZ+P) basis set may be designated N(9s5p1d/4s2p1d). The DZ basis thus consists of 60 contracted Gaussian functions and the DZ+P basis 96 contracted functions. All results presented here were obtained at the self-consistent-field (SCF) level of theory. It was possible to obtain configuration interaction (CI) wave functions and energies for a few selected geometries but the SCF results (to be described below) indicated that such a procedure could be very misleading.

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(5) E. A. Chandross and G. Smolinsky, *Tetrahedron Lett.*, **13**, 19 (1960).

(6) G. L. Closs and A. M. Harrison, *J. Org. Chem.*, **37**, 1051 (1973).

(7) A. Vogler, R. E. Wright, and H. Kunkely, *Angew. Chem., Int. Ed. Engl.*, **19**, 717 (1980).

(8) See J. D. Roberts, "Notes on Molecular Orbital Calculations", W. A. Benjamin, New York, 1962, p 77.

(9) M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *Tetrahedron Lett.*, **47**, 4659 (1973).

(10) M. H. Palmer, A. J. Gaskell, and R. H. Findlay, *J. Chem. Soc., Perkin Trans. 2*, 778 (1974).

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(12) J. S. Wright, *Theor. Chim. Acta*, **36**, *37* (1974).

(13) M. J. S. Dewar, *Pure Appl. Chem.*, **44**, 767 (1975).

(14) T.-K. Ha, R. Cimiraglia, and M. T. Nguyen, *Chem. Phys. Lett.*, **83**, 317 (1981).

(15) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).

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(18) H. Huber, *Angew. Chem., Int. Ed. Engl.*, **21**, 64 (1982). Huber's basis set is not precisely described, but yields an energy of −325.988 hartrees for N_6, or about 0.3 hartree higher than the standard DZ SCF energies seen in Table I.

(19) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(20) T. H. Dunning, *J. Chem. Phys.*, *53*, 2823 (1970).

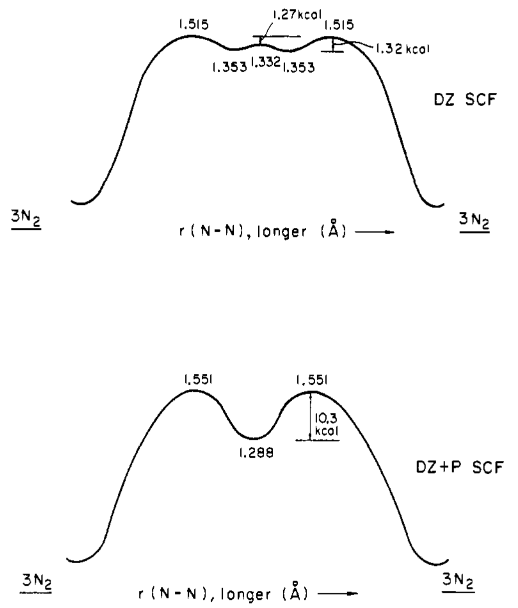

Figure 1. Qualitative sketches of the potential energy surfaces connecting D_{6h} hexaazabenzene with three infinitely separated N_2 molecules. As a one-dimensional reaction coordinate, the longer of the two distinct N–N distances in D_{3h} N_6 was chosen. Of course, the two N–N distances coalesce as one passes from D_{3h} to D_{6h} point group.

That is, the N_6 potential energy hypersurface is so flat near the constrained D_{6h} minimum that anything short of a complete geometrical optimization and harmonic vibrational analysis would appear to be of limited value.

Stationary point molecular geometries were determined using both analytic gradient[21] and direct energy search methods. The latter, although no longer generally helpful, proved useful in this context owing to the extreme flatness of the N_6 energy surface and the small number of independent geometrical parameters (one for D_{6h} structures, two for D_{3h} structures). Given the D_{6h} stationary point structures, quadratic force constants were obtained as differences of analytic forces and subjected to standard harmonic vibrational analyses. DZ+P basis computation times on the Harris 800 minicomputer for SCF plus gradient were typically 7 h for geometries of C_{2v} symmetry and 15 h for point group C_s, with only a single reflection plane.

Structures and Energetics

The DZ SCF and DZ+P SCF descriptions of N_6 turned out to be very different, even in a qualitative sense. Therefore, the lower level of theory will be discussed first. As seen in Figure 1, there are no less than *three* N_6 stationary points in the vicinity of the anticipated D_{6h} hexazine structure. As will be demonstrated in the next section, the D_{6h} structure is indeed a transition state, as suggested by the nearly comparable 4-31G study of Ha, Cimiraglia, and Nguyen[14] and the work of Huber,[18] carried out with a small DZ basis set. Not mentioned by Ha or Huber is the fact that a very shallow (with respect to the D_{6h} transition state) D_{3h} minimum occurs nearby at the DZ SCF level of theory. This D_{3h} minimum lies only 0.05 kcal below the D_{6h} transition state and has unique bond distrances r_1(N–N) = 1.295 Å, r_2(N–N) = 1.353 Å, as seen in Figure 2. These distances correspond to an increase of 0.031 Å in one bond distance and a compression of 0.027 Å in the other, relative to the D_{6h} perfectly "aromatic" structure.

Since a D_{3h} equilibrium geometry was found by DZ SCF there must be a second transition state (in addition to the D_{6h} structure) connecting the N_6 minimum with (the energetically much lower) three separated N_2 molecules. This transition state is shown in Figure 1 and 2 and is quite well separated structurally from the other stationary points. Specifically, the longer N–N distance is increased by 0.193 Å and the shorter distance decreased by 0.098 relative to the D_{6h} transition state. Despite this rather large shift in geometry, from two equal bond distances of 1.322 Å to long and short N–N distances differing by 0.291 Å, the accompanying energy difference is only 1.27 kcal. This finding suggests that the N_6 energy difference is extraordinarily flat in the region of the D_{6h} hexaazabenzene structure. Although the DZ SCF characterization of the D_{6h} structure as a transition state will shortly be challenged, this more general conclusion of flatness is supported by the higher level results to be presented.

Contrary to previous theoretical studies,[13,14,18] the highest consistent level of theory yet used to address this problem suggests that D_{6h} hexazine *is* a relative minimum on the N_6 energy surface. The fact that the DZ+P SCF method yields this result is demonstrated in Figure 1, with Figure 2 and Table I and II providing additional details. The predicted N–N separation of the hexaazabenzene miminum is 1.288 Å, or only 0.034 Å shorter than the analogous DZ D_{6h} stationary point prediction. The striking difference, of course, is that with DZ SCF the D_{6h} structure is a transition state, while adding a set of d functions to each nitrogen atom transforms hexazine into a genuine potential minimum. Since the D_{6h} structure is a minimum with DZ+P SCF, there must be a transition state separating if from the dissociation limit of three nitrogen molecules. This transition state is seen in Figures 1 and 2, which show alternating bond distances of 1.178 and 1.551 Å. Comparison of the DZ and DZ+P SCF results shows the surprising (relative to the structures of normal closed-shell molecules[16]) result that d functions *increase* the longer predicted N–N distance, by 0.036 Å. The shorter N–N distance, which

Table I. Total Energies (hartrees) and Relative Energies (kcal/mol) for N_6 Stationary Points at Various Levels of Theory[a]

	DZ SCF		DZ+P SCF	
	total energy	rel energy	total energy	rel energy
D_{6h} N_6	−326.265 67[b]	0.00	−326.514 27	0.00
D_{3h} N_6 minimum	−326.265 74	−0.05		no such stationary point
D_{3h} N_6 transition state	−326.263 64	+1.27	−326.497 84	+10.3
three N_2 molecules	−326.634 93	−231.7	−326.876 98	−227.6

[a] Relative energies are given with respect to the benzene-like D_{6h} stationary point. Note that while the D_{3h} structures reported here are definitely stationary points, they have not been proven by normal coordinate analysis to be minima and transition states, respectively. [b] An energy of −326.26557 hartrees (0.0001 hartree higher) was reported by Ha, Cimiraglia, and Nguyen[14] apparently using the identical DZ SCF method. Their D_{6h} geometry is r(N–N) = 1.320 Å, while the present stationary point geometry is r(N–N) = 2.4974 bohrs = 1.322 Å.

Table II. Predicted Vibrational Frequencies (in cm^{-1}) for Hexaazabenzene Compared with Those Known Experimentally for Benzene[a]

normal mode	hexazine DZ SCF	hexazine DZ+P SCF	benzene exptl	benzene assignments
		In-Plane Frequencies		
E_{2g}	1539	1722 (1550)	1599	C–C stretching[
E_{1u}	1257	1412 (1271)	1482	C–C stretching
B_{1u}	1160	1262 (1136)	1010	C–C–C trigonal bending
A_{1g}	1083	1184 (1066)	993	breathing
E_{2g}	769	809 (728)	606	C–C–C in-plane bending
B_{2u}	232i	330 (297)	1309	C–C stretching (Kekulé)
		Out-of-Plane Frequencies		
B_{2g}	913	959 (863)	707	C–C–C puckering
E_{2u}	366	318 (287)	404	C–C–C out-of-plane bending

[a] To provide a more realistic comparison, the DZ+P SCF harmonic frequencies have also been reduced by 10%, and these empirically corrected frequencies are given in parentheses. Experimental frequencies and assignments are from ref 26.

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(21) P. Pulay, "Modern Theoretical Chemistry", Vol. 4, H. F. Schaefer, Ed., Plenum Press, New York, 1977, pp 153–185.

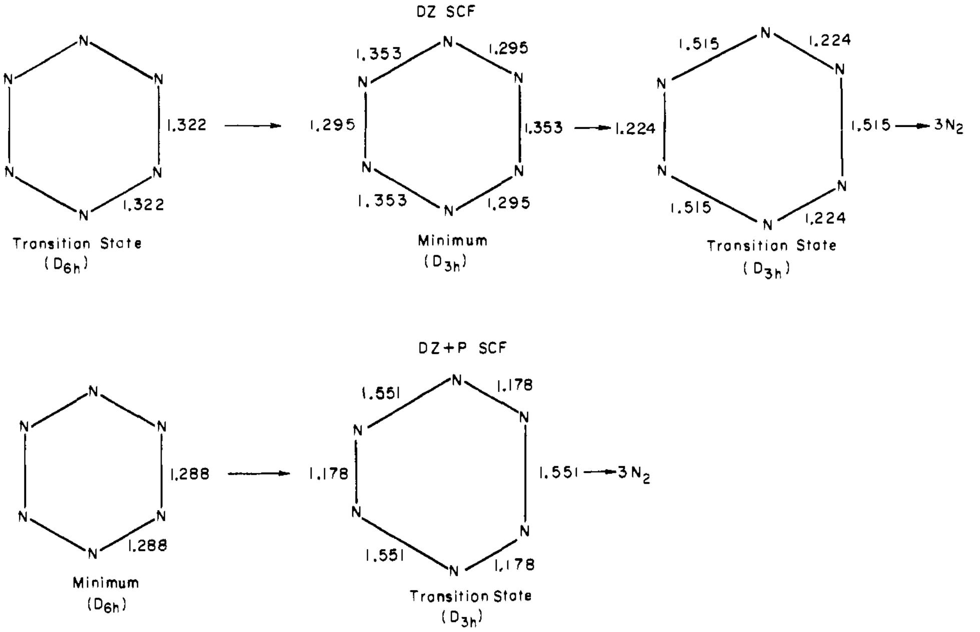


Figure 2. Stationary point geometrical structures for N_6. N–N bond distances are given in Å. Note in Figure 1 that the DZ SCF and DZ+P SCF potential surfaces are very different.

is much more like that in isolated N_2, shows the expected decrease (by 0.046 Å) when polarization functions are added to the basis.

Quite unexpected relative to earlier theoretical work is the DZ+P SCF prediction (see Table I) that the D_{6h} N_6 minimum is separated by a barrier of 10.3 kcal from the energetically much lower $3N_2$ asymptote. Such a barrier is surprisingly large and, if correct, would readily explain Vogler's apparent low-temperature observation[7] of N_6. Even if the precise value of the N_6 dissociation barrier from DZ+P SCF theory is too high, the fact that the energy changes by so very little for such a broad range of N–N separations (1.551–1.178 = 0.373 Å) is encouraging in terms of experimentally trapping N_6 via matrix isolation techniques.

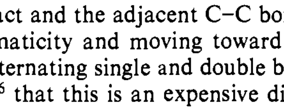
A matter of lesser interest here is the energy difference between D_{6h} hexaazabenzene and three separated N_2 molecules. Previous theoretical studies[10–14] have demonstrated that hexazine lies energetically far above three N_2 molecules. To make this comparison, the structure of the N_2 molecule was optimized at the DZ SCF (r_e = 1.100 Å) and DZ+P SCF (r_e = 1.083 Å) levels of theory. The predicted bond distances are in acceptable agreement with the experimental value[22] r_e = 1.098 Å. Three times the SCF energies of N_2 are given in Table I, from which a bit of subtraction shows that hexazine lies 231.7 kcal above $3N_2$ with the DZ SCF method and 227.6 kcal above $3N_2$ with DZ+P SCF. As Ha[14] has noted, correlation effects will reduce these energy differences, inasmuch as D_{6h} N_6 is described more poorly in the Hartree–Fock approximation than is the $3N_2$ asymptote.

Vibrational Frequencies of Hexaazabenzene

Consideration of the structure alone of D_{6h} hexazine would lead one to believe that it is, if anything, even more aromatic than benzene. Benzene has a C—C bond distance intermediate between typical C═C and C—C distances, being a bit closer to the former. However, the predicted N—N distance in D_{6h} hexazine (1.322 Å DZ, 1.288 Å DZ+P) is very much closer to the double-bonded diimide value[23] [r(N═N) = 1.25 Å] than to that of the single bond in hydrazine[24] [r(N—N) = 1.447 Å]. Furthermore, the predicted N—N distance is a bit shorter than the 1.32 Å found from the crystal structure[25] of the aromatic s-tetrazine molecule 5c. Thus the analogy between hexazine and benzene would appear to be a very good one based on the structural data presented here.

However, the predicted vibrational frequencies demonstrate clearly the dramatic differences between hexaazabenzene and benzene itself. These frequencies are given in Table II, where comparison is made with the benzene vibrational frequencies[26] associated with the carbon skeleton. Of course, some mixing between the C–H and C–C degrees of freedom is inevitable for benzene, so the comparison is not a perfect one.

From the DZ SCF results alone it is apparent that the B_{2u} vibrational frequencies of hexazine and benzene are about as different as one could imagine. The B_{2u} mode allows one C–C distance to contract and the adjacent C–C bond to expand, destroying the aromaticity and moving toward a structure with distinguishable alternating single and double bonds. It has been known for years[26] that this is an expensive displacement energetically for benzene, and this is reflected in the observed Kekulé stretching frequency of 1309 cm^{-1}. However, for hexaazabenzene as modeled by DZ SCF, the B_{2u} mode becomes an ***imaginary*** vibration frequency (232 i); i.e., the D_{6h} structure is a maximum with respect to B_{2u} displacements. Thus the harmonic vibrational analysis of this species demonstrates conclusively that at the DZ SCF level of theory, hexazine is a transition state for nitrogen–nitrogen bond switching. One can imagine a degenerate isotopic reaction that would employ such a transition state, but termolecular reactions of this general type are thought to be relatively unlikely.[27]



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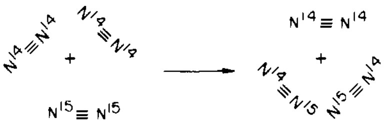

(4a)

$$2\,N_2^{14} + N_2^{15} \longrightarrow N_2^{14} + 2\,N^{14}N^{15} \quad (4b)$$

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[23] M. Carlotti, J. W. C. Johns, and A. Trombetti, *Can. J. Phys.*, **52**, 340 (1974).

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Table III. Total Energies (in hartrees) and Relative Energies (in kcal/mol) from Correlated Wave Functions for N_6[a]

	DZ CI		DZ+P CI	
	total energy	rel energy	total energy	rel energy
D_{6h} N_6	−326.808 02	0.0	−327.282 47	0.0
D_{3h} N_6 minimum	−326.808 84	−0.5	no minimum	
D_{3h} N_6 transition	−326.822 66	−9.2	−327.280 35	+1.3
three N_2 molecules	−327.174 98	−230.3	−327.616 38	−209.5

[a] Relative energies are given with respect to the benzene-like D_{6h} stationary point. Note that the geometries used here are those in Figure 2, i.e., optimized at the single configuration SCF level of theory. Thus reoptimizing the structures (*assumed* here) at the CI level could significantly affect these predictions.

It is not without precedent for the nature of a stationary point to change in going from DZ to DZ+P SCF theory. For example, in the SH_4 molecule, the SF_4-like C_{2v} minimum disappears when polarization functions are added to the basis set.[28] Similarly for the H_7^+ complex $H_3^+(H_2)_2$ the known equilibrium geometry is predicted to be a transition state when CI is carried out with a DZ basis set.[29] In the same vein, the DZ SCF D_{6h} transition state becomes a minimum when d functions are added to the N_6 basis set.

Of particular interest in Table II is the B_{2u} vibrational frequency predicted by DZ+P SCF. This frequency, while no longer imaginary (as with the DZ SCF method), is nevertheless very different from the experimental value for benzene. Specifically, Table II shows that the carbon skeletal B_{2u} frequency in C_6H_6 is 1309 cm^{-1}, while the analogous DZ+P SCF frequency for hexazine is 330 cm^{-1}, almost a factor of 4 smaller. This is, of course, further concrete evidence that the N_6 potential energy hypersurface is very flat in the region of the D_{6h} stationary point. The lowest DZ+P SCF vibrational frequency is not the B_{2u} mode but rather the degenerate E_{2u} frequency at 318 cm^{-1}. This is an out-of-plane bending mode quite analogous to that observed at 404 cm^{-1} for benzene. Thus one sees that the N_6 energy hypersurface is only marginally flatter than benzene with respect to this ring deformation. In this general vein, one concludes that the DZ+P SCF N_6 vibrational frequencies are all roughly comparable to the analogous skeletal modes of benzene except for the ring-stretching B_{2u} Kekulé displacement.

Preliminary Results from Correlated Wave Functions

As noted earlier, it was not considered feasible at the present time to determine stationary point geometries and vibrational frequencies at the configuration interaction (CI) level of theory. However, *assuming* the SCF stationary point structures in Figure 2, single-point CI wave functions were determined including all valence single and double excitations with respect to the N_6 Hartree–Fock reference configuration. In C_{2v} point group (the symmetry of the SCF transition states for $N_6 \rightarrow 3N_2$ is actually higher, D_{3h}), there are a total of 33 320 configurations with the DZ basis set and 142 130 configurations with the DZ+P basis. These variational calculations were made possible by use of the recently developed shape-driven graphical unitary group approach,[30] and the larger CI required 12 h on the Harris Corp. Series 800 minicomputer.

The results obtained from correlated wave functions are summarized in Table III. One sees first that electron correlation reduces the exothermicity of the $N_6 \rightarrow 3N_2$ process by only ~17 kcal, to ~211 kcal. A much greater reduction (~115 kcal) in this exothermicity was earlier predicted by Ha, Cimiraglia, and Nguyen,[14] and we suspect that the latter result is not reliable, perhaps because of an improper use of configuration selection techniques.

With geometries determined at the SCF level of theory, the effect of electron correlation is apparently to raise the energy of the D_{6h} stationary point relative to adjacent regions of the N_6 energy hypersurface. Thus with the larger DZ+P basis set the barrier to N_6 dissociation is seemingly reduced to 1.3 kcal from the SCF value of 10.3 kcal. Moreover, appendage of the Davidson correction[31] for unlinked clusters further reduces the energy of the geometry corresponding to the DZ+P SCF transition state, to 3.8 kcal below the energy of the analogous hexazine structure.

It is at best difficult to assess the significance of the correlated energy differences just reported. If the results obtained had involved complete geometry optimization at the correlated levels of theory, then one would be inclined to doubt the existence of hexazine as a relative minimum on the N_6 potential surface. However, we must emphasize that no such correlated geometry determination was attempted and thus the results may be misleading. It should also be recalled that a counterintuitive result was found (in the longer of the alternating N–N distances for the N_6 dissociation transition state) in going from the DZ to the DZ+P basis set. Thus it may not be possible to reliably estimate the effects of correlation of the N_6 stationary point geometries. In conclusion, great progress has been made along the path to a reliable prediction of the properties of hexazine, but the process has not yet been carried to an entirely satisfactory conclusion.

Concluding Remarks

The present theoretical study, carried out at a significantly higher level and degree of thoroughness than previous work, predicts the D_{6h} structure of hexaazabenzene to be a relative minimum on the N_6 potential energy hypersurface. More pictorially, hexaazabenzene is predicted to be a dimple on top of a mountain. A question that must be addressed in this context is, "Do the authors believe this result to be definitive?" To that question we must in candor give an equivocal answer. In the sense that we are confident that raising the level of theory applied will ultimately give correct answers to all such problems, then the DZ+P SCF prediction that N_6 is a minimum must be considered more "reliable" than previous theoretical predictions to the contrary. However, this line of reasoning only suggests a most probable result and carries with it not a trace of infallibility. The primary and definitive conclusion of this research is rather that the N_6 energy surface is very flat in the vicinity of the D_{6h} hexaazabenzene structure. Changes in the N–N bond distance of up to 0.37 Å may be accommodated with a rise in the total energy of only 10 kcal.

Has hexaazabenzene actually been made[7] by Vogler, Wright, and Kunkely? At this point it appears to the present authors a bit premature to form an educated judgment. Further experiments are absolutely essential in this regard, and it is hoped that the vibrational frequencies predicted here might assist in a matrix infrared spectroscopic identification of N_6. In any case, the unusual broadness of the N_6 potential surface near the hexaazabenzene stationary point does support the view that D_{6h} N_6 might be trapped in a low-temperature matrix, as claimed by VWK.[7]

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