Title
CYCLIC D6h HEXAZABENZENEu-A RELATIVE MINIMUM ON THE N6 POTENTIAL ENERGY HYPERSURFACE?

Permalink
https://escholarship.org/uc/item/4434j59n

Author
Schaefer, H.F.

Publication Date
1982-07-01
Submitted to the Journal of the American Chemical Society

CYCLIC D$_6$h HEXAAZABENZENE--A RELATIVE MINIMUM ON THE N$_6$ POTENTIAL ENERGY HYPERSURFACE?

Paul Saxe and Henry F. Schaefer III

July 1982

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Cyclic $D_{6h}$ Hexaazabenzene--A Relative Minimum on the $N_6$
Potential Energy Hypersurface?

Paul Saxe and Henry F. Schaefer III

Department of Chemistry and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720
U.S.A.

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 zeta (DZ) and double zeta 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 $r_1(N-N) = 1.178\,\text{Å}$, $r_2(N-N) = 1.551\,\text{Å}$.

Harmonic vibrational frequencies for hexaazabenzenzene 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 hexaazabenzen is the final member of the series of aromatic and potentially aromatic molecules.

In this series of thirteen unsubstituted compounds, seven are well known and at least reasonably stable: 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 and an improved synthesis reported in 1974, but 4b is apparently not well known, since a recent review states that "the parent of this class has never been prepared."

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 in 1960, and seventeen additional 1,2,3 triazenes are
noted in Neunhoeffer's 1978 review. Based on the stability of the 4,5,6-trimethyl-1,2,3 triazine, reported by Closs and Harrison in 1972, it has been suggested that the parent 4 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 5).

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 D₆h structure, all six CH fragments having been replaced by nitrogen atoms. For these reasons, the report by Vogler, Wright, and Kunkely of evidence for the formation of hexaazabenzene was a startling one. These authors studied the low-temperature photolysis of the azide complex cis-[Pt(N₃)₂(PPh₃)₂] and analyzed the photoproducts in glasses of organic solvents (ethanol or methyltetrahydrofuran) at 77°C. A yellow coloration rapidly occurred (absorption maximum at λ = 380 nm) which on warming the matrix immediately disappeared with simultaneous evolution of N₂. Vogler, Wright, and Kunkely (VWK) concluded that the N₆ molecule is formed as the azide ligands are cleaved, i.e.,

$$\text{cis}[\text{Pt(N}_₃\text{)}₂(\text{PPh}_₃\text{)}₂] \rightarrow \text{Pt(PPh}_₃\text{)}₂ + \text{N}_₆$$  (1)
At room temperature, flash photolysis of the same platinum azide in the same solvents gave a similar UV absorption at $\lambda = 380$ nm.

Prior to the VWK experiment, there had already been at least six theoretical investigations of hexazabenzene. As early as 1962, Roberts 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. VWK state that Wright's calculations "lead to the conclusion that $N_6$ is slightly stabilized," whereas in fact Wright only suggested that $D_{6h} N_6$ 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 MNDO/1 studies of the dissociation process

$$D_{6h} N_6 \rightarrow N_2 + N_2 + N_2$$

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.\textsuperscript{14} Using a 4-31G basis set\textsuperscript{15} (of nearly double zeta quality\textsuperscript{16}) they conclude (in concurrence with Dewar\textsuperscript{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\textsuperscript{14} predicted an $n^*\pi^*$ electronic transition at 391 nm, in reasonable agreement with VWK's observed\textsuperscript{7} $\lambda_{\text{max}} = 380$ nm. Ha concluded that harmony with the VWK experiment might be reached if hexazine were stabilized by the ethanol matrix at 77°F.

As this manuscript was in the final stages of preparation, a semi-popular review of theoretical aspects of the $N_6$ problem appeared.\textsuperscript{17} This review focussed our attention on the 1982 $N_6$ publication of Huber,\textsuperscript{18} who applied the SCF method with a small double zeta 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

Thus the best theoretical calculations to date concur that hexaaazabenzene is not a minimum on the $N_6$ potential energy hypersurface. Although Ha\textsuperscript{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 hexaaazabenzene 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\textsuperscript{16} were used in the present research. The first was the standard $N(9s5p/4s2p)$ double zeta (DZ) basis of Huzinaga\textsuperscript{19} and Dunning.\textsuperscript{20} In the second basis, a set of six cartesian d-like functions (polarization
functions) with orbital exponent $\alpha=0.8$ were added to each nitrogen atom. This double zeta plus polarization (DZ+P) basis set may be designated N(9s 5p 1d/4s 2p 1d). 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) wavefunctions and energies for a few selected geometries, but the SCF results (to be described below) indicated that such a procedure could be very misleading. 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\textsuperscript{21} and direct energy search methods. The latter, although no longer generally helpful, proved useful in this context due to the extreme flatness of the $N_6$ energy surface and the small number of independent geometrical parameters (1 for $D_{6h}$ structures, 2 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 seven hours for geometries of $C_{2v}$ symmetry and fifteen hours 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 and the work of Huber, 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 distances $r_1(N-N) = 1.295 \, \text{Å}$, $r_2(N-N) = 1.353 \, \text{Å}$, 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 Figures 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 $D_{6h}$ hexaazabenzenne 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, 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 Tables I and II providing additional details. The predicted N-N separation of the hexaazabenzenne 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 it 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) result that d functions increase the longer predicted N-N distance, by 0.036 Å. The shorter N-N distance,
which is much more like that in isolated $\text{N}_2$, 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 $D_{6h}$ $\text{N}_6$ minimum is separated by a barrier of 10.3 kcal from the energetically much lower three $\text{N}_2$ asymptote. Such a barrier is surprisingly large and, if correct, would readily explain Vogler's apparent low temperature observation $^7$ of $\text{N}_6$. Even if the precise value of the $\text{N}_6$ 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 $\text{N}_6$ via matrix isolation techniques.

A matter of lesser interest here is the energy difference between $D_{6h}$ hexaazabenzenes and three separated $\text{N}_2$ molecules. Previous theoretical studies $^{10-14}$ have demonstrated that hexazine lies energetically far above three $\text{N}_2$ molecules. To make this comparison, the structure of the $\text{N}_2$ 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 $\text{N}_2$ are given in Table I, from which a bit of subtraction shows that hexazine lies 231.7 kcal above 3$\text{N}_2$ with the DZ SCF method and 227.6 kcal above 3$\text{N}_2$ 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 \(^{23}\) \([r(N=N) = 1.25 \text{ Å}]\) than to that of the single bond in hydrazine \(^{24}\) \([r(N-N) = 1.447 \text{ Å}]\). 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
hexaazabenzenne 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

\[ \begin{align*}
N^{14} & \equiv N^{14} + N^{14} \equiv N^{14} \\
N^{15} & \equiv N^{15} + N^{15} \equiv N^{15}
\end{align*} \]  

(4a)

\[ \begin{align*}
2N_2^{14} + N_2^{15} & \rightarrow N_2^{14} + 2N_2^{14} N^{15}
\end{align*} \]  

(4b)
that would employ such a transition state, but termolecular reactions of this general type are thought to be relatively unlikely.\textsuperscript{27}

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 \( \text{SH}_4 \) molecule, the \( \text{SF}_4 \)-like \( C_{2v} \) minimum disappears when polarization functions are added to the basis set.\textsuperscript{28} Similarly for the \( \text{H}_7^+ \) complex \( \text{H}_3^+ (\text{H}_2)_2 \) the known equilibrium geometry is predicted to be a transition state when CI is carried out with a DZ basis set.\textsuperscript{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 \( C_6\text{H}_6 \) is 1309 cm\(^{-1}\), while the analogous DZ+P SCF frequency for hexazine is 343 cm\(^{-1}\), almost a factor of four 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 320 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\textsubscript{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 \( N\textsubscript{6} \) 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, and the larger CI required 12 hours on the Harris Corporation 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 \( \sim 17 \) kcal, to \( \sim 211 \) kcal. A much greater reduction (\( \sim 115 \) kcal) in this exothermicity was earlier predicted by Ha, Cimiraglia, and Nguyen,\textsuperscript{14} and we suspect that the latter result is not reliable, perhaps due to 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 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 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 $D_{6h}^6 \text{N}_6$ might be trapped in a low-temperature matrix, as claimed by VWK.\textsuperscript{7}

**Acknowledgments**

This research was supported by the U.S. National Science Foundation under Grant Number CHE-8009320 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
References


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


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 hartrees higher than the standard DZ SCF energies seen in Table I.


Table I. Total energies (hartrees) and relative energies (kcal/mole) for N₆ stationary points at various levels of theory. Relative energies are given with respect to the benzene-like D₆h stationary point. Note that while the D₃h structures reported here are definitely stationary points, they have not been proven by normal coordinate analysis to be minima and transition states, respectively.

<table>
<thead>
<tr>
<th></th>
<th>DZ SCF</th>
<th>DZ+P SCF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Energy</td>
<td>Relative Energy</td>
</tr>
<tr>
<td>D₆h N₆</td>
<td>-326.26567</td>
<td>0.000</td>
</tr>
<tr>
<td>D₃h N₆ minimum</td>
<td>-326.26574</td>
<td>-0.05</td>
</tr>
<tr>
<td>D₃h N₆ transition state</td>
<td>-326.26364</td>
<td>+1.27</td>
</tr>
<tr>
<td>Three N₂ molecules</td>
<td>-326.63493</td>
<td>-231.7</td>
</tr>
</tbody>
</table>

An energy of -326.26557 hartrees (0.0001 hartree higher) was reported by Ha, Cimiraglia, and Nguyen⁴⁴ apparently using the identical DZ SCF method. Their D₆h geometry is \( r(N-N) = 0.320 \) 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. 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 reference 26.

<table>
<thead>
<tr>
<th>Normal Mode</th>
<th>Hexazine DZ SCF</th>
<th>Hexazine DZ+P SCF</th>
<th>Benzene Experimental</th>
<th>Benzene Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hexazine</td>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In-plane frequencies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_{2g})</td>
<td>1539</td>
<td>1723 (1551)</td>
<td>1599</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>(E_{1u})</td>
<td>1257</td>
<td>1412 (1271)</td>
<td>1482</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>(B_{1u})</td>
<td>1160</td>
<td>1258 (1132)</td>
<td>1010</td>
<td>C-C-C trigonal bending</td>
</tr>
<tr>
<td>(A_{1g})</td>
<td>1083</td>
<td>1185 (1067)</td>
<td>993</td>
<td>breathing</td>
</tr>
<tr>
<td>(E_{2g})</td>
<td>769</td>
<td>809 (728)</td>
<td>606</td>
<td>C-C-C in-plane bending</td>
</tr>
<tr>
<td>(B_{2u})</td>
<td>2321</td>
<td>343 (309)</td>
<td>1309</td>
<td>C-C stretching (Kekulé)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Out-of-plane frequencies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_{2g})</td>
<td>913</td>
<td>959 (863)</td>
<td>707</td>
<td>C-C-C puckering</td>
</tr>
<tr>
<td>(E_{2u})</td>
<td>288</td>
<td>320 (288)</td>
<td>404</td>
<td>C-C-C out-of-plane bending</td>
</tr>
</tbody>
</table>
Table III. Total energies (in Hartrees) and relative energies (in kcal/mole) from correlated wave functions for \( \text{N}_6 \). 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 effect these predictions.

<table>
<thead>
<tr>
<th></th>
<th>DZ CI</th>
<th>DZ+P CI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Energy</td>
<td>Relative Energy</td>
</tr>
<tr>
<td>( D_{6h} ) ( \text{N}_6 )</td>
<td>-326.80802</td>
<td>0.0</td>
</tr>
<tr>
<td>( D_{3h} ) ( \text{N}_6 ) minimum</td>
<td>-326.80884</td>
<td>-0.5</td>
</tr>
<tr>
<td>( D_{3h} ) ( \text{N}_6 ) transition state</td>
<td>-326.82266</td>
<td>-9.2</td>
</tr>
<tr>
<td>Three ( \text{N}_2 ) molecules</td>
<td>-327.17498</td>
<td>-230.3</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. Qualitative sketches of the potential energy surfaces connecting $D_{6h}$ hexaazabenzen 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.

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.
1.353

DZ SCF

1.32 kcal

1.332

DZ+P SCF

1.288

10.3 kcal

$\text{D}3\text{N}_2$

$r (N-N),\text{ longer (Å)}$ ---

$\text{D}3\text{N}_2$

Figure 1
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.