AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **62**, 350 (1975); doi: 10.1063/1.430492
View online: http://dx.doi.org/10.1063/1.430492
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/62/2?ver=pdfcov
Published by the AIP Publishing

Potential energy surface for the model unimolecular reaction HNC → HCN

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(Received 13 September 1974)

Ab initio electronic structure theory has been used to determine the more important features of the potential energy surface for the simple isomerization reaction HNC → HCN. Extended basis sets were used in conjunction with both self-consistent-field (SCF) and configuration interaction (CI) wavefunctions. For nonlinear or C_s geometrical arrangements of the three atoms, the CI included 11 735 configurations, i.e., all single and double excitations. This large scale CI reproduces the HCN ground state geometry quite accurately and has been used to tentatively identify HNC in the interstellar medium. The SCF calculations predict HNC to lie 9.5 kcal/mole above HCN, while CI yields 14.6 kcal/mole. Similarly, barrier heights of 40.2 and 34.9 kcal/mole are predicted by SCF and CI. Thus, the SCF approximation is qualitatively reasonable for HNC → HCN. If HNC is designated by a reaction angle of 180° and HCN by 0°, then the saddle point or transition state is predicted to lie at 73.7°, significantly closer to HCN. A reaction path is determined from the SCF potential surface. The surface will be used in RRKM and classical trajectory studies of the dynamics of this reaction.

INTRODUCTION

Traditional chemical interest in the isomerization of HNC is limited by the fact that the free HNC molecule has never been observed in the laboratory. However, in the present context this is not a serious disadvantage. The HNC system was chosen because it is small enough to be treated with a wide variety of theoretical techniques, which may then be compared quantitatively. In this way, it is hoped that HNC → HCN will become an important model system for the theory of unimolecular reactions.

This work began largely as an extension of previous work on the methyl isocyanide → methyl cyanide rearrangement. Liskow *et al.*[1,2] derived certain geometrical and energetic features of the $CH_3NC \rightarrow CH_3CN$ potential energy surface, in part in order to help Bunker[3] explore an apparent failure of the RRKM model in the case of this reaction. Unfortunately, CH_3CN has so many degrees of freedom that a thorough *ab initio* study of the reaction would be both costly and difficult to interpret. Consequently, we settled upon the idea of replacing the methyl group with a single atom, thereby removing nine confusing (and hopefully immaterial) degrees of freedom.

Substituting a hydrogen atom for the methyl group leaves the prominent features of the reaction roughly unchanged. The exothermicity for the rearrangement is similar (15 kcal vs 15–17 for CH_3NC), and the barrier to rearrangement is quite close (35 kcal vs 38 for CH_3NC).

It is therefore intriguing that although CH_3NC and CH_3CN have both been prepared in the laboratory, all attempts to make free HNC have failed.

A note from the astrophysical literature[4] makes this puzzle still more interesting. In 1971, radioastronomers Snyder and Buhl[4] conjectured that an unidentified microwave emission line at 90.665 GHz in galactic sources W51 and DR21 could come from the $J = 1 \rightarrow 0$ rotational transition of the HNC molecule. Thorough *ab initio* calculations[5] have recently predicted a moment of inertia for HNC consistent (within the accuracy of the calculations)[6] with this identification. The possibility that this elusive species exists in interstellar space is tantalizing indeed.

The present paper represents one step toward an *a priori* understanding of the HNC isomerization. Here we restrict ourselves to a discussion of the potential energy surface for this model reaction. A second paper[7] will describe a thorough RRKM treatment of the dynamics of HNC → HCN. Future work will include a classical trajectory study of the same reaction.

PRELIMINARIES

It is helpful to begin with a qualitative familiarity with the expected potential energy surface.

First, note that three parameters may be used to determine the relative orientations of the atoms. Let us take them to be R_{CN}, the CN bond length; R_{MH}, the distance from the hydrogen atom to the C–N center of mass (the C–N bond midpoint would be equally good, but the center of mass was chosen to conform with previous work[1,2]); and θ, the angle between the CN and HM vectors. As the rearrangement proceeds from CNH to HCN, θ will go from 180° to 0°. This coordinate system is sketched in Fig. 1.

Since three parameters are required to define the geometry, the potential energy surface is actually a 3-dimensional manifold in 4-space, thus not easily envisioned. Fortunately, variation in the C–N bond length does not play a crucial role in the reaction, and we can for the present hold the C–N bond fixed. There then

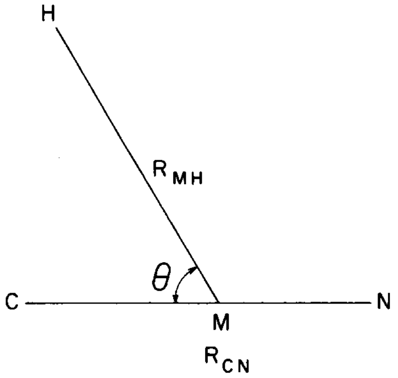

FIG. 1. Illustration of the three coordinates R_{CN}, R_{MH}, and θ, in terms of which the potential energy surface is described.

remain two degrees of freedom, those describing the position of a hydrogen atom around a rigid CN radical. An approximate contour map of the potential energy field experienced by this hydrogen atom is shown in Fig. 2. Note that the absolute minimum lies to the left of the carbon atom, corresponding to the stable HCN. A *local* minimum exists to the right of the nitrogen nucleus, corresponding to HNC. (The difference in depth between the two minima is not apparent because it is smaller than the contour interval.) The floor of the elliptical valley containing these two minima rises substantially between them, the highest point in the valley floor being roughly halfway between the minima. This pass, or highest point of the valley floor, is generally called a "saddle point" (reference to the negative curvature of the surface at such a point) or a "critical configuration."[8]

Traditional discussions of chemical kinetics center on the "reaction path" or "minimum energy path," which follows the valley floor from one minimum over the saddle point to the other minimum. (For the sake of rigor, it must be noted that the minimum energy path described thus is not uniquely defined in any physically meaningful sense; transformation to another set of coordinates would shift the valley and thus the minimum energy path. Only the two local minima and the saddle point are guaranteed to map onto themselves under a coordinate transformation.)

A number of ways to construct a curve approximating the minimum energy path have been published. One such approach involves selecting some coordinate which varies monotonically in the course of the reaction, then for various values of that coordinate finding the values of the remaining coordinates for which the energy is lowest. For example, in the HNC → HCN rearrangement, we might pick θ as our "reaction coordinate." Then for values of θ varying from 0° to 180°, search for values of R_{CN} and R_{MH} such that $E(R_{CN}, R_{MH}, \theta)$ is minimized. This procedure defines functions $R_{CN}(\theta)$, $R_{MH}(\theta)$, and $E(\theta)$ which parametrically define a curve in 4-space lying in the potential energy surface. We might want to associate this curve with the minimum energy path.[9]

This approach was used in the current work. However, it was used only because there was no particular need for a very accurate energy path; for the reader already may know, as shown elsewhere,[10] that the minimum energy path thus described is by no means unique. Indeed, for most bimolecular reactions, the simplest choice of an independent coordinate can produce intuitively inappropriate and even discontinuous reaction paths.[11]

Another method of picking a minimum energy path (hereinafter MEP, with cautionary quotation marks implied) is the gradient-following method, in which one finds a curve connecting the two minima, passing over the saddle point, and everywhere tangent to the gradient of the potential energy function. This curve would be the curve followed by a ball rolling on the potential energy surface immersed in infinitely viscous molasses. This curve also is not mapped onto itself under a coordinate transformation (as shown in Ref. 10), and therefore is not uniquely defined in physical terms.

SCF STUDIES

The region near the MEP was extensively explored with self-consistent-field (SCF) calculations. The basis set in terms of which the molecular orbitals were expanded was of type "double zeta plus polarization," meaning that two basis functions were used for each orbital in an occupied shell, and one additional set of polarization functions was included on each nucleus.[6] The polarization functions on each nucleus have an angular momentum quantum number one greater than that of the highest occupied shell and are needed to describe the distortion in the occupied orbitals when bonds are formed. Thus the basis set contained two s-type functions and a set of p-type functions centered on the hydrogen nucleus; and four s, two sets of p, and one set of d functions on carbon and on nitrogen. These basis functions were in turn expressed as fixed linear combinations of a larger number of Gaussian functions. On hydrogen, four s-type Gaussian functions were "contracted" to make the two s-type basis functions, while the p-type set was taken to be a single p-type Gaussian function. The total contraction scheme was thus ($4s$ $1p/2s$ $1p$) for hydrogen, and, in similar notation, ($9s$ $5p$ $1d/4s$ $2p$ $1d$) on carbon and nitrogen. (Aside from the polarization functions, this is Dunning's contraction[12] of Huzinaga's primitive Gaussian basis set.)[13] Such

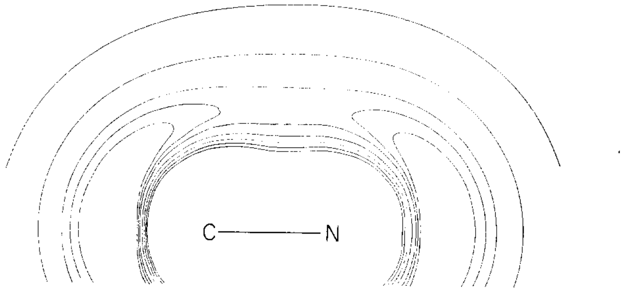

FIG. 2. Contour plot approximately representing the potential energy surface for a hydrogen atom moving around a rigid CN radical. The two local minima at opposite ends of the radical are not of equal depth, although they may appear so because their energies differ by less than the contour interval.

basis sets have been found to yield fairly reliable predictions of one-electron properties.[6]

The SCF calculations were performed on a Univac 1108 using the MOLE Quantum Chemistry System described by Rothenberg *et al.*[14] Calculation of the energy at each nuclear geometry required 35–40 min of 1108 time.

For each chosen value of θ, minimization of E with respect to R_{CN} and R_{MH} proceeded as follows. Energies were calculated at nuclear geometries chosen by educated guess until the acquired data points seemed to enclose a local minimum. Then a quadratic polynomial in R_{CN} and R_{MH} was fit to these points, and the minimum of the polynomial located. If this minimum was poorly defined (as when the accumulated data points were poorly situated), more calculations were performed in the neighborhood of the predicted minimum, and the process repeated.

When this procedure had been completed for $\theta = 0°$, 30°, 60°, 90°, 120°, 150°, and 180°, a search for the saddle point began in the region of 72°. Although interpolated values for R_{CN} and R_{MH} from the neighboring angles could be expected to provide a fairly good guess at the values of these coordinates at the saddle point, locating a saddle point is a substantially more difficult procedure than is locating a minimum.

The over-all approach was similar to the minimization. A quadratic polynomial was fit to calculated points and the saddle point of the polynomial determined. More points were calculated around this refined guess at the saddle point, and a new polynomial fit, until the predicted saddle point fell fairly close to the calculated points. The increased difficulty, over that of the minimizations, was due partly to the additional variable (for now all three coordinates are being varied) and partly to the conceptual elusiveness of the multidimensional saddle point. The higher dimensionality makes it more difficult to choose points which will result in a linearly independent set of equations for the polynomial coefficients. Further, if the points for the fit are very widely spaced, one may find that the matrix of the quadratic coefficients of the polynomial has no negative eigenvalue, or *two* negative eigenvalues, instead of the single negative eigenvalue required of a saddle point.

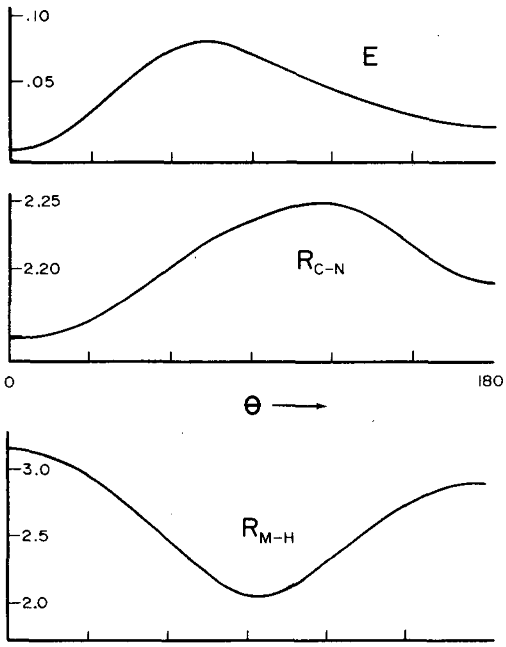

FIG. 3. Plot of the functions parametrically defining the minimum energy path, as determined in the SCF approximation. The abscissa, θ, varys from 0° (HCN) to 180° (CNH).

TABLE I. Values of the three coordinates θ, R_{CN}, and R_{MH}, and the energy E along the minimum energy path as calculated in the SCF approximation. Values are in atomic units.[15]

θ	E	R_{CN}	R_{MH}
0.	0.	2.1478	3.1640
30.	0.02637	2.1608	2.9659
60.	0.07409	2.2010	2.4738
70.2	0.07918	2.218	2.272
90.	0.06786	2.2363	2.0290
120.	0.04483	2.2479	2.2806
150.	0.02460	2.2166	2.7051
180.	0.01518	2.1895	2.8739

The calculated MEP is most easily presented by plotting the energy and the two distances as functions of the angle θ. This is done in Fig. 3; the corresponding data[15] are tabulated in Table I.

The plot of the energy along the MEP bears delightful resemblance to the traditional, very qualitative, energy curves used to illustrate various reaction rate theories.[16] The C–N bond is seen to lengthen substantially as the hydrogen comes alongside, possibly reflecting the hydrogen's interference in the C–N bonding. The shortening of the M–H distance around 90° shows that the path followed by the H is more elliptical than circular (see the contour plot, Fig. 2). Note that the scales are different for the two distances; variations in the C–N bond length are much smaller (~0.1 bohr) than those in the M–H distance (~1 bohr).

Properties of the predicted SCF potential energy surface are presented in Table II.

CONFIGURATION INTERACTION SURFACE

The reliability of the SCF approximation for exploration of potential energy surfaces has been but scantily studied. Reference 10 reviews results of SCF and configuration interaction (CI) calculations for a few atom-plus-diatom reactions ($F + Li_2$, $F + H_2$, $H + F_2$, and $H + H_2$), from which a couple of rules may be inferred (but by no means proven):

(1) When bonding is primarily ionic, the SCF approximation is adequate (as in $Li_2 + F$).

(2) Critical configurations involving the addition of a covalent bond are poorly described by the SCF approximation (as in $F + H_2$, $H + F_2$, and $H + H_2$), and the corresponding barrier heights are consequently exaggerated.

TABLE II. Properties of the HCN–HCN potential energy surface, predicted within the SCF approximation. (Experimental values in parentheses.) The millihartree (mh) is 10^{-3} hartree.

HNC	
H–N bond length	1.8631 a_0 = 0.9859 Å
N–C bond length	2.1895 a_0 = 1.1586 Å
Energy	−92.87454 hartree
HCN	
H–C bond length	2.0077 a_0 (2.014) = 1.0624 Å
C–N bond length	2.1478 a_0 (2.179) = 1.1366 Å
Energy	−92.88972 hartree
Critical configuration	
M–H distance	2.272 a_0 = 1.202 Å
C–N bond length	2.218 a_0 = 1.174 Å
θ	70.2°
Energy	−92.81054 hartree
Exothermicity	15.18 mh = 9.5 kcal
Barrier to HNC	64.0 mh = 40.2 kcal

Unfortunately, the existing collection of potential surface explorations is not sufficient to establish these rules firmly. Furthermore, the application of these rules to the HNC rearrangement is ambiguous; the binding is presumably covalent throughout the rearrangement, but the critical configuration does not involve the assimilation of an additional unpaired electron into a second covalent bond, as is the case for all the examples cited for Rule 2. Therefore configuration interaction calculations were undertaken to assess the performance of the SCF approximation.

The CI wavefunction used was expressed as a linear combination of many configurations (6343 for linear HNC 11 735 for the nonlinear geometries), each configuration being a proper singlet spin function. The configuration list used comprises all single and double replacements from the reference or SCF configuration. The one-electron functions were themselves expressed in terms of a contracted Gaussian basis set described as (11*s* 6*p* 1*d*/6*s* 3*p* 1*d*) on carbon and nitrogen, and (6*s* 1*p*/3*s* 1*p*) on hydrogen, using the notation introduced above. The coefficients of the configurations in the wavefunction were determined by the method of Roos.[17]

TABLE III. Properties of the HNC–HCN potential energy surface, as predicted by configuration interaction calculations. (Experimental values in parentheses.)

HCN	
H–N bond length	1.8813 a_0 = 0.9955 Å
N–C bond length	2.2103 a_0 = 1.1696 Å
Energy	−93.16916 hartree
HCN	
H–C bond length	2.014 a_0 (2.014) = 1.066 Å
C–N bond length	2.173 a_0 (2.179) = 1.150 Å
Energy	−93.19241 hartree
Critical configuration	
M–H distance	2.226 a_0 = 1.178 Å
C–N bond length	2.232 a_0 = 1.181 Å
θ	73.7°
Energy	−93.1135 hartree
Exothermicity	23.25 mh = 14.6 kcal
Barrier height to HNC	55.66 mh = 34.9 kcal

TABLE IV. Values of the three coordinates and the energy along the minimum energy path, calculated by adjusting the SCF values to conform with the values predicted by CI calculations at 0°, 73.7°, and 180°. Values are in atomic units.[15]

θ	E	R_{CN}	R_{MH}
0.	0.0	2.173	3.184
30.	0.02658	2.184	2.984
60.	0.07351	2.216	2.484
73.7	0.07891	2.232	2.226
90.	0.06904	2.243	2.031
120.	0.04856	2.253	2.291
150.	0.03076	2.230	2.727
180.	0.02325	2.210	2.902

The predicted properties of the potential energy surface, as determined in these CI calculations, are presented in Table III. Comparison with the SCF results in Table II reveals the following:

(1) The SCF bond lengths for HCN and HNC are 0.3%–1.2% too short. This is a well-known[6] aberration of the SCF approximation. It may arise from the fact that as two covalently-bonded nuclei separate, one electron from the bonding pair should withdraw with one nucleus, the other electron with the other nucleus. Use of a single configuration to describe the wavefunction requires that these two electrons continue to share a single orbital, an approximation which is worse for larger internuclear separations and which therefore causes the energy to rise too rapidly with increasing bond length.

(2) The SCF-predicted distances in the critical configuration differ from the CI by 1%–2%. Because of the nature of saddle points, the generalization about SCF bond lengths does not apply here.

(3) The angle at the critical configuration differs by 3.5° between the two calculations.

(4) The SCF exothermicity is 5 kcal too small.

(5) The barrier to rearrangement seen by the HNC molecule is 5 kcal higher in the SCF approximation. This 5 kcal difference may be thought of as being due to the difference in predicted exothermicities; the barrier viewed from the HCN side is essentially the same (49.5 kcal vs 49.7) in two models.

In summary, the SCF approximation provides a fairly accurate description of the potential energy surface. The most important discrepancy is the 5 kcal exothermicity error.

Since it is hoped that classical trajectory studies will be based on the potential energy surface presented here, an effort has been made to combine the SCF data with the more accurate (but less abundant) CI data, to produce a description of the surface which agrees with the

CI data at the three stationary points and mimics the SCF data between. This was done very simply by applying a three-parameter transformation of the form

$$E_{\text{new}} = a + bE_{\text{old}} + c\theta$$

to the values of E, R_{CN}, and R_{MH} given in Table I. For each property, a, b, and c were picked to make the "new" property agree with the CI-calculated property at the three CI points. The resultant data are tabulated in Table IV.

ACKNOWLEDGMENTS

This research was supported in part by the National Science Foundation, Grants GP-31974 and 41509X. Helpful discussion with Dr. Bowen Liu and Dr. Stephen Rothenberg are gratefully acknowledged.

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