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SOME FEATURES OF THE $\text{CH}_3\text{NC} \longrightarrow \text{CH}_3\text{CN}$ POTENTIAL SURFACE*Dean H. Liskow, Charles F. Bender,[†] and Henry F. Schaefer III^{**}

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ABSTRACT

Nonempirical self-consistent-field calculations are reported for about 75 points on the potential surface for the $\text{CH}_3\text{NC} \longrightarrow \text{CH}_3\text{CN}$ isomerization. Due to interest in the possible non-RRKM behavior of CH_3NC , the magnitude of the barrier to rotation of the methyl group is examined as a function of the reaction coordinate. The transition state or saddle point geometry is determined by minimizing the potential energy with respect to five geometrical parameters and maximizing with respect to a sixth. The geometries of CH_3NC and CH_3CN are also predicted and found to agree closely with experiment. Finally, it is established that, contrary to semi-empirical results, the present theoretical approach does not predict the existence of a relative minimum in the reaction coordinate.

In an earlier paper¹ we reported ab initio self-consistent-field (SCF) electronic structure calculations for CH_3NC , CH_3CN , and several points along the reaction coordinate. The emphasis of that paper was on the geometry of the transition state (a pyramidal CH_3 group was predicted) and the changes in electronic structure accompanying the reaction. Two recent developments have led us to carry out further calculations on $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$. These developments are best understood in light of our coordinate system, seen in Fig. 1. During the reaction, the angle θ goes from 180° (CH_3NC) to 0° (CH_3CN).

One of the most intriguing aspects of recent discussions of the methyl isocyanide isomerization is the prediction by Harris and Bunker² that CH_3NC may be a non-RRKM (Rice, Ramsperger, Kassel, and Marcus)³ molecule. That is, Harris and Bunker suggested that intramolecular vibrational relaxation does not occur rapidly in CH_3NC . Very recently, Bunker⁴ has concluded that the non-RRKM prediction (based on classical trajectory studies⁵) is substantially weakened by the neglect of rotational effects in the earlier work.² A completely unequivocal resolution of this problem would of course require knowledge of the entire potential surface. However, one feature which appears⁶ particularly important is the barrier to internal rotation of the methyl group in Fig. 1. Let us use the symbol ϕ to represent this angle of rotation. We define ϕ to be 0° when the N atom is eclipsed to one of the H atoms; then $\phi = 60^\circ$ when the rotating C atom in Fig. 1 is eclipsed to an H atom.

To determine the magnitude of the rotational barrier, additional ab initio calculations of the type described in Ref. 1 were carried out. Briefly, the calculations are of the single configuration SCF variety and use a "double


zeta" basis set.⁷ Table I shows the results thus obtained. Note that the geometrical parameters (other than θ and ϕ) used for these calculations were those determined in Ref. 1 for $\theta = 90^\circ$. Although it is hazardous to estimate the errors involved in such predictions, similar calculations⁸ on known rotational barriers suggest the present calculated barriers are within 20% of the exact (unknown) values.

It was initially something of a surprise to us that the rotational barrier changes sign in going from $\theta = 135^\circ$ to $\theta = 90^\circ$. In retrospect, however, it is obvious that at $\theta = 135^\circ$, when $\phi = 0^\circ$, the N atom is quite close to the H atom with respect to which it is eclipsed. Thus this conformation lies higher in energy than the $\phi = 60^\circ$ case, where the N atom is staggered with respect to two of the H atoms. Further it would have been difficult to predict with confidence the sign or magnitude of the barrier at $\theta = 90^\circ$ without a calculation such as the present one. In conclusion, we hope that the present rotational barrier results will be helpful in the quest^{2,4} for an understanding of the dynamics of the CH_3NC isomerization.

The second impetus to the present work was the appearance of a paper⁹ by Dewar and Kohn, who carried out a semi-empirical MINDO calculation of the reaction coordinate. The results of Dewar and Kohn are for the most part consistent with our previous ab initio calculations.¹ In particular, the CH_3 group is predicted to remain pyramidal throughout the reaction coordinate, and the bonding remains covalent; that is a planar $[\text{CH}_3^+](\text{CN}^-)$ structure does not form the transition state, as Van Dine and Hoffman¹⁰ suggested several years ago.

However, the most interesting aspect of the paper by Dewar and Kohn is the prediction of a stable triangular intermediate. That is, they predict a relative minimum in the reaction coordinate for $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$. Dewar and Kohn⁹ point out that such an intermediate would be unique, since "no case has yet been reported of a stable, neutral, metal-free organic π complex." They further suggest that such complexes might be more readily detectable experimentally if appropriate substitutions of the methyl group were made.

Although we wholeheartedly agree with Dewar and Kohn concerning the potential importance of the existence of such intermediates, we were less convinced of the reliability of their calculations. This was particularly true in light of the MINDO prediction¹¹ that C_3 is an equilateral triangle; C_3 of course is well known¹² to be linear. It therefore seemed possible that their semi-empirical method artificially favored triangular, as opposed to linear, conformations. We note that the present ab initio approach correctly predicts¹³ the $^1\Sigma_g^+$ ground state of C_3 to be linear.

Therefore, we first carried out a much more thorough search for the $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ transition state. In the earlier work we constrained the three C-H distances to be 1.10Å, and assumed (following the prediction of Van Dine and Hoffman¹⁰) the transition state to occur at $\theta = 90^\circ$. In the present geometry search our only constraints were that the methyl group retain C_{3v} local symmetry and that the center of the  triangle lie coplanar to the three heavy atoms. In addition, the geometries of CH_3NC and CH_3CN were optimized as a gauge of the reliability of our saddle point prediction.

The geometry predictions are summarized in Table II. X is the center of mass of the CN group. There it is seen that the theoretical structures of

CH_3NC and CH_3CN agree well with the experiment. The largest errors occur in the CH distances, which are predicted to be 0.02\AA too short for both molecules. The predictions of Dewar and Kohn⁹ for these two molecules are reasonable, but uniformly less accurate. For example, they predict the C-N distances in the two molecules to be 0.029 and 0.030\AA too long. On this basis it is to be expected that our transition state prediction is more reliable than that of Dewar and Kohn.

The potential energy is maximized for an angle $\theta = 100.8^\circ$, somewhat greater than the 90° assumed in the earlier work.¹ The H-C-X angle is 106.2° , nearly the same as predicted earlier, and this prediction is strengthened by the accurate H-C-X angles predicted for CH_3NC and CH_3CN . The CH distance is decreased by nearly 0.01\AA from the values for CH_3NC and CH_3CN and the CN distance is increased by 0.031\AA over CH_3NC . Finally, the distance from the methyl carbon to the CN center-of-mass is decreased by 0.145\AA from that predicted for CH_3NC . The largest single discrepancy between the present work and that of Dewar and Kohn is for $R(\text{CX})$, which they predict to be $\sim 1.43\text{\AA}$.

To examine the prediction¹¹ of a stable intermediate, we carried out the calculations reported in Table III. There we see that the energy decreases monotonically as θ is either increased or decreased from the saddle point value, 100.8° . Except for $\theta = 100.8^\circ$, the points in Table III do not fall on the reaction coordinate. By varying the energy at each θ value with respect to the five additional geometrical parameters seen in Table II, one could obtain points essentially on the reaction coordinate. However, the resulting minimizations would serve only to lower the energy of these points with respect to the transition state. Thus, it seems clear that the present theoretical approach denies the existence of a relative minimum in the reaction coordinate.

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FOOTNOTES AND REFERENCES

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Table I. Methyl rotational barrier accompanying the isocyanide isomerization. θ is defined by Fig. 1 and ϕ in the text. The energy in hartrees is given above the relative energy in kcal/mole.

θ	135°	90°	45°
ϕ			
0°	-131.80106 1.48	-131.75698 0.00	-131.80074 0.00
20°	-131.80167 1.10	-131.75664 0.21	-131.79999 0.47
40°	-131.80284 0.36	-131.75599 0.62	-131.79847 1.42
60°	-131.80342 0.00	-131.75568 0.82	-131.79770 1.91

Table II. Geometries and energies of three points on the minimum energy path for $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$. Unless indicated experimental values, given in parentheses, are from C. C. Costain, J. Chem. Phys. 29, 864 (1958).

Parameter	CH_3NC	Saddle Point	CH_3CN
θ	180° (180°)	100.8°	0° (0°)
ϕ	--	0°	--
HCX Angle	110.0° (109.1)	106.2°	110.0° (109.5°)
R(CH)	1.081Å (1.101)	1.074Å	1.082Å (1.102)
R(CX)	1.967Å (1.962)	1.822Å	2.086Å (2.081)
R(CN)	1.167Å (1.166)	1.198Å	1.146Å (1.157)
E(hartrees)	-131.85166	-131.75546	-131.87927
E(kcal/mole)	0.0	60.4 (38.4^a)	-17.3 ($14.7-16.8$) ^b

^aExperimental activation energy of F. W. Schneider and B. S. Rabinovitch, J. Am. Chem. Soc. 84, 4215 (1962).

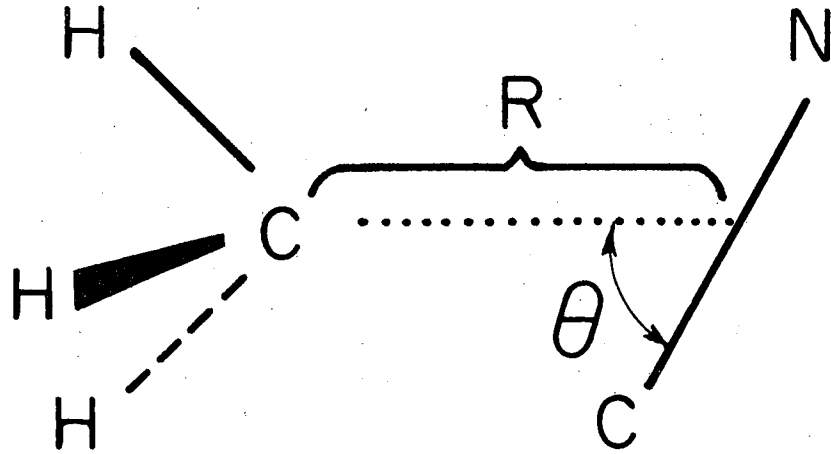
^bSee heat of formation data given in Ref. 9.

Table III. Some points near the saddle point on the $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ potential surface. All geometrical parameters except θ (see Fig. 1) are those predicted for the saddle point (middle column, Table II).

θ	E(hartrees)	E(kcal/mole)
130.8	-131.77609	47.42
120.8	-131.76518	54.27
110.8	-131.75971	57.70
105.8	-131.75593	60.07
100.8	-131.75546	60.37
95.8	-131.75614	59.94
90.8	-131.75782	58.88
80.8	-131.76353	55.30
70.8	-131.77171	50.17
60.8	-131.78183	43.82

FIGURE CAPTION

Fig. 1. Coordinate system used to describe the methyl isocyanide isomerization.



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Fig. 1

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