energy quantities quoted in section III which differ only in the second place in electron volts, must be viewed with some degree of caution since the molecular geometries were not optimized for any of the molecules treated here. However, we are very encouraged by the results obtained thus far and are presently analyzing CC bonds in hydrocarbons in the same way. We also are in the process of making models for the LMO's themselves and studying different classes of organic compounds, such as fluorides and carbonyls.

Theoretical Reaction Coordinate for the Methyl Isocyanide Isomerization[1]

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Abstract: *Ab initio* self-consistent-field calculations have been carried out to approximately determine the minimum energy path for the $CH_3NC \rightarrow CH_3CN$ reaction. A set of four s and two p functions on C and N and two s functions on H was used. The predicted exothermicity was 17.4 kcal/mol, in reasonable agreement with Benson's empirical estimate of 15 kcal. The calculated barrier height was 58.8 kcal compared to Rabinovitch's experimental value of 38.4 kcal. This difference is ascribed to an expectation that electron correlation will be greater for the transition state than for either CH_3NC or CH_3CN. The calculations differ from the extended Hückel treatment of Van Dine and Hoffmann in that we predict the CH_3 group to remain pyramidal (HCX angle 106°) at the saddle point. The planar CH_3 structure lies 14 kcal higher in energy. The question of changes in "charge" on the methyl carbon is investigated in detail. Mulliken atomic populations suggest that the charge on the methyl carbon at the transition state is intermediate between CH_3NC and CH_3CN. This is completely consistent with the conclusions of Casanova, Werner, and Schuster. However, it is suggested that several other properties (including the potential at each nucleus, the 1s electron binding energies, and the electric field gradients) give a more reliable picture of the changes in electronic structure. These properties suggest that at the transition state there is somewhat more charge on the methyl carbon than in either the product or reactant. The unfavored transition state, in which the CH_3 group is forced to be planar, has a large amount of charge on the methyl carbon, resulting in an electronic structure approaching $[CH_3^+][CN^-]$.

The $CH_3NC \rightarrow CH_3CN$ reaction is one of the simplest examples of a unimolecular isomerization. The kinetics of this reaction have been studied exhaustively by Rabinovitch and coworkers[2,3] over the past decade. Rabinovitch's work has yielded a wealth of information concerning the mechanism of the isomerization, energy transfer, and the suitability of various theoretical models[4] (*e.g.*, RRKM) for describing the kinetics of the reaction. Recently, Harris and Bunker[5] have taken another significant step toward an understanding of the dynamics of the $CH_3NC \rightarrow CH_3CN$ reaction. Using a model potential energy surface, Harris and Bunker[5a] carried out classical trajectory studies[6] of the isocyanide isomerization. Their most important conclusion was that, given an initial internal energy of 150–300 kcal/mol, intramolecular energy transfer into the reaction coordinate probably does not occur for times t less than 10^{-10} sec. In a recent communication,[5b] Harris and Bunker emphasize the non-RRKM behavior of CH_3NC.

It seems clear that an accurate *a priori* potential energy surface for the CH_3CN isomerization would be of great value in providing insight concerning the reaction dynamics. The first step in this direction was taken by Van Dine and Hoffmann,[7] who constructed a CH_3CN potential energy surface from extended Hückel calculations. Van Dine and Hoffmann predicted the saddle point (transition state) to occur for a nearly isosceles CNC triangular arrangement. Their calculated barrier height (activation energy) was 40.8 kcal/mol, in surprisingly good agreement with experiment, 38.4 kcal/mol. Another interesting feature of the Van Dine–Hoffmann calculations is the prediction that the methyl group becomes planar (120° HCH angle) at the saddle point. In the isolated CH_3CN molecule, the HCC angle is 109.5°.

In the present paper, we take a second step toward obtaining a reliable potential surface for $CH_3NC \rightarrow CH_3CN$, a series of nonempirical self-consistent-field calculations. We began this study with the expectation that the Hartree-Fock approximation would be inherently incapable of describing the potential surface in a quantitatively correct manner. In particular, one expects the correlation energy to be significantly greater near the saddle point geometry than for either the reactant CH_3NC or the product CH_3CN.[8] Thus we can

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

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Table I. Summary of Self-Consistent-Field Energies for the Methyl Isocyanide Rearrangement[a]

Description	θ, deg	R	Other geometrical parameters	E, hartrees	E, kcal
CH_3NC	180	1.971	Standard	−131.8507	0.0
	135	1.864	Standard	−131.8034	29.7
Saddle point	90	1.802	$R(CN) = 1.203$, $\theta(HCX) = 106°$	−131.7570	58.8
Rotated saddle point	90	1.802	$R(CN) = 1.203$, $\theta(HCX) = 106°$	−131.7557	59.6
Planar CH_3	90	2.013	$R(CN) = 1.2$, $\theta(HCX) = 90°$	−131.7346	72.9
	45	1.990	Standard	−131.7979	33.1
CH_3CN	0	2.097	Standard	−131.8785	−17.4

[a] Distances are given in Ångströms; θ and R are defined in Figure 1.

predict with little hesitation that the Hartree–Fock barrier height will be significantly higher than the experimental activation energy. However, it is now well established that self-consistent-field (SCF) calculations, even using relatively small basis sets, yield rather reliable molecular geometries.[9] Therefore we expect the SCF minimum energy path or reaction coordinate to be rather reliable. At some later time we hope to report an *ab initio* potential surface explicitly including electron correlation for the methyl isocyanide rearrangement.

Basis Set and Computational Details

The calculations were carried out in terms of the primitive Gaussian basis sets of Huzinaga,[10] (9s, 5p) for carbon and nitrogen and (4s) for hydrogen. Following Dunning,[11] these C and N basis sets were optimally contracted to four s and two p functions. The hydrogen (4s) basis was similarly contracted to (2s). Thus for CH_3CN, 84 primitive Gaussians were used to form 36 contracted functions in this "double ζ" basis set. Based on previous experience,[12,13] we expect the present basis set to yield total SCF energies for CH_3CN about 0.15 hartree above the true (complete basis set) Hartree–Fock energies.

On the basis of previous calculations on the FH_2 potential surface,[14] we expect certain errors in the *shape* of the predicted CH_3CN surface. However, these errors may be due more to the neglect of electron correlation than to the limited size of our basis set. For the $F + H_2 \rightarrow FH + H$ reaction, the SCF barrier height (using a basis comparable to the present one) is 34.3 kcal/mol, as opposed to the experimental activation energy, 1.7 kcal. With this same basis, configuration interaction calculations yield a barrier height of 5.7 kcal.[14] However, the estimated Hartree–Fock barrier height is 15 kcal/mol. We see that in order to accurately describe the FH_2 surface, the incorporation of correlation effects using a modest basis set is more effective than going to a very large basis within the Hartree–Fock approximation.

For a number of geometries (*e.g.*, ordinary CH_3CN), the SCF procedure consistently diverged, even though several different sets of starting orbitals were used. This problem was eventually solved using the very effective extrapolation procedure of Winter and Dunning.[15]

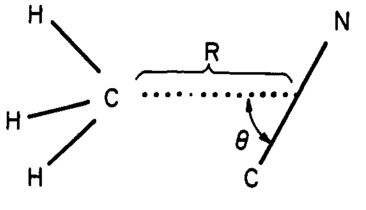

Figure 1. Coordinate system used to describe $CH_3NC \rightarrow CH_3CN$.

Geometries Considered

A complete potential energy surface for CH_3CN would involve $[3(6) - 6] = 12$ independent geometrical parameters. The variation of these 12 parameters is clearly beyond the feasibility of the present *ab initio* investigation. In fact, we have carried out a very restricted series of geometry variations within this 12 dimensional space.

Figure 1 helps to illustrate the geometries considered in the present work. Following Van Dine and Hoffmann,[7] the reaction coordinate was taken to be the angle θ describing the rotation of the CN group about its center of mass. The CN center of mass is constrained to lie on the line which is perpendicular to and passes through the center of the HHH triangle. For all values of θ considered (0, 45, 90, 135, and 180°) the distance R between the methyl carbon and the CN center of mass was varied. The two parameters θ and R are thus assumed to be the most important in the determination of the reaction coordinate.

Other restrictions adopted in the selection of geometries included the following. (a) The CH_3 group was required to have at least C_{3v} local symmetry. (b) The three CH distances were fixed at 1.10 Å. In CH_3CN and CH_3NC, this bond distance is 1.103 and 1.101 Å.[16] (c) Except at $\theta = 90°$, the CN distance was fixed at 1.16 Å. For comparison, this distance is 1.157 Å in CH_3CN and 1.166 Å in CH_3NC. (d) Except at $\theta = 90°$, the HCX angle was fixed at 110°. X represents the position of the CN center of mass. In CH_3CN and CH_3NC, this angle is[16] 109° 30′ and 109° 7′. (e) Except at 90°, the C atom was held eclipsed with respect to one of the three H atoms. Thus the nitrogen atom is staggered with respect to the other two H atoms.

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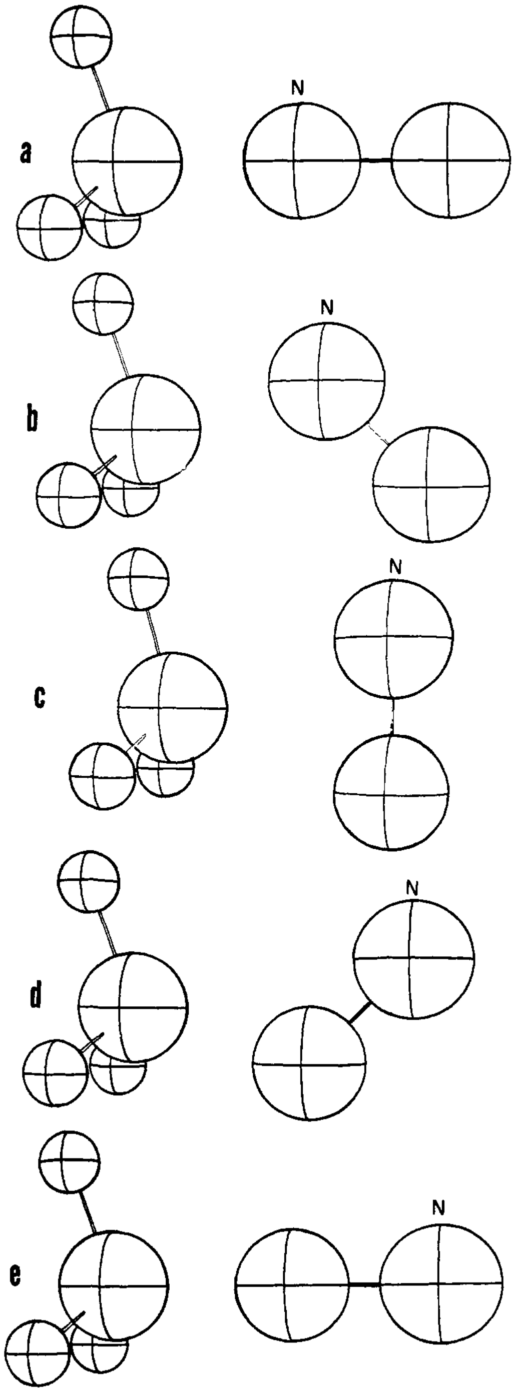

Figure 2. Three-dimensional perspectives of the molecular geometry along the reaction coordinate for $CH_3NC \rightarrow CH_3CN$: (a) CH_3NC, $\theta = 180°$, $E = 0.0$ kcal; (b) θ 135°, $E = 29.7$ kcal; (c) approximate saddle point, $\theta = 90°$, $E = 58.8$ kcal; (d) $\theta = 45°$, $E = 33.1$ kcal; (e) CH_3CN, $\theta = 0°$, $E = -17.4$ kcal.

Features of the Reaction Coordinate

Our results are summarized in Table I. Five points on the reaction coordinate are indicated graphically in Figure 2. The theoretical exothermicity is seen to be 17.4 kcal/mol. Although the energy difference between CH_3NC and CH_3CN is not known, Benson[17] has empirically estimated a value of 15 kcal/mol. Since the correlation energies of CH_3NC and CH_3CN are likely to be nearly equal, our predicted value should be fairly reliable.

Table I shows the predicted activation energy to be 58.8 kcal, or 1.5 times the experimental value of 38.4 kcal. Since we expect a single-configuration wave function to be a poorer approximation for the saddle point geometry than for either the reactant or product, this result is qualitatively reasonable. As discussed above, we expect that a modest amount of configuration interaction[14] will bring the predicted activation energy into much better agreement with experiment.

A feature of considerable interest is the saddle point geometry. In the present work, we have assumed that the saddle point occurs for $\theta = 90°$. Reasons for this assumption are (a) the calculated energies for $\theta = 45°$ and $\theta = 135°$ are nearly the same, (b) $\theta = 90°$ is the logical halfway point between CH_3CN and CH_3NC, and (c) the extended Hückel calculations of Van Dine and Hoffmann[7] predict $\theta = 92°$. Therefore, at $\theta = 90°$, we simultaneously optimized R (see Figure 1), the CN distance, and the HCX bond angle. Our results are seen in Table I and show that the distance between the methyl carbon and the CN center of mass is 1.802 Å, significantly shorter than in either CH_3NC or CH_3CN. At the saddle point the CN distance is predicted to be 1.203 Å, slightly longer (0.03–0.04 Å) than in CH_3NC and CH_3CN. The HCX angle is predicted to be 106° at the saddle point, only about 3° less than in the two stable molecules.

There is one feature concerning which the present potential surface differs qualitatively from the extended Hückel surface of Van Dine and Hoffmann: namely, their prediction that the CH_3 group is nearly planar at the saddle point. Table I shows clearly that the present calculations predict a nearly tetrahedral CH_3 group. For comparison with the Van Dine–Hoffmann results we carried out several additional calculations with the CH_3 group restricted to be planar. With this restraint at $\theta = 90°$, a much longer optimum distance R (2.013 Å) was found, in qualitative agreement with Van Dine and Hoffmann. However, our planar CH_3 saddle point geometry lies at 72.9 kcal, while for θ(HCX) = 106°, the barrier height is lower, 58.8 kcal.

At the saddle point there is a small barrier to internal rotation. That is, one of the hydrogen atoms may be eclipsed with respect to either the C or N atom of the CN group. All but two of the calculations reported here were carried out for the carbon atom eclipsed with respect to H. After the variation of geometrical parameters at the saddle point was completed, a single calculation was carried out with the nitrogen atom eclipsed; that is, in Figure 1, the upper H, the two C's, and the N atom all lie in the same plane. As Table I shows, this conformation lies 0.8 kcal below the arrangement in which the carbon atom is eclipsed. Thus, 0.8 kcal would appear to be a reasonable value for this small barrier.

Interpretive Aspects

A point of considerable interest concerning the $CH_3NC \rightarrow CH_3CN$ reaction is the change in electron distribution during the rearrangement. In addition to the well-known studies of Rabinovitch,[2,3] the experimental work of Casanova, Werner, and Schuster[18] is pertinent in this regard. By studying a variety of

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(18) J. Casanova, N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).

reactions RNC → RCN, Casanova and coworkers[18] were able to conclude that "the bond-breaking and bond-making processes are essentially synchronous." This implies, in a simple point-charge model, that the "charge" on the CH_3 group is nearly constant during the $CH_3NC \rightarrow CH_3CN$ rearrangement.

Van Dine and Hoffmann[7] have discussed the change in atomic charges (from Mulliken population analyses[19]) based on their extended Hückel calculations. However, they arrive at rather different conclusions than Casanova and coworkers.[18] In particular, Van Dine and Hoffmann find the charge at the methyl carbon to be $+0.19$ for CH_3NC and $+0.02$ for CH_3CN, but $+0.42$ for the transtition state geometry. That is, they find a significant increase in positive charge at the methyl carbon in the transition state. Thus Van Dine and Hoffmann conclude, in disagreement with Casanova,[18] that there is definite ionic character, $[CH_3^{+0.59}]$-$[CN^{-0.59}]$, at the saddle point geometry. Since it is generally accepted that carbonium ions have trigonal (*e.g.*, planar CH_3^+) geometry, Van Dine and Hoffmann were not surprised to find the methyl group to be predicted planar in the transition state from their extended Hückel calculations.

Table II shows population analyses extracted from our wave functions at four geometries. In addition to the reactant, saddle point (θ(HCX) = 106°), and product, a population analysis is included for the transition state constrained to have a planar CH_3 group. Again, it should be stressed that our calculations (see Table I) predict the true transition state to have a nonplanar CH_3 arrangement and the planar transition state to lie 14.1 kcal/mol higher in energy. Table II shows that the present population analyses are consistent with the conclusions of Casanova, Werner, and Schuster.[18] That is, the charge on the methyl carbon progresses from -0.41 for CH_3NC to -0.52 at the saddle point to -0.58 for CH_3CN. Similarly the charge on the CN group varies from -0.27 to -0.22 to -0.12. That is, the *ab initio* saddle point is even less ionic than ordinary CH_3NC. However, if we constrain the CH_3 group to be planar (at a cost of 14.1 kcal), Table III shows that the transition state does become more ionic, $[CH_3^{+0.40}][CN^{-0.40}]$. It should be noted that our calculated populations for CH_3CN and CH_3NC are in qualitative agreement with the earlier *ab initio* calculations of Clementi and Klint.[20]

Table II. Population Analyses and Potential Calculated at Each Nucleus in CH_3CN

	CH_3NC	Saddle point, θ(HCX) = 106°	Planar saddle point, θ(HCX) = 90°	CH_3CN
		Atomic Charges		
H	0.22	0.26	0.28	0.23
C_{methyl}	−0.41	−0.52	−0.43	−0.58
N	−0.20	−0.21	−0.28	−0.10
C	−0.07	−0.01	−0.12	−0.02
		Potentials		
H	−1.062	−1.032	−0.999	−1.048
C_{methyl}	−14.6463	−14.6277	−14.6071	−14.6661
N	−18.3329	−18.3274	−18.3526	−18.3408
C	−14.6965	−14.6913	−14.7163	−14.6783

Table III. Orbital Energies (in Hartrees) for Four CH_3CN Geometries

		Saddle point		
	CH_3N	Lowest energy θ(HCX) = 106°	Planar θ(HCX) = 90°	CH_3CN
E(total)	−131.8507	−131.7570	−131.7346	−131.8785
1a′	−15.5993	−15.6235	−15.5963	−15.6035
2a′	−11.3136	−11.3371	−11.3675	−11.3061
3a′	−11.3006	−11.3102	−11.2835	−11.2946
4a′	−1.2874	−1.2937	−1.2551	−1.2517
5a′	−1.0341	−0.9772	−0.9927	−1.0400
6a′	−0.7376	−0.6899	−0.6900	−0.6948
7a′	−0.6414	−0.5737	−0.5819	−0.6281
8a′	−0.4780	−0.5336	−0.4780	−0.5517
9a′	−0.4643	−0.4610	−0.4426	−0.4682
1a″	−0.6414	−0.6413	−0.6689	−0.6281
2a″	−0.4780	−0.4814	−0.4649	−0.4682

The population analysis is an inherently arbitrary method for studying the electron distribution in a molecule. Thus one would like to confirm the qualitative results of the previous paragraph in terms of quantities which are, at least in principle, observable. One observable property which may be nicely correlated with "atomic charges" is the inner shell ionization potential at a particular atom.[21,22] That is, the greater the inner shell ionization potential, the more positive charge may be thought to reside on the atom in question. A quantity related to the inner shell ionization potential and hence to the concept of atomic charge is the potential at a nucleus.[23,24] The calculated potentials at each nucleus are seen in Table II, while the orbital energies or Koopmans theorem ionization potentials are given in Table III. In all four calculations the 1a′ orbital corresponds to nitrogen 1s. For CH_3CN the 2a′ orbital is the CN carbon and the 3a′ orbital corresponds to the methyl carbon 1s. For CH_3CN the 2a′ orbital is the CN carbon and the 3a′ orbital corresponds to the methyl carbon 1s. However, for the other three calculations (first three columns of Table III) the 2a′ orbital is the methyl carbon 1s.

There is a one-to-one correspondence between the calculated inner shell ionization potentials and the potential at each nucleus. Limiting ourselves to the point discussed by Casanova, *et al.*,[18] and by Van Dine and Hoffmann,[7] the charge at the methyl carbon, the following is implied. (a) The methyl carbon has a greater positive charge (or, if one prefers, a smaller negative charge) in CH_3NC than in CH_3CN. (b) At the transition state the methyl carbon becomes somewhat more positive than for CH_3NC. (c) At the constrained planar CH_3 saddle point, the methyl carbon takes on a rather large positive charge, indicating a significant amount of $[CH_3^+][CN^-]$ character.

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Table IV. Some Molecular Properties (in Atomic Units) for CH_3CN[a]

	CH_3NC	Saddle point θ(HCX) = 106°	Saddle point θ(HCX) = 90°	CH_3CN
		Dipole Moment		
μ_y	−1.46 (−1.51 ± 0.02[b])	−1.135	−1.76	−1.66 (−1.54 ± 0.02[b])
μ_z	0.0	−0.013	−0.009	0.0
		Quadrupole Moment Tensor		
θ_{xx}	1.19	0.92	1.31	1.12
θ_{yy}	−2.39 (−2.0 ± 1.2[c])	2.34	1.89	−2.24 (−1.3 ± 0.9[c])
θ_{zz}	1.19	−3.25	−3.21	1.12
θ_{yz}	0.00	0.01	−0.01	0.00
		Second Moments of the Electron Distribution		
$\langle x^2 \rangle$	−19.05 (−19 ± 2[c])	−19.52	−19.82	−19.05 (−19 ± 1[c])
$\langle y^2 \rangle$	−116.64 (−116 ± 2[c])	−82.75	−90.49	−126.91 (−124 ± 1[c])
$\langle z^2 \rangle$	−19.05 (−19 ± 2[c])	−39.00	−39.45	−19.05 (−19 ± 1[c])
$\langle yz \rangle$	0.00	−0.02	−0.02	0.00
		Electric Field Gradient Tensor at Methyl Carbon		
q_{xx}	0.23	0.32	0.46	0.14
q_{yy}	−0.46	−0.66	−0.94	−0.28
q_{zz}	0.23	0.34	0.48	0.14
q_{yz}	0.00	−0.03	−0.03	0.00

[a] For CH_3NC and CH_3CN at equilibrium, the *y* axis contains the CN group. At the saddle point the *z* axis includes the CN group. Experimental values are in parentheses. [b] S. N. Ghosh, R. Trambarulo, and W. Cordy, *J. Chem. Phys.*, **21**, 308 (1953). [c] Reference 25.

The above potential–ionization potential picture is *not* completely consistent with the Mulliken atomic charges in Table II. The primary difference is that the population analysis suggests the methyl carbon has *less* charge at the saddle point than for CN_3NC. Both analyses agree that the planar saddle point has the most ionic electron distribution. We tend to prefer the potential–ionization potential picture due to the necessary arbitrariness of the population analysis.

To further investigate the changes in electron distribution along the reaction coordinate, several additional molecular properties were computed, some of which are seen in Table IV. The fact that the SCF and experimental dipole moments[24] for CH_3CN and CH_3NC agree well is not too surprising since the molecules are quite polar. In general, however, larger basis sets are required for good agreement between SCF and experimental dipole moments.[8] Interestingly, the calculations predict the transition state to have a smaller dipole moment than CH_3NC or CH_3CN. This result is consistent with Casanova's conclusions, but not those of Van Dine and Hoffmann. As expected the planar saddle point has a much larger (0.41 atomic unit = 1.0 debye) dipole moment. The calculated electric field gradient tensor shows the same type of behavior as the potentials at each nucleus and the inner shell electron binding energies. That is, the largest *q* values are found for the planar CH_3 arrangement and the smallest values for CH_3CN. The transition state field gradient tensor is intermediate between that of CH_3NC and the planar saddle point. Finally, it should be pointed out that our calculated quadrupole moment elements along the molecular axis are in good agreement with the experimental values of Pochan, Shoemaker, Stone, and Flygare.[25]

Concluding Remarks

The most important finding of our theoretical study is that the transition state or saddle point for the $CH_3NC \rightarrow CH_3CN$ isomerization involves a pyramidal CH_3 group (HCX angle 106°). The planar methyl saddle point is predicted to lie 14.1 kcal higher and a variety of calculated molecular properties indicate significant ionic $[CH_3^+][CN^-]$ character. The question of change in "atomic charge" on the methyl carbon along the reaction coordinate is investigated by a number of means. The most obvious conclusion is that the predicted transition state is far less ionic (less charge on methyl carbon) than the planar CH_3 structure mentioned above. Mulliken population analyses suggest that the electron distribution changes smoothly between CH_3NC and CH_3CN. However, more reliable indicators, namely calculated potentials at each nucleus, inner shell ionization potentials, and electric field gradients, suggest that the transition state involves a methyl carbon somewhat more positively charged than in either CH_3NC or CH_3CN.

Acknowledgments. Helpful discussions with Professors Andrew Streitwieser and Roald Hoffmann are sincerely appreciated. The wise counsel of Dr. Nicholas W. Winter concerning the convergence of SCF calculations is gratefully acknowledged. Mr. Peter K. Pearson generated *via* computer the pictures of CH_3CN along the reaction coordinate.

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