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The Methyl Isocyanide Isomerization: A CNDO/2 Study with Partitioning of Energy

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CNDO/2 calculations together with a partitioning of the energy into various one- and two-centre components have been performed on CH_3CN, CH_3NC, and a large number of nuclear configurations formed by placing the methyl group at various positions with respect to the fixed CN group. A complete potential energy surface was obtained showing that a minimum in energy occurred for a pyramidal CH_3 group placed at approximately 90° to the CN axis. The barrier to the reaction $CH_3NC \rightarrow CH_3CN$ is calculated as 32.9 kcal, in reasonable agreement with 38.4 kcal, the experimental value of Rabinovitch. A charge separation equivalent to $[CH_3^{+0.22}][CN^{-0.22}]$ is found for the intermediate compared to $[CH_3^{+0.08}][CN^{-0.08}]$ and $[CH_3^{+0.12}][NC^{-0.12}]$ for the cyanide and isocyanide, respectively.

Key words: Energy partitioning – Isomerization – Cyanide – Methyl isocyanide

Introduction

As Ivar Ugi points out in his preface to the book "Isonitrile Chemistry" [1], the chemistry of isonitriles is not just the chemistry of one of the many functional classes of organic compounds, but it is remarkably different from the remainder of organic chemistry because the isonitriles form the only class of stable organic compounds containing formally divalent carbon. Our interest in this laboratory has to this point centered around nitriles and their reactions [2], but it is perhaps not unnatural that in considering "simple" reactions of nitriles, isomerization would come to mind.

The rearrangement of isonitriles to nitriles has been known for over half a century [3], and the isomerization of methyl isocyanide is now one of the most completely studied unimolecular reactions, at least from the standpoint of its kinetic behaviour [4]. In the last five years a number of purely theoretical approaches to the study of methyl isocyanide and its isomerization have been taken. Van Dine and Hoffmann [5] employed the extended Hückel method to calculate a potential energy surface for methyl cyanide and found a barrier height of 40.8 kcalories per mole, compared to 38.4 kcalories per mole from experiment. *Ab initio* calculations [6] have recently been performed on both methyl cyanide and isocyanide and have shown that the highest occupied orbitals in the two molecules are π and carbon lone pair, respectively. Clementi and Klint [7] earlier reported on the results of some *ab initio* SCF calculations on CH_3CN and CH_3NC done as part of a larger study on the cyano group.

Dewar and Kohn [8], by means of the MINDO/2 method, calculated a reaction path for the isomerization. These authors found the heats of formation of methyl isocyanide and cyanide to be 26.3 and 16.8 kcal/mole, respectively, compared to observed values of 35.6 and 20.9 kcal/mole [9]. In addition the heat of reaction and the activation energy were calculated to be -9.5 and 34.3 kcal/mole compared to -14.7 and 38.4 kcal/mole, respectively, the former estimated [10], the latter from experiment [11], and the intermediate was predicted to be triangular in shape. Even more recently and after the present calculations had been completed, *ab initio* selfconsistent field calculations using contracted sets of Gaussian functions [12] were performed on the cyanide, the isocyanide and three intermediate positions for both pyramidal and planar CH_3. The predicted exothermicity of the reaction was 17.4 kcal/mole and the activation energy was calculated as 58.8 kcal/mole, the size of the latter relative to the experimental value being ascribed to a greater electron correlation in the transition state than in either of the stable molecules.

In the present work, the CNDO/2 method [13] with the original parametrization of Pople and Segal is utilized to perform calculations on a variety of nuclear configurations. The method of partitioning of energy within the CNDO/2 method, proposed originally by Fischer and Killmar [14] and tested by them on hydrocarbons, has been shown by us [15] to be applicable to molecules containing the CN single, double, and triple bonds. This method has been applied in the present work in an attempt to provide further elucidation of the mechanism of the isomerization. In this method the partitioned quantity which is taken to be characteristic of the chemical bond AB is

$$E^R_{AB} = 2 \sum_{\substack{\mu \in A \\ \nu \in B}} S_{\mu\nu} \beta_{\mu\nu} P_{\mu\nu}$$

where the summation extends over all orbitals μ and ν associated with atoms A and B, respectively, $P_{\mu\nu}$ and $S_{\mu\nu}$ are the $\mu\nu_{\text{th}}$ elements of the bond order and overlap matrices, respectively, and $\beta_{\mu\nu}$ is a parameter occurring in the CNDO method. Equations for both one-centre and two-centre terms have been given previously [14, 15] and will not be repeated here.

Results and Discussion

In order to employ a convenient method for systematizing the various nuclear configurations involved in the calculations, the carbon of the cyanide or isocyanide group was labelled C_2, and the C_2N bond was placed along the x-axis so that the nitrogen atom was 0.6003 Å in the positive x-direction, and the C_2 was 0.5659 Å in the negative x-direction (Fig. 1). The C_1 carbon atom of the methyl group could then be placed at any point in space and the axis of symmetry of the CH_3 group is extended through C_1 to the origin (0) so that an angle θ is defined with the nitrogen atom ($< C_1ON$). For an angle θ of 0 degrees the nuclear configuration of isocyanide is reproduced while for 180 degrees the cyanide is represented. The nuclear configuration of both the cyanide and isocyanide together with any intermediate position of the C_1 atom may then be specified by the value of the angle θ and the distance d between the origin and C_1 atom. Calculations were performed for a variety

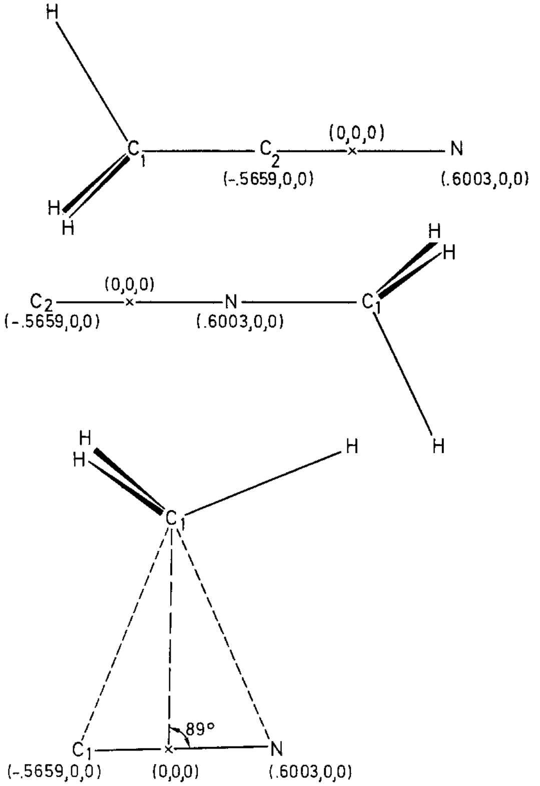

Fig. 1. Assignment of coordinates for the specification of MeCN, MeNC, and intermediates

of (θ, d) coordinates with the pyramidal CH_3 group in three different orientations. No attempt was made to perform calculations for different C–H or $C{\equiv}N$ bond lengths.

Table 1 contains the two nuclear configurations used for methyl cyanide and that used for the isocyanide. The calculated atomic charge distributions, calculated and experimental dipole moments, ionization potentials, and total electronic energies are also given. Not unexpectedly the atomic charge distributions in the cyanide and isocyanide are quite different. The charges on the methyl carbon, nitrile carbon, and nitrogen change sign in passing to the isocyanide. The calculated values of dipole moments and ionization potentials agree with experimental to the extent expected for the CNDO/2 method [16] although the calculated value for the dipole moment for methyl isocyanide seems, perhaps fortuitously, to be unexpectedly good.

To permit comparisons with the previous *ab initio* work [6], Table 2 lists the energies of the occupied and the first unoccupied orbitals for the three configurations of Table 1. As with the *ab initio* calculations the highest occupied orbital of methyl cyanide is a π-orbital while that for the isocyanide is a carbon lone pair orbital.

Table 1. Geometry and calculated properties of methyl cyanide, isocyanide and the predicted intermediate

Configuration	Geometry (Å)					Charge distribution				Dipole moment (debye)		*I.P.* (e.V.)		E^e (hartree)
	$<HC_1H$	C_1H	C_1N	C_1C_2	NC_2	H	C_1	N	C_2	Calc.	Exptl.	Calc.	Exptl.	
MeCN[a] (I)	109.5	1.1025	2.6154	1.4583	1.1571	+0.030	−0.018	−0.178	+0.105	3.14	3.97[c]	15.82	12.21	−27.8908
[b] (II)	109.1	1.1015	2.5901	1.4239	1.1662	+0.031	−0.018	−0.179	+0.103	3.19	—	15.64	—	−27.8988
MeNC[a] (III)	109.1	1.1015	1.4239	2.5901	1.1662	+0.015	+0.074	+0.031	−0.149	3.93	3.83[d]	15.60	11.27	−27.7787
Intermediate (IV)	109.1	1.1015	1.5228	1.5284	1.1662	+0.044 −0.01 −0.01	+0.193	−0.074	−0.145	3.12	—	14.23	—	−27.8273

[a] Ref. [17].

[b] Ref. [17] with coordinates of C_2 and N interchanged.

[c] Smith, J. W., Witten, L. B.: Trans. Faraday Soc. **47**, 1304 (1951).

[d] Ghosh, S. N., Trambarulo, R., Gordy, W.: J. Chem. Phys. **21**, 308 (1953).

[e] Ref. [6].

Table 2. Molecule orbital energies (hartree) of methyl cyanide and isocyanide

Configuration	CH_3CN I	CH_3CN II	CH_3NC III
Occupied orbitals	-1.5001σ	-1.5092σ	-1.5955σ
	-1.3395σ	-1.3429σ	-1.2443σ
	-0.8509π	-0.8587π	-0.8648π
	-0.8509π	-0.8587π	-0.8648π
	-0.8395σ	-0.8423σ	-0.8604σ
	-0.6384σ	-0.6382σ	-0.5921π
	(lone pair)	(lone pair)	
	-0.5848π	-0.5748π	-0.5921π
	-0.5848π	-0.5784π	-0.5730σ
			(lone pair)
Lowest unoccupied orbital	0.2145π	0.2079π	0.2261π

1 hartree = 27.2097 eV.

Tables 3, 4, and 5 record the total electronic energies calculated for a range of (θ, d) values, that is, with the C_1 of the methyl group at various orientations with respect to the CN bond. In addition, in Tables 3 to 5 different orientations of the methyl hydrogens with respect to the C_2N axis are considered. The results in Table 3 and 4 are obtained with a C_1–H bond in plane with the C_2N bond, where as those in Table 5 are obtained with a staggered configuration of the hydrogen atoms. The orientation of the hydrogen atoms in the methyl group has a small but not a negligible effect on the total electronic energies of the molecule. Additional calculations to obtain a more refined energy surface were done for the particular orientation of the hydrogen atoms which produced the lowest energy for the intermediate and these are also reported in Table 3.

The values given in Table 3 for one orientation of the CH_3 group are shown diagrammatically in Fig. 2. As can be seen, a minimum energy corridor passes between the two extremes, the cyanide and isocyanide, and lies between d values of 1.4 and 1.8 Å. It should also be noticed that Fig. 2 illustrates the presence of a metastable intermediate, as Dewar [8] predicted by MINDO/2 calculations, and the larger activation barrier lies between the intermediate and CH_3CN. The minimum intermediate electronic energy calculated was -27.8266 hartree for a θ value of $89 \pm 3°$ and a d value of 1.4 ± 0.05 Å. However, graphical interpolation produced a value of -27.8273 hartree at 89° and 1.408 Å. The difference between the energy of the intermediate and that of the isocyanide is 30.5 kcal. The activation barrier for the isocyanide isomerization is 32.9 kcal/mole^{-1} which agrees well with the experimental value of 38.4 kcal/mole^{-1} [4]. For the nuclear configuration of the intermediate the angle formed by the methyl hydrogen, carbon and the origin is 109.8°. Although the location of the origin along the CN axis in the present work is not identical to that used by Liskow, Bender, and Schaefer (LBS), the difference is sufficiently small (0.12 Å) that this angle may be compared directly with the corresponding value of 106° found by LBS by taking the origin at the centre of mass of the CN axis.

Table 3. Total electronic energies[a] of possible intermediates of the cyanide-isocyanide isomerization

d(Å)							
θ(degree)	1.2	1.4	1.6	1.8	2.0	2.2	2.4
0			(27.77873 at $d = 2.02423$ Å)				
5			27.16875	27.66634	27.76172	27.67830	27.53436
15			27.26067	27.68408	27.74794	27.65471	27.50990
25			27.40067	27.70636	27.71977	27.60974	27.46492
35			27.54266	27.71390	27.67328	27.54782	27.40558
45	26.36153	27.28455	27.64629	27.70277	27.61581	27.47914	27.34232
55	26.96387	27.53909	27.71191	27.67912	27.55719	27.41505	27.28510
65	27.36494	27.69971	27.74406	27.65118	27.50880	27.36540	27.24245
75	27.59933	27.78784	27.75723	27.62975	27.47758	27.33543	27.21761
85	27.70158	27.82373	27.75996	27.62035	27.46591	27.32581	27.21085
95	27.69855	27.81963	27.76041	27.62627	27.47569	27.33722	27.22279
100	27.59912	27.77974	27.76018	27.64886	27.50821	27.37212	27.25627
115	27.39850	27.70081	27.75694	27.68709	27.56422	27.43159	27.31110
125	27.08257	27.57431	27.74458	27.73489	27.63715	27.50882	27.38213
135	26.63155	27.39140	27.71254	27.77992	27.71484	27.59334	27.46030
180			(27.89883 at $d = 2.02423$ Å)				

	1.3	1.35	1.4	1.45	1.5	1.55
77	27.74953	27.78223	27.79842	27.80321	27.79553	27.78043
80	27.77199	27.79984	27.81126	27.81161	27.80141	27.78325
83	27.78773	27.81114	27.81972	27.81744	27.80524	27.78572
86	27.79785	27.81815	27.82538	27.82089	27.80728	27.78667
89	27.80081	27.82062	27.82661	27.82153	27.80797	27.78687
92	27.79808	27.81851	27.82458	27.82034	27.80681	27.78639

[a] All energies (a. u.) are negative.

(Orientation of hydrogen atoms of the methyl group corresponds to that in Fig. 1).

1 hartree = 27.2097 eV.

Table 4. Total electronic energies[a] of possible intermediates of the cyanide-isocyanide isomerization

d(Å)							
θ(degree)	1.2	1.4	1.6	1.8	2.0	2.2	2.4
45	26.40135	27.30269	27.65364	27.70567	27.61696	27.47949	27.34251
55	26.99318	27.55418	27.71858	27.68198	27.55835	27.41533	27.28534
65	27.38277	27.70929	27.74852	27.65324	27.50970	27.36578	27.24252
75	27.60626	27.79192	27.75923	27.63063	27.47806	27.33568	27.21754
85	27.69916	27.82275	27.75955	27.62013	27.46591	27.32578	27.21078
95	27.68712	27.81326	27.75734	27.62488	27.47504	27.33696	27.22276
105	27.57687	27.76732	27.75391	27.64613	27.50706	27.37177	27.25607
115	27.36313	27.68132	27.74792	27.68323	27.56284	27.43105	27.31099
125	27.03317	27.54932	27.73399	27.73074	27.63580	27.50845	27.38190
135	26.57416	27.36681	27.70348	27.77673	27.71361	27.59293	27.46031

[a] All energies are negative and in a. u.

(Orientation of hydrogen atoms of the methyl group corresponds to that in Fig. 1 but with the methyl group rotated about the carbon atom by 180°).

1 hartree = 27.2097 eV.

Table 5. Total electronic energies[a] of possible intermediates of the cyanide-isocyanide isomerization

d(Å) θ(degree)	1.2	1.4	1.6	1.8	2.0	2.2	2.4
45	26.38272	27.29361	27.64980	27.70407	27.61566	27.47919	27.34218
55	26.97847	27.54651	27.71498	27.68004	27.55765	27.41504	27.28511
65	27.37326	27.70424	27.74609	27.65202	27.50911	27.36566	27.24223
75	27.60188	27.78951	27.75810	27.63007	27.47778	27.33557	27.21759
85	27.69936	27.82286	27.75949	27.62007	27.46587	27.32558	27.21072
95	27.69203	27.81610	27.75867	27.62540	27.47516	27.33707	27.22264
105	27.58759	27.77324	27.75677	27.64725	27.50754	27.37199	27.25594
115	27.38138	27.69115	27.75238	27.68503	27.56334	27.43117	27.31091
125	27.06015	27.56236	27.73903	27.73259	27.63646	27.50847	27.38193
135	26.60870	27.37956	27.70773	27.77805	27.71396	27.59309	27.46004

[a] All energies (a.u.) are negative.

(Orientation of hydrogen atoms of the methyl group corresponds to that in Fig. 1 but with the methyl group rotated about the carbon atom by 90°).

1 hartree = 27.2097 eV.

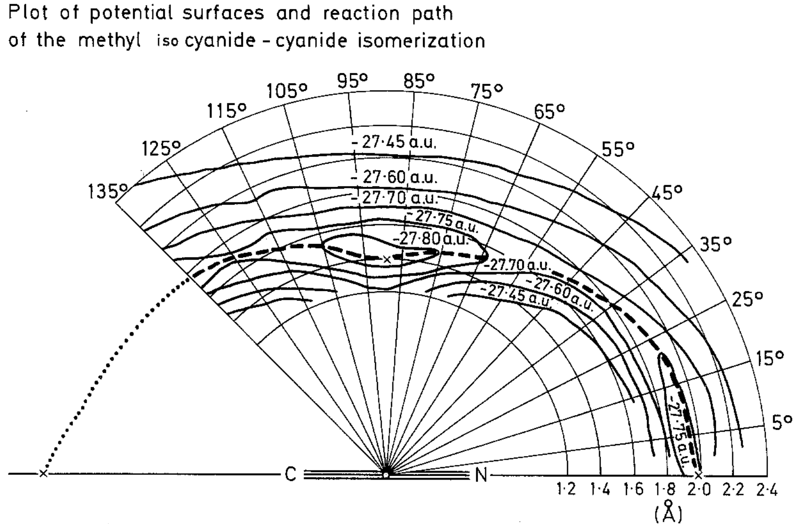

Fig. 2. Energy surface for $CH_3NC \rightarrow CH_3CN$ as a function of (θ, d)

Table 6 displays the one-center energy terms for the atoms of methyl cyanide (configurations I and II), methyl isocyanide (III) and the intermediate (IV). E_A^U is the total (one center) atomic orbital energy of the electrons on atom A, E_A^J is the electronic repulsion of the electrons on atom A, and E_A^K is the electronic exchange interaction of the electrons on atom A, and E_A is the sum of these three terms. As expected the values obtained for the two configurations of methyl cyanide are quite similar. However, with methyl isocyanide, the isocyanide carbon C_2 has a more negative E_A^U value than the cyanide, while that of the nitrogen is less negative. This reflects the shift in electron population from the nitrogen to the carbon when the cyanide is converted to the isocyanide. The remainder of the one-center terms for C_2 and N in the isocyanide also display the behaviour expected. Although the

Table 6. One-center energy terms[a] of methyl cyanide, isocyanide and the intermediate

Configuration		C_1	C_2	N	H	
I	E_A^U	−9.4375	−9.1823	−18.6202	−0.6193	
	E_A^J	4.7651	4.4779	9.4968	0.3525	
	E_A^K	−0.5967	−0.5621	− 1.3038	−0.1763	
	E_A	−5.2692	−5.2665	−10.4271	−0.4430	
II	E_A^U	−9.4352	−9.1851	−18.6237	−0.6188	
	E_A^J	4.7646	4.4823	9.4988	0.3520	
	E_A^K	−0.5967	−0.5624	− 1.3043	−0.1760	
	E_A	−5.2673	−5.2652	−10.4292	−0.4428	
III	E_A^U	−9.2361	−9.9401	−17.7223	−0.6291	
	E_A^J	4.5506	5.0813	8.7457	0.3638	
	E_A^K	−0.5718	−0.8155	− 1.0980	−0.1819	
	E_A	−5.2573	−5.6744	−10.0746	−0.4472	
IV	E_A^U	−8.9360	−9.8872	−18.2235	−0.6449	−0.6103
	E_A^J	4.2772	5.0701	9.1174	0.3824	0.3424
	E_A^K	−0.5389	−0.8032	− 1.2917	−0.1912	−0.1712
	E_A	−5.1978	−5.6203	−10.3979	−0.4538	−0.4391

[a] All energies in a.u.
1 hartree = 27.2097 eV.

nuclear configuration of the intermediate has the methyl group approximately at 90° to the CN bond, it is surprising to find that the one-center terms of the carbon C_2 of the intermediate more closely resemble those of the isocyanide. Again this coincides with a similarity between the charges of C_2 in the intermediate and the isocyanide (−0.145 and −0.149, respectively). In contrast, the one-center terms on the nitrogen of the intermediate are approximately midway in value between those for the cyanide and those for the isocyanide, the exception being for the exchange interaction term of the intermediate, which is almost equal to the corresponding term for the cyanide. As will be seen, a similar behaviour is exhibited by the two-center terms.

Table 7 contains values of the two-center terms, E_{AB}^R and E_{AB} for the most interesting pairs of atoms. As expected, values of both such terms are quite small in all the configurations for pairs of atoms not directly bonded to each other. In both methyl cyanide and isocyanide, the results obtained for the bonded pairs are in the range expected from previous work [15]. In the case of the intermediate, the E^R values reflect a decrease in the triple bond characteristic of the $C \equiv N$ bond. The values for C_1N and C_1C_2 are both quite negative, suggesting that the intermediate can be viewed as a 3-membered ring structure. Figure 3 shows the E^R values for various pairs of atoms in two configurations with angle θ of 45° and 135°. The increasing and decreasing of the E^R values for C_1N and C_1C_2 to form and break the ring is readily evident.

In previous work [15] it has been demonstrated that typical E_{AB}^R terms for C–N, C=N, and C≡N lie in the vicinity of the values −1.10, −1.60, −2.30 hartree, respectively, while those for C–C and C≡C are approximately −1.30 and −2.30 hartree, respectively. Further reference to Table 7 shows that, in the isomerization of the isocyanide the C_2N bond appears to lose a portion of its triple bond charac-

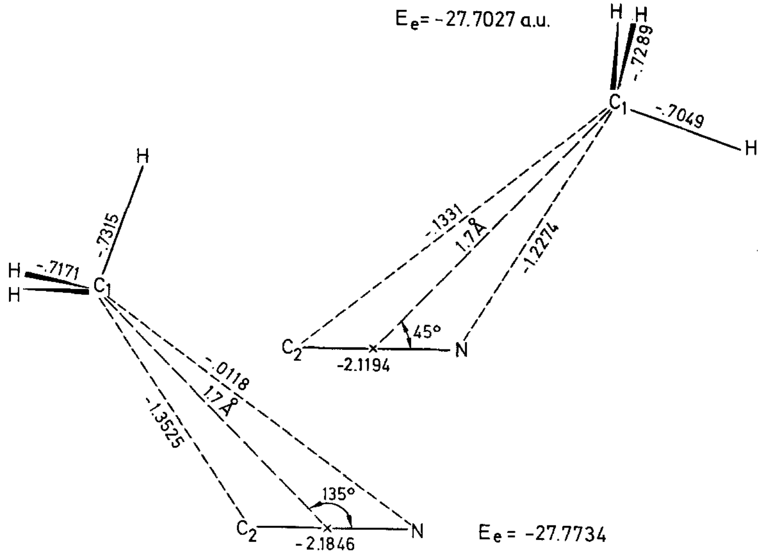

Fig. 3. E^R_{AB} values of various atomic pairs for two orientations of the methyl group

Table 7. Two-center energy terms[a], E^R_{AB} and E_{AB}, of methyl cyanide, isocyanide and the intermediate

Configuration		C_1H	C_1N	C_1C_2	C_2N
I	E^R_{AB}	−0.7297	0.0143	−1.2687	−2.3424
	E_{AB}	−0.7417	0.0146	−1.1909	−2.1873
II	E^R_{AB}	−0.7277	0.0142	−1.3212	−2.3176
	E_{AB}	−0.7379	0.0147	−1.2130	−2.1828
III	E^R_{AB}	−0.7382	−1.2048	0.0147	−2.2653
	E_{AB}	−0.7517	−1.1293	0.0138	−2.0894
IV	E^R_{AB}	−0.7071 −0.7119	−0.7504	−0.8567	−1.9733
	E_{AB}	−0.7051 −0.7182	−0.6791	−0.7604	−1.6810

[a] All energies in a.u.
1 hartree = 27.2097 eV.

ter on formation of the intermediate, while the formerly nonexistent C_1C_2 bond in the isocyanide attains an E^R value in the intermediate near that expected for a C–C bond. Table 8 shows the results of further decomposition into the portions contributed by each of the basis functions S, P_x, P_y, P_z on each atom to the E^R_{AB} values. The C_2N bond is placed along the x-axis, and the CH_3 group is considered to move in the xy plane. It may be seen that, in the formation of the intermediate from the isocyanide, the $P_z - P_z$ component is virtually unchanged, while the contribution of the $P_y - P_y$ and s-P_x components are decreased. Similarly, from Table 7 it may be seen that the C_1N bond which existed as a single bond in the isocyanide suffers a change in character so that the C_1C_2 and the C_1N bonds in the inter-

Table 8. Atomic orbital contributions to E^R_{AB} for MeCN, MeNC, and the intermediate

Bond	C_1N			C_2N			C_1C_2		
Configuration	I	IV	III	I	IV	III	I	IV	III
SS	−0.0013	−0.0735	−0.1576	−0.3041	−0.2108	−0.2689	−0.2019	−0.1129	−0.0030
SX	0.0040	−0.0201	−0.2103	−0.4053	−0.4021	−0.5472	−0.2437	−0.0269	0.0054
SY	0.0	−0.1386	0.0	0.0	0.0	0.0	0.0	−0.1580	0.0
SZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
XS	−0.0010	−0.0154	−0.3701	−0.3851	−0.2476	−0.2571	−0.3652	−0.1597	−0.0044
XX	0.0104	−0.0076	−0.3523	−0.2706	−0.3266	−0.2639	−0.3024	−0.0208	0.0155
XY	0.0	−0.0384	0.0	0.0	0.0	0.0	0.0	−0.0288	0.0
XZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
YS	0.0	−0.1573	0.0	0.0	0.0	0.0	0.0	−0.1946	0.0
YX	0.0	−0.0585	0.0	0.0	0.0	0.0	0.0	−0.0666	0.0
YY	0.0010	−0.2058	−0.0571	−0.4887	−0.3198	−0.4629	−0.0778	−0.1653	0.0005
YZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ZS	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ZX	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ZY	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ZZ	0.0010	−0.0353	−0.0571	−0.4887	−0.4646	−0.4629	−0.0778	−0.0649	0.0005
total	0.0142	−0.7504	−1.2048	−2.3424	−1.9733	−2.2653	−1.2687	−0.8567	0.0146

1 hartree = 27.2097 eV.

mediate take on quite similar E^R values. Reference to Table 8 reveals that, among other things, the $P_y - P_y$ components of both C_1C_2 and C_1N have increased in contribution considerably in passing from the isocyanide to the intermediate. Although other terms alter as well, this change in $P_y - P_y$ components suggests that the labelling of the intermediate as a π complex as suggested by Dewar [8] is at least in part a reasonable one.

Although no investigation of the energy difference between the planar and pyramidal forms of CH_3 for the nuclear configuration of the intermediate was made, CNDO/2 calculations performed using the intermediate geometry of Van Dine and Hoffmann [5] showed that the planar and pyramidal forms had energies of −27.388 and −27.395 hartree, respectively, or approximately 4 kcal. energy difference, compared to 14 kcal found in the *ab initio* work [12].

It is of interest to consider the charge distribution found in the present work as compared with experimental and other theoretical results. Casanova, Werner, and Schuster [18] concluded from their experimental studies that little charge separation develops in the transition state. However, Van Dine and Hoffmann [5] find a significant increase in positive charge at the methyl carbon in the transition state, and conclude that the intermediate has an ionic character, $[CH_3^{+0.59}][CN^{-0.59}]$. The present results suggest that the transition state could be represented as $[CH_3^{+0.22}][CN^{-0.22}]$. Similarly the *ab initio* results predict that the transition state with pyramidal CH_3 can be written as $[CH_3^{+0.26}][CN^{-0.22}]$ which is rather close to the present findings. For the cyanide itself the present results lead to $[CH_3^{+0.08}][CN^{-0.08}]$ compared to $[CH_3^{+0.088}][CN^{-0.088}]$ as obtained by Clementi and Klint [7].

In summary, the present results predict a height of the barrier to isomerization as 32.9 kcal, quite close to the experimental value of 38.4 kcal/mole^{-1}. The intermediate is predicted to be one with a pyramidal CH_3 situated at very close to 90° from the CN axis. The predicted ionicity of the intermediate, at least based on Mulliken population analyses, is significant, and is quite similar to that found by the same method in *ab initio* studies [12].

Finally it may be useful to note some of the previous work involving studies of energy changes by semiempirical methods. Gordon [19] has applied the CNDO/2 molecular orbital method to predict and attempt to explain the barriers to internal rotation in a number of molecules. He concluded that the CNDO method would be applicable to such barrier studies only if nonbonded interactions involving highly electronegative atoms (e.g., F) are unimportant. In contrast, applications of both EXH and CNDO methods by Snyder [20] to the transformation, classical 2-phenylethyl → phenonium cation produced results which, in both cases, do not show quantitative agreement with experiment. The CNDO method has been applied to a conformational analysis of acetanilide [21] and to a study of the barrier to internal rotation in 0-chloronitrobenzene and σ-dinitrobenzene [22] with good agreement with experimental results. However, Combs and Holloman [23] have recently reported on observations of several apparently false energy minima in their semiempirical calculations of potential barriers in the internal rotation of such molecules as FNO_2, and suggest that the most obvious defect is the lack of consideration of lone-pair electron interactions. Earlier work in this laboratory [24] successfully predicted, in advance of the definitive experiments [25], that cyanamide exhibits a non-planar structure. The predicted angle (46–56°) was, however, somewhat larger than that ultimately measured experimentally (38°).

While the results for the isomerization of methyl isocyanide given in the present paper are encouraging certainly there are hazards in accepting too readily the results of semiempirical calculations. The mixed results reported in the literature attest to these dangers. It appears, at this time, that what is needed are a number of experimentally well-worked, relatively simple reactions on which calculations of both the *ab initio* and semiempirical type may be performed. With such information at hand it might then become possible to make generalizations as to the applicability of semiempirical methods in the construction of meaningful potential energy surfaces.

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