# The Isocyanide–Cyanide and Isoelectronic Rearrangements

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**Abstract:** Potential surfaces for the isocyanide–cyanide rearrangement of a hydrogen, methyl, and phenyl are constructed from extended Hückel calculations. The reaction path for a methyl group rearranging moves it on an approximate semicircle around the center of the CN bond, with the CN bond lengthening and the methyl group flattening as it shifts, always keeping the same face toward CN. A phenyl group shifts by a $\pi$ route rather than $\sigma$, and this preference is rationalized from an interaction diagram. Excited states may have bent cyanide and isocyanide minima but large activation energies to interconversion. The rearrangement should also be feasible in the isolectronic diazonium and acetylide ions.

The thermal rearrangement of isocyanides (I) to cyanides (II) has been known for some time. The

$$\underset{\text{I}}{\mathrm{RN{\equiv}C}} \xrightarrow{\Delta} \underset{\text{II}}{\mathrm{N{\equiv}CR}}$$

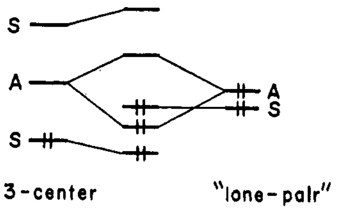
reaction is a prototype of a true unimolecular process and its kinetics have been carefully studied in both vapor phase and solution by Rabinovitch and coworkers.[1] These studies made it unlikely that the rearranging group R could become completely detached during the isomerization. It was further shown by Casanova and coworkers[2] that stereochemical integrity was maintained at the migrating atom.

In this work we have investigated the potential surface for the rearrangement by means of extended Hückel calculations.[3] The cases studied in detail include R = hydrogen, methyl, and phenyl. In addition we have considered analogous rearrangements of the isolectronic species, diazonium cations[4] III and acetylide anions IV.

$$\underset{\text{III}}{\mathrm{RN^{+}{\equiv}N}} \qquad\qquad \underset{\text{IV}}{\mathrm{RC{\equiv}C^{-}}}$$

Aided in part by the hindsight obtained from the calculations we will describe below, we can sketch the evolution of orbitals in these rearrangements. Let us begin with the symmetric case of a diazonium ion isomerization. In a semilocalized view the essential orbitals in the reactant, transition state, and product are shown in Figure 1. They are an N–R $\sigma$ bond, an N–N $\pi$ bond, and a nitrogen lone pair. Another N–N $\pi$ bond has the reaction plane as its nodal plane and so is not much affected by the rearrangement, provided that the rearranging group R has no $\pi$ orbitals. The molecular orbital calculations of course lead to delocalization of the above semilocalized set.

As the rearrangement proceeds the bonding changes until in the transition state we can describe it as follows. There is a pair of nitrogen lone pairs, and a three-center bond involving one orbital from each of the nitrogens and the rearranging group. The three-center orbitals form a familiar triplet,[5] in order of increasing energy S (symmetric), A (antisymmetric), and S with respect to the symmetry plane perpendicular to and bisecting the N–N axis. A simple interaction diagram shown below illustrates that as a result of the interaction of three-center A level with a lone-pair combination of the same symmetry a stable closed-shell six-electron configuration is obtained. There are thus no high-lying energy levels in the transition state and the rearrangement is a symmetry-allowed thermal process.[6]



Let us now return to the calculations we carried out. Figure 2 shows the calculated potential surface for the motion of an H atom in the space around a C–N group with a fixed C–N distance of 1.20 Å.[7] The two minima for linear HCN and HNC are apparent, as well as the saddle-point nature of the transition state for the rearrangement. In further calculations with R = methyl or phenyl, we did not construct a full potential energy surface but instead studied several sections through it. The sections were defined in terms of an origin at the midpoint of the C–N bond, a distance $r_1$ from this origin to the R group, and an angle $\theta$ measured from the "N side" (see Figure 3). While we will consistently refer to a fixed CN group and a moving R group, it should be kept in mind that the motion is relative, and that one could just as well think of the R group fixed and CN moving.

**Methyl Isocyanide.** The extended Hückel method in general gives poor bond lengths.[3] The calculated energy minima occurred at $CH_3$–CN 1.53 Å (observed 1.46[7]) and $CH_3$–NC 1.63 Å (observed 1.44[7]), which

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[1] G. H. Kohlmaier and B. S. Rabinovitch, *J. Phys. Chem.*, **63**, 1793 (1959); F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962); **85**, 2365 (1963).

[2] J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).

[3] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2047, 2474, 2745 (1964), and subsequent papers. The parameters used here are the same except that the H 1s exponent is chosen as 1.3.

[4] There is some evidence for this rearrangement of aryldiazonium ions: E. S. Lewis and R. E. Holliday, *J. Am. Chem. Soc.*, **88**, 5043 (1966); E. S. Lewis and J. M. Insole, *ibid.*, **86**, 32 (1964); but see A. K. Bose and I. Kugajevsky, *ibid.*, **88**, 2325 (1966).

[5] See, for example, F. A. Cotton, "Chemical Applications of Group Theory," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1963, p 155.

[6] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965); to be published; R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); *Accounts Chem. Res.*, **1**, 17 (1968).

[7] C–N distances in cyanides and isocyanides are not very different; in $CH_3$–CN 1.16 Å (L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955)), in $CH_3$–NC 1.17 Å (M. Kessler, H. Ring, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **79**, 54 (1950)).

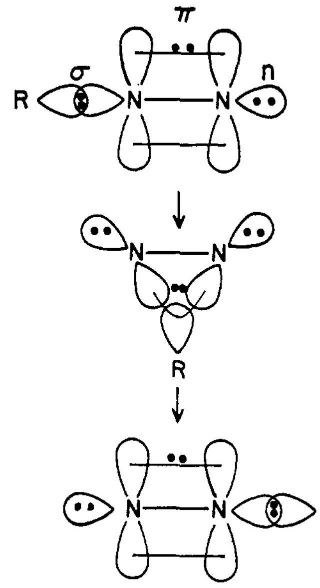


Figure 1. The essential semilocalized orbitals in the degenerate diazonium ion rearrangement.

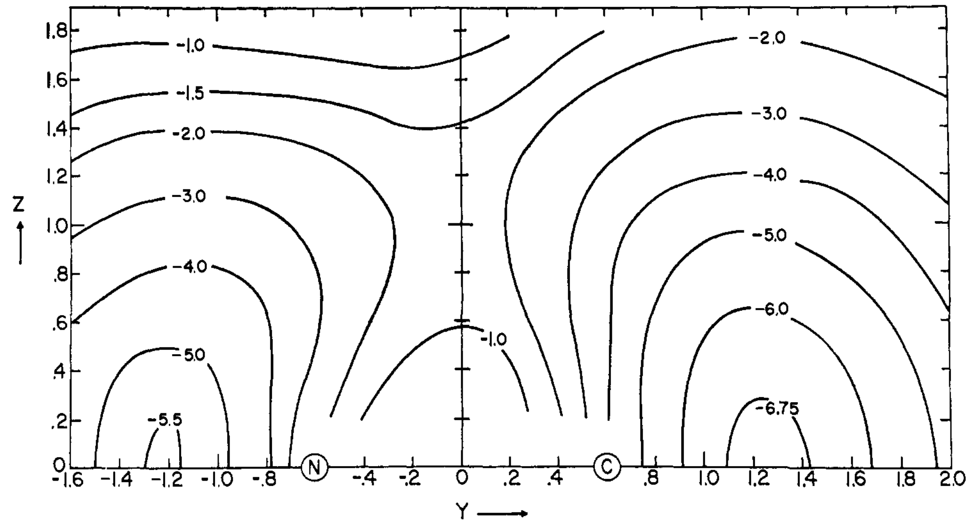


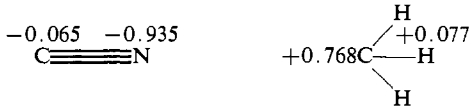
Figure 2. Energy contours (in electron volts) for the motion of a hydrogen near a C-N framework with fixed C-N distance of 1.20 Å. The axes are Cartesian coordinates in Å for the hydrogen. The energy surface has cylindrical symmetry around the C-N axis.

were better than anticipated. Figure 4 shows the total energy along the reaction coordinate $\theta$, the energy at each point being a minimum with respect to variation of $r_1$. This is a section through the potential surface $E(\theta, r_1)$ which is close to a semicircle. Some lines on that surface are shown in Figure 5; these represent variation of $E$ with $r_1$ at fixed values of $\theta$. The vertical arrows indicate the "reaction path" over the energy surface, *i.e.*, the curve in Figure 4.

The first point to be noted from Figure 4 is that the top of the activation barrier comes at approximately $\theta = 88°$; that is, in the transition state the methyl group is nearly equidistant from C and N. At $\theta = 88°$ and $r_1 = 2.15$ Å, $CH_3$-N is 2.21 Å and $CH_3$-C is 2.25 Å.

The calculated activation energy for the rearrangement is 40.8 kcal/mol starting on the isocyanide side. That this figure agrees so well with the observed vapor phase value of 38.4 kcal/mol[1] is surely an accident, since the calculated $\Delta H$ for the reaction is $-25.2$ kcal/mol compared to the empirically estimated $-15$ kcal/mol.[8]

A significant feature of Figure 5 is the minimum in the potential energy curve even in the transition state. The depth of the well relative to complete separation of methyl cation and $CN^-$ ($r_1 = \infty$) is calculated as approximately 13 kcal, though we consider the magnitude unreliable. This leads naturally to the question of how much net charge is on the rearranging group R in the transition state. Figure 6 shows the charges calculated from a Mulliken population analysis. Qualitatively, slight additional positive charge (approximately 0.2 unit) develops at the methyl carbon in the transition state. The actual values should not be taken too seriously, but the trend is real.[9] For comparison the charges in isolated $CN^-$ and $CH_3^+$ fragments of geometry similar to those used in studying the rearrangement are shown below.


$$\overset{-0.065}{C}\equiv\overset{-0.935}{N} \qquad +0.768\,C(H)_3,\ H\ +0.077$$

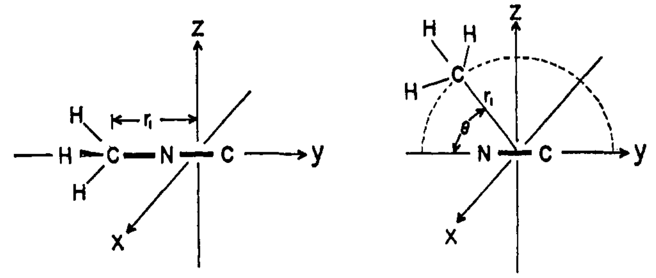


Figure 3. Variables defining the rearrangement. The origin is at the midpoint of the C-N bond. $r_1$ is the distance from the origin to R and $\theta$ is an angle of rotation of the R group around the $x$ axis, with $\theta = 0$ corresponding to R lying on the negative $y$ axis.

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(8) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(9) Extended Hückel calculations exaggerate charge separation. Approximate SCF calculations by the CNDO/2 method (J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129, S133 (1965); **44**, 3289 (1966)) lead to a much more uniform charge distribution.

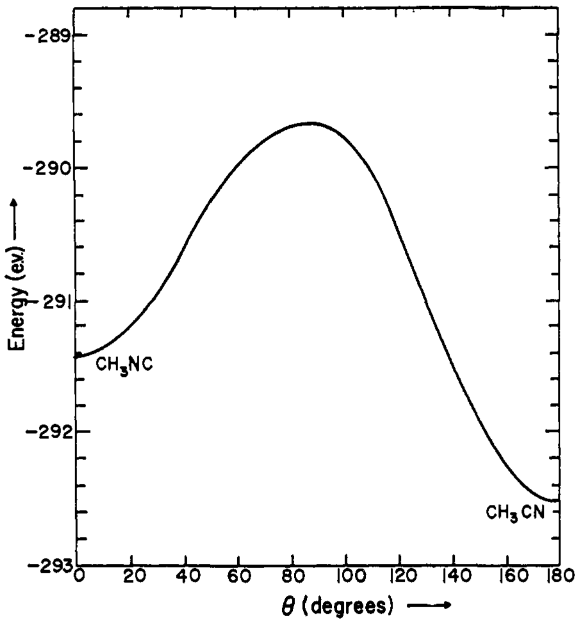


Figure 4. Total energy as a function of $\theta$, minimized with respect to $r_1$ at each point.

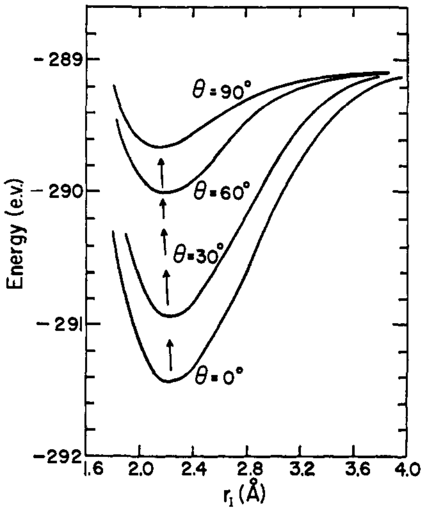


Figure 5. Some linear sections through the energy surface for the methyl isocyanide–cyanide rearrangement.

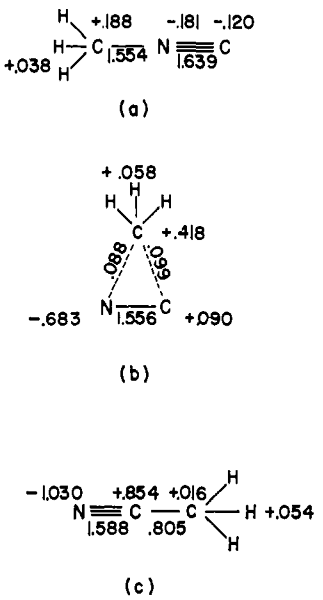


Figure 6. Mulliken population analysis for (a) $CH_3NC$, (b) the rearrangement transition state, and (c) $CH_3CN$. The signed numbers are net charges, the unsigned ones overlap populations. The three methyl hydrogens are slightly nonequivalent in the transition state; the charge given is averaged.

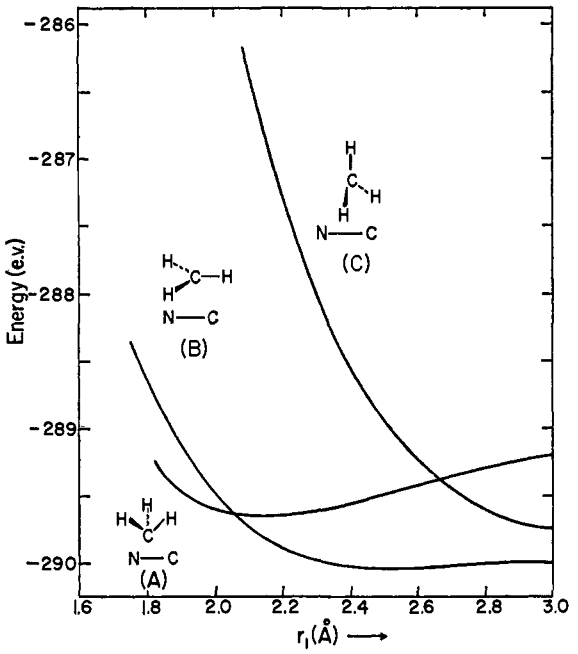


Figure 7. Energy sections at $\theta = 90°$ for (A) tetrahedral $CH_3$, (B) trigonal $CH_3$, (C) inverting trigonal $CH_3$, *i.e.*, a trigonal $CH_3$ in *xz* plane (see Figure 3).

Experimentally, two pieces of evidence have been presented[2] which indicate *little or no charge* at the rearranging carbon. First, when R = cyclobutyl, no cyclopropylcarbinyl rearrangement products are formed. Second, the substituent effect on rate is very small when R is *para*-substituted phenyl ($\rho = -0.12$). To the extent that these experimental observations reflect the ionic character of the transition state, they seem to be out of line with our calculated charge distribution. In spite of this, we find in every case studied (isocyanides as well as diazonium ions) there is an increase in positive charge at C-1 in the transition state.

If there is positive charge developing at the rearranging R group, it might reflect itself in a change of geometry of the moving $CH_3$ group. Since the preferred equilibrium geometry of carbonium ions appears to be trigonal, we envisaged a flattening of the $CH_3$ group in the transition state. This is confirmed in Figure 7 where energy sections at $\theta = 90°$ are shown for trigonal and tetrahedral $CH_3$ groups. Thus the inclusion of this further degree of freedom in the rearrangement as well as inspection of the overlap populations of Figure 6 hints at the following description of the rearrangement process. The rearranging group moves on a very approximate semicircle about the middle of the CN bond. As it shifts the CN bond lengthens slightly then contracts once again. The rearranging methyl group flattens from a tetrahedral to a nearly trigonal configuration and then folds again to a pyramidal form, all the while maintaining bonding on one and the same face with CN.

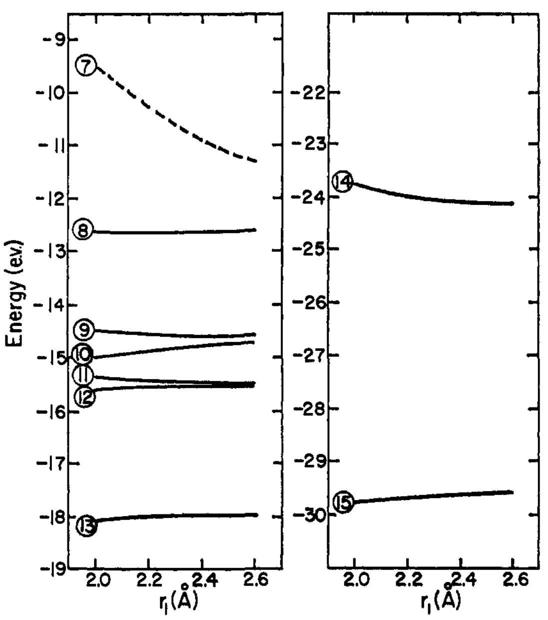


Figure 8. The change in energy with $r_1$ of individual levels in the methyl isocyanide transition state. Orbitals 8–15 are occupied; orbital 7 is empty.

It is interesting to decompose the reduced overlap populations between the $CH_3$ and CN groups into individual atomic orbital overlap populations, as shown in Table I.

Table I. Orbital Overlap Populations for Methyl Isocyanide Rearrangement Transition State, $\theta = 88°$

| | $C_1(2s)$ | $C_1(2p_x)$ | $C_1(2p_y)$ | $C_2(2p_z)$ |
|---|---|---|---|---|
| C(2s) | 0.0022 | 0 | 0.0002 | 0.0434 |
| $C(2p_x)$ | 0 | −0.0006 | 0 | 0 |
| $C(2p_y)$ | −0.0057 | 0 | −0.0015 | −0.0353 |
| $C(2p_z)$ | 0.0157 | 0 | 0.0079 | 0.0726 |
| N(2s) | −0.0043 | 0 | 0.0004 | 0.0042 |
| $N(2p_x)$ | 0 | −0.0014 | 0 | 0 |
| $N(2p_y)$ | −0.0029 | 0 | −0.0012 | −0.0195 |
| $N(2p_z)$ | 0.0158 | 0 | 0.0028 | 0.0945 |

Thus, it can be seen that the largest single contribution to the bonding of the $CH_3$ group in our transition state is from the σ bonding between $C_1(2p_z)$ and the C and N $2p_z$ orbitals. It is the third highest of the eight filled molecular orbitals in the transition state which appears to be mainly responsible for this bonding.

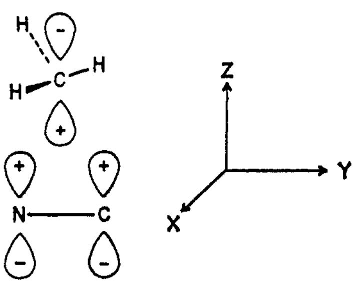


Figure 8 shows the variation with distance $r_1$ of the individual orbital energies. The orbital indicated above is no. 10 in Figure 8. While it would be tempting to single out this σ ($2p_z$–$2p_z$) orbital, it is obvious from Figure 8 that it is really a combination of orbital energy variations with distance which adds up to a total energy curve which has a minimum.

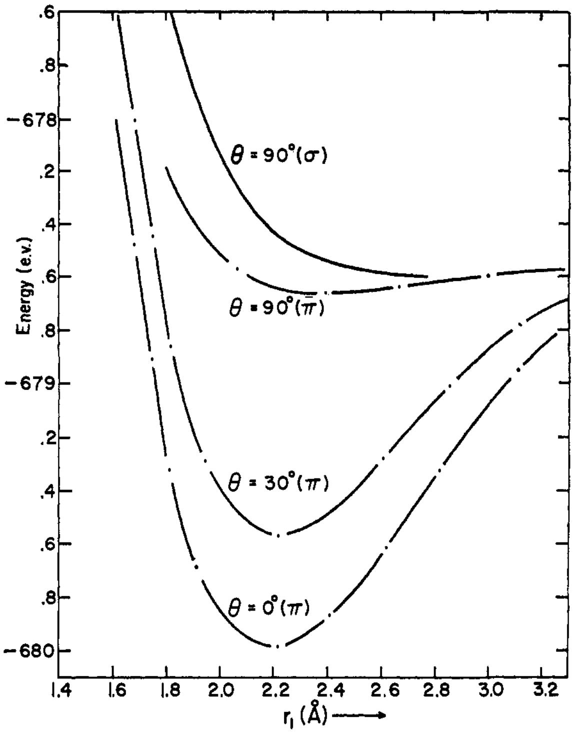
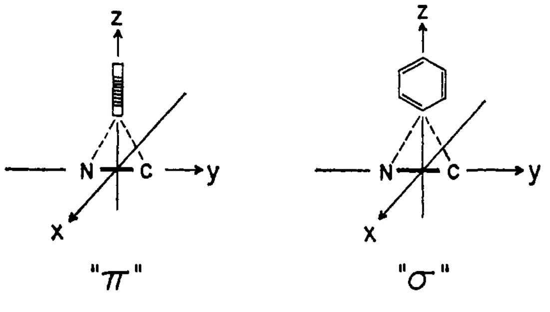


Figure 9. Some sections through the potential surface for the phenyl isocyanide rearrangement. The σ and π geometries are defined in the text.

**Phenyl Isocyanide.** The phenyl group introduces an additional degree of freedom, namely the orientation of the plane of the benzene ring with respect to the rearrangement plane. Two extremes of geometry are recognizable, which we will call the "σ" and "π" routes.

In the σ route the three-center bond in the transition state is formed with a σ orbital of the phenyl ring, and all the atoms lie in one plane throughout the reaction. In the π route the three-center bond utilizes a p orbital of the phenyl ring, and the plane of the ring remains perpendicular to the plane defined by CN and the bonded phenyl carbon. Figure 9 shows some calculated sections through the rearrangement potential surface.[10] At every θ (0° < θ < 180°) a π conformation is preferred to a σ. σ and π sections at θ = 90° may be compared in Figure 9.



The σ transition state is not bound with respect to dissociation to $C_6H_5^+$ and $CN^-$. The calculated barrier to rotation of the phenyl group is 8 kcal/mol in the

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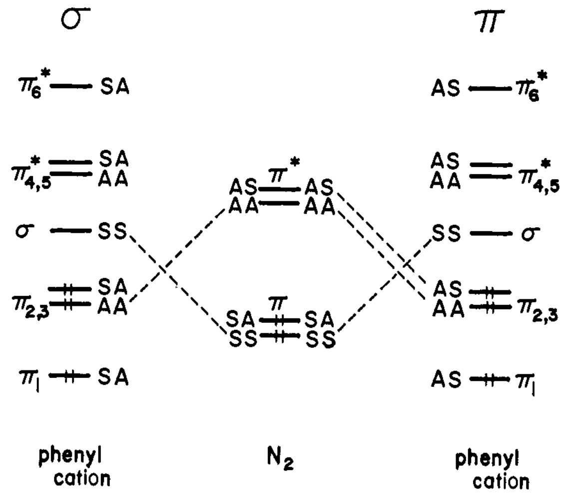
(10) A hexagonal benzene ring with C–C 1.40 Å, C–H 1.10 Å, was maintained throughout the rearrangement.

transition state. The calculated activation energy is 30.8 kcal/mol with the transition state at $r_1 = 2.4$ Å, $\theta = 85°$. The experimental value for the activation energy of the closest studied derivative, *p*-tolyl isocyanide, is 33.8 kcal/mol in the gas phase.[1] Figure 10 shows the calculated charge distribution in the isocyanide and the transition state.

Experimental information on the geometry of the phenyl isocyanide rearrangement is lacking. Kohlmaier and Rabinovitch[1] have studied the kinetics of the rearrangement of *p*-tolyl isocyanide both in the gas and in the liquid (Nujol) phase. These authors assumed two models for the transition state, and calculated rough values for $\Delta S^{\ddagger}$ for each model: (1) free rotation of the phenyl group, calculated $\Delta S^{\ddagger} = 2.2$ eu; (2) three-membered ring rigid structure model, calculated $\Delta S^{\ddagger} = -1.1$ eu. On the basis of their observed $\Delta S^{\ddagger} = -4.8$ eu, they concluded that the somewhat rigid ring model, with a rotational barrier, was the better representation of the transition state. This is in accord with our calculations.

There is a simple orbital explanation for the preferred π route. It is based on differences in the possible interactions of π orbitals of the CN and phenyl fragments. To get maximum aid from simple symmetry arguments, let us go to the diazonium rearrangement and consider the σ and π transition states as arising from the interaction of a phenyl cation and a nitrogen molecule. We will classify all levels as symmetric (S) or antisymmetric (A) with respect to first, the *xz* plane, and second, the *yz* plane (see illustration in which σ and π routes are defined). The relevant orbitals are the six π levels of the benzene and a vacant σ orbital at the migrating carbon, as well as the two π and two π* levels of the nitrogen molecule. To construct an interaction diagram we place the center of gravity of the N–N π bonds lower than that of the C–C, and the phenyl σ orbital at approximately nonbonding. The symmetry properties of the benzene π levels are familiar[11] and so the interaction diagram can be completed as below.



A simple and familiar perturbation argument indicates that the chemically significant interaction is between the unoccupied orbitals of one component and the occupied levels of the other, and that the magnitude of this stabilizing interaction is inversely proportional to the energy difference between the interacting levels. In the above interaction diagram we have not indicated the position of the energy levels but only shown by dashed lines the major stabilizing interactions. These are between π* orbitals of the $N_2$ and bonding benzene π levels, as well as the three-center bond construction from the SS levels. There are two of the former interactions in the π transition state and one in the σ. The σ transition state is thus the less stable. When the symmetry is partially broken, as in the isocyanide–cyanide rearrangement transition state, we can no longer obtain such a simple argument from symmetry alone. But in essence nothing much changes and the major interactions remain precisely those indicated in the symmetric case.

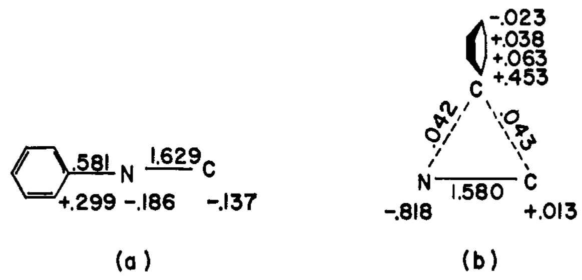
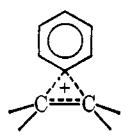


Figure 10. Population analysis results on phenyl isocyanide and the transition state for its rearrangement to phenyl cyanide. The signed numbers are net charges, the unsigned ones Mulliken overlap populations.

It should also be noted that a similar argument can be used to stabilize a π over a σ transition state in the phenonium ion rearrangement,[12] though classical reasoning would provide the answer anyway. Here there



is only a single π level of the ethylene component (SS) and a single π* level (AS). There is one stabilizing interaction in the π transition state, none in the σ.

Our calculated activation energy for a π-route phenyl rearrangement is 31 kcal, for a σ route 39, and for the methyl rearrangement 41. The similarity of the last two numbers, both σ routes, raised in our minds the question of the relative feasibility of a π route for the methyl rearrangement. Now a π route for an alkyl rearrangement implies a shift with inversion. The transition state would have a planar $CH_3$ group approximately in the *xz* plane. A potential energy curve for this geometry may be found in Figure 7. The approach is of high energy and not bound. It seems that a shift with inversion (π route) is preferred unless, as happens in the case of methyl, the π route is sterically encumbered and σ route favored.

**Excited-State Rearrangement.** The tendency of excited HCN to bend was clearly analyzed by Walsh in his important series of papers in 1953.[13] The study of the far-ultraviolet spectrum was initiated by Price and

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[11] See, for example, J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p 125.

[12] D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964), and references therein.

[13] A. D. Walsh, *J. Chem. Soc.*, 2288 (1953).

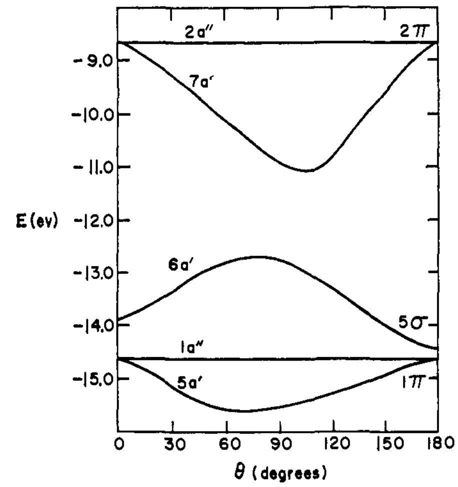

Figure 11. Energy levels near nonbonding along a semicircular section of the potential surface for the HNC to HCN rearrangement. $r_1$ is fixed at 1.70 Å as $\theta$ varies. The levels are labeled to correspond with those of ref 17.

Walsh[14] and continued by Herzberg and Innes.[15] Three bands were analyzed and the transitions assigned in order of increasing energy to the following upper states: $^1A''$ (HCN angle 125°), $^1A''$ (114.5°), $^1A'$ (140°).

Figure 11 shows the behavior of some of our one-electron energy levels as $\theta$ is varied at $r_1 = 1.70$. MO calculations close to the Hartree-Fock level[16,17] consistently place the $5\sigma$ level below the $1\pi$ for HCN, and so our calculations are out of line here. The energy level trends resemble closely those proposed by Walsh[13] except for the discrepancy in the behavior of the a′ levels[18] noted by Pan and Allen.[17] Thus, Walsh's conclusions about geometry changes in excited states are not much altered in our approximation. We obtain some states in which the minima remain at HCN and HNC linear, some in which there is a linear HNC but a bent HCN minimum, and some with bent minima on the HCN and HNC sides. A potential surface for one of the latter cases, the A′ state arising from 6a′ to 7a′ excitation, is shown in Figure 12. We find it interesting that, while two bent minima are created which are formally separated by a *lesser* motion of the H atom than in the ground state, the barrier separating them is *greater* in the excited state than in the ground state.

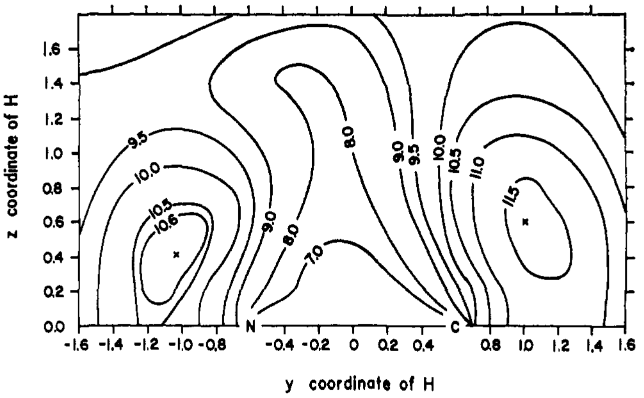

Figure 12. Calculated potential surface for the A excited state of HCN and HNC arising from a 6a′ to 7a′ excitation. The convention is that of Figure 2.

The $CH_3CN$ excited state curves resemble those of HCN. The rearrangement has been carefully studied,[19] but we find our calculations do not contribute to an analysis of the experimental results. In the case of $C_6H_5CN$ the lowest excited states involve excitations primarily in the benzene ring.

**Isoelectronic Rearrangements.** We investigated several diazonium and acetylide rearrangements and obtained potential energy curves very similar to those exhibited for the isocyanide–cyanide case. Some sample activation energies which we calculate are (kilocalories/mole): methyldiazonium ion, 42; phenyldiazonium ion, 39; phenylacetylide ion, 58. Though the acetylide value is significantly higher than the other activation energies we have calculated, we think it would be worthwhile to search for this rearrangement experimentally.

**Acknowledgment.** We are grateful to the National Science Foundation, the National Institutes of Health, the Sloan Foundation, and the Chevron Research Company for financial support of this work.

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[14] W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 381 (1945).

[15] G. Herzberg and K. K. Innes, *Can. J. Phys.*, **35**, 842 (1957).

[16] A. D. McLean, *J. Chem. Phys.*, **37**, 627 (1962).

[17] D. C. Pan and L. C. Allen, *ibid.*, **46**, 1797 (1967).

[18] While both we and Pan and Allen[17] have 5a′ decreasing in energy with bending and 6a′ increasing, our 5a′ originates from $1\pi$ while theirs arises from $5\sigma$. This is an accident of our incorrect ordering of $5\sigma$ and $1\pi$ in linear HCN; the compositions of 5a′ and 6a′ are probably the same in both calculations at intermediate bending angles.

[19] D. H. Shaw and H. O. Pritchard, *J. Phys. Chem.*, **70**, 1230 (1966).