the NDDO approximation instead of INDO. While we are studying the parametrization of NDDO, the results are not yet sufficient to show whether the ad- vantages gained compensate for the additional com- putation time (greater by a factor of 2–3 over MINDO/ 2).

Ground States of σ-Bonded Molecules. XVI.[1] The Rearrangement of Methyl Isocyanide to Acetonitrile[2]

Michael J. S. Dewar* and M. C. Kohn

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received August 13, 1971

Abstract: The MINDO/2 method has been used to calculate the reaction path for the conversion of methyl iso- cyanide into acetonitrile. The calculated heat of reaction and activation energy are in reasonable agreement with experiment as also are the geometries and heats of formation of reactant and product. The reaction is predicted to involve a stable triangular intermediate with the properties expected of a π complex rather than an ion pair.

Some time ago one of us interpreted[3] the thermal conversion of methyl isocyanide (1) to acetonitrile (2) as an intramolecular rearrangement involving an intermediate π complex (3), *i.e.*, a species in which methyl is linked to the CN moiety by a three-center covalent bond. According to the π-complex theory[3,4] the bond in 3 should, so far as the methyl group is concerned, be no different in kind from the normal two-center bond CX in a methyl derivative H_3CX; the migrating methyl group should therefore on this basis retain its stereochemistry during the reaction and the intermediate phases should not differ much in polarity from the starting material and reactant.
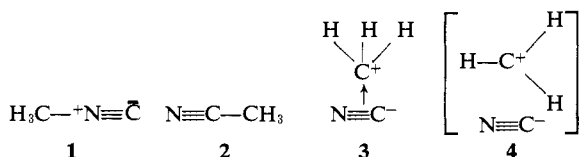
The rearrangement of 1 to 2 has been studied in detail by Schneider and Rabinovitch;[5] the reaction takes place homogeneously in the gas phase, following kinetics characteristic of a unimolecular process. Rabinovitch, *et al.*, concluded that the migration of methyl must be intramolecular, the transition state having a triangular geometry (*cf.* 3).

This conclusion was supported by Casanova, *et al.*,[6] who showed that optically active derivatives of 1 re- arrange with complete retention of configuration of the migrating group. Further light was shed on the nature of the transition state by a study of alkyl deriva- tives of 1, the relative rates of rearrangement of methyl, ethyl, isopropyl, and *tert*-butyl isocyanides being

5.6:7.8:2.6:1.0; the lack of any consistent trend along the series suggests that the transition states must differ little in polarity from the reactants and also that the migrating carbon retains its tetrahedral geometry.

These results clearly provide strong support for the π-complex mechanism.

Recently Van Dine and Hoffmann[7] have studied the rearrangement of 1 to 2 by the "extended Hückel" method, assuming a fixed CN bond length (1.20 Å) and fixed geometries for the methyl group. When the latter was assumed to remain pyramidal throughout, the transition state was predicted to have the geometry indicated below (CN and CC distances (Å), and formal charges on methyl and CN, calculated by Van Dine and Hoffmann[7] for the rearrangement 1 → 2), the
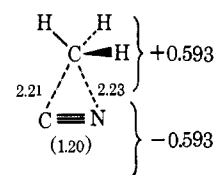
methyl–carbon and methyl–nitrogen distances being similar and very long, with large formal charges on the methyl and CN groups. Since this result seemed to suggest that the reaction was tending to pass through an intermediate ion pair 4, they recalculated the energy of the symmetrical intermediate, assuming the methyl group to be planar, for various methyl–CN distances. Then equilibrium methyl–CN distance increased from *ca.* 2.1 Å to *ca.* 2.5 Å and the energy at the minimum decreased by *ca.* 0.4 eV. While they do not quote charges for this structure, it seems reasonable to assume that it must have corresponded closely to 4.

The procedure used by Van Dine and Hoffmann is admittedly far from reliable, leading to predicted heats of formation and molecular geometries that are greatly in error. Moreover it seems to be particularly un- satisfactory in the case of unusual ("nonclassical") structures; thus cyclopropanone (5) was predicted[8]

(1) Part XV: M. J. S. Dewar and M. C. Kohn, *J. Amer. Chem. Soc.,* **94,** 2699 (1972).
(2) This work was supported by the Air Force Office of Scientific Re- search through Contract F44620-70-C-0121.
(3) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.
(4) M. J. S. Dewar, *Nature (London),* **156,** 789 (1945); *J. Chem. Soc.,* 406, 777 (1946); *Bull. Soc. Chim. Fr.,* C71, 18 (1951).
(5) F. W. Schneider and B. S. Rabinovitch, *J. Amer. Chem. Soc.,* **84,** 4215 (1962).
(6) J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.,* 31, 3473 (1966).

(7) G. W. Van Dine and R. Hoffmann, *J. Amer. Chem. Soc.,* **90,** 3227 (1968).
(8) R. Hoffmann, *ibid.,* **90,** 1475 (1968).

Table I. Properties of Methyl Isocyanide and Acetonitrile

| | Heat of formation (25°), kcal/mol | | Bond lengths, Å | | | | Dipole moment, D | |
| | | | —C—C or C—N— | | C≡N | | | |
Compound	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
CH₃—N⁺C⁻	26.3	35.6,[a] 35.9[b]	1.402	1.424[c]	1.195	1.166[c]	3.80	3.85[d]
CH₃—C≡N	16.8	20.9,[a] 19.1[e]	1.430	1.458[f]	1.187	1.157[f]	3.88	3.92[d]

[a] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxel, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," National Bureau of Standards Publication NSRDS-NBS-26, Washington, D. C., 1969. [b] "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, Washington, D. C., 1952. [c] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). [d] "Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970, p E-70. [e] From heats of formation of HCH and C₂H₅CN: S, W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [f] C. Matsumara, E. Hirota, T. Oka, and Y. Morino, *J. Mol. Spectrosc.*, **9**, 366 (1962).

to be less stable by 1.0 eV (23 kcal/mol) than the isomeric Favorskii intermediate **6**, a conclusion at variance with experiment and MINDO/2 calculations.[9]
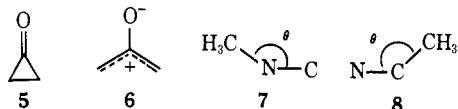
The heat of formation of the ion pair CH₃⁺CN⁻ at the separation estimated by Van Dine and Hoffmann[7] (2.5 Å) can be estimated from the heats of formation of CH₃⁺ (262 kcal/mol; Table I, ref a) and CN⁻ (50 kcal/mol[10]) together with their electrostatic energy of attraction (−83 kcal/mol). The resulting value (229 kcal/mol) is greater than that (74 kcal/mol) for the gaseous transition state[13] by no less than 155 kcal/mol. This difference is so enormous that it could not possibly be countered by any possible errors in the data or by exchange interactions between the components at a distance of 2.5 Å. The structure predicted by Van Dine and Hoffmann for the transition state therefore seems somewhat unrealistic.

The matter is of theoretical interest since a number of other molecular rearrangements can be interpreted in terms of similar π-complex mechanisms,[3] in particular rearrangements of carbonium ions,[14] and since the existence of π complexes in which olefins act as donors to metals[4] is now well established. We have therefore reexamined the rearrangement of **1** to **2** by a more reliable MO procedure.

Theoretical Procedure

The calculations were carried out using a recently developed semiempirical SCF-MO treatment (MINDO/2[9,15]) which has been shown to give good estimates of ground-state properties. The original version suffered from several defects, in particular a tendency to overestimate dipole moments and a systematic lengthening of CH bonds by 0.1 Å. These particular deficiencies have been overcome by a minor modification[16] of the parameters, and we used these modified parameters in the calculations reported here.

(9) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 2854 (1970).

(10) Estimated from the heat of formation of CN radidal (109 kcal/mol)[11] and its electron affinity (59 kcal/mol).[12]

(11) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(12) H. O. Pritchard in "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1970, p E73.

(13) Estimated from the heat of formation of methyl isocyanide (36 kcal/mol; Table I) and the gas-phase activation energy (38 kcal/mol)[5] for **1 → 2**.

(14) M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965).

(15) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(16) (a) M. J. S. Dewar, D. H. Lo, and N. Trinajstić, submitted for publication; (b) N. Bodor, M. J. S. Dewar, and D. H. Lo, submitted for publication.

The energy of the system was calculated as a function of the CH₃-N-C bond angle θ (see **7**) and the N-C-CH₃ bond angle θ' (see **8**). For each value of θ or θ' the energy was minimized with respect to all bond lengths and all the other bond angles and dihedral angles, using a program based on the SIMPLEX algorithm,[17] written by Dr. A. Brown and modified by Dr. D. H. Lo.

Results and Discussion

Table I compares our calculated heats of formation, geometries, and dipole moments of **1** and **2** with experiment. The agreement is reasonably satisfactory and our calculated heat of reaction (−9.5 kcal/mol) is quite close to that (−14.7 kcal/mol) estimated by Benson[18] (*cf.* the heats of formation in Table I).

Figure 1 shows a plot of the calculated reaction path as a function of the reaction coordinates θ (see **7**) and θ' (see **8**). It will be seen that the reaction is predicted to involve the reversible formation of an intermediate, the main activation barrier lying between the intermediate and **2**. The calculated overall activation energy (34.3 kcal/mol) is in reasonable agreement with the experiment (38.4 kcal/mol).[5]
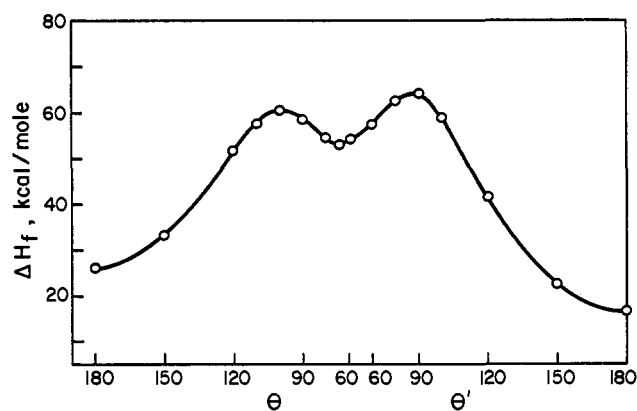

Figure 1. Plot of energy *vs.* θ and θ' (see **7** and **8**) for the conversion of **1** to **2**.

Figure 2a shows the geometry calculated for the intermediate; the methyl–carbon and methyl–nitrogen distances are quite short and the HCH bond angles (H (in plane) CH (out of plane), 105.5°; both H out of plane, 108.4°) are similar to the corresponding angles calculated for **1** (108.3°) and **2** (108.0°). This structure clearly corresponds very nicely to that expected[3,4] for the π complex **3**; it is quite different from that de-

(17) J. A. Nelder and R. Mead, *Comput. J.*, 7, 308 (1964).
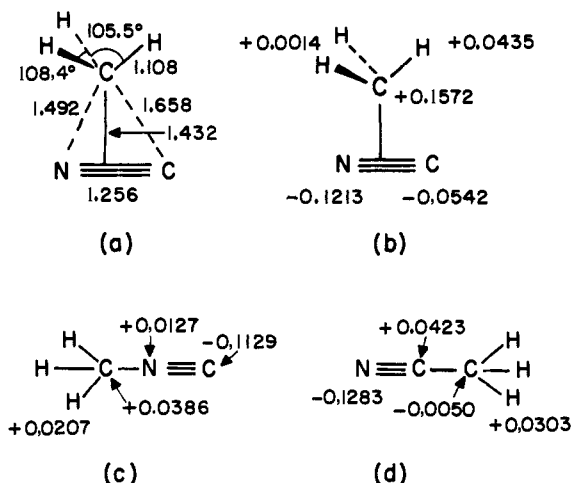
(18) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

Figure 2. (a) Calculated bond lengths (Å) and HCH bond angle in 3; (b, c, and d) calculated formal charges in 3, 1, and 2, respectively. The CH bond lengths in (a) are the same, as are the charges at H in (c) and (d).

duced[7] by Van Dine and Hoffmann for their transition state.[14]

Figures 2b–d compare calculated formal charges in the intermediate with those in 1 and 2. It will be seen that the intermediate is predicted to be little more polar than either "classical" isomer, as again would be expected for the π complex 3. In confirmation, the calculated dipole moment of 3 (2.70 D) is in fact somewhat smaller than those for 1 and 2 (Table I). Note also the preferred conformation of the methyl group in 3 (Figure 2a); this would be expected since it should maximize hyperconjugative back-coordination[4] due to overlap of the CH bond MO with the empty antibonding CN π MO. In confirmation, the calculated positive charge on the in-plane hydrogen is greater than that on either of the other two (Figure 2b).

A further interesting feature of our calculation is the prediction that the π complex 3 should revert to 1 more readily than it undergoes conversion to 2, in spite of the fact that the latter process is more exothermic. This is because 3 is predicted to be unsymmetrical, the apical methyl lying nearer nitrogen than carbon, a result in agreement with the predictions of π-complex theory[3] because the π electrons of the C≡N bond must be polarized toward nitrogen, nitrogen being more electronegative than carbon.

In the original presentation[3,4] of the π-complex theory, it was deduced that the π complex formed by a given acceptor X$^+$ with an unsymmetrical olefin should show a similar polarization. Thus the π electrons in propene would be expected to show the polarization indicated in 9 owing to the inductive effect of methyl; this is supported by the formal charges calculated by MINDO/2, indicated in 9. The propene–X$^+$ π complex should have a correspondingly distorted structure 10, X$^+$ lying nearer to the unsubstituted end of the double bond. In that case attack by a nucleophile Y$^-$ on 10 should take place at the carbon atom adjacent to methyl, both because the electron density there is lower and because the reaction then leads to a product 11 in which X has attached itself to the nearest available carbon atom. The calculations reported here for 3 support this interpretation[3,4] of the orientation of electrophilic addition to olefins, i.e., of Markovnikov's rule.
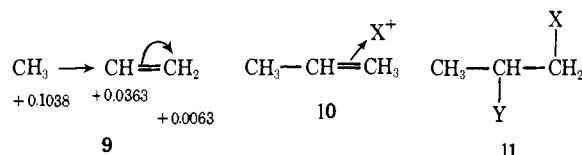
The prediction that 3 should exist as a stable intermediate is interesting in that no case has as yet been reported of a stable, neutral, metal-free organic π complex. If 3 is indeed stable, the corresponding intermediate in the rearrangement of an aryl isocyanide should be still more so,[3] particularly if the aryl group is of electron-deficient type (e.g., picryl or 4-pyrimidyl); attempts to detect such intermediates would be of interest. Indeed, it might be possible to obtain such evidence even for 3 itself.
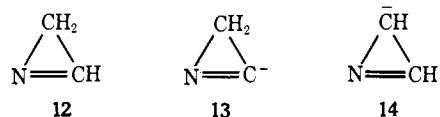
If 3 is in fact stable, the azirene 12 might undergo exchange of its methylene hydrogens for deuterium on treatment with, e.g., a mixture of a teriary amine and deuterioacetic acid, by reversible conversion to 3 via the anion 13. If such exchange were observed, it would in turn provide strong evidence for this mechanism and so for the existence of 3 as a stable species because the methylene protons in 12 should be only very weakly acidic, the corresponding anion 14 being antiaromatic.