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CNDO/2 CALCULATIONS AND ENERGY PARTITIONING IN THE FORMATION OF ACRYLONITRILE AND PROPIOLONITRILE FROM ACETYLENE AND HYDROCYANIC ACID

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Abstract—Calculations within the CNDO/2 approximation have been performed on HCN and HC≡CH oriented in a variety of ways with respect to each other. Total electronic energies and partitioned energies have been obtained which predict that an intermediate forms. Additional calculations on a variety of related configurations have also been carried out and a qualitative mechanism for the homogeneous, high temperature formation of both acrylonitrile and propiolonitrile from HCN and HCCH has been proposed.

INTRODUCTION

The formation of nitriles, particularly by convenient and inexpensive routes, is of great practical interest. For example, both adiponitrile and acrylonitrile are precursors to widely used polymeric products, and as such their production is of great concern to the chemical industry. Our interest in the physical and chemical properties of molecules containing the C≡N bond has led to the study, through quantum chemical means, of the manner in which such molecules react. Hydrocyanic acid (HCN) is the simplest uncharged, closed-shell nitrile, and in addition, one on which substantial experimental and theoretical studies have been performed. In addition, the reactions of HCN are of substantial practical utility. It is well known that the addition of HCN to acetylene over solid catalysts at 300–800°C produces acrylonitrile.[1] Numerous patents on this process exist.[2] A recent theoretical study on this reaction has been performed.[3] However, it has been pointed out by Krebaum[4] that none of the many patents mentions formation of acetylenic nitriles under any conditions but several workers concede unattractive yields of acrylonitrile in the range of 700–900° in the absence of catalysts. Krebaum demonstrates that, at 770 to 975° and in the absence of added catalysts, acetylene and hydrocyanic acid react to form propiolonitrile, acrylonitrile, cyanogen, and hydrogen. As the temperature is increased the yield of propiolonitrile increases while the yield of acrylonitrile decreases. For example, the thermal cyanation of acetylene with hydrocyanic acid produces, at 770°, yields of 2 and 22% of P and A, respectively based on C_2H_2 converted while at 900°C the yields have reversed to 31 and 21, respectively. Further, pyrolysis of acrylonitrile at 770 to 935° gave low yields of propiolonitrile, suggesting that acrylonitrile is not an intermediate in the production of propiolonitrile.

The present work was initiated in an attempt to elucidate the mechanism of the process of formation of both acrylonitrile and propiolonitrile (especially in the light of Krebaum's demonstration that the presence of a catalyst is not necessary) by means of semi-empirical quantum chemical calculations (in this case, CNDO/2 calculations[5]) and application of a technique for the partitioning of the total electronic energy.[6,7] The calculations were carried out using the original parameters with a modification to calculate energy partitioning. Both closed-shell and open-shell versions of CNDO/2 were employed.

RESULTS AND DISCUSSION

Nuclear configurations for the reactant and product molecules are given in Table 1. The notation for other configurations is given in Fig 1. Calculations were also performed on CN^-, the CN radical, the H—C≡C· radical, and acrylonitrile with one of the hydrogen atoms or the CN group removed to form a radical or an ion. In these calculations the geometry employed for the radicals or ions is that given for the parent molecule in Table 1. A complete energy surface for the interaction between hydrogen cyanide and acetylene was determined. HCN was allowed to approach HCCH with the axes of these linear molecules at various angles and distances from each other. For these calculations the molecular geometry of the two molecules was kept fixed at the values given in Table 1.

The configuration (9 of Fig 1) of the two molecules which produced the lowest total electronic energy, −34·7163 hartree,† was that in which the internuclear axis of HCN was perpendicular to that of HCCH and 2·43 bohr from it. The center of the CN bond was approximately over the center of the CC bond of acetylene. For purposes of comparison, it is recorded that the "parallel" configuration gave an energy of −34·5755 hartree.

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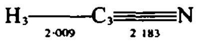
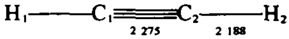
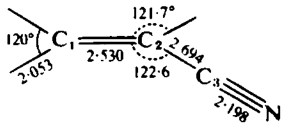
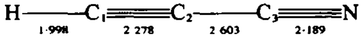
†1 hartree = 27·2097 eV = 627·709 kcal mole^{-1}.

Table 1. Nuclear configurations and labelling of atoms employed for reactants and products

Molecule	Nuclear configuration and labelling of atoms
HCN[8]	
HCCH[9]	
CH_2CHCN[10]	
CHCCCN[11]	

All bond lengths are given in bohr, where 1 bohr = 0·529 Å.

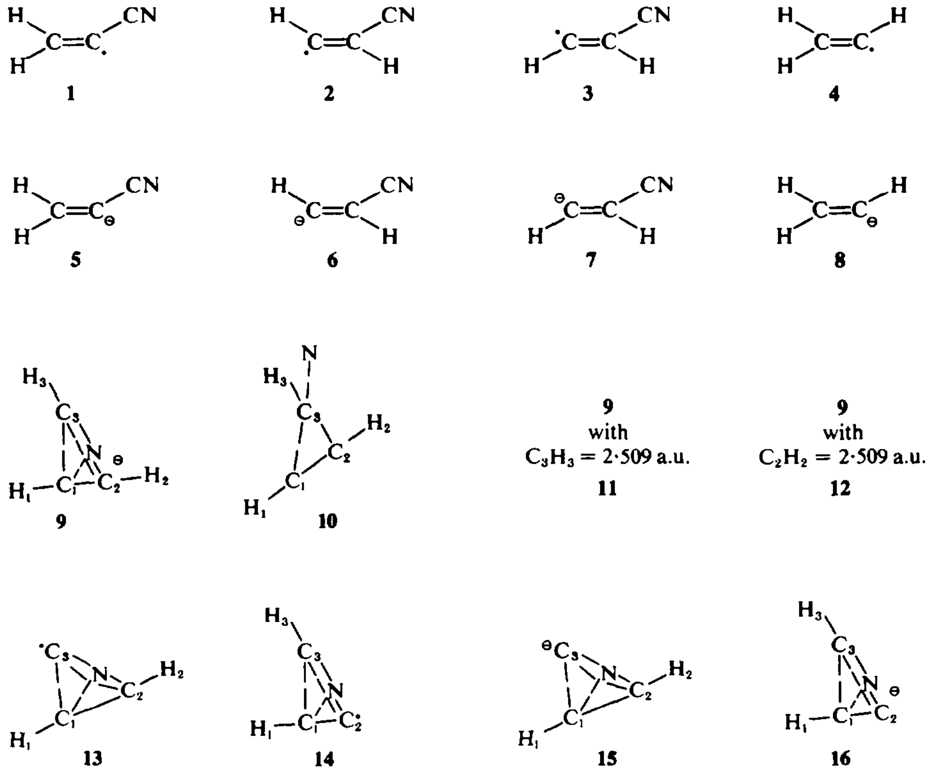


Fig 1. Nuclear configurations of intermediates.

In addition, calculations were performed on configuration **9** in which the C_3N bond is moved so that the H_3C_3N angle is 90° and the C_3N bond is perpendicular to the HCCH axis (configuration **10**, Table 2). Calculations were also performed on configuration **9** with either a H atom or a proton removed from one of two positions (configurations **13** to **16** of Fig 1) and with the C_3H_3 or C_2H_2 internuclear distances increased to 2·509 hartree.

Table 2 presents a summary of the calculated total electronic energies with their partitioned total one-center terms and two-center E^R_{AB} terms where

$$E^R_{AB} = 2 \sum_{\substack{\mu \in A \\ \nu \in B}} P_{\mu\nu} \beta^0_{\mu\nu} S_{\mu\nu}.$$

It is this latter term which has been demonstrated[6,7] to be characteristic of the particular bond con-

Table 2. Two-centre energy, E^{R}_{AB}‡

Config.	C_1C_2	C_1C_3	C_1N	C_1H_1	C_1H_2	C_1H_3	C_2C_3	C_2N	C_2H_1	C_2H_2	C_2H_3	C_3N	C_3H_1	C_3H_2	C_3H_3	NH_1	NH_2	NH_3
HCN	–	–	–	–	–	–	–	–	–	–	–	−2·3733	–	–	−0·7964	–	–	+
HCCH	−2·3984	–	–	−0·7295	–	–	–	–	–	−0·7295	–	–	–	–	–	–	–	–
CH_2CHCN	−1·7048	−0·0249	+	−0·7544	−0·0004	−0·7556	−1·3270	+	+	−0·7408	+	−2·3190	−0·0027	−0·0010	+	0	+	−0·0001
CHCCN	−2·3509	+	+	−0·7977	–	–	−1·4396	+	+	–	–	−2·3276	+	–	–	+	–	–
CN^-	–	–	–	–	–	–	–	–	–	–	–	−2·3393	–	–	–	–	–	–
CN:	–	–	–	–	–	–	–	–	–	–	–	−2·3308	–	–	–	–	–	–
HCC·	−2·3715	–	–	−0·7186	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1	−1·7442	−0·0244	+	−0·7363	–	−0·7450	−1·3612	+	−0·0084	–	+	−2·2947	−0·0025	–	+	+	–	+
2	−1·7357	−0·0418	+	−0·7401	−0·0009	–	−1·3087	+	+	−0·7297	–	−2·3174	+	−0·0057	–	0	+	–
3	−1·7438	−0·0290	+	−0·7392	−0·0109	–	−1·3168	+	+	−0·7170	–	−2·3183	−0·0022	−0·0063	–	+	+	–
4	−1·7869	–	–	−0·7330	+	−0·7448	–	–	−0·0100	−0·7416	−0·0006	–	–	–	–	–	–	–
5	−1·7217	−0·0335	+	−0·7435	–	−0·7384	−1·3537	+	–	–	+	−2·2819	−0·0033	–	+	+	–	−0·0005
6	−1·6623	−0·0283	+	−0·7283	+	–	−1·3270	+	−0·0028	0·7317	–	−2·2973	+	+	–	0	+	–
7	−1·6906	−0·0226	+	−0·7266	+	–	−1·3357	+	−0·0015	−0·7195	–	−2·2984	−0·0031	+	–	+	+	–
8	−1·8330	–	–	−0·7048	+	−0·7212	–	–	−0·0271	−0·7365	−0·0121	–	–	–	–	–	–	–
9	−1·6192	−0·7693	−0·6616	−0·7188	+	−0·0019	−0·7693	−0·6616	+	−0·7188	−0·0019	−1·5630	+	+	−0·7768	+	+	+
10A*	−2·0819	−0·8161	−0·0036	−0·7181	+	+	−0·8161	−0·0036	+	−0·7181	+	−1·9354	+	+	−0·6992	+	+	+
10B†	−1·8918	−0·9684	+	−0·9684	+	+	−0·9684	+	+	−0·7054	+	−1·7629	+	+	−0·6246	+	+	+
11	−1·6184	−0·7775	−0·6592	−0·7187	+	+	−0·7775	−0·6592	+	−0·7187	+	−1·5609	+	+	−0·5983	+	+	+
12	−1·6195	−0·7682	−0·6613	−0·7184	+	+	−0·7774	−0·6625	+	−0·6033	+	−1·5618	+	+	−0·7768	+	+	+
13	−1·6770	−0·7693	−0·6456	−0·7169	+	–	−0·7315	−0·6456	+	−0·7169	–	−1·6884	−0·0018	−0·0018	–	+	+	–
14	−1·7132	−0·7315	−0·6476	−0·7156	–	−0·0011	−0·7278	−0·6231	+	–	−0·0033	−1·6423	−0·0016	–	−0·7748	+	–	+
15	−1·5296	−0·7730	−0·6581	−0·7078	+	–	−0·7730	−0·6581	+	−0·7098	–	−1·6070	+	+	–	+	+	–
16	−1·6324	−0·7706	−0·6566	−0·7055	–	+	−0·7692	−0·6456	+	–	−0·0003	−1·4935	+	–	−0·7714	+	–	+

***10A** refers to configuration **10** of Fig 1.

†**10B** refers to configuration **10** with H_1 and H_2 placed so that that angles formed by $H_1C_1C_2$ and $C_1C_2H_2$ are both 120°.

‡Entries containing only a − sign indicate that the pair of atoms does not exist in the molecule, while a + sign refers to an antibonding interaction between the specified pair of atoms.

sidered. As has been mentioned, the configuration (containing HCN and HCCH) for which the lowest energy is produced is that in which these two molecules have a perpendicular orientation. It is interesting to note that the total electronic energy of this configuration **9** is lower than the sum of those of HCN and HCCH. Hence, it seems not unreasonable to suggest that a structure resembling that of configuration **9** may form. Of course its lifetime may be very short. It may also be noted that acrylonitrile has a somewhat lower energy than **9**.

It is of interest to examine the two-center E^R_{AB} terms for **9**. $-E^R_{AB}$ for both the pairs C_1C_2 and C_3N is shown to be much smaller than that found with the individual molecules HCCH and HCN, thus suggesting a weakening of these bonds. However, the corresponding values for C_1C_3, C_1N, C_2C_3 and C_2N, the pairs involved with the linking of HCN and HCCH together, are increased from zero to significant quantities. Although $-E^R_{AB}$ is a function of bond length, it has been shown[6,7] that values for C—C and C—N lie in the region of 1·0 to 1·5. Hence values given in Table 2 for the pairs of atoms linking HCN and HCCH reflect bonding equivalent to somewhat less than a classical single bond.

At the high temperatures considered by Krebaum[4] it is not unreasonable to suggest that configuration 9 may pass through a number of different vibrational variations, one of which is labelled configuration **10A**. Here there are essentially only two atom-pair linkages between the reactant molecules, namely C_1C_3 and C_2C_3. Both of these reflect, in their E^R_{AB} values, somewhat stronger binding than found for the corresponding pairs in **9**.

In order to provide some hypothesis as to the next step in the mechanism it is of value to consider the various possibilities at temperatures of 770 to 975°. Let us assume that **9** and its vibrationally distorted form **10** may exist as metastable intermediates. At such high temperatures the most likely occurrence presumably is that of the intermediate "decomposing" to form the two reactant molecules. This may account for the relatively low conversions found by Krebaum[4] at 720°. There is also the possibility that one of the bonds (other than those linking HCN and HCCH to each other) might break. As evidenced by the sizes of the E^R_{AB} terms, considerable bonding energy still exists in the C_3N_3 and C_1C_2 terms. In addition each of the atoms, C_1, C_2, C_3, and N_3, is apparently bonded to more than one other in this list, thus providing further reason for suggesting that the C_3N_3 and C_2C_1 pairs are less likely to break. If such arguments are valid, configuration **9** is more probable than **10**, as further evidenced by the total electronic energies. Further, it then appears possible that a C—H bond scission might occur. On the basis of the similarity between E^R_{CH} values for the various C—H bonds it appears reasonable to suggest that breaking of these is approximately equally probable.

Calculations were performed on configurations **13** to **16** to examine the effect of removing either an H atom or a proton from either the C_2 or C_3 position. The results suggest that the radical forms are more stable (the presence of an additional electron in the ionic forms must be kept in mind) than the ionic configurations, while the E^R_{AB} values for a given directly bonded pair vary little from one form to the other.

It thus appears possible to consider the mechanism for the formation of acrylonitrile and propiolonitrile in the following manner. HCN and HCCH react to form the metastable intermediate (**9**) which can, of course, revert to the reactants at high temperatures or alternatively, perhaps through a vibrationally excited form of **9**, such as **10**, form unstable radicals such as **13** and **14** by loss of a hydrogen atom. These configurations may then be converted to one or more of configurations **1**, **2** and **3** from which acrylonitrile can form on addition of a hydrogen atom. Alternatively either configurations **13** and **14** or configurations **1**, **2**, **3** may lose a second hydrogen atom and be converted to propiolonitrile.

The present mechanism supports the contention of Krebaum[4] that acrylonitrile is not an intermediate in the formation of propiolonitrile. In addition, the conventional mechanism involving the formation of H atoms from HCN and the subsequent attack of such radicals on the triple CC bond appears to be less favourable than the preliminary formation of the intermediate **9** of lower total electronic energy followed by loss of one or more H atoms. Since the intermediate **9** is predicted to form spontaneously from the reactants, and the configurations **1**, **2** and **3** form from **13** or **14** with relatively little change in energy, the activation energy for the overall reaction presumably is encountered in the passage of **9** to **13** to **14** and is estimated to be approximately 200 kcal $mole^{-1}$. Finally, the nature of the assumptions involved in this work should be emphasized. The method employed involves semi-empirical solutions of the electronic part of the Schrödinger equation after application of the Born-Oppenheimer approximation. Hence only electronic energies are considered and no account is taken of the influence of the temperatures of 700 to 900°, on the "nuclear" energies, such as those associated with translation and rotation. Further the present method considers only the encounter between two isolated molecules, each in their electronic ground states. Although it may be argued that the greater part of energy changes in a reaction probably are electronic in nature, nevertheless only semi-quantitative or qualitative significance may be attached to the present results.

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