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Energy-Conformation Studies of HCN, HNC and CN^-: A Comparison of Results from EH–SCC and SCF Molecular Orbital Calculations

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We have made an Extended Hückel Self Consistent Charge (EH–SCC) molecular orbital calculation for hydrogen cyanide, hydrogen isocyanide and cyanide ion. The main purpose of this calculation was to compare the EH–SCC and the more accurate SCF MO calculations for HCN in order to evaluate the method we used here for future use. Specifically, we have calculated and compared the following properties of HCN: total energy, binding energy, variation of ground state energy with geometric conformation, ionization potential and dipole moment. In addition, we have extended previous calculations of HCN by also considering its energy variation with bond angle for two excited state configurations and deducing some of the characteristics of its electronic spectra. Finally we have also made an MO calculation of the isocyanide isomer HNC and CN^- ion to compare with and add to the known characterization of the H, C, N, system.

Rechnungen nach der erweiterten Hückeltheorie werden für HCN, HNC und CN^- durchgeführt und mit *ab initio* Resultaten verglichen. Im einzelnen wurden Gesamtenergie, Bindungsenergie in Abhängigkeit von der geometrischen Struktur, Ionisierungspotential und Dipolmoment von HCN berechnet und außerdem die Energie für zwei doppelt angeregte Konfigurationen in Abhängigkeit vom Bindungswinkel bestimmt. Darüber hinaus sind MO-Rechnungen für HNC und CN^- gemacht worden.

1. Introduction and Background

Many important properties of HCN such as its total binding energy [1, 2], dissociation energies [1, 2], ionization potential [2, 3], dipole moment [4] and electronic spectra [5] have been extensively studied and are well characterized experimentally. In addition, several accurate ab initio molecular orbital calculations have been reported [6–8], which yield excellent ground state total energies, verify some of the above mentioned experimentally determined properties and calculate others such as electric polarizability and quadrople moments. In one of these studies, [8] the variation of total energy of HCN as a function of bond angle was determined, resulting in the correct prediction of a linear ground state molecule. Why, then, another theoretical Calculation at this time? In answer to this question, we shall briefly discuss the aims of the present calculation.

We have recently been using a semi-empirical one electron model for molecular orbital calculations, the Extended Hückel Self Consistent Charge method (EH–SCC) to study a series of polymers of HCN, namely the dimer [9a, b], trimer and tetramer, and other related nitriles, amines and imines. These molecules are all possible precursors in the abiotic syntheses of biologically interesting molecules such as purines, proteins and amino acids under simulated primitive earth conditions [10–13]. Beside HCN, none of the remaining molecules in our proposed series have been treated by the more exact molecular orbital methods. Thus, before continuing with out planned use of the EH–SCC MO method, we wished to test its validity by comparing the results obtained from it with the results obtained from the more exact calculations for HCN on the one hand and from experimental results on the other. The main purpose of the present study then, is just such a calibration of the EH–SCC MO method, i.e., a determination of its area of useful application and its limitations.

The EH method was first applied to the study of transition metal complexes [14]. It has since been used for the study of a variety of different molecules [15], for example, a series of methylene compounds [15a], carbonium ions [15b] metal porphyrins [15c, d] and purines and pyrimidines [15e]. The details of this method have therefore been described elsewhere [16, 15b, c] and we shall not repeat them here. The method is characterized by the use of a semi-empirical, one electron, effective molecular Hamiltonian in which one electron energy matrix elements between atomic orbitals are estimated from the ionization potential of these orbitals. In the version of this model which we use here, we include all valence orbitals and electrons, one Slater type function is used for each orbital [STO], and all overlaps between atomic orbitals are calculated. In addition, we use a charge iteration scheme [15c] to successively diagonalize the energy-overlap matrix until the input and output charge distribution agree to a stipulated consistency. This self-consistent charge aspect is a way of including some electron correlation in this essentially one electron model.

The results of such a diagonalization represent the interaction of all the valence electrons in the nuclear framework chosen. A set of molecular orbitals, all of which are linear combinations of the original valence atomic orbitals, are obtained which gives the distribution of electrons in the molecule, together with a corresponding set of one electron molecular orbital energies. The sum of these energies, for all occupied orbitals is the valence configuration energy of the molecule. This is only part of the total electronic energy which can be calculated with this model. The energy of the individual orbitals depends somewhat on the way in which they are filled. Specifying the occupancy specifies a configuration. Differences in configuration energies allow the approximate determination of electronic spectra. The energy of the highest filled orbital is an estimate of the first ionization potential of a given configuration. Finally, a determination of the net charge on each atom allows the calculation of a molecular dipole moment.

Specifically then, in this study we have used the EH–SCC model to calculate compare and discuss the following properties of HCN: its total energy, binding energy, the variation of its ground state energies with geometric conformation, its first ionization potential and dipole moment. In addition we have extended the results of previous HCN calculations by also considering its energy variation with bond angle for two excited configurations and deducing some of the characteristics of its electronic spectra. A further extension is that in addition to the HCN calculation, we also present a study of the isocyanide isomer HNC and the cyanide ion CN^-.

2. Total Molecular Energies

The accurate molecular orbital calculations made for HCN are based on a Hartree Fock Self Consistent Field procedure for the solution of the Schroedinger Equation with the exact spin independent molecular Hamiltonian. Variations within this framework include the choice of atomic orbital functions and the number of such functions chosen to represent each orbital. In 1962, McLean published an LCAO–SCF calculation for HCN [6], with what is called a limited basis set of functions, i.e., one for each atomic orbital included. He used a Slater type orbital (STO) for each of the 14 atomic orbitals of HCN with modified best-atom values for the orbital exponents. The exact Hamiltonian was used and numerical calculation made of exact energy and overlap matrix elements. In 1966, McLean and Yoshimine repeated the HCN calculation varying their earlier one in two ways [7]. They used an extended STO basis set i.e. more than one such function for each atomic orbital, in one calculation and a different type of basis set, called the double zeta function, in another. In 1967, Pan and Allen [8] made an LCAO–SCF calculation of HCN using still two different types of basis set functions: Gaussian and "Adjusted Gaussian" functions. One of the objects of all these calculations was to obtain a good ground state energy for the linear singlet HCN molecule. The value of the total energies obtained from these five SCF–LCAO calculations are given in Table 1. From a best ground state energy criteria alone, then, the extended STO SCF calculation appears to be the most accurate. Let us now compare these total energies with that calculated from the EH–SCC MO method.

The total energies calculated above can be written as a sum of 4 terms:

$$E_T = \sum_{i}^{\text{val}} \varepsilon_i(mo) + \sum_{i}^{\text{core}} \varepsilon_i(mo) = E_{ee} + E_{nn} \tag{1}$$

where the first term is the valence electron configuration energy, the second the core electron configuration energy, the third the electron correlation energy and the fourth the nuclear repulsion energy.

To see the relative magnitudes of the contribution of each term to the total energy, the results of the 1962 McLean Calculation can be written as follows:

$$E_T = -7.249 \quad -54.3358 \quad -55.1484 \quad +23.8762 \tag{2}$$

Table 1. *Total molecular energies and binding energies of* HCN *from different* MO *calculations*

	McLean [6]	Yoshimine and McLean [7]		Pan and Allen [8]		EH–SCC	Experiment
	L.S–STO	Extended STO	Double ζ	Gaussian	Adj. Gaussian	LS–STO	
E_T	−92.5474 au	−92.9147 au	92.8369 au	−92.6713 au	−92.8286 au	−7.0 au	
BE	4.2 eV[a]	9.12 eV	—	2.82 eV	7.10 eV	20.2 eV	13.52 eV

[a] 1 a.u. = 27.2 eV.

with the terms written in the same order as in Eq. (1). By comparing expression (1) and (2), we see that the valence configuration energy is by far the smallest part of the total energy. It is this electronic energy alone which the EH–SCC model allows us to calculate. Thus we cannot expect our one electron molecular orbital model to give us total molecular energies.

We can however, compare the value we obtain for the first term from the EH–SCC MO method, with the value from the SCF MO calculation. In our EH–SCC calculation, we used the same basis set of functions that McLean did in his 1962 calculation; STO's with best atomic orbital exponents but only include the valence orbitals. However, we do not, as he did, actually calculate energy matrix using the exact molecular Hamiltonian. Instead, as we have mentioned above, an empirical evaluation of one electron energy matrix element is made and the orbital functions used only to calculate overlap integrals. For a linear HCN molecule, with $r_{CH} = 1.152$, and a totally paired configuration, we obtain a value of 7.0 a.u. for term 1 in expression (1) compared to the SCF value of -7.25. Thus we see that while we calculate only this small part of the total energy, and by a very different process than the more exact molecular orbital calculations do, we obtain reasonable agreement with them using the same set functions. There has even been some suggestion [15b] that the EH–SCC method leads to somewhat more accurate values of single molecular orbital energies, being designed as it is to optimize these energies. The question remains as to what use can be made of these small pieces of the total molecular energies. As we shall see in the next two sections, they can be used to determine approximate values of total binding energies and more importantly to determine the most stable molecular conformations.

3. Binding Energies

Of more chemical interest than total molecular energy is the binding energy of a molecule i.e. the small difference between the total molecular energy and the combined energies of the separated atoms of the molecule. This difference is usually $< 1\%$ of the total molecular energy. Thus, to obtain binding energies, very accurate MO calculations and analagous AO energy calculations are usually performed. The same method is used for each calculation with the hope that the uncertainties in each will cancel and provide reasonable values for the binding energies. Just how much this hope is realized for the previous SCF MO calculations of HCN may be seen in Table 1, where the total binding energies calculated from the four MO studies as well as the experimental value are given. We see from this table that all four HCN calculations yield low values of the total binding energy. The best result of 9.12 eV is obtained from an extrapolation to the Hartree-Fock limit of Yoshimine and McLean's best total energy [7]. It is 30% too low while the worst results give only 25% of the total binding energy, indicating the elaborateness of the MO calculation needed to obtain good binding energies.

We may use the results of the simpler McLean calculation of the binding energy [6] to see how each of the four energy terms contribute to it. Below is a term for term comparison of the molecular energy and sum of the atomic energies of H, C and N.

$$E_T = -7.249 \quad -54.3358 \quad -54.8384 \quad +23.8762 \tag{3}$$

$$\sum E_A = -6.124 \quad -53.9198 \quad -32.3160 = 0.0 \tag{4}$$

$$BE = -1.125 \quad -0.3860 \quad -22.5224 \quad +23.8762 \tag{3–4}$$

$$BE = \Delta E_1 \quad + \Delta E_2 \quad + \Delta E_3 \quad + \Delta E_4$$

$$BE = 0.156 \text{ a.u.} = 4.2 \text{ eV}.$$

Several interesting observations can be made from the results of this tabulation. The per cent change in core electron energy ΔE_2 in molecule formation is $< 1\%$ while the change in valence electron energy ΔE_1 is 17%, thus verifying that the outer electrons are more perturbed in bonding. The main contribution by far to the additional stabilization of the molecule comes from the non-classical electron correlation or exchange term ΔE_3. However, it may also be seen that this contribution is balanced by the added nuclear repulsion term ΔE_4 which does not exist for the separated atoms. Thus the difference between these two largest terms, each of which is 50 × greater than the one electron stabilization energies, makes a net contribution to the binding energy $\Delta E_4 - \Delta E_3 = 1.354$ eV of the same order of magnitude as ΔE_1 and ΔE_2. The *BE* obtained from this MO calculation is only 1/3 of the experimental value.

The valence state configuration energy term alone will be a good approximation to the binding energy in so far as the sum of three remaining terms $\Delta E_2 + \Delta E_3 + \Delta E_4$ cancel, which could occur in some molecules. In the case of HCN, if only the difference in valence electron configuration energy ΔE_1 were used it would yield a value of the binding energy for HCN about twice that observed. This is better than the *BE* obtained from total energy differences in this and the two Pan and Allen results [8]. However, from the EH–SCC MO we do not obtain the same numerical value for ΔE_1 as in the SCF method. This is because our estimate of the valence molecular configuration energy is different. Also, we obtain atomic energies empirically from the valence state ionization potentials of the atomic orbitals. For linear HCN in its ground state configuration we obtain as our approximation to the binding energy:

$$BE \cong \Delta E_1 = 182.4 - 162.2 = 20.2 \text{ eV}.$$

while this value is 50% higher than the experimental value it is as accurate an estimate on the high side as all but the most accurate MO calculations [7] are on the low side. Thus we may draw two conclusions from this analysis of calculated molecular binding energies. One is that the simple one electron EH–SCC model, with the above reservations, does give some indication of at least the order of magnitude of dissociation energies. In addition, it is quite difficult for even the more accurate MO calculations to obtain accurate binding energies. Therefore, the calculation of more accurate binding energies alone should not be the main reason for doing more accurate molecular orbital calculations, unless one can proceed to the ultimate in sophisticated numerical molecular orbital procedures for the molecule under consideration. So far this is possible only for a limited number of molecules.

4. Variation of Energy with Molecular Geometry: HCN Ground State

We should like very much to use the valence molecular configuration energies calculated from the EH–SCC MO method, to study the relative stabilities of various geometric conformations of a given molecule. We were therefore quite interested by the analysis made by Pan and Allen [8] of both the total energy and valence configuration energy variation as a function of the HCN bond angle in its ground state configuration. From the variation in the total energy, they were successful in predicting a linear ground state molecule in agreement with observation, although the variation was only 0.54 eV as the bond angle varied from 140° to 180°. However, from the variation of the value $\sum_i^{\text{val}} \varepsilon_i$ (MO) only with angle, they find the opposite trend i.e. the molecule is somewhat less stable in the linear form. This small part in the total energy however appears to be extremely insensitive to bond angle variation, changing only by 0.09 eV. Thus for HCN, both the total energy and the valence configuration energy calculated as a part of it by Pan and Allen, are quite insensitive to bond angle variation with one barely predicting a linear ground state and the other even more marginally predicting a bent state. Thus they find that HCN is indeed a "borderline" case as predicted earlier by Walsh from his "rules" i.e. correlations of empirically determined variation of valence configuration energies with bond angle in linear triatomic molecules [17a]. On the basis of his rules, Walsh predicted that triatomic molecules HAB containing 10 or less valence electrons should be linear in their ground state while those with > 10 should be bent [17b]. Thus HCN is a borderline linear molecule both by Walsh's criteria and by the more elaborate MO calculation of total energy variation with angle.

Using the EH–SCC MO model, the calculation of the valence configuration energies is not the same as when it is part of an SCF MO calculation like that of Pan and Allen, nor is it as empirical as the original basis for the Walsh correlations. The results of our calculation of valence configuration energies for three bond angles for the ground state configuration of HCN is given in Table 2a, along with the analogous variations obtained by Pan and Allen. We see immediately from the total valence configuration energies in this table that our results predict a linear ground state and that the variation of configuration energy with

Table 2a. *Energy variation of ground state configuration of* HCN *with geometry*

$r_{\text{CH, NC}}$	Bond angle	$\sum_i^{\text{val}} E_i$(MO) (eV)	E_{σ_1} (eV)	E_{σ_2} (eV)	E_{π_x} (eV)	E_{π_y} (eV)	E_{σ_3} (eV)
exp.	140 SCF	−206.873	−35.158	−21.787	−14.96	−14.78	−16.728
exp.	120 EH	−179.2	−28.846	−19.380	−14.674	−14.179	−12.52
exp.	150 SCF	−206.829	−34.854	−21.896	−14.919	−14.816	−16.727
exp.	150 EH	−181.4	−28.89	−20.03	−14.44	−14.48	−13.06
exp.	180 SCF	−206.785	−34.753	−22.034	−14.848	−14.848	−16.703
exp.	180 EH	−182.4	−29.04	−20.15	−14.41	−14.41	−13.20
longer	180 EH	−180.0	−28.31	−20.31	−13.93	−13.93	−13.50

angle from 120° to 180° is 3.2 eV; much greater than the opposite variation of 0.09 eV from the Pan and Allen results. Comparing the behavior of the individual molecular orbitals with bond angle bending, we see that the lowest energy orbital σ_1, and the highest, σ_3, are both destabilized in our calculation, but are stabilized with bending in the Pan and Allen calculation, while the other three orbitals have the same qualitative behavior in both cases. It was these same two orbital energies, σ_1, and σ_3, that Walsh also found to be destabilized with bending and which led him also to the prediction of a linear HCN ground state.

Having established reasonable behavior of the ground state configuration energy with bond angle, we wished to further test its sensitivity by varying the bond lengths. We therefore, used somewhat longer bond distances as determined for an excited state of HCN from its spectra [5], and recalculated the energy of the linear, ground state configuration. The results are also given in Table 2a. We see that the total mo energy is 2.4 eV less stable than for the known equilibrium bond distances. Once again the valence state configuration energies calculated from the EH–SCC model were able to distinguish the correct nuclear geometry. In a subsequent analysis in the same paper [8], Pan and Allen show that, contrary to the results they obtained with HCN, the valence configuration energy variation with molecular conformation does in general follow that of the total energy and that indeed the conditions imposed by a Hartree Fock solution for molecular energies assures this parallel behavior except for highly polar molecules. It may be then that the EH–SCC method as we have already mentioned is particularly suited for obtaining good single molecular orbital energies. Thus, their general analysis of the validity of using configuration energy instead of total energy variations, and the fact that our determination of the configuration energies led to the correct results for HCN, strongly indicate that we may proceed to study relative stabilities of various conformations of molecules using the EH–SCC MO method.

5. Excited States of HCN: Conformations and Electronic Energies

Using the EH–SCC MO procedure we have calculated the configuration energy as a function of bond angle for two excited state configurations of HCN. From Table 2a, it may be seen that the ground state configuration we obtain for the linear molecule is: $(\sigma_1)^2\,(\sigma_2)^2\,(\pi_1)^4\,(\sigma_3)^2$. The highest filled orbital is essentially a non-bonding nitrile nitrogen orbital and the two π orbitals are degenerate in the linear molecule. The two excited state configurations chosen for study were as follows:

$$(1)\quad (\sigma_1)^2\,(\sigma_2)^2\,(\pi_1)^4\,(\sigma_3)\,(\pi_2^*)\qquad n\rightarrow\pi^*\,,$$

$$(2)\quad (\sigma_1)^2\,(\sigma_2)^2\,(\pi_1)^2\,(\pi_1)^1\,(\sigma_3)^2\,(\pi_2^*)\qquad \pi\rightarrow\pi^*\,.$$

The first excited state configuration corresponds, to an $n-\pi^*$ transition while the second corresponds to a $\pi-\pi^*$ transition. From experiments, it is known that the first excited state of HCN is bent with an angle of about 125° and slightly longer bond distances than in the ground state i.e. $r_{\mathrm{CH}} = 1.14$ and $r_{\mathrm{CN}} = 1.297$ Å. Using these bond distances, we have calculated the configuration energy variation

Table 2b. *Energy variation of excited state configuration 1:* $(\sigma_1)^2\,(\sigma_2)^2\,(\pi_x)^2\,(\pi_{1_y})^2\,(\sigma_3)\,(\pi_{2_x})$

Bond angle	$\sum_i^{\text{val}} E_i(\text{MO})$ (eV)	E_{σ_1}	E_{σ_2}	$E_{\pi_{1x}}$	$E_{\pi_{1y}}$	E_{σ_3}	$E_{\pi_{2x}}$
120	−175.32	−28.32	−19.61	−14.59	−13.96	−13.08	−9.28
150	−174.67	−28.30	−19.94	−14.29	−13.96	−13.42	−8.77
180	−173.28	−28.11	−20.05	−13.78	−13.78	−13.61	−8.23

Table 2c. *Energy variation of excited configuration 2:* $(\sigma_1)^2\,(\sigma_2)^2\,(\pi_1)^2\,(\pi_1\,1)^1\,(\sigma_3)^2\,(\pi_2)$

Bond angle	$\sum_i^{\text{val}} E_i(\text{MO})$ (eV)	E_{σ_1}	E_{σ_2}	$E_{\pi_{1x}}$	$E_{\pi_{1y}}$	E_{σ_3}	$E_{\pi_{2x}}$
120	−174.56	−28.35	−19.72	−14.59	−13.95	−12.98	−9.31
150	−175.01	−28.36	−20.09	−14.32	−14.00	−13.32	−8.85
180	−174.71	−28.33	−20.30	−13.95	−13.95	−13.56	−8.42

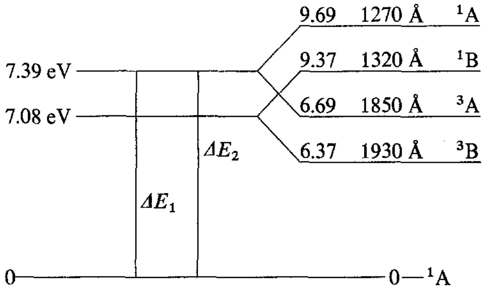

Fig. 1. Calculated electronic energy levels of HCN

of these configurations as a function of bond angle. Table 2b and 2c give the results of these calculations. We see from these tables that configuration 1 ($n \to \pi^*$) is most stable at an angle of 120° in excellent agreement with experiment. The energy of configuration 2, ($\pi \to \pi^*$) appears to be much less sensitive to angle variation and more marginally predicts an angle of 150°. We may also see from these tables how the individual MO energies vary with bond angle for each configuration and that the two orbitals which are degenerate in the linear molecule separate in energy as it is bent. An estimate of the electronic transition energies may be obtained from the configuration energies listed in Table 2a, b, c. Using the lowest conformation energy for each configuration we obtain:

$$\Delta E_{1\,0}(n \to \pi^*) = E_1(120°) - E_0(180°) = 182.4 - 173.32 = 7.08\ eV,$$

$$\Delta E_{2\,0}(\pi \to \pi^*) = E\ \ (150°) - E_0(180°) = 182.4 - 175.01 = 7.39\ eV$$

where subscripts refer to the ground state, first and second excited state configurations and the bond angles are given in parenthesis. These energy differences are shown schematically in Fig. 1.

These are, however, configuration energy differences only. Each excited state configuration gives rise to two total states of the system, a singlet and triplet state. This is also shown schematically in Fig. 1. The energy separation between states of the same configuration is due to electron repulsion and is of the order of several eV, with the triplet state usually lying lower. The configuration energy is presumed to be the weighted average of the energy of all states arising from it. We have corrected the total state energies for an electron repulsion energy separation of 3 eV ± 1. As seen in Fig. 1, we obtain a series of 4 possible electronic transition energies all above 2000 Å with the lower energy transitions being singlet-triplet spin forbidden. These results are in good agreement with the general aspects of the experimental spectra obtained for HCN [5]. There are no absorption bands below 2000 Å, between 1700 – 2000 there is very weak absorption, between 1350 – 1550 there is weak and sharp absorption and at wave lengths shorter than 1120 extremely strong and diffuse absorption.

6. Ionization Potential and Dipole Moment of HCN

Table 3 gives the ionization potential and dipole moment determined for the linear ground state HCN molecule from the previous SCF calculations and from the present EH–SCC calculation. The lowest ionization potential is the energy of the highest filled MO of the ground state. In our calculations this highest filled MO is a non-bonding nitrile nitrogen σ orbital, while in the SCF calculations the highest filled MO's are the degenerate nitrile π bonding orbitals as also indicated in Table 3. We have listed two values of the lowest ionization potentials for each type of calculation. We see from the Table that both SCF calculations with the STO basis sets yielded the same value of ionization potential in good agreement with experiment [4]. One of the Pan and Allen calculations also let to a good value, while the other gave a value about 15 % too high. In our calculation we obtain a value about 4% too low. If however we vary the input values of atomic orbital ionization potentials we can exactly reproduce the observed ionization potential. We have done this latter variation, mainly as an exercise to determine the sensitivity of the values obtained to one of our most crucial input parameter, the ionization potentials of the atomic orbitals.

All the molecular orbital calculations allow the determination of the dipole moment of the molecule. In the SCF method these are calculated as the expectation value of the dipole moment operator for the ground state. Our program calculates

Table 3. *Ionization potential and dipole moment of* HCN

Source of value	IP (eV)	D.M(B.M.)	Highest filled MO	Atomic charge distribution		
				H	C	N
Experimental	13.56–13.92	2.986				
McLean [6]	13.8	1.54	π	0.08	−0.16	−0.08
McLean-Yoshimine [7]	13.8	3.29	π			
Pan and Allen [8] (Gauss)	15.81	2.72	π			
Pan and Allen [8] (Adj. Gauss)	13.69	3.36	π			
EH–SCC	13.20	1.77	$\sigma(nb)$	0.14	0.03	−0.17
EH–SCC (vary α^a)	13.92	2.72	$\sigma(nb)$	0.10	0.29	−0.39

[a] α = Atomic orbital energy.

the net charge on each atom from a Mullikan Population analysis [18] of the filled MO's. From this charge and the known position of the atoms, the classical expression for dipole moment is used to determine the dipole moment.

We see from the results listed that the simpler McLean calculation gives a less accurate dipole moment than ours, but that all the other SCF calculations are better. However, the same EH–SCC calculation, varying input atomic orbital energies which gave good agreement for the ionization potential also gives very good agreement with the measured dipole moment. Thus our model does contain the possibility of obtaining reasonable to good ionization potentials and dipole moments. The charge distribution corresponding to the two values of dipole moment we obtain, and those from McLean's simpler calculations are given in the last column of Table 3.

7. Dissociation of HCN: The CN Ion

We have made an EH–SCC MO calculation of the behavior of linear HCN as the H–C bond length increases from its normal value to 6 times normal. At this distance, the H no longer interacts with the CN entity and the bond appears to cleave heterolytically into H^+ and CN^- ions. The negative charge appears to be evenly distributed on the C and N atoms with no non-bonding orbitals on either one.

Our calculated ionization potential for the CN^- ion is -12.96 eV, which is then our estimate of the electron affinity of the CN radical. Since it is only slightly less than the ionization potential of the H atom i.e. 13.59 eV, our results indicate that there would not be much energy difference between the heterolytic and homolytic dissociation energy of H–CN. From our calculated results, we can determine the heterolytic dissociation energy in two different ways. An estimate of this quantity can be determined directly by comparing the total electronic configuration energy of HCN and of the $H^+ + CN^-$ systems:

$$D_0(H^+ - CN^-) = E_T(HCN) - E_T(H^+ + CN^-) = -182.4 + 188.4 = 5.8 \text{ eV}.$$

This value is somewhat greater than the several experimentally determined values of the homolytic dissociation energy: 5.50 eV [1a] and 5.17 eV [2]. We can also use this experimental value together with our predicted value of electron affinity of CN^- and the known ionization of H atom to obtain another estimate of the heterolytic dissociation energy:

$$\begin{array}{lll}
(1) & HCN \rightleftarrows H + CN & D_0(\text{exp}) = 5.41 \text{ eV}, \\
(2) & H \rightarrow H^+ + e & IP(\text{exp}) = 13.59 \text{ eV}, \\
(3) & CN + e \rightarrow CN^- & EA(\text{CALC}) = -12.96 \text{ eV} \\
\hline
 & HCN \rightleftarrows H^+ + CN^- & D_0 = 6.04 \text{ eV}.
\end{array}$$

Thus our directly calculated value of D_0 and the one obtained from our calculated value of electron affinity of CN and experimental values of homolytic dissociation agree quite well, indicating internal consistency in our calculations.

Recently [1b], however, there has been an experimental determination of the heterolytic bond dissociation energy $D_0(H^+ - CN^-)$ from an analysis of the mass spectrum obtained by photoionization of HCN. The value determined from this analysis which involves several experimental steps and assumptions about other thermodynamic quantities is 15.18 eV. This is more than twice the value we determine and corresponds to an ionization potential of 3.82 for the CN ion. In another recent publication [19], the ionization potential of CN^- is given as 6.05 eV. Thus it appears that uncertainties in both experimental and theoretical procedures have only established a range of values for the ionization potential of CN^- and the heterolytic dissociation energy of H–CN.

8. Hydrogen Isocyanide: An Alternate Isomer

Though HNC has never been isolated, we thought it would be of interest to calculate some of its characteristics, to compare with HCN on the one hand and also as the parent compound of a series of more stable alkyl isocyanides. These compounds are of special interest because they are part of a class of reactive carbene compounds with anomalous carbon atom bonding. We have thus calculated the valence configuration energy as a function of bond angle for the ground state of HNC, using a value of $r_{CN} = 1.16$ Å found in methyl isocyanides and $r_{NH} = 0.96$ Å. The results are presented in Table 4, along with the variation in binding energy, the ionization potential, dipole moment and promotion energy to the lowest empty orbital for each conformation. The energy of the highest filled orbital is stabilized as the angle increases as may be seen from the values of the ionization potentials given in column 4. The result of this and the other individual orbital energy variations is that, as can be seen from column 2 of Table 4, we predict a linear ground state for the HNC molecule. While HNC has never been isolated, a structural determination has been made for isolated CH_3CN [20]. It has a linear $C{-}N{\equiv}C$ conformation in accord with our prediction of a linear HNC molecule. The magnitude of the dipole moment does not vary very much with angle, though its direction changes. The energy values listed in the last column represent approximations to the $n \rightarrow \pi^*$ transition for this molecule. They are the promotion energies from a σ_3 to a π_2 orbital in the ground state configuration. In Table 4 is also presented for comparison our results for the linear ground state HCN molecule. We see that our calculation predicts that this isomer is more stable than the isocyanide by 4.2 eV if we compared the difference in valence configuration energies or by 2.0 eV from the difference in their binding energies obtained from our calculation. Thus for the equilibrium:

$$\mathrm{HCN} \rightleftarrows \mathrm{HNC} \quad \Delta E \cong 2-4\ \mathrm{eV} \cong 50-100\ \mathrm{Kcal/mole}$$

Table 4. *Comparison of linear and bent* HNC

	E_T (eV)	BE(eV)	IP(eV)	DM(BM)	ΔE_1 (eV)	H	C	N
HNC(180)	−178.03	18.2	−12.55	1.58	5.9	0.22	−0.11	−0.12
HNC(150)	−177.0	17.6	−12.34		5.4			
HNC(120)	−173.80	11.1	−11.79	1.60	4.6			
HCN(180)	−182.40	20.2	−13.20	1.77	6.2	0.14	0.03	−0.17

and we would expect negligible amounts of HNC to be present at normal temperatures. Our results then are in accord with the observation that no HNC is detected in solutions of HCN and that it also would be too unstable with respect to that isomer to be easily isolated. We also see from Table 4, that the predicted ionization potential of HNC is somewhat lower than for HCN as is its promotion energy, and its dipole moment. In the corresponding charge distributions for the two isomers, also presented in Table 4, we see that the isonitrile carbon is negative while the nitrile carbon is positive and that the isonitrile nitrogen has a smaller negative charge than the nitrile nitrogen. The reason for these rather different charge distributions lies in the differences in bonding and behavior of the atoms in the two isomers. These differences will be discussed in another report, where the more chemical properties of the three species HCN, HNC, and CN^- will be considered.

9. Summary

In the preceding analysis, we have evaluated the EH–SCC MO method both with respect to more accurate MO methods and with predictibility of observed properties. This method cannot be used to determine total energies of molecules nor to determine the relative energies of total states arising from the same molecular configurations. It appears that it can, however, be used to calculate the relative stability of various molecular conformations. Thus, we correctly predict from it a linear ground state and a bent excited state for HCN and that it is energetically favored over HNC in its ground state. We also predict a linear HNC molecule in agreement with the known CH_3NC structure. In addition, the EH–SCC MO method appears to yield as good molecular binding energies as most of the more exact MO calculations, and to give reasonable values of first ionization potentials, dipole moments and the charge distribution in the molecule. We shall show, in the next paper how the results of the EH–SCC method can also be used to obtain some insight into the chemical reactivities of the HCN, NHC and CN^- molecules which have been discussed here.

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References

1. a) Berkowitz, J.: J. chem. Physics **36** # 1D, 2533 (1962).
   b) — Chupka, W. A., Walter, T. A.: J. chem. Physics **50** # 4, 1497 (1962).
2. Dubler, V. H., Liston, S. K.: J. chem. Physics **48** # 10, 4765 (1962).
3. Field, F. H., Franklin, J. L.: Electron impact phenomena, p. 273. New York: Academic Press Inc. 1957.
4. Bhattacharya, B. H., Gordy, W.: Physic. Rev. **119**, 144 (1960).
5. Herzberg, G.: Canad. J. Physics **35**, 842 (1957).
6. McLean, A. D.: J. chem. Physics **37**, 627 (1962).
7. Yoshimine, M., McLean, A. D.: Computed ground state enengus and dipole moments for some linear molecules, IBM, San Jose Laboratory Research Note, January 1966.
8. Pan, D. C., Allen, L. A.: J. chem. Physics **46** # 5, 1797 (1967).

9. Loew, G. H.: Conformation of HCN dimer and its role in chemical evolution, submitted to J. theoret. Biol.
   b) — Chang, S.: Quantum chemical study of HCN dimer and its role in chemical evolution. Submitted to Tetrahedron.
10. a) Kliss, R. M., Matthews, C. N.: Proc. nat. Acad. Sci. **48**, 1300 (1962).
   b) Matthews, C. N., Moser, R. E.: Proc. nat. Acad. Sci. **56**, 1087 (1966).
   c) — — Nature **215**, 1230 (1967).
   d) Moser, R. E., Matthews. C. N.: Experientia **24**, 658 (1967).
11. a) Ferris, J. P., Orgel, L. E.: J. Amer. chem. Soc. **88**, 1074 (1966).
   b) Sanchez, R. A., Ferris, J. P., Orgel, L. E.: J. molecular Biol. **38**, 121 (1968).
   c) Ferris, J. P., Kuder, J. E., Catalano, A. W.: Science **166**, 765 (1969).
   d) — — J. Amer. chem. Soc. **92**, 2527 (1970).
12. Chang, S., Flores, J., Ponnamperuma, C.: Proc. nat. Acad. Sci. **64**, 1011 (1969).
13. a) Moser, R. E., Claggett, A. R., Matthews, C. N.: Tetrahedron Letters **1969**, 1605.
   b) — — — Tetrahedron Letters **1968**, 1599.
14. Wolfberg, M., Helmholz, L.: J. chem. Physics **20**, 837 (1952).
15. a) Hoffman, R., Zeiss, G. D., Van Dine, G. W.: J. Amer. chem. Soc. **90**, 1485 (1968).
   b) — J. chem. Physics **40**, # 9, 2480 (1964).
   c) Zerner, M., Gouterman, M.: Theoret. chim. Acta (Berl.) **4**, 44 (1966).
   d) — — Kobayashi, H.: Theoret. chim. Acta (Berl.) **6**, 363 (1966).
   e) Pullman, B., Pullman, A.: Prog. in Nucleic Acid Res. and Molecular Biology **9**, 327 (1969).
16. Hoffman, R.: J. chem. Physics **39**, 1397 (1963).
17. a) Walsh, A. D.: J. chem. Soc. (London) **1953**, 2288.
   b) — J. chem. Soc. (London) **1953**, 2260.
18. Mullikan, R. S.: J. chem. Physics **23**, 1833, 2338, 2343 (1955).
19. Pearson, R. G.: J. Chem. Ed. **45** # 10, (1968).
20. Kessler, M., Ring, H., Trambarulo, R., Gordy, W.: Physic. Rev. **79**, 54 (1950).

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