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# QUANTUM CHEMICAL STUDY OF HCN DIMER AND ITS ROLE IN CHEMICAL EVOLUTION

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**Abstract**—An Extended Huckel Self Consistent Charge (EH-SCC) molecular orbital calculation has been made for eight geometric conformations of the two tautomeric forms of hydrogen cyanide dimer: amino cyanomethylene and cyanoformaldimine, both of which are possible precursors in abiotic syntheses of purines and proteins. In addition to their relative energies, we have determined such properties as the dipole moment, first ionization potential and lowest lying electronic transitions for each of the eight conformations. The main focus of attention in this paper is however a comparison of the chemical properties of the lowest energy conformations for each tautomeric form, deduced from the bonding picture which emerges from the MO calculation. Since no form of the dimer has ever been definitively isolated, our predicted properties are compared with some indirect observations and also with the known behaviour of other related amine, imine and methylene compounds. Also, based on their predicted chemical reactivities, the possible role of each hydrogen cyanide dimer tautomeric form in abiotic synthesis is discussed.

## I. *Introduction and background*

During the past ten years, several investigators have proposed that a dimer of HCN is a key intermediate in the abiotic synthesis of purines and proteins under conditions consistent with those on the primitive earth.[1] The hypothesized role of this molecule is based on the assumption that its lowest energy form is the planar, linear, 1, 3-biradical, aminocyanomethylene: $H_2N—C{=}C{=}N$.[1a] Presumably this form readily polymerizes to form the HCN tetramer, diaminomaleonitrile, and higher polymers. The tetramer has been shown to undergo photorearrangement leading to the formation of purine precursors[2] and also to be a condensing agent for amino acids in aqueous solution.[3] The higher polymers, though inadequately characterized, have been proposed as non-amino acid precursors of primitive proteins.[1d], [4] Since the dimer has never been isolated in any form, the main support for the lowest energy aminocyanomethylene structure is provided by a quantum mechanical calculation made in 1964.[5]

We have recently made a more complete and extensive quantum chemical calculation of the dimer. Using the EH-SCC molecular model, we have considered 8 possible conformations of the dimer shown in Fig 1: the *trans*(IA) and *cis*(IB) isomers of the cyanoformaldimine form and 6 conformations of the aminocyanomethylene form, three planar conformations (IIA, B, C) each having different bond angles at the carbene carbon and likewise three non-planar conformations (IIIA, B, C) with a tetrahedral amino nitrogen. For each of these eight conformations, we have considered both the lowest lying singlet and triplet states. In an initial report of the results for the dimer,[6]

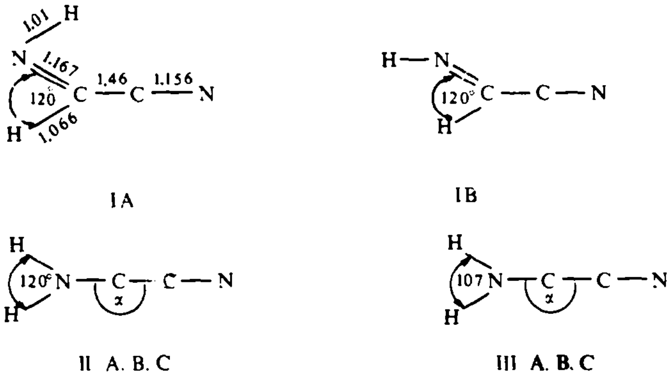


FIG 1. Different conformations for the two tautomeric forms of HCN dimer. IA, IB are the cis and trans forms of the cyanoformaldimine. IIA,B,C are planar conformations of the amino-cyanomethylene with varying methylene carbon bond angle. IIIA,B,C are non-linear conformations of the amino isomer with varying bond angle.

we indicated that the lowest energy form is the singlet *trans*-cyanoformaldimine (IA), in direct contradiction to the previous calculation.[5] Clearly, the hypothetical role proposed earlier[1–3] for aminocyanomethylene in prebiotic synthesis must be re-evaluated. Our results indicate also that the lowest energy aminocyanomethylene is the singlet, bent planar form (IIB). In this report we wish to focus attention on the properties and discuss the expected behaviour of the lowest energy forms of the HCN dimer, *trans*-cyanoformaldimine (IA) and aminocyanomethylene (IIB), both in a singlet state.

In our initial report on the dimer, we compared our present calculation with the one made previously and pointed out, on the one hand, the more complete nature of the present one, and, on the other hand, the limitations of this method of calculation. The set of approximations and assumptions inherent in an EH-SCC molecular orbital calculation has already been discussed in detail in many places.[7]

The present calculation included all 20 valence electrons of the six atoms of the dimer. Atomic orbital energies, based on valence state ionization potentials, are used as input to evaluate one electron matrix element. A single Slater orbital is used for each atomic orbital included in the calculation. An iterative solution of the energy overlap matrix is performed until the input and output charges on each atom agree within specified limits. From the resulting charge distribution, the dipole moment of the molecule can be calculated. Most important, from the final matrix diagonalization, MO functions are obtained which are linear combinations of the original atomic orbital functions interacting in the nuclear framework, along with corresponding MO energies. It is these MO energies, which we have used to obtain relative stabilities of the various states and conformations of the dimer discussed in our initial report. In addition, the energy of the highest filled MO is a reasonable estimate of the first ionization potential of the molecule. In the next section, we shall briefly review the results of our energy study and also tabulate the dipole moments and ionization potentials calculated for the 8 conformations of the HCN dimer studied.

In many MO calculations, attention is focused on obtaining the best possible total molecular energies and also on calculating more extensive physical properties of the molecule in addition to dipole moments, such as quadrupole moments, electric polarizability, nuclear electric shielding factors. Very often, the MO's themselves are presented only as a table of coefficients of basis set atomic orbitals. The more exact energy calculation, the less resemblance a description of a single atomic orbitals has to an easily recognizable atomic electron density distribution, *i.e.*, 2s, 2p, etc. Instead each atomic orbital is represented by a set of analytic or numerical functions of varying form depending on the specific calculation. From MO results presented in this way it is difficult to extract information about the nature of the bonding in the molecule in a fashion which can be easily related to the chemical properties of the molecule. It is precisely this type of information, rather than the additional physical properties, which we wish to extract from the MO's of this calculation.

In Section III of this report we focus attention on an analysis of the spatial distribution of the electrons in all of the filled MO's of the 2 isomers we are considering. This analysis classifies orbitals into types such as pi-bonding, non-bonding, sigma-bonding, etc. From this analysis we then obtain a composite picture of the way in which each atom bonds in two forms (IA and IIB) of the HCN dimer. In so doing, we essentially translate the MO picture of the bonding to a modified valence bond picture, the sum of specified MO's leading to an approximate valence bond notation for the bonding.

In Section IV we discuss the chemical implications of the bonding of each isomer described in the previous part. Predictions are made of chemical behaviour and compared with that of known molecules. Finally, consideration is given to the possible role of both forms of the dimer in chemical evolution.

## II. *Calculated properties of conformations of the dimer*

In Table I are presented the relative energies of the lowest state of each of the eight dimer conformations, in order of increasing energy. As we have already mentioned, the lowest energy conformation is the *trans*-cyanoformaldimine form (IA) of the dimer. Because geometrical isomers of aliphatic imines have never been isolated, interconversion of *trans*(IA)- and *cis*-cyanoformaldimine (IB) is expected to be easy. The lowest energy aminocyanomethylene is the singlet, planar bent conformation (IIB) which lies 3·3 ev above IA. The lowest energy triplet aminocyanocarbene is the planar

TABLE I. PHYSICAL PROPERTIES OF HCN DIMERS

| Conformation | Lowest energy state | Relative energy (ev) | Dipole moment (Debye) | Ionization potential (ev) |
|---|---|---|---|---|
| IA *trans*-cyanoformaldimine | $^1A_1$ | 0 | 1·91 2·78 | −10·50 |
| IB *cis*-cyanoformaldimine | $^1A_1$ | 0·67 | 1·89 3·31 | −11·0 |
| IIB Planar-120° aminocyanomethylene | $^1A_1$ | 3·3 | 1·39 7·87 | −10·10 |
| IIA Planar-180° aminocyanomethylene | $^3A_2$ | 4·5 | 1·87 8·86 | −9·66 |
| IIIA non-planar-180° aminocyanomethylene | $^1A_1$ | 4·9 | 4·56 8·69 | −9·30 |
| IIIB non-planar-126° aminocyanomethylene | $^1A_1$ | 7·4 | 5·35 8·54 | −9·2 |
| IIIC non-planar-103° aminocyanomethylene | $^3A_2$ | 8·3 | 1·40 7·92 | −9·19 |
| IIC Planar-103° aminocyanomethylene | $^1A_1$ | 9·0 | 1·70 6·58 | −10·0 |

linear form (IIA) thought previously to be the ground state, but found here to be about 4–5 ev less stable than IA.

Methylene, $CH_2$, has been the subject of numerous and extensive theoretical and experimental investigations. Only recently, however, have substituted methylenes received careful study from the MO standpoint.[8] For the variety of substituted methylenes examined the reliable calculations usually predicted bent triplet ground states, except for the linear triplets, cyanomethylene, dicyanomethylene and propargylene. Only in the cases of formylmethylene and difluoromethylene were bent singlet ground states considered possible. Experimental evidence is consistent with a linear or near linear triplet ground state for methylene,[9] bent triplet ground states for phenylmethylene,[10] diphenymethylene,[11] trifluoromethylmethylene[12] and di(trifluoromethyl)methylene[12] and linear triplet ground states for cyanomethylene,[13] dicyanomethylene[14] and propargylene.[13a, 15] Chloromethylene,[16] fluoromethylene[16] and difluoromethylene,[17] however, appear to be ground state singlets. Generally, the nature of methylene ground state symmetries and geometries as preducted by MO calculations[8] are in agreement with experimental results. Our conclusion that aminocyanomethylene is also a ground state singlet is consistent with Hoffman's emperical criterion for deciding ground state symmetries of substituted methylenes,[8a] and is consistent with esr studies.[18]

Also included in Table 1 are the calculated dipole moments and first ionization potentials obtained for each form. Perhaps in future work, correlation of experimentally determined and calculated values could provide evidence of the identity of dimer forms. In particular, all of the methylene forms have an unusually high dipole moment and could easily be distinguished from the imine forms.

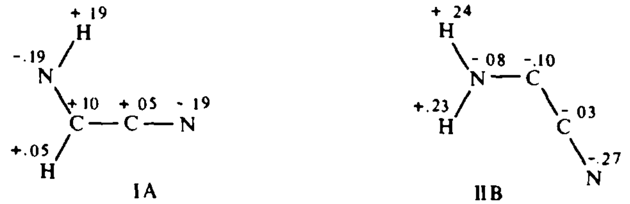


FIG 2. Charge distribution of the two tautomeric forms of HCN dimer in their lowest energy conformations.

In Fig 2, we show the net charge calculated on each atom in the two forms of the dimer we are considering. Comparison of the *trans*-cyanoformaldimine (IA) and the aminocyanomethylene (IIB) reveals several striking differences. In the former, the two nitrogens have about the same negative charge, while in the latter, the nitrile nitrogen is substantially more negative and the amino nitrogen is much less negative. In IA, the two hydrogens are quite inequivalent, with the H-bonding to the nitrogen having a greater positive charge than the one bonding to the carbon. In IIB, the two hydrogens are somewhat inequivalent because of the 120° bond angle at the methylene carbon but both are substantially more positive than the imine hydrogens in IA. In the linear methylene (IIA) the two amino hydrogens become equivalent. In IA, the imine carbon has a small positive charge, while the methylene carbon of IIB has a small negative charge. The nitrile carbon in IA has an even smaller positive charge than the imine carbon, whereas the same carbon in IIB has a small negative charge. These charge differences on the atoms result from dissimilar bonding between atoms in IA and IIB, as discussed in the next section.

### III. *The nature of the bonding in the two dimer tautomers*

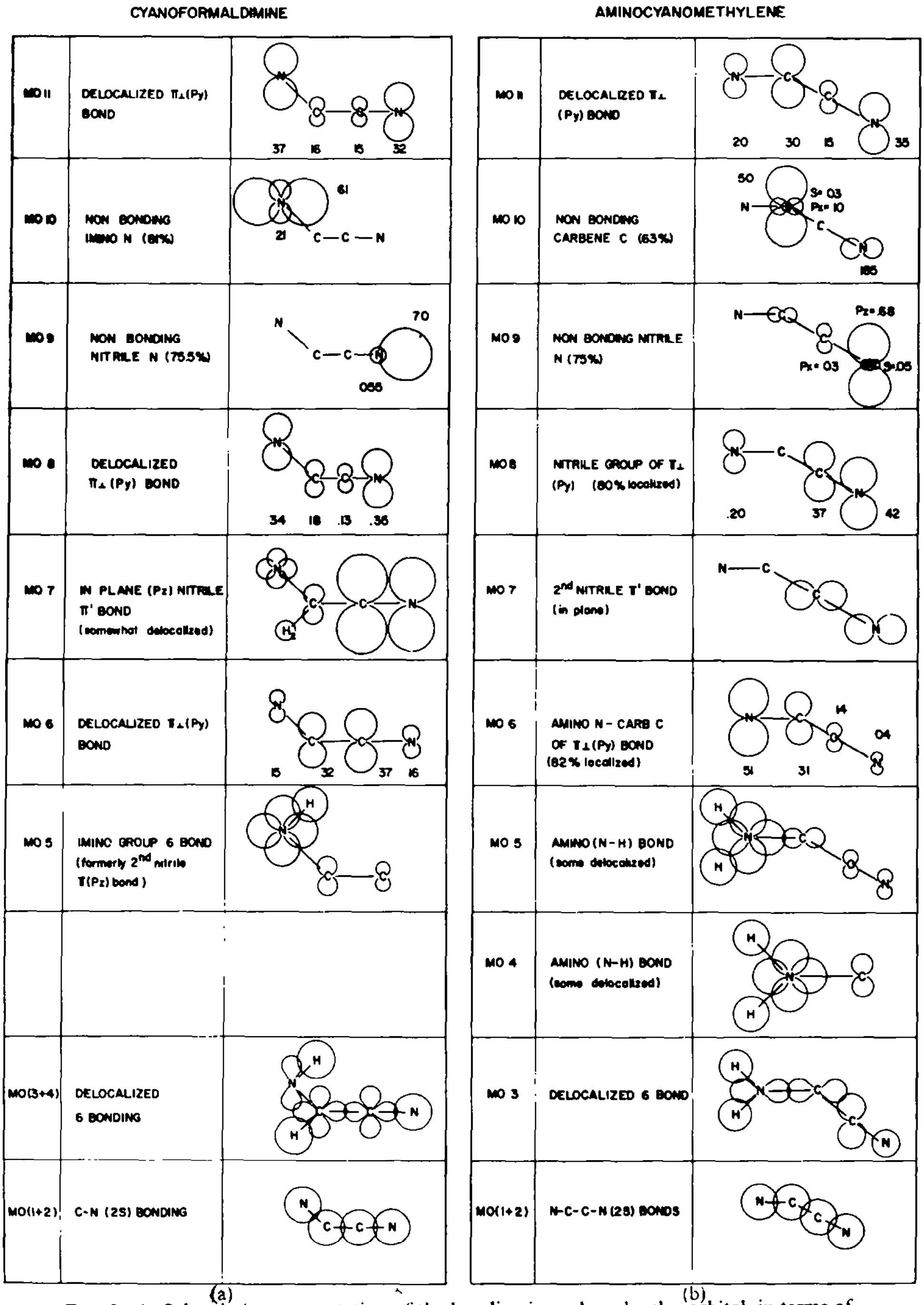
A. *Characterization of the molecular orbitals.* The HCN dimer has 20 valence electrons and 18 valence atomic orbitals. Thus, after interaction in the molecule, there are 18 MO's, 10 of which are filled in the totally paired configuration. From our calculation, we obtain an expression for each MO in terms of linear combinations of atomic orbital coefficients. Using a Mullikan population analysis, these coefficients can be transformed into an electron density distribution over the atomic orbital in a given MO. If we do this and consider also the charge density between atoms, we can classify each MO in terms of its most salient features. In Figs 3a and 3b are summarized the results of such a classification. The two top filled orbitals in each tautomer have substantially non-bonding character, with the greater part of the electron density centred on a single atom in the molecule. In IA, the top filled orbital (10) is essentially a non-bonding imine nitrogen orbital with 82 % of the electron density on that atom. This electron density is distributed in the planar $p_z$ and $p_x$ orbitals. Similarly the next lowest orbital (9), is non-bonding with 75 % of the electron density centered on the nitrile nitrogen, mostly in the $p_x$ orbital.

For IIB, the highest orbital (10) is also primarily a non-bonding orbital with more delocalization than the corresponding non-bonding orbital of 1A; thus only 63% of the electron density resides on the methylene carbon, with the remaining on the nitrile nitrogen. The next lower orbital (9) of IIB has exactly the same character as orbital 9 of IA.

In addition to non-bonding orbitals, there is a pi-bonding system in both dimers composed of MO's (6) and (8) in each case. These pi orbitals are linear combinations of the py atomic orbitals of the carbons and nitrogens with no electron density in the xz plane of the molecule. In IA, both pi orbitals are delocalized on all four C and N atoms, with more electron density on the two nitrogens in (8) and more electron density on the two carbons in (6). In IIB, the nature of each pi orbital is quite different. One, (8), is essentially the pi orbital of the nitrile group with a little overlap onto the amino nitrogen; while the second, (6), is essentially a pi bond between the amino nitrogen and the methylene carbon. Apparently in IIB, the pi system is divided at the methylene carbon into two somewhat localized regions, while in IA there is more extensive delocalization. The lowest unfilled orbital (11) in each system is also a delocalized pi orbital which, in the triplet state of these molecules, is half filled by promotion of one electron from MO (10). The nature of these triplet states for the eight conformations of the dimer have been discussed in our initial report.[6]

A third type of orbital is exemplified by (7) in both isomers. It represents the second, in-plane pi bond of the nitrile group, but with some delocalization onto the other atoms. Thus for both IA and IIB, the lowest unfilled and five highest filled MO's are either non-bonding or pi-bonding.

The remaining five lowest energy orbitals form what might be called the sigma bonding system of the molecule. Within this fourth category, there are subsets. The two lowest orbitals in IA and IIB for example, involve only the 2s orbitals of the



Figs 3a, b. Schematic representation of the bonding in each molecular orbital, in terms of participating atomic orbitals. In each figure, the size of atomic orbitals is proportional to the electron density in each orbital. Overlapping orbitals on adjacent atoms signify sigma bonding, while Po bonds are represented by non-overlapping atomic p orbitals. In 3a) are the mo's for cyanoformaldimine (IA) and 3b) for aminocyanomethylene (IIB).

carbons and nitrogens and hence correspond to delocalized, non-directed bonding over these atoms. In IA, orbitals (3) and (4) add some p character to the C–N sigma bonding and also involve bonding to the H atoms. MO (5) is essentially a unique imine nitrogen bonding orbital and completes the sigma bonding system for IA. In IIB, both MO's (4) and (5) represent primarily bonding of the amino nitrogen to its two hydrogens, with the nitrogen using primarily a $p_z$ orbital to do so. There is no suggestion of a second pi bond between the amino nitrogen and the methylene carbon. MO(3) brings some p character to the C–N sigma bonding and some additional bonding to the H atoms.

B. *Composite picture of bonding of each atom in the HCN dimer.* Having characterized each MO, we can now form from them a complete picture of the nature of each bond in the molecule, that is, determine how each atom uses its atomic orbital density in bonding. In Tables 2A and 2B are summarized the bonding description of each atom in cyanoformaldimine (IA) and the aminocyanomethylene (IIB), respectively. In these Tables, for each atom, column 1 identifies and lists its bonds, column 2 gives the MO's which have contributed to the formation of each bond, column 3 indicates the specific s and p orbitals used in forming each bond and the number of electrons in each, and column 4 gives the total number of electrons the atom contributes to each bond.

From Table 2A, it may be seen that the imine nitrogen in IA forms two very inequivalent sigma bonds. Its bond to H has totally in-plane *p*-character, while its bond to carbon is almost 2s in nature. Nitrogen donates 1·3 electrons to each of these bonds. In addition there are 1·6 non-bonding electrons with in-plane p-character and one electron in a delocalized pi bond. This distribution of electrons in the bonding of the imine nitrogen in the dimer accounts for the 5 original electrons and the additional 0·2 charge acquired in the molecule. We can compare the description of bonding which comes from our MO calculation of charge distribution in the molecule with the one obtained from the usual simplified valence bond approach based on partial correlations between the bond symmetry of a given atom, the bond strength, the bond angles and the necessary hybridization to obtain such bond angles. For an imine nitrogen, the resulting general description of the bonding depends only on its being planar and having 120° bond angles. With such geometry the imine nitrogen is assumed to form three equivalent $sp^2$ in-plane orbitals, two of which are used to form equivalent bonds to H and C, with one electron in each corresponding to the electron distribution $1/3\,(s + p_x + p_z)$, while the third $sp^2$ orbital would contain 2 non-bonding electrons distributed as $2/3\,(s + p_x + p_z)$. In addition, one electron would be part of a pi-bonding system. Thus, the MO calculations reveal a picture of bonding and electron distribution quite different from that based on the simple valence-bond correlations which are normally used to describe chemical bonding characteristics of atoms in molecules.

Proceeding to the nitrile nitrogen, it is clear that the resultant bonding picture also differs from the usual description of nitrile nitrogen bonding which involves two equivalent $sp_x$ orbitals, one of which has one electron participating in bonding to the C and the other of which has two non-bonding electrons. Our results indicate that there are about 1·5 electrons primarily in a 2S bonding orbital and 1·51 electrons principally in a $p_x$ non-bonding orbital. Our description of the two additional bonds formed by the nitrile nitrogen conform more closely to the classical one, placing almost one electron each in in-plane and out-of-plane pi-bonds to the carbon with a

TABLE 2. BONDING PICTURE FOR EACH ATOM IN IA AND IIB: DISTRIBUTION OF ATOMIC ORBITAL ELECTRON DENSITY IN MOLECULAR ORBITALS AFTER BOND FORMATION

2A: *trans*-cyanoformaldimine (IA)

| *Imino* N | contributing MO's | Bond character | # electrons in bond |
|---|---|---|---|
| σ Bond to $C_m$ | 1,2,3,4 | $1\cdot24s + \cdot06p_z$ | 1·3e |
| σ Bond to H | 3,4,5 | $0\cdot8p_z + \cdot5p_x$ | 1·3e |
| π Bond: Delocal | 6,8 | 1p | 1·0e |
| N.B. Character: Local | 10 | $1\cdot2p_x + 0\cdot4p_z$ | 1·6e |
| *Nitrile* N | | | |
| σ Bond to C | 1,2,3,4 | $1\cdot22s + 0\cdot23p_x$ | 1·56e |
| π Bond to $C_n$ | 7 | $1\cdot08p_z$ | 1·08e |
| π Bond. Delocal | 6,8 | $1\cdot0p_v$ | 1·02e |
| N.B. Character · Local | 9 | $1\cdot4p_x + \cdot11s$ | 1·51e |
| *Imine C* | | | |
| σ Bond to N and C | 1,2,3,4 | $\cdot962 + 48p_x + \cdot48p_z$ | 1·92e |
| σ Bond to H | 3,4,5 | $\cdot06 + \cdot43p_x + \cdot47p_z$ | 0·96e |
| π Bond: Delocal | 6,8 | 1·02 | 1·02e |
| *Nitrile* C | | | |
| σ Bond to N and C | 1,2,3,4 | $1\cdot1s + \cdot85p_x$ | 2·0e |
| σ Bond to N | 7 | $\cdot95p_z$ | 1·0e |
| π Bond: Delocal | 6,8 | 1·0 | 1·0e |

2B aminocyanomethylene (IIB)

| *Amino* N | contribution MO's | bond character | # Electrons in band |
|---|---|---|---|
| σ Bond to C | 1,2,3 | | |
| 2 σ Bonds to H | 3,4,5 | $1\cdot24s + 1\cdot18p_x + 1\cdot23p_z$ | 3·65e |
| π Bond: Delocal | 6,8 | $1\cdot42p_y$ | 1·42e |
| N.B. Character | — | — | — |
| *nitrile* N | | | |
| σ Bond to C | 1,2 | $1\cdot34s + 0\cdot16p_z + 0\cdot1p_x$ | 1·6e |
| π Bond to C | 7 | $1\cdot25p_x$ | 1·25e |
| π Bond to C: Delocal | 6,8 | 0·920 | 0·92e |
| N.B. Character: Local | 9 | $1\cdot38p_z + \cdot05p_y + \cdot09s$ | 1·52e |
| *methylene* C | | | |
| 2 σ Bonds to N and C | 1,2,3 | $1\cdot15s + 0\cdot8p_x + 0\cdot35p_z$ | 2·30e |
| N.B. Character: Local | 10 | $1\cdot0p_z + 0\cdot2p_x$ | 1·2e |
| π Bond to C | 6,8 | $0\cdot62p_y$ | 0·6e |
| *nitrile* C | | | |
| 2 σ Bonds to N and C | 1,2,3 | $1\cdot15s + 0\cdot58p_z + 0\cdot25p_x$ | 2·0e |
| π Bond to N | 7 | $0\cdot75p_x$ | 1·0e |
| π Bond to N | 6,8 | $0\cdot93p_y$ | 0·93e |

little delocalization of the former and considerable delocalization of the latter to other atoms.

The imine carbon, planar with 120° bond angles, has three sigma bonds which do not conform to three equivalent $sp^2$ hybridized bonds. Instead, its sigma bonds to nitrogen and carbon are sp; that is, are $(1/4)(2s + p_x + p_z)$ while its bond to hydrogen is almost pure $p_x$. There is about one electron in each of these three bonds, and, in agreement with the standard chemical description of trivalent planar double bonded carbon, there is about 1 electron in a py (pi) bond.

The linear divalent nitrile carbon conforms more closely than any other of the atoms to the conventional description of its bonding. Its two sigma bonds are approximately equivalent, almost $sp_x$ bonds, with slightly more s character than this equal mixing implies, and contain one electron in each bond. In addition, it has two pi bonds, one in-plane and fairly localized, and one delocalized pi bond, each with about one electron in it.

The two imine hydrogens use their single 1s orbital in bonding which is their only option in this calculation. Because of the positive charge which develops on them in the molecules, they have slightly less than one electron in each bond.

We turn now to Table 2B for a similar description of the aminocyanomethylene. For this form of the dimer, we considered six conformations in which the amine nitrogen had both a tetrahedral bonding symmetry similar to that of ammonia and a planar symmetry with three 120° bond angles. The planar nitrogen conformations had the lower energies. We can see why by examining the nature of the bonding of the amino nitrogen shown in Table 2B. It has three almost equivalent $sp^2$ bonds each containing about 1·2 electrons. However, there is more s character in its bond to carbon and more p character in its bond to the two hydrogens. In addition, the amino nitrogen forms a delocalized pi bond with the methylene carbon and the nitrile group involving 1·42 electrons. Unlike ammonia then, the amino nitrogen in the dimer does not have any non-bonding electrons. In the non-planar amino nitrogen conformations (IIIA-C) there is also no non-bonding electron character in the amino nitrogen. Apparently, when there is opportunity, electrons of an amino nitrogen will form a delocalized pi bond with neighboring atoms in a molecule, rather than remain non-bonding and localized on the nitrogen. Furthermore, when it does so, a planar conformation at the nitrogen is favored over a tetrahedral one.

The nitrile nitrogen on the IIB form of the dimer has substantially the same character as it does in IA. It is involved in sigma bonding to the nitrile carbon with 1·6 electrons, has 1·5 non-bonding electrons with only p character, and two pi bonds. The only difference is that in IIB the negative charge on the nitrile nitrogen is substantially increased to $-{\cdot}27$, which is reflected in the slightly greater electron density in each bond.

The nitrile carbon is also substantially the same as in IA and again conforms most closely to the standard description of it, with two sp sigma bonds and two pi bonds each containing about one electron. It does, however, have a slight negative charge in this form as compared to a slight positive charge in the imine form of the dimer.

The two amino hydrogens in IIB are both much more positive than either of the hydrogens in IA and again confined to use of their only valence atomic orbital, the 1s orbital, in bonding.

The methylene carbon in IIB is, of course, substantially different from the imine carbon of IA. In our results, the nature of the bonding at the methylene atom in the linear methylene IIA is about the same as that in IIB. From Table 2B, we see that the two sigma bonds of the carbon are approximately sp in nature, although the bond angle is 120°, and contain somewhat more than one electron in each bond. In addition, the methylene carbon contributes 0·6 electrons to a delocalized pi-bonding system with the other C and N atoms. Finally, it does appear to have 1·2 fairly localized non-bonding electrons in what is primarily an in-plane pi orbital. However, because this orbital is only 63 % localized on the methylene carbon, it does have some bonding character. The result of the charge distribution gives the methylene carbon a small negative charge of −0·1.

Clearly, the methylene carbon in IIB differs quite markedly in its bonding and electron distribution from a normal singlet divalent methylene carbon in which one of the two remaining orbitals contains two spin-paired non-bonding electrons, while the second remains empty. It is the empty orbital in the divalent carbon of typical methylenes that leads to their electrophilic nature.[19] In IIB not only is there no empty orbital, there is just slightly more than one non-bonding electron associated with the methylene carbon. That carbon is more accurately described as trivalent, suggesting greater kinship to a radical rather than a methylene carbon. On the other hand, the non-bonding electron on that carbon is spin-paired, unlike the case in free radicals. In summary, it appears that IIB resembles a spin-paired biradical in which slightly more than one electron is localized on the "methylene" carbon and somewhat less than one electron is delocalized throughout the pi system.

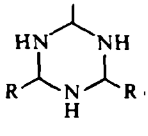
## IV. *Predictions of chemical behavior for IA and IIB and their possible role in prebiotic synthesis*

The bonding description and charge distributions which arise from the calculations permit some predictions about the chemical behavior of forms IA and IIB of the HCN dimer. Two important considerations are the basicity of the N atoms and the electrophilicity of the C atoms in each. Some of the predictions and correlations are part of a larger more general study[20] aimed at obtaining at least semi-quantitative calibration points for characteristics which determine N basicity, particularly in the small N-containing molecules which are considered important in prebiotic synthesis.

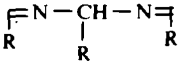
Three criteria by which to gauge N basicity are : (1) net charge on the N atom, (2) the number of non-bonding electrons associated with the N atom, and (3) the nature of the non-bonding electrons, *i.e.*, the degree of localization and the hybridization. The higher the net negative charge, the more localized the non-bonding electrons and the greater the p-character of the non-bonding orbital, the greater the basicity.[20] Both N atoms in IA are remarkably similar with respect to these criteria (Fig 2, Tables 2A and 2B). The net charge on the two atoms is the same, −0·19. The imine N has 1·6 electrons in an orbital which is totally p-sigma in character, and the nitrile N has 1·5 electrons in a predominantly p-sigma orbital with about 7% s-character. In both cases, the electrons are localized on the N atom. If we consider the N in HCN, which has essentially the same bonding characteristics as the corresponding N in IA, but with slightly less negative charge (−0·17), we expect at first glance that the basicity of both the imine and the nitrile N of IA should be similar to that of HCN. On the other hand, our calculations on $NH_3$[20] show that the N atom has a negative charge of −0·34 and 1·96 non-bonding electrons localized in a primarily p orbital with slight s-character. Since there is virtually no difference in the hybridization of the N orbital containing the non-bonding electrons in HCN and $NH_3$, the obviously great disparity in N basicity apparently reflects small differences in negative charge and especially in the total number of non-bonding electrons. Thus, although there is only a slight difference in the electron density at the imine (1·6 electrons) and nitrile N (1·5 electrons), the difference may be sufficient to lead to greater basicity at the former site. We conclude that both N atoms in IA are only weakly basic, but the imine N is probably more basic than the nitrile N. This is a surprising conclusion because, although the basicity of simple imines has not been directly measured, there is evidence that they are moderately basic, though not as basic as the corresponding amine.[21] In more classical terms, however, one might expect a substantial lowering of the basicity of the imine N in IA due to the strong inductive effect of the nitrile group.

Data in IA in Fig 2 indicate that the imine and nitrile C atoms are nearly neutral, the former having a slightly greater positive charge than the latter. The extensively delocalized pi-bonding system encompasses both carbons, but the nitrile C has an additional pi bond to the nitrile N while the imine C bonds in sigma fashion to hydrogen. It is not clear how the difference in bonding at the two carbons affects, stereoelectronically, their relative electrophilicity. We do not know the relative energies required for bond rehybridization and alteration of molecular geometry which would result from bonding to an attacking nucleophile at either C atom in IA. High s-character in the orbitals at C is expected to enhance electrophilicity; however, the amount of s-character at both C atoms in IA is essentially the same. On the basis of charge distribution and orbital s-character on the two C atoms, both appear to be equally susceptible to nucleophilic attack, a reaction mode common to most imines and nitriles.[21]

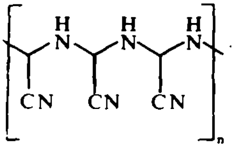
Simple aliphatic amines without substituents on the nitrogen undergo rapid polymerization.[21] In aqueous media, they hydrolyze readily, particularly in the presence of acids. Polymerization has been found to affect symmetrical hexahydrotriazines (III) and trimethylene diamines (IV), the latter accompanied by loss of ammonia. Analogous reactions are possible for IA. More extensive linear polymerization could lead to polmers containing partial structures such as V and/or VI, which like III and IV (R = CN) are gem-diamines and would be expected to yield glycine and glyoxalic acid after vigorous acid hydrolysis. Additions to the imine double bond of IA are likely, and in the presence of HCN, aminomalononitrile, the trimer of HCN, could be readily formed and further polymerization to tetramer and higher polymers could take place. Clearly, in aqueous media, hydrolysis will complete with polymerization and addition reactions.



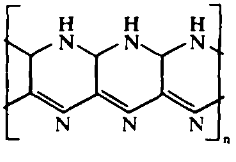
III


$\underset{R}{=}N-\underset{R}{CH}-N\underset{R}{=}$

IV



V



VI

In the case of aminocyanomethylene (IIB), bonding in the nitrile group is essentially the same as that in IA and HCN, indicating similar reactivity in terms of N basicity and C electrophilicity. Although the charges on the N and C in the nitrile group are slightly more negative than in IA and HCN, the net polarization between the two atoms is essentially the same. The amino N in IIB, however, is expected to be atypical, much more weakly basic than in amines and probably less basic than even the imine N in IA, because it has no non-bonding electrons and only a net negative charge of $-0{\cdot}08$. On the basis of our criteria, the nitrile N in IIB should be more basic than the amino N.

The "methylene" carbon is expected to be the most reactive site in IIB. But the apparent spin-paired biradical-like nature of the molecule indicates that IIB will not undergo reactions typical of electrophilic methylenes.[19] In addition to polymerization reactions, dimerization of two molecules of IIB to the HCN tetramer, diaminomaleonitrile, should be relatively facile. The bond angle of 120° at the methylene carbon is retained in the tetramer. Two bonds can easily be formed between the two methylene carbons of each dimer molecule, one in-plane sigma bond from the electrons in non-bonding orbitals and one pi bond from electrons in p pi orbitals of the two methylene carbons. Consistent with this view is the report [18] that singlet aminocyanomethylene dimerized to diaminomaleonitrile, but could not be captured by typical methylene traps such as olefins, triphenylphosphine. The only other products appeared to be intractable polymers. Such polymers were also the only products obtained when aminocyanomethylene was generated in the presence of hydroxylic solvents, even in trace amounts. If IIB can be captured with highly electrophilic olefins such as tetracyanoethylene, some similarity may be drawn between IIB and so-called "nucleophilic" methylenes.[22]

## *V. Conclusion*

One of the most ubiquitous and abundant primary products of prebiotic synthesis experiments involving primitive atmospheres is HCN[23]. Its subsequent polymerization, which necessarily proceeds through the dimer stage, affords a number of compounds which are precursors for amino acids and purines, amino acid condensing agents, and possibly peptides. Under the conditions of a variety of prebiotic-type experiments,[2b, 4, 24] there does not appear to be any reasonable pathway for formation of an aminocyanomethylene (IIB) from two molecules of HCN. Formation of cyanoformaldimine, however, can be readily viewed as addition of HCN across the triple bond of a second HCN molecule. Because cyanoformaldimine IA appears to be 3·3 ev lower in energy than IIB, it is reasonable to assume that formation of IA will not be followed by conversion to IIB. Since the dimer and trimer of HCN have never been detected in experiments where the polymerization was closely studied, they undoubtedly react as soon as they are formed to produce higher polymers of HCN. We conclude that the chemistry of HCN polymerization reflects the reactivity of the dimer IA and other higher oligomers of HCN rather than that of aminocyanomethylene.

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