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The Electronic Structure of the HCN Dimer and Trimer

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The electronic structure and energy of dimerization and trimerization of HCN are computed with an STO-3G basis and the results found to be in good agreement with the experimental ΔE. Unlike CNDO/2, this small *ab initio* basis predicts the correct geometry for the dimer of hydrogen cyanide. The charge redistribution effects found in this H-bond involving a C–H proton donor and *sp* hybridized acceptor are similar to those found in previous H-bonded studies.

Hydrogen cyanide, unlike water [1] and hydrogen fluoride [2][1], forms a well-characterized dimer in the gas phase. As early as in 1939, definitive thermodynamic measurements [3] on the gas phase association of HCN gave an enthalpy of dimerization of −3.3 kcal/mole and an enthalpy of trimerization of −8.7 kcal/mole.

There have been two previous attempts to calculate the energy of dimerization of HCN. One, by Hoyland and Kier [4] used the CNDO/2 semi-empirical molecular orbital method [5] and found cyclic $(HCN)_2$ far more stable than the linear structure found experimentally [6]. This failure of CNDO/2 was in contrast to the success it enjoyed in predicting properties of other H-bonded systems [5, 7] and indicated that this system would be a very interesting one to study with a minimum *ab initio* basis set.

Rae has computed [8] the dimerization energy and minimum energy geometry for the HCN linear dimer and found a dimerization energy of 4.7 kcal/mole and $R(\mathrm{N}\ldots\mathrm{C}) = 3.3$ Å. He used a very good SCF wave function for the HCN monomer and separately computed the electrostatic, polarization, exchange repulsion and dispersion contribution to the intermolecular energy.

We have computed the energy for both the linear (HCN...HCN) and cyclic $\begin{pmatrix}\mathrm{H{-}C{\equiv}N}\\ \mathrm{N{\equiv}C{-}H}\end{pmatrix}$ structures of $(HCN)_2$ as well as the energy for the linear trimer (HCN...HCN...HCN) at $R_1(\mathrm{N}\ldots\mathrm{C}) = R_2(\mathrm{N}\ldots\mathrm{C}) = 3.2$ Å using an STO-3G basis set and the results of the calculations are listed in Table 1.

The monomer geometry was assumed fixed at the experimental value [10], this approximation has been found to be excellent in previous studies of weak hydrogen bonds [11]. Unlike the CNDO/2 results, we found the cyclic dimer very

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[1] HF forms mainly a hexamer but IR studies indicate that under appropriate conditions, the dimer could be characterized.

Table 1

HCN monomer

$E = -91.67527$ a. u.

$r(\mathrm{C{-}H}) = 1.07$ Å

$r(\mathrm{C{\equiv}N}) = 1.15$ Å

Linear dimer $\mathrm{HC}\overbrace{\mathrm{N}\ldots\mathrm{HC}}^{R}\mathrm{N}$

R (N...C) (Å)	E (a. u.)
2.7	−183.31595
3.0	−183.35563
3.2	−183.35640
3.3	−183.35634
3.6	−183.35522

Cyclic dimer $\left.\begin{array}{l}\mathrm{H{-}C{\equiv}N{-}}\\ \mathrm{N{\equiv}C{-}H{-}}\end{array}\right] R$

R (between monomers) (Å)	E (a. u.)
2.0	−183.25790
2.6	−183.34160
2.9	−183.34942
3.2	−183.35164
3.5	−183.35207
3.8	−183.35210

Linear trimer $\mathrm{HC}\overbrace{\mathrm{N}\ldots\mathrm{HC}}^{R_1}\overbrace{\mathrm{N}\ldots\mathrm{HC}}^{R_2}\mathrm{N}$

$R_1(\mathrm{N}\ldots\mathrm{C}) = R_2(\mathrm{N}\ldots\mathrm{C}) = 3.2$ Å

$E = -275.03854$ a. u.

little stabilized relative to the HCN monomers and the linear dimer was found to have a stabilization energy of 3.7 kcal/mole at $R(\mathrm{C}\ldots\mathrm{N}) = 3.2$ Å, the same length as found in the crystal [12] where the HCN molecules form infinite linear chains. The neglect of three and four center repulsions in CNDO/2 clearly is the cause why a cyclic structure, with the 2C's and N's close together, is computed to be especially stable in a CNDO/2, calculation. Our ΔE is in better agreement with the experimental value than Rae's, mainly because a molecular orbital calculation does not include the attraction due to dispersion forces, which Rae finds to be 1.3 kcal/mole at the minimum energy geometry. The ΔE calculated by us is too large probably because charge transfer and polarization effects are exaggerated in this minimal basis calculation. Our calculated $R(\mathrm{C}\ldots\mathrm{N})$ length is probably a bit too short, since one would expect the dimer length to be longer than that found in the crystal.

The stabilization energy for the linear trimer at $R_1(\mathrm{C}\ldots\mathrm{N}) = R_2(\mathrm{C}\ldots\mathrm{N}) = 3.2$ Å was calculated to be 8.1 kcal/mole which is in good agreement with the experimentally found value.

The charge distribution changes found for the linear dimer and trimer are given in Table 2. The calculated dipole moments for the monomer and dimer are

Table 2

Monomer population		
H	0.8502	
C	5.9896	
N	7.1602	
Linear dimer $R = 3.2$ Å		
	Population	Δ population[a]
H	0.8407	0.0095
C	5.9688	0.0208
N	7.1748	−0.0146
H	0.8231	0.0271
C	6.0098	−0.0202
N	7.1828	−0.0226
Linear trimer $R_1 = R_2 = 3.2$ Å		
	Population	Δ population
H	0.8391	0.0111
C	5.9664	0.0232
N	7.1783	−0.0181
H	0.8140	0.0362
C	5.9890	0.0006
N	7.1974	0.0372
H	0.8208	0.0294
C	6.0107	−0.0211
N	7.1843	−0.0241

[a] Δ population = (monomer population)–(polymer population). Negative sign denotes increase of electronic charge on atom.

Table 3. Dipole moments

Configuration	Dipole moment (D)
Monomer	2.48
Linear dimer ($R = 3.2$ Å)	5.58

presented in Table 3. The enhancement of the dipole moment due to H-bonding is of the same magnitude as found for the water dimer [13].

As has been found in previous studies on H-bonding, the proton donor hydrogen loses charge on hydrogen bond formation, and the C≡N of the proton donor fragment gains. On the proton acceptor, nitrogen actually gains electrons at the expense of the less electronegative C and H atoms, who are big losers of charge. It is very interesting to note that in the linear trimer, the central HCN stays nearly neutral (−0.0004) and acts as a charge transmitter from one end fragment (+0.0162) to the other (−0.0158). This phenomenon has been previously observed in CNDO/2 calculations on HF and water polymers containing as many as 12 monomers [15]. In the cyclic dimer, as the fragments approach each other the charge shifts from H→N in each fragment.

The field gradient at the proton is 0.362 a. u. in the monomer, 0.335 a. u. at the H-bonded proton in the linear dimer. This field gradient for the monomer is 20% smaller than the experimental value [16]; but the interesting fact is that the percent decrease of the field gradient going from monomer → dimer (8%) is similar to that found in the water dimer (9%) [15].

These calculations add additional support for the adequacy of a small contracted *ab initio* basis to represent the energies and geometries of hydrogen bonding found experimentally and encourages the use of this basis on larger systems where an extensive basis set calculation would be prohibitive. This basis set tends to underestimate the distance between monomers by 0.1–0.3 Å and to overestimate the dimerization energy by 20–40% [14].

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