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## Electronic Structure and One-Electron Properties of the Isoelectronic Molecules HCN, HNC, HBO, HOB, HBF<sup>+</sup>, and HFB<sup>+</sup>

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A double  $\zeta$  quality basis set was used to determine the equilibrium geometries, energies, and one-electron properties of a number of isoelectronic molecules. The properties determined included multipole moments, electric field gradients, and diamagnetic susceptibilities. The geometries and properties were compared with experimental results and previous calculations where available.

### Introduction

While there have been numerous theoretical investigations of the equilibrium geometries and energies of at least some of the molecules to be considered here, particularly HCN and HNC, the same cannot be said regarding calculation of the one-electron properties of these molecules. The means for calculating a wide range of

one-electron properties including multipole moments and diamagnetic susceptibilities and shielding are incorporated in both the POLYATOM/2<sup>1</sup> and the IBMOL5A<sup>2</sup> ab initio program packages. Snyder and Basch<sup>3</sup> have in fact utilized the POLYATOM/2 program to provide listings of the one-electron properties output for a number of molecules including HCN but without giving any analysis of the data

TABLE I: Equilibrium Geometries and Energies for the HXY Species<sup>a</sup>

	$R_{H-X}, \text{\AA}$	$R_{X-Y}, \text{\AA}$	total energy	$-V/2T$
HCN	1.056 (1.066) <sup>5</sup>	1.145 (1.153) <sup>5</sup>	-92.8427	0.99985
lit. values	1.063 <sup>14</sup>	1.137 <sup>14</sup>		
HNC	0.981 (0.9940) <sup>6</sup>	1.160 (1.1689) <sup>6</sup>	-92.8383	0.99954
lit. values	0.986 <sup>14</sup>	1.159 <sup>14</sup>		
HBO	1.154	1.202	-100.1439	0.99980
lit. values	1.179, <sup>21</sup> 1.153, <sup>22</sup> 1.157 <sup>23</sup>	1.177, <sup>21</sup> 1.199, <sup>22</sup> 1.205 <sup>23</sup>		
HOB	0.937	1.275	-100.0968	0.99927
lit. values	0.936, <sup>22</sup> 0.950 <sup>23</sup>	1.298, <sup>22</sup> 1.295 <sup>23</sup>		
HB <sup>+</sup> F	1.159	1.248	-124.3805	1.00035
lit. values	1.160, <sup>22</sup> 1.199 <sup>24</sup>	1.242, <sup>22</sup> 1.227 <sup>24</sup>		
HF <sup>+</sup> B	0.932	1.985	-124.3042	0.99988
lit. values	0.945 <sup>22</sup>	1.877 <sup>22</sup>		

<sup>a</sup> Values in parentheses are experimental results. Superscripts indicate the appropriate reference source. Energies are given in Hartrees.

or comparison with experimental results. Of the molecules being considered here only HCN and HNC have experimentally determined geometries, and experimentally measured one-electron properties are available only for HCN. The molecule, HBO, has been prepared by using matrix isolation techniques and its infrared spectrum has been obtained.<sup>4</sup>

The experimental geometry of HCN<sup>5</sup> indicates a linear structure with an H-C bond length of 1.066 Å and a C-N bond length of 1.153 Å. Creswell and Robiette,<sup>6</sup> using the data from the analysis of the millimeter wave spectrum of HNC by Pearson et al.,<sup>7</sup> determined the equilibrium bond lengths in HNC to be H-N = 0.9940 Å and N-C = 1.1689 Å. Bhattacharya and Gordy<sup>8</sup> obtained a dipole moment for HCN of 2.986 D and also determined the <sup>14</sup>N quadrupole coupling constant in H<sup>12</sup>C<sup>14</sup>N to be -4.714 MHz. There have been a number of experimental determinations of the deuteron quadrupole coupling constant in DCN giving values of 194 ± 2,<sup>9</sup> 199.0 ± 3,<sup>10</sup> and 202.18 ± 0.31 kHz.<sup>11</sup> Hartford et al.<sup>12</sup> found the quadrupole moment for HC<sup>15</sup>N along the molecular axis to be 3.1 ± 0.6 esu-cm<sup>2</sup>. Gierke and Flygare<sup>13</sup> used the atom dipole method to obtain the average diamagnetic shieldings  $\sigma_{av}^{d(1H)}$ ,  $\sigma_{av}^{d(13C)}$ , and  $\sigma_{av}^{d(14N)}$  in HCN to be 97, 326, and 381 ppm, respectively. There is no similar experimental information available for the other molecules.

Numerous ab initio calculations have been performed on HCN and on HNC with the primary purpose of obtaining equilibrium geometries. Pearson et al.<sup>14</sup> reported equilibrium geometries and dipole moments for HCN and HNC with both a double  $\zeta$  plus polarization basis set and CI. The double  $\zeta$  plus polarization basis set gave a H-C bond length of 1.063 Å, a C-N bond length of 1.137 Å, and a dipole moment of 3.22 D while for HNC it gave a H-N bond length of 0.986 Å, a N-C bond length of 1.159 Å, and a dipole moment of 2.91 D. The CI calculation resulted in a geometry for HCN almost identical with the experimentally determined one and a dipole moment of 3.012 D. In addition, a variety of workers using a variety of basis sets have determined particular one-electron properties for HCN. Kern and Karplus<sup>15</sup> have calculated quadrupole coupling constants for DCN and HCN as have Bonaccorsi, Scrocco, and Tomasi.<sup>16</sup> Ditchfield<sup>17</sup> has determined magnetic shielding constants for H<sup>13</sup>CN and HC<sup>14</sup>N. Kato, Fujimoto, and Saika<sup>18</sup> have obtained diamagnetic susceptibilities and anisotropies for HCN. Gready et al.<sup>19</sup> have determined a number of one-electron properties, including multipole moments for both HCN and HNC. Barfield and Grant<sup>20</sup> calculated average diamagnetic shieldings  $\sigma_{av}^{d(1H)}$ ,  $\sigma_{av}^{d(13C)}$ , and  $\sigma_{av}^{d(14N)}$  for HCN in the INDO approximation, but including certain two-center integrals, to be 101.3, 324.8, and 377.9 ppm, respectively. Thomson and Wishart<sup>21</sup> used a double  $\zeta$  plus polarization basis set on

HBO to give an equilibrium geometry (H-B = 1.179 Å, B-O = 1.177 Å), a dipole moment (3.261 D), and atom-centered quadrupole moments and field gradients. Summers and Tyrrell,<sup>22</sup> using a 4-31G basis set, obtained optimized geometries for HBO (H-B = 1.153 Å, B-O = 1.199 Å) and for HOB (H-O = 0.936 Å, O-B = 1.298 Å). Recently Botschwina<sup>23</sup> has used PNO-CI and CEPA techniques to obtain optimized geometries for HBO (H-B = 1.157 Å, B-O = 1.205 Å) and for HOB (H-O = 0.950 Å, O-B = 1.295 Å). Equilibrium geometries have also been calculated for HB<sup>+</sup>F by Jansen and Ros<sup>24</sup> and by Summers and Tyrrell<sup>22</sup> and for HF<sup>+</sup>B.<sup>22</sup> Taylor et al.<sup>25,26</sup> pointed out that by using progressively larger basis sets along with "singles and doubles" CI makes the agreement between the calculated and experimental geometry of HCN progressively worse. The answer to the problem according to Taylor et al.<sup>25,26</sup> is not in extending the basis set but in the inclusion of multiple excitations as evidenced by the importance of unlinked clusters.

The purpose of this investigation was to determine a variety of one-electron properties at the equilibrium geometry for the isoelectronic molecules being studied. These calculated properties will be compared and contrasted with available experimental and theoretical results.

## Method and Results

Calculations were carried out on an IBM 370-158 computer by using double  $\zeta$  quality basis sets (18S, 7P/4S, 2P) for boron, carbon, nitrogen, oxygen, and fluorine and (6S/2S) for hydrogen, optimized by Huzinaga and Sakai.<sup>27</sup> The IBMOL5A ab initio program package developed by Clementi et al.<sup>2</sup> was utilized. The one-electron property part of the package is essentially identical with that employed in the POLYATOM/2 program.<sup>1</sup> The geometries were optimized by using a 0.005-Å grid and optimizations were repeated for each parameter till self-consistency was achieved. The points on the energy surfaces showed no evidence of random errors giving smooth potential surfaces. The minima were graphically determined, the uncertainty in the geometrical parameters being less than 0.001 Å. Table I gives the equilibrium geometries and total energies for all of the systems studied. Also included are the virial theorem results for these optimized systems. Some one-electron properties, relative to the center of mass of the respective molecules, are given in Table II, all properties being given in atomic units with the appropriate conversion factors given in Table III. The coordinate system used in all cases has the Z axis in the direction Y → H. Positive signs on the dipole moment indicate H<sup>+</sup>XY<sup>-</sup> polarity. Atom-centered one-electron properties are given in Table IV. Again all properties are given in atomic units and reference should be made to Table III for the conversion factors. Table V lists the various quadrupole

TABLE II: Center-of-Mass One-Electron Properties for HXY<sup>a</sup>

	HCN	HNC	HBO	HOB	HB <sup>+</sup> F	HF <sup>+</sup> B
potential						
electronic	-10.5315	-10.7841	-10.4730	-10.9004	-11.0796	-8.7294
total	1.7959	1.9762	1.5222	1.8099	1.9789	0.6814
electric field						
electronic	-0.3780	2.1336	-2.5655	4.2059	-4.2698	3.9304
total	-0.3408	-2.9299	1.1966	-4.0441	2.2780	-0.9056
field gradient						
electronic	7.8573	8.5748	7.9351	9.0547	9.6676	5.7439
total	-12.7197	-16.0501	-11.3487	-17.0852	-13.0738	-3.6847
dipole moment						
electronic	-0.1659	-0.1489	0.3035	-0.5420	0.4623	-2.8556
total	1.3454	1.2183	1.3722	1.5471	2.0288	-0.7359
quadrupole moment						
electronic	-22.9904	-21.9391	-28.3007	-25.2161	-28.5848	-45.6662
total	1.5754	1.3447	-0.4514	-0.2851	2.2785	8.8376
second moment						
electronic	-50.5186	-49.5548	-53.3575	-52.8980	-47.0482	-66.1189
total	-25.9528	-26.2710	-25.5081	-27.9671	-16.1849	-11.6151
octupole moment						
electronic	-16.1124	6.6109	-42.2758	29.4993	-46.2732	45.4076
total	9.2121	19.9838	-3.2858	35.9306	3.3407	16.0238
av diam susceptibility	40.30	39.53	42.57	42.20	37.53	52.75

<sup>a</sup> All properties are in atomic units except for average diamagnetic susceptibility which is in units of cm<sup>3</sup>/mol × 10<sup>6</sup>.

TABLE III: Atomic Unit Conversion Factors

potential	1 au = 9.07618 esu/cm
electric field	1 au = 0.171524 × 10 <sup>8</sup> dyn/esu
field gradient	1 au = 0.324123 × 10 <sup>16</sup> esu/cm <sup>3</sup>
dipole moment	1 au = 2.54177 D
quadrupole moment	1 au = 1.34504 × 10 <sup>-26</sup> esu·cm <sup>2</sup>
second moment	1 au = 0.2800285 × 10 <sup>-16</sup> cm <sup>2</sup>
octupole moment	1 au = 0.711766 × 10 <sup>-34</sup> esu·cm <sup>3</sup>
diamagnetic susceptibility	1 au = 1.188028 × 10 <sup>-6</sup> cm <sup>3</sup> /mol
diamagnetic shielding	1 au = 17.75 ppm
energy	1 au = 627.5 kcal/mol

coupling constants obtained by using the values for the nuclear quadrupole moments given in the footnotes. Table VI compares the present results for a number of one-electron properties of HCN with experimental and previous calculated results.

## Discussion

The geometries and energies given in Table I show similar patterns to those observed in a more extensive set of calculations for the same isoelectronic series with a 4-31G basis set.<sup>22</sup> This is not unexpected since the basis set used in the present work, while much larger than the 4-31G basis set, does use a similar contraction scheme for the valence shell. In all instances the species HXY, where X is the less electronegative atom, is more stable than where X is the more electronegative of the two heavy atoms. Further, for the less stable member of each pair of molecules the highest occupied valence orbital is a nonbonding orbital associated with the less electronegative heavy atom. On the other hand, the highest occupied molecular orbitals in the more stable member of each pair are two degenerate  $\pi$  orbitals except in the case of HB<sup>+</sup>F. In both HB<sup>+</sup>F and HF<sup>+</sup>B it would be more correct to describe the degenerate  $\pi$  orbitals as fluorine nonbonding orbitals. The bond lengths between the two heavy atoms are consistently shorter in the species where the hydrogen is bound to the less electronegative atom.

TABLE IV: Atom-Centered, One-Electron Properties for HXY<sup>a</sup>

	HCN	HNC	HBO	HOB	HB <sup>+</sup> F	HF <sup>+</sup> B
potential <sup>b</sup>						
H	-5.6264	-6.1617	-5.1012	-6.5786	-4.9242	-6.6291
X	-18.4013	-21.5931	-15.3464	-24.9314	-15.1598	-28.2367
Y	-21.3247	-18.1211	-24.7535	-14.9466	-28.5167	-13.5441
electric field <sup>c</sup>						
H	0.0708	0.0725	0.0821	0.0760	0.0919	0.0901
X	0.0835	0.0731	0.0340	0.0087	0.0454	-0.1277
Y	-0.1995	-0.1408	-0.2129	-0.0774	-0.2658	-0.0248
electric field gradient <sup>c</sup>						
H	-0.3800	-0.5113	-0.2614	-0.5944	-0.2361	-0.5380
X	0.4096	-0.1815	0.4161	-1.6379	0.6014	-3.2824
Y	1.2074	0.9789	0.4361	0.4422	-1.6082	0.0412
quadrupole moment						
H	-6.6122	-5.3765	-9.7804	-8.4968	0.5185	22.5195
X	-1.2426	-0.8596	-3.7955	-3.0180	-1.4080	12.3367
Y	4.5796	4.4815	2.4383	4.4371	7.2452	11.3273
av diamagnetic shielding						
H	-99.87	-109.37	-90.55	-116.77	-87.40	-117.67
X	-326.62	-383.28	-272.40	-442.53	-269.09	-501.20
Y	-378.51	-321.65	-439.37	-265.30	-506.17	-240.41

<sup>a</sup> All properties are in atomic units except average diamagnetic shielding which are in parts per million (ppm). <sup>b</sup> Only electronic contribution to potential. <sup>c</sup> Total contribution to electric field.

TABLE V: Quadrupole Coupling Constants ( $-eqQ/h$ )<sup>a</sup>

	HCN	HNC	HBO	HOB	HBF <sup>+</sup>	HFB <sup>+</sup>
<sup>2</sup> H	0.2498	0.3361	0.1718	0.3907	0.1552	0.3536
<sup>14</sup> N	-4.4891	0.6746				
<sup>10</sup> B			-8.4105	-8.9372	-12.1560	-0.8333
<sup>11</sup> B			-4.1075	-4.3647	-5.9367	-0.4070
<sup>17</sup> O			2.7315	-10.2585		

<sup>a</sup> Units are MHz.  $O^2H = +0.002\,796\,5\,b$ ,  $O^{14}N = +0.015\,82\,b$ ,  $O^{10}B = +0.086\,b$ ,  $O^{11}B = +0.042\,b$ ,  $O^{17}O = -0.026\,65\,b$ .

TABLE VI: One-Electron Properties of HCN<sup>a</sup>

	this work	experimental	other work
dipole moment, D	3.420	2.986 <sup>8</sup>	3.26, <sup>16</sup> 3.244, <sup>17</sup> 3.04, <sup>26</sup> 3.22, <sup>14</sup> 3.325 <sup>19</sup>
quadrupole moment, (esu·cm <sup>2</sup> ) × 10 <sup>26</sup>	2.12	3.1 ± 0.6 <sup>12</sup>	1.93, <sup>27</sup> 2.03 <sup>19</sup>
octupole moment, (esu·cm <sup>3</sup> ) × 10 <sup>34</sup>	6.56		6.37 <sup>19</sup>
quadrupole coupling constant, MHz			
<sup>2</sup> H	0.2498	0.194, <sup>9</sup> 0.199, <sup>10</sup> 0.20218 <sup>11</sup>	0.208 <sup>16</sup>
<sup>14</sup> N	-4.489	-4.714 <sup>8</sup>	-4.65 <sup>16</sup>
av diamagnetic shielding, ppm			
$\sigma_{av}^d(H)$	99.87	101.72 <sup>32</sup>	97 <sup>13</sup>
$\sigma_{av}^d(C)$	326.62	326.75 <sup>32</sup>	326 <sup>13</sup>
$\sigma_{av}^d(N)$	378.51	377.62 <sup>32</sup>	381 <sup>13</sup>

<sup>a</sup> Superscripts indicate the appropriate reference sources.

The geometries obtained for both HCN and HNC give bond lengths which are consistently about 0.01 Å shorter than the experimental values. It should be pointed out that the bond lengths calculated correspond to  $r_e$  values. There is excellent agreement between the present geometry for HBO and that obtained by Botschwina<sup>23</sup> while both differ significantly from the results of Thomson and Wishart.<sup>21</sup> On the other hand, the present result for the geometry of HOB has both bond lengths coming out 0.01–0.02 Å shorter than the values obtained by Botschwina.<sup>23</sup> The geometry for HBF<sup>+</sup> is in good agreement with the previous 4-31G basis set results<sup>22</sup> while the geometry for HFB<sup>+</sup> emphasizes even more than the 4-31G basis set results<sup>22</sup> the picture of HFB<sup>+</sup> as essentially HF<sup>+</sup> + B<sup>+</sup>.

The only experimental dipole moment available for the systems presently being considered is for HCN which has a value of 2.986 D<sup>8</sup> so that our calculated value of 3.4 D is somewhat large. Many large basis set calculations of the dipole moment of HCN do overestimate its value; for example, Bonaccorsi et al.<sup>16</sup> obtained 3.26 D, Ditchfield et al.<sup>17</sup> obtained 3.244 D, Johansson et al.<sup>28</sup> 3.04 D, and Pearson et al.<sup>14</sup> 3.22 D. On the other hand, minimal basis sets or semiempirical calculations significantly underestimate the dipole moment. Similarly for HNC our calculated value for the dipole moment (3.094 D) is in reasonably good agreement with Pearson et al.<sup>14</sup> (2.91 D) but somewhat larger. The dipole moment obtained by Thomson and Wishart<sup>21</sup> for HBO (3.261 D) is about 0.2 D smaller than our result (3.485 D). All of the calculated dipoles are in the same direction except that of HFB<sup>+</sup> which would indicate a HFB<sup>+</sup> polarity. In all cases except HFB<sup>+</sup> the nuclear contribution to the dipole dominates and determines the sign of the dipole. The contribution of the  $\pi$  orbitals increases in magnitude and changes sign in going from the more stable to the less stable member of each HXY pair of molecules as is also the case with the  $\sigma_{X-Y}$  contribution. The  $\sigma_{H-X}$  contribution, however, decreases in magnitude in going from the more stable to the less stable member of each HXY pair and in addition retains its sign. It should be noted that in the more stable member of each pair the  $\sigma_{H-X}$  contribution is of the opposite sign to that of the  $\pi_{X-Y}$  and  $\sigma_{X-Y}$  contributions while in the less stable member all bonding orbitals contribute in the same sense. The dipole moment is invariant to

choice of origin only in those species with no net charge.

The quadrupole moments,  $\Theta_{ZZ}$ , and the octupole moments,  $\Omega_{ZZZ}$ , are given relative to the center of mass of the molecule in Table II. The only experimental value available for comparison is  $\Theta_{ZZ} = 3.1 \pm 0.6$  esu·cm<sup>2</sup> for HC<sup>15</sup>N.<sup>12</sup> This can be compared with the values of 0.93 and 1.93 esu·cm<sup>2</sup> obtained by using STO-5G and 4-31G basis sets, respectively,<sup>29</sup> with the value of 2.03 esu·cm<sup>2</sup> obtained by Gready et al.<sup>19</sup> and the present value of 2.12 esu·cm<sup>2</sup>. The quadrupole and octupole moments for HCN and HNC are in good agreement with the values obtained by Gready et al.<sup>19</sup> Pan and Allen<sup>30</sup> calculated the quadrupole moment at the carbon in HCN to be  $1.624 \times 10^{-26}$  esu·cm<sup>2</sup> which compares well with the value of  $1.671 \times 10^{-26}$  esu·cm<sup>2</sup> obtained in the current investigation. The atom-centered quadrupole moments for HBO should be compared with those of Thomson and Wishart<sup>21</sup> which are of the same sign and of similar relative magnitude but approximately a factor of 2 larger. This discrepancy may be due to the method of definition of the quadrupole moment. The definition used in this work is that due to Buckingham<sup>31</sup> but some workers use the definition given by Townes and Schawlow<sup>32</sup> which increases the moment by a factor of 2. The nuclear and electronic contributions to the quadrupole moments are similar in magnitude but of opposite sign with the nuclear contributions dominating in HCN, HNC, HBF<sup>+</sup>, and HFB<sup>+</sup> while the reverse is true for HBO and HOB. All molecular orbital contributions to the quadrupole moments are of the same sign with the dominant ones being due to the outermost nonbonding orbital and the  $\sigma_{H-X}$  orbital. The nuclear contributions to the octupole moments are positive except in the case of HFB<sup>+</sup> and are in every case much larger for the more stable member of each pair of HXY molecules. The electronic contributions, on the other hand, alternate in sign, being negative for the more stable member of the pair. The dominant molecular orbital contributions are due to the highest nonbonding orbital and the  $\sigma_{H-X}$  orbital. These contributions retain their sign in going from one member of each pair to the other while the remaining bonding orbital and nonvalence orbital contributions switch signs.

The field gradients measured relative to the atom centers can be used to determine quadrupole coupling constants,  $-eqQ/h$ , if the appropriate atomic quadrupole moment,  $Q$ , is known. Pan and Allen<sup>30</sup> determined the

field gradient at the hydrogen in DCN and at the carbon in  $\text{H}^{14}\text{CN}$  to be 0.472 and -0.481 au, respectively, which should be compared to the values obtained in the present calculation of -0.380 and 0.410 au, respectively. The sign difference is due to Pan and Allen having the positive direction of the  $Z$  axis pointing toward the nitrogen. The only experimental values for the quadrupole coupling constants are those for  $^2\text{H}$  in  $^2\text{HCN}^{9-11}$  and for  $^{14}\text{N}$  in  $\text{HC}^{14}\text{N}^8$  and the present values of 249.8 kHz and -4.489 MHz, respectively, should be compared with these and with the calculated values of 208 kHz and -4.65 MHz, respectively, obtained by Bonaccorsi et al.<sup>16</sup> Particularly noticeable are the large changes in the quadrupole coupling constants at the various nuclei for the isoelectronic pairs of molecules. This is especially noticeable for  $^{14}\text{N}$  in HCN and HNC and for  $^{17}\text{O}$  in HBO and HOB and is attributable primarily to large changes in the electronic contribution to the field gradient at these centers. On the other hand, the boron quadrupole coupling constants in HBO and HOB show only a small variation and in this case the electronic contribution to the field gradient at the boron in these two molecules shows little variation.

For an exact Hartree-Fock wave function the Hellman-Feynman theorem predicts that the sum of the forces on all the nuclei should be zero for all internuclear distances.<sup>33</sup> The net force on each nucleus should be zero for the equilibrium geometry determined by using an approximate Hartree-Fock wave function which is fully optimized. This net force is the product of the electric field at the nucleus times the charge on the nucleus. This corresponds to total forces at the nuclei ranging from  $1.708 \times 10^{-2}$  dyn in the negative  $Z$  direction for  $\text{HBF}^+$  to  $2.147 \times 10^{-3}$  dyn in the same direction for HNC so the Hellman-Feynman is not in fact satisfied. Presumably these deviations from the Hellman-Feynman theorem are due, at least in part, to incompletely optimized wave functions. It is interesting that the total forces at the nuclei are smaller for the less stable member of each HXY pair.

The average diamagnetic susceptibility,  $\chi_{\text{av}}^{\text{d}}$ , of the molecule can be determined from the electronic contribution to the second moment of the charge distribution relative to the center-of-mass with the relation

$$\chi_{\text{av}}^{\text{d}} = (-e^2 N / 6mc^2) \langle r^2 \rangle_{\text{CM}}$$

The results are shown in Table II. The sign of these quantities is positive because of the choice of axes directions. Unfortunately no experimental data are available for comparison, the only measured quantity being  $\chi_{\perp} - \chi_{\parallel} = 7.2 \pm 0.4 \times 10^{-6} \text{ cm}^3/\text{mol}$ . The calculated value of  $\chi_{\text{av}}^{\text{d}}$  obtained by Kato et al.<sup>18</sup> of  $-14.87 \times 10^{-6} \text{ cm}^3/\text{mol}$  for HCN is more than a factor of 2 smaller than the present result.

The electronic contribution to the potential at a specific atom in a molecule can be used to determine the average diamagnetic shielding at that atom by using the relation

$$\sigma_{\text{av}}^{\text{d}}(\text{A}) = (e^2 / 3mc^3) \langle 1/r \rangle_{\text{A}}$$

where  $\sigma_{\text{av}}^{\text{d}}(\text{A})$  is the average diamagnetic shielding at atom A in parts per million (ppm). The results are given in Table IV. The values for HCN are in excellent agreement with the experimental results obtained by Garvey and DeLucia<sup>34</sup> for  $\sigma_{\text{av}}^{\text{d}}(^1\text{H})$ ,  $\sigma_{\text{av}}^{\text{d}}(^{13}\text{C})$ , and  $\sigma_{\text{av}}^{\text{d}}(^{14}\text{N})$  of 101.72, 326.75, and 377.62 ppm, respectively, and with the results of Gierke and Flygare.<sup>13</sup> The significant changes in  $\sigma_{\text{av}}^{\text{d}}$  at a particular atom in going from one molecule to another are worth noting. Generally, theories of chemical shifts in molecules assume that they arise primarily from changes in paramagnetic terms. The present results are in agreement with other recent calculations<sup>20</sup> in suggesting that diamagnetic effects must also be taken into account.

In conclusion it does appear that the calculated one-electron properties, where they can be compared with experimental results, are in quite good agreement with these results. On the basis of comparison with experimental data, where available, the present calculated bond lengths are too short by approximately 0.01 Å and the dipole moments are too large by about 15%. While the inclusion of polarization functions has generally been found to lead to improvements in the one-electron properties calculated at a specific geometry, somewhat the reverse effect has been observed in geometry optimization of bond lengths. One would therefore expect that use of a double  $\zeta$  plus polarization basis set would give better one-electron properties for the particular equilibrium geometry obtained but that equilibrium geometry would not agree as well with the experimental geometry as the one obtained by using the double  $\zeta$  basis set. The error in the calculated dipole moments is at least in part due to the insufficiency of the present basis sets in describing the behavior of electrons distant from the nuclei. It is difficult to determine how accurately other multipole moments are calculated because of the lack of experimental data but the present results are in good agreement with previous calculations, where available. The discrepancy between the present calculated value of the deuteron quadrupole coupling constant for DCN and the experimental and calculated values (Table VI) is directly attributable to the sensitivity of this quantity to the D-C bond distance. Bonaccorsi's<sup>16</sup> calculated value was obtained at a D-C bond distance of 1.065 Å compared to the 1.056 Å distance in the present calculation. Those properties which are less sensitive to geometry or electron distribution far from the nuclei, such as the  $^{14}\text{N}$  quadrupole coupling constant and average diamagnetic shielding, are in good agreement with experiment where such comparison is possible.

## References and Notes

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