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The 14-Electron Isoelectronic Series. Some ab Initio Calculations on a Series of Related Molecules

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Received August 20, 1976

Abstract: Ab initio calculations on a number of related 14-electron molecules have been carried out using a 4-31G basis set and the equilibrium geometries and the electronic structure of the molecules in these geometries are presented. A primary purpose of this investigation was to detect patterns in the total energies, geometries, and ordering of the molecular orbitals for these related isoelectronic systems. Such patterns have been observed and are discussed and where possible interpreted. In addition, the results of protonation are described and a preliminary result of the study of the potential energy surface for the protonation of NO^+ is given. The study also provides equilibrium geometries for a number of previously uninvestigated molecular species which will hopefully be of assistance to experimentalists interested in detecting and identifying such species.

The 14-electron isoelectronic series contains a number of important and thoroughly investigated molecules such as carbon monoxide, nitrogen, hydrogen cyanide, and acetylene. It also contains a number of molecules which have recently been identified as being present in interstellar space and have more recently still been produced and studied in the laboratory. These are the molecular species HCO^+ , HNN^+ , and HNC . Individual members of this series have been studied using ab initio molecular orbital techniques and a wide variety of basis sets. Among these are CF^+ ,^{1,2} HBNH ,^{3,4} NO^+ ,² CO ,⁵ HCO^+ ,⁶⁻⁸ N_2 ,⁹ NNH^+ ,^{2,8,10,11} CN^- ,¹² HCN ,¹³ HNC ,¹⁴⁻¹⁶ HCNH^+ ,¹⁷ HBO ,¹⁸ C_2^{2-} ,¹⁹ HCCH ,²⁰ BF ,⁹ HBF^+ ,²¹ and O_2^{2+} .¹⁹ While much effort has been expended, with some success, in empirical and semiempirical calculations, using a consistent methodology, to study series of related molecular systems with the hope of discovering patterns of behavior in the energies, molecular orbital order, and other electronic properties there is little or no evidence of similar studies, using a consistent basis set, in ab initio calculations. The work re-

ported here deals with such a set of calculations involving a group of isoelectronic molecules and using a 4-31G Gaussian basis set. The results obtained are analyzed with a view to observing regularities in the ordering of energies of the molecules, the molecular orbitals, and the geometry parameters.

Within the group of isoelectronic molecules studied are subgroups related by the presence or absence of one or more protons. Another purpose of this study was to investigate the effect of protonation on the orbital energies and total energies and to observe what changes in electron density distribution occur. A set of calculations on the single protonation of BF , CO , and N_2 ²¹ discussed the systems HBF^+ , HCO^+ , COH^+ , and NNH^+ but used a smaller basis set than the one employed here and provide no information on the total energy or equilibrium geometry of COH^+ .

A number of the molecular systems discussed in this study have either never been previously investigated, have been studied using a smaller basis set, or have been subject to only partial optimization. It is hoped that the equilibrium geome-

Table I. Molecular Properties for the Minimum Energy Forms of CF^+ , HCF^{2+} , and HFC^{2+} ^a

	CF^+	HCF^{2+}	HFC^{2+}
RC-F, Å	1.187	1.142	1.342
RC-H, Å		1.190	
RF-H, Å			1.148
Total electronic energy	-160.704 08	-166.205 20	-163.176 65
Nuclear repulsion energy	24.073 32	29.732 23	26.716 49
Total energy	-136.630 76	-136.472 97	-136.460 16
Electron density			
C	4.921	4.816	4.505
F	9.079	8.889	9.352
H		0.295	0.143
Valence orbital energies	-2.2304 $3\sigma^2$ -1.3553 $4\sigma^2$ -1.1876 } $1\pi^4$ -1.1876 } $1\pi^4$ -0.9851 $5\sigma^2$	-2.6192 $3\sigma^2$ -1.7049 $4\sigma^2$ -1.5447 } $1\pi^4$ -1.5447 } $1\pi^4$ -1.5413 $5\sigma^2$	-2.4474 $3\sigma^2$ -1.7162 $4\sigma^2$ -1.4664 } $1\pi^4$ -1.4664 } $1\pi^4$ -1.3002 $5\sigma^2$

^aAll energies in hartrees.

tries obtained for these molecules will aid in their identification by, for example, assisting in the assignment of lines in the microwave or millimeter wave spectrum.

Method and Results

The calculations were carried out using an ab initio program developed by Hehre and Pople²² and available through the Quantum Chemistry Program Exchange. In all instances the basis set used was the 4-31G extended Gaussian basis set. In the determination of the Cartesian coordinates used, the atomic weights were those of the most abundant isotope and were taken from the 1972-73 CRC Handbook.²³ Calculations were carried out for individual geometries until an energy minimum was obtained using geometry variations in the region of the minimum of 0.001 Å in bond lengths and 1° in bond angles. The results obtained for the equilibrium geometries of the systems studied are given in Tables I–XI. Table XII lists the results obtained for the equilibrium structures of the system HNO^{2+} at N–H distances corresponding to the equilibrium structure, the structure at the barrier top, and the structure corresponding to complete separation of H^+ from NO^+ . The equilibrium rotational constants, B_e , for those molecules for

Table II. Molecular Properties for the Minimum Energy Forms of HBC^{2-} , HCB^{2-} , and $HBCH^-$ ^a

	HBC^{2-}	HCB^{2-}	$HBCH^-$
RB-C, Å	1.364	1.383	1.303
RB-H, Å	1.231		1.183
RC-H, Å		1.098	1.063
Total electronic energy	-77.549 54	-77.964 25	-83.442 31
Nuclear repulsion energy	15.011 42	15.436 74	19.951 34
Total energy	-62.538 12	-62.527 51	-63.490 96
Electron density			
H(-B)	1.421		1.173
B	5.855	5.871	5.350
C	6.724	6.949	6.521
H(-C)		1.179	0.956
Valence orbital energies	-0.2304 $3\sigma^2$ -0.0481 $4\sigma^2$ +0.2043 $5\sigma^2$ +0.2687 } $1\pi^4$ +0.2687 } $1\pi^4$	-0.2877 $3\sigma^2$ -0.0506 $4\sigma^2$ 0.2525 } $1\pi^4$ 0.2525 } $1\pi^4$ 0.2590 $5\sigma^2$	-0.5716 $3\sigma^2$ -0.3597 $4\sigma^2$ -0.2824 $5\sigma^2$ -0.0308 } $1\pi^4$ -0.0308 } $1\pi^4$

^aAll energies in hartrees.

which geometries were not previously available are listed in Table XIII.

Discussion

A primary purpose of this investigation was to determine the equilibrium structure of a series of related molecules using a consistent basis set and to observe and interpret patterns in the electronic properties and geometries of the systems studied. A second and related reason for this study was to investigate the effect of single and double protonation particularly with regard to changes in orbital energies and electron distribution. For this reason the series of isoelectronic molecules is broken down in Tables I–XI into sets of subgroups differing only in terms of the number of protons present. The discussion will concern itself first with the patterns observed and with their interpretation. Second, the effects of protonation are given and interpreted. Finally, the equilibrium geometries and electronic structures of those molecules not previously investigated are discussed.

An initial observation that can be made in comparing all of the diatomic species studied is that in all of the heteronuclear

Table III. Molecular Properties of the Minimum Energy Forms of BN^{2-} , HBN^- , HN^- , and $H-B-N-H^a$

	BN^{2-}	HBN^-	HN^-	$HBNH$
RB-N, Å	1.304	1.251	1.292	1.227
RB-H, Å		1.176		1.156
RN-H, Å			0.980	0.976
Total electronic energy	-92.794 51	-98.118 53	-98.788 98	-104.274 11
Nuclear repulsion energy	14.203 11	18.580 93	19.279 33	24.091 43
Total energy	-78.591 41	-79.537 60	-79.509 65	-80.182 68
Electron density				
H(-B)		1.167		0.958
B	5.866	5.080	5.177	4.554
N	8.134	7.753	8.068	7.862
H(-N)			0.754	0.627
Valence orbital energies	-0.4163 $3\sigma^2$ -0.1040 $4\sigma^2$ 0.2263 } $1\pi^4$ 0.2263 } $1\pi^4$ 0.2598 $5\sigma^2$	-0.7411 $3\sigma^2$ -0.3481 $4\sigma^2$ -0.1690 $5\sigma^2$ -0.0821 } $1\pi^4$ -0.0821 } $1\pi^4$	-0.8054 $3\sigma^2$ -0.4337 $4\sigma^2$ -0.1213 } $1\pi^4$ -0.1213 } $1\pi^4$ -0.0253 $5\sigma^2$	-1.1095 $3\sigma^2$ -0.7366 $4\sigma^2$ -0.6087 $5\sigma^2$ -0.4222 } $1\pi^4$ -0.4222 } $1\pi^4$

^aAll energies in hartrees.

Table IV. Molecular Properties of the Minimum Energy Forms of NO⁺ and HNO²⁺ ^a

	NO ⁺	HNO ²⁺
RN-O, Å	1.048	1.039
RN-H, Å		1.218
Total electronic energy	-156.945 78	-161.901 99
Nuclear repulsion energy	28.276 11	33.437 88
Total energy	-128.669 67	-128.464 11
Electron density		
H		0.144
N	6.191	6.199
O	7.809	7.657
Valence orbital energies		
	-2.2491 3σ ²	-2.6042 3σ ²
	-1.3504 4σ ²	-1.7394 4σ ²
	-1.1774 } 1π ⁴	-1.5901 5σ ²
	-1.1774 }	-1.5230 } 1π ⁴
	-1.1459 5σ ²	-1.5230 }

^a All energies in hartrees.

diatomics the highest occupied orbital is the nondegenerate σ-type orbital and that in general the separation between the degenerate π orbitals and the highest occupied orbital increases with increasing electronegativity difference or core charge difference ranging from 0.010 hartree in the case of CN⁻ to 0.309 hartree in the case of BF. In the homonuclear diatomics the reverse ordering of the orbitals holds with the degenerate π orbitals being the highest occupied ones and the separation between these orbitals and the next lower occupied orbital ranging from 0.002 hartree for O₂²⁺ to 0.014 hartree for C₂²⁻. Also notable is that in every case, for the diatomic systems studied, the lowest energy virtual orbitals are degenerate π* type orbitals.

When the results for the triatomic systems are considered the first point to be noted is that in every case, as one would expect from Walsh's rules²⁴ since these systems all possess 10 valence electrons, they are all linear. Also if we compare the species HAB and ABH where B is taken as the more electronegative atom or the atom with larger core charge, the species HAB are more stable, i.e., have lower (more negative) total energy, than the species ABH which is, interestingly, in agreement with what would be expected using the concept of core-core repulsions.²⁵ Also in all the systems studied except those involving fluorine the degenerate pair of π orbitals are the highest occupied in the HAB molecules while a nondegenerate σ-type orbital is the highest occupied orbital in the

Table VI. Molecular Properties of the Minimum Energy Forms of N₂, HNN⁺, and HNNH²⁺ ^a

	N ₂	HNN ⁺	HNNH ²⁺
RN-N, Å	1.085	1.077	1.063
RN-H, Å		1.017	1.081
Total electronic energy	-132.652 10	-138.436 84	-143.721 55
Nuclear repulsion energy	23.89787	29.486 58	34.865 16
Total energy	-108.754 23	-108.950 26	-108.856 39
Electron densities			
N	7.00	6.610	
N(-H)		7.013	6.738
H		0.376	0.262
Valence orbital energies			
	-1.5341 2σ _g ²	-1.9067 3σ ²	-2.2585 2σ _g ²
	-0.7687 2σ _u ²	-1.3238 4σ ²	-1.6416 2σ _u ²
	-0.6300 3σ _g ²	-1.0246 5σ ²	-1.5480 3σ _g ²
	-0.6263 } 1π _u ⁴	-0.9979 } 1π ⁴	-1.3461 } 1π _u ⁴
	-0.6263 }	-0.9979 }	-1.3461 }

^a All energies in hartrees.

ABH molecules. The pattern for the ABH molecules also holds true for HFC²⁺ and BFH⁺. In the case of HCF²⁺ and HBF⁺ the σ orbital is the highest occupied but it is notable that the energy separation between this orbital and the lower degenerate π orbitals is significantly smaller in the case of HCF²⁺ (0.003 hartree) compared to HBF⁺ (0.055 hartree). In the systems HNN⁺ and HCC⁻ the degenerate π orbitals are the highest occupied. In fact where the two heavy atoms are identical the degenerate π orbitals remain the highest occupied in all the systems based on them. In every case in going from the systems HAB to ABH one observes a significant destabilization of the highest occupied σ-type orbital. In all cases except for the fluorine-containing systems there is also a slight stabilization of the degenerate π orbitals resulting in these systems in the switch over of orbitals already mentioned. In the fluorine-containing systems the π orbitals are slightly destabilized in going from HAB to ABH. In fact, in the fluorine-containing systems the degenerate pair of orbitals would be better described as nonbonding fluorine orbitals than as π orbitals. Another feature is that there is no noticeable pattern of behavior for the total electronic energy and the nuclear re-

Table V. Molecular Properties of the Minimum Energy Forms of CO, HCO⁺, HOC⁺, and HCOH²⁺ ^a

	CO	HCO ⁺	HOC ⁺	HCOH ²⁺
RC-O, Å	1.128	1.098	1.160	1.115
RC-H, Å		1.078		1.128
RO-H, Å			0.976	1.046
Total electronic energy	-135.070 12	-140.803 05	-140.465 08	-145.849 76
Nuclear repulsion energy	22.517 75	28.023 73	27.720 43	33.159 65
Total energy	-112.552 36	-112.779 32	-112.744 65	-112.690 11
Electron densities				
H(-C)		0.484		0.351
C	5.607	5.364	5.090	4.979
O	8.393	8.152	8.571	8.436
H(-O)			0.340	0.233
Valence orbital energies				
	-1.5574 3σ ²	-1.9372 3σ ²	-1.9182 3σ ²	-2.2748 3σ ²
	-0.7940 4σ ²	-1.2056 4σ ²	-1.3601 4σ ²	-1.6530 4σ ²
	-0.6401 } 1π ⁴	-1.0951 5σ ²	-1.0193 } 1π ⁴	-1.4497 5σ ²
	-0.6401 }	-0.9973 } 1π ⁴	-1.0193 }	-1.3540 }
	-0.5488 5σ ²	-0.9973 }	-0.8773 5σ ²	-1.3540 }

^a All energies in hartrees.

Table VII. Molecular Properties of the Minimum Energy Forms of CN⁻, HCN, HNC, and HCNH⁺ ^a

	CN ⁻	HCN	HNC	HCNH ⁺
RC-N, Å	1.170	1.140	1.163	1.124
RC-H, Å		1.051		1.067
RN-H, Å			0.979	0.997
Total electronic energy	-111.131 34	-116.939 13	-117.101 32	-122.840 02
Nuclear repulsion energy	18.995 74	24.207 20	24.384 53	29.817 66
Total energy	-92.135 60	-92.731 94	-92.716 79	-93.022 36
Electron densities				
H(-C)		0.674		0.512
C	6.306	5.989	5.698	5.487
N	7.694	7.337	7.738	7.541
H(-N)			0.564	0.460
Valence orbital energies				
	-0.9085 3σ ²	-1.2697 3σ ²	-1.2776 3σ ²	-1.6286 3σ ²
	-0.2918 4σ ²	-0.8076 4σ ²	-0.8782 4σ ²	-1.1916 4σ ²
	-0.1544 } 1π ⁴	-0.5723 5σ ²	-0.5171 } 1π ⁴	-1.0787 5σ ²
	-0.1544 }	-0.5008 }	-0.5171 }	-0.8563 }
	-0.1441 5σ ²	-0.5008 } 1π ⁴	-0.4777 5σ ²	-0.8563 } 1π ⁴

^a All energies in hartrees.**Table VIII.** Molecular Properties of the Minimum Energy Forms of BO⁻, HBO, HOB, and HBOH⁺ ^a

	BO ⁻	HBO	HOB	HBOH ⁺
RB-O, Å	1.248	1.199	1.298	1.222
RB-H, Å		1.153		1.155
RO-H, Å			0.936	0.952
Total electronic energy	-116.348 57	-121.766 93	-121.964 58	-127.524 71
Nuclear repulsion energy	16.960 49	21.748 25	22.014 30	27.215 85
Total energy	-99.388 09	-100.018 68	-99.950 28	-100.308 86
Electron densities				
H(-B)		0.934		0.410
B	5.163	4.471	4.617	4.076
O	8.837	8.594	8.875	8.767
H(-O)			0.508	0.746
Valence orbital energies				
	-1.0051 3σ ²	-1.3452 3σ ²	-1.4076 3σ ²	-1.7296 3σ ²
	-0.3147 4σ ²	-0.6722 4σ ²	-0.8680 4σ ²	-1.1822 4σ ²
	-0.1968 } 1π ⁴	-0.6091 5σ ²	-0.5805 } 1π ⁴	-0.9279 5σ ²
	-0.1968 }	-0.5170 }	-0.5805 }	-0.8947 }
	-0.0574 5σ ²	-0.5170 } 1π ⁴	-0.3433 5σ ²	-0.8947 } 1π ⁴

^a All energies in hartrees.**Table IX.** Molecular Properties of the Minimum Energy Forms of C₂²⁻, HCC⁻, and HCCH ^a

	C ₂ ²⁻	HCC ⁻	HCCH
RC-C, Å	1.271	1.234	1.190
RC-H, Å		1.057	1.051
Total electronic energy	-90.112 20	-95.888 03	-101.756 01
Nuclear repulsion energy	14.988 21	19.827 26	25.044 59
Total energy	-75.123 99	-76.060 76	-76.711 42
Electron densities			
C	7.000	6.344	
C(-H)		6.745	6.296
H		0.910	0.704
Valence orbital energies			
	-0.3481 2σ _g ²	-0.6981 3σ ²	-1.0327 2σ _g ²
	0.1158 2σ _u ²	-0.4309 4σ ²	-0.7568 2σ _u ²
	0.2356 3σ _g ²	-0.1120 5σ ²	-0.6761 3σ _g ²
	0.2495 } 1π _u ⁴	-0.0815 }	-0.4056 }
	0.2495 }	-0.0815 }	-0.4056 }

^a All energies in hartrees.

pulsion energy other than that the changes in these in going from HAB to ABH are small except in the fluorine-containing

compounds where they are very much larger. Also observable is the fact that in the HAB systems, ignoring the fluorine-containing compounds, there is a regular pattern of change in the separation of the highest occupied π and σ orbitals increasing for example in the series HBC²⁻, HBN⁻, HBO. The lowest energy virtual orbitals are degenerate π* orbitals except in CCH⁻, BNH⁻, HBC²⁻, and HCB²⁻ where the lowest is a σ*-type orbital.

Patterns of behavior can also be identified in the bond distances. In every case the A-B distance decreases in going from AB to HAB while there is no consistent pattern in going to ABH. The A-B distance is consistently shorter in the HAB series than in the ABH series. Finally the H-A distance is in every case longer than the B-H distance.

In the tetratomic systems the degenerate π orbitals are the highest occupied except in the case of HBFH²⁺ where they are more correctly described as fluorine nonbonding orbitals. When one looks at the separation of the degenerate π orbitals from the highest occupied σ orbital the pattern observed for the appropriate heavy atoms is BC (0.252 hartree), BN (0.187 hartree), BO (0.033 hartree), and BF (-0.186 hartree). In other words as the electronegativity difference or core charge difference increases the separation decreases and eventually reverses the ordering of the orbitals. The lowest energy virtual orbitals are in all cases a pair of degenerate π* orbitals. The A-B distance is always shortened in going from ABH to HABH while there is no consistent pattern in going from HAB

Table X. Molecular Properties of the Minimum Energy Forms of BF, HBF⁺, HFB⁺, and HBFH²⁺ ^a

	BF	HBF ⁺	HFB ⁺	HBFH ²⁺
RB-F, Å	1.310	1.242	1.877	1.345
RB-H, Å		1.160		1.190
RF-H, Å			0.945	1.050
Total electronic energy	-142.114 94	-147.667 46	-142.797 11	-151.729 68
Nuclear repulsion energy	18.177 50	23.436 34	18.663 74	27.594 63
Total energy	-123.937 44	-124.231 12	-124.133 37	-124.135 05
Electron densities				
H(-B)		0.723		0.577
B	4.563	4.004	4.103	3.765
F	9.437	9.273	9.498	9.460
H(-F)			0.399	0.198
Valence orbital energies				
	-1.6684 3σ ²	-2.0284 3σ ²	-1.8937 3σ ²	-2.3728 3σ ²
	-0.8100 4σ ²	-1.1426 4σ ²	-1.1013 4σ ²	-1.6049 4σ ²
	-0.7108 } 1π ⁴	-1.0478 } 1π ⁴	-0.9458 } 1π ⁴	-1.4121 } 1π ⁴
	-0.7108 }	-1.0478 }	-0.9458 }	-1.4121 }
	-0.4017 5σ ²	-0.9933 5σ ²	-0.7675 5σ ²	-1.2264 5σ ²

^a All energies in hartrees.**Table XI.** Molecular Properties of the Minimum Energy Form of O₂²⁺ ^a

	O ₂ ²⁺
RO-O, Å	1.012
Total electronic energy	-181.424 04
Nuclear repulsion energy	33.465 12
Total energy	-147.958 92
Electron densities	
O	7.000
Valence orbital energies	
	-3.0256 2σ _g ²
	-2.0046 2σ _u ²
	-1.7915 3σ _g ²
	-1.7900 1π _u ⁴
	-1.7900

^a All energies in hartrees.**Table XII.** Molecular Properties of HNO²⁺ at Different H-N Distances ^a

	(a)	(b)	(c)
RN-O, Å	1.048	1.042	1.039
RN-H, Å	90.000	1.529	1.218
Total electronic energy	-157.027 58	-160.969 48	-161.901 99
Nuclear repulsion energy	28.363 76	32.508 11	33.437 88
Total energy	-128.663 82	-128.461 37	-128.464 11
Electron density			
H	0.0	0.079	0.144
N	6.191	6.216	6.199
O	7.809	7.705	7.657
Valence orbital energies			
	-2.2549 3σ ²	-2.5488 3σ ²	-2.6042 3σ ²
	-1.3561 4σ ²	-1.6542 4σ ²	-1.7394 4σ ²
	-1.1832 } 1π ⁴	-1.5066 5σ ²	-1.5901 5σ ²
	-1.1832 }	-1.4697 }	-1.5230 }
	-1.1518 5σ ²	-1.4697 } 1π ⁴	-1.5230 } 1π ⁴

^a All energies in hartrees.

to HABH. Again as with the triatomics and in accord with Walsh's rules the tetratomics investigated are all linear.

In all of the heteronuclear diatomics the highest occupied orbital (5σ²) has a considerable amount of nonbonding char-

Table XIII. Equilibrium Rotational Constants, B_e^a (MHz), for Compounds Not Previously Investigated

Molecule	B _e , MHz	Molecule	B _e , MHz
HCF ²⁺	38 621.57	HCOH ²⁺	36 092.63
HFC ²⁺	31 666.27	HNNH ²⁺	38 424.34
HBC ²⁻	35 279.16	BO ⁻	49 759.50
HCB ²⁻	36 170.89	HBO	39 645.97
HBCH ⁻	31 371.18	HOB	38 660.39
BN ²⁻	48 220.53	HBOH ⁺	32 799.14
HBN ⁻	38 706.12	HBF ⁺	34 984.48
HNB ⁻	40 070.86	HFB ⁺	18 608.00
HNO ²⁺	45 440.04	HBFH ²⁺	26 317.91
HOC ²⁺	44 577.26		

^a B_e (MHz) = 5.05377 × 10⁵/I (amu Å²).

acter associated with the less electronegative atom A. The result of the approach of a proton to form HAB is that this orbital now takes on σ bonding character and is significantly stabilized relative to the π orbitals leading to the switch in order previously discussed. Even in the case of HCF²⁺ and HBF⁺ where the order does not change from that in CF⁺ and BF respectively the σ type orbital undergoes significant stabilization relative to the π orbitals. In the case of the approach of a proton to form ABH the orbital involved (4σ²) is one on the B atom which is lower lying than the π orbitals and the ordering of the outer occupied molecular orbitals is not affected. The relatively greater enhancement of the stability of the 5σ² orbital in HAB relative to the 4σ² orbital in ABH as a result of protonation is significant in terms of the general observation that the HAB species is always more stable, in terms of total energy, than the corresponding ABH species.

The addition of a further proton to form HABH results in all cases as observed, except for HBFH²⁺, in the π orbitals becoming the highest occupied. This is because in the case of the protonation of ABH the highest occupied orbital (5σ²) is associated with the A atom and takes on H-A bonding character resulting in enhanced stability and the switching of the orbital order. In the case of protonation of HAB it is the 4σ² orbital which is involved and the ordering of the outer occupied orbitals is unchanged.

In all instances of protonation where the species being protonated has a negative charge or is neutral the molecule formed has enhanced stability in terms of total energy over the reactant. However, where the reactant is already positively charged the protonated species formed is less stable. An example of the

latter case is the protonation of NO^+ to form HNO^{2+} (Table XII). In NO^+ the highest occupied orbital is predominantly nonbonding on the nitrogen while the lowest virtual orbitals are a pair of degenerate π^* orbitals. At a distance of 90 Å from the nitrogen the proton has not significantly affected the occupied orbitals but the lowest virtual orbital is now a hydrogen 1s orbital. An energy maximum is reached at an H-N distance of 1.529 Å at which point the N-O distance has shortened to 1.042 Å and the highest occupied orbitals are now a pair of degenerate π orbitals, i.e., the ordering of the highest occupied orbitals has been altered even though the H 1s orbital is present significantly only in the lowest virtual orbital. Closer approach of the proton produces a minimum at an H-N distance of 1.218 Å, the hydrogen 1s orbital now contributing to the fourth and fifth occupied orbitals and the lowest virtual orbitals becoming once again a degenerate pair of π^* orbitals. The energy barrier to formation of HNO^{2+} from NO^+ is approximately 130 kcal/mol.

All of the doubly charged species except for O_2^{2+} have not previously been described in the literature. A number of the singly charged species such as HBCH^- and HBN^- and the neutral species HOB also are new. The data provided in the Tables I-XI are generally self-explanatory. One interesting feature is the unusual length of the B-F bond in BFH^+ (1.877 Å). It appears as if the approach of a proton to the fluorine in BF results in a structure which is largely $\text{B}^+\text{F}-\text{H}$ with the hydrogen gaining electron density primarily at the expense of the boron.

It should be pointed out that the equilibrium rotational constants, B_e , given in Table XIII differ from the effective rotational constants, B_v , experimentally determined because of the vibrational dependence of the effective moments of inertia as given by

$$I_v = I_e + \sum_s (v_s + \frac{1}{2}d_s)\epsilon_s$$

where I_v is the effective moment of inertia, I_e is the moment of inertia of the equilibrium configuration corresponding to the minimum in the potential surface, the summation is over the vibrational states each characterized by a quantum number v_s plus a degeneracy d_s , and ϵ_s is a complex factor of both harmonic and anharmonic force constants. In general, for polyatomic molecules there is no clear-cut relation between the effective moments of inertia and the equilibrium geometry. However, it is hoped that the parameters listed in Table XIII will provide a useful first estimate in determining the wave-length regions to be searched for possible transitions.

In considering the reliability of the bond lengths obtained in the present calculations, particularly relative to other possible basis sets, it should be pointed out that Pople²⁶ has found that for a variety of simple organic molecules SCF bond distance errors using a double- ζ basis set of the 4-31G type are one-third to one-half as great as those resulting from the use

of a minimum basis set. Further, Schaefer²⁷ indicates that improving the basis set further does not necessarily improve the reliability of the geometries obtained and that, for the single configuration Hartree-Fock approximation, the double- ζ SCF level may be a good stopping point for the purpose of geometry predictions.

This paper has indicated a number of observed patterns in the electronic and geometric properties of a series of related molecules using the same basis set for all calculations. The effects of protonation have also been studied and again definite patterns were observed in comparing the various subgroups of systems investigated. Finally the equilibrium geometries and electronic structures of a number of new molecular species are described. While the advantage of using a single basis set for a series of molecules has been demonstrated it should be pointed out that some of the patterns observed might be an artifact of the basis set used and further studies on the same systems using a different basis set would be valuable for comparison with the present results.

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