Self-Consistent Molecular Orbital Methods. 21. Small Split-Valence Basis Sets for First-Row Elements

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Abstract: Two new split-valence basis sets, termed 6-21G and 3-21G, are proposed for use in molecular orbital calculations on molecules containing first-row elements. The valence functions for the smaller representation (3-21G) have been taken directly from the larger (6-21G), preventing their collapse inwards to make up for deficiencies in the inner-shell region. This is necessary to ensure a good description of bonding interactions which necessarily involve overlap of valence functions. Equilibrium geometries, vibrational frequencies, relative energies, and electric dipole moments calculated using the 3-21G basis set are nearly identical with those obtained from the larger 6-21G representation. Compared to experiment they are consistently superior to properties derived from the STO-3G minimal basis set, and of comparable quality to those obtained from the larger 4-21G and 4-31G representations. One notable exception is that the 4-31G basis set yields hydrogenation energies in significantly better agreement with experiment than those obtained from 3-21G. The 3-21G basis set comprises the same number of primitive Gaussian functions as STO-3G (although nearly twice the number of basis functions) and should be nearly as efficient computationally as that representation for applications which require evaluation of energy derivatives as well as the energy itself (e.g., determination of equilibrium geometry and calculation of vibrational frequencies). It is less costly to apply than either the 4-21G or 4-31G split-valence basis sets, and in those areas where the performance of the two is comparable it would appear to be the method of choice.

Introduction

Gaussian-type basis sets used in ab initio molecular orbital computations usually involve some compromise between computational cost and accuracy. Small sets can be used for a wider range of chemical problems but involve some loss of flexibility in the resulting molecular orbitals. The simplest level of basis is *minimal* and corresponds to one basis function per atomic orbital. The next level is *split-valence* in which two basis functions are used for each valence atomic orbital. This second level is known to give a better description of the relative energies and of some geometrical features of molecules. Further improvement of a basis set requires addition of functions of higher angular quantum numbers (polarization functions). Application of basis sets of this type is generally limited to relatively small molecules.

The basis functions are normally *contracted.* This means that each is a linear combination of a number of primitive Gaussian functions. A considerable increase in computational efficiency can be achieved if the exponents of the Gaussian primitives are shared between different basis functions.[2a] At the split-valence level, this has been exploited by sharing primitive exponents between s and p functions for the valence functions. In particular, a series of basis sets has been defined and designated *K-LM*G where *K*, *L*, and *M* are integers. Such a basis for a first-row element (Li to Ne) consists of an s-type inner-shell function with *K* Gaussians, an inner set of valence s- and p-type functions with *L* Gaussians, and another outer sp set with *M* Gaussians. Both valence sets have shared exponents. For hydrogen, only two s-type valence functions (with *L* and *M* Gaussians) are used. One such split-valence basis set (4-31G), defined for hydrogen and the first-row elements boron to fluorine, has already received widespread application.[2b,c] Two larger basis sets of this type (5-31G and 6-31G) have been proposed but have not been as widely applied.[3]

Since the 4-31G basis was proposed, computer programs have been developed which calculate analytically the derivatives of the energy with respect to nuclear coordinates. These are of great value in investigations of equilibrium structures, transition structures, force constants, and molecular vibrational frequencies. However, as several authors have pointed out, derivative programs increase greatly in efficiency as the number of primitive Gaussians is reduced.[4] This is not necessarily true for single-point (nonderivative) calculations where the computation is often dominated by the self-consistent field (SCF) procedure, which depends only on the number of basis functions and not on the number of primitives. There is, therefore, considerable motivation for the development of smaller split-valence basis sets with fewer primitives. In an important recent paper, Pulay, Forgarasi, Pang, and Boggs (PFPB)[4b] have developed such a smaller basis for hydrogen and boron through fluorine (denoted by 4-21G). They found for a series of small molecules that structures, force constants, dipole moments, and derivatives could be determined as well at this level as with the 4-31G basis.

The original 4-31G, 5-31G, and 6-31G split-valence basis sets were obtained by optimizing all Gaussian exponents and contraction coefficients to give the lowest Hartree–Fock (spin-unrestricted or UHF)[5] energy for the atomic ground state. However, difficulties are encountered if this procedure is followed using a small number of primitives, particularly if only a small number is used for the inner-shell basis function. If there are few valence electrons (e.g., Li or Be), there is a tendency for the valence functions to "fall inward" toward the nucleus. This presumably occurs because the total energy minimization criterion prefers additional functions in the inner-shell region rather than a good description of the valence region. This happened with attempts to find a 4-31G basis for lithium and beryllium which ultimately proved largely unsuccessful. Consequently, a 5-21G basis for these atoms was proposed for use in conjunction with the 4-31G set for other first-row atoms.[3b]

The "falling inward" of the valence part of split-valence basis is clearly undesirable since a good description of bonding interactions must involve the overlap of valence basis functions on neighboring atoms, which must in turn depend on a good description of the outer part of the atomic structure. Ideally, the valence part of a split-valence basis should be determined with a very good inner-shell function to prevent such an unwanted collapse. Thus, for example, we might define a "best" 21G valence part of a split-valence *K*-21G basis as one in which all parameters are optimized with *K* large (i.e., approximating an ∞ − 21G basis). Such a basis would no longer be computationally efficient because of the large value of *K*. However,

0002-7863/80/1502-0939$01.00/0

Table I. 21G Basis Functions for Hydrogen and Helium

atom	α'_1	d'_s	α''_1
H	4.501 80	1.562 85 (−1)	1.513 98 (−1)
	6.814 44 (−1)	9.046 91 (−1)	
He	1.362 67 (+1)	1.752 30 (−1)	3.829 93 (−1)
	1.999 35	8.934 83 (−1)	

the inner-shell basis function could then be replaced by one with fewer primitives (smaller K) *without reoptimizing the valence functions*. This would yield a computationally efficient basis set in which the valence functions would not have collapsed to an appreciable extent.

In this paper we explore this route to obtaining efficient split-valence sets for first-row atoms. The first step is to determine and evaluate 6-21G basis sets, simulating "perfect inner-shell" ∞ − 21G sets. The 6G inner-shell functions are then replaced by smaller (less primitives) 3G inner-shell functions, and the resulting basis set is evaluated and compared with 6-21G.

Atomic Basis Sets

For atoms Li to Ne, the *K-LMG* basis functions are defined as

$$\begin{aligned}
\varphi_{1s}(\mathbf{r}) &= \sum_{k=1}^{K} d_{1s,k} g_s(\alpha_{1k}, \mathbf{r}) \\
\varphi'_{2s}(\mathbf{r}) &= \sum_{k=1}^{L} d'_{2s,k} g_s(\alpha'_{2k}, \mathbf{r}) \\
\varphi'_{2p}(\mathbf{r}) &= \sum_{k=1}^{L} d'_{2p,k} g_p(\alpha'_{2k}, \mathbf{r}) \\
\varphi''_{2s}(\mathbf{r}) &= \sum_{k=1}^{M} d''_{2s,k} g_s(\alpha''_{2k}, \mathbf{r}) \\
\varphi''_{2p}(\mathbf{r}) &= \sum_{k=1}^{M} d''_{2p,k} g_p(\alpha''_{2k}, \mathbf{r})
\end{aligned} \tag{1}$$

where g_s and g_p are normalized s- and p-type Gaussian functions, respectively. For hydrogen and helium, only two s-type basis functions are used containing L and M primitives. Thus

$$\begin{aligned}
\varphi'_s(\mathbf{r}) &= \sum_{k=1}^{L} d'_{s,k} g_s(\alpha'_k, \mathbf{r}) \\
\varphi''_s(\mathbf{r}) &= \sum_{k=1}^{M} d''_{s,k} g_s(\alpha''_k, \mathbf{r})
\end{aligned} \tag{2}$$

The basis sets introduced in this paper have $L = 2$ and $M = 1$. Values of K of 3 and 6 are considered.

The 6-21G basis is first obtained by minimization of the UHF atomic energies, all d coefficients and α exponents being varied subject to normalization. Numerical procedures have been discussed elsewhere.[2b] For atoms H, He, B, C, N, O, F, and Ne, the atomic ground state is used. For Be, the $(1s)^2(2s)(2p)^3P$ excited state is used to obtain a good simultaneous description of valence s- and p-type orbitals. For Li, the s-type basis functions are determined using the $(1s)^2(2s)^2S$ ground state and the contraction coefficients for p functions are found subsequently using the $(1s)^2(2p)^2P$ excited state, holding the other parameters fixed. Complete results are given in Tables I and II. The hydrogen and helium values have been obtained previously by van Duijneveldt.[6] All values are given with six figures and need to be slightly renormalized when used in practice.

As mentioned in the Introduction, our interest is to find valence basis functions close to those appropriate for perfect inner-shell functions. To test whether this level is adequately approached with $K = 6$, an 8-21G basis was found for carbon using the same technique. All parameters for the valence functions were found to be within 1% of the 6-21G values; this is judged to be sufficiently close. No further investigations were undertaken with $K > 6$.

Having found the complete 6-21G basis, the next step is to formulate K-21G bases for Li to Ne with smaller K, holding the valence part fixed. This is done by reoptimizing the φ_{1s} parameters for the atomic ground states (except ^3P for beryllium). The resulting values for $K = 3$ are listed in Table III. Finally, 6-21G and 3-21G atom energies are found in Table IV.

Molecular Scaling Factors

The basis sets listed in the previous section are appropriate to atoms. For use in molecular calculations, our previous practice[2b,c,3] has been to rescale the functions

$$\varphi^{\text{molecule}}(\mathrm{r}) = \zeta^{3/2}\varphi(\zeta r) \tag{3}$$

choosing the ζ values to be optimum for some "average molecular environment". This has long been known to be particularly important for hydrogen. To study possible rescaling of the K-21G basis sets, we have optimized the energies of some small molecules with respect to both geometrical parameters and separate scaling factors ζ' and ζ'' for the inner and outer valence functions. Results for AH_n molecules with only one nonhydrogen atom are listed in Table V. Corresponding results for some diatomic molecules are in Table VI.

These optimum scale factors show considerable variation. In our previous development of the 4-31G basis,[2b,c] we proposed a somewhat arbitrary set of "average molecular scaling factors" for use in calculations on molecules. However, for atoms Li to Ne, we elect not to do this with the 6-21G and 3-21G basis sets, so that the basis functions will be used without further modification. There are two main reasons for this. In the first place, optimum ζ values both greater and less than unity are found for all atoms except boron. Secondly, if the basis sets are to be used for exploration of reactive potential surfaces where atoms are partly removed from molecules, a good description of the free atom is also important. The most serious inadequacy of using unit scale factors occurs for lithium, where an optimum value of 1.5 is found for ζ''_{Li} in lithium fluoride. This reflects contracted character for the valence functions in this highly ionic compound. However, as is evident in the next section, use of a scale factor of unity does not have a major adverse effect on the calculated properties of even this system.

We shall continue to treat hydrogen as an exception. The optimum scale factors are almost always greater than unity. Nevertheless, the scale factors used previously[2b] ($\zeta' = 1.20$, $\zeta'' = 1.15$) are based too heavily on hydrogen in polar bonds. To give a better average description and to give greater weight to hydrogen is partially broken bonds, we propose to use $\zeta' = \zeta'' = 1.10$ in the 6-21G and 3-21G basis sets.

Performance of the 6-21G and 3-21 Split-Valence Basis Sets[7]

Equilibrium Geometry Comparisons. Equilibrium geometries calculated for hydrogen and for the one heavy-atom hydrides of lithium to fluorine using the 6-21G and 3-21G basis sets are presented in Table VII. Here they are compared to experimental data where available as well as to previously obtained results[10] at the minimal basis STO-3G,[11] the PFPB 4-21G,[4b] and 4-31G[2] split-valence basis levels. Mean absolute deviation

Table II. 6-21G Basis Functions for Lithium to Neon

	α_1	d_{1s}	α'_2	d'_{2s}	d'_{2p}	α''_2
Li	6.424 18 (+2)	2.150 96 (−3)	5.402 05 (−1)	−2.631 27 (−1)	1.615 46 (−1)	2.856 45 (−2)
	9.651 64 (+1)	1.626 77 (−2)	1.022 55 (−1)	1.143 39	9.156 63 (−1)	
	2.201 74 (+1)	7.763 83 (−2)				
	6.176 45	2.464 95 (−1)				
	1.935 11	4.675 06 (−1)				
	6.395 77 (−1)	3.469 15 (−1)				
Be	1.264 50 (+3)	1.943 36 (−3)	1.295 48	−4.210 64 (−1)	2.051 32 (−1)	7.735 01 (−2)
	1.899 30 (+2)	1.482 51 (−2)	2.688 81 (−1)	1.224 07	8.825 28 (−1)	
	4.312 75 (+1)	7.206 62 (−2)				
	1.208 89 (+1)	2.370 22 (−1)				
	3.807 90	4.687 89 (−1)				
	1.282 66	3.563 82 (−1)				
B	2.082 12 (+3)	1.849 86 (−3)	2.281 87	−3.686 62 (−1)	2.311 52 (−1)	1.243 28 (−1)
	3.123 10 (+2)	1.412 77 (−2)	4.652 48 (−1)	1.199 44	8.667 64 (−1)	
	7.088 74 (+1)	6.926 97 (−2)				
	1.985 25 (+1)	2.323 93 (−1)				
	6.291 61	4.701 54 (−1)				
	2.128 62	3.602 88 (−1)				
C	3.047 52 (+3)	1.825 88 (−3)	3.664 98	−3.958 97 (−1)	2.364 60 (−1)	1.958 57 (−1)
	4.564 24 (+2)	1.405 66 (−2)	7.705 45 (−1)	1.215 84	8.606 19 (−1)	
	1.036 53 (+2)	6.875 70 (−2)				
	2.922 58 (+1)	2.304 22 (−1)				
	9.348 63	4.684 63 (−1)				
	3.189 04	3.627 80 (−1)				
N	4.150 11 (+3)	1.845 41 (−3)	5.425 22	−4.133 01 (−1)	2.379 72 (−1)	2.832 05 (−1)
	6.200 84 (+2)	1.416 45 (−2)	1.149 15	1.224 42	8.589 53 (−1)	
	1.416 88 (+2)	6.863 25 (−2)				
	4.033 67 (+1)	2.285 74 (−1)				
	1.302 67 (+1)	4.661 62 (−1)				
	4.470 03	3.656 72 (−1)				
O	5.472 27 (+3)	1.832 17 (−3)	7.402 94	−4.044 53 (−1)	2.445 86 (−1)	3.736 84 (−1)
	8.178 06 (+2)	1.410 47 (−2)	1.576 20	1.221 56	8.539 55 (−1)	
	1.864 46 (+2)	6.862 62 (−2)				
	5.302 30 (+1)	2.293 76 (−1)				
	1.718 00 (+1)	4.663 99 (−1)				
	5.911 96	3.641 73 (−1)				
F	6.783 19 (+3)	1.884 63 (−3)	9.777 59	−4.073 27 (−1)	2.466 80 (−1)	4.823 83 (−1)
	1.042 44 (+3)	1.381 21 (−2)	2.086 17	1.223 14	8.523 21 (−1)	
	2.423 98 (+2)	6.624 93 (−2)				
	6.963 20 (+1)	2.218 75 (−1)				
	2.268 94 (+1)	4.608 42 (−1)				
	7.796 36	3.784 53 (−1)				
Ne	8.785 83 (+3)	1.780 77 (−3)	1.248 30 (+1)	−4.099 22 (−1)	2.474 60 (−1)	6.062 50 (−1)
	1.323 90 (+3)	1.357 90 (−2)	2.664 51	1.224 31	8.517 43 (−1)	
	3.007 95 (+2)	6.708 47 (−2)				
	8.518 91 (+1)	2.268 25 (−1)				
	2.765 34 (+1)	4.650 53 (−1)				
	9.530 39	3.689 95 (−1)				

of both 6-21G and 3-21G AH bond lengths from experiment is 0.016 Å (six comparisons). The corresponding deviations in the STO-3G and 4-31G bond lengths are 0.035 and 0.014 Å, respectively. The 6-21G and 3-21G bond angles in ammonia and water are closer to experimental values than those obtained with the 4-31G basis, although they are still too large. This improvement has already been noted by PFPB in their work using a 4-21G basis set.[4b] STO-3G bond angles for these two molecules are smaller than the experimental values.

A larger set of 6-21G and 3-21G geometries for two-heavy atom systems for which experimental structural data are available is presented in Table VIII. Again comparisons are drawn with the results of STO-3G, 4-21G, and 4-31G calculations, some of which have previously been published.[2b,4b,12] Note that here, as in the case of the one heavy-atom hydrides, equilibrium geometries calculated using the 6-21G and 3-21G basis set are nearly identical. For example, the mean absolute deviations from experiment of 6-21G and 3-21G AB bond lengths are 0.016 and 0.016 Å, respectively (45 comparisons). These errors compare to deviations of 0.028 and 0.016 Å for the STO-3G and 4-31G calculations, respectively. Thus, again it would appear that equilibrium structures calculated using any of the 6-21G, 3-21G, or PFPB 4-21G basis sets are of comparable quality to those derived from 4-31G and superior to geometries obtained at the STO-3G level. Certain failures of this type of basis set (no polarization functions) are common to 3-21G, 6-21G, and 4-31G. Most notable is the incorrect prediction of a trans structure for hydrogen peroxide.

Calculated 6-21G, 3-21G, and 4-31G total energies for the one- and two-heavy-atom molecules for which theoretical equilibrium geometries have been determined are given in Table IX. STO-3G total energies have been published previously.[12a]

Molecular Vibrational Frequencies. Vibrational frequencies

Table III. 3-21G Inner-Shell Basis Functions for Lithium to Neon

	3-21G	
	α_1	d_{1s}
Li	3.683 82 (+1)	6.966 86 (−2)
	5.481 72	3.813 46 (−1)
	1.113 27	6.817 02 (−1)
Be	7.188 76 (+1)	6.442 63 (−2)
	1.072 89 (+1)	3.660 96 (−1)
	2.222 05	6.959 34 (−1)
B	1.1634 (+2)	6.296 05 (−2)
	1.743 14 (+1)	3.633 04 (−1)
	3.680 16	6.972 55 (−1)
C	1.722 56 (+2)	6.176 69 (−2)
	2.591 09 (+1)	3.587 94 (−1)
	5.533 35	7.007 13 (−1)
N	2.427 66 (+2)	5.986 57 (−2)
	3.648 51 (+1)	3.529 55 (−1)
	7.814 49	7.065 13 (−1)
O	3.220 37 (+2)	5.923 94 (−2)
	4.843 08 (+1)	3.515 00 (−1)
	1.042 06 (+1)	7.076 58 (−1)
F	4.138 01 (+2)	5.854 83 (−2)
	6.224 46 (+1)	3.493 08 (−1)
	1.343 40 (+1)	7.096 32 (−1)
Ne	5.157 24 (+2)	5.814 30 (−2)
	7.765 38 (+1)	3.479 51 (−1)
	1.681 36 (+1)	7.107 14 (−1)

Table IV. Energies of Atomic Ground States (hartrees)

atom	6-21G	3-21G
H[a]	−0.496 979	−0.496 979
He	−2.835 680	−2.835 680
Li[b]	−7.430 630	−7.381 513
Be[c]	−14.569 304	−14.486 820
B	−24.516 842	−24.389 762
C	−37.658 966	−37.481 070
N	−54.342 410	−54.105 390
O	−74.700 940	−74.393 657
F	−99.230 341	−98.845 009
Ne	−128.275 846	−127.803 825

[a] Scaled value = −0.496 199. See text following for discussion. [b] Value for ^2P state (6-21G): −7.363 352. [c] Value for ^3P state (6-21G): −14.506 096.

for the water and ammonia molecules obtained from the 6-21G and 3-21G basis sets are compared to experimental values in Table X. Also included are frequencies calculated using the STO-3G and 4-31G methods.[13] Theoretical frequencies have been calculated by determination of the complete quadratic force field (matrix of second derivatives) evaluated at the theoretical equilibrium geometry, anharmonic effects being neglected. Calculated frequencies corresponding to bond stretching modes are consistently higher than the corresponding experimental values for all levels of theory. Frequencies obtained from quadratic force constants calculated from the 6-21G and 3-21G basis sets are in best accord with the experimental quantities; those derived from the minimal STO-3G representation are most in error. The calculated bending mode frequency in water is overestimated by all levels of theory, the three split-valence basis sets yielding comparable results, the minimal STO-3G representation a value which is 35% too high. The same situations holds for the degenerate pair of bending vibrational modes in ammonia. The frequency associated with the symmetrical bend in ammonia (the mode leading to inversion at the nitrogen center) is, on the other hand, underestimated by all three split-valence levels, the 6-21G and 3-21G results being significantly closer to the experimental value than the frequency derived from 4-31G calculations. The STO-3G basis set again overestimates the magnitude.

Energy Comparisons. Theoretical energies for complete hydrogenation of two heavy-atom molecules (the same set as previously discussed) are presented in Table XI. Results obtained at the 6-21G and 3-21G levels have been compared both to experimental values (enthalpies) and to those derived from STO-3G and 4-31G calculations.[14] In general, the 6-21G and 3-21G reaction energies are similar, the largest difference between the two being 4.5 kcal mol^{-1} for the complete hydrogenation of nitrogen. Although the theoretical hydrogenation energies at either of these levels are clearly superior to those obtained using the minimal basis set STO-3G method (mean absolute deviations of 6-21G and 3-21G hydrogenation energies from experiment are 8.9 and 9.8 kcal mol^{-1}, respectively, for 18 comparisons, and 22.2 kcal mol^{-1} for STO-3G) they are not in as good agreement with the experimental enthalpies as those obtained at 4-31G (mean absolute deviation of 6.8 kcal mol^{-1}). The largest errors occur for saturated systems and for molecules with highly electronegative atoms. The significant deviation from the 4-31G results is presumably a consequence of the fact that, owing to a decrease in the number of Gaussian functions employed in the description of the valence atomic orbitals, the 6-21G and 3-21G functions are not as diffuse as the corresponding 4-31G representations.

A comparison of calculated (6-21G, 3-21G, STO-3G, and 4-31G levels) and experimental relative isomer energies is presented in Table XII.[15] STO-3G optimized geometries have been employed throughout.[16] Again the 6-21G and 3-21G energy differences are very similar, and generally are superior to the corresponding STO-3G values but not quite as good as the 4-31G results. Mean absolute deviations between 6-21G and 3-21G relative energies and experimental enthalpy differences are 5.7 and 6.0 kcal mol^{-1}, respectively (nine comparisons). Corresponding deviations for the STO-3G and 4-31G basis sets are 13.6 and 5.2 kcal mol^{-1}, respectively. The 6-21G and 3-21G basis sets perform most poorly in the comparison of acyclic and small-ring isomers (e.g., propyne/cy-

Table V. Optimum Geometries[a] and Valence Scale Factors for Molecules AH_n (6-21G)

molecule	R	θ	ζ'_A	ζ''_A	ζ'_H	ζ''_H	E
LiH	1.635		1.028	1.064	1.208	1.157	−7.979 15
BeH_2	1.336		1.022	.955	1.329	1.343	−15.757 41
BH_3	1.187		1.010	1.004	1.133	1.196	−26.363 19
CH_4	1.081		1.013	1.112	1.090	0.996	−40.153 44
NH_3	0.997	113.4	0.983	0.977	1.150	1.080	−56.106 12
OH_2	0.969	108.4	0.987	0.977	1.203	1.173	−75.891 25
FH	0.932		0.994	0.985	1.270	1.333	−99.84512

[a] Each molecule has equal AH bond lengths R and equal HAH bond angles θ. Angles for BeH_2, BH_3, and CH_4 are fixed by symmetry constraints, $D_{\infty h}$, D_{3h}, and T_d.

Table VI. Optimum Geometries and Valence Scale Factors for Molecules AB (6-21G)

molecule AB	R	ζ'_A	ζ''_A	ζ'_B	ζ''_B	E
Li_2	2.823	0.905	0.950	0.905	0.950	−14.867 77
LiF	1.526	1.129	1.503	0.998	0.982	−106.793 53
N_2	1.082	0.986	1.006	0.986	1.006	−198.773 49
CO	1.127	1.006	0.984	1.007	1.028	−112.574 64
F_2	1.398	1.011	1.019	1.011	1.019	−198.415 30

Table VII. Calculated and Experimental Equilibrium Geometries for Hydrogen and One-Heavy-Atom Hydrides

molecule	point group	geometrical parameter	6-21G	3-21G	STO-3G	4-21G[4b]	4-31G	exptl[a]
H_2	$D_{\infty h}$	r(HH)	0.735	0.735	0.712	0.732	0.730	0.741
LiH	$C_{\infty v}$	r(LiH)	1.636	1.640	1.510		1.637	1.595
BeH_2	$D_{\infty h}$	r(BeH)	1.338	1.339	1.291		1.332	
BH_3	D_{3h}	r(BH)	1.187	1.188	1.160	1.183	1.183	
CH_4[b]	T_d	r(CH)	1.083	1.083	1.083	1.082	1.081	1.086
NH_3	C_{3v}	r(NH)	1.003	1.003	1.033	1.000	0.991	1.012
		∠(HNH)	112.1	112.4	104.2	112.6	115.8	106.7
OH_2[c]	C_{2v}	r(OH)	0.968	0.967	0.990	0.963	0.950	0.959
		∠(HOH)	107.5	107.6	100.0	108.1	111.2	103.9
FH	$C_{\infty v}$	r(FH)	0.939	0.937	0.956	0.936	0.922	0.917

[a] Experimental data for diatomic molecules from S. Boucier, "Spectroscopic Data Relative to Diatomic Molecules", Vol. 17 of "Tables of Constants and Numerical Data", Pergamon Press, Elmsford, N.Y., 1970, or from G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1970. For polyatomic molecules from J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, "Structure Data on Free Polyatomic Molecules", Vol. 7 of Landolt-Bornstein, "Numerical Data and Function Relationships in Science and Technology", New Series, K. H. Hellwege, Ed., Springer-Verlag, West Berlin, 1976. [b] Experimental r_e reported by A. G. Robiette, at the Seventh Austin Symposium on Gas Phase Molecular Structure, University of Texas, Austin, Texas, 1978. [c] Experimental equilibrium structure from R. L. Cook, F. C. De Lucia, and P. Helminger, *J. Mol. Spectrosc.*, **53**, 62 (1974).

clopropene) where the methods unduly favor the open-chain system. This is also a documented failing of the 4-31G basis set.[15] Another conspicuous failing of the 6-21G and 3-21G methods is in the comparison of the relative stabilities of *trans*-ethanol and dimethyl ether. Here both levels underestimate the experimental difference (12.2 kcal mol^{-1}) by more than half.

Electric Dipole Moments. Electric dipole moments calculated using the 6-21G, 3-21G, and PFPB 4-21G basis sets are presented in Table XIII. These are compared both with experimental values and with results of STO-3G and 4-31G calculations.[17] As anticipated on the basis of our other studies, the two new split-valence basis sets yield results which are nearly identical. The calculated 6-21G and 3-21G dipole moments are generally, but not always, higher than the corresponding experimental values, the same trend as previously noted for the 4-31G split-valence basis set. Similar trends are shown by the 4-21G basis.[4b] On the other hand, the STO-3G minimal basis set generally underestimates the magnitudes of electric dipole moments. Mean absolute deviations between calculated and experimental electric dipole moments are 0.47 and 0.48 for the 6-21G and 3-21G basis sets (13 comparisons), smaller than the corresponding mean deviations from the STO-3G and 4-31G calculations, 0.72 and 0.52 D, respectively.

Conclusion

Two new split-valence basis sets (termed 6-21G and 3-21G) have been constructed for use in molecular orbital calculations on molecules containing first-row elements. Their performance, with regard to the calculation of equilibrium geometries and molecular vibrational frequencies and in the description of relative molecular energies, has been assessed, enabling the following general conclusions to be drawn.

Equilibrium geometries, vibrational frequencies, relative energies, and electric dipole moments calculated using the 3-21G basis set are very close to those obtained using the 6-21G representation, which, with its improved inner-shell description, does lead to significantly lower total energies. It is likely that other properties which do not depend to a significant extent on the description in the region of the atomic nuclei will likewise be handled equally by the two basis sets.

Equilibrium geometries calculated using the 6-21G and 3-21G basis sets are (in the mean) superior to those obtained from STO-3G calculations. They are approximately equal to 4-31G level structures, and superior with regard to the description of bond angles involving heteroatoms. Vibrational frequencies obtained using either of the 6-21G or 3-21G basis sets are also of comparable quality if not superior to those derived from 4-31G, and significantly closer to experiment than STO-3G values. The 6-21G and 3-21G basis sets do not fare as well as 4-31G with regard to the calculation of the energies of complete hydrogenation, although all three basis sets perform significantly better than STO-3G. On the other hand, calculated 6-21G and 3-21G relative isomer energies are of comparable quality to those obtained at the 4-31G values. Finally, 6-21G and 3-21G electric dipole moments are, in the mean, closer to experimental values than are those obtained either from 4-31G (which are generally larger) or STO-3G (which are generally smaller).

The 3-21G basis set contains fewer primitive Gaussian functions than the previously introduced 4-31G and PFPB 4-21G representations and, therefore, offers a significant computational advantage, particularly in applications which call for evaluation of energy derivatives (e.g., geometry optimizations and force constant evaluations). Preliminary explorations with even smaller representations (e.g., 3-11G and 1-21G) suggest that it is about the simplest split-valence basis set which performs moderately well with regard to the calculation molecular properties.[18] The 3-21G representation contains the same number of primitives as the widely used STO-3G minimal basis set, although it comprises almost twice the number of basis functions per atom (two for hydrogen and helium and nine for lithium to neon, vs. one and five basis

Table VIII. Calculated and Experimental Equilibrium Geometries for Two-Heavy-Atom Molecules

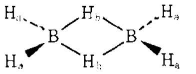
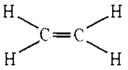
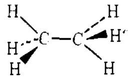
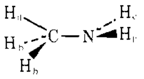
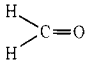
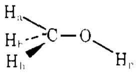
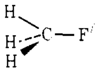
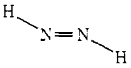
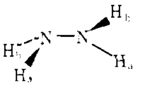
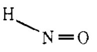
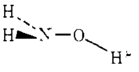
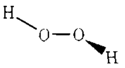
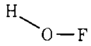
molecule	point group	geometrical parameter	6-21G	3-21G	STO-3G	4-21G[4b]	4-31G	exptl[a]
Li—Li	$D_{\infty h}$	r(LiLi)	2.818	2.816	2.698		2.803	2.672
Li—O—H[b]	$C_{\infty v}$	r(LiO)	1.536	1.537	1.432		1.577	1.582
		r(OH)	0.956	0.955	0.971		0.941	
Li—F	$C_{\infty v}$	r(LiF)	1.522	1.520	1.407		1.561	1.564
	D_{2h}	r(BB)	1.789	1.786	1.805		1.792	1.770
		$r(BH_a)$	1.182	1.182	1.154		1.178	1.192
		$r(BH_b)$	1.315	1.315	1.327		1.315	1.329
		$\angle(H_aBH_a)$	122.2	122.4	122.6		122.1	121.8
H—C≡C—H	$D_{\infty h}$	r(CC)	1.188	1.188	1.168	1.185	1.190	1.203
		r(CH)	1.051	1.051	1.065	1.051	1.051	1.061
	D_{2h}	r(CC)	1.315	1.315	1.306	1.312	1.316	1.330
		r(CH)	1.074	1.074	1.082	1.073	1.073	1.076
		∠(HCH)	116.2	116.2	115.6	116.0	116.0	116.6
	D_{3d}	r(CC)	1.542	1.542	1.538	1.541	1.529	1.526
		r(CH)	1.084	1.084	1.086	1.083	1.083	1.088
		∠(HCH)	108.0	108.1	108.2	108.0	107.7	107.4
H—C≡N	$C_{\infty v}$	r(CN)	1.139	1.137	1.153	1.137	1.140	1.153
		r(CH)	1.051	1.050	1.070	1.051	1.051	1.065
$H-\overset{+}{N}\equiv C^{-}$[d]	$C_{\infty v}$	r(NC)	1.161	1.160	1.170	1.162	1.162	1.165
		r(NH)	0.983	0.983	1.011	0.980	0.979	0.994
	C_s	r(CN)	1.472	1.471	1.486	1.474	1.450	1.471
		$r(CH_a)$	1.091	1.090	1.093	1.089	1.089	1.099
		$r(CH_b)$	1.083	1.083	1.089	1.081	1.081	1.099
		$r(NH_c)$	1.004	1.004	1.033	1.000	0.993	1.010
		$\angle(NCH_a)$	114.9	114.8	113.7	114.6	114.5	114.6
		$\angle(NCH_{bb})$	123.3	123.4	124.0		124.2	123.6
		$\angle(H_bCH_b)$	107,6	107.6	108.2		107.3	108.0
		$\angle(CNH_{cc})$	134.8	135.3	119.1	135.0	144.4	125.7
		$\angle(H_cNH_c)$	111.0	111.2	104.4	110.9	113.4	107.1
$\bar{C}\equiv O^+$	$C_{\infty v}$	r(CO)	1.131	1.129	1.146	1.130	1.128	1.128
	C_{2v}	r(CO)	1.209	1.207	1.217	1.208	1.206	1.203
		r(CH)	1.084	1.083	1.101	1.084	1.081	1.101
		∠(HCH)	115.2	115.0	114.5	115.2	116.4	116.5
	C_s	r(CO)	1.444	1.441	1.433	1.446	1.430	1.421
		$r(CH_a)$	1.079	1.079	1.092	1.079	1.076	1.093
		$r(CH_b)$	1.085	1.085	1.095	1.085	1.083	1.093
		$r(OH_c)$	0.967	0.966	0.991	0.962	0.950	0.963
		$\angle(OCH_a)$	106.2	106.3	107.7		106.3	107.0
		$\angle(OCH_{bb})$	130.6	130.5	130.4		129.6	129.8
		$\angle(H_bCH_b)$	108.7	108.7	108.1		109.2	108.5
		$\angle(COH_c)$	110.1	110.3	103.8	110.4	113.2	108.0
	C_{3v}	r(CF)	1.408	1.404	1.384		1.412	1.383
		r(CH)	1.080	1.080	1.097		1.076	1.100
		∠(HCH)	109.5	109.5	108.3		110.7	110.6
N≡N	$D_{\infty h}$	r(NN)	1.084	1.083	1.134	1.084	1.085	1.094
	C_{2h}	r(NN)	1.240	1.239	1.267		1.226	1.252
		r(NH)	1.022	1.021	1.061		1.012	1.028
		∠(NNH)	108.9	109.0	105.3		110.5	106.9
	C_2	r(NN)	1.451	1.451	1.459		1.401	1.447
		$r(NH_a)$	1.003	1.003	1.037		0.992	1.008
		$r(NH_b)$	1.007	1.007	1.040		0.995	1.008
		$\angle(NNH_a)$	109.0	109.0	105.4		113.0	109.2
		$\angle(NNH_b)$	113.4	113.3	109.0		116.6	109.2
		$\angle(H_aNH_b)$	111.8	111.8	104.6		115.0	113.3
		$\omega(H_aNNH_b)$	93.7	93.8	91.5		92.1	88.9
	C_s	r(NO)	1.218	1.217	1.231		1.197	1.212
		r(NH)	1.037	1.036	1.082		1.026	1.063
		∠(ONH)	109.5	109.4	107.6		110.7	108.6
	C_s	r(NO)	1.476	1.472	1.427		1.442	1.453
		r(NH)	1.003	1.002	1.044		0.998	1.016
		r(OH)	0.960	0.959	0.995		0.951	0.962
		$\angle(ONH_2)$	114.7	114.7	113.8		119.2	112.7
		∠(HNH)	109.7	109.6	103.3		111.5	107.1
		∠(NOH)	103.4	103.6	101.4		106.0	101.4
O=O	$D_{\infty h}$	r(OO)	1.241	1.241	1.217		1.196	1.207
	C_2	r(OO)	1.478	1.473	1.395		1.468	1.475
		r(OH)	0.972	0.971	1.001		0.955	0.950
		∠(OOH)	99.4	99.4	101.1		100.8	94.8
		ω(HOOH)	180.0	180.0	125.3		180.0	120.0

Table VIII (*Continued*)

molecule	point group	geometrical parameter	6-21G	3-21G	STO-3G	4-21G[4b]	4-31G	exptl[a]
	C_s	r(OF)	1.442	1.439	1.355		1.443	1.442
		r(OH)	0.977	0.976	1.006		0.961	0.964
		∠(HOF)	99.0	99.0	101.4		99.7	97.2
F—F	$D_{\infty h}$	r(FF)	1.406	1.402	1.315		1.413	1.416

[a] Except where otherwise noted, experimental data for diatomic molecules from S. Boucier, "Spectroscopic Data Relative to Diatomic Molecules", Vol. 17 of "Tables of Constants and Numerical Data", Pergamon Press, Elmsford, N.Y., 1970, or from G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1970. For polyatomic molecules from J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, "Structure Data on Free Polyatomic Molecules", Vol. 7 of Landolt-Bornstein, "Numerical Data and Function Relationships in Science and Technology", New Series, K. H. Hellwege, Ed., Springer-Verlag, West Berlin, 1976. [b] Estimate of LiO bond length from M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3,** 311 (1974). [c] See: L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.*, **63,** 4750 (1975), for an estimate of experimental r_e structure. [d] Experimental r_e structure from G. L. Blackman, R. D. Brown, P. D. Godfrey, and H. I. Gunn, *Nature* (*London*), **261,** 395 (1976); E. F. Pearson, R. A. Creswell, M. Winnewisser, and G. Winnewisser, *Z. Naturforsch. A*, **31,** 1394 (1976). [e] Experimental r_s structure from M. C. L. Gerry, R. M. Lees, and G. Winnewisser, *J. Mol. Spectrosc.*, **61,** 231 (1976). [f] Experimental r_s structure from N. W. Clark and F. C. De Lucia, *J. Mol. Struct.*, **32,** 29 (1976). [g] Experimental r_s structure from S. Tsunekawa, *J. Phys. Soc. Jpn*, **41,** 2077 (1976).

Table IX. Energies of Molecules (hartrees)

molecule	6-21G//6-21G	3-21G//3-21G	4-31G//4-31G	molecule	6-21G//6-21G	3-21G//3-21G	4-31G//4-31G
H_2	−1.122 96	−1.122 96	−1.126 38	HNC	−92.747 31	−92.339 71	−92.716 78
LiH	−7.978 84	−7.929 84	−7.977 35	CH_3NH_2	−95.084 98	−94.681 66	−95.071 66
BeH_2	−15.755 29	−15.673 78	−15.754 61	CO	−112.572 47	−112.093 30	−112.552 36
BH_3	−26.362 27	−26.237 30	−26.349 27	H_2CO	−113.698 54	−113.221 82	−113.692 62
CH_4	−40.149 26	−39.976 88	−40.139 77	CH_3OH	−114.872 52	−114.398 02	−114.871 52
NH_3	−56.103 65	−55.872 20	−56.106 69	CH_3F	−138.836 23	−138.281 89	−138.858 61
OH_2	−75.888 43	−75.585 96	−75.908 64	N_2	−108.771 00	−108.300 95	−108.754 22
FH	−99.842 40	−99.460 22	−99.887 29	N_2H_2	−109.821 12	−109.354 77	−109.812 69
Li_2	−14.866 74	−14.769 25	−14.860 66	N_2H_4	−111.012 54	−110.550 00	−111.006 75
LiOH	−82.803 81	−82.453 25	−82.817 01	HNO	−129.576 56	−129.038 29	−129.579 22
LiF	−106.784 09	−106.354 19	−106.824 09	NH_2OH	−130.789 76	−130.256 29	−130.791 88
B_2H_6	−52.745 20	−52.497 81	−52.719 40	O_2	−149.380 36	−148.769 08	−149.392 96
C_2H_2	−76.744 11	−76.395 96	−76.711 41	H_2O_2	−150.551 80	−149.945 82	−150.559 91
C_2H_4	−77.947 98	−77.600 99	−77.922 16	HOF	−174.487 55	−173.800 67	−174.515 85
C_2H_6	−79.138 02	−78.793 95	−79.115 93	F_2	−198.412 51	−197.644 24	−198.458 43
HCN	−92.760 38	−92.354 08	−92.731 93				

Table X. Calculated and Experimental Vibrational Frequencies (cm^{-1})

molecule	vibrational mode	6-21G	3-21G	STO-3G	4-31G	exptl[a]
H_2O	symmetric stretch	3780	3809	4133	3951	3657
	bend	1801	1801	2171	1745	1595
	antisymmetric stretch	3918	3941	4384	4102	3756
NH_3	symmetric stretch	3631	3639	3828	3761	3337
	bend	877	856	1412	623	950
	degenerate stretch	3789	3796	4103	3958	3444
	degenerate bend	1859	1858	2077	1821	1627

[a] Experimental frequencies from T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", *Natl. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 39** (1972).

Table XI. Calculated and Experimental Energies of Hydrogenation Reactions (kcal mol^{-1})

hydrogenation reaction	6-21G//6-21G	3-21G//3-21G	STO-3G//STO-3G	4-31G//4-31G	exptl[a]
Li—Li + H_2 → 2LiH	18.2	18.5	18.5	20.6	19.8
Li—OH + H_2 → LiH + H_2O	35.4	36.0	35.6	36.3	30.5
Li—F + H_2 → LiH + HF	51.9	52.7	34.1	54.1	49.6
CH_3—CH_3 + H_2 → 2CH_4	−25.5	−25.0	−18.8	−23.0	−18.1
CH_3—NH_2 + H_2 → CH_4 + NH_3	−30.1	−29.8	−20.0	−30.1	−25.7
CH_3—OH + H_2 → CH_4 + H_2O	−28.4	−28.2	−16.4	−34.1	−30.3
CH_3—F + H_2 → CH_4 + HF	−22.3	−22.2	−8.2	−26.1	−29.5
NH_2—NH_2 + H_2 → 2NH_3	−47.0	−46.7	−28.4	−50.1	−50.0
HO—OH + H_2 → 2H_2O	−66.0	−66.6	−30.9	−81.9	−86.8
F—F + H_2 → 2HF	−95.6	−98.1	−29.2	−118.8	−133.8
CH_2=CH_2 + 2H_2 → 2CH_4	−69.4	−70.9	−90.8	−65.1	−57.2
H_2C=O + 2H_2 → CH_4 + H_2O	−62.3	−63.5	−64.9	−64.1	−57.3
HN=NH + 2H_2 → 2NH_3	−91.8	−94.0	−74.6	−92.3	−83.5
HN=O + 2H_2 → NH_3 + H_2O	−110.3	−113.0	−77.7	−114.5	−102.9
HC≡CH + 3H_2 → 2CH_4	−122.2	−124.3	−153.7	−117.7	−105.4
HC≡N + 3H_2 → CH_4 + NH_3	−83.3	−84.9	−97.0	−84.1	−76.8
C^-≡O^+ + 3H_2 → CH_4 + H_2O	−66.2	−68.9	−72.0	−72.5	−63.9
N≡N + 3H_2 → 2NH_3	−48.0	−52.5	−36.2	−49.4	−37.7

[a] Experimental thermochemical data from S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1968.

Table XII. Calculated and Experimental Relative Isomer Energies (kcal mol^{-1}), STO-3G Optimized Geometries

formula	isomer	6-21G// STO-3G	3-21G// STO-3G	STO-3G// STO-3G	4-31G// STO-3G	exptl[a]
C_3H_4	propyne	0	0	0	0	0
	allene	2.1	2.9	17.1	0.8	1.6
	cyclopropene	40.5	39.9	30.0	36.4	22.3
C_3H_6	propene	0	0	0	0	0
	cyclopropane	15.8	14.5	−3.7	13.2	7.9
C_2H_3N	acetonitrile	0	0	0	0	0
	methyl isocyanide	18.2	20.2	24.1	20.6	16.8
C_2H_7N	*trans*-ethylamine	0	0	0	0	0
	dimethylamine	5.2	5.2	2.3	6.8	6.5
C_2H_4O	acetaldehyde	0	0	0	0	0
	vinyl alcohol	9.3	9.5	18.5	11.7	8 ± 2
	oxacyclopropane	35.2	35.2	11.0	37.8	27.1
C_2H_6O	*trans*-ethanol	0	0	0	0	0
	dimethyl ether	5.1	5.2	−0.8	9.5	12.2
CH_3NO	formamide	0	0	0	0	0
	nitrosomethane	66.5	68.4	23.9	65.7	60.5

[a] Experimental thermochemical data from S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

Table XIII. Calculated and Experimental Electric Dipole Moments (D)

molecule	6-21G//6-21G	3-21G//3-21G	STO-3G//STO-3G	4-21G//4-21G/[4b]	4-31G/4-31G	exptl[a]
LiH	5.95	5.99	4.84		5.97	5.88
NH_3	1.77	1.75	1.87	1.76	1.42	1.47
OH_2	2.37	2.39	1.71	2.19	2.49	1.85
HF	2.15	2.17	1.25	2.19	2.29	1.82
LiF	5.73	5.74	3.11		6.42	6.33
HCN	3.03	3.04	2.45	3.08	3.21	2.98
CH_3NH_2	1.44	1.44	1.62	1.48	1.25	1.31
CO	0.40	0.40	0.12	0.60	0.60	0.11
H_2CO	2.64	2.66	1.54	2.80	3.02	2.33
CH_3OH	2.10	2.12	1.51	2.21	2.28	1.70
CH_3F	2.32	2.34	1.15		2.63	1.85
N_2H_4	2.22	2.24	2.22		1.93	1.75
NH_2OH						0.59[b]
H_2O_2	0.00	0.00	1.30		0.00	2.20

[a] Except where otherwise noted experimental data from R. D. Nelson, D. R. Lide, and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **No. 10** (1967). [b] S. J. Tsunekawa, *J. Phys. Soc. Jpn.*, **38**, 167 (1972).

functions, respectively, for a minimal set). Therefore, 3-21G computations which are heavily dominated by derivative evaluation should be of comparable cost to those at the minimal basis STO-3G level, while "single-point" calculations, which are often dominated by the SCF procedure, are apt to be significantly most costly. Although the 3-21G basis set does not perform as well as 4-31G with regard to the calculation of reaction energies, its performance in other areas (e.g., equilibrium geometries, vibrational frequencies and electric dipole moments) is equal to or better than that of 4-31G. Furthermore, it is clearly superior to STO-3G both as a means for determining equilibrium geometries and force constants and for assessing relative molecular energies. Because of its increased number of basis functions (but not of primitive Gaussians), the range of application of the 3-21G basis to large molecules may be more limited than STO-3G. Nevertheless, where size limitations do not restrict its use, we suggest that the 3-21G split-valence basis set provides a reasonable alternative to the minimal STO-3G as a general tool for the investigation of molecular structure.

Acknowledgments. We are indebted to Dr. P. Pulay for an advance copy of ref 4b. This research was supported by grants from the National Science Foundation (Grant CHE75-09808 at Carnegie-Mellon University and Grant CHE77-04977 at the University of California).

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(1) (a) Carnegie-Mellon University; (b) University of California.

(2) (a) See: J. A. Pople and W. J. Hehre, *J. Comput. Phys.*, **27**, 161 (1978); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); (c) W. J. Hehre and J. A. Pople, *ibid.*, **56**, 4233 (1972).

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(6) F. B. van Duijneveldt, "Gaussian Basis Sets for the Atoms H-Ne for Use in Molecular Calculations", IBM Publication RJ 945 (No. 16437).

(7) All molecular calculations have been carried out using the GAUSSIAN 77/UCI program[8] on a Harris Corp. Slash 6 digital computer and the GAUSSIAN 78/CMU program[9] on a Digital Equipment Corp. Vax 11/780 digital computer.

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(16) We propose a nomenclature A//B to indicate calculations which have been performed at level A using a geometry which is optimum for level B. Thus 3-21G//STO-3G indicates a 3-21G level calculation using an optimum STO-3G geometry.

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A Theoretical Study of the Structure and Charge Distribution of Some Alkynylcarbenium Ions

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Abstract: We have carried out STO-3G minimal basis set "ab initio" calculations to determine the structure and charge distribution, using the YSP population analysis, of the propargyl cation and some of its mono-, di-, and trisubstituted derivatives. Our results indicate that progressive α substitution favors a greater participation of mesomeric form $\mathrm{XYC}_\alpha{}^+ - \mathrm{C}_\beta{=}\mathrm{C}_\gamma - \mathrm{Z}$, while γ substitution increases the contribution of form $\mathrm{XYC}_\alpha{=}\mathrm{C}_\beta{=}\mathrm{C}_\gamma{}^+ - \mathrm{Z}$. The relative stability of the different derivatives is also discussed.

I. Introduction

Alkynylcarbenium ions were directly observed first by Richey, Philips, and Rennick[1] in 1965. Ever since, the number of experimental and theoretical studies on these (and related) cations has been considerable.[2] This interest is justified because alkynyl cations are directly related to and can be a convenient model[3] for vinyl cations, which are, in turn, intermediates in solvolyses of vinyl halides,[4-7] vinyl triflates,[7,8] and the electrophilic addition to alkynes.[9]

Alkynyl cations can exist in the two mesomeric forms presented in Figure 1.

Since the paper of Richey et al.[1] was published, a considerable experimental effort was devoted to studying the inherent stabilities, structure,[10,11] and charge distribution[3] of these cations. This last aspect constitutes one of the most recent and interesting applications of ^{13}C magnetic resonance spectroscopy, since it has been proved[12] that chemical shifts reflect the charge densities on carbons of similar hybridization and substitution.

All these experimental studies[3,10,11] indicate that mesomeric form II is an important contributor to the stability of these cations. However, little can be said on how substituents might change the relative importance of these mesomeric forms, because only tertiary ions are stable, and this makes observation of electronic changes at C_α, C_β, or C_γ impossible.[3] However, theoretical work can yield valuable information on this problem.

The first members of this family, propargyl cation and its possible isomers, have been already studied at the "ab initio" level, using different basis sets.[13] However, no effort was devoted to evaluate the structure and charge distribution of alkynyl cations, with the only exception being the semiempirical calculations of Pittman et al.[14]

In this paper we present an "ab initio" study of some alkynylcarbenium ions. We will center our discussion on the relative stability of mesomeric forms I and II and on the influence of the substituents on the stability of either form, in each particular case. We will calculate the charge distribution using the YSP population analysis,[15] which has been proved very reliable[16] to evaluate charge densities in neutral and charged systems.

YSP population analysis is a density-partitioning technique based on the representation of the electron density $\rho(r)$ by an expansion in terms of spherical atomic density basis functions which do not present the limitations of the Mulliken population analysis, in the sense that the charge distributions obtained do not depend on the details of the basis set used in spanning the molecular wave function.

II. Calculations

We have carried out a geometry optimization of these mono-, di-, and trisubstituted propargyl cation derivatives (IIIa–l), presented in Figure 2, using a STO-3G minimal basis set.[17]

In the optimization process for IIIb–f, the following restrictions were adopted: the methyl group was kept unchanged, assuming local C_{3v} symmetry with CH bond lengths equal to 1.10 Å and HCH bond angles equal to 109.47°. For IIIl cation, the NH_2 group was also kept unchanged and in the same plane of the molecule, assuming local C_{2v} symmetry with NH bond length equal to 1.0 Å and the NHN bond angle equal to 120°. In all cases (IIIa–l) we have taken the C_α–C_β–C_γ skeleton as linear.

With these restrictions, all the remaining parameters were optimized, until changes in the total energy were less than 10^{-5} au for variations of ± 0.005 Å in the bond lengths and 0.1° in the bond angles.

III. Monosubstituted Derivatives

We present in Table I the optimized geometry of propargyl

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