

**Figure 2.** Calculated and observed<sup>33</sup> perpendicular and parallel contributions to the RR spectrum of the Q band of a typical porphyrin: (a) the calculated contribution of the A term to  $I_{||}$ ; (b) the calculated B term contribution to  $I_{||}$  of the  $B_{1g}$  and  $A_{1g}$  modes (the calculated intensities of the  $B_{2g}$  modes are much smaller); (c) the observed  $I_{||}$  of Cu-porphine<sup>33</sup> (the line at 1498  $\text{cm}^{-1}$  is much weaker in other porphyrins where other strong  $B_g$  lines appear at  $\sim 1550 \text{ cm}^{-1}$ ); (d) the observed  $I_{\perp}$  for Cu-porphine; (e) the calculated B term contribution to  $I_{\perp}$ .

the effect of protonation on absorption and resonance Raman spectra are straightforward. The proton charge is distributed as a  $\sigma$  charge between the proton and the atoms at the protonation site (the  $\sigma$  charge distribution can be determined by all-valence-electron calculations). This  $\sigma$  charge is treated simply as any other  $\sigma$  charge by eq 13, including the modifications of  $W_{\mu}$  by adding the  $Q_{\mu}^{\sigma\gamma_{AA}}$  term associated with the new  $\sigma$  charge. This type of calculation was used extensively in studying the effect of protonation on the spectrum of protonated Schiff bases of retinal.<sup>38,42</sup>

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## V. Concluding Remarks

This paper presents an extension of the QCFF/PI method to heteroatom-containing conjugated molecules. The extension involves incorporation of the  $\sigma$  charges into the  $\pi$ -electron Hamiltonian by treating formally the SCF equation as an all-valence-electron problem, assuming zero  $\sigma$ - $\pi$  overlap, and then fixing the  $\sigma$ -electron bond orders. The resulting submatrix of the  $\pi$  orbitals is the one used for the  $\pi$ -electron calculations. The incorporation of the potential from the  $\sigma$  atom of a given molecule in its  $\pi$ -electron Hamiltonian is generalized to incorporate potential from charges and induced dipoles of neighboring molecules (eq 21). This offers a simple and reliable way of incorporating environmental effects in calculations of spectroscopic properties of biological chromophores. This can be applied in detailed studies of spectral shifts of substrates or prosthetic groups in active sites of proteins with known X-ray structure. Such a study is demonstrated here for the spectral shift of hemoglobin upon  $r \rightarrow t$  transition. Other related studies are now underway in our laboratory.

Incorporation of external potentials from neighboring molecules in  $\pi$ -electron calculations might be crucial for consistent study of the important class of charge-transfer crystals of TCNQ and related molecules.<sup>43</sup> In such cases, the present method can be implemented in the Molecular Crystal Analysis (MCA) program.<sup>44,45</sup>

The extension of the QCFF/PI method to conjugated molecules allows for interpretation of RR spectra of most biological chromophores. This is demonstrated here by the normal mode analysis of a porphyrin. Other studies are reported in ref 3. The present approach also offers the possibility of studying environmental effects on RR spectrum of biological chromophores. Such studies may be done by simply using eq 21 in calculating RR spectrum of chromophores in protein active sites.

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## Study of Additivity of Correlation and Polarization Effects in Relative Energies

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**Abstract:** Calculations are reported at the 6-31G and 6-31G\*\* level with and without inclusion of all double excitations (CID/6-31G and CID/6-31G\*\*). The relative effects of polarization or correlation are compared with calculations involving polarization and correlation. The error in additivity is  $\sim 2$  kcal/mol for systems involving simple geometric changes and  $\sim 4$  kcal/mol for systems involving dimerization and molecular combination. These results are especially interesting in electron-deficient systems involving relatively large corrections due to differences in classical vs. nonclassical bonding. We emphasize that additivity in total energies is neither expected nor observed.

As computers become more efficient and computer methods more effective, the problem of correlation is becoming more tractable. Several prominent groups in theoretical chemistry have recently<sup>1,2</sup> solved the problem of determining analytical gradients





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from correlated wave functions. Other groups are concerned with CI effects and geometries<sup>3</sup> notably Kutzelnigg<sup>4-9</sup> and Meyer.<sup>10,11</sup>

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Table I. Differences in Total Energy Lowerings (kcal/mol) from DZ Basis (6-31G) with Further Levels of Approximation

molecule	CID/6-31G (MP3)	6-31G**	sum	CID + pol	geometry, Å	exptl
H <sub>2</sub> O, B-A	3.06 (2.93)	9.72	12.78 (12.65)	10.69	A, linear; B, bent	OH, 0.957 <sup>a</sup> HOH, 105.0
NH <sub>3</sub> , B-A	0.98 (0.78)	7.73	8.71 (8.51)	8.34	A, planar; B, pyramidal	NH, 1.033 <sup>b</sup> HNH, 106.7
N <sub>2</sub> , B-A	14.39 (7.14)	-4.80	9.59 (2.34)	9.72	A, 1.194; B, 1.294	NN, 1.194 <sup>c</sup>
F <sub>2</sub> , B-A	9.21 (7.13)	-5.72	3.49 (1.41)	3.09	A, 1.418; B, 1.518	FF, 1.418 <sup>d</sup>
B <sub>2</sub> H <sub>4</sub> , B-A	22.26 (22.31)	12.69	34.95 (35.00)	33.24	A,  ; B, 	
B <sub>2</sub> H <sub>4</sub> , C-A	1.84 (2.05)	-1.20	0.64 (0.85)	0.29	A,  ; C, 	
BH <sub>3</sub> ...H <sub>2</sub> , B-A	1.33 (1.42)	1.16	2.49 (2.58)	3.00	A, 1.60; B, 1.45	e
BH <sub>3</sub> ...H <sub>2</sub> , C-A	2.65 (2.84)	2.24	4.89 (5.08)	6.23	A, 1.60; C, 1.30	e
BH <sub>3</sub> , B-A	10.59 (11.24)	8.93	19.52 (20.17)	23.38	A, BH <sub>3</sub> , H <sub>2</sub> ; B, BH <sub>3</sub>	
B <sub>2</sub> H <sub>6</sub> , B-A	14.30 (15.22)	7.69	21.99 (22.91)	24.89	A, 2 BH <sub>3</sub> ; B, B <sub>2</sub> H <sub>6</sub>	





<sup>a</sup> Benedict, S. W.; Gailar, N.; Plyler, E. K. *J. Chem. Phys.* 1956, 24, 1139. <sup>b</sup> Kuchitsu, K.; Guillory, J. P.; Bartell, L. S. *Ibid.* 1968, 49, 2488. <sup>c</sup> Herzberg, G. "Spectra of Diatomic Molecules"; Van Nostrand: Princeton, NJ, 1950. <sup>d</sup> Andrychuk, D. *Can. J. Phys.* 1951, 29, 151. <sup>e</sup> See ref 31.

There is no question that CI effects are important for geometries and relative energies. Very few workers, however, have simultaneously considered the effect of correlation and polarization on systems of more than three nonhydrogen atoms. A CI calculation in the much expanded polarized space is often too great a demand on computer time to be feasible. The approach explored here is to combine the effect of polarization and correlation, which implies that energy lowering due to excitations to polarization orbitals is either equal for the systems considered or negligibly small. It is also necessary that the polarization functions act to increase the angular flexibility of the basis set but not be significantly occupied. According to Hurley<sup>12</sup> excitations to high-lying virtual or "external" orbitals are almost independent of nuclear configuration and therefore cancel when comparing energies of the same molecular formula. These are the justifications. But in practice, how well does the approximation hold? This approximation has been used<sup>13</sup> but not justified, tested extensively, or even suggested to have some generality.

### Method

Calculations were made at two geometries for each geometry (A and B) and at a third (C) for B<sub>2</sub>H<sub>4</sub> and BH<sub>3</sub> by using the Gaussian 80 program package.<sup>14</sup> For the first four molecules the experimental geometries were used for geometry A, and for geometry B the indicated deformation was made. All boron-containing compounds were optimized at the 3-21G level<sup>15</sup> and compared with STO-3G optimizations in Table II. At these geometries calculations were made at the CID/6-31G level<sup>16</sup> and at the CID/6-31G\*\* level. These two calculations provide the 6-31G and 6-31G\*\* energies as well as the Møller-Plesset correlation correction estimates and the correction due to all double

Table II. Optimized Geometries (Å)

molecule	variable	3-21G <sup>a</sup>	STO 3G <sup>b</sup> except BH <sub>3</sub>	exptl
H <sub>2</sub>	HH	0.7349 <sup>c</sup>	0.712 <sup>c</sup>	0.742 <sup>d</sup>
BH <sub>3</sub>	BH	1.1877 <sup>c</sup>	1.160	
BH <sub>3</sub> (C <sub>2v</sub> ), 	a	1.2592	1.27 <sup>e</sup>	
	b	1.2739	1.27	
	c	1.1836	1.19	
	α	100.41	102.0	
	β	127.49	120.0	
B <sub>2</sub> H <sub>6</sub>	BB	1.7852 <sup>c</sup>	1.805	1.770 <sup>f</sup>
	BH <sub>t</sub>	1.1823	1.154	1.192
	BH <sub>b</sub>	1.3147	1.327	1.329
	H <sub>t</sub> BH <sub>t</sub>	122.37	122.6	121.8
	BB	1.7477	1.713	
B <sub>2</sub> H <sub>4</sub> (A), 	BH <sub>t</sub>	1.1921	1.162	
	H <sub>t</sub> BH <sub>t</sub>	116.42	116.7	
	BB	1.4939		
	BH <sub>t</sub>	1.1584		
	BH <sub>b</sub>	1.2629		
B <sub>2</sub> H <sub>4</sub> (B), 	BB	1.6618	1.644	
	BH <sub>t</sub>	1.1939	1.162	
	H <sub>t</sub> BH <sub>t</sub>	116.40	117.2	
	BB	1.6618	1.644	
	BH <sub>t</sub>	1.1939	1.162	
B <sub>2</sub> H <sub>4</sub> (C), 	BB	1.6618	1.644	
	BH <sub>t</sub>	1.1939	1.162	
	H <sub>t</sub> BH <sub>t</sub>	116.40	117.2	
	BB	1.6618	1.644	
	BH <sub>t</sub>	1.1939	1.162	

<sup>a</sup> This work. <sup>b</sup> Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* 1975, 97, 3402. <sup>c</sup> Also see ref 15. <sup>d</sup> Footnote c, Table I. <sup>e</sup> Better than DZ: Hoheisel, C.; Kutzelnigg, W. *J. Am. Chem. Soc.* 1975, 97, 6970. <sup>f</sup> Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. "Structure Data on Free Polyatomic Molecules", Vol. 7 of Landolt-Bornsteins' "Numerical Data and Function Relationships in Science and Technology", New Series; Hellwege, K. H., Ed.; Springer-Verlag: West Berlin, 1976.

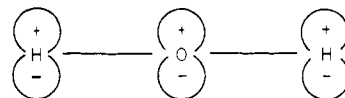


Figure 1.

excitations. The relative effects of correlation and polarization are next computed.

$$(\text{CID}/6\text{-}31\text{G} - 6\text{-}31\text{G})_{\text{B}} - (\text{CID}/6\text{-}31\text{G} - 6\text{-}31\text{G})_{\text{A}} = \Delta_{\text{CI}}$$

$$(6\text{-}31\text{G}^{**} - 6\text{-}31\text{G})_{\text{B}} - (6\text{-}31\text{G}^{**} - 6\text{-}31\text{G})_{\text{A}} = \Delta_{\text{pol}}$$

$$(\text{CID}/6\text{-}31\text{G}^{**})_{\text{B}} - (\text{CID}/6\text{-}31\text{G}^{**})_{\text{A}} = \Delta_{\text{pol}+\text{CI}}$$

Table I reports the  $\Delta_{\text{CI}}$ ,  $\Delta_{\text{pol}}$  and  $\Delta_{\text{pol}+\text{CI}}$  values for the molecules studied. Møller-Plesset corrections<sup>17</sup> to third order<sup>18</sup> are given in parentheses.

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Table III. Relative Energies<sup>a</sup> (kcal/mol)

molecule	6-31G	CID/6-31G**
H <sub>2</sub> O, A	26.27	36.95
B	0	0
NH <sub>3</sub> , A	0	7.09
B	1.26	0
N <sub>2</sub> , A	0	0
B	38.35	28.63
F <sub>2</sub> , A	0	0
B	4.91	1.82
B <sub>2</sub> H <sub>4</sub> , A	11.71	12.00
B	58.12	25.17
C	0	0
BH <sub>3</sub> ...H <sub>2</sub> , A	8.76 <sup>b</sup>	-0.15 <sup>b</sup>
B	11.40	-0.51
C	15.61	0.46
BH <sub>3</sub> , A	0	0
B	29.43	6.06
B <sub>2</sub> H <sub>6</sub> , A	13.70	38.58
B	0	0

<sup>a</sup> Positive energies are less stable, relative to the reference energy at zero; conversion factor, 1 hartree = 627.4898 kcal/mol. <sup>b</sup> With respect to BH<sub>3</sub> + H<sub>2</sub>.

### Discussions and Results

**H<sub>2</sub>O.** The two geometries studied were linear (A) and bent (B) water. The bent geometry is favored by both polarization and correlation because many interactions are eliminated by symmetry in the linear case. The total additive stabilization 12.78 kcal/mol is over 2 kcal/mol more than the  $\Delta_{CI+pol}$  value. The reason for this is that the  $\pi_u$  occupied orbital of linear H<sub>2</sub>O exhibits a significant hyperconjugative effect from the hydrogen p orbitals and the oxygen p orbital (Figure 1). The CID/6-31G will not contain this interaction, and therefore excitations from this orbital are ignored. An additional lowering of the linear structure by 2 kcal/mol through excitations from this orbital would account for the nonadditivity. A very accurate study<sup>19</sup> of the potential energy hypersurfaces for H<sub>2</sub>O predicts the linear form to be 34.5 kcal/mol higher than the bent form for a polarized basis set which decreases to 34.1 kcal/mol when single and double excitations are included. The present result of 35.99 kcal/mol (6-31G\*\*) increases to 36.95 kcal/mol (CID/6-31G\*\*; Table III) with inclusion of all double excitations.

**NH<sub>3</sub>.** From Table I it is seen that the planar geometry (A) is actually preferred at the 6-31G level. It has previously been found<sup>20</sup> that if a very large basis set of s and p functions is used, the HNH angle opens to 120°. Polarization is found to be the major source of the inversion barrier (calculated CID/6-31G\*\* 7.09 kcal/mol, experimental<sup>21</sup> 5.8 kcal/mol). A large STO calculation (5,4,1/2,1 + CI) by Stevens<sup>23</sup> has predicted a 5.9-kcal/mol barrier with only a 0.34-kcal/mol contribution from correlation. This is comparable with a correlation contribution of 0.61 kcal/mol calculated here. These results are also in complete agreement with previous results as reviewed by Payne and Allen.<sup>22</sup>

**N<sub>2</sub> and F<sub>2</sub>.** When the effects of polarization and correlation are compared, it is seen that polarization favors the shorter bond length (experimental) while correlation favors the longer. The effects are additive at the CID level, but at the MP3 level the relative correlation is underestimated. A good study has been made<sup>24</sup> and reviewed<sup>12</sup> of CI effects and the potential surface of F<sub>2</sub>; comparisons of CI vs. polarization effects were not made.

**Boron Compounds.** The next three molecules are electron-deficient compounds of boron which have been optimized at the

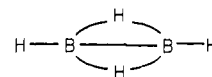


Figure 2.

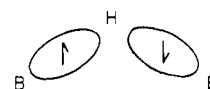


Figure 3.



Figure 4.

6-31G level and are compared in Table II with STO-3G optimized variables.

The three geometries of B<sub>2</sub>H<sub>4</sub> require polarization and correlation corrections which greatly favor the nonclassical structure. The total relative energy at the CID/6-31G\*\* level indicates the classical form A to be more stable by 13.17 kcal/mol and C by 25.17 kcal/mol than the nonclassical form (Table III). The relative difference between the D<sub>2h</sub> and D<sub>2d</sub> forms (12.00 kcal/mol, CID/6-31G\*\*) compares well with a value of 10.5 kcal/mol reported<sup>15</sup> at the 6-31G\* level. In the classical forms the ten bonding electrons are distributed in one BB bond and four BH terminal bonds. In geometry B there are two terminal bonds, two symmetrical BHB bonds and one BB bond (Figure 2). The system is expected to be strained as, in contrast to all known boron hydrides, the two borons are bonded by a direct bond as well as by two hydrogen bridges.

The additional correlation for the nonclassical form can be pictorially understood from Figures 3 and 4. It is much easier for opposite spin electrons to correlate their orbitals in Figure 3 and to remain separated by a proton than for the case in Figure 4. This is intended as only a pedagogic picture, as accurate molecular electron density maps<sup>25</sup> from a correlated wave function are known for the prototype hydrogen bridge system, B<sub>2</sub>H<sub>6</sub>, and isolated lobes as shown in Figure 3 are not indicated.

The next two boranes BH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> are among the simplest boron hydrides known to undergo reactions. Diborane has been widely studied,<sup>25-27</sup> and the results here agree very well with the work of Bartlett and co-workers,<sup>27</sup> who have applied many-bodied perturbation theory to diborane. With use of the relative 6-31G results in Table III, the dimerization energy is 34.60 by using the additivity rule and using the CID/6-31G\*\* basis 38.58 kcal/mol which compares well with the experimental value of 35.5 kcal/mol.<sup>28</sup> The molecule BH<sub>3</sub> has been well studied<sup>29-31</sup> and is predicted to exist as a weak complex only by the most sophisticated calculation<sup>30</sup> (UMP2/6-31G\*\*) in agreement with experimental observations.<sup>32</sup> Calculations were repeated on 4-31G optimized geometries<sup>30</sup> to determine if a stable adduct is also predicted at the additive level. The three geometries studied were the optimum UMP2/6-31G\*\* structure ( $r_0 = 1.45$  Å) and structures varied by 0.15 Å with the B-H<sub>2</sub> distance as reaction coordinate. The system is predicted unbound by the 6-31G, 6-31G\*\*, and CID/6-31G levels but bound (0.54 kcal/mol;  $r_0 = 1.48$ -Å parabolic fit) by CID/6-31G\*\*. Pople and co-workers<sup>30</sup> found a stability of 1.70 kcal/mol for the adduct at the UMP2/6-31G\*\*

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Table IV. Absolute Energies (Hartrees)<sup>a</sup>

molecule	6-31G	6-31G**	CID/6-31G (MP3/6-31G)	CID/6-31G**
H <sub>2</sub> O, A	-75.942 312	-75.965 830	-76.069 838 (-76.067 228)	-76.168 974
B	-75.984 176	-76.023 193	-76.116 574 (-76.113 601)	-76.227 861
NH <sub>3</sub> , A	-56.163 065	-56.184 910	-56.288 802 (-56.285 283)	-56.386 971
B	-56.161 063	-56.195 223	-56.288 361 (-56.284 530)	-56.398 267
N <sub>2</sub> , A	-108.838 792	-108.906 527	-109.081 736 (-109.066 000)	-109.238 813
B	-108.777 681	-108.837 765	-109.043 553 (-109.016 266)	-109.193 189
F <sub>2</sub> , A	-198.646 073	-198.673 139	-198.912 473 (-198.904 040)	-199.040 897
B	-198.638 252	-198.656 198	-198.919 321 (-198.907 585)	-199.038 002
B <sub>2</sub> H <sub>4</sub> , A	-51.595 950	-51.621 757	-51.721 908 (-51.714 929)	-51.821 821
B	-51.521 985	-51.568 009	-51.683 418 (-51.676 529)	-51.800 828
C	-51.614 609	-51.638 492	-51.743 503 (-51.736 856)	-51.840 947
BH <sub>3</sub> ...H <sub>2</sub> , A	-27.489 628	-27.515 103	-27.591 723 (-27.585 891)	-27.672 450
B	-27.485 430	-27.512 764	-27.589 645 (-27.583 945)	-27.673 032
C	-27.478 720	-27.507 770	-27.585 026 (-27.579 496)	-27.671 478
BH <sub>5</sub> , A	-27.503 593	-27.524 199	-27.600 089 (-27.593 593)	-27.672 214
B	-27.456 688	-27.491 525	-27.570 053 (-27.564 611)	-27.662 563
B <sub>2</sub> H <sub>6</sub> , A	-52.753 566	-52.785 738	-52.897 082 (-52.888 566)	-53.014 522
B	-52.775 392	-52.819 813	-52.941 705 (-52.934 650)	-53.076 007

<sup>a</sup> Correlation energies are for a "frozen-core" model and include a size-consistency correction (see ref 16).

level which compares well with the value calculated here (1.49 kcal/mol) at the same level. Significantly, when the polarization and correlation effects are added, a stable adduct persists [0.15 kcal/mol (0.17 kcal/mol);  $r_o = 1.54 \text{ \AA}$  ( $r_o = 1.53 \text{ \AA}$ ) parabolic fit to additive CID (MP3) energies], though more shallow and at a longer B-H<sub>2</sub> distance.

The C<sub>2v</sub> structure of BH<sub>5</sub>, believed to be a transition state/intermediate<sup>28,30</sup> in the hydrolysis and deuterolysis of the borohydride ion, was optimized at the 3-21G level which upon reoptimizing at the 6-31G\*\* level yielded an energy 0.05 kcal/mol lower (energies reported are at the 3-21G geometry). From Table I, BH<sub>5</sub> is 9.92 kcal/mol more unstable than BH<sub>3</sub> + H<sub>2</sub> by using the additivity rule and 6.05 kcal/mol more unstable than BH<sub>3</sub> + H<sub>2</sub> by using the CID/6-31G\*\* basis. This compares well with a value of 7 kcal/mol calculated by Hoheisel and Kutzelnigg.<sup>31</sup> For BH<sub>5</sub> and B<sub>2</sub>H<sub>6</sub> the additivity rule underestimates the relative effect of correlation by almost 4 kcal/mol. This difference is attributable to the larger virtual CI space of BH<sub>5</sub> and B<sub>2</sub>H<sub>6</sub> as compared to their constituent parts. The number of molecular orbital integrals created for the combined system is approximately 3 times the number created for the two parts. Excitations to the high-lying virtual orbitals, though contributing very little individually, are very numerous. Still, additivity in these cases gives a lower bound to their relative energy. Further if we accept the rule of additivity, this size effect (different relative energies for different basis sets: this should not be confused with size consistency<sup>16</sup>) amounts to ~3.5 kcal/mol in the systems studied. The problem of consistent CI corrections for composite systems needs further investigation. A summary of total energies is given in Table IV.

### Conclusion

Several representative molecular systems were studied to determine the additivity of polarization and correlation effects. It

was found that in cases tested here, which do not involve population of the polarization orbitals or a composite system, the additivity of CI effects (all double excitations) and polarization (d orbitals on all first-row elements; p orbitals on hydrogens) is accurate to about 0.5 kcal/mol. The third-order Møller-Plesset CI correction is less accurate especially for systems involving a large number of lone pairs. In composite systems the difference in relative virtual spaces yields lower CI energies for the combined system in the full polarized space. In these cases additivity provides a lower bound to the relative energy.

Total energies are not expected to be additive due to the neglect of all configurations involving polarized orbitals. At best one may hope that this difference is about constant for systems that have the same molecular composition and some similarities of chemical bonding. In the present study we have shown that this approximation is useful for conformational isomers and simple reactions not involving unpairing of electrons. Problems are anticipated for systems involving open shells, metastable or transition states, and elements beyond the first row of the periodic table. We shall explore other systems, other levels of approximation, and possible subtle cancellations which may lead to appropriate limits of relative energy additivity.

**Acknowledgment.** We wish to thank the National Science Foundation (Grant CHE 77 19899) and the National Institutes of Health (Grant GM 06920) for support. We also acknowledge NSF grant PCM 77-11398 for the computational laboratory. We are indebted to J. A. Pople for making the Gaussian 80 program available.

(33) Additivity at the MP3/6-31G and MP2/6-31G\*\* levels has been used very recently by: Nobes, R. H.; Rodwell, W. R.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1980**, *103*, 1913. See also: Komornicki, A.; Dykstra, C. E.; Vincent, M. A.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 1652.