suggests a strong interaction between the radical and $SnCl_4$.

Figure 5 represents the variation of the ESR spectra of the complexed radical **2** with temperature; [**1**] = [$SnCl_4$] = 1.00 M. Such variation of the spectra is completely reversible except that the radical decays at high temperature (over about 60 °C). Therefore, the variation is not due to another new radical produced by the reaction of the complexed radical. It is clear that the change of the central absorption lines is much larger than that of the wings of the spectrum. Analyses of the signals reveal that it is due to the larger variation of the $a_{\beta\text{-H}}$ value than the $a_{\gamma\text{-H}}$, $a_{\delta\text{-H}}$, and a_{Cl} values; e.g., $a_{\beta\text{-H}} = 7.96$ and 9.91 G, $a_{\gamma\text{-H}} = 2.36$ G, $a_{\delta\text{-H}} = 2.30$ G, $a_{^{35}\text{Cl}} = 0.25$ G, and $a_{^{37}\text{Cl}} = 0.21$ G at 60 °C.

It is well-known that the $a_{\beta\text{-H}}$ value is dependent on both the spin density ρ on the radical carbon and the time-average dihedral angle θ between the β hydrogen and the $2p_z$ orbital on the carbon.[14] Although it is now difficult to determine the exact θ value since the ρ value is expected to be reduced by complexation,[11] it seems that $SnCl_4$ regulates the rotation between β hydrogen and the carbon p_z orbital to some extent, $\theta = 54$–$57°$ at 23 °C, based on the $a_{\beta\text{-H}}$ value of 17.6 G for 1-methoxy-1-(methoxycarbonyl)ethyl radical,[15] in which the methyl group rotates freely, $\langle\theta\rangle = 45°$.

Restriction of such free rotation was clearly demonstrated by using $(CH_3)_3CCH_2\dot{C}(OCD_3)COOCD_3$, as shown in Figure 6, where [deuterated **1**] = [$SnCl_4$] = 1.00 M. The doublet of doublets at 23 °C, consistent with a conformationally locked structure, was converted to a triplet with increasing temperature. Small absorptions denoted in this figure by downward arrows are assigned to doublet splitting by ^{115}Sn, ^{117}Sn, and ^{119}Sn nuclei, $a_{Sn} = 8.85$ and 9.63 G at 40 and 60 °C,[8] which clearly supports the spectral analysis previously mentioned.

Acknowledgment. We express our cordial thanks to Dr. Y. Miura (Osaka City University, Japan) for his helpful discussion.

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(15) This radical was produced by the hydrogen abstraction from methyl 2-methoxypropionate by *tert*-butoxy radical in chlorobenzene under UV light irradiation at 23 °C.

Origin of Deuterium Isotope Effects on Carbon-13 Chemical Shifts

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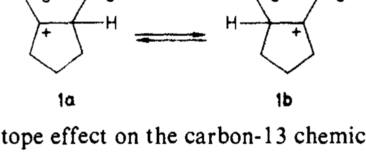
Abstract: In an attempt to model deuterium isotope effects on carbon-13 chemical shifts in the NMR spectra of aliphatic molecules and carbocations, ab initio calculations have been performed at the STO-3G level. The total charge and the gross orbital charges on the nuclei in these compounds were calculated as a function of the C–H bond lengths. The gross atomic charge and the gross orbital charges vary linearly with the bond length for small displacements around the equilibrium bond length. Assuming a charge shift relationship and reasonable values of the isotope effect on bond displacement, the magnitude and directions of the variations of electron density with C–H bond length were found to be sufficiently large to account for the magnitude and sign of the chemical shift isotope effects in acetone and the 2-propyl cation. The sign of β-deuterium isotope effects in cations with two-electron three-center bonds is not adequately accounted for.

The substitution of deuterium for hydrogen in organic compounds can alter the carbon-13 chemical shift of carbon atoms as many as six bonds removed from the site of substitution.[1] Saunders et al.[2] have shown that when deuterium is substituted for hydrogen at positions β to the cationic carbon in equilibrating carbenium ions, the equilibrium is shifted toward the carbenium ion isotopomer which has hydrogen β to the formally charged carbon. For example, in the 1,2-dimethyl-1-cyclopentyl cation, **1a** is favored, $K = [\textbf{1a}]/[\textbf{1b}] > 1$. Examination of the two-bond deuterium isotope effect on the carbon-13 chemical shift in nonequilibrating β-deuterated carbocations has shown the sign and magnitude of the effect at the positively charged carbon to depend upon the electron-demand and -delocalization mechanism at the cationic center. Servis and Shue[3] reported that β-deuterium substitution in classical static carbenium ions produces a downfield shift of the cationic carbon-13 resonance. In addition, Servis and Shue reported that the positively charged carbons in allylic and benzylic conjugated cations are unaffected by β-deuterium substitution. The β effect for such ions was related to the demand for hyperconjugative stabilization. Forsyth et al.[4] recently provided additional evidence for the hyperconjugative origin of the isotope effect arising from β-deuterium substitution in classical carbocations.



1a 1b

In three cases where the carbocations are believed to be σ-delocalized, β-deuterium substitution produces a shielding of the cationic carbon. The β effect in these ions arises from an isotopic perturbation of resonance. The electron distribution in the bridging three-center two-electron bond is perturbed by the replacement of hydrogen by deuterium.

The chemical shielding of a nucleus in a molecule is a function of the internuclear separations.[5] In principle, chemical shifts could be calculated by integrating the chemical shielding of the nucleus as a function of distance over the vibrational potential surface. Since vibrations are in general anharmonic, bonds are more or

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(2) Saunders, M; Wiberg, K. B.; Pratt, W.; Kater, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8072.

(3) Servis, K. L.; Shue, F. F. *J. Am. Chem. Soc.* **1980**, *102*, 7233.

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0002-7863/86/1508-2211$01.50/0

less deformed from the equilibrium configuration when the bond vibrates. The isotope effects could be obtained by comparison of integrated chemical shieldings for the two isotopomers over their respective vibrational potential surfaces. Full dynamical calculations of the variation of shielding with internal coordinates have been reported for a few diatomic molecules.[5] Recently, the isotope effects on the mean bond displacements in methane were calculated.[6] By neglecting all but the linear terms and assuming that the reported deuterium isotope effect on the carbon-13 chemical shift results from the calculated mean bond displacements, the sensitivity of the carbon-13 shielding to the C–H bond distance, $(\delta\sigma^{c}/\delta\Delta r_{CH})_e$, was found to be equal to -35 ppm/Å for the primary isotope effect. These methods have clarified the origin of the one-bond deuterium isotope effect on carbon-13 chemical shifts but are not easily extended to the molecules of interest here.

The merits of charge-shift relationships between carbon-13 NMR chemical shifts and atomic electron populations in a series of related compounds have been assessed.[7] When the various contributions to the shielding were examined, the local paramagnetic terms was found to govern the changes in total shielding[8] in a series of closely related compounds, and consequently, under these circumstances correlations between NMR shifts and local electron populations occur. Since isotopomers are the most closely related of compounds, any change in atomic electron populations which result from isotopic substitution should produce NMR shift changes.

We have attempted to assess whether the isotope effects on the chemical shift can be modeled by examining the effect of an artificial shortening of the C–H bond length at the site of isotopic substitution. This artificial shortening of the C–H bond mimics the decrease in the average internuclear separation which occurs upon isotopic substitution. Calculations of the electron density at each nucleus in a molecule or ion as a function of the variation of a specific C–H bond length should provide a measure of the change in the average electron density which results from isotopic substitutions at this site. An attempt to use semiemperical MO calculations to model the isotope effects on the C-13 shifts in naphthalene and azulene has been reported.[9] These calculations were stated not to account for the deuterium isotope effects at remote positions although no details were given.

We report here the results of the calculation of the variation in average electron densities at the carbon atoms in several molecules and carbocations and a comparison with reported chemical shift isotope effects in these or related compounds. These calculations provide insight into the origins of chemical shift isotope effects in carbon-13 NMR spectra.

Results

The STO-3G GAUSSIAN 70 program of Pople and Hehre[10,11] was used for the calculation of electron densities in several molecules and cations. The geometries used in the calculation are listed in the supplementary material and were taken from the literature where possible.[12] The structures of the cationic species were obtained from previously reported higher level calculation when available.[13]

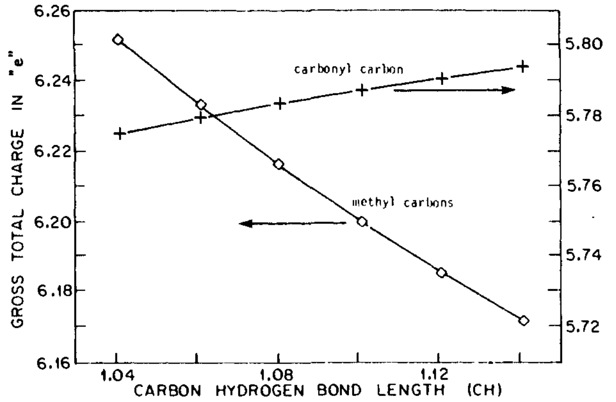

Figure 1. Plot of the gross total charge vs. the C–H bond length of the carbon atoms in acetone.

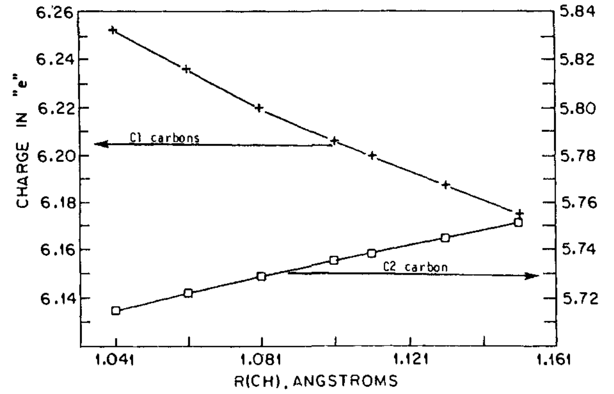

Figure 2. Plot of the gross total charge vs. C–H bond length of the carbon atoms in the 2-propyl cation.

Table I. Dependence of the Total Gross Atomic Charge on C–H Bond Length[a]

compound	C–H bond length varied	carbon	dq/dr, e/Å
acetone	1,1,1,3,3,3	C1	−0.80
		C2	+0.19
2-fluoro-2-propyl cation	1,1,1,3,3,3	C1	−0.76
		C2	+0.29
2-propyl cation	1,1,1,3,3,3	C1	−0.73
		C2	+0.33
propane	1,1,1,3,3,3	C1	−0.77
		C2	+0.17
1-phenyl-1-ethyl cation	1,1,1	C1	−0.77
		C2	+0.13
2,3-dimethyl-2-butene	1,1,1,1′,1′,1′	C1	−0.74
		C2	+0.20
2,3-dimethyl-2-butene chloronium ion	1,1,1,1′,1′,1′	C1	−0.78
		C2	+0.18
2-methyl-2-norbornyl cation (bridged structure)	8,8,8 (–CH_3)	C8	−0.56
		C2	+0.13
nonclassical 2-norbornyl cation (bridged structure)	3,3	C3	−0.47
		C2	+0.06

[a] Slopes of the plots of total gross atomic charge vs. C–H bond length are in units of electrons per angstroms.

Structural data were unavailable for the 1-phenyl-1-ethyl cation, the 2-fluoro-2-propyl cation, the 2-propyl cation, the 2-methyl-2-norbornyl cation, and the 2,3-dimethyl-2-butene chloronium ion, so appropriate values from structurally related compounds were

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used. For the phenyl ring of the 1-phenyl-1-ethyl cation, the C-C bond lengths were set to 1.340 Å, the C-H bond lengths were set to 1.040 Å, and the *ipso*-Cl bond length was set to 1.342 Å. The C2-H bond length of the 2-propyl cation was initially set at 1.09 Å and the calculations repeated with $r(HC^+) = 1.00$ Å. The C-F bond length employed for the 2-fluoro-2-propyl cation was 1.320 Å, which is slightly shorter than the average carbon-fluorine bond length found in perfluorohydrocarbons (1.34 Å).[14] The calculation for the 2-methyl-2-norbornyl cation employed the nonclassical structure of Goddard et at.,[13] except that the hydrogen attached to C2 was replaced by a methyl group at a distance of 1.522 Å.

The molecules and ions were oriented so that the p orbital at the carbon atom at the site adjacent to the C-H bond being varied was oriented along the x axis of a right-handed Cartesian coordinate system. Gross atomic charges and gross atomic orbital charges were determined by a standard Mulliken population analysis which was performed by the GAUSSIAN 70 program.

In these calculations, the changes in gross atomic and gross orbital charge upon gradual expansion of the internuclear separation of specific carbon hydrogen bonds were determined. The carbon hydrogen bond lengths were varied between 1.04 and 1.14 Å in increments of 0.010-0.040 Å. Both the gross total charge on individual nuclei and the gross atomic orbital charges were plotted as a function of carbon-hydrogen bond length.

Typical plots of the charge vs. C-H bond length are presented in Figures 1 and 2. These plots appear to be nearly linear for small displacements about the equilibrium bond length. The slopes of these plots are listed in Table I. The slopes of the atomic charge vs. carbon hydrogen bond length for the carbon atom at which the carbon-hydrogen bond length was being varied ranged from -0.73 to -0.80 e/Å (mean -0.76, standard deviation ±0.02) for the neutral molecules acetone, 2,3-dimethyl-2-butene, and propane as well as the classical 2-propyl cation, the classical 2-fluoro-2-propyl cation, and the resonance-stabilized 1-phenyl-1-ethyl cation. For the 2-norbornyl cation, variation of the C3-H bond lengths produced a change in the electron density at the C3 carbon of -0.47 e/Å. For the 2-methyl-2-norbornyl cation, variation of the methyl C-H bond length induced a charge variation at C8 of -0.56 e/Å. At the carbon β to the C-H bond being varied, the slopes of total charge vs. C-H bond length ranged from +0.33 to +0.06 e/Å.

Two separate calculations were performed for the 2-propyl cation employing C2-H bond lengths of 1.000 and 1.091 Å, respectively. The gross total charges and gross orbital charges obtained from both of these calculations were graphed as a function of the carbon-hydrogen bond length. The two slopes obtained from these two calculations for the 2-propyl cation indicate that the slope of the plot of the charge vs. C-H bond length does not vary with small variations in other specific geometrical parameters. The gross orbital charges and the total charge on individual atoms are listed in the supplementary material.

Discussion

The reported values for the one-bond and two-bond deuterium isotope effects on the carbon-13 chemical shifts for relevant compounds are listed in Table II. The notation for the isotope effect on the chemical shift is $^n\Delta C(D)$ where n is the number of bonds separating the observed carbon from the site of deuterium substitution.[15] A negative value indicates that the C-13 resonance in the deuterated isotopomer is upfield of the corresponding one in the nondeuterated analogue. For compounds for which the isotope effect has not been reported, those for closely related compounds have been used. Although the isotope effects in propane-*1,1,1,3,3,3*-d_6 have not been measured, the effects in a large number of related aliphatic compounds have been determined[11] and do not vary significantly. The 2-propyl cation cannot be prepared directly but isotope effects for other aliphatic cations are known to be reasonably constant;[3] the values for $CH_3{}^+C(CD_3)_2$ have been included in Table II. Isotope effects for 2-phenyl-2-propyl,[3] 2-*p*-tolyl-2-propyl,[3] and 1-*p*-fluoro-1-ethyl[16] cations have been reported; Table II includes values for the 2-phenyl-2-propyl cation. The isotope effect included for the 2-norbornyl-*3,3*-d_2 cation is that for the 2-methyl-2-norbornyl-*3,3*-d_2 cation.[16]

In all cases, the values for $^1\Delta C(D)$ are negative with a magnitude that does not change appreciably from one structure to another. This observation is consistent with an isotope-induced bond shortening which leads to increased shielding of the carbon nucleus. The values for $^2\Delta C(D)$, Table II, vary from +0.8 ppm for the 2-methyl-2-propyl cation to -2.5 ppm for the 2-methyl-2-norbornyl-*3,3*-d_2 cation. Short of full dynamical calculations, there is no way of assessing whether these results can be reconciled with the variation in shielding with internal coordinates for the two isotopomers.

In order to evaluate whether the isotopes can be modeled by using a charge-shift relationship and a calculation of the effect of isotopic bond displacements on atomic electron populations, the isotope effects on the C-13 chemical shifts need to be compared with the calculated changes in atomic electron populations induced by bond displacement. The rovibrationally averaged bond length for a C-H bond is measurably longer than for a C-D bond. The deuterium isotope effect on the average bond length has been reported to be as large as 0.012 Å.[9,17]

To complete the comparison, the change in electron density needs to be converted into a change in the chemical shift. The best estimates for this value come from examination of a series of compounds in which the hybridization is constant but the charge varies. In monocyclic conjugated hydrocarbons, the C-13 chemical shielding is increased by 160 ppm for each unit increase in the π-electron density.[18] If the total net atomic charge is used, the correlation line indicates a change of 300 ppm/e.[8]

We have determined the deuterium isotope effect on the carbonyl carbon-13 chemical shift in acetone-d_6 to be +0.32 ± 0.010 ppm.[19] Assuming a value of 160 ppm/e for the charge-shift relationship, a change of 0.32 ppm would result from a decrease in the carbonyl carbon π-electron density of -0.0020 e. If the value of 300 ppm/e is used, a change of -0.0011 e in the total net atomic charge would produce a shift of 0.32 ppm. Similarly the deuterium isotope effect on the methyl carbon-13 chemical shift in acetone of -0.86 ppm[20] would correspond to an increase in the electron density of +0.0054 e using 160 ppm/e or +0.0029 e using 300 ppm/e. The bond shortening resulting from isotopic substitution by deuterium will produce an increased atomic electron population at the methyl carbon and a decreased atomic electron population at the carbonyl carbon in acetone. Both the opposite sign and the relative magnitude of the calculated shifts in electron density are consistent with the opposite directions and relative size of the observed deuterium isotope effects on the C1 and C2 chemical shifts for acetone.

From the slopes listed in Table I, stretching a C-H bond removes the electron density from the carbon attached to the hydrogen. The calculations also indicate that the hydrogen gains a portion of this charge (see supplementary material). The remaining charge is lost to the electron-deficient carbon whose unoccupied p orbital hyperconjugates with the C-H σ bond.

The dependence of the total atomic charge on the C-H bond length, dq/dr, at the β carbon varies from one system to another

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(15) This is the same notation used in ref 11 except that upfield shifts by the heavier isotope have a negative sign. The conventional procedure is to treat upfield substituent effects as negative. Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, **1980**.

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Table II. Deuterium Isotope Effects on Chemical Shifts and Dependence of the Gross Atomic Charge and Gross Orbital Charges on C–H Bond Length for Several Selected Compounds

compound	C–H bond length varied	carbon	ΔC(D), ppm	variation in gross atomic charge, dq/dr[a]	variation in gross orbital charge, dq/dr[a]			
					2s	$2p_z$	$2p_y$	$2p_x$
propane	1,1,1,3,3,3	C1	–0.8[b]	–0.77	+0.32	–0.38	–0.33	–0.44
		C2	–0.2[b]	+0.17	+0.03	+0.04	+0.08	+0.03
acetone	1,1,1,3,3,3	C1	–0.9[h]	–0.80	+0.32	–0.40	–0.31	–0.43
		C2	+0.32[h]	+0.19	+0.04	+0.04	+0.08	+0.05
2-propyl cation	1,1,1,3,3,3	C1	–0.8[c]	–0.73	+0.27	–0.38	–0.22	–0.44
		C2	+0.8[c]	+0.33	+0.01	–0.03	+0.07	+0.31
1-phenyl-1-ethyl cation	2,2,2	C2	–1.0[f]	–0.77	+0.29	–0.37	–0.26	–0.41
		C1	0.0[f]	+0.13	+0.02	+0.01	+0.04	+0.05
2,3-dimethyl-2-butene	1,1,1,1′,1′,1′	C1	–0.9[e]	–0.74	+0.32	–0.25	–0.42	–0.44
		C2	–0.2[e]	+0.20	+0.04	+0.11	+0.03	+0.02
2-norbornyl cation (bridged structure)	3,3	C3	–0.9[d]	–0.47	+0.23	–0.30	–0.14	–0.25
		C2	–2.5[d]	+0.06	+0.01	0.00	+0.04	+0.01
2-methyl-2-norbornyl cation (bridged structure)	8,8,8 (CH_3)	C8	–0.8[g]	–0.56	+0.38	–0.44	–0.15	–0.36
		C2	–2.2[g]	+0.13	+0.07	+0.04	+0.10	–0.11

[a] In electrons per angstrom. [b] Value for 2-propanol in ref 11. [c] Value for $CH_3C^+(CD_3)_2$. See ref 3. [d] Unpublished results for the 2-methyl-2-norbornyl-3,3-d_2 cation. [e] Servis, K.; Domenick, R. *J. Am. Chem. Soc.* **1985**, *107*, 7186. [f] Value for 2-phenyl-2-propyl cation. See ref 3. [g] Reference 3. [h] Reference 16.

for the compounds listed in Table II. The value of dq/dr at the β carbon in the 2-propyl cation is +0.33 e/Å. The value of dq/dr at the C1 carbon in the 1-phenyl-1-ethyl cation is +0.13 e/Å, while the value obtained for C2 in the nonclassical structure of the 2-norbornyl cation is +0.06 e/Å. The variation in dq/dr for these systems appears to reflect the varying degrees of electron demand at the β carbons in these electron-deficient systems. Why the value for propane (+0.17 e/Å) is comparable to that in acetone (+0.19 e/Å) is not clear.

These values of dq/dr would suggest that 2ΔC(D) in all systems would be deshielding, and in fact many are not.[2,3,4,11,21] In aliphatic compounds, the two-bond deuterium isotope effect is generally negative as a result of increased inductive electron release. In classical carbocations where hyperconjugation is important, $^2\Delta C(D)$ is generally positive as a result of the decrease in hyperconjugative electron release by the vicinal C–D bond.

In an attempt to determine whether these phenomenological rationalizations were reflected in the STO-3G calculations, the contributions of the individual gross orbital charges to the total gross atomic charge were examined. Hyperconjugative effects should appear as an enhanced dependence of the gross orbital charge on C–H bond length for the empty $2p_x$ orbital of the cation, while inductive effects should appear in the dependence of the gross orbital charge on the C–H bond length for 2s, $2p_z$, and $2p_y$ orbitals. In Table II, the values of some selected examples are presented along with their respective deuterium isotope effects.

A comparison of the dependence of the gross orbital charge on the C–H bond length with the isotope effect on the chemical shift for the β carbon (Table II) indicates a roughly parallel behavior. In the 2-propyl cation, dq/dr for the $2p_x$ orbital is +0.31 e/Å and $^2\Delta C(D)$ is approximately 0.8 ppm. In the 1-phenyl-1-ethyl cation dq/dr for the $2p_x$ orbital is +0.05 e/Å and $^2\Delta C(D)$ is 0.0 ppm. In the 2-methyl-2-norbornyl cation, dq/dr for the $2p_x$ orbital is –0.11 e/Å and $^2\Delta C(D)$ is –2.22 ppm. Although there does not appear to be a linear relationship between the calculated dq/dr values and the experimental $^2\Delta C(D)$ value, the general trend appears to be in the correct direction.

The fact that the $^2\Delta C(D)$ effects in the 2-methyl-2-norbornyl cation are of opposite sign to those in the other cations has been attributed to an isotopic perturbation of resonance.[3] The calculations suggest that if the deuterium isotope effects were solely of hyperconjugative origin as in other classical cations, the induced shifts would be of the same sign. The failure of these calculations to reproduce the sign of $^2\Delta C(D)$ in the 2-methyl-2-norbornyl cation is consistent with the view that the isotope effects are of a different origin. It might be possible to model isotopic perturbation of resonance by allowing minimization of other geometric parameters as the C–H bond lengths are varied, but this has not been attempted. The large upfield shifts ($^2\Delta C(D) \approx -2$) in cations with two-electron three-center bonds are not readily accounted for.

Acknowledgment. The numerical calculations were carried out at the University of Southern California Computing Center. We thank Prof. Gerald A. Segal for his assistance with the calculations and for making the programs available.

Supplementary Material Available: Tables of geometries used in the calculations, gross orbital charges, total charges on individual atoms, and Cartesian coordinates for compounds in this study (35 pages). Ordering information is given on any current masthead page.

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