J. Phys. Chem. A **2001,** *105,* 7297−7307

An Exploration of Long Range Electronic Effects in Substituted Alkanes

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Received: March 5, 2001; In Final Form: May 24, 2001

An analysis of the results of ab initio quantum mechanical calculations has been performed on a large number of substituted ethanes, pentanes, hexanes, and dodecanes. The bond critical points of the Atoms in Molecules (AIM) method have been ascertained for these molecules and each is expressed as a FCP, which is defined as the fraction of the bond distance at which the critical point is located. In the ethyl derivatives, the FCPs for the methyl C−H bonds correlate with the charge on the hydrogen atoms. In the longer chain compounds, the FCP for the C_m-C_n bond of charged substituents is related to the difference in inverse distances of the carbon atoms from the charged substituent. An investigation of the amount of s character used in bonds showed that two measures of this quantity, a partial Mulliken overlap population analysis, and a method involving orthogonal Natural Bonding Orbital (NBO) theory orbitals, correlate well with the methylene H−C−H bond angle. In the NBO results for most C−C bonds, the amount of s orbital used in a hybrid orbital is proportional to the amount of the NBO localized hybrid orbital used in the bond. Further analysis shows that the amount of hybrid orbital used by a carbon atom in a bond to a neighboring carbon atom predicts the FCP; there is a relationship between the topological based method of the atoms in molecules approach and the NBO localization procedure. The s character in bonds is determined by the same inverse distance dependence found for the FCP. A similar result holds for the energies of carbon 1s orbitals. Atomic dipole vectors were studied; both their length and direction are influenced by charged substituents. The charged substituent exerts a perturbation on the atomic basin of the carbon atoms in long-chain alkanes that is propagated through space. This distortion determines the values of all investigated parameters.

Introduction

Knowledge of the effect of a substituent on the electronic properties of other atoms in a molecule is the cornerstone of modern physical organic chemistry.[1] Two aspects of this endeavor are pertinent in our studies. The electronic property most often discussed is atomic charge. This subject is uncertain, despite its great appeal, because there is no quantum mechanical operator associated with the charge on an atom in a molecule.[2] Many different methods of charge assessment exist[3−7] and often these give very different results.[8,9] In addition, there remains some question about the means by which the perturbation introduced by the substituent is transmitted to remote sites. Many argue that this transmission is dominantly by a through-space or field effect,[10−17] although others do not accept this assessment.[18−22] We became interested in the method of transmission of a perturbation during a study of the charge variation on carbon and hydrogen atoms in substituted alkanes.[23] In that study, we found that charged substituents transmitted that charge to the hydrogen atoms on the periphery of the molecules, but the carbon atoms in the substituted alkanes, other than the geminal ones, showed no systematic response to the substituent. As a result of these findings, we became interested in learning what properties, if any, of carbon atoms in alkyl chains are influenced by the substituent. For instance, does the polarization of the electron density around a carbon atom change? Does the bonding interaction change? In this work, we examine a number of quantum mechanically derived parameters and ascertain their response to substituents, especially charged ones. We report on two parameters that result from topological analysis of the electron density in a molecule[24,25] and two that result from analysis of wave functions.[26−29] Our aim is to use these parameters to probe how a substituent's charge is expressed in the carbon backbone. In contrast to the lack of meaningful variation of the carbon atom charge, these other variables show strong dependence upon the charge of the substituent and the detailed geometry of the molecules.

We have investigated the bond critical point and atomic dipole moments obtained from the electron density analysis of the Atoms in Molecules (AIM) method.[25] The bond critical point is the minimum on the path of maximum electron density between two nuclei. The bond critical point has been shown to move closer to the atom of lower electron withdrawing ability.[30−32] Because a substituent should change the relative electron withdrawing ability of a carbon atom, we expect that the bond critical points may reflect this perturbation. The atomic dipole is another parameter that is obtained from an AIM analysis of the topology of the charge density. The atomic dipole is the first moment of the charge density, a measure of the lack of spherical symmetry of the electron density. Bader[25] has interpreted the cause of this atomic dipole as a polarization of electron density around an atom that is a direct result of the perturbation by a neighboring atom. For instance, in CO, there is a dipole due to net electron transfer from carbon to oxygen that is significantly offset by the polarization of the atomic densities as measured by the atomic dipoles of C and O. We use such electronic polarization to probe the nature of the electron density in the atomic basin of carbon atoms in substituted, charged alkanes.

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10.1021/jp010833r CCC: $20.00

TABLE 1: Fractional Bond Critical Points and Atomic Dipole Vectors in CH_3CH_2X[a]

	FCP				atomic dipole[b]	
X	C_1-X	C_2-C_1	$H_{ap}-C_2$	H_g-C_2	C_1	C_2
			neutral X			
F	0.316	0.483	0.371	0.368	0.692 (1°)	0.105 (−11°)
OH	0.317	0.486	0.373	0.369	0.672 (1°)	0.092 (−9°)
NH_2	0.358	0.504	0.373	0.374	0.528 (3°)	0.007 (125°)
CH_3	0.502	0.498	0.373	0.374	0.037 (56°)	0.018 (20°)
CF_3	0.436	0.485	0.369	0.367	0.263 (−5°)	0.108 (−1°)
NF_2	0.319	0.479	0.370	0.365	0.617 (0°)	0.128 (−3°)
H	0.627	0.500	0.373	0.373	0.027 (−108°)	0.027 (0°)
SiH_3	0.625	0.499	0.372	0.372	1.359(180°)	0.043 (−5°)
SiF_3	0.624	0.490	0.369	0.369	1.364 (180°)	0.085 (−4°)
NH_2*c*	0.359	0.495	0.373	0.368, 0.374[d]		
			charged X			
CH_2^-	0.543	0.532	0.385	0.379	0.241 (−167°)	0.121 (−176°)
CF_2^-	0.515	0.516	0.386	0.373	0.116 (167°)	0.030 (142°)
BH_3^-	0.694	0.529	0.387	0.378	1.194 (−176°)	0.098 (−170°)
BF_3^-	0.694	0.522	0.385	0.376	1.190 (−178°)	0.054 (−170°)
$B(OH)_3^-$	0.694	0.525	0.387	0.376	1.191 (−176°)[e]	0.064 (−169°)[e]
O^-	0.331	0.534	0.388	0.379	0.662 (−8°)	0.133 (−168°)
NH_3^+	0.317	0.461	0.355	0.363	0.569 (−5°)	0.184 (−1°)
NF_3^+	0.303	0.437	0.352	0.355	0.544 (13°)	0.284 (−1°)
PH_3^+	0.625	0.464	0.355	0.363	1.064 (177°)	0.182 (71°)

[a] H_{ap} is the hydrogen antiperiplanar to the X group. H_g is the hydrogen gauche to the X group. [b] The length in atomic units is given with the angle with respect to the C_1-X and C_2-C_1 bonds in paranthesis for C_1 and C_2, respectively. See text for a description of the sign of the angles. [c] This molecule has the NH_2 group rotated so that one of the hydrogen atoms on the nitrogen is antiperiplanar to the C−C bond. [d] The first value is for the methyl hydrogen atom on the same side of the C−C−N plane as the lone pair on the nitrogen. The AIM charges are −0.003 and −0.029, respectively. [e] The atomic dipoles in these cases are slightly out of the plane defined by the two carbon atoms and the boron atom.

In addition to parameters derived from topological analysis of electron density, there are several other parameters obtainable from quantum calculations that seem well suited to probe the long-range perturbations. One of these is the carbon 1s orbital energy levels. The 1s orbitals of first row elements have been shown experimentally, via ESCA experiments,[33] to be sensitive to the environment of the atom in the molecule. We are also interested in the evaluation of the 2s character used in the bonding of carbon atoms. This parameter has a rich history, starting with the early work of Coulson,[34] which was continued by Bent[35] and others.[3,36] We approach the 2s character in bonds through a Mulliken population analysis[37] as well as with the Natural Bonding Orbital (NBO) method.[26−29] The latter also provides us with the relative composition of bonds between carbon atoms, a feature that gives us insight into the bonding of carbon atoms in alkanes.

Computational Methods

Calculations were performed using Gaussian-94, Revision B.1 and B.2[38] and Gaussian-98, Revision A.7,[39] on an SGI Power XZ Indigo2 running IRIX 6.2 or on a Dell OptiPlex GX1p machine running Linux, Red Hat Version 6.0 and 7.0. All structures were optimized with the 6-31+G* basis set. We chose this basis set because it contains polarization functions, required for the successful calculation of anionic materials, but is not so large as to inhibit our study of an extensive set of molecules. All results were obtained using both the SCF=Tight and Opt=Tight convergence criteria. In our evaluation of the Mulliken overlap population[37] we calculated the wave function using the STO-3G basis set with the geometry fixed at the value optimized with the 6-31+G* basis set. We made extensive use of the visualization software Ampac 6.0 GUI.[40] The NPA method, Natural Bonding Orbital Version 3.1,[26−29] was implemented through Link 607 of the Gaussian package. The AIM procedure was carried out using the programs EXT94b and PROAIMV[41] as downloaded[42] and compiled on our machines. In several cases where we found an AIM analysis using PROAIM led to unreasonable values of atomic charges, we used the PROMEGA program that is part of the PROAIMV package.

Results and Discussion

Bond Critical Point Displacements. The bond critical point is usually defined by specification of the distance from that point to each of the two nuclei involved. To compare bonds of different lengths, we prefer to express the bond critical point as the fraction of the distance between the two nuclei that the point is located. We define the fractional bond critical point of a bond, the FCP, in a substituted alkane, as the fractional distance from the atom furthest from the X group at which the critical point is found. For instance, the FCP of the C_3 to C_2 bond is the fraction of the C_3-C_2 bond length from C_3 at which the critical point is located.

In Table 1 we give the FCP for the C−X, C−C, and methyl C−H bonds in a number of neutral ethane derivatives. These data show the expected behavior in the C−X bond. As X becomes more electron withdrawing, the FCP moves toward the methylene carbon atom because X claims a larger amount of electron density in the internuclear region. It is interesting to note that the FCP of the C_1-X bond becomes smaller in all cases where hydrogen atoms are replaced by fluorine atoms in the X group. Examination of the FCP in the C_2-C_1 bond for the compounds with neutral X shows some tendency for this effect to be propagated, as conventional wisdom would suggest: a CH_2X group, where X is electron withdrawing, should be more electron-withdrawing than a CH_3 group. In general, however, the magnitude of the variation of the FCP of the C_2-C_1 bond is only about one-quarter to one-tenth of that of the C_1-X bond. Two of the data are at odds with this conclusion. First, the FCP in the C_2-C_1 bond for $X=NH_2$ is greater than 0.500, in striking contrast to the low value of the FCP for the C_1-X bond in this compound. We have investigated the role of the lone pair in this situation by studying a compound in which the C_2-C_1-N-H dihedral angle is set to 180° (the actual computed value for the minimized structure is 176°) so that the lone pair is no longer antiperiplanar to the C−C bond. For this conformer of ethylamine, the C_1−X FCP does not change significantly, but the C_2−C_1 FCP is lowered to 0.495, in better agreement with our expectations. The result for the normal ethylamine is consistent with the dipole set up by the nitrogen lone pair, which causes a polarization of the electrons within the C_2−C_1 bond that moves the FCP toward C_1. Second, the FCP for the C_2−C_1 bond with X=SiH_3 is not greater than 0.5 as we would expect. We do not have an explanation for this observation. Table 1 also gives the values of the FCP for the H−C_2 bonds. Because the variation is very small, it is only with considerable imagination that we can conclude that these data show signs of a propagation of the FCP of the C_1−X bond into the H−C_2 bond.

The FCPs for CH_3CH_2X in which X is charged show the FCP trend for the C_1−X bond that follows expectations based on the nature of X. Those compounds in which the atom attached to C_1 is of higher ionization energy than the carbon atom have smaller values of the FCP in the C_1−X bond whereas compounds containing an X with an atom attached to C_1 that is of lower ionization energy have larger values. This phenomenon is independent of the charge on the X substituent: both X=O^- and X=NH_3^+ have small FCPs. In contrast to the neutral X, there is a distinct behavior of the FCP of the C_2−C_1 bond and the two different kinds of H−C_2 bonds. The FCP of these bonds are dependent upon the *charge* of X, not the *nature* of the atom attached to C_1. It is the FCP data for the C_2−C_1 bond that shows this most clearly. Even though the FCP in the C_1−X bond for X=O^- and X=NH_3^+ are similar, the FCP for the C_2−C_1 bond show distortion in opposite directions. Also, the C_2−C_1 FCP of X=NH_3^+ and X=PH_3^+ are similar, even though the FCP of the C_1−X bonds are very different. *Whereas the nature of X determines the* C_1−X *FCP, the charge on X determines the* C_2−C_1 *FCP*. This occurs in the FCP of the H−C_2 bonds as well. In the charged compounds, the H−C_2 FCP might be thought of as a direct consequence of the distribution of charge onto the peripheral atoms of the molecule.[23] The positively charged substituents cause the methyl hydrogen atoms to become positively charged, which makes them effectively more electron withdrawing from the carbon atom. The FCP moves toward the hydrogen atom. A plot of the FCP of the methyl hydrogen atoms vs the AIM charges[43] is an excellent straight line over the entire range of compounds listed in Table 1-see Figure 1. It is especially noteworthy that the rotated X=NH_2 group has two nonequivalent gauche hydrogen atoms of significantly different charge and both of these points are on the line. Clearly the H−C_2 FCP results support the charge data reported earlier.

To further pursue the critical point variations at atoms remote from the perturbation, we have examined the FCP in a number of substituted pentanes and hexanes; the data are in Table 2. The compounds with neutral X establish that the FCP for the C−C bonds past C_2−C_1 show little variation and are relatively close to 0.50, the value of an electronically symmetrical bond. The FCP is slightly lower for X=EF_n than for X=EH_n. A similar observation can be made from the comparison of hexylammonium ion with hexyltrifluoroammonium ion, indicating that fluorine atoms have some effect on the FCP at remote distances, but this effect is small compared to the more significant effect of charge. For those cases in which X is charged positively, the FCP shows a distortion toward the higher numbered carbon atom in the C_n−C_{n-1} bond (the FCP value is less than 0.50). The FCP is distorted toward the lower numbered carbon atoms for negative X. As we observed for the ethyl derivatives, this distortion is charge dependent and not dependent on the FCP of the C_1−X bond. The effect also appears to be long-range: the FCP in the C_n−C_{n-1} bond with $n = 5$ for NH_3^+ is 0.487, which can be compared with values of 0.498−0.499 for neutral X. A comparison of the hexyl- and pentyammonium ions establishes the effect of a charged X group on the FCP of interior C−C bonds is independent of the length of the alkyl chain. Furthermore, all the data in Table 2 establish that the CH_3−C FCP is larger than those of adjacent interior bonds.[44]

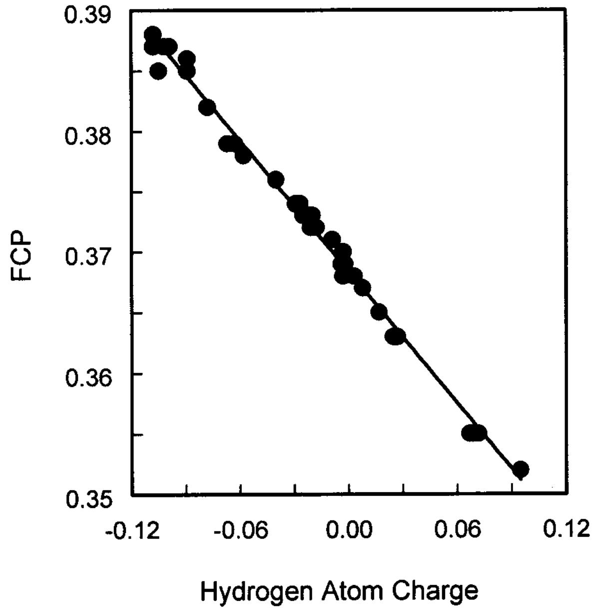


Figure 1. Fractional critical point, FCP, vs the calculated AIM charge on methyl hydrogen atoms for the compounds listed in Table 1.

TABLE 2: Fractional Bond Critical Points for Carbon−Carbon Bonds in Substituted Alkanes

X	C_1−X	C_2−C_1	C_3−C_2	C_4−C_3	C_5−C_4	C_6−C_5
			hexanes			
H	0.373	0.498	0.500	0.500	0.500	0.502
F	0.316	0.480	0.496	0.496	0.498	0.501
NH_2	0.358	0.500	0.499	0.499	0.499	0.502
SiH_3	0.625	0.496	0.498	0.499	0.499	0.502
SiF_3	0.624	0.487	0.493	0.496	0.498	0.501
CF_3	0.435	0.481	0.493	0.495	0.498	0.501
BH_3^-	0.695	0.530	0.524	0.516	0.512	0.510
CH_2^-	0.546	0.533	0.524	0.515	0.511	0.510
NH_3^+	0.316	0.455	0.471	0.481	0.487	0.493
NF_3^+	0.302	0.429	0.465	0.476	0.484	0.491
PH_3^+	0.625	0.459	0.472	0.482	0.487	0.494
			pentanes			
F	0.316	0.480	0.496	0.496	0.500	
CH_3	0.498	0.500	0.500	0.500	0.502	
NH_3^+	0.316	0.456	0.471	0.481	0.490	
O^-	0.331	0.534	0.526	0.515	0.514	
1	0.316	0.456	0.482	0.488	0.487	
2[a]	0.695	0.529	0.513	0.511	0.514	
3[b]	0.316	0.456	0.482	0.487	0.485	0.497
4[c]	0.315	0.446	0.459	0.464	0.461	0.460
SiH_3*d*	0.625	0.495	0.499	0.500	0.501	

[a] This is a twisted conformer with X=BH_3^- and approximately the same dihedral angles as **1**. The actual values are −57.7° and −62.2°. [b]Twisted nonylammonium ion twisted as described in text. The remaining three FCP values are 0.502, 0.491, and 0.502, for C_7, C_8, and C_9, respectively. [c]Zwitterionic hexane with NH_3 attached at C_1 and BH_3 attached at C_6. The FCP for the B−C_6 bond is 0.305. [d]Twisted conformer with dihedrals angles approximately the same as in **1**. The actual values are given in ref 62.

To test if the mechanism of this long-range effect of charge is through-bond or through-space, we must vary the spatial separation of the perturbing charge and a given carbon atom,

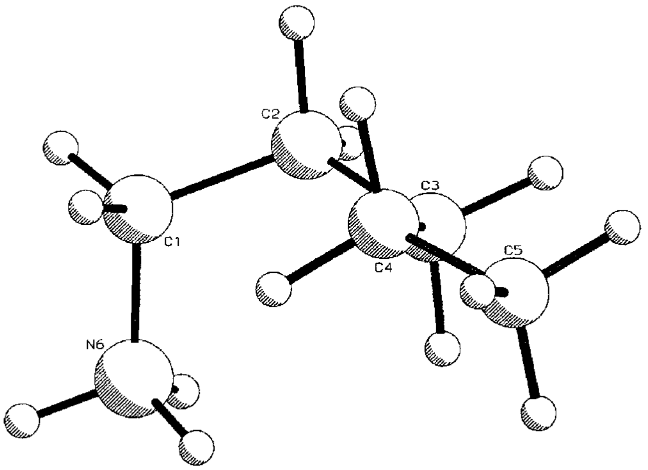


Figure 2. Optimized geometry of pentyammonium ion, $C_5H_{11}NH_3^+$ **1**, in the conformation in which the $C_3-C_2-C_1-N$ and $C_4-C_3-C_2-C_1$ dihedral angles are set to about −60°.

while keeping the number of bonds between these two groups the same. Twisted conformers of the alkyl chains satisfy this requirement. The minimized geometry of pentylammonium ion, **1**, with the $C_3-C_2-C_1-N$ and $C_4-C_3-C_2-C_1$ dihedrals set at about −60°, (in minimized form, the values are −57.7° and −62.2°) is shown in Figure 2. These twists bring carbon atoms 3, 4, and 5 closer to the positive charge, which we assume is centered roughly on the nitrogen atom,[45] than in the all antiperiplanar, C_s, conformer. Importantly, the distance between C_3 and N decreases from 3.86 to 3.08 Å, but the distance between C_4 and the N decreases by nearly 50% more, from 5.04 to 3.74 Å. If the perturbation of the FCP is caused by a through-space effect, the larger change in the C_4-N distance compared to the C_3-N distance will change the FCP of the C_4-C_3 bond in the twisted conformer compared to that bond in the C_s conformer. If the distortion of the FCP is governed by the difference in electron withdrawing ability of the carbon atoms involved in the bond, and the latter is dictated by the difference in the potential caused by the positive charge, then the closer a carbon atom is to the positive charge, the higher its apparent electron-withdrawing ability. Because the difference between the $N-C_4$ and $N-C_3$ distances changes from 1.18 Å in the C_s conformer to 0.66 Å in the twisted conformer, we expect the C_4-C_3 FCP to be closer to 0.5 in the latter. The data in Table 2 show the twisting does not affect the FCP for the C_2-C_1 bond but does influence in the expected direction the FCP of the C_4-C_3 bond in **1.** Similar comparisons can be made in the C_s and twisted conformer of pentylborohydride, **2**. Even more dramatic is the data on a longer chain twisted compound, the nonylammonium ion, **3,** shown in Figure 3, with similar values for the $C_3-C_2-C_1-N$ and $C_4-C_3-C_2-C_1$ dihedrals as in **1** (−56.2° and −58.2°, and also $C_6-C_5-C_4-C_3$, −61.0°, $C_7-C_6-C_5-C_4$, −59.4°, and $C_9-C_8-C_7-C_6$, −65.9°). The FCP data for the C−C and C−N bonds in this compound are given in Table 2. Especially noteworthy is the FCP of greater than 0.50 in the C_7-C_6 bond. In **3**, C_7 is closer to the positive charge than C_6, 4.53 Å compared to 4.90 Å, respectively. A reversal of the direction of the FCP is exactly what is predicted on the basis of the perturbation of the positive charge acting through space. Distance and FCP data for all of these alkylammonium ions, including the C_s conformers of dodecylammonium ion, are given in Table S1 (Supporting Information). A through-space perturbation should cause the FCP to be proportional to the *difference* in the inverse distances of the carbon atoms from the charge: The distortion of the FCP in the C_n-C_{n-1} bond of substituted ammonium ions should be proportional to $(1/r_{n(N)} - 1/r_{n-1(N)})$, where $r_{n(N)}$ is the distance between the carbon atom *n* and the nitrogen atom. In Figure 4 we show this functional relationship for all C−C bonds in the C_s conformers of pentyl-, hexyl-, and dodecylammonium ions and **2** and **3**. The agreement is reasonable. We have carried out a similar treatment for the C−C bonds in the C_s conformers of hexyl- and dodecylborohydride and **2** with similar results. In this case, the slope of the plot is opposite, as expected from the fact that the charge centered on the BH_3 group is opposite.

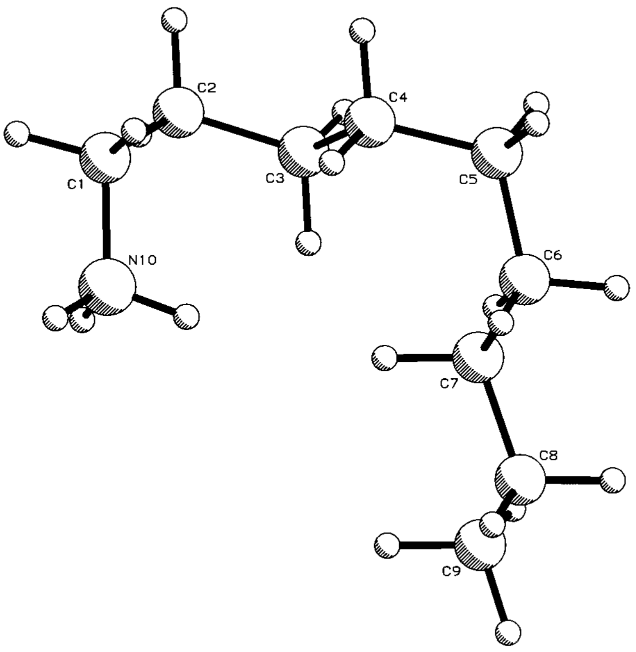


Figure 3. Optimized geometry of nonylammonium ion, **3**, in a conformation in which the $C_3-C_2-C_1-N$, $C_4-C_3-C_2-C_1$, $C_6-C_5-C_4-C_3$, $C_7-C_6-C_5-C_4$, and $C_9-C_8-C_7-C_6$ are set to about −60°, whereas other backbone dihedrals remain at about 180°.

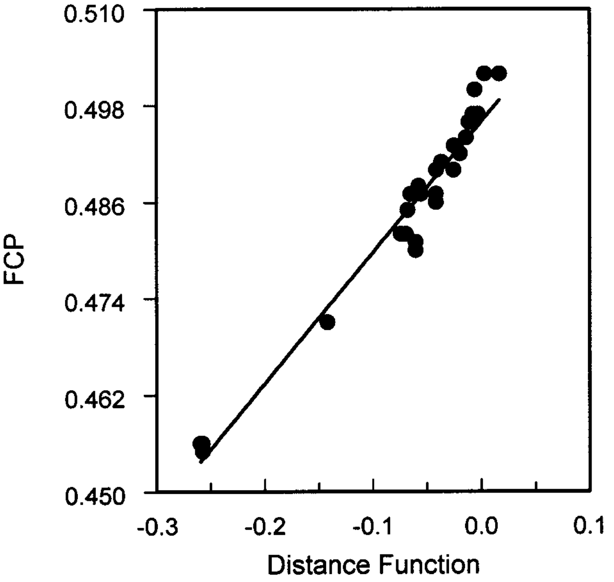


Figure 4. FCP for carbon−carbon bonds vs the distance function, $(1/r_{n(N)} - 1/r_{n-1(N)})$, where $r_{n(N)}$ is the distance between the nitrogen atom of a substituted ammonium ion and the *n*th carbon atom, C_n.

That the phenomena we observe are caused by long-range charge effects is supported by the zwitterionic species, $BH_3(CH_2)_6NH_3$, **4**.[46] In this compound, the positively charged nitrogen end of the molecule pushes the FCP of the C−C bond away from itself, lowering the numerical value of the FCP. In contrast, the negatively charged BH_3 group pulls the FCPs toward the boron atom. Thus, these two effects support each other in the zwitterion. This can be seen in the bonds in the middle of the molecule, see Table 2. The FCP of the C_4-C_3 bond is 0.464, closer to C_4 than the corresponding bond in pentyl- or hexylammonium ion, 0.481. From the point of view of the boron end of the molecule, the C_4-C_3 bond has an FCP of 0.536; this is to be compared with the value 0.516 for the C_4-C_3 bond in hexylborohydride.

The long-range perturbation of the FCP of C−C bonds by charged substituents supports our earlier observation[23] of a long-range effect on the charge on hydrogen atoms in substituted alkanes. These changes in the FCP occur even though there is no evidence of a propagation of charge on the carbon atoms themselves. For instance, the NBO (AIM) charges on interior carbon atoms of dodecylammonium ion range from −0.465 (0.081) on C_2 to −0.437 (0.096) on C_{11}, with values between of −0.434 (0.088), −0.429 (0.090), −0.428 (0.088), −0.427 (0.087), −0.426 (0.087), −0.426 (0.086), −0.427 (0.086), and −0.428 (0.086) for C_3 to C_{10}, respectively.[23] These FCP distortions must be caused by a polarization of charge within the atomic basin (in the language of the AIM method), rather than a motion of charge from one carbon atom to another as in a classical inductive effect. We find additional evidence for this polarization in an examination of the variation of three other electronic properties in substituted alkanes, the atomic composition of carbon−carbon bonds, the energy of the 1s carbon orbitals, and the atomic dipoles.

Propagation of s Overlap Population in Carbon−Carbon Bonds. Following the Coulson[34] and Bent[35] arguments, we anticipate that the bond between the fluorine atom and the carbon atom in CH_3CH_2F will use an orbital on the carbon atom that has relatively little s character. The enhanced p character used by C_1 in the C_1-F bond allows this carbon atom to donate electron density to the fluorine atom in accordance with the relative ionization energies of the two atoms. If C_1 uses little s character in the bond to F, it should have enhanced s character in the bonds to its other three substituents. This enhanced s character of C_1 in the bond to C_2 should, because of the small radial extension of the s orbital, result in enhanced p character of C_2 in the bond to C_1.[35] This inversion of the bonding character in C_n and C_{n-1} in the C_n-C_{n-1} bond is a prime example of a through-bond phenomenon. In this section, we look at three measures of the s character in C−C bonds to determine whether s character is propagated down an alkyl chain.

Bent[35] postulated “a relatively large (small) angle between equivalent hydrid orbitals implies that the s content of the orbitals is relatively large (small).” To measure the angle between the hybrid orbitals, Bent suggested that the angle between two equivalent atoms be measured, although more recently it was suggested that the angle between the bond paths,[25] as defined by the AIM technique, should be used.[47] Following Bent, we expect for X═F in CH_3CH_2X, the s character of C_1 in the C_1-F bond will be small, the s character of C_1 in the C_1-H bond large, and the H−C−H angle large. Indeed, the 6-31+G* computed H−C−H bond angles change as expected, 109.2°, 107.8°, 106.4°, and 106.3° for X═F, OH, NH_2, and CH_3. Previous examples of this kind of observation applied to H−C−H angles[48] as well as C−C−C angles[36] have been reported. We also find the angle for X═CF_3 (107.6°) is larger than that of X═CH_3, X═NF_2 (108.0°) greater than X═NH_2, X═NF_3^+ (111.1°) greater than X═NH_3^+ (109.1°), and X═BF_3^- (105.9°) greater (barely) than X═BH_3^- (105.4°), all as expected. The exception to this behavior is the angle for X═SiH_3 (105.9°), which is the same as that for X═SiF_3. The positively charged substituents have larger values for the methylene H−C−H angle than do the negatively charged substituents. This last comparison seems reasonable in that a positively charged substituent is more electron-withdrawing than is a negatively charged one. We also note that the electron density at the bond critical point in the C_1-H bonds decreases from X═F to X═CH_3. This follows the suggestion that the amount of s character in C−H bonds is larger when charge density at the bond critical point is larger.[49] To be able to judge if the cause of the H−C−H angle variation is due to s character changes, we need to assess the amount of s character in the C_1-H bonds.

Nearly 50 years ago, Mulliken developed the concept of overlap population[37] as a means of obtaining a intuitive interpretation of the results of molecular orbital calculations. The overlap population between two basis set orbitals, ϕ_κ and ϕ_λ, is given by $P_{\kappa\lambda}S_{\kappa\lambda}$ where

$$P_{\kappa\lambda} = 2 \sum_{i}^{\text{occupied}} c_{\kappa i} c_{\lambda i} \tag{1}$$

is an element of the density matrix, $S_{\kappa\lambda}$ is the overlap integral between orbitals ϕ_κ and ϕ_λ, and $c_{\kappa i}$ is the coefficient of the basis set orbital κ in the molecular orbital i. Although this method is susceptible to problems,[50,51] it is sometimes useful in comparisons.[52] We assume that the s character that a given atom uses in a bond is given by the overlap population of that atom’s valence shell s orbital with all valence orbitals on the neighboring atom. We call this restricted overlap population the SOP. To calculate the SOP, we use the orbitally based STO-3G basis set, which does not have diffuse functions that are known to give strange results in the Mulliken population analysis,[51] at the geometry minimized with the 6-31+G* basis set. The SOP is a relative number because some of the s character in a Mulliken approach is assigned to the atom. We therefore look at the percentage SOP used in the C_1-H bond compared to the total SOP in all bonds from C_1. The results-see Table 3-for X═F, OH, NH_2, and CH_3 is a monotonic variation from 29.4% to 24.1%, in agreement with the H−C−H bond angle variations.

Because of the potential difficulties with SOP values, we also considered a measure of s character in bonds[53] that utilizes the NBO analysis.[26−28] In this method, the delocalized molecular orbital wave functions are transformed into a set that corresponds to localized bonds. This generates a set of orthogonal hybrid orbitals on each atom in a molecule and identifies the hybrid orbital on C_n that is used to bond with C_m. These localized bond orbitals are of the form

$$\psi = c_m(c_{ms}\phi^m_{2s} + c_{mpx}\phi^m_{2px} + c_{mpy}\phi^m_{2py} + \Omega) + c_{\mathrm{n}}(c_{ns}\phi^n_{2s} + c_{npx}\phi^n_{2px} + c_{npy}\phi^n_{2py} + \Omega) \tag{2}$$

where the c’s are coefficients, the φ are atomic wave functions, and Ω are terms, generally small, involving other members of the 6-31+G* basis set. The amount of s character used by C_n in the bond to C_m is $c_n c_{\mathrm{ns}}$ and we label this product the NBOC. Because we are using normalized orbitals, the sum of the $(c_n c_{\mathrm{ns}})^2$ over all bonding, antibonding, and Rydberg levels is unity.

The SOP and NBOC results for several substituted ethyl compounds are given in Table 3. The SOP values roughly parallel those of the NBOC. The SOP and the NBOC of C_1 in the bond to X increase from F to CH_3, as anticipated on the basis of the electron withdrawing ability of X.[35] The SOP in

TABLE 3: SOP from Mulliken Population Analysis and NBOC from NBO Localized Orbitals in $CH_3CH_2X^a$

	SOP					NBOC				
X	C_2-C_1-X		$\mathbf{C_1}-H$	$H_{ap}-\mathbf{C_2}-C_1$		C_2-C_1-X		$\mathbf{C_1}-H$	$H_{ap}-\mathbf{C_2}-C_1$	
F	0.110	0.043	0.110	0.108	0.103	0.386	0.218	0.390	0.384	0.365
OH	0.118	0.065	0.109	0.110	0.107	0.382	0.259	0.385	0.382	0.365
NH_2	0.109	0.088	0.110	0.109	0.108	0.376	0.309	0.380	0.385	0.373
CH_3	0.116	0.116	0.108	0.110	0.112	0.368	0.368	0.374	0.385	0.371
CF_3	0.112	0.081	0.109	0.110	0.106	0.381	0.341	0.388	0.387	0.357
SiH_3	0.105	0.101	0.101	0.109	0.110	0.373	0.438	0.378	0.388	0.365
SiF_3	0.104	0.080	0.100	0.110	0.107	0.384	0.409	0.394	0.391	0.357
CH_2^-	0.084	0.121	0.098	0.096	0.110	0.348	0.428	0.352	0.366	0.399
BH_3^-	0.093	0.127	0.093	0.100	0.119	0.342	0.489	0.347	0.368	0.397
BF_3^-	0.095	0.104	0.093	0.102	0.118	0.352	0.469	0.363	0.372	0.387
O^-	0.084	0.062	0.090	0.102	0.098	0.350	0.327	0.350	0.366	0.400
NH_3^+	0.120	0.038	0.123	0.114	0.096	0.401	0.237	0.405	0.399	0.344
NF_3^+	0.123	0.005	0.126	0.113	0.086	0.418	0.184	0.420	0.397	0.333
PH_3^+	0.115	0.059	0.116	0.114	0.095	0.400	0.338	0.403	0.402	0.336

[a] In each column, the numbers refer to the s character in the atom that is bold. For the Mulliken analysis, the left-hand number is the s character in the overlap population (STO-3G basis set) to the left-hand atom, and the right-hand number is to the right-hand atom. For the NBO analysis, the numbers are the coefficient of the s orbital of the bold atom in the localized wave function (6-31+G*) binding that atom to the left and right atoms, respectively. See text, especially eq 2.

the C_1-X bond with $X=SiH_3$ is slightly less than that anticipated on the basis of the electron withdrawing ability of silicon, although the NBOC value seems reasonable. For both $X=CF_3$ and $X=SiF_3$, the SOP and NBOC in the C_1-X bond are smaller than for the corresponding compounds with hydrogen atoms, as anticipated. The compounds with charged X are more complex. The data suggest that both the electron-withdrawing nature of the atom in X that is attached to C_1 and the charge on X determine the SOP and NBOC of the C_1-X bond. Generally, the positively charged X have smaller SOP and NBOC, while the negatively charged X have larger ones. For instance, the C_1 SOP of the C_1-X bond for $X=NH_3^+$ is less than that of $X=NH_2$. With the data in Table 3 we have the ability to test if the use of a large amount of s character by C_1 in the C_1-X bond causes little use of s character by C_1 in its bonds to other atoms. For the neutral compounds, the SOP data show no systematic variation of s character of C_1 in the bonds to C_2 or methylene hydrogen atoms, although the NBOC data indicate a slight systematic variation in these bonds. The negatively charged substituents, on the other hand, have values of both SOP and NBOC for C_1 in the C_1-C_2 bond and the C_1-H bonds that are smaller than the values found for the neutral compounds; the reverse holds for positively charged X. Thus, charge has a significant role in dictating the s character used by C_1 in the bond to adjacent atoms.

What effect does the X group have on the use of s character in the bonding of C_2? Does little s character in the C_1-X bond lead to little from C_2 in the C_2-C_1 bond as a through-bond argument would suggest? For the neutral compounds, the data in Table 3 give little indication of a propagation of the distorted use of s character in the bonding. The SOPs used by C_2 in the bonds to C_1 parallel those of the C_1 to X bonds, but the NBOC are ambiguous. For the charged species, the s character used by C_2 in bonding to C_1 shows a clear trend. It is not, however, dependent upon the s character used by C_1 in the bond to X, but is dictated by the *charge* on X. We see this more clearly in an examination of long-chain substituted alkanes.

Data for the SOP and NBOC for some pentanes and hexanes are given in Table 4. A comparison of the data in Table 3 and Table 4 shows that C_1 responds in a nearly identical manner in the long chain alkanes as it does in the ethyl derivatives, and that the data for the substituted pentanes and substituted hexanes show great similarity. For the neutral compounds, there is very little difference between the SOP at C_3 for $X=H$ compared to $X=F$ or $X=SiH_3$. On the other hand, for negatively charged X, the SOP from C_n to C_{n-1} is larger, and the SOP from C_n to C_{n+1} is smaller than for the neutrals, even at $n = 5$. The reverse trend occurs with the positively charged X, and both of these behaviors are also reflected in the NBOC. It is especially significant how the NBOC of C_1 with $X=O^-$ changes from a small value in the C_1-X bond, characteristic of an electron-withdrawing X, to large values for C_n in the C_n-C_{n-1} bond, characteristic of negatively charged X. A similar effect is observed with $X=PH_3^+$. To further probe this effect, we studied the three $C_{12}H_{25}X$ compounds, $X=BH_3^-$, CH_2^-, and NH_3^+. The value of the SOP on C_{12} in the bond from C_{12} to C_{11} is 0.112, 0.112, and 0.111, respectively. These data, and those in Table 4 for neutral X, suggest 0.112 is the value of the SOP for an unperturbed methyl group. A similar relationship holds for the NBOC data where the unperturbed value is about 0.371. Although the perturbation from this value is small, it is clearly seen at C_6 for charged X. Examination of the long chain compounds, dodecylborohydride and ammonium ions, and tridecylcarbanion also show a long-range effect-see Table S3. Inspection of the data for the s character used by C_n in bonding to other carbon atoms in Table 4 for neutral X with $n > 3$ shows an unpertubed or “normal” SOP of 0.108 to 0.109 and a “normal” NBOC of 0.368 to 0.370 for methylene carbons. In the dodecylborohydride ion, the values for the SOP for carbons $n = 1$ to $n = 5$ are very similar to those for hexylborohydride. The SOP at C_8 in the C_8-C_7 bond is 0.111, larger than the “normal” value. Likewise, in dodecylammonium ion, the NBOC at C_8 is 0.365 for the C_8-C_7 bond, smaller than the “normal” value. These results show that the perturbation of the s character, as measured by both the SOP and NBOC, is still significant, albeit small, at very large distances (C_8 is 10.1 Å from the nitrogen atom). To verify a relationship between our SOP and the Bent angle criterion for s character, we have plotted the H−C−H bond angle vs the percentage of the SOP used in the C−H bond; we find a rough linear correlation-see Figure 5.[54] These data confirm that the calculational methods of measuring the s character in bonds is supported by the empirical relationship suggested by Bent.

To investigate the nature of the charge dependent interaction that produces the change in s character in long-chain substituted alkanes, we have measured these parameters in a number of twisted conformers. The data for the s character in twisted conformers are given in Table 5. Comparison of Table 4 and

TABLE 4: SOP from Mulliken Population Analysis and NBOC from NBO Localized Orbitals in Substituted Pentanes and Hexanes[a]

X	$C_2-\mathbf{C_1}-X$		$C_3-\mathbf{C_2}-C_1$		$C_4-\mathbf{C_3}-C_2$		$C_5-\mathbf{C_4}-C_3$		$C_6-\mathbf{C_5}-C_4$		$\mathbf{C_6}-C_5$
					SOP						
H	0.112	0.110	0.109	0.108	0.109	0.109	0.109	0.109	0.108	0.109	0.112
F	0.110	0.043	0.108	0.100	0.109	0.107	0.109	0.108	0.108	0.109	0.112
SiH_3	0.106	0.101	0.108	0.108	0.109	0.108	0.109	0.109	0.108	0.109	0.112
CH_2^-	0.082	0.120	0.095	0.106	0.102	0.114	0.105	0.113	0.106	0.112	0.114
BH_3^-	0.094	0.127	0.099	0.118	0.103	0.114	0.105	0.113	0.106	0.112	0.114
BF_3^-	0.096	0.104	0.101	0.116	0.104	0.114	0.106	0.113	0.106	0.112	0.114
NH_3^+	0.120	0.036	0.113	0.090	0.113	0.097	0.112	0.103	0.111	0.105	0.110
NH_3^{+b}	0.120	0.037	0.113	0.090	0.113	0.097	0.111	0.103		0.108	
NF_3^+	0.123	0.005	0.111	0.079	0.113	0.093	0.112	0.101	0.111	0.104	0.109
					NBOC						
CH_3	0.368	0.369	0.369	0.369	0.369	0.369	0.369	0.369	0.369	0.368	0.372
F	0.385	0.219	0.369	0.362	0.373	0.364	0.370	0.365	0.370	0.366	0.370
SiH_3	0.374	0.438	0.372	0.363	0.369	0.367	0.369	0.369	0.370	0.368	0.371
CH_2^{-c}	0.345	0.430	0.352	0.395	0.359	0.388	0.362	0.380		0.380	
BH_3^-	0.340	0.489	0.352	0.395	0.358	0.388	0.361	0.382	0.364	0.377	0.378
BH_3^{-b}	0.341	0.489	0.352	0.395	0.357	0.388	0.361	0.381		0.380	
BF_3^-	0.350	0.428	0.356	0.385	0.359	0.384	0.361	0.380	0.364	0.376	0.377
O^{-b}	0.346	0.329	0.352	0.396	0.358	0.389	0.361	0.381		0.381	
PH_3^+	0.402	0.338	0.390	0.330	0.382	0.345	0.378	0.355	0.376	0.358	0.364
NH_3^+	0.403	0.237	0.387	0.340	0.382	0.344	0.378	0.353	0.376	0.357	0.364
NH_3^{+b}	0.402	0.237	0.387	0.340	0.382	0.345	0.378	0.352		0.361	
NF_3^+	0.421	0.183	0.387	0.326	0.386	0.337	0.380	0.349	0.377	0.355	0.363

[a] See footnote *a* to Table 3. [b] Pentyl compound. [c] $C_5H_{11}-CH_2^-$, a pentane in our nomenclature.

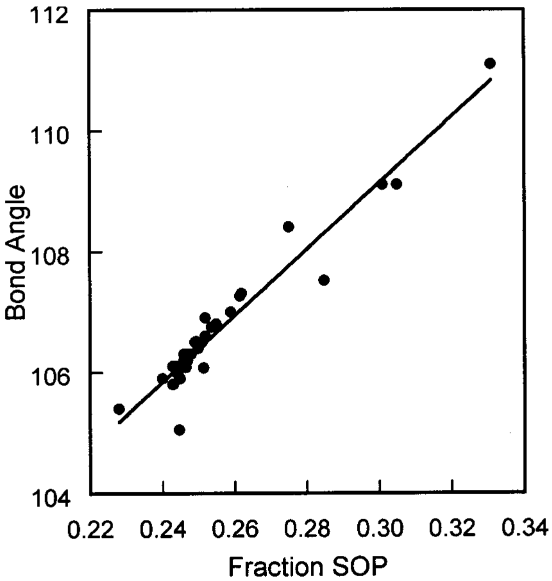


Figure 5. H−C−H methylene carbon bond angle vs the Mulliken s overlap population, SOP, for methylene carbon atoms in hexane, 1-fluorohexane, hexylsilane, hexylcarbanion, hexylborohydride ion, hexylammonium ion, hexyltrifluoroborate ion, hexyltrifluoroammonium ion, and hexylphosphonium ion. The data are tabulated in Tables S2 and S3 of Supporting Information.

Table 5 reveals the data for the neutral compounds are largely independent of the geometry of the molecule. An exception to this observation is the s character on C_2 in the C_2-C_3 bond of hexylfluoride, where both the SOP and NBOC have larger values in the twisted isomer. There are, however, significant differences between the C_s and the twisted conformers in the charged species. Although it is possible to imagine that through-bond interactions are sensitive to the relative orientation of the bonds, the correlation with direct distance dependence that we establish below make the through-space interpretation more likely.

Our data indicate the s character varies significantly down the alkyl chain only for charged substituents. Furthermore, we find the s character of a given atom is dependent upon the distance of that atom from the charge and not on the amount of s character used by C_1 in the C_1-X bond. How do we connect s character with the charge on the substituent? Our approach is to examine more carefully the localized bonding orbital of the NBO approach, which has the form given in eq 2. Because ψ_m and ψ_n, the hybrid orbitals on C_m and C_n, respectively, are orthogonal, the contribution of ψ_n to the bond is given by c_n^2. We have found by examination of the various coefficients in the localized bonding orbitals of the NBO method that c_{ns} is proportional to c_n as long as $n \neq 1$. It follows that the NBOC, $c_n c_{ns}$ is proportional to c_n^2 if $n \neq 1$. All of the arguments for the NBOC, therefore, hold for c_n^2, the fraction of the bond that is provided by carbon atom C_n. Furthermore, we also discovered an excellent correlation between c_n^2 and the FCP. In Figure 6 we show this relationship for all the bonds between methylene carbons of pentyl-, hexyl-, and dodecylammonium ions, dodecylborohydride **1**, **2**, **3**, and hexylphosphonium ion (except for the C_2-C_1 bond of the substituted ammonium compounds-see below). The correlation for the methyl carbon atom for each of these species is also given. This feature of our analysis is fascinating as it links the results of the NBO method, a method based on localized wave functions, with those of the AIM procedure, which is based on the topology of the electron density.[55] Because of the parallel between NBOC and c_n^2, an equally good correlation exists between the FCP and the NBOC. It is especially noteworthy that c_n^2 has a value of 0.502 for the C_7-C_6 bond in nonylammonium ion. This is the bond where the FCP switches from a value of less than 0.50, found in all other bonds between methylene carbons in positive ions, to a value of 0.502. The topological FCP parameter and the NBO hybrid orbital analysis agree about the unusual situation found in the C_7-C_6 bond.

What factor is responsible for this correlation between c_n^2 and the FCP? The FCP might be thought to be shifted from the atom of relatively high ionization energy toward the one of relatively low ionization energy because of the distortion of the coefficients in the wave function for the bonding orbital between those two atoms.[56] The data presented in Figure 6 support this

TABLE 5: SOP from Mulliken Population Analysis and NBOC from NBO Localized Orbitals in Twisted Pentane Isomers[a]

X	C_2-C_1-X		$C_3-\mathbf{C_2}-C_1$		$C_4-\mathbf{C_3}-C_2$		$C_5-\mathbf{C_4}-C_3$		$\mathbf{C_5}-C_4$
					SOP				
CH_3	0.109	0.108	0.108	0.108	0.109	0.109	0.108	0.109	0.112
F	0.110	0.042	0.111	0.100	0.109	0.107	0.108	0.108	0.112
BH_3^-, **2**	0.093	0.127	0.103	0.117	0.106	0.113	0.104	0.104	
NH_3^+, **1**	0.120	0.036	0.114	0.089	0.112	0.101	0.112	0.104	
					NBOC				
CH_3	0.368	0.367	0.367	0.367	0.366	0.370	0.369	0.368	0.371
F	0.386	0.216	0.375	0.361	0.367	0.362	0.370	0.367	0.370
BH_3^-, **2**	0.341	0.487	0.357	0.394	0.358	0.380	0.360	0.376	0.381
NH_3^+, **1**	0.402	0.235	0.381	0.338	0.376	0.354	0.380	0.357	0.359
NH_3^{+b}, **3**	0.402	0.236	0.381	0.338	0.376	0.353	0.380	0.356	0.355

[a] See footnote *a* to Table 3. [b]Nonylammonium ion. The values for the last bonds are: $C_6-\mathbf{C_5}$, 0.369; $C_7-\mathbf{C_6}-C_5$, 0.366 0.365; $C_8-\mathbf{C_7}-C_6$, 0.0.376 0.368; $C_9-\mathbf{C_8}-C_7$, 0.30.368 0.362; $C_9-\mathbf{C_8}$, 0.370.

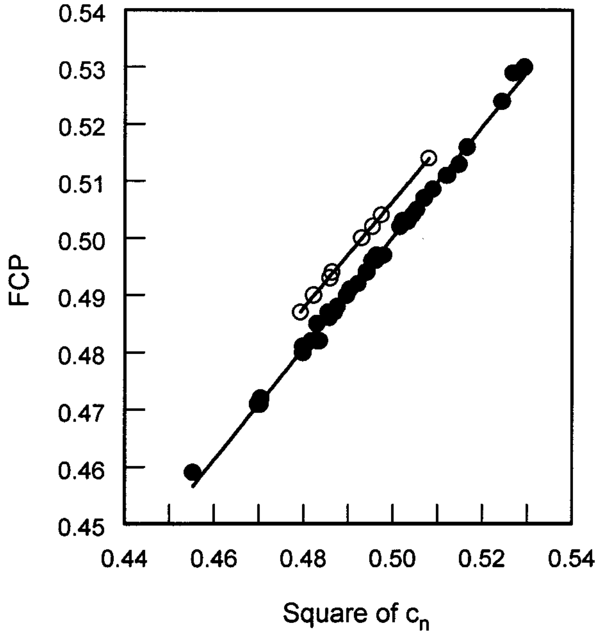


Figure 6. Fraction bond critical point of the carbon−carbon bonds, C_n-C_{n-1}, vs the square of the coefficient of the hybrid orbital on C_n used in bonding to C_{n-1} according to an NBO analysis. Data are for the C_s conformers of dodecyl-, hexyl-, pentylammonium ions **1**, **2**, **3**, dodecylborohydride ion, and hexylphosphonium ion. The solid circles are for methylene carbons, the open circles for the methyl carbon atoms at the end of the chain. Data points for the C_2-C_1 bond for the five ammonium ions have not been plotted-see text.

view. If C_n is a carbon atom close to the source of positive charge, it experiences an effective potential that makes it act as if it has a higher ionization energy. Therefore, the wave function of the localized bond contains more C_n character. It seems reasonable that this would shift the FCP further from C_n as the FCP must occur at some point where the bonding wave functions of both C_n and C_m are small. This explains the correlation between c_n^2 and the FCP. The exceptions to this correlation are the substituted ammonium ions. In these, the C_2-C_1 bonds have c_2^2 values that are larger than the FCPs. That is, the c_2^2 value predicts the critical point will be too close to C_2. These molecules are unusual compared to the other charged species because they have very small values of the SOP and the NBOC in the C_1-N bond. As a consequence of the Coulson/Bent argument, the C_2-C_1 bond contains significant s character from C_1 and very little from C_2. This makes the C_1 atom have a larger atomic basin and moves the FCP toward C_2 relative to the value predicted by c_2^2. The wave functions for the localized bonds indicate this is true. This is a case of a short-range propagation of s character in a through-bond sense superimposed upon the long-range through-space charge effect.

Energies of 1s Orbitals. Both of the parameters that we have discussed above depend on the bonding interaction of two atoms. In this section we examine the energy of core electrons, which are known from ESCA studies[57,58] to be sensitive to environmental parameters, including charge.[33,59,60] The substituted alkanes we have studied have very stable molecular orbitals that are largely localized on a given atom. For instance, in fluoropentane, the lowest lying mo (−26.28 hartrees) is 99% fluorine 1s, with some small amounts of higher fluorine s orbitals mixed in. The next four mo's, lying in energy between −11.304 and −11.217 hartrees are mainly carbon 1s in character: they are essentially carbon 1s atomic orbitals. The next lowest level is at −1.586 hartrees, which means these lowest five mo's are isolated in energy. Not surprisingly, the orbital in fluoropentane that is on C_1 is considerably more stable than those orbitals on the remaining carbon centers because the fluorine atom creates positive charge on C_1. The difference in energy of the C_1 orbital in fluoropentane relative to that in pentane, −0.088 hartrees, determined using the 6-31+G* level of theory, compares favorably with the difference between CH_3F and CH_4, −0.096 hartrees, obtained with a more sophisticated basis set.[61] The 1s orbitals of the remaining carbon atoms in both the C_s and a twisted conformer of fluoropentane, which has a structure similar to **1**,[62] show relatively little variation in energy, ranging from −11.213 to −11.230 hartrees. These values should be compared to the values for carbon atoms in pentane that range from −11.210 to −11.216 hartrees. In contrast to these values, the energy of the 1s orbitals of carbon atoms in the substituted alkanes with charged substituents show a considerably wider range of values. These data are given in Table 6.

For the C_s isomers listed in Table 6, the energy of the carbon 1s orbital increases (decreases) monotonically as the carbon is further from the source of positive (negative) charge. The data in the fourth and fifth columns clearly show that the twisted conformers of ammonium ions have energies for the carbon 1s orbitals that differ from the corresponding atoms in the C_s conformers. Although the first two carbons for the C_s and twisted pentanes have, within 0.002 hartrees, the same 1s orbital energy, C_3 of **1** has a value 0.013 hartrees more negative than the corresponding C_s isomer. This corresponds to the fact that C_3 in the twisted conformer is 0.8 Å closer to the nitrogen atom than is C_3 of the C_s conformer. Likewise, C_7 of **3** has an energy that is more stable than that of C_6 of this conformer; C_7 is, in fact, 0.4 Å closer to the nitrogen than is C_6. Similar results, in the opposite direction, are seen with $X{=}BH_3^-$ for the C_s and the twisted conformer, **2**. ESCA peaks, which correspond to the energies of the 1s levels, corrected for rearrangement

TABLE 6: Energies[a] of 1s Orbitals of Carbon Atoms in Substituted Alkanes

	NH_3^{+b}	NH_3^{+c}	NH_3^{+d}	NH_3^{+e}	NH_3^{+f}	NF_3^{+b}	BH_3^{-b}	BH_3^{-g}
C_1	−11.4769	−11.4761	−11.4749	−11.4752	−11.4707	−11.5298	−11.0014	−11.0023
C_2	−11.3975	−11.3965	−11.3950	−11.3977	−11.3934	−11.4231	−11.0531	−11.0548
C_3	−11.3598	−11.3585	−11.3566	−11.3729	−11.3683	−11.3798	−11.0837	−11.0688
C_4	−11.3342	−11.3304	−11.3279	−11.3555	−11.3496	−11.3440	−11.1080	−11.0862
C_5	−11.3082	−11.3217	−11.3072	−11.3251	−11.3279	−11.3227	−11.1187	−11.1007
C_6		−11.2925	−11.2926		−11.3213	−11.2999		
C_7			−11.2814		−11.3273			
C_8			−11.2729		−11.3137			
C_9			−11.2661		−11.3061			

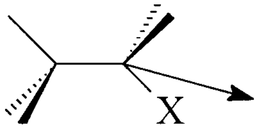
[a] In hartrees [b]C_s isomer of the pentane derivative. [c]C_s isomer of hexane derivative. [d]C_s conformer of the dodecane derivative. The remaining carbons have values of −11.2609, −11.2586, and −11.2490. [e]Conformer **1**. [f]Twisted nonylammonium ion, **3**. [g]Conformer **2.**

energies,[59] can be accounted for by a potential model that involves through-space action of charges on the various atoms in the molecule.[57,58] Our attempts to fit the 1s energy levels of dodecylammonium ion to an equation of the type suggested previously,[63] where we use either the AIM or the NBO charges on each atom in the molecule, gives significant scatter (correlation coefficient of 0.93). The data are, however, fit quite well (correlation coefficient of 0.99) by a modification of this formula, namely

$$\frac{\Delta E}{\Delta q_i} = k + \frac{1}{\Delta q_i r_{ij}} \tag{3}$$

where ΔE and Δq_i are the difference in carbon 1s energy and charge, respectively, between the ammonium derivative and the corresponding alkane, r_{ij} is the distance between the carbon atom and the nitrogen atom in the ammonium compound, and k is a constant. These data establish that the energy of the carbon 1s orbitals in charged substituted alkanes are perturbed through space.

Atomic Charge Polarization. Bader has discussed the polarization of electron density around an atom by the charge on a neighboring atom.[25] The dipolar part of this polarization is expressed in the AIM analysis in terms of an atomic dipole vector. We note that both the length and direction of the dipole vectors in charged species, such as the carbon atoms in our molecules, are origin dependent. In the AIM analysis, the origin of the dipole is chosen as the nuclear center. We express all atomic dipoles in atomic units. We also must state the direction in which the atomic dipole vector points. For the C_s conformers, the atomic dipoles of the carbon atoms are constrained to be in the plane of symmetry, but there is still an ambiguity with respect to the angle an atomic dipole vector makes with respect to a bond vector. We will view our molecules as shown in **5**, with the X group to the lower right. An angle between the atomic dipole vector and a bond is defined as negative if a clockwise rotation of less than 180° moves the bond vector onto the atomic dipole and positive if a counterclockwise rotation is necessary.



5

The atomic dipoles for the neutral ethyl derivatives, CH_3CH_2X, are given in Table 1. The length of the atomic dipole vectors on C_1 decrease down the series X═F, OH, NH_2, CH_3, which is consistent with the Bader treatment.[25] In the first three cases, the dipole vector points at the X atom, consistent with the more negative charge on the fluorine, oxygen, or nitrogen atom compared to the carbon atom. Also as expected, the direction of the atomic dipole vector for X═SiH_3 and X═SiF_3 are opposite to those of the X groups with atoms of higher ionization energy adjacent to C_1. The atomic dipoles on C_2 of the neutral ethyl derivatives are generally smaller than those on C_1. There is no obvious pattern to the magnitude or orientation of the dipoles of C_2. Data for the atomic dipoles of CH_3CH_2X compounds with charged X are also given in Table 1. The direction of the atomic dipole vector on C_1 of the charged compounds is determined by the relative electron withdrawing ability of the group in X to which C_1 is attached, and is independent of the charge.

Some typical data for the long chain compounds are given in Table 7. As in the ethyl derivatives, C_1 has a very large polarization, essentially the same in both direction and magnitude as that found in the ethyl compounds. The data in Table 7 for neutral X show a rapid decrease in the length of the atomic dipole as one moves down the chain from X. These results contrast sharply with the values for charged X. For the case of X═NH_3^+, the magnitude of the atomic dipole vector is still 0.1 for C_4, three times that of X═F and 30 times that of X═SiH_3 at this carbon. Also, the charged species differ significantly in the direction of the dipole. For positively charged X, the dipole points toward the preceding carbon atom, independent of the direction of the dipole at C_1. Thus, for X═PH_3^+ the dipole at C_1 points in the same direction as that for X═SiH_3, but for the other carbons, it points in the same direction as do those for X═NH_3^+. For negatively charged X, the dipoles point away from the preceding atom, independent of the direction of the dipole on C_1. That the dipole at C_n with $n \geq 2$ depends only on the charge of X supports a through-space perturbation.

We have also examined the atomic dipoles in **1**, **2**, **3**, and a pentylsilane with the approximately the same dihedral angles[64] as **1**. These data are also given in Table 7. The length of the atomic dipoles for the twisted conformer with X═SiH_3 are somewhat larger than those of the C_s conformer, but small compared to those of the charged compounds, either the C_s or the twisted conformers. The atomic dipole vectors of C_1 and C_2 in **1** and **3** are very similar in direction and magnitude to those found for the same two carbons in the all antiperiplanar conformer of pentyl- and hexylammonium ions. The lengths of the atomic dipoles at the remaining carbon atoms are somewhat smaller than the corresponding value for the C_s chain compounds. A similar analysis for the lengths of the dipoles holds for pentylborohydride, although some of the lengths are a little greater in **2** than in the C_s conformer. The lack of a plane of symmetry in the twisted conformers makes a description of the direction of the atomic dipoles difficult. In Table 7 the angles the dipole on C_n makes with two other vectors in the molecule,

TABLE 7: Lengths and Angles of Atomic Dipole Vectors for Substituted Alkanes[a]

X	C_1	C_2	C_3	C_4	C_5	C_6
			hexanes			
F	0.696 (3°)	0.098 (−6°)	0.030 (−12°)	0.030 (12°)	0.028 (−56°)	0.024 (−13°)
CF_3	0.268 (9°)	0.098 (−1°)	0.033(6°)	0.025 (−5°)	0.020 (−55°)	0.024 (−7°)
SiH_3	1.352 (180°)	0.029 (6°)	0.009 (30°)	0.003 (−74°)	0.009 (−90°)	0.020 (−12°)
NH_3^+	0.578 (8°)	0.207 (−16°)	0.148 (12°)	0.100 (−13°)	0.070 (−4°)	0.056 (−6°)
PH_3^+	1.069 (176°)	0.202 (−15°)	0.143 (14°)	0.093 (−14°)	0.069 (−3°)	0.056 (−6°)
BH_3^-	1.191 (−176°)	0.151 (158°)	0.125 (−161°)	0.082 (155°)	0.065 (−141°)	0.016 (−132°)
O^-[b]	0.656 (−7°)	0.191 (166°)	0.129 (−163°)	0.086 (150°)	0.032 (166°)	
			twisted pentanes[c]			
SiH_3	1.359 (178°, 178°)	0.029 (33°, 60°)	0.014 (89°, 143°)	0.020 (80°, 108°)	0.019 (112°, 38°)	
1	0.576 (8°, 8°)	0.191 (15°, 44°)	0.090 (32°, 58°)	0.064 (28°, 26°)	0.080 (7°, 26°)	
3[d]	0.566 (9°, 9°)	0.190 (13°, 43°)	0.127 (27°, 82°)	0.071 (38°, 42°)	0.068 (47°, 79°)	0.006 (40°, 91°)
BH_3^-	1.218 (178°, 178°)	0.157 (176°, 143°)	0.154 (103°, 149°)	0.084 (124°, 151°)	0.037 (174°, 146°)	

[a] The angle is in paranthesis. The angle is between the atomic dipole on the indicated carbon and the vector defined by the indicated carbon and the atom proceeding it in the chain. See text for definition of sign. [b] Pentane derivative. [c] See text for discussion of angles. [d] The atomic dipole vectors and the angles on C_7, C_8, and C_9 are 0.059, (98°, 20°); 0.041, (29°, 26°); and 0.024, (62°, 34°), respectively.

the C_n-C_{n-1} vector and the C_n-X vector are given. For the neutral pentylsilane, the directions of these vectors seem almost random. But in **1** and **3**, nearly all of the angles between the atomic dipole vector and the two nuclear vectors are less than 90° (for the exceptions, see below). This is in contrast to the data for **2**, where all the angles are greater than 90°. These data for the charged X are in agreement with those for the C_s compounds in which the direction of the atomic dipole vectors is always toward the X atom for positively charged X and away from it for negatively charged X.

How can we account for the rather substantial lengths of the atomic dipole data for carbon atoms other than C_1 in the charged species? A reasonable model is that the charged X group simply polarizes the electron density around other atoms in the molecule. In the case of the charged alkanes studied here, this hypothesis cannot be valid because the direction of the atomic dipole vector is incorrect: the atomic dipoles essentially point at the NH_3 group for $X{=}NH_3^+$, whereas for $X{=}BH_3^-$, they point away from the BH_3 group. We believe the direction of the atomic dipole is determined largely by the distortion of the atomic basin, a distortion shown in the position of the FCP. Consider the C_n-C_{n-1} bond in a molecule with a positive charge, where C_{n-1} is closer to that charge. We postulate that C_{n-1} will have a larger effective ionization energy and hence will push the atomic basin and the bond critical point toward C_n by contributing a greater amount of wave function to the bond. Likewise, in the C_n-C_{n+1} bond, C_{n+1} will pull the atomic basin of C_n toward itself. These movements of the electron density toward C_n from C_{n-1} and from C_n toward C_{n+1} contribute significantly to the atomic dipole vector, and cause the positive end to point toward the perturbing positive charge. In the C_s-substituted alkanes, where the vector from the charged substituent makes a small angle with the bond direction, this model accounts for both the length and direction of the atomic dipoles. In the twisted conformers, the analysis is more difficult because of the loss of symmetry. As a consequence, the vector from the positive charge to C_n is no longer approximately parallel to the bond vectors, so the distortion of the atomic basin is less readily understandable. Nevertheless, what is striking in the data in Table 7 is the angles of less than 90° the atomic dipoles on C_n of substituted ammonium complexes make with the C_n-N vector. Similarly, the angles in **2** are much greater than 90°. Further, the two atoms in nonylammonium ion that have odd values of the dipole moment length and angle, C_6, and C_7, are exactly those that are in unique positions in the molecule: C_6 is further from the N atom that either of its neighbors, and C_7 is closer than either of its neighbors.

Conclusions

We have established that charged substituents in long-chain alkanes influence a number of parameters of the carbon atoms and the carbon−carbon bonds of those compounds by a through-space mechanism. We have calculated two properties resulting from analysis of topological aspects of the wave function using the AIM technique, the critical point position (FCP) and the atomic dipoles. We use the FCP data to argue that the basin of electron density around a carbon atom is distorted by the potential produced by the charge on X, even though there is no systematic effect on the charge of the carbon atoms, at least as calculated by either the AIM or the NBO method.[23] The length and direction of the atomic dipoles support this assignment. These distortions, especially in conformers that are twisted, establish that this effect operates through space. We have also established a similar phenomenon occurs with the energy of the core electrons of the carbon atoms. An examination of the s orbital participation in bonding shows the variation is determined by a through-space effect. Our exploration of these various long-range electronic effects complements our earlier data[23] concerning charge distribution in substituted alkanes with charged substituents. Finally, we have analyzed the orbitals that result from the localized bond analysis generated by an NBO treatment of the charged substituted alkanes. For the carbon−carbon bonds, the fraction of the hybrid used by C_n in the bond to C_m shows a parallel to the position of the FCP of that bond. This remarkable agreement between the orbitally based NBO method and the topological AIM method stands in striking contrast to the disagreement these two methods produce with respect to assignment of charge to atoms.[9] From our atomic dipole vector analysis, we conclude that although carbon atoms in charged substituted alkanes do not gain or lose substantial electron density to neighboring carbon atoms, the atomic basin around those atoms-as measured by the FCP, the atomic dipole vectors, and the s orbital participation is significantly distorted.

Acknowledgment. We appreciate a grant from the Fisher Foundation that partially supported the Calculation Chemistry Laboratory at Smith College. E.M.N. thanks the Arnold and Mable Beckman Foundation for financial support.

Supporting Information Available: Table S1, Table S2, Table S3. These material are available free of charge via the Internet at http://pubs.acs.org

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