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Charge Variations in Substituted Alkanes: Evidence for a Through-Space Effect

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Abstract: Ab initio quantum mechanical calculations at the 6-31+G* basis set are reported on over 75 substituted ethanes and higher alkanes. The charges on the carbon and hydrogen atoms of these species are determined by topological- and orbital-based methods. The relative change in charge is used to determine how a substituent group affects atoms remote from it. Arguments are presented to account for the charge on the hydrogen atoms in substituted ethanes and higher alkanes. Fluorine atoms within about 2.7 Å of hydrogen atoms cause an increase in positive charge on those hydrogen atoms. Charge is moved to the periphery of the molecule when a charged substituent is present. A model that involves through-space interactions between the charged group and the alkane framework accounts for these data. The charge calculations indicate a substituted carbon atom has a charge that is more dependent on the nature of the atom to which it is attached than on that atom's charge or on other atoms in the substituent. No evidence of systematic charge variation on nonsubstituted carbon atoms was found. Energy changes for some isodesmic reactions are explained on the basis of the model of charge distribution. The results are applicable to studies of the Hammett equation.

Introduction

The interpretation of the results of chemical reactions often depends on the concept of the charge on atoms in molecules. The influence the charge at one point in a molecule has on properties or reactivities at another site is critical to our understanding of chemistry. It has, however, often been emphasized[1,2] that charge is not readily available by quantum mechanical calculations as there is no atomic charge operator. Bachrach[1] has associated attempts to use quantum mechanical calculations of charge in chemistry as a part of "finding the Grail." We have been investigating, by quantum mechanical calculations, the variation in bond length in some simple carbon-based compounds, mainly those of the type ZCH_2CH_2X.[3] In the process of analyzing our calculational results, we found ourselves, as have many others before us, drawn to interpretations based on the variation of charge on the atoms in our species. Given the uncertainty of the quantum mechanical meaning of charge, our preoccupation reminds us of Touchstone's saying: "The fool doth think he is wise, but the wise man knows himself to be a fool."[4] Nevertheless, we believe that our investigation of charge variation reveals aspects of substituent effects that can be meaningfully applied to an understanding of chemical systems.

Attempts to assign charges to atoms in molecules based on the wave function for those molecules have been pursued since the earliest quantum mechanical calculations. Mulliken population analysis[5] has been widely used, and widely criticized for its basis set dependence[6] and arbitrary division of the shared charge between two atoms.[1,7] Another orbitally based method has been developed—the natural population analysis (NPA) of Weinhold and co-workers.[8,9] There has also been work on a topological analysis of the total electron density (AIM), which has been developed by Bader and co-workers.[10] A wide variety of methods sometimes called "physically oriented" schemes[11] also exist, which are useful in molecular simulations where atomic charges are fit to reproduce electrostatic potentials.[12] Bachrach[1] and Wiberg and Rablen[13] have previously compared these various methods. Their results show that the absolute magnitude of the charge on a given atom varies significantly from method to method. We find this also, as we will illustrate below. Our aim, however, is neither to compare the methods nor to attempt to find the "real" value of the charge, whatever that is taken to mean. Rather we attempt to ascertain what aspects of the charge on atoms in molecules are common to some of these methods and hence can be used to predict properties of simple carbon-based compounds such as CH_3CH_2X where X varies over a large range and includes groups that are charged, both positively and negatively. We have also expanded our investigations to several longer chain compounds, from butyl derivatives to dodecyl ones, to determine if the charge on the carbon and hydrogen atoms remote from the perturbing center can be influenced by that substituent. From these we find long-range variation in charge. We also address the issue of whether there are any energetic consequences of this long-range variation in charge.

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Computational Methods

Calculations were performed using Gaussian-94, revisions B.1 and B.2[14] and Gaussian-98, revision A.7,[15] on an SGI Power XZ Indigo2 running IRIX 6.2 or on a Dell OptiPlex GX1p machine running Linux, Red Hat Version 6.0. The structures used in the calculations were optimized with the basis sets indicated in the text. The results were obtained using both the SCF = Tight and Opt = Tight convergence criteria. We made extensive use of the visualization software Ampac 6.0 GUI.[16] The NPA method, Natural Bonding Orbital Version 3.1,[17−19] was implemented through Link 607 of the Gaussian package. The AIM procedure was carried out using the programs EXT94b and PROAIMV[20] as downloaded[21] and compiled on our machines. For EXT94b to run successfully, we had to modify the program slightly. In cases where we found an AIM analysis using PROAIM led to unreasonable values of atomic charges, presumably because integration rays went through the interatomic surface, we used the PROMEGA program that is part of the PROAIMV package. In these instances, we found that the program MORPHY98_SGI,[22−27] which uses a different integration algorithm, gave results that appear reasonable and generally agreed with those from the PROMEGA program.

Results

The Effect of Basis Set Variation. One of the major criticisms of the Mulliken population analysis (MPA) is that it is very dependent upon the choice of basis set.[1] It has been claimed[1,13,28] that the newer procedures, such as the NPA and AIM methods, are not as dependent on the choice of basis set. We find that the changes in charge for some atoms in CH_3CH_2X for X = F and X = SiH_3 are quite sensitive to a change in basis set, even in the NPA or AIM method. For instance, using basis sets between 6-31G and 6-31+G(3df,3pd), as listed in Table S1, the MPA charge on the methyl carbon of X = F varies over a range of 0.34 charge units, whereas there is a maximum change of 0.13 (NPA) or 0.18 (AIM) charge units with the newer methods. Although the MPA analysis is known to fail for augmented basis set calculations,[29] the NPA and AIM methods are only somewhat less sensitive to a change in basis set.

Our concern, however, is not with the absolute magnitude of the charge on any given atom, but with relative magnitudes. Here all methods of population analysis produce more consistent answers—Table S1—especially the NPA and AIM methods. For instance, the difference in charge on the hydrogen atoms that are antiperiplanar and gauche, respectively, to the X = F group show an average (standard deviation) of -0.005 ± 0.002, and a maximum variation of 0.006 with the NPA method and -0.012 ± 0.001 and 0.004 with the AIM method. Similar comparisons hold for X = SiH_3. In addition, an especially useful comparison is the value of the charge difference between the methylene carbon for X = F and that carbon for X = SiH_3. Though the values of these absolute charges calculated with the NPA method range over about 0.13 charge units for each X as the basis set is changed, the difference has a standard deviation of a factor of 6 less, 1.021 ± 0.021. We conclude comparisons are largely independent of basis set.

We chose the 6-31+G* basis set for our work because we wished to analyze charge differences involving a large number of compounds, neutral as well as ones with positive and negative charges. Molecules with negative charges are known to require basis sets with diffuse functions.[7] The 6-31+G* basis set is a compromise because it contains diffuse functions, yet requires only moderate calculational times.

There is one further aspect that is critical to our application of charge calculations to the interpretation of chemical behavior: we will not attempt to interpret those situations in which the two methods of charge analysis produce differences that are inconsistent with each other. We have chosen to focus on charge assessment methods based on orbital—NPA—or topological—AIM—analyses, rather than those derived from the fit to electrostatic potentials or other methods.[30] The former two methods, as has been discussed several times in the literature—see especially the discussion about the role that charge plays in the rotation about the C−N bond in amides[31−37]—differ dramatically in the magnitude of the absolute charge assigned to various atoms. Our interest in *differences* in charges usually removes this issue. Since we do not wish to speculate about the more appropriate of the two methods of charge determination, we will not analyze those situations in which the two methods disagree about relative differences in charge.

Charge Variations on Hydrogen Atoms in Compounds with Charged X. We have studied the variation in the charge on the atoms in a number of ethyl derivatives. The data for the calculated charges are given in Tables 1 and 2. In Figure 1, we present the relationship between the charge calculated by the AIM method and that calculated by the NPA method for the

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Table 1. NPA Charge on Atoms in $CH_3CH_2X^a$

X	H_{ap}	H_g	C of CH_3	H of CH_2	C of CH_2	X
F	0.223	0.230	−0.685	0.184	0.086	−0.453
SO_2F	0.243	0.248	−0.667	0.271	−0.698	0.085
OH	0.218	0.227	−0.659	0.179	−0.044	−0.326
CF_3	0.231	0.234	−0.655	0.246	−0.518	−0.016
H	0.216	0.216	−0.649	0.216	−0.649	−0.216
NH_2	0.220	0.212	−0.657	0.211	−0.234	−0.175
NF_2	0.230	0.240	−0.675	0.294	−0.266	−0.247
SiH_3	0.223	0.219	−0.640	0.242	−0.937	0.433
SiF_3	0.229	0.229	−0.646	0.260	−1.048	0.489
CH_3	0.220	0.214	−0.640	0.216	−0.448	0.008
Li	0.186	0.191	−0.626	0.186	−1.139	0.845
CH_2Li	0.201	0.206	−0.637	0.191	−0.447	0.088
CH_2^-	0.164	0.192	−0.644	0.177	−0.461	−0.797
CF_2^-	0.176	0.216	−0.653	0.194	−0.553	−0.810
BH_3^-	0.169	0.197	−0.624	0.176	−0.691	−0.600
BF_3^-	0.175	0.208	−0.631	0.190	−0.799	−0.541
$B(OH)_3^-$	0.160	0.208	−0.629	0.185	−0.762	−0.558
NH_3^+	0.278	0.245	−0.686	0.261	−0.229	0.625
NF_3^+	0.291	0.269	−0.707	0.288	−0.197	0.500
OH_2^+	0.286	0.254	−0.712	0.262	−0.026	0.421
FH^+	0.332	0.304	−0.806	0.254	0.327	0.031

[a] Data are for the 6-31+G* basis set

Table 2. AIM Charge on Atoms in $CH_3CH_2X^a$

X	H_{ap}	H_g	C of CH_3	H of CH_2	C of CH_2	X
F	−0.009	0.003	0.077	0.007	0.659	−0.747
SO_2F	0.018	0.030	0.081	0.064	−0.023	−0.262
OH	−0.021	−0.002	0.080	−0.031	0.667	−0.658
CF_3	−0.002	0.008	0.074	0.020	0.153	−0.263
H	−0.024	−0.024	0.072	−0.024	0.072	−0.024
NH_2	−0.020	−0.028	0.042	−0.020	0.549	−0.476
NF_2	−0.003	0.017	0.075	0.030	0.483	−0.651
SiH_3	−0.018	−0.021	0.073	−0.012	−0.730	0.743
SiF_3	−0.004	−0.004	0.078	0.015	−0.806	0.712
CH_3	−0.024	−0.027	0.060	−0.036	0.107	−0.018
Li	−0.064	−0.070	0.072	−0.070	−0.590	0.902
CH_2Li	−0.053	−0.040	0.049	−0.078	0.112	0.122
CH_2^-	−0.105	−0.067	0.013	−0.097	0.125	−0.703
$CF_2^{-\,b}$	−0.089	−0.025	0.044	−0.071	0.113	−0.876
BH_3^-	−0.102	−0.058	0.046	−0.108	−0.431	−0.173
BF_3^-	−0.089	−0.040	0.052	−0.083	−0.498	−0.222
$B(OH)_3^-$	−0.099	−0.040	0.047	−0.094	−0.469	−0.219
NH_3^+	0.072	0.027	0.074	0.076	0.330	0.318
NF_3^+	0.095	0.069	0.090	0.140	0.201	0.194
OH_2^+	0.086	0.043	0.083	0.120	0.289	0.216
FH^+	0.147	0.126	0.107	0.217	0.005	0.009

[a] Data are for 6-31+G* basis set. [b] These values was computed with PROMEGA and MORPHY98_SGI. The PROMEGA data are listed above.

gauche and antiperiplanar hydrogen atoms of the methyl group. The magnitude of the charge assigned to hydrogen atoms by these two methods differ significantly; however, the charges on these two types of hydrogen atoms apparently respond to a common factor independent of the method of analysis.

We consider first the ethyl derivatives with charged X groups, the five negative groups CH_2^-, CF_2^-, BH_3^-, BF_3^-, and $B(OH)_3^-$; and three positive groups, NH_3^+, NF_3^+, and OH_2^+.[38] It is clear from the data in Tables 1 and 2 that the positively charged compounds have extensive positive charge placed upon the hydrogen atoms of the ethyl group. For instance, if we add a proton to $CH_3CH_2NH_2$ to form $CH_3CH_2NH_3^+$, the antiperiplanar and gauche hydrogen atoms become more positive by 0.058 and 0.033 charge units (NPA), and by 0.092 and 0.055 charge units (AIM). The methyl carbon atom, on the other hand, changes by only 0.029 (NPA) or 0.032 (AIM) charge units. Likewise, if we remove a proton from the antiperiplanar site of one methyl group on propane, the antiperiplanar hydrogen of the other methyl group becomes more negative by 0.056 (NPA) or 0.081 (AIM) charge units. The methyl carbon atom changes by only 0.004 and 0.047 charge units, respectively.

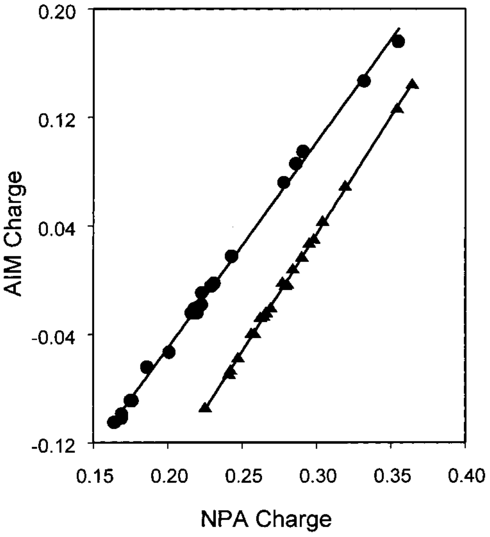

Figure 1. Calculated AIM charge versus calculated NPA charge for the methyl hydrogen atoms in CH_3CH_2X at the 6-31+G* level. The antiperiplanar hydrogen atoms are displayed as circles, and the gauche hydrogen atoms, as triangles. For the gauche hydrogen atoms, 0.05 charge units were added to the NPA data for clarity.

Another way to look at this phenomenon is to consider the formal reaction

$$X{-}X + (CH_3)CH_2{-}CH_2(CH_3) = 2\,(CH_3)CH_2{-}X \quad (1)$$

The total charge on each half of the butane is zero, and the total charge on each half of X_2 is zero for uncharged X or ±1 for the charged X. Using the charges on each atom in butane, we can compute the change in charge on each atom in an ethyl fragment upon going from butane to the corresponding CH_3CH_2X. If $X = BH_3^-$, for instance, we find the total change in charge on the ethyl fragment in a NPA analysis is −0.401 charge units, of which −0.149 charge units is on atoms other than the methylene carbon. We expect the methylene carbon will be reasonably negative because the electrons in the B−C bond will be polarized toward the carbon. The remaining 0.149 units of negative charge are mostly localized on the antiperiplanar hydrogen of the methyl group (−0.051) and the methylene hydrogen atoms (−0.038 each). The AIM charge data produce comparable results for this analysis. In a similar fashion, we find that the positively charged materials localize positive charge on the hydrogen atoms of the ethyl fragment. For instance, with $X = NH_3^+$, the total change in charge on the ethyl fragment is 0.685 charge units (AIM), of which 0.448 is on atoms other than the methylene carbon. Most of this positive charge change from butane is localized on the hydrogen atoms of the ethyl group, 0.096 units on the antiperiplanar hydrogen, 0.054 units on each of the gauche hydrogen atoms, and 0.115 units on each of the methylene hydrogen atoms. This analysis demonstrates the charge an ethyl fragment carries in CH_3CH_2X compounds (X charged) is spread mostly onto the periphery of the molecule, onto the hydrogen atoms. This was previously suggested,[39] but was not as thoroughly established as by our data.

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(38) We also performed calculations on $X = FH^+$. This species is, however, essentially an ethylcarbenium ion solvated by HF. We will not use this species in our arguments.

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Table 3. NPA Charges on Hydrogen Atoms in Long Chain, C_s, Compounds[a]

X	H on C_1	H on C_2	H on C_3	H on C_4	H on C_5	H on C_6
			Butyl			
H	0.215	0.214	0.214	0.215, 0.220		
F	0.182	0.227	0.217	0.218, 0.223		
CH_2^{-b}	0.177	0.194	0.201	0.205, 0.196		
BH_3^-	0.177	0.199	0.200	0.206, 0.196		
O^-	0.076	0.193	0.220	0.204, 0.193		
NH_3^+	0.257	0.236	0.232	0.226, 0.247		
			Pentyl			
H	0.214	0.214	0.212	0.214	0.214, 0.220	
F	0.182	0.227	0.216	0.217	0.215, 0.223	
CH_2^{-b}	0.177	0.195	0.200	0.207	0.208, 0.203	
BH_3^-	0.177	0.200	0.199	0.207	0.207, 0.203	
NH_3^+	0.257	0.236	0.230	0.224	0.223, 0.239	
			Hexyl			
H	0.214	0.214	0.213	0.213	0.214	0.214, 0.220
F	0.182	0.227	0.216	0.216	0.215	0.215, 0.221
CF_3^b	0.244	0.232	0.216	0.216	0.215	0.215, 0.222
SiF_3	0.258	0.226	0.215	0.215	0.215	0.215, 0.222
NH_2	0.209	0.210	0.214	0.213	0.214	0.214, 0.221
SiH_3	0.240	0.217	0.214	0.213	0.214	0.215, 0.220
CH_2^{-b}	0.177	0.195	0.201	0.206	0.209	0.210, 0.207
BH_3^-	0.177	0.200	0.200	0.206	0.208	0.210, 0.206
NH_3^+	0.257	0.236	0.230	0.221	0.221	0.220, 0.235

[a] The values in the last column for each chain are for the gauche and antiperiplanar positions, respectively. [b] For these X groups, C_1 is the methylene carbon to which CH_2^- or CF_3 is attached.

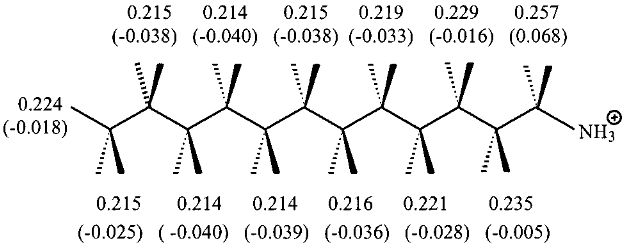
Table 4. AIM Charges on Hydrogen Atoms in Hexyl Derivatives of C_s Symmetry[a]

X	H on C_1	H on C_2	H on C_3	H on C_4	H on C_5	H on C_6
H	−0.027	−0.039	−0.042	−0.042	−0.039	−0.027, −0.024
F	0.003	−0.015	−0.038	−0.037	−0.038	−0.025, −0.021
CF_3	0.016	−0.010	−0.037	−0.037	−0.038	−0.025, −0.021
SiF_3	0.012	−0.022	−0.037	−0.038	−0.038	−0.025, −0.021
NH_2	−0.023	−0.045	−0.040	−0.041	−0.038	−0.027, −0.023
SiH_3	−0.015	−0.037	−0.040	−0.041	−0.039	−0.027, −0.023
CH_2^-	−0.098	−0.071	−0.060	−0.052	−0.047	−0.035, −0.045
BH_3^-	−0.107	−0.062	−0.062	−0.052	−0.048	−0.035, −0.045
NH_3+	0.068	−0.004	−0.015	−0.028	−0.028	−0.017, 0.000

[a] The values for the hydrogen atoms on C_6 are for the gauche and antiperiplanar positions, respectively.

Our understanding of this localization of charge relies upon consideration of longer chain compounds. In Tables 3 and 4 we present data for some long chain compounds with C_s symmetry: that is, compounds in which all carbon−carbon bonds are antiperiplanar to each other. There are several observations to make about these data. First, the values of the charges on the methylene hydrogen atoms as we move down the chain are nearly independent of the chain length. This observation is not particularly unexpected, as chemists have always believed that the environment around an atom in a carbon chain depends most strongly on the non-carbon, non-hydrogen neighbors. Second, the hydrocarbons (X = H) and the remote end of long chain compounds with neutral X, show the antiperiplanar hydrogen at the end of the chain always has a charge that is more positive than the gauche hydrogen on this methyl group by 0.006 (NPA) or 0.003 (AIM) charge units. The cause of this difference is not clear to us.[40] Third, when X is neutral, the methylene hydrogen atom charges become independent of X by C_3. In contrast, the effect of a charged X on the hydrogen atoms is still evident at C_6. For example, the antiperiplanar hydrogen on the C_6 methyl group of hexylammonium ion has a charge about 0.014 (NPA) or 0.021 (AIM) charge units more positive than the corresponding hydrogen with X = H, F, CF_3, or SiF_3, all of which have the "normal" charge pattern for this environment. The difference in charge, antiperiplanar hydrogen minus gauche hydrogen, on the terminal carbon of the pentyl and hexyl chains is still more positive for X = NH_3^+ and more negative for X = BH_3^- than the normal value for neutral X (between 0.006 and 0.008 charge units), just as they are in the substituted ethanes. This observation establishes that the antiperiplanar hydrogen atom is more sensitive than the gauche hydrogen atoms to the charge on the molecule. Finally, since charged X groups modify the charges on the hydrogen atoms on C_6, we are dealing with a long-range effect. [41]

Because the effect of a charged X extends to the end of a five- or six-membered chain, we have studied the charges on the hydrogen atoms of substituted dodecanes, $C_{12}H_{25}X$, for X = NH_3^+, CH_2^-, and BH_3^-. We illustrate the charges on the hydrogen atoms with X = NH_3^+ in **1**. The NPA data and the AIM data are presented with the latter listed in parentheses. The charge on the hydrogen atoms of C_1 through C_5 parallel closely the corresponding charges in hexylammonium ion. After C_5, with the exception of a slightly positive antiperiplanar hydrogen atom at C_{12} for X = NH_3^+ and a slightly negative antiperiplanar hydrogen atom at C_{12} for X = BH_3^-, **2**, and X = CH_2^- (Supporting Information), the charge stops varying and becomes close to that characteristic of the methylene groups in the middle of a hydrocarbon. These data strongly support our



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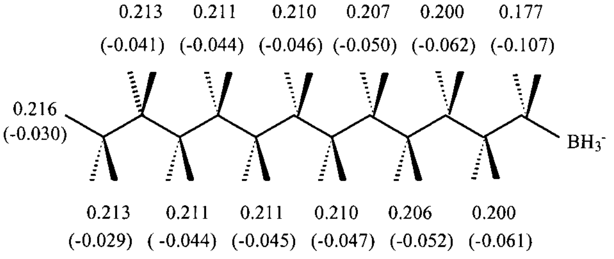

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(40) We have performed experiments that show it is insensitive to changes in bond lengths or angles. The antiperiplanar site differs from the gauche site in its proximity to neighboring C−H bonds, especially the C−H bonds on the β carbon. It is possible that weak dipolar interactions play a role. We do not believe an attempt to be more quantitative is warranted here because of the small difference in charge, although the generality of the difference is impressive.

(41) Although this effect is very subtle, the change in charge on the hydrogen atoms with increasing carbon number follows a slightly different decay for even-numbered and odd-numbered carbons. An excellent example of this effect occurs in the pentyl system with X = BH_3^-. Using the NPA method, we find the charges on the hydrogens on odd carbons are 0.177, 0.199, 0.207 (gauche), whereas those on the even carbons are 0.200, 0.207. There is actually a small reversal of the decay pattern as the carbon number goes up, but the pattern is of increasing positive charge with distance from the BH_3^- center is preserved within either only the odd- or only the even-numbered atoms.

conclusion, given above, that a long-range phenomenon is influencing the charge of the hydrogen atoms in substituted alkanes that carry charge.

To verify that the charges on the hydrogen atoms are being influenced by the charged groups in a systematic manner we turned to the zwitterionic material, BH_3-$(CH_2)_6$−NH_3. The hydrogen atoms near the nitrogen end of this molecule, from which we start our numbering, have charges more positive than the corresponding hydrogen atoms in hexane (C_1 and C_2, 0.253 and 0.230, NPA; 0.062 and −0.013, AIM, respectively). These charges are not as positive as those found in the hexylammonium ion because the boron center reduces that positive value. Likewise, the hydrogen atoms at C_5 and C_6, which are close to the boron, have a charge more negative than in hexane, 0.181 and 0.207 (NPA) and −0.101 and −0.051 (AIM), respectively, but more positive than in **2** and hexylborohydride due to the presence of the protonated nitrogen. These data clearly show a long-range effect of charged substituents.

Hydrogen Charges in Neutral CH_3CH_2X. The charge variations in compounds with neutral X are not as obvious as those in which X is charged. The neutral CH_3CH_2X do not have large charge variations on the methyl hydrogen atoms, especially if we discount the compounds containing Li, which are essentially solvated carbanions due to the long C−Li bond, (2.016 Å in X = Li and 2.013 Å in X = CH_2Li). Nevertheless, the data for all neutral CH_3CH_2X fall on the line in Figure 1, showing that both the NPA and AIM methods give similar results. Second, the X groups that we studied—see Tables 1 and 2—can be divided into three groups. The members of the first group, like the cationic species, have values of the charge on the antiperiplanar hydrogen minus that on the gauche ones that are positive, X = NH_2, CH_3, SiH_3. For the second group this value is zero (X = H, of necessity, and X = SiF_3), and for the third, the value is negative, as it is for the anionic substances. These classes of X are independent of method of charge analysis and basis set. In addition, we performed charge calculations on X = SiH_3 and X = F as representatives of the first and third classes using a density functional method to determine if the classification is dependent upon lack of electron correlation correction. We obtained the same result for these charge differences using B3LYP/6-31+G*, where we found the difference is positive for X = SiH_3 (0.003, NPA; 0.004, AIM) and negative for X = F (−0.003, NPA; −0.008, AIM).

A third observation concerns the differences between compounds that contain F and those that do not. We find that compounds in which a fluorine atom is present in X generally have more positive values of charge on the methyl hydrogen atoms. It is useful to compare sets of compounds with similar environments, X = NH_2 with X = NF_2, for instance. The antiperiplanar hydrogen is 0.010 (NPA) and 0.017 (AIM) charge units more positive in the latter, and the gauche hydrogen atoms are 0.028 (NPA) and 0.045 (AIM) charge units more positive. This is a general pattern: all hydrogen atoms become more positive in compounds containing fluorine (including charged ones), but the gauche hydrogen atoms are more affected. An obvious rationalization for the more positive hydrogen atom charge in compounds with fluorine atoms in the X group is the electron-withdrawing power of F. Indeed, in both the NPA and AIM methods of analysis, the X = SO_2F group, a strongly electron-withdrawing group, has the most positive values for the charge on methyl hydrogen atoms. This electron withdrawing analysis suggests that we should find that motion of electrons in the formal reaction 1 from the ethyl group to the X group should occur, as it does, in the order F > OH > NH_2 > CH_3. Furthermore, the AIM results show there is more electron transfer to YF_n than to the YH_n group (Y=C, Si, N), in agreement with the requirements of our model. The NPA analysis agrees for Y=N, but has small changes for Y=C and Y=Si (which are reversed in the Y=Si case). The two methods agree reasonably with the role of fluorine as an electron withdrawing atom.

The data for the methylene hydrogen atoms in the neutral compounds is also presented in Tables 1 and 2. These data show, as expected, sensitivity to the nature of X. We find, however, no correlation between the values calculated by the NPA method and those calculated by the AIM method. For instance, in the AIM analysis the methylene hydrogen atoms for X = F have a charge that is between the values for X = SiF_3 or CF_3 and those of X = SiH_3 or CH_3. In the NPA method, however, the methylene hydrogen atoms for X = F have the lowest charge of any neutral except X = OH and the compounds with X that contain Li. This situation makes it impossible for us to find a physical explanation for the variations without deciding upon a "correct" method of computing charge. This is disappointing to us because of the sensitivity of the methylene hydrogen charges to X. We could construct a model using one of the charge methods, but it would then be incorrect for the other. There is some phenomenon in one or both of the two methods of analysis that causes the lack of correlation between them.

Charge Variations on Carbon Atoms. The perturbation of the carbon atoms in substituted alkanes and the effect of that perturbation at remote sites has been extensively studied in organic chemistry, normally under the guise of Hammett relationships.[42,43] An electron-withdrawing X should generate relatively positive carbon atoms, and the amount of positive charge on these atoms should decrease with distance from X. In one of the earliest calculations addressing this issue, Pople and Gordon used the CNDO method[44] and suggested there was charge alternation down the aliphatic chain. An experiment that assumed point charges at atomic centers suggested this alternation is not present.[45] More recently, Wiberg and co-workers have shown using the AIM procedure that there is little charge propagation down the carbon atom chain in butyl[39] and ethyl[46] derivatives. In Tables 1 and 2, we present comprehensive data for the charges on carbon atoms in substituted ethanes. An analysis of the values in these tables reveals patterns of behavior that, to us, are sometimes unexpected.

Our criterion for a carbon atom charge deserving interpretation is that the NPA and AIM methods predict the same trend. A plot of the data shows *some* agreement between the NPA and AIM methods for the methylene carbon atom charges for neutral CH_3CH_2X (correlation coefficient of only 0.92). There is no correlation between the NPA and AIM charge assignments for the methylene carbon atoms[47] in the charged species. As a result, we cannot make any reasonable conclusions about the charge on these particular atoms. There are, however, interesting features present in the values for methylene carbon charges that we discuss below.

We begin with consideration of the data for the methylene carbon atom in the neutral compounds. As the X group is

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[47] We compared our results with those of Wiberg and Laidig—see ref 46—who used a 6-31G**//6-31G* basis set and the AIM method. There is a linear correlation between our AIM data and that of Wiberg and Laidig (r^2 = 0.999).

changed from F to OH to NH_2 to CH_3 the NPA procedure shows the methylene carbon atom charge becomes more negative. The AIM procedure shows a similar trend, although the charges for F and OH are reversed. What we find surprising is that both methods show the methylene carbon atom has a similar charge with X = SiF_3 and X = SiH_3 and with X = CF_3 and X = CH_3, respectively. These observations suggest the charge on the methylene carbon atom is significantly more sensitive to the *nature* of the atom to which it is attached than it is to the charge on that atom (as varied by changing the other atoms, Y, in the groups SiY_3 and CY_3). This phenomenon is also apparent in a comparison of X = SiH_3 and X = CF_3. In an NPA analysis, the central atom of these groups have charges of 1.109 and 1.240, respectively. Despite this similarity, the charge on the methylene carbon atoms in X = SiH_3 and X = CF_3 are notably different: −0.937 in the former and −0.518 in the latter. The same observations hold for the AIM analysis. This result is consistent with a previous study.[48]

The NPA and AIM procedures show very different behavior for the methylene carbon atom in molecules with charged X groups. The NPA method shows the charge on the methylene carbon differs by about 0.01 charge units for X = NH_2 and NH_3^+, for X = OH and OH_2^+, and for X = CH_3 and CH_2^-. Although small, the variations are in the expected directions. The AIM analysis also shows the methylene carbon atom charge is rather insensitive to the change from X = CH_3 to X = CH_2^-, but the similarity in methylene carbon atom charges determined by the two methods ends here. Dramatic changes in charge occur with the AIM method when X is changed from NH_2 to NH_3^+, and from OH to OH_2^+. These variations are counterintuitive: a positively charged molecule apparently creates a more negatively charged methylene carbon atom. These results strikingly contrast with those generated by the NPA method, but they are not completely unexpected given the reported AIM analysis of alkoxide ions, which exhibit similar behavior.[49] For the NPA method, these results augment our earlier observation about the charge depending upon the *nature* of the substituent. Not only does this hold for the substituent variation (X = CH_3 to X = CF_3), but it also holds for a charge variation on the substituent (X = NH_2 to X = NH_3^+).

The methyl carbon atom charges presented in Tables 1 and 2 provide additional evidence for concluding that the charge on the methylene carbon atom depends on the nature of the substituents. The charge on the methyl carbon shows very little variation, a range of only 0.059 (NPA) and 0.038 (AIM) charge units for the neutral compounds. If the methyl carbon atom charge is primarily sensitive to the nature of the four atoms it is attached to, then the charge should vary little as there are always three hydrogen atoms and another carbon. We tested this conclusion through examination of over 50 disubstituted compounds, ZCH_2CH_2X. The charge on the carbon atom in the $CH_2X(Z)$ fragment is dependent upon X(Z) but independent of Z(X). In $FCH_2CH_2SiH_3$, for example, the NPA method gives a charge of 0.092 on the carbon of the CH_2F fragment and −0.965 on the carbon atom of CH_2SiH_3 fragment compared to values of 0.086 and −0.937, respectively, in the corresponding monosubstituted ethanes. These results are consistent with earlier studies,[28,39,46,50,51] which showed there is no change in charge on the methyl carbon with a change in substituent on the other terminus of the molecule. How general is the conclusion that the charge of an atom depends on the nature of the substituents and not on the more remote environment around that substituent? It is consistent with an AIM analysis of the fluorine atom charge in CF_nH_{4-n} and the silicon atom charge in $C(SiH_3)_nH_{4-n}$,[50] and with an NPA analysis of the silicon atom charge in $NH_n(SiH_3)_{3-n}$.[51] In contrast, this conclusion is not true for the AIM charge on the cyano carbon in $CH_n(CN)_{4-n}$ or of chlorine charge in CH_nCl_{4-n}.[50]

Table 5. NPA Charges on Carbon Atoms in Substituted Hexanes of C_s Symmetry

X	C_1	C_2	C_3	C_4	C_5	C_6
H	−0.636	−0.437	−0.429	−0.429	−0.437	−0.636
F	0.101	−0.475	−0.435	−0.428	−0.437	−0.637
CF_3	−0.509	−0.443	−0.427	−0.429	−0.437	−0.637
SiF_3	−1.037	−0.434	−0.428	−0.430	−0.437	−0.637
NH_2	−0.222	−0.444	−0.432	−0.428	−0.437	−0.636
SiH_3	−0.925	−0.427	−0.426	−0.430	−0.436	−0.636
CH_2^-	−0.448	−0.435	−0.426	−0.424	−0.434	−0.633
BH_3^-	−0.680	−0.419	−0.422	−0.427	−0.434	−0.633
NH_3^+	−0.216	−0.466	−0.435	−0.432	−0.440	−0.641

We extended our carbon atom charge analyses to a number of long chain compounds. We present the NPA charge data in several substituted hexanes in Table 5 and the AIM results in Table S2. We also calculated the NPA and AIM charges on a number of substituted butanes and pentanes; these data parallel those of the hexanes. The two methods predict similar overall behavior of the carbon atoms in these extended systems. The NPA and AIM charges on C_1 for the substituted hexanes parallel the methylene carbon atom charges in the substituted ethanes (slope 0.997 and 1.004 respectively, correlation coefficients both 1.00): the charge on the carbon atom in a CH_2X fragment is independent of whether that fragment is attached to a methyl or an extended methylene chain. Further, whatever factor causes the lack of correlation between the NPA results and the AIM data is also independent of those attachments. The data for C_2 show the charge varies over only a range of 0.056 (NPA) and 0.033 (AIM) charge units. With the exception that C_2 is most positive for X = F from both NPA and AIM perspectives, there is no pattern of variation shared between the methods: we do not believe an attempt at analysis is worthwhile. As we move down the chain, the charge on the carbon atoms show, not surprisingly, less and less variation as X is changed, but still without systematic pattern. Further, in contrast to the hydrogen charge data, there is no indication that the carbon atom charges respond in any particular manner to charged X groups.

Discussion

Is the Variation in Hydrogen Charge Through Space? In the published work on substituent effects, there are "inductive," "resonance," and "polarization" effects.[42,43,52] The phenomenon that we are discussing, in which there is not a conjugated double bond system, should be classified as an inductive effect. Inductive effects have been broken down into sub-categories, through-space and through-bond processes. The current interpretation seems to favor a through space effect,[52−55] although some authors do not believe this point has been established.[52,56,57] In this section, we explore how well a field effect

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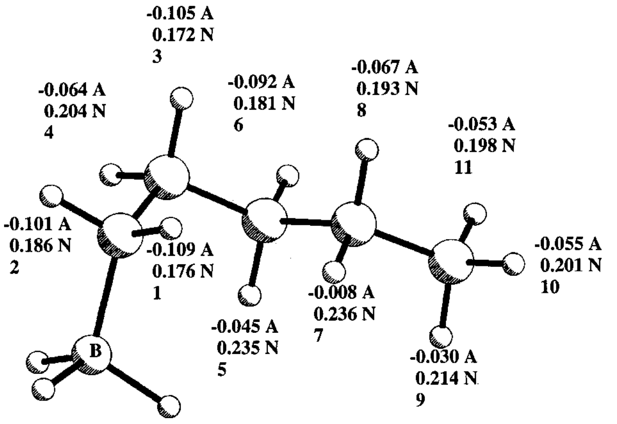

Figure 2. Optimized geometry of twisted $C_5H_{11}BH_3^-$, **3**, at the 6-31+G* level and hydrogen atom numbering scheme. The AIM (labeled A) and NPA (labeled N) charges for the hydrogen atoms are listed.

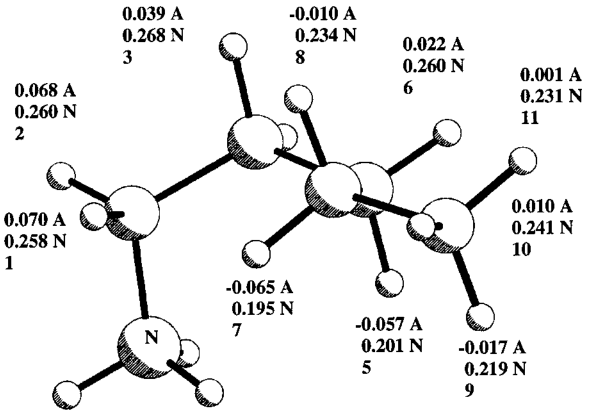

Figure 3. Optimized geometry of twisted $C_5H_{11}NH_3^+$, **4**, at the 6-31+G* level and hydrogen numbering scheme. The AIM (labeled A) and NPA (labeled N) charges for the hydrogen atoms are listed. The unmarked hydrogen atom is 4 and carries a charge of 0.001 (AIM) and 0.242 (NPA).

(through space) explains the trends discussed in the last section as well as the data we obtained for two twisted pentyl derivatives. In Figure 2, we give the structure of a $C_5H_{11}BH_3^-$ conformer in which the $C_3-C_2-C_1-B$ and $C_4-C_3-C_2-C_1$ dihedral angles are about $-60°$ (in the minimized structure the angles are $-57.7°$ and $-62.2°$, respectively). We also indicate the charges on the various hydrogen atoms in this molecule. Figure 3 does the same for the pentylammonium ion in the same conformation. The charges are approximately the same for hydrogen atoms 1−4 as they are for hydrogen atoms in similar positions in the ethylborohydride ion and ethylammonium ion. There are, however, several remarkable aspects to these compounds. As shown in Figure 2, the two hydrogen atoms labeled H_5 and H_7 are more positively charged than any hydrogen in the corresponding compounds with C_s symmetry. In fact, these two hydrogen atoms on a negative ion have charges that are as *positive* as the charges on the hydrogen atoms of C_2 of the alkylammonium ions. On the other hand, H_6 and H_8 are quite negative compared to hydrogen atoms on carbons 3 and 4 of the all antiperiplanar conformer. Similar observations hold for the pentylammonium ion in Figure 3. For instance, we find H_5 and H_7 are significantly more *negative* than any hydrogen atoms in the pentylammonium ion of C_s symmetry and H_6 and H_8 are quite positive.

Because these hydrogen atom charges differ so drastically from those of the all antiperiplanar, C_s, structure of these molecules, it seems unlikely that a classical through-bond inductive effect occurs. Most explanations of a through-bond effect have suggested there is an attenuation of the perturbation by between 0.3 and 0.4 for each bond.[56] It is, therefore, difficult for us to see how we can have such an effect still obviously manifest at the end of a six carbon chain, much less still have a minor perturbation at the end of a twelve carbon chain. Further, the fact that the antiperiplanar hydrogen in the ethyl derivatives is more strongly perturbed by charged X than are the gauche hydrogen atoms is consistent with a through-space effect, with a definite angular dependence—see below. Is it possible to model a through-space effect in a quantitative or semiquantitative manner? A major difficulty with attempting to be quantitative concerns the real charge distribution in the molecule. It has often been pointed out that atoms in molecules are not spherical and the center of charge does not necessarily correspond with the nuclear center.[10,58] Notwithstanding this, simple electrostatic models in which charge is centered at nuclei or bond dipoles are placed at the center of bonds are commonly used to explain chemical behavior in carbon based compounds. Recently, for instance, it has been suggested that the relative stability of the diaxial conformation of 1,4-dichlorocyclohexane is electrostatic in nature. An electrostatic calculation of the stability of this isomer[59] using charges obtained by the CHELPG method[60] agrees quantitatively with the observed stability. To ascertain how the method of computing charge affects this calculation, we have determined the NPA charges in the various conformers of 1,4-dichlorocyclohexane at the geometries previously used.[59] Calculations using the NPA charges give the same direction of stability as do the CHELPG numbers, but produce numerical answers that are widely deviant from the observed energy differences. It seems to us that attempts to use point charges to determine energy differences quantitatively are questionable, although a qualitative approach seems reasonable.

We attempt here to rationalize the relative charges that we see on the hydrogen atoms in substituted, charged ethanes. In the anions of the ethyl derivatives, the excess negative charge is distributed over the entire molecule, but a significant fraction resides on the hydrogen atoms. A similar situation prevails for the positive charge of the cations. We reason that electrons (or the lack thereof) around the methylene carbon of the ethyl derivatives affect all methyl hydrogens approximately equally and therefore do not lead to any differentiation. The relative difference in the charge on the hydrogen atoms of the methyl group is caused by the charge on the X group. We apply a simple electrostatic field model to these compounds to predict relative charge. We compute the electrical field component arising from the charge on X at electrons in the C−H bond *along the axis* of that bond. Since we desire a simple model, we do not want to integrate the charge distribution of electrons, but rather assign the sum of the charges on all atoms in X to a position at the atom attached to the methylene carbon. This charge creates a field component to which the electrons in the bonds of the antiperiplanar and gauche hydrogen atoms respond. Because the value of the angle, θ, between the vector from X to the center of the C−H bond and the C−H bond vector, is smaller for the antiperiplanar hydrogen atom, it responds to the field more strongly ($\cos\theta$ is larger) than do the gauche ones. When the substituent is positively charged, the field withdraws

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Table 6. Charges on Hydrogen Atoms in Various Fluoropropanes

X	H, α[a]	F, α[b]	q_{ap}[c]	q_g[c]	*d*, F−H_g
CF_3	- - -	180.0, ±60.18	0.231, −0.002	0.234, 0.008	2.682
CF_3	- - -	0.0[d], ±120.31	0.229, −0.004	0.232, 0.004	2.657
CF_2H	180.0	±59.05	0.225, −0.012	0.232, 0.005	2.657
CF_2H	0.0[d]	±120.99	0.232, −0.003	0.222, −0.015	3.483
CFH_2, **5**	55.93, 178.71	−62.71	0.228, −0.018	0.233, 0.004	2.679
				0.215, −0.025	3.347
CFH_2, **6**	±61.30	180.0	0.230, −0.008	0.218, −0.028	4.057

[a] The dihedral angle H−C_1−C_2−C_3. [b] The dihedral angle F−C_1−C_2−C_3. [c] The first value is the NPA charge, the second the AIM charge. [d] Fixed at 0.0°.

electrons from the antiperiplanar hydrogen more than the gauche ones, and visa versa for a negative X. This model accounts for the more positive antiperiplanar hydrogen for the positive X and a less positive one for the negative. It does not, however, account for the magnitude of the difference in charge between the antiperiplanar and gauche hydrogen atoms, for a given X, which is remarkably constant among the various charged X. Although the hydrogen atoms have similar values of cos θ as X is varied, our charge assessments for X vary significantly as it is changed and this should cause a change in the magnitude of the differences in the charges between the antiperiplanar and gauche hydrogen atoms. Obviously, as the model does not pretend to be able to accurately assess the absolute charge on X, it fails to account for the absolute magnitude of the value of the charge on the antiperiplanar hydrogen.

A reasonable extension of this model accounts for the charges on the hydrogen atoms in the long chain, all antiperiplanar, compounds given in Tables 3 and 4. We mentioned above that this depends on whether the hydrogen atom is attached to an even or odd numbered carbon atom. The value of θ is larger for the odd numbered carbon atoms than for even numbered ones.[61] A more convincing test to determine if this model is self-consistent can be achieved if we examine the structures **3** and **4**, Figures 2 and 3, respectively. Because a twist about the C_2−C_3 bond changes the distances and the value of θ, these conformers should have very different hydrogen charges than the all antiperiplanar species. The change of the C_3−C_2−C_1-X and C_4−C_3−C_2−C_1 dihedral angles from 180° to −60° causes H_5 and H_7 to orient such that the values of θ are 110° and 118°, respectively. This means that the field component at the center of the C−H bond induced by the charge at the X center is in the opposite direction from the field component exerted on those electrons in the all antiperiplanar conformers, where all angles are less than 90°. When X is negative, as in **3**, the field component gives a more positive charge to the hydrogen atom; and conversely when X is positive. On the other hand, the value of θ for H_6 and H_8 are reasonably small, 27° and 54°, respectively. Further, H_6 and H_8 are closer to the X group than the corresponding hydrogen atoms on the all antiperiplanar molecule. These two factors give H_6 and H_8 a more negative charge for negative X and a more positive charge for positive X than the corresponding hydrogen atoms in the all antiperiplanar conformers.

This long-range, through-space model for charge variation on the hydrogen atoms in these charged species seems reasonably successful at rationalizing the charges determined by the NPA or AIM methods. We have found further evidence, which we will present subsequently,[3] for this through-space mechanism in studies of bond critical points and atomic dipole moments,[10] and in other electronic properties.

Hydrogen Atom Charge and Fluorine Proximity. We remarked above that the charge on an antiperiplanar hydrogen of a methyl group is less positive than that on a gauche hydrogen when the molecule contains one or more fluorine atoms in X. Although this effect is not large, we believe it is real. We have carried out some additional experiments on fluoropropanes that establish the important parameter in this phenomenon is the distance of separation between the fluorine atoms in the molecule and the hydrogen atoms in question. We present the data in Table 6, where the arrangement of groups is indicated by giving the dihedral angle that each substituent on C_1 has with respect to the C_2−C_3 bond. For the substance that is in an eclipsed conformation, the indicated dihedral angle was frozen; all other variables were optimized.

The data in Table 6 show the gauche hydrogen atom(s) has a more positive charge than the antiperiplanar hydrogen atom of the methyl group in CH_3CH_2X when a fluorine atom is within 2.7 Å of the gauche hydrogen atom(s). In terms of the orientation of the substituents on C_1, all compounds with a fluorine that has a dihedral angle of 0° or 60° (F−C_1−C_2−C_3) show charges with $H_g > H_{ap}$, whereas those with a dihedral angle of 120° or 180° have charges with $H_{ap} > H_g$. The case of **5** is especially interesting because there are two symmetry nonequivalent C−H_g bonds. The one that is closer to the fluorine (2.679 Å) has a charge greater than that of the antiperiplanar hydrogen, and also greater than that of the other gauche hydrogen, which is 3.348 Å from the fluorine. The gauche hydrogen remote from the fluorine atom and the antiperiplanar hydrogen in **5** are close to the charges they have in **6**, where the fluorine atom is remote from all methyl hydrogen atoms. We also investigated a $C_5H_{11}F$ conformer that is related to the charges species shown in Figures 2 and 3, but with X = F instead of X = BH_3^- or NH_3^+. In this species, most hydrogen atoms have charges about the same as those in the all antiperiplanar conformer. We find, however, that H_5 (see Figure 2 for numbering) has a charge significantly larger (0.231, NPA) than the value of a hydrogen on C_3 in the C_s conformer. The twist has moved this hydrogen atom to a distance of 2.646 Å from the fluorine atom. We note H_7, which is significantly affected by the charge in the corresponding X = BH_3^- and X = NH_3^+ compounds, is not influenced by the fluorine in X = F. This hydrogen atom is 3.314 Å from the fluorine, outside the apparent range for effective perturbation.

We cannot definitively establish the cause of the increased charge on hydrogen atoms close to a fluorine atom in these substituted hydrocarbons. There is considerable controversy about the role that a C−F bond can play in interactions with a hydrogen atom even if it is attached to an oxygen.[62−65] In any case, the distance at which we find the fluorine exerts some effect on the hydrogen atom's charge (2.7 Å) is considerably

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(61) For instance, with X = BH_3^- in $C_{12}H_{25}X$, the angles at C_2 and C_3 are 79.4° and 74.4°, respectively. Since the field component varies as cos θ, this factor makes the charge on the corresponding hydrogen atoms more negative for C_3 than for C_2. The hydrogen atoms at C_3, however, are further from the negative perturbation, which decreases their negative charge. The interplay of these two factors causes the charge on the hydrogen atoms to vary as observed.

larger than the best estimates of a hydrogen bonding distance (2.2 Å).[65] It has been argued that C−F- - - -H−C interactions at distances between 2.4 and 2.8 Å play a role in determining crystal structures in fluorobenzenes.[66] Perhaps the interaction we observe is similar. Whatever the cause, our data require that the interaction dies more quickly with increased distance than a simple electrostatic effect.

Long-Range Energetic Consequences of Charged Substituents. We have shown that long-range perturbations occur when the substituent on an alkyl chain is charged. There are energetic consequences of this phenomenon. To illustrate these consequences we calculate the energy change, Δ*E*, for the isodesmic reaction shown below

$$Z(CH_2)_nCH_3 + CH_3CH_2X = Z(CH_2)_nCH_2X + C_2H_6 \qquad (2)$$

where *n* is 0, 1,... For all cases but $n = 0$, this process breaks two C−C bonds and forms two C−C bonds. For $n = 0$, we break and form one Z−C bond and one C−C bond. We calculated ΔE for over fifty compounds with varying X, Z, and *n*. With the exception of the reaction in which FCH_2CH_2F is formed (3.1 kcal/mol), and several compounds containing lithium atoms that we discuss below, all compounds with neutral Z and X have Δ*E* values in the range of −0.8 to 1.6 kcal/mol. For charged X groups, we find Δ*E* is substantially greater, especially for compounds in which Z contains fluorine atoms. We give the latter data in Table 7. We contend several lithium containing neutral compounds have large values of Δ*E* (FCH_2CH_2Li, −8.4 kcal/mol; $F(CH_2)_3Li$, −3.6 kcal/mol) because the carbon containing fragment is anionic.

Although we can imagine a number of explanations for this energetic interaction between Z and X separated by two methylene groups, the fact that the phenomenon is found in longer chain compounds as well—see Table 7—restricts the number of these possibilities. For instance, in the series of compounds with $Z = SiF_3$ and $X = CH_2^-$, the interaction is −12.2 kcal/mol for a separation of two methylene groups, and slowly drops to −6.2 kcal/mol when there are four methylene groups between Z and X. Similarly, for $Z = SiF_3$ and $X = BH_3^-$, the value of ΔE with four intervening methylene groups is 50% of the value for separation by two methylene groups. Clearly the interaction between Z and X is long range.

We can account for this long-range energy effect using our model, presented above, for the change in charge on hydrogen atoms upon replacement of a neutral X with a charged X. The model has part of the charge on the X group distributed to the periphery of the molecule, to the hydrogen atoms. In the case of disubstituted compounds containing F, we believe that charge will again be pushed to the periphery of the molecule; however, the periphery contains hydrogen atoms and fluorine atoms. Thus, when $X = CH_2^-$ or BH_3^-, negative charge is partially delocalized onto the fluorine atoms of the Z group. Delocalization of negative charge onto fluorine atoms is an energy stabilizing effect, which is what we see in Δ*E* for reaction 2 when we combine a negative X with a Z containing fluorine atoms. In contrast, when $X = NH_3^+$, positive charge is transmitted to the fluorine atoms, which has an energy destabilizing effect. As we showed above in the discussion of the charges on hydrogen atoms, the magnitude of the effect of a charged X depends on the distance between the charged center and the hydrogen atom. Likewise, in the fluorine-substituted Z groups, the increased distance diminishes the buildup of charge (in both the positive and negative sense, depending upon X) and we find that absolute value of Δ*E* diminishes with distance, but is still reasonably large with four methylene groups between X and Z. The NPA charge data for the fluorine atoms presented in Table 7 support these assertions. In, $SiF_3CH_2CH_3$, for instance, the NPA charge on the antiperiplanar and gauche fluorine atoms are −0.704 and −0.702, respectively. These both become more negative in $SiF_3CH_2CH_2BH_3^-$ or $SiF_3CH_2CH_2CH_2^-$. As the chain separating the SiF_3 group from the negatively charged group increases from two methylene groups to four, the charge on the fluorine atoms become more positive, but never as positive as in trifluorosilylethane. In contrast, when the charge on the fluorine atoms in $SiF_3CH_2CH_3$ are compared with the charges on those atoms in the disubstituted compounds with $Y = SiF_3$ and $X = NH_3^+$, the charges are more positive. Once again, however, even with four methylene groups separating the trifluorosilyl group from the ammonium group, the charge remains more positive than in trifluorosilylethane.

Table 7. Energy Changes for Reaction 2 and NPA Charges

compound	Δ*E* (kcal/mol)	Y_{ap}, Y_g
$SiF_3-(CH_2)-CH_2^-$	−18.9	−0.734, −0.722[a]
$SiF_3-(CH_2)_2-CH_2^-$	−12.2	−0.721, −0.717
$SiF_3-(CH_2)_3-CH_2^-$	−8.9	−0.716, −0.711
$SiF_3-(CH_2)_4-CH_2^-$	−6.2	−0.712, −0.709
$SiF_3-(CH_2)-BH_3^-$	−19.7	−0.731, −0.720
$SiF_3-(CH_2)_2-BH_3^-$	−12.8	−0.721, −0.717
$SiF_3-(CH_2)_3-BH_3^-$	−8.9	−0.716, −0.711
$SiF_3-(CH_2)_4-BH_3^-$	−6.4	−0.712, −0.709
$SiF_3-(CH_2)-NH_3^+$	20.7	−0.670, −0.687
$SiF_3-(CH_2)_2-NH_3^+$	8.4	−0.682, −0.691
$SiF_3-(CH_2)_3-NH_3^+$	6.2	−0.687, −0.696
$SiF_3-(CH_2)_4-NH_3^+$	4.7	−0.691, −0.698
$SiFH_2-(CH_2)_4-NH_3^+$ [b]	2.4	−0.691[c]
$CF_3-(CH_2)_2-CH_2^-$	−10.7	−0.443, −0.433
$CF_3-(CH_2)_2-BH_3^-$	−12.4	−0.444, −0.434
$CF_3-(CH_2)_4-BH_3^-$	−5.7	−0.432, −0.426
$CF_3-(CH_2)_2-NH_3^+$	12.2	−0.388, −0.406
$CF_3-(CH_2)_4-NH_3^+$	5.8	−0.403, −0.414
$F-(CH_2)_2-CH_2^-$	−9.6	−0.502[d]
$F-(CH_2)_2-BH_3^-$	−10.7	−0.502[d]
$F-(CH_2)_2-NH_3^+$	12.0	−0.402[d]
$HO-(CH_2)_2-CH_2^-$	−3.5	−0.842, 0.467[e]
$HO-(CH_2)_2-BH_3^-$	−4.3	−0.841, 0.465
$HO-(CH_2)_2-NH_3^+$	4.0	−0.797, 0.526
$H_2N-(CH_2)_2-CH_2^-$	−3.8	−0.954, 0.364[f]
$H_2N-(CH_2)_2-BH_3^-$	−4.2	−0.951, 0.362
$H_2N-(CH_2)_2-NH_3^+$	2.3	−0.924, 0.408

[a] For $Z = SiF_3$ and $Z = CF_3$ these values represent the NPA charges for the antiperiplanar and gauche fluorine atoms, respectively. [b] The fluorine is antiperiplanar to a carbon−carbon bond. [c] This is the charge on the fluorine atom. [d] These values are the NPA charges for the fluorine atom in Z = F. [e] These are the NPA charges for the O atom and the H atom in Z = OH, respectively. [f] These are the NPA charges for the N atom and the H atom in $Z = NH_2$, respectively.

Our argument that the Δ*E* values arise form the same factor(s) that cause the charge variation on the hydrogen atoms in the substituted alkanes finds further support in a semiquantitative relationship between the charges we calculate on the hydrogen atoms by either the AIM or the NPA methods and the energies. As previously shown for long chain alkanes, the NPA charge on the terminal antiperiplanar hydrogen is 0.220 whereas that on the terminal gauche hydrogen atoms is 0.214. When we substitute an antiperiplanar hydrogen on one end of an alkane

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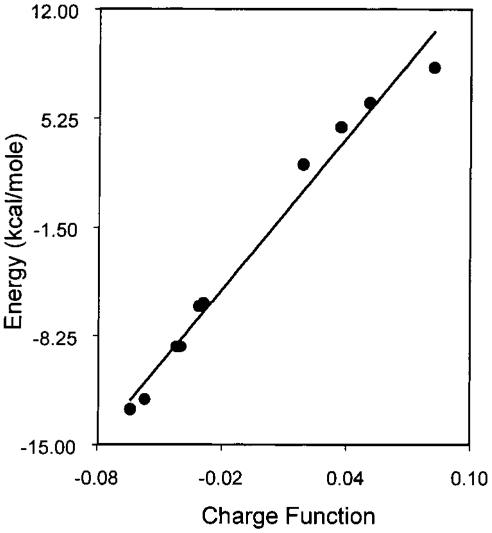

Figure 4. Energy of reaction 2 versus the charge function (see text).

with a charged X, the charges on the hydrogen atoms at the other end change. We calculated the difference between the charge on a hydrogen atom of a methyl group with X = H to that when X is charged. Now we consider replacing the methyl group with a SiF_nH_{3-n} group. We define the "charge function" as the sum of the charge differences over the n sites and we postulate the charge function will be proportional to the value of ΔE. In Figure 4, we show a plot of the charge function versus ΔE for $SiF_nH_{3-n}(CH_2)_mX$ for various X, n, and m. (In this process we chose to use a silicon substituent only because we had more data available.) The agreement is reasonable, especially considering that the nature of the X group varies from BH_3^- and CH_2^- to X = NH_3^+ and that we have used charges on methyl groups to predict results on substituted silicon atoms.

We can apply these notions to ZCH_2CH_2X compounds where Z is OH or NH_2. Both of these groups are electron-withdrawing and should have $\Delta E < 0$ for negative X and $\Delta E > 0$ for positive X. In addition, we would anticipate that the absolute magnitude of ΔE would decrease in the order F > OH > NH_2. The data in Table 7 support the first argument: both Z = OH and Z = NH_2 do show stability for reaction 2 with negative X and instability with positive X. Both Z = OH and Z = NH_2 have smaller magnitudes of ΔE than F, although the former two are approximately equal for negative X rather than show the greater absolute energy change for Z = OH than Z = NH_2.

Conclusions

We establish in substituted alkanes that the relative charge on the hydrogen atoms calculated by the NPA and AIM methods are highly correlated. With charged substituents, we find the charge resides on the periphery of the molecule, the hydrogen atoms. The charge on the hydrogen atoms calculated by either the AIM or NPA method is propagated by a long-range, through-space, interaction between the X group and the carbon−hydrogen bonds. In neutral substituted alkanes, antiperiplanar hydrogen atoms on the terminal methyl groups are more positive in charge than are the gauche ones. This arrangement is reversed by the presence of fluorine atoms within 2.7 Å of a gauche hydrogen atom. Any hydrogen atom within 2.7 Å of a fluorine atom is more positive than anticipated. We find no interpretable result for the charges of carbon atoms other than those adjacent to X. These latter carbon atoms show a charge that appears to be sensitive to the nature of the substituent, but not particularly to the presence of charge on the substituent. Also, any atoms attached to a substituent atom, such as hydrogen or fluorine, have a minimal effect on the charge on the adjacent carbon atom. As a result, SiH_3 and SiF_3 have similar charges on a substituted carbon.

Our results, especially those concerning the value of ΔE for reaction 2 can be used to understand chemical results. In this work we have generally treated the charged groups X as if they are the source of the perturbation. But we could just as well treat the fluorine atoms substituted at the periphery of the molecule as the perturbing source and ask about the effect *on* the charged substituent. From this point of view, our work fits in closely with the general studies of the how substituents affect charged centers at remote points in molecules.[42,43,67] This is a classic area of study in physical organic chemistry when those charge sites are involved in phenomena including the acidity of carboxylic acids and transition states for solvolysis.

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Supporting Information Available: Table S1, Table S2, NPA and AIM hydrogen atom charges in $C_{12}H_{25}CH_2^-$, and Table S3, the calculated energies for the molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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