Charge Competition in Halogenated Hydrocarbons

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ABSTRACT: The distribution of electronic charge in a molecule plays a major role in determining the molecule's physical, chemical, and biological properties. For studies of charge distributions, halogenated hydrocarbons are especially informative prototype systems, because the overall charge distributions depend strongly on both the identities and relative positions of the halogen substituents. In this report, we examine how the placement and identities of the halogen substituents affect the natural population analysis, atoms in molecules, and Gasteiger partial atomic charge distributions in representative saturated (methanes and ethanes), unsaturated (ethylenes), and aromatic (benzenes) halogenated hydrocarbons, using density functional calculations. The results are interpreted in terms of the electronegativities and the charge capacities of the halogens. The relationships of these charge distributions to the electrostatic potential maps of the compounds are also explored. ©2011 Wiley Periodicals, Inc. Int J Quantum Chem 112: 219–229, 2012

Key words: partial atomic charges; electrostatic potential maps; electronegativity; charge capacity; halogenated hydrocarbons

Introduction

The electronic probability distribution of a molecule results from a complex web of interactions between the molecule's constituent atoms and depends on both the mutual connections of the atoms and their inherent electronic properties. The resulting charge distribution, in turn, largely determines the molecule's physical, chemical, and biochemical properties. In this report, we examine the electronic charge distributions in several representative classes of halogenated hydrocarbons in an attempt to gain a perspective on how the individual atomic properties and their connections influence the overall molecular electronic charge distributions in these molecules.

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The halogens provide an important series of molecular substituents with electronegativities extending over a range from fluorine (Pauling electronegativity $\chi = 3.98$, the highest in the periodic table) through chlorine ($\chi = 3.16$), bromine ($\chi = 2.96$), and iodine ($\chi = 2.66$) [1, 2]. These atoms are all more electronegative than carbon ($\chi = 2.55$) and hydrogen ($\chi = 2.20$), and on that basis might be expected to drain electronic charge from carbon in halogen-substituted hydrocarbon compounds. The electonegativity χ_i of atom i in a molecule depends on its effective charge Q_i, which to a first approximation can be written as $\chi_i(Q) = \chi_i(Q)_{Q=0} + bQ$, where $b = (\partial\chi/\partial Q)_{Q=0}$ [3]. According to Sanderson's principle of electronegativity equalization, charge will flow within the molecule until at equilibrium the electronegativities $\chi_i(Q_i)$ of all the atoms are equal [4, 5]. The coefficient b is related inversely to a second important atomic property, the charge-carrying capacity κ. This property, first emphasized by Huheey [6], reflects the ability of the atom to absorb or release additional charge. For example, although fluorine has the highest electronegativity in the halogen group, it has a lower ability than the other halogens to accommodate additional charge. The concept of atomic charge capacity has been further examined and elaborated by Politzer et al. [7, 8].

It is well known that the "charge" on a particular atom in a molecule is not a proper quantum mechanical observable. Nonetheless, the concept of an atomic charge in a molecule has historically been an especially important tool for chemists, and a variety of schemes, both quantum chemical and empirical, have been proposed to represent partial atomic charges [9, 10]. Among the quantum chemical schemes, charges based on the natural population analysis (NPA) approach of Reed et al. [11] and the atoms in molecules (AIM) approach of Bader [12] have been shown in earlier studies to correlate strongly with variations in a variety of molecular physical and chemical properties, such as inversion barriers and pK_as [13–16], and these measures of partial atomic charge have therefore been examined in the present work. Also, charges calculated by the empirical method of Gasteiger et al. [17–19], which is based on Sanderson's principle of electronegativity equalization, were determined.

Cramer has divided partial atomic charge models into four classes [20]: Class I charges are not determined directly from quantum chemical calculations, but rather from some more empirical approach; Class II charges are determined from orbitals derived from quantum chemical calculations; Class III charges are based on a partitioning scheme for the wave function or probability distribution of the molecule; Class IV charges are developed by altering Class II or III charges to match some experimentally observed property [20]. Within this classification, Gasteiger charges fall within Class I, NPA charges fall in Class II, and AIM charges fall in Class III. Electrostatic potential (ESP) charges, which we shall briefly examine, also fall into Class III.

The interpretation of the distribution of atomic charges derived from quantum chemical calculations also warrants further examination, in particular in light of recent developments in the area of "halogen bonding" (for a review of this field see Ref. 21). It has long been recognized that, due to the presence of electron lone pairs, polarization effects, and so on, the partial atomic charges obtained from different schemes can neither be thought as point charges [22] nor should the charges be considered to be uniformly distributed over atomic spheres. Over the past several years, studies of ESP surfaces have revealed many instances of positive regions falling within otherwise negative regions on the exposed potential surface maps [23]. These nonuniform potential surfaces can be understood using the "σ-hole" theory of Clark et al. [24, 25] wherein highly electron-withdrawing substituents drain electron density from sp-hybridized orbitals in polarizable atoms. An interesting and extreme example of this phenomenon is chlorotrinitromethane, $ClC(NO_2)_3$ [26], which exhibits especially long C—N bonds (1.538–1.544 Å, compared with the more customary 1.47 Å) and an especially short C—Cl bond (1.712 Å) in electron diffraction (1.694 Å from X-ray diffraction [27]). The ESP surface of this compound reveals a strong positive region on the isodensity surface of the chlorine atom, and its unusual features can be rationalized in terms of natural bond orbital analysis and σ-hole theory. Thus, it was of interest to us to compare the partial atomic charges of the halocarbons studied with features revealed on their ESP surfaces.

Methods

The calculations were performed using the Gaussian98 suite of programs [28] and the

TABLE I

Natural population analysis (NPA), AIM, Gasteiger, and electrostatic potential (ESP) charges for the fluorinated, chlorinated, and brominated methanes.

		Fluoro (X = F)				Chloro (X = Cl)				Bromo (X = Br)			
		NPA	AIM	Gast	ESP	NPA	AIM	Gast	ESP	NPA	AIM	Gast	ESP
0	C	−0.807	−0.006	−0.078	−0.894	−0.807	−0.006	−0.078	−0.894	−0.807	−0.006	−0.078	−0.894
	H	0.202	0.002	0.020	0.224	0.202	0.002	0.020	0.224	0.202	0.002	0.020	0.224
1	C	−0.080	0.531	0.079	−0.257	−0.530	0.101	0.011	−0.552	−0.600	−0.027	−0.008	−0.652
	H	0.151	0.030	0.058	0.154	0.201	0.052	0.039	0.217	0.208	0.055	0.035	0.237
	X	−0.373	−0.621	−0.253	−0.205	−0.072	−0.256	−0.129	−0.097	−0.024	−0.138	−0.095	−0.060
11	C	0.482	1.095	0.230	0.156	−0.363	0.202	0.097	−0.362	−0.511	−0.062	0.059	−0.392
	H	0.122	0.067	0.098	0.125	0.205	0.095	0.060	0.229	0.213	0.098	0.050	0.209
	X	−0.363	−0.614	−0.213	−0.203	−0.023	−0.196	−0.108	−0.048	0.042	−0.067	−0.080	−0.013
111	C	0.926	1.703	0.380	0.426	−0.274	0.294	0.181	−0.043	−0.508	−0.098	0.124	−0.191
	H	0.112	0.116	0.141	0.123	0.204	0.134	0.081	0.178	0.209	0.134	0.066	0.172
	X	−0.346	−0.606	−0.174	−0.183	0.023	−0.143	−0.087	−0.044	0.100	−0.010	−0.063	0.007
1111	C	1.305	2.362	0.561	0.706	−0.258	0.384	0.266	0.096	−0.593	−0.141	0.189	0.089
	X	−0.326	−0.591	−0.140	−0.176	0.064	−0.095	−0.067	−0.023	0.148	0.035	−0.047	−0.022

Spartan'08, and Spartan'10 programs [29]. AIM charges were determined using wavefunctions from Gaussian98 and the AIMALL collection of programs [30]. The quantum chemical calculations were generally performed at the density functional theory B3LYP/6-311G** level. Gasteiger charges were calculated from an on-line site, using SMILES notations for the compounds [31]. ESP maps were constructed on the 0.002 bohr^{-3} probability surface.

Results and Discussion

METHANES

The NPA, AIM, and Gasteiger charges on the fluoromethanes, chloromethanes, and bromomethanes are summarized in Table I and illustrated in Figure 1. Table I also gives ESP charges for these compounds. It is clear that the different charge measures examined here provide very different absolute partial atomic charge values, and the patterns of their variations with successive substitution also show some differences. In general, the AIM partial atomic charges for the halogen atoms are the most negative of those examined, the NPA charges the least negative, and the Gasteiger charges intermediate between the other values. The ESP fluorine charges were typically close to the Gasteiger values but were closer to the NPA charges for the chloromethanes and bromomethanes. As discussed below, the charges on the hydrogen and carbon atoms show different variations resulting from halogen substitution.

With successive fluorination, the NPA fluorine charges fall steadily, from −0.373 in fluoromethane to −0.326 in tetrafluoromethane. The AIM fluorine charges, which are considerably more negative, fall only slightly, from −0.621 to −0.591 in this sequence, the Gasteiger charges fall from −0.253 to −0.140, and the ESP charges fall from −0.205 to −0.176. The charges on the central carbon increase in the same order, reaching +1.305 for the NPA charge in CF$_4$, +2.362 for the AIM charge, +0.561 for the Gasteiger charge, and +0.706 for the ESP charge. Interestingly, the NPA and ESP hydrogen charges become less positive with successive fluorine substitution, indicating that the electron density is being drawn mainly from the central carbon, whereas both the AIM and Gasteiger hydrogen charges become more positive with successive fluorine substitution, suggesting a sharing of the charge depletion between the carbon and hydrogen atoms.

In chloromethane, the NPA and ESP charges show the central carbon as a highly negative position, with the positive charge residing completely on the three hydrogen atoms. For the chloromethane series, the NPA chlorine charges change from −0.072 in chloromethane to a positive +0.023 charge in trichloromethane and +0.064 in tetrachloromethane. Thus, despite the greater electronegativity of chlorine compared with carbon, in CCl$_4$ the NPA charges show the chlorines as positive and the central carbon as negative. In

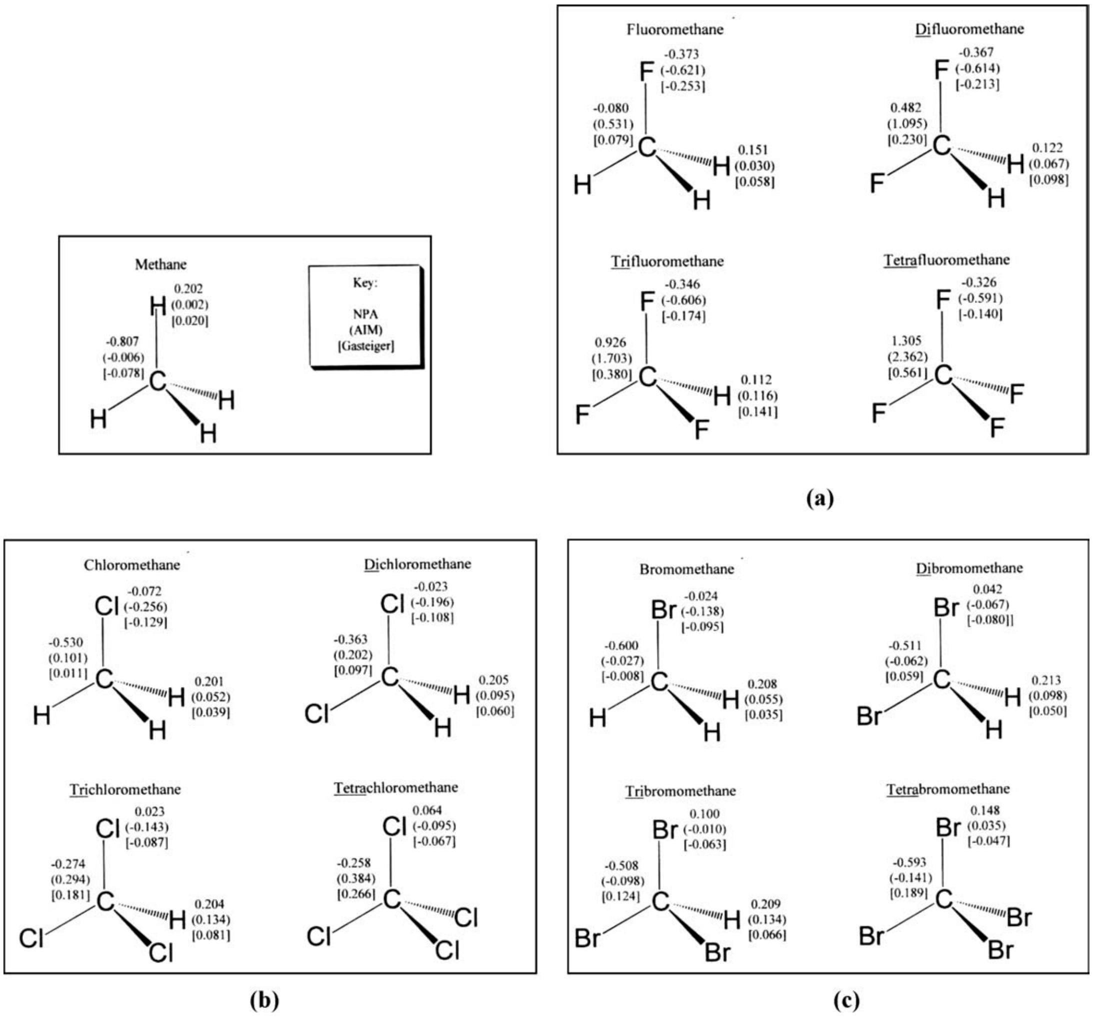


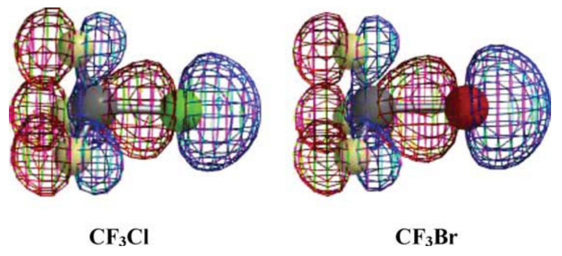
FIGURE 1. NPA, AIM, and Gasteiger charges for the halomethanes studied in this work.

contrast, the AIM, Gasteiger, and ESP chlorine charges are negative in all of the chlorinated methanes, with the AIM chlorine charge decreasing from -0.256 in $CClH_3$ to -0.095 in CCl_4, the Gasteiger charge decreasing from -0.129 to -0.067, and the ESP decreasing from -0.097 to -0.023 in this same series. The AIM and Gasteiger charges on the hydrogens are much smaller than the NPA charges, whereas the ESP hydrogen charges are similar to the NPA hydrogen values.

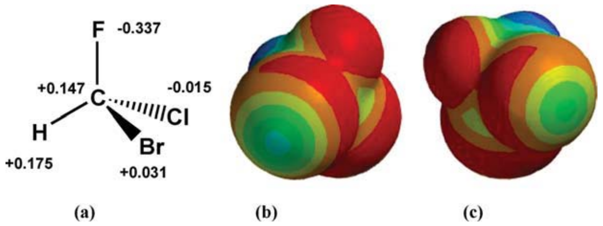
For the bromomethane series, the NPA charge on the bromine is negative only for bromomethane itself and becomes increasingly positive in CBr_2H_2, CBr_3H, and CBr_4. The NPA charge on the central carbon is strongly negative in all the bromo compounds. In this case, the AIM bromine charges are negative for the first three members of the series but become positive in tetrabromomethane. The Gasteiger charges decrease as the number of bromine atoms increases but show the bromines carrying a negative charge for all members of the series. The ESP bromine charges are negative for all the bromomethanes except $CHBr_3$, where the bromines are very slightly positive.

For the fluoromethanes, although the absolute values of the partial atomic charges determined using the three measures used here differ substantially from one another, the overall variations in these charges are strongly correlated (correlation coefficients R from 0.89 to 0.96). In the case of chloromethanes and bromomethanes, the correlations between the different charge measures are generally much lower.

As noted in the Introduction section, ESP maps for halogenated compounds often display a much more nuanced picture of the charge distributions than do the partial atomic charge distributions. The most striking σ-hole effects occur for compounds with a highly polarizable atom connected to a strong electron-withdrawing group [23, 24, 26]. In the halomethanes, this can be illustrated by the series CF_3—F, CF_3—Cl, and CF_3—Br. Figure 2 compares the NPA partial atomic charges and ESP surfaces of these compounds. (The ESP surfaces for these compounds were earlier reported by Politzer et al. [25].) The σ-holes are the positive (blue) regions on the chlorine and bromine ESP surfaces. The σ-orbitals in CF_3Cl and CF_3Br presumably responsible for this phenomenon are illustrated below:



As a further illustration, we present the NPA charges and ESP surface of bromochlorofluoromethane, CBrClFH, a compound sometimes used to illustrate the concept of a chiral center. The NPA partial atomic charges and two views of the ESP surface of CBrClFH are shown below: (a) NPA charges, (b) the ESP surface as seen facing the bromine atom, and (c) the ESP surface as seen facing the chlorine atom (positive regions shown in blue, negative regions in red).



It is apparent from the ESP maps above and those in Figure 2 that the depiction of an atomic charge in a molecule as a single number, despite the usefulness of such numbers in numerous applications [10, 14–16], is clearly limited and fails to represent the complexity of the actual charge distribution. Note the positive regions (blue and green) on the bromine ESP surface and (green) on the chlorine surface. The hydrogen atom is seen in the background as the most positive (blue) center.

HALOETHANES

The NPA, AIM, and Gasteiger charges for the halogenated ethanes are shown in Table II. For the singly substituted haloethanes, all of the charge measures show the halogen substituents to have negative partial charges. Of the three charge schemes, the AIM scheme yields the most negative values for the halogen charges in these compounds. The NPA scheme shows the substituted carbon to be negative for the monosubstituted chlorine and bromine compounds, whereas the AIM and Gasteiger schemes show the substituted carbons as positive. The NPA charges for the unsubstituted carbon atoms remain strongly negative, and the other schemes show the unsubstituted carbons as either slightly positive (AIM) or slightly negative (Gasteiger).

For the disubstituted haloethanes, the AIM scheme again yields the most negative partial charge values for all of the halogens. All of the charge schemes show that introduction of a second halogen decreases the negative partial charge on both halogens, although the effect is greater for substitution on the same carbon, as might be expected. The NPA treatment of 1,1-dibromoethane shows both bromine atoms as slightly positive, an effect not seen at this stage in the AIM and Gasteiger charges. Moreover, in 1,2-dihaloethanes, small differences are evident between the halogen partial charges for the trans and gauche conformers in both the NPA and AIM schemes. The Gasteiger scheme, which is topological, does not exhibit these differences.

Continuing halogen substitution further reduces the halogen charges as these atoms compete for the electronic probability distribution with the other atoms of the molecules. Notably, in

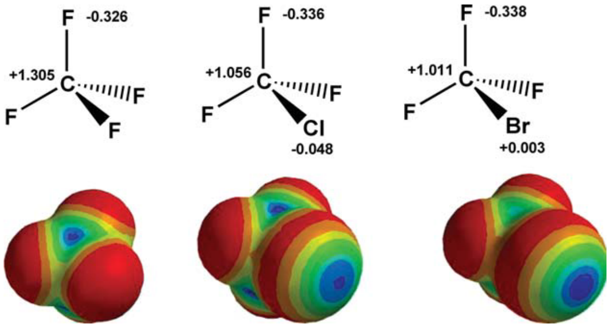


FIGURE 2. Comparison of the NPA charges and ESP maps for CF_4, CF_3Cl, and CF_3Br.

TABLE II

NPA, AIM, and Gasteiger charges for the ethanes studied.

		Fluoro (X = F)			Chloro (X = Cl)			Bromo (X = Br)		
Compound		NPA	AIM	Gast.	NPA	AIM	Gast.	NPA	AIM	Gast.
0	C	−0.572	0.035	−0.068	−0.572	0.035	−0.068	−0.572	0.035	−0.068
	H	0.191	−0.012	0.023	0.191	−0.012	0.023	0.191	−0.012	0.023
1	C	−0.619	0.031	−0.037	−0.600	0.040	−0.052	−0.602	0.043	−0.056
	Cx	0.100	0.522	0.087	−0.319	0.116	0.020	−0.378	0.005	0.001
	Hg	0.203	0.012	0.025	0.207	0.015	0.024	0.208	0.015	0.024
	Ht	0.203	0.006	0.025	0.208	0.007	0.024	0.208	0.007	0.024
	Hx	0.150	0.020	0.061	0.196	0.041	0.043	0.202	0.044	0.038
	X	−0.390	−0.625	−0.249	−0.096	−0.278	−0.126	−0.049	−0.174	−0.092
11	C	−0.652	0.036	−0.004	−0.618	0.050	−0.035	−0.623	0.052	−0.043
	Cxx	0.631	1.054	0.237	−0.168	0.203	0.105	−0.301	−0.041	0.067
	Hgg	0.216	0.038	0.028	0.220	0.028	0.026	0.220	0.036	0.053
	Hgt	0.213	0.027	0.028	0.220	0.037	0.026	0.220	0.028	0.025
	Hxx	0.131	0.060	0.101	0.201	0.087	0.063	0.207	0.090	0.025
	Xx	−0.376	−0.618	−0.210	−0.037	−0.215	−0.105	0.028	−0.095	−0.076
12T	Cx	0.065	0.535	0.118	−0.353	0.125	0.036	−0.415	0.011	0.013
	Hxg	0.158	0.041	0.064	0.210	0.062	0.044	0.217	0.066	0.039
	Xt	−0.380	−0.617	−0.246	−0.068	−0.251	−0.124	−0.019	−0.143	−0.091
12G	Cx	0.051	0.534	0.118	−0.361	0.126	0.036	−0.426	0.004	0.013
	Hxg	0.166	0.048	0.064	0.213	0.064	0.044	0.218	0.065	0.039
	Hxt	0.161	0.034	0.064	0.212	0.054	0.044	0.219	0.058	0.039
	Xg	−0.378	−0.615	−0.246	−0.065	−0.245	−0.124	−0.012	−0.128	−0.091
111	C	−0.672	0.057	0.031	−0.632	0.063	−0.018	−0.641	0.063	−0.030
	Cxxx	1.078	1.628	0.387	−0.105	0.281	0.188	−0.329	−0.088	0.133
	Hggt	0.223	0.048	0.032	0.229	0.044	0.027	0.229	0.042	0.026
	Xxx	−0.359	−0.610	−0.171	0.017	−0.159	−0.084	0.094	−0.033	−0.060
112C_s	Cx	0.028	0.560	0.150	−0.389	0.138	0.053	−0.462	0.008	0.026
	Cxx	0.588	1.085	0.267	−0.214	0.212	0.121	−0.355	−0.041	0.080
	Hxgt	0.169	0.053	0.067	0.223	0.070	0.046	0.230	0.073	0.040
	Hxxt	0.134	0.068	0.105	0.215	0.096	0.065	0.224	0.100	0.054
	Xgg	−0.362	−0.601	−0.243	−0.036	−0.214	−0.123	0.018	−0.091	−0.090
	Xxg	−0.363	−0.607	−0.206	−0.011	−0.186	−0.103	0.058	−0.060	−0.075
112C_1	Cx	0.027	0.553	0.150	−0.387	0.135	0.053	−0.457	0.017	0.026
	Cxx	0.593	1.073	0.267	−0.207	0.208	0.121	−0.346	−0.042	0.080
	Hxgg	0.172	0.066	0.067	0.223	0.079	0.046	0.229	0.081	0.040
	Hxgt	0.169	0.056	0.067	0.224	0.075	0.046	0.232	0.077	0.040
	Hxxg	0.139	0.082	0.105	0.214	0.105	0.065	0.221	0.107	0.054
	Xgt	−0.369	−0.609	−0.243	−0.043	−0.227	−0.103	0.009	−0.111	−0.090
	Xxg	−0.362	−0.608	−0.206	−0.006	−0.183	−0.103	0.064	−0.053	−0.075
	Xxt	−0.368	−0.611	−0.206	−0.018	−0.197	−0.123	0.049	−0.077	−0.075
1112	Cx	0.004	0.587	0.185	−0.416	0.147	0.069	−0.494	0.020	0.038
	Cxxx	1.036	1.671	0.418	−0.142	0.297	0.204	−0.373	−0.086	0.144
	Hxggt	0.179	0.074	0.071	0.232	0.086	0.047	0.239	0.087	0.041
	Xggt	−0.357	−0.598	−0.240	−0.021	−0.205	−0.121	0.033	−0.084	−0.089
	Xxxg	−0.344	−0.600	−0.168	0.044	−0.131	−0.082	0.124	0.001	−0.059
	Xxxt	−0.353	−0.603	−0.168	0.028	−0.149	−0.082	0.108	−0.025	−0.059
1122T	Cxx	0.564	1.110	0.298	−0.241	0.222	0.137	−0.385	−0.029	0.092
	Hxxgg	0.146	0.099	0.108	0.222	0.116	0.066	0.228	0.118	0.056
	Xxgt	−0.355	−0.602	−0.203	0.010	−0.169	−0.102	0.078	−0.042	−0.074

(Continued)

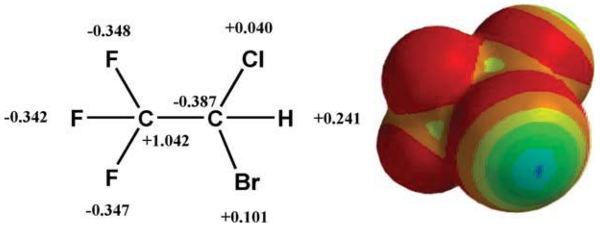
TABLE II
(Continued).

Compound		Fluoro (X = F)			Chloro (X = Cl)			Bromo (X = Br)		
		NPA	AIM	Gast.	NPA	AIM	Gast.	NPA	AIM	Gast.
1122G	Cxx	0.564	1.108	0.298	−0.235	N/A	0.137	−0.392	−0.038	0.092
	Hxxgt	0.142	0.089	0.108	0.219	N/A	0.116	0.233	0.114	0.056
	Xxgg	−0.348	−0.596	−0.203	0.016	N/A	−0.102	0.087	−0.026	−0.074
	Xxgt	−0.359	−0.603	−0.203	0.000	N/A	−0.102	0.072	−0.052	−0.074
11122	Cxx	0.541	1.156	0.332	−0.275	0.240	0.154	−0.430	−0.025	0.105
	Cxxx	1.006	1.712	0.451	−0.176	0.308	0.220	−0.414	−0.085	0.157
	Hxxggt	0.151	0.106	0.111	0.229	0.122	0.068	0.238	0.123	0.057
	Xxggt	−0.344	−0.593	−0.199	0.027	−0.152	−0.100	0.098	−0.021	−0.073
	Xxxgg	−0.331	−0.590	−0.165	0.064	−0.110	−0.080	0.144	0.024	−0.058
	Xxxgt	−0.340	−0.595	−0.165	0.052	−0.125	−0.080	0.133	0.004	−0.058
111222	Cxxx	0.983	1.765	0.488	−0.211	0.323	0.237	−0.457	−0.073	0.169
	Xxxggt	−0.328	−0.586	−0.163	0.070	−0.106	−0.079	0.152	0.026	−0.056

Notations: G= gauche, T = trans, C_s and C_1 are the symmetry species.

1,1,1,-trichloroethane, the chlorine atoms are seen as becoming slightly positive in the NPA scheme, although these atoms remain negative for the 1,1,2-tricloroethane species. Only at the pentasubstituted stage does the AIM bromine partial atomic charge become slightly positive. The Gasteiger charges for all of the halogens remain negative throughout this series. Both the NPA and AIM schemes picture the bromine atoms as positive in hexabromoethane.

For illustration, the NPA charges and the ESP map for the substituted ethane anesthetic halothane (CF_3—CBrClH) are shown below.



It is notable that the NPA charges show the carbon of the trifluoromethane group to be strongly positive, as expected, whereas the second carbon, despite being bonded to two formally more electronegative atoms, is negative, and the bromine and chlorine NPA charges are positive. The ESP map shows a much more nuanced distribution over the potential energy surface, with bromine (facing) displaying evidence of a σ-hole. In this and other cases, the fluorine atoms (appearing on the left) exhibit uniformly negative (red) potential maps.

HALOETHENES

The charges in the halogenated ethenes are shown in Table III. Fluorine substitution in ethene leads to a rather drastic realignment of the electronic charges. The carbon NPA charge in unsubstited ethene is −0.366: substitution of a single fluorine alters the charge on the substituted carbon to +0.254 and that on the unsbstituted carbon to −0.483. The AIM carbon charges change from −0.041 in ethene to +0.452 at the fluorinated position and to −0.001 at the unsubstituted carbon in fluoroethene. The changes in the Gasteiger charges on fluorine substitution are more subdued. The fluorine charges reported for fluoroethene are −0.342 (NPA), −0.622 (AIM), and −0.214 (Gasteiger). Further fluorine substitution does not drastically alter these values, although there is evidence of charge competition. The fluorine charges in tetrafluoroethene are −0.303 (NPA), −0.587 (AIM), and −0.167 (Gasteiger).

As an illustration, the NPA charges and ESP map for 1-bromo-1-chloro-2-fluoroethene are shown below.

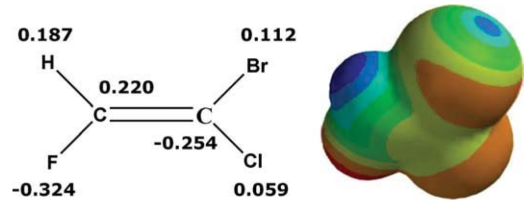


TABLE III

Natural population, AIM, and Gasteiger charges for the haloethenes.

		Fluoro (X = F)			Chloro (X = Cl)			Bromo (X = Br)		
		NPA	AIM	Gast.	NPA	AIM	Gast.	NPA	AIM	Gast.
0	C	−0.366	−0.041	−0.106	−0.366	−0.041	−0.106	−0.366	−0.041	−0.106
	H	0.183	0.021	0.053	0.183	0.021	0.053	0.183	0.021	0.053
1	C	−0.483	−0.001	−0.071	−0.397	0.004	−0.088	−0.392	0.006	−0.092
	Cx	0.254	0.452	0.080	−0.196	0.028	−0.003	−0.261	−0.112	−0.026
	Hc	0.206	0.055	0.056	0.204	0.053	0.054	0.204	0.053	0.054
	Ht	0.206	0.048	0.056	0.206	0.028	0.054	0.206	0.046	0.054
	Hx	0.159	0.070	0.094	0.201	0.076	0.074	0.206	0.078	0.069
	X	−0.342	−0.622	−0.214	−0.019	−0.212	−0.093	0.037	−0.070	−0.059
11	C	−0.569	0.088	−0.034	−0.413	0.053	−0.069	−0.413	0.048	−0.078
	Cxx	0.768	0.991	0.263	−0.096	0.104	0.100	−0.242	−0.191	0.054
	Hct	0.220	0.071	0.059	0.219	0.067	0.056	0.219	0.066	0.055
	Xx	−0.319	−0.610	−0.173	0.036	−0.148	−0.071	0.109	0.004	−0.043
12 (cis)	Cx	0.156	0.520	0.115	−0.237	0.083	0.016	−0.305	−0.075	−0.012
	Hxt	0.170	0.087	0.097	0.218	0.089	0.076	0.225	0.091	0.070
	Xc	−0.327	−0.606	−0.212	0.018	−0.173	−0.091	0.080	−0.017	−0.058
12 (trans)	Cx	0.160	0.516	0.115	−0.227	0.087	0.016	−0.292	−0.063	−0.012
	Hxc	0.171	0.094	0.097	0.216	0.096	0.076	0.223	0.098	0.070
	Xt	−0.332	−0.611	−0.212	0.011	−0.182	−0.091	0.069	−0.034	−0.058
112	Cx	0.076	0.609	0.151	−0.259	0.132	0.034	−0.333	−0.034	0.002
	Cxx	0.681	1.079	0.298	−0.128	0.162	0.118	−0.276	−0.152	0.067
	Hxct	0.182	0.107	0.010	0.230	0.105	0.077	0.238	0.107	0.071
	Xct	−0.322	−0.599	−0.208	0.038	−0.154	−0.090	0.101	0.004	−0.057
	Xxc	−0.306	−0.594	−0.170	0.067	−0.116	−0.070	0.144	0.047	−0.042
	Xxt	−0.311	−0.599	−0.170	0.053	−0.132	−0.070	0.127	0.021	−0.042
1122	Cxx	0.605	1.172	0.334	−0.156	0.211	0.136	−0.312	−0.110	0.081
	Xxct	−0.303	−0.587	−0.167	0.078	−0.106	−0.068	0.156	0.055	−0.041

Abbreviations: o = ortho, m = meta, p = para, X, x = halogen.

Note that although carbon is more electronegative than hydrogen, the carbon on the left has a more positive charge than the hydrogen bonded to it. In the same manner, although both chlorine and bromine are more electronegative than carbon, the carbon on the right exhibits a substantial negative charge while both the halogens bonded to it show positive NPA charges. Thus, at least so far as the NPA charges are concerned, chemical reasoning about partial atomic charges based simply on electronegativities can be misleading. Here too the ESP map displays a much more complex pattern than one might discern from the partial atomic charges.

HALOBENZENES

The NPA, AIM, and Gasteiger charges for the halogen-substituted benzenes are given in Table IV. It is interesting that for benzene itself, the three different charge schemes studied here paint quite different pictures. The NPA charges for carbon and hydrogen are substantially different (−0.203 and +0.203), whereas there is little difference between the C and H AIM charges (−0.018, +0.018). The Gasteiger C and H charges fall between these values (−0.062, +0.062). Single halogen substitution by any of the halogens displays the expected ortho/para-directing effect on the carbon positions. Fluorine substitution has the strongest effect at the substituted (ipso) carbon position, with the AIM charges being the most extreme. The three charge schemes for fluorobenzene yield quite different fluorine charges, again with the AIM fluorine charge (−0.626) being the greatest, compared with the NPA (−0.341) and Gasteiger (−0.205) charges. Single chlorine and bromine substitutions cause much more modest charge reallignments, although it can be noted that even at the singly substituted stage, the NPA charge on the bromine atom is slightly positive.

TABLE IV
NPA, AIM, and Gasteiger charges for the halobenzenes.

		Fluoro			Chloro			Bromo		
Compound		NPA	AIM	Gast.	NPA	AIM	Gast.	NPA	AIM	Gast.
0	C	−0.203	−0.018	−0.062	−0.203	−0.018	−0.062	−0.203	−0.018	−0.062
	H	0.203	0.019	0.062	0.203	0.019	0.062	0.203	0.019	0.062
1	Co	−0.272	0.004	−0.059	−0.231	0.013	−0.060	−0.232	0.014	−0.061
	Cm	−0.184	−0.006	−0.026	−0.185	−0.008	−0.043	−0.185	−0.009	−0.048
	Cp	−0.222	−0.013	−0.062	−0.207	−0.011	−0.062	−0.205	−0.011	−0.062
	Cx	0.413	0.465	0.123	−0.020	0.046	0.041	−0.082	−0.096	0.018
	Ho	0.221	0.050	0.065	0.221	0.046	0.063	0.221	0.045	0.063
	Hm	0.207	0.029	0.062	0.209	0.029	0.062	0.209	0.030	0.062
	Hp	0.207	0.025	0.062	0.208	0.027	0.062	0.208	0.027	0.062
	X	−0.341	−0.626	−0.205	−0.010	−0.220	−0.084	0.052	−0.078	−0.050
12	Com	−0.258	0.014	−0.024	−0.211	0.021	−0.042	−0.212	0.023	−0.047
	Cmp	−0.203	−0.002	−0.059	−0.191	−0.003	−0.060	−0.190	−0.005	−0.061
	Cxo	0.350	0.505	0.158	−0.058	0.081	0.059	−0.125	−0.069	0.032
	Hom	0.225	0.058	0.065	0.224	0.053	0.063	0.225	0.051	0.063
	Hmp	0.211	0.034	0.062	0.213	0.035	0.062	0.213	0.035	0.062
	Xo	−0.325	−0.611	−0.202	0.023	−0.184	−0.082	0.089	−0.033	−0.049
13	Coo	−0.341	0.025	0.009	−0.260	0.042	−0.025	−0.263	0.045	−0.034
	Cop	−0.291	0.008	−0.026	−0.235	0.018	−0.043	−0.234	0.020	−0.048
	Cmm	−0.166	0.007	−0.056	−0.168	0.003	−0.059	−0.169	0.001	−0.060
	Cxm	0.429	0.480	0.126	−0.007	0.055	0.042	−0.070	−0.090	0.019
	Hoo	0.238	0.079	0.067	0.237	0.071	0.065	0.237	0.068	0.064
	Hop	0.225	0.055	0.065	0.225	0.052	0.063	0.225	0.051	0.063
	Hmm	0.212	0.039	0.062	0.215	0.039	0.062	0.215	0.039	0.062
	Xm	−0.335	−0.622	−0.205	0.005	−0.204	−0.084	0.069	−0.058	−0.050
14	Com	−0.253	0.017	−0.024	−0.212	0.023	−0.042	−0.214	0.023	−0.047
	Cxp	0.396	0.476	0.124	−0.028	0.054	0.041	−0.090	−0.092	0.018
	Hom	0.225	0.059	0.065	0.226	0.055	0.063	0.226	0.054	0.063
	Xp	−0.339	−0.624	−0.205	0.001	−0.209	−0.084	0.065	−0.062	−0.050
123	Comp	−0.275	0.016	−0.023	−0.217	0.026	−0.042	−0.217	0.028	−0.047
	Cmmp	−0.185	0.012	−0.056	−0.177	0.007	−0.059	−0.177	0.004	−0.060
	Cxoo	0.288	0.556	0.193	−0.096	0.113	0.078	−0.167	−0.045	0.046
	Cxom	0.364	0.521	0.161	−0.042	0.086	0.061	−0.108	−0.068	0.033
	Homp	0.228	0.063	0.065	0.228	0.057	0.063	0.228	0.055	0.063
	Hmmp	0.215	0.044	0.062	0.218	0.042	0.062	0.218	0.042	0.062
	Xoo	−0.310	−0.596	−0.199	0.054	−0.149	−0.081	0.123	0.008	−0.048
	Xom	−0.320	−0.607	−0.202	0.032	−0.174	−0.082	0.099	−0.023	−0.049
124	Coom	−0.325	0.034	0.012	−0.241	0.051	−0.024	−0.244	0.053	−0.033
	Comm	−0.239	0.024	−0.021	−0.194	0.030	−0.041	−0.196	0.030	−0.046
	Comp	−0.272	0.022	−0.024	−0.219	0.027	−0.042	−0.220	0.027	−0.047
	Cxom	0.368	0.526	0.161	−0.044	0.091	0.061	−0.111	−0.062	0.033
	Cxop	0.334	0.510	0.159	−0.065	0.085	0.059	−0.131	−0.068	0.032
	Cxmp	0.412	0.492	0.126	−0.015	0.065	0.042	−0.078	−0.084	0.019
	Hoom	0.242	0.087	0.068	0.240	0.076	0.065	0.241	0.073	0.064
	Homm	0.229	0.067	0.065	0.230	0.061	0.063	0.230	0.059	0.063
	Homp	0.229	0.064	0.065	0.229	0.059	0.063	0.229	0.057	0.063
	Xom	−0.319	−0.607	−0.202	0.036	−0.170	−0.082	0.103	−0.016	−0.050
	Xop	−0.324	−0.609	−0.202	0.031	−0.175	−0.082	0.099	−0.020	−0.049
	Xmp	−0.333	−0.620	−0.205	0.012	−0.197	−0.083	0.077	−0.047	−0.049
135	Coop	−0.358	0.030	0.009	−0.265	0.046	−0.025	−0.266	0.049	−0.034
	Cxmm	0.445	0.502	0.129	0.006	0.071	0.044	−0.058	−0.079	0.020

(Continued)

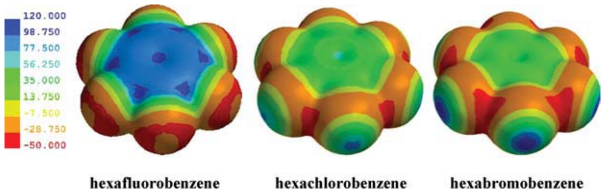
TABLE IV
(Continued).

Compound		Fluoro			Chloro			Bromo		
		NPA	AIM	Gast.	NPA	AIM	Gast.	NPA	AIM	Gast.
	Hoop	0.242	0.084	0.067	0.241	0.075	0.065	0.240	0.072	0.064
	Xmm	−0.329	−0.617	−0.205	0.018	−0.190	−0.083	0.083	−0.040	−0.050
1234	Commp	−0.258	0.027	−0.021	−0.203	0.033	−0.041	−0.204	n/a	−0.046
	Cxoom	0.302	0.568	0.196	−0.080	0.121	0.079	−0.150	n/a	0.047
	Cxomp	0.348	0.532	0.161	−0.050	0.091	0.061	−0.115	n/a	0.033
	Hommp	0.232	0.072	0.065	0.232	0.064	0.063	0.232	n/a	0.063
	Xoom	−0.305	−0.592	−0.199	0.062	−0.140	−0.080	0.131	n/a	−0.048
	Xomp	−0.319	−0.605	−0.202	0.039	−0.167	−0.082	0.106	n/a	−0.049
1235	Coomp	−0.342	0.038	0.012	−0.248	0.056	−0.024	−0.250	0.058	−0.033
	Cxoop	0.272	0.564	0.194	−0.103	0.118	0.078	−0.173	−0.042	0.046
	Cxomm	0.380	0.540	0.164	−0.028	0.097	0.062	−0.095	−0.059	0.034
	Cxmmp	0.428	0.515	0.129	−0.004	0.074	0.044	−0.067	−0.079	0.020
	Hoomp	0.245	0.091	0.068	0.243	0.079	0.065	0.243	0.076	0.064
	Xoop	−0.309	−0.594	−0.199	0.061	−0.142	−0.082	0.131	0.018	−0.049
	Xomm	−0.315	−0.603	−0.202	0.044	−0.161	−0.082	0.112	−0.007	−0.050
	Xmmp	−0.328	−0.615	−0.205	0.023	−0.185	−0.081	0.089	−0.033	−0.049
1245	Coomm	−0.311	0.039	0.015	−0.223	0.058	−0.022	−0.226	0.060	−0.032
	Cxomp	0.351	0.537	0.161	−0.052	0.092	0.061	−0.118	−0.062	0.033
	Hoomm	0.246	0.095	0.068	0.243	0.081	0.065	0.244	0.077	0.064
	Xomp	−0.318	−0.605	−0.202	0.042	−0.164	−0.082	0.110	−0.007	−0.049
12345	Coommp	−0.329	0.042	0.015	−0.232	0.062	−0.022	−0.235	n/a	−0.032
	Cxoomm	0.315	0.583	0.199	−0.064	0.126	0.080	−0.134	n/a	0.048
	Cxoomp	0.286	0.573	0.196	−0.087	0.122	0.079	−0.157	n/a	0.047
	Cxommp	0.363	0.547	0.164	−0.037	0.099	0.062	−0.103	n/a	0.034
	Hoommp	0.249	0.100	0.068	0.246	0.084	0.065	0.246	n/a	0.064
	Xoomm	−0.301	−0.588	−0.199	0.069	−0.131	−0.080	0.139	n/a	−0.048
	Xoomp	−0.304	−0.590	−0.199	0.067	−0.135	−0.080	0.137	n/a	−0.049
	Xommp	−0.313	−0.601	−0.202	0.048	−0.157	−0.082	0.116	n/a	−0.048
123456	Cxoommp	0.299	0.586	0.199	−0.073	0.128	0.080	−0.143	n/a	0.048
	Xoommp	−0.299	−0.586	−0.199	0.073	−0.128	−0.080	0.143	n/a	−0.048

Abbreviations: o = ortho, m = meta, p = para, X, x = halogen.

Further fluorine substitution on the benzene skeleton shows that the influence of charge competition falls off with distance between the substituted positions, as might be expected. Eventually, in perfluorinated benzene, the AIM charges display the most extreme carbon/fluorine charge disparity (±0.586), compared with the NPA (±0.299) and Gasteiger (±0.199) charges. Multiple chlorine and bromine substitutions cause much more modest charge alterations. Even at the doubly substituted stage, the NPA charges on the chlorines are slightly positive, although both the AIM and Gasteiger chlorine charges remain negative throughout the series. (Note that we were unable to determine AIM charges for two of the more highly substituted bromobenzenes.)

The ESP maps for the perhalogenated benzenes display some interesting patterns (shown below). Perfluorobenzene shows a positive interior and, uncharacteristically, even some variation within the negative (red/orange) exterior surface representing the fluorine atoms. Normally fluorine atoms show solid red surfaces. Perchlorobenzene and perbromobenene display modestly positive interiors and evidence of positive σ-hole regions on their exterior regions.



Conclusions

We have investigated the competition for electronic probability density arising from halogen substitution in four representative series of compounds: methanes, ethanes, ethenes, and benzenes. Three measures of partial atomic charge—NPA, AIM, and Gasteiger charges—have been used. The variations in these charge measures for the fluorinated species are generally strongly correlated, although the absolute values of the charges determined tend to be quite different. For the chlorinated and brominated species, the correlations between the charge measures tend to be much lower. The NPA approach indicates that the partial atomic charges on chlorine and bromine atoms, due to their larger charge capacities, often take on positive values, but this effect does not appear within the AIM and Gasteiger schemes (with the exception here of penta- and hexa-bromoethane for the AIM charges). Selected examples of ESP surface maps show that the actual distribution of the charge tends to be much more complex than might be inferred from single number partial atomic charges.

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