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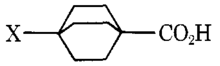
Effect of Substituents on the Electron Densities in Methane. σ and π Interactions in Saturated Systems

Kenneth B. Wiberg

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received April 2, 1979*

Abstract: Wave functions for a series of methyl derivatives have been converted into electron-density distributions. The space about the carbon has been separated into regions which may be attributed to each of the atoms, and the electron populations have been obtained for each region by numerical integration of the electron densities. Although it was not readily possible to assign a unique electron population to the methyl hydrogens, because of the dependence on the size chosen for the volume element about carbon, the charge shifts at hydrogen were found to be relatively unaffected by the carbon size. The charge shifts have been determined and have been separated into σ and π components. Substituents may be σ acceptors or donors, and π acceptors or donors, and affect methane in much the same fashion as has been found for benzene derivatives.

Substituents have important effects on the properties of organic compounds and on the rates and courses of reactions. Much work has been done in trying to describe the effects of substituents in a quantitative fashion, usually in the form of linear free energy relationships.[1] Thus, substituent effects in aromatic systems have been described in terms of field and resonance effects,[2] and in saturated systems they have frequently been described in terms of field effects.[3] Despite a very large number of studies there remain some fundamental questions which have not been answered. Their nature may be indicated by considering the well-studied case of the pK_as of the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids (1).



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It has been shown that the change in pK_a with a change in substituent (X) can be accommodated by the purely Coulombic field effect.[4] However, this requires the use of a simplified model for the effective dielectric constant of the medium between X and CO_2H and it may be considerably in error. On the basis of the presently available information it is not possible to state what fraction of the change in pK_a is due to the Coulombic interaction between the C-X dipole and the negative charge in the carboxylate anion, and what fraction is due to a change in electron density at C_1 caused by the substituent.

We wish to determine the distance and conformational components of the substituent effect using an unambiguous method which will not be influenced by solvent effect, ion pairing, and other phenomena. Thus we were led to examine the effect of substituents on electron distributions in hydrocarbons. As the first step in this investigation, we have examined methyl derivatives and the results are reported herein.

Electron density distributions may be obtained from the wave functions derived from ab initio molecular orbital calculations. These distributions have been applied to the study of a variety of chemical problems, and have been the subject of a comprehensive review,[5] as well as two monographs.[6,7] Recent applications include the charge distribution in acetaldehyde,[8] the bond character of C-Li bonds,[9] the study of the lone pairs,[10] the charge distribution in XCCH and XCN molecules,[11] and the study of nucleophilic displacement reactions.[12]

The accuracy of the calculated electron density distributions depends on the quality of the basis set used in the calculation.[5,13] We have studied the effect of basis set on the calculated properties (geometry, force constants, dipole moment, and dipole moment derivatives) of methyl fluoride and methyl chloride,[14] and found that they could be reproduced satisfactorily if a split-valence (4-31G[15] or 6-31G[16]) basis set is augmented by either bond functions[17] (i.e., s orbitals at centers of C-H bonds and a set of s and p orbitals at centers of C-X bonds) or polarization functions[18] (d orbitals at carbon and p orbitals at hydrogen). In this context, the dipole-moment derivatives are probably the most important of the properties since they reflect local electron densities. The basis sets which reproduce these quantities probably will lead to satisfactory electron-density distributions.

In order to make meaningful comparisons among the methyl derivatives it will be necessary to use the same geometry for all of the compounds studied. Fortunately, with these compounds the C-H bond lengths and the H-C-X bond angles are almost invarient with a change in substituents (1.09 ± 0.01 Å, 109.5 ± 0.5°).[19] Since the extended basis set calculations give geometries close to the experimental values, the above geometry along with the experimental C-X lengths was used.

It is known that, whereas the atomic charges for hydrogen fluoride derived from a population analysis[20] are strongly dependent on the basis set used, the electron-density distribution shows only a small dependence.[21] We first wished to determine if this also was true for methyl derivatives. Therefore, the effect of basis set was examined again using methane, methyl fluoride, and methyl chloride as examples. The basis sets are listed

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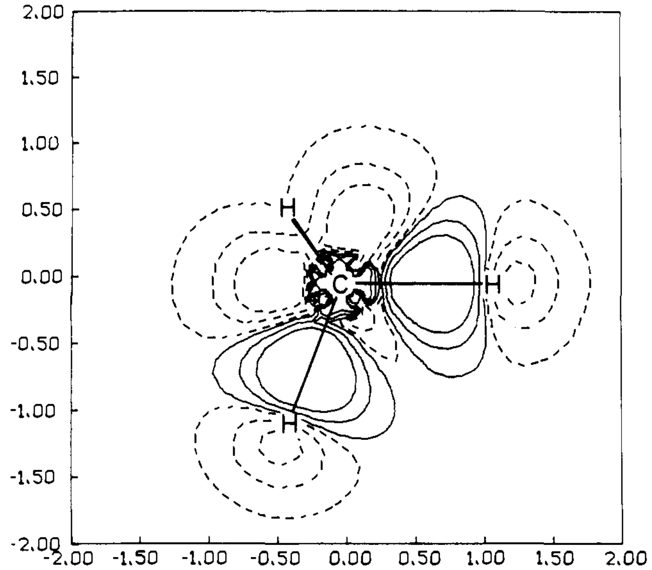

Figure 1. Difference in electron-density distribution in a H-C-H plane for methane using the 4-31G and 6-31G** basis set. The solid lines indicate greater electron density for the latter. The solid lines represent 0.001, 0.005, and 0.01 e contours, and the dashed lines represent −0.001, −0.005, and −0.01 e contours.

Table I. Basis Functions

description	derived from	comments
4-31G		standard basis[7]
4-31G + BF	4-31G	C-H s bond function with $\alpha = 0.7$ and C-X s and p bond functions with $\alpha = 0.7$
4-31G + 2BF	4-31G	same as above with added C-X s and p bond functions with $\alpha = 0.2$
6-31G		standard basis[8]
6-31G*	6-31G	d-polarization functions added to C and X[8]
6-31G**	6-31G	same as above plus p-polarization functions added to H[8]

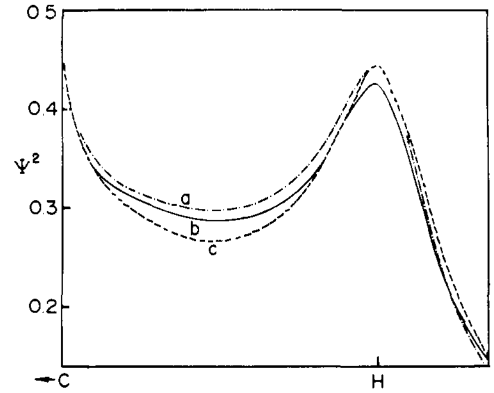

Figure 2. Electron-density distribution along a C-H bond in methyl fluoride for (a) the 6-31G** basis set; (b) 4-31G + 2BF; (c) 4-31G.

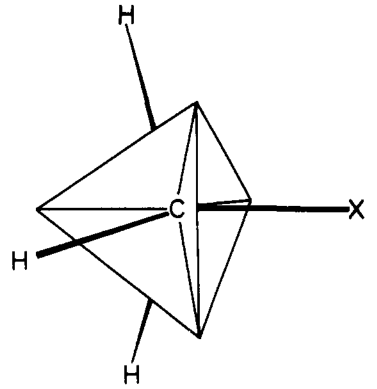

Figure 3. Separation of electron densities into regions for C-H bonds. Each bond angle is bisected by a plane, and the six planes form pyramidal regions with the carbon at the apex. Numerical integration of the electron densities within each region gives the electron populations.

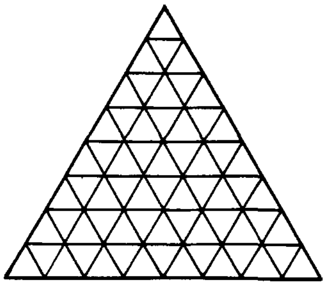

Figure 4. Detail of a plane perpendicular to a C-H bond and bounded by the planes shown in Figure 3. The equilateral triangle thus formed is divided into smaller triangles as shown, and the electron density is calculated at the center of each triangle. The values are multiplied by the area of the triangles and summed to give the electron-density function for the plane.

in Table I and the results of the calculations are summarized in Table II. In each case, the 6-31G basis set gives a significantly lower energy than 4-31G. This is largely a result of a better description of the core orbitals on carbon, fluorine, and chlorine, and does not significantly affect the calculated dipole moments or the population analysis. The addition of bond functions to the 4-31G basis set or polarization function to the 6-31G basis set leads to a decrease in energy and a decrease in the calculated dipole moment to a value close to the experimental moment. At the same time, there is a marked change in the electron densities obtained from the population analysis.

The nature of the changes in the electron-density distribution which results from a change in basis set is indicated in Figures 1 and 2. The difference in ψ^2 between the 4-31G and 6-31G** sets in a CH_2 plane of methane is shown in Figure 1. It can be seen that the latter leads to more electron density being concentrated in the C-H bonding region. The 4-31G + BF basis leads to an intermediate electron-density distribution which is close to that for 6-31G**. The changes for methyl fluoride are shown in Figure 2, where the values of ψ^2 are plotted along the C-H bond axis. Here again, the 6-31G** basis is the most effective in concentrating electron density in the bonding region, with 4-31G + 2BF a close second. The 4-31G basis gives a significantly smaller electron density.

It would be helpful to have a way in which to apportion electron density between carbon and hydrogen in methane so as to avoid the difficulties associated with the population analysis.[22] In linear or planar systems, this has been done by dividing the region between atoms by planes and then integrating the electron-density distribution between the planes.[5,9,11,23,24] In the case of methane, the electron density about carbon may be partitioned in an analogous fashion as shown in Figure 3.

The volume element about the methyl carbon is divided into four equal segments by a set of planes which bisect H-C-H bond angles. Planes normal to the C-H bonds will then create equilateral triangles with the C-H bonds passing through their centers (Figure 4). The electron-density function over the area of a given triangle may be obtained by numerical integration. This is conveniently done by dividing each triangle into a set of smaller triangles (Figure 4). The value of ψ^2 is calculated at the center of each smaller triangle and multiplied by the area element. Summation of these quantities gives the electron-density function. The value of this function along the C-H

Table II. Effect of Basis Set on Energies and Electron Populations

				electron populations						
				population analysis			integration			
compd	basis set	E, au	μ, D	C	H	X	C	H	X	time, s
CH_4	4-31G	−40.139 55		6.610	0.847		5.792	1.052		3.3
	4-311G	−40.140 87		6.511	0.872					10.3
	4-31G + 1BF	−40.149 92		6.415	0.896		5.796	1.051		6.7
	6-31G	−40.180 38		6.621	0.845		5.792	1.052		3.6
	6-31G*	−40.195 06		6.659	0.835		5.786	1.054		12.5
	6-31G**	−40.201 59		6.472	0.882		5.782	1.054		37.2
CH_3F	4-31G	−138.857 65	2.499[a]	6.027	0.839	9.457	5.796	1.024	9.131	7.3
	4-311G	−138.870 22	2.519	6.193	0.864	9.214				24.1
	4-31G + 1BF	−138.894 72	2.058	5.997	0.909	9.275				17.4
	4-31G + 2BF	−138.903 67	1.833	6.149	0.883	9.202	5.706	1.030	9.206	24.7
	6-31G	−138.993 30	2.500	6.021	0.842	9.452	5.688	1.022	9.246	8.1
	6-31G*	−139.034 15	2.064	6.065	0.843	9.406	5.691	1.030	9.218	52.6
	6-31G**	−139.039 33	2.056	5.916	0.891	9.413	5.681	1.029	9.231	99.7
CH_3Cl	4-31G	−498.539 12	2.411[b]	6.537	0.784	17.112	5.714	1.024	17.214[c]	12.0
	4-31G + 1BF	−498.573 89	2.107	6.339	0.860	17.081				26.6
	4-31G + 2BF	−498.576 20	1.932	6.231	0.871	17.156	5.695	1.024	17.233	38.6
	6-31G	−499.07782	2.614	6.657	0.753	17.085	5.786	1.020	17.154	26.9
	6-31G*	−499.114 05	2.224	6.494	0.765	17.212				114.4
	6-31G**	−499.120 62	2.237	6.309	0.817	17.238	5.745	1.022	17.189	189.0

[a] μ_{obsd} = 1.859 D (Wofsy, S. C.; Muenter, J. S.; Klemperer, W. *J. Chem. Phys.*, **1972**, 44, 607). [b] μ_{obsd} = 1.869 (Shulman, R. G.; Dailey, B. P.; Townes, C. H. *Phys. Rev.* **1950**, *78*, 145). [c] The chlorine electron populations were taken as 26.0 less the C and H populations.

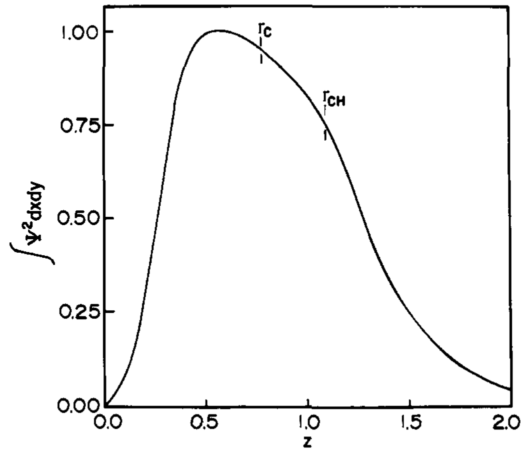

Figure 5. Values of the electron-density function in planes perpendicular to a C-H bond of methane, and with the volume element shown in Figure 3. The z coordinate lies along the C-H bond, with the origin at the carbon.

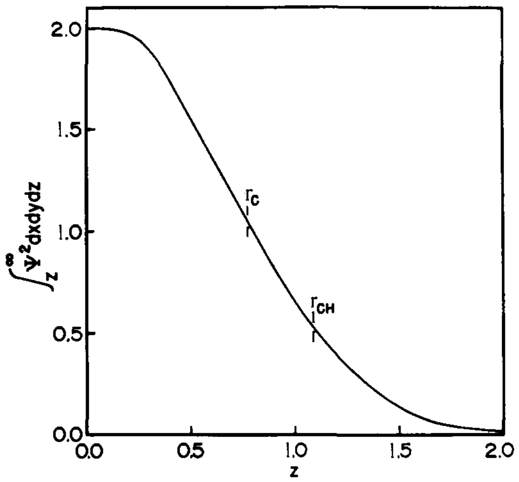

Figure 6. Electron populations for methane obtained by integrating the electron-density function.

bond is shown in Figure 5. The area under the curve gives the total electron population in the C-H bond, and was found to be 2.000 electrons. This procedure involves an arbitrary choice that the volume element, and consequently the electron density in the bond, goes to zero at the carbon. At any reasonable distance from the carbon, this choice has no effect.

The electron-density functions starting at a large distance from the carbon may be summed to give the total electron population in the C-H bond for a given distance to infinity. This is shown in Figure 6. From the hydrogen outward there is found 0.517 electron. The choice of a dividing line between carbon and hydrogen is arbitrary. We have chosen to take one-half the carbon-carbon bond length in ethane (i.e., 0.766 Å = r_C in Figure 6) as an appropriate distance since this will facilitate a later examination of ethyl derivatives. With this choice, the electron population associated with the hydrogen in methane becomes 1.054 electrons, using the 6-31G** basis set. It must be remembered that this value will change with different choices of r_C. For example, with r_C = 0.850 Å the electron population associated with the hydrogen in methane is reduced to 0.907.[25] Thus the absolute values should not be given too much significance. However, differences are significant and can be used to explore both the effect of basis-set changes and the effect of substituents.

The values of electron population obtained in this way for methane are shown in Table II under the heading "integration". The basis-set dependence is quite small, and all basis sets give essentially the same values. It can be seen that the changes found in the population analysis are not reflected in the distribution of electron population between carbon and hydrogen.

Let us next examine the effect of introducing a substituent. The difference between the electron distribution in a H-C-F plane in methyl fluoride and that in a H-C-H plane in methane is shown in Figure 7a. The corresponding difference between methyl chloride and methane is shown in Figure 7b. In the case of methyl fluoride, it can be seen that electron density along the C-F bond axis is shifted from carbon to fluorine. However, the electron density in the C-H bond in methyl fluoride is greater than that in methane! The case of methyl chloride is more complex, but it is clear that here also electron density has been transferred into the C-H bonds.

Again, we wish to separate regions of space which may be attributed to the different atoms. In doing so, we proceed in the same fashion as indicated above. Since the geometry was

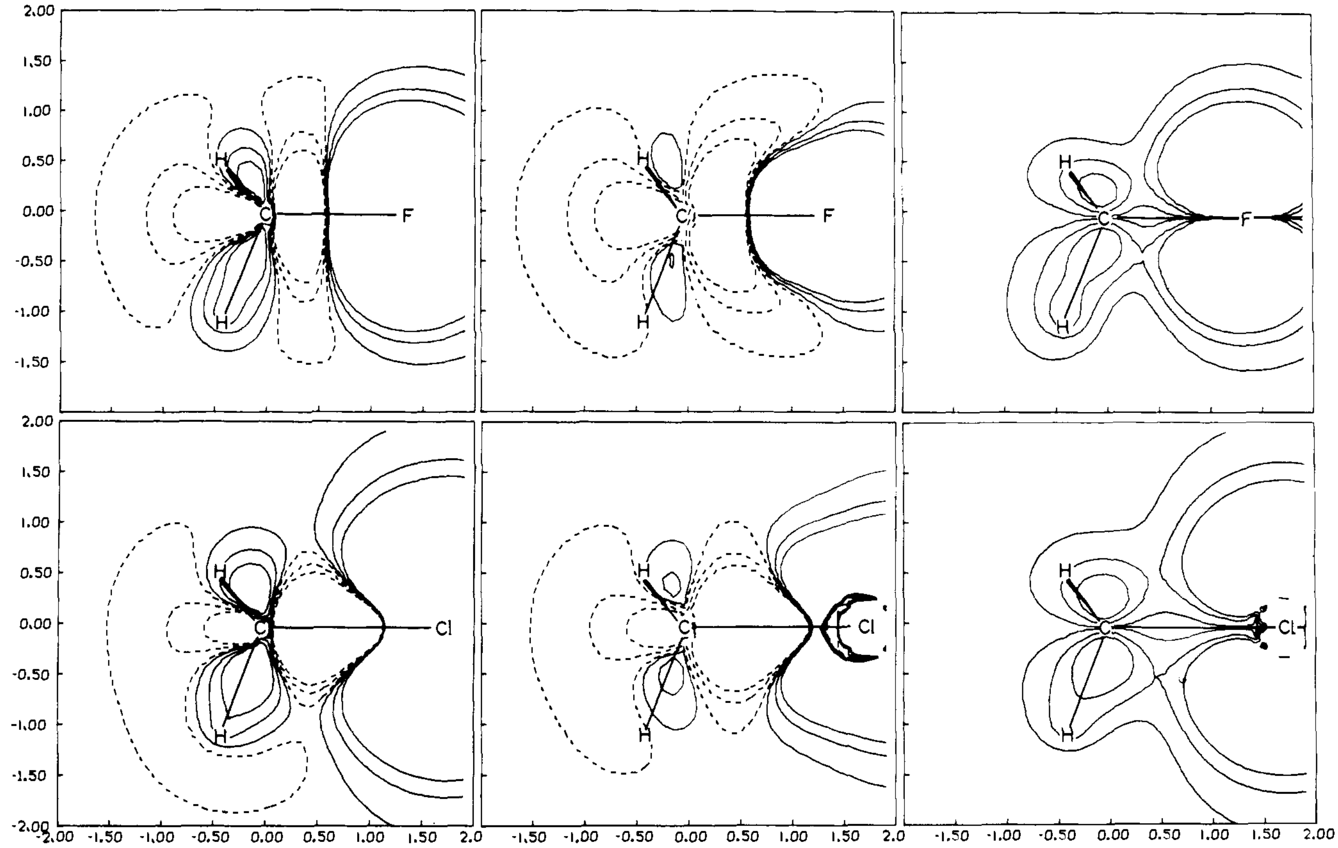

Figure 7. Difference in electron-density distribution in a H-C-X plane between a methyl halide and methane using 6-31G** wave functions. The upper plots (a) are for methyl fluoride and the lower plots (b) are for methyl chloride. In each case, the first plot is for all the electrons, the second is for the σ valence electrons, and the third is for the π valence electrons. Solid lines indicate a greater electron density in the methyl halide than in methane. The solid lines represent 0.001, 0.005, and 0.01e contours, and the dashed lines represent −0.001, −0.005, and −0.01 e contours.

maintained constant, the volume element about the methyl carbon again was divided into four equal segments and numerical integration was performed within each region. It was possible that this procedure might transfer some electron density from a large substituent such as chlorine to the methyl hydrogens. As a test, the substituent was placed along the $+z$ axis, and the summation of the methyl hydrogens was eliminated for a $z > 0.8$ Å. This distance was chosen since electron-density plots indicated a minimum in the region between the hydrogen and chlorine of methyl chloride at about $z = 0.8$ Å. Using this z cutoff and $r_C = 0.766$ Å, methane, methyl fluoride, and methyl chloride gave decreases in electron populations at the methyl hydrogens of 6, 5, and 12 me. The electron populations obtained without a z cutoff were used for methane and methyl fluoride, whereas the corresponding population for methyl chloride was decreased by 6 me.

The values obtained in this fashion are given in Table II. Again, it is seen that the electron populations associated with the several atoms do not change markedly on going from one basis set to another. The 4-31G + 2BF and 6-31G** basis sets give essentially the same charge distribution. The similarity of the values derived from the extended basis sets makes it possible to use the 4-31G + 2BF set for calculations on a series of methyl derivatives. The last column in the table gives the execution times using a CDC-7600 computer. It can be seen that the cost associated with the use of the 4-31G + 2BF set is considerably less than for the 6-31G** set, making it practical to carry out calculations on larger systems.

Why should there be such a large difference in electron population between the population analysis and direct summation of the square of the wave function?[26] The molecular orbitals are formed from linear combinations of atomic orbitals. The population analysis places the electron density derived from a given atomic orbital at the associated atom. However, once they are part of a molecular orbital, the atomic orbitals no longer have an existence of their own. The molecular-orbital calculation forms the combination of these functions which best reproduces the true electron-density distribution. When the electron density is distributed in a purely geometrical fashion, the atomic orbital from which it was derived is no longer of concern.

Before proceeding to an examination of the effect of other substituents it will be helpful to consider the molecular orbitals used by the compounds which have a C_3 symmetry axis.[27] They are shown in Figure 8 and do not include the inner 1s orbitals on C and X. The lowest energy MOs utilize linear combinations of the 2s AOs on C and X. The next orbitals are a degenerate pair of π-type orbitals formed by the positive linear combination of the $2p_x$ and $2p_y$ orbitals C and X (π^+). At a somewhat higher energy is found the σ-type orbital formed by the $2p_z$ orbitals at C and X (p-σ). The highest occupied MOs are a degenerate pair of π-type orbitals formed by the negative linear combination of the $2p_x$ and $2p_y$ orbitals at C and X (π^-).

Since all the methyl derivatives which have C_3 symmetry utilize σ and π orbitals, it is useful to separately examine the charge shifts for the two types of orbitals. The effects in the xz plane for methyl fluoride and methyl chloride are shown in Figure 7. In each case, the plots show the difference between the electron density for the methyl halide and that for methane itself. It can be seen that the σ orbitals lead to a general electron transfer from the carbon to the halogen, whereas the π orbitals lead to electron transfer from the halogen to the methyl group. The net effect in the C-H bond is to increase the electron density over than in methane. This is further illustrated in Figure 9, which shows the electron densities along a C-H bond of methane and of methyl fluoride. Here, only a small change is seen in the σ orbitals, whereas there is a considerable

Table III. Molecular Geometries,[6] Energies, and Dipole Moments

compd	$r_{\mathrm{C-X}}$	r_{XY}	∠CXY	τ_{HCXY}	r_{YZ}	∠CXY′	E, au	μ_{calcd}	μ_{obsd}	t, s
CH_3F	1.382						−138.903 67	1.83	1.86	25
CH_3Cl	1.785						−498.576 20	1.93	1.96	39
CH_3CH_3	1.534	1.090	109.47	60.0			−79.137 00			72
$CH_3NH_3^+$	1.470	1.000	109.47	60.0			−95.470 22			78
CH_3CN	1.460	1.157	180.0				−131.778 34	4.06	3.92	113
CH_3NC	1.427	1.167	180.0				−131.745 36	3.42	3.83	115
CH_3OH	1.425	0.945	108.5	180.0			−114.912 93	1.90	1.71	38
CH_3SH	1.818	1.329	100.3	180.0			−437.232 12	1.59	1.42	62
CH_3NH_2	1.474	1.011	112.0	59.4			−95.102 53	1.49	1.33	62
CH_3O^-	1.430						−114.256 80			34
CH_3S^-	1.820						−436.619 22			40
$CH_3C{\equiv}CH$	1.460	1.207	180.0		1.060		−115.736 09	0.73	0.83	123
CH_3CHO	1.512	1.207	120.3	0.0	1.114	115.3	−152.751 89	2.98	2.69	186

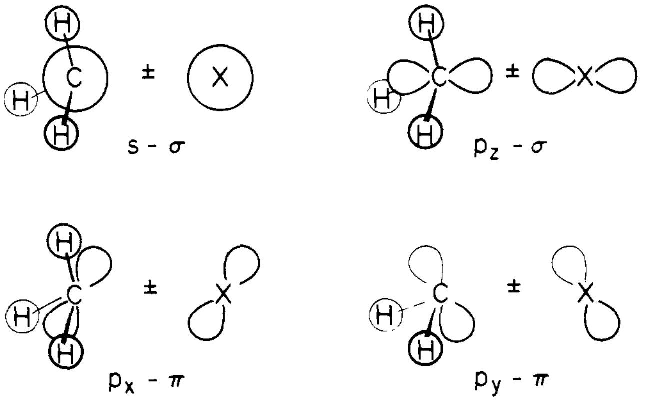

Figure 8. Molecular orbitals of methyl derivatives.

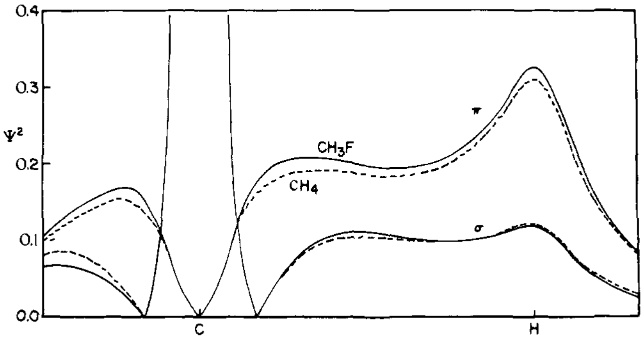

Figure 9. Electron densities along a CH bond of methane and of methyl fluoride separated into σ and π components. In each case the solid line is for methyl fluoride.

increase in electron density in the π orbitals along the CH bond of methyl fluoride as compared to methane.

We are now in a position to examine the effects of a variety of substituents on the charge distribution in a methyl group. The results of calculations carried out using the 4-31G + 2BF basis set are given in Table III. It can be seen that the dipole moments are satisfactorily calculated, suggesting that a reasonable charge distribution has been obtained for all of these compounds.[28]

The effect of substituents on the MO energy levels of methane is illustrated in Figure 10. The s-σ orbitals show the largest effect of substituents. This is expected since the s orbitals are more strongly affected by the nuclear charge than are the p orbitals. When C_3 symmetry is lost, as with methanol, methylamine, and methanethiol, the separation into σ and π orbitals is not complete, and the π^+ and π^- orbitals are split in energy. The MO energies correlate well with the ionization potentials derived from photoelectron spectroscopy,[29] as shown in Figure 11. The correlation is given by

$$-\mathrm{IP} = 0.83\epsilon - 1.5$$

This is close to the result previously obtained in examining the energy levels in a series of alkenes.[30]

The electron populations derived from a population analysis, and from numerical integration of the wave functions, are shown in Table IV. In addition to the total electron population, the values for the σ and π orbitals have been obtained separately for $r_C = 0.766$ Å. For comparison, the total electron population at hydrogen using $r_C = 0.850$ Å also is given. When necessary, a correction for the substituent's contribution to the hydrogen electron population was made in the same fashion as was described for methyl chloride (see calculation section for details). It can be seen that the change in this value using methane as the reference is essentially the same for the two volume elements assigned to carbon. The calculated electron densities at carbon should not be interpreted too closely because the separation between the carbon and the substituent depends on the use of a constant $r_C = 0.766$ Å. However, this may not be appropriate in all cases. Large changes probably are significant, but small changes may be insignificant. The hydrogen charges, on the other hand, should be quite satisfactory since the C–H bond distance and angle remain constant throughout the series. The effects at hydrogen are relatively simple and will be considered first.

All substituents except hydrogen have the potential for interacting with the σ and π orbitals of the methyl group in the same fashion as has been found with benzene derivatives[31] and other unsaturated systems.[32] As a result there should be four types of substituents: (1) σ and π donors; (2) σ acceptor and π donor; (3) σ donor and π acceptor; (4) σ and π acceptor. If we examine the hydrogen electron populations in the σ orbitals, we see that only O^- and S^- are σ donors. All other substituents, except methyl, are σ acceptors. The hydrogen electron populations in the π orbitals indicate that O^- and S^- are the most effective π donors. Compared to hydrogen as the substituent, both methyl and fluorine are weak π donors. The other substituents are π acceptors. Three of the possible types of substituents are found among those studied. The remaining type, σ donor and π acceptor, would probably be found with BH_2 as the substituent.

The results obtained with fluorine as the substituent may at first appear anomalous: an increase in electron density in the C–H bond region but a decrease in electron population at hydrogen. This simply indicates that at least part of the increased electron density in the C–H bond is taken from the region about the hydrogen.[33]

The substituents without cylindrical symmetry are examined in Table V.[34] Here, the methyl hydrogens are no longer equivalent. The hydrogens which are trans to a lone pair have a larger electron population than those which are trans to a substituent X–H bond. With a staggered arrangement, a back-bonding by the lone pairs can only involve the trans

Table IV. Electron-Density Distributions in Methyl Derivatives with C_{3v} Symmetry

compd	population analysis			integration											
				r_c = 0.766									r_c = 0.850		
				σ			π			total			total		
	C	H	δH	C	H	δH	C	H	δH	C	H	δH	C	H	δH
CH_3O^-	6.233	1.028	0.132	1.972	0.327	0.002	1.788	0.817	0.091	5.760	1.144	0.094	6.423	0.996	0.091
CH_3S^-	6.276	0.981	0.085	2.014	0.338	0.013	1.756	0.777	0.051	5.770	1.115	0.065	6.377	0.967	0.062
CH_3CH_3	6.255	0.915	0.019	2.030	0.323	−0.002	1.790	0.737	0.011	5.820	1.060	0.010	6.458	0.914	0.009
CH_4	6.415	0.896	0.000	2.050	0.325	0.000	1.750	0.726	0.000	5.800	1.050	0.000	6.380	0.905	0.000
CH_3F	6.149	0.883	−0.013	1.788	0.294	−0.031	1.922	0.736	0.010	5.710	1.030	−0.020	6.366	0.886	−0.019
CH_3Cl	6.231	0.871	−0.025	1.823	0.305	−0.020	1.875	0.722	−0.004	5.698	1.027	−0.023	6.292	0.883	−0.022
$CH_3C{\equiv}CH$	6.091	0.870	−0.026	2.025	0.316	−0.009	1.840	0.716	−0.010	5.865	1.032	−0.018	6.483	0.888	−0.017
CH_3NC	6.024	0.858	−0.038	1.892	0.302	−0.023	1.896	0.718	−0.008	5.788	1.020	−0.030	6.425	0.877	−0.028
CH_3CN	6.013	0.848	−0.048	2.006	0.312	−0.013	1.860	0.702	−0.024	5.866	1.014	−0.036	6.482	0.870	−0.035
$CH_3NH_3^+$	6.065	0.818	−0.078	1.874	0.296	−0.029	1.936	0.688	−0.038	5.810	0.984	−0.066	6.432	0.840	−0.065

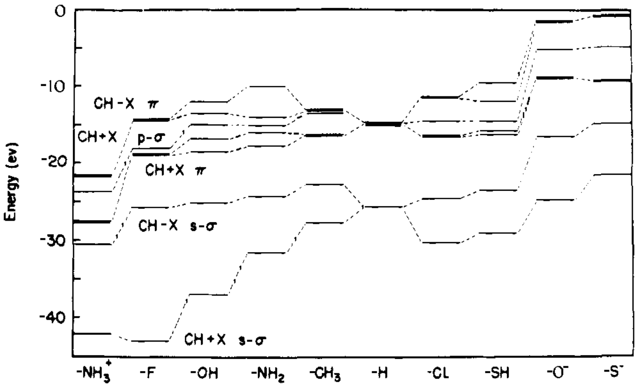

Figure 10. MO energy levels for CH_3-X compound.

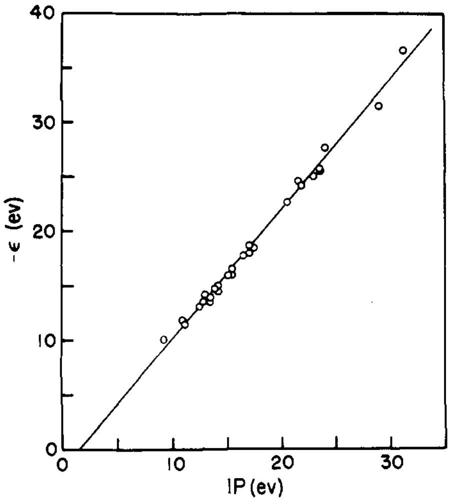

Figure 11. Correlation between MO energies and ionization potentials.

methyl hydrogens. A π interaction involving the X-H bond is much less effective than that involving a lone pair.

It was of interest to see if there were a relationship between the charge shifts for the methyl hydrogens as obtained from a population analysis and those obtained by integration of the electron-density distribution. This is examined in Figure 12. Although the correlation is not perfect, it is reasonably good. Thus, at positions past the α carbon, the population analysis is a useful guide to charge shifts. It might be noted that the electron populations at hydrogen obtained by integration of the wave functions using r_C = 0.850 Å are rather close to the values obtained via the population analysis.

It may be recognized that the pattern of σ inductive effects and π interactions which has been observed with the methyl derivatives is closely related to the effects of these substituents in aromatic systems. We have previously noted a linear relationship between the charge shifts obtained from the population analysis and the Hammett σ values for substituents on benzene rings.[35] A similar relationship is obtained with the

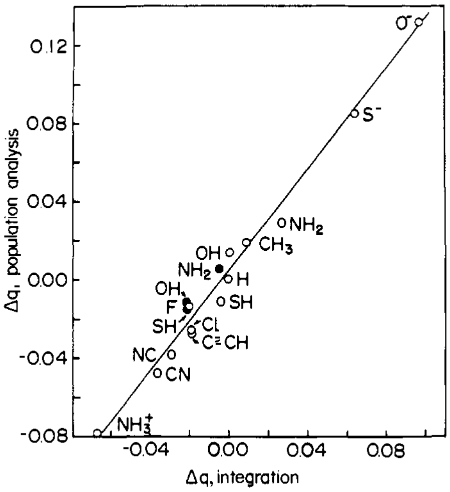

Figure 12. Relation between the charge shifts at hydrogen derived from the population analysis and those derived by integration of the wave functions.

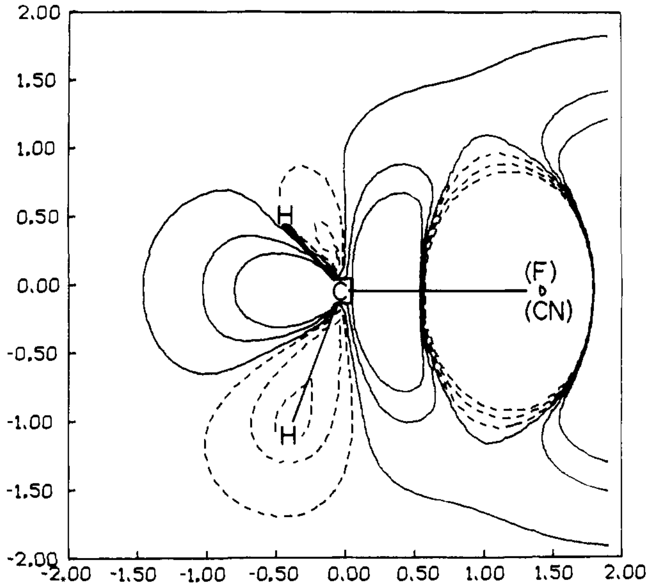

Figure 13. Electron-density difference in the H-C-X plane between acetonitrile and methyl fluoride. Solid lines indicate greater electron density in acetonitrile and dashed lines indicate greater electron density in methyl fluoride. The contour values are 0.001, 0.005, 0.01, −0.001, −0.005, and −0.01.

charge shifts derived by integration. σ and π interactions are possible with longer chain saturated aliphatic compounds, and it will be of interest to determine how the σ and π orbitals affect the electron densities at the β, γ, and δ carbons. It is possible that the σ effect will decrease monotonically on going down the chain, and that the π effect may yield an alternating

Table V. Electron-Density Distributions in Methyl Derivatives with C_s Symmetry

compd	population analysis			integration					
				$r_c = 0.766$			$r_c = 0.850$		
	C	H	δH	C	H	δH	C	H	δH
CH_4	6.415	0.896	0.000	5.807	1.048	0.000	6.389	0.903	0.000
CH_3NH_2	6.149	0.902[a]	0.006	5.783	1.043	−0.005	6.413	0.898	−0.005
		0.925[b]	0.029		1.075	0.027		0.926	0.023
CH_3OH	6.139	0.885[a]	−0.011	5.749	1.026	−0.022	6.392	0.883	−0.020
		0.910[b]	0.014		1.053	0.005		0.909	0.006
CH_3SH	6.422	0.882[a]	−0.014	5.758	1.026	−0.022	6.354	0.884	−0.019
		0.885[b]	−0.011		1.044	−0.004		0.900	−0.003

[a] Trans to X–H bond. [b] Trans to lone pair.

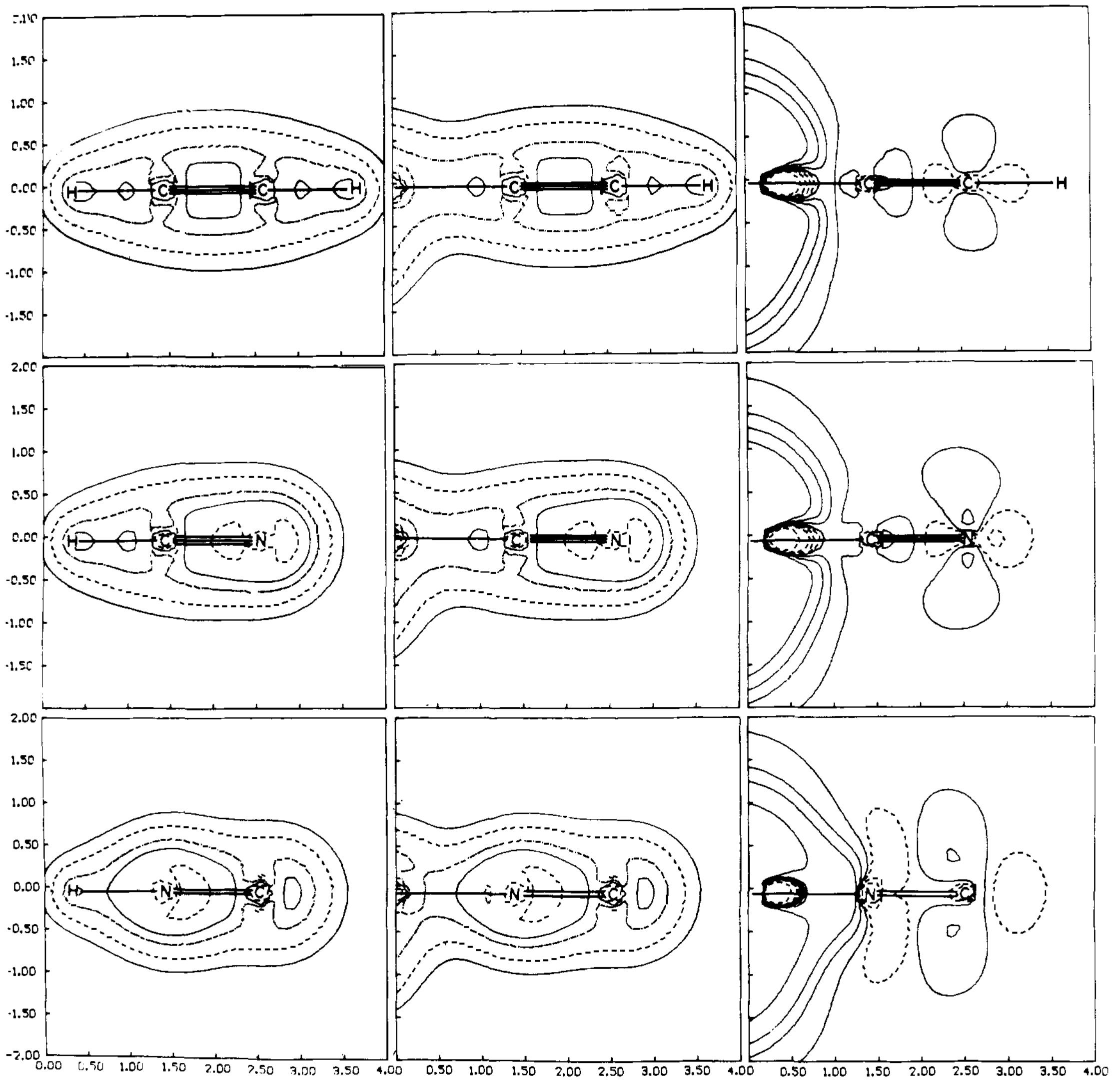

Figure 14. Effect of a methyl group on the electron-density distribution in acetylene (top), hydrogen cyanide (center), and hydrogen isocyanide (bottom). From left to right the plots give the electron density distribution in a plane for (a) the unsubstituted compound; (b) the methyl-substituted compound; (c) the difference between the two. In (a) and (b) the contour values are 0.02, 0.05, 0.1, and 0.2 e, whereas in (c) they are 0.001, 0.005, 0.01, −0.001, −0.005, and −0.01 e.

pattern of electron densities as found in conjugated systems. Longer aliphatic chains are now being examined.

The electron populations at the α carbon are more difficult to interpret. Although our scheme for obtaining the charge shifts at the methyl hydrogens is reasonably independent of the nature of the substituent, the corresponding quantities at the α carbon depend on how the C–X bond electron densities are distributed between C and X. The use of a constant value of r_C with varying C–X bond lengths may not be appropriate. With this in mind, we shall see if any information may be derived from the calculated carbon electron populations.

The population arising from the σ orbitals changes in accord with the electronegativity of the substituent, and even O^- and S^- lead to reduced populations. The electron populations found with the π orbitals show a more complex pattern. There is a very rough inverse relationship with the σ population suggesting that the π system attempts to minimize the C–X bond dipole created in the σ system. The net result is a relatively small range of total electron populations at carbon.

According to the population analysis, the electron population at the methyl carbon is greater in methyl fluoride than in acetonitrile. However, the population derived from the electron-density distribution has the reverse order. The case may be examined with the aid of a plot of the difference in electron density between acetonitrile and methyl fluoride in the H-C-X plane (Figure 13). The most obvious feature is the decrease in electron density in the methyl C-H bond on going from $X = F$ to $X = CN$. This is in good accord with the calculated hydrogen charge shifts. The effect at carbon is less clear, but, since most of the region about carbon has greater electron density with $X = CN$ than with $X = F$, the values derived by integration appear reasonable.

It seems pointless to consider the carbon shifts further at this time because of the complex interaction between σ inductive an π acceptor/donor effects and the uncertainty in the values themselves. These problems should not be as important at the β and γ positions, and here the charge shifts at carbon should be of greater significance.

So far, the effect of substituents on the methyl group has been of primary interest. Information also may be gained concerning the substituents. It is known that methyl substitution stabilizes triple bonds in acetylene and nitriles by about 5 kcal/mol.[35] In order to see what changes in electron distribution accompany this stabilization, we have examined the electron-density distributions for acetylene, hydrogen cyanide, methylacetylene, and acetonitrile (Figure 14). It can be seen that methyl substitution leads only to minor σ-π reorganization at the remote carbon or nitrogen. The major effect is the σ and π donation from the methyl group to the adjacent atom, and the effects are similar for the two cases.[36] Hydrogen isocyanide and methyl isocyanide also were examined, and, although methyl substitution does not appear as important as with the triple bonds, the effect on the electron-density distribution was similar to that found in the other cases.

Calculations

The molecular orbital calculations were carried out using GAUSSIAN-76[37] and the CDC-7600 computer at Brookhaven National Laboratory. The separation of electron density into regions attributed to the various atoms was carried out as indicated in the text and Figure 3. Each triangle (Figure 4) was divided into n^2 smaller triangles where n is the number of slices parallel to the base. Initially $n = 16$ and this was increased with increasing z until at the hydrogen $n = 30$. A constant value of n was used thereafter. The electron density was calculated at the center of each triangle and summed to give the electron-density function for the plane. The planes were taken at 0.05-Å intervals along z for $z = 0.0$-0.5 Å, and at 0.10-Å intervals thereafter. In one case the values of n were increased to 32-60 and 0.05-Å increments were used throughout. There was no significant change in the calculated electron-density function. The electron population was obtained by numerical integration of the electron-density function over the appropriate range of z coordinates.

The total electron population in a C-H bond in methane was found to be 2.000 e for each basis set, indicating that the numerical integrations had been carried out correctly. As an additional check, the integrations were carried out over planes parallel to one H-C-H plane, again dividing the space as shown in Figure 3. The populations obtained in this fashion agreed with those from the first method within 0.001 e. The numerical integrations using a PDP-11/45 computer required between 4 (CH_4) and 16 h (CH_3CN).

In the cases in which the integration for one C-H bond might pick up some electron density from a large substituent such as chlorine, the numerical integrations were carried out with the carbon at the origin and the substituent on the z axis. The summations for the C-H bonds were cut off when z reached 0.8 Å. For methane and methyl fluoride, the electron population was found to be decreased by 0.006 e as compared to the use of no z cutoff. Thus, when the cutoff was used, the calculated populations were increased by 0.006 e to obtain the final values shown in the tables.

In the case of ethane, the midpoint of the C-C bond (0.766 Å) was used to separate the electron density for the two methyl groups, and the populations were calculated accordingly. With the methylammonium ion, a plane 0.766 Å from the carbon was used to separate the methyl and ammonium groups. The electron population for a methyl hydrogen between two amino hydrogens in methylamine was treated in the same fashion, whereas a methyl hydrogen trans to the hydroxyl hydrogen in methanol was treated in the same fashion as for the methyl halides. The methyl hydrogens between a hydrogen and a lone pair were given a value halfway between those derived by the two methods given above.

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References and Notes

(1) For a recent general review, see: Topsom, R. D. *Prog. Phys. Org. Chem.* **1976,** *12,* 1.

(2) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968,** *90*, 4328. Dewar, M. J. S.; Grisdale, P. J. *Ibid.* **1962,** *84*, 3539. Brownlee, R. T. C.; DiStefano, J.; Topsom, R. D. *Spectrochim. Acta, Part A* **1975,** *31*, 1685. Taft, R. W.; Grob, C. A. *J. Am. Chem. Soc.* **1974,** *96*, 1236.

(3) Westheimer, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1938,** *6*, 513. Cole, T. W., Jr.; Mayers, C. J.; Stock, L. M. *J. Am. Chem. Soc.* **1974,** *96*, 4555. Liotta, C. L.; Fisher, W. F.; Slightom, E. L.; Harris, C. L. *Ibid.* **1972,** *94*, 2129. Taft, R. W. "Steric Effects in Organic Chemistry", Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

(4) Roberts, J. D.; Moreland, W. T. *J. Am. Chem. Soc.* **1953,** *75*, 2167. Holtz, H. D.; Stock, L. M. *Ibid.* **1964,** *86*, 5188. Wilcox, C. F., Jr.; McIntyre, J. S. *J. Org. Chem.* **1965,** *30*, 777. Liotta, C. L. Fisher, W. F.; Greene, G. H., Jr.; Joyner, B. L. *J. Am. Chem. Soc.* **1972,** *94*, 4891.

(5) Bader, R. F. W. *MTP Int. Rev. Sci.; Phys. Chem., Ser. Two* **1975,** *1*, 43. *Acc. Chem. Res.* **1975,** *8*, 34.

(6) Van Wazer, J. R.; Abser, I. "Electron Densities in Molecules and Molecular Orbitals"; Academic Press: New York, 1975.

(7) Streitwiesser, A., Jr.; Owens, P. H. "Orbital and Electron Density Diagrams: An Application of Computer Graphs"; Macmillan: New York, 1975.

(8) Streitwieser, A., Jr.; Collins, J. B.; McKelvey, J. M.; Grier, D.; Sender, J.: Toczko, A. G. *Proc. Natl. Acad. Sci. U.S.A.* **1979,** *76*, 2499.

(9) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratros, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976,** *98*, 4778.

(10) Daudel, R.; Stephens, M. E.; Csizmadia, I. G.; Kozmutza, C.; Kapuy, E.; Goddard, J. D. *Int. J. Quantum Chem.* **1977,** *11*, 665. Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975,** *97*, 7391.

(11) Politzer, P.; Kasten, S. D. *J. Phys. Chem.* **1976,** *80*, 283.

(12) Bader, R. F. W.; Duke, A. J.; Messer, R. R. *J. Am. Chem. Soc.* **1973,** *95*, 7715.

(13) One also assumes that correlation effects which are neglected in single determinant SCF calculations will not have an important effect on the calculated distribution.[5]

(14) Wiberg, K. B. *J. Am. Chem. Soc.* **1979,** *101*, 1718.

(15) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971,** *54*, 724.

(16) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972,** *16*, 217. In the case of chlorine, the basis set of Dunning, T. H., Jr. *Ibid.* **1970,** *7*, 423, was used.

(17) Vladimiroff, T. *J. Phys. Chem.* **1973,** *77*, 1983, has shown that for diatomics the use of bond functions is nearly as effective as the use of polarization functions. For application of bond functions to first-row polyatomic molecules see: Meyer, W.; Pulay, P. *J. Chem. Phys.* **1972,** *56*, 2109. Jalosovszky, G.; Pulay, P. *J. Mol. Struct.* **1975,** *26*, 277. Carlsen, N. R. *Chem. Phys. Lett.* **1977,** *51*, 192.

(18) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972,** *16*, 217.

(19) Methyl halides: Duncan, J. L. *J. Mol. Struct.* **1970,** *6*, 447. Methanol: Lees, R. M.; Baker, J. G. *J. Chem. Phys.* **1968,** *48*, 5299. Methylamine: Lide, D. R., Jr. *Ibid.* **1957,** *27*, 343. Acetonitrile: Duncan, J. L. *J. Mol. Struct.* **1974,** *22*, 225. Methanethiol: Kojima, J.; Nishikawa, T. J. *J. Phys. Soc. Jpn.* **1957,** *12*, 680. Ethane: Bartell, L. S.; Higginbotham, H. K. *J. Chem. Phys.* **1965,** *42*, 851. Propyne: Duncan, D. L. *J. Mol. Struct.* **1974,** *22*, 225.

(20) Mulliken, R. S. *J. Chem. Phys.* **1962,** *36*, 3428.

(21) Politzer, P.; Mulliken, R. S. *J. Chem. Phys.* **1971,** *55*, 5135.

(22) Davidson, E. R. *J. Chem. Phys.* **1968,** *46*, 3320. Fliszár, S.; Kean, G.; Macaulay, R. *J. Am. Chem. Soc.* **1974,** *96*, 4353.

(23) (a) Politzer, P.; Harris, R. R. *J. Am. Chem. Soc.* **1970,** *92*, 6451. (b) Bader, R. F. W.; Beddall, P. M.; Cade, P. E. *Ibid.* **1971,** *93*, 3095.

(24) The electron density may also be partitioned in other ways. Cf. Daudel, R.; Bader, R. F. W.; Stephens, M. E.; Borrett, D. S. *Can. J. Chem.* **1974,** *52*, 1310. Srebrenik, S.; Bader, R. F. W.; Ngugen-Dang, T. T. *J. Chem. Phys.* **1978,** *68*, 3667. Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979,** *101*, 1389.

(25) The electron population assigned to hydrogen is close to a linear function of r_C over the range of 0.75-0.85 Å.

(26) For a discussion of the general problem of assigning electron populations, see: Julg, A. *Top. Curr. Chem.* **1975,** *58*, 1, and ref 23.

(27) Excellent pictorial representations of these orbitals are given in Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

(28) The calculation of a dipole moment in accord with the experimental value is a necessary but not sufficient requirement for a good wave function. The main argument for the use of the 431G + 2BF wave functions is the

agreement in the calculated electron populations with those calculated with 631G** basis set.

(29) Potts, A. W.; Lempka, H. J.; Streets, D. G.; Price, W. C. *Philos. Trans. R. Soc. London, Ser. A.* **1970,** *268,* 59. Potts, A. W.; Williams, T. A.; Price, C. W. *Faraday Discuss. Chem. Soc.* **1972,** *54,* 104. The compounds included in Figure 11 are methane, ethane, methyl fluoride, methyl chloride, methanol, and methylamine.

(30) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* **1976,** *98,* 7179.

(31) Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; p 374 ff.

(32) Bernardi, F.; Bottoni, A.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978,** *100,* 7205.

(33) Another way in which to compare the hydrogen electron populations for methane and methyl fluoride makes use of the calculated populations from the proton to infinity, which are 0.517 for methane and 0.507 for methyl fluoride. The hydrogen populations may be approximated as twice this value, or 1.034 and 1.014 e, respectively. The difference, 0.020 e, agrees with the value given in Table IV.

(34) Lone-pair interactions have received extensive study; Wolfe, S.; Schlegel, B.; Whangbo, M.-H. *Can. J. Chem.* **1974,** *52,* 3787. Wolfe, S.; Rauk, A.; Tel, L. M.; Csizmadia, I. G. *J. Chem. Soc. B* **1971,** 136. Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972,** *94,* 2371. The effect of lone-pair interactions on C–H stretching frequencies and bond lengths is reviewed: McKean, D. C. *Chem. Soc. Rev.* **1978,** *3,* 399.

(35) Wiberg, K. B. *J. Am. Chem. Soc.* **1979,** *101,* 2204.

(36) The effect of fluorine and lithium substitution on the electron populations in acetylene has been examined by Politzer and Harris (ref 23a), and the effect of methyl substitution on anions has been examined: Pross, A; Radom, L. *J. Am. Chem. Soc.* **1978,** *100,* 6572.

(37) Binkley, J. S.; Whitehead, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978,** *11,* 368.

Nonexponential Proton Spin–Lattice Relaxation and Internal Rotation of Methyl Groups

E. Haslinger* and W. Robien

Contribution from the Institut für Organische Chemie der Universität Wien, A-1090 Wien, Austria.

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Abstract: Nonexponential relaxation has been analyzed by direct observation of the null points of the two coincident components of a methyl signal after a 180° pulse. From these observations correlation times for both internal rotation of the methyl group and local reorientation were determined. The method has been used to study association behavior and internal mobility of medium and large molecules and to assign methyl resonances. This method is generally applicable to study internal mobility and solute-solvent interactions in medium or large molecules which are bearing methyl groups.

Introduction

In an NMR experiment absorption of electromagnetic radiation by a spin system causes transitions from a lower to an upper energy level. The radiationless return to equilibrium requires radio-frequency power of the same energy which is provided by fluctuating magnetic fields. This process is called spin–lattice relaxation and is dependent on the details of the molecular motion.[1] It can be observed by measuring the time dependence of the longitudinal magnetization which is usually exponential and can be characterized by a relaxation time T_1. If the overall motion of a system of three or more spins is highly anisotropic, cross correlation may give rise to a nonexponential relaxation pattern and slows down the relaxation rate.[5-8] Therefore a number of papers have been devoted to the study of the relaxation behavior of methyl groups; however, only few observations of nonexponential spin–lattice relaxation in solutions have been reported.[2-4] In these cases the T_1 decay has been analyzed as a sum of two exponentials by a nonlinear least-squares fit, which cannot be done very accurately.[3,4] Recently it has been shown that the two components of the longitudinal magnetization can be resolved and their individual relaxation rates have been measured.[9] After a 180° pulse the two components relax independently so that near the null point the faster relaxing component may be positive, while the other is still negative. In the extreme narrowing limit, they also have different T_2 values, thus giving rise to a difference signal (Figure 1). From a series of these spectra the T_1 values for both components and their relative contributions could be obtained.

We have used this method to investigate the internal mobility of methyl groups in several medium and large molecules.

Theory

The theory of three relaxing spins ($I = \frac{1}{2}$) in an equilateral triangle has been treated in various degrees of sophistication.[5-8] Some of these models are too complex for our experiments, where the extreme narrowing approximation is valid and there are only three observed quantities. One has therefore to assume that the methyl group is rotating relative to an isotropically reorienting framework. It is known from the composite particle method of spectral analysis[10-12] that a methyl group is represented by a doublet and a quartet state. The total z magnetization is also made up of a doublet and a quartet component. These components have different relaxation rates, which are coupled together. They are therefore mixed into two components M_A and M_B with relaxation times $T_1{}^A$ and $T_1{}^B$. If the extreme narrowing approximation is valid, the faster relaxing component has the shorter T_2 value and hence the greater line width. Using the matrix elements given by Bain and Lynden-Bell[13] one can write the relaxation matrix in terms of the total magnetization (M_T) which is the observed quantity and the difference between the doublet and the quartet magnetization:[9]

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} M_T \\ M' \end{bmatrix} = -\begin{bmatrix} 10_{x'} + 2_{\eta'} & -2\sqrt{5}x' \\ -2\sqrt{5}x' & 4x - 2x' + 6\eta - 5\eta \end{bmatrix}\begin{bmatrix} M_T - M_T{}^0 \\ M' \end{bmatrix} \quad (1)$$

x is the contribution to the dipolar relaxation of the methyl protons, which is proportional to the time integral of the self-correlation function between proton pairs; x' is the contribution arising from the correlation between the dipolar coupling of

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