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Substituent Effects. 1. Methyl Derivatives

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Abstract: The structures of 35 monosubstituted methanes were calculated with the 6-31G* basis set. Bent C-H bonds were found in most cases. The bond path angles for the H-C-X bonds were found to correlate with the electronegativity of X. The electron populations for each of the atoms were determined by direct integration of 6-31G** wave functions calculated at the 6-31G* geometries. The populations also were correlated with the electronegativity of the substituents. The changes in population result from a combination of a charge shift toward the more electronegative atom in a bond and a movement of the bond critical point toward the less electronegative atom. The relative importance of these two terms was estimated.

Substituent effects continue to be of interest to chemists,[1] but even the simplest of organic compounds have not as yet received a detailed systematic investigation. Our interest in these effects has led us to begin such an investigation, and we now report the results we have obtained in examining methane singly substituted with a variety of groups.[2] The analysis is based on 6-31G**[3] wave functions, which have been calculated by using the 6-31G*-optimized geometries,[4] and includes both the structural changes and the changes in electron populations caused by the substituents.

The calculated energies and geometries for the compounds with C_{3v} symmetry are given in Table I and are compared with the observed structures. There is generally good agreement between the observed and calculated bond angles. The distances from carbon to other first- or second-row elements are uniformly ~1% too short.[5,6] There is more scatter for the CH bond lengths, but this is at least in part due to systematic differences in observed bond lengths between microwave spectroscopy and electron diffraction.[7]

The one surprising structural parameter derived from the calculations is the short C-O bond length in methoxide ion, 1.311 Å as compared to 1.400 Å in methanol. It was possible that this was an artifact resulting from the oxygen lone pairs trying to use carbon orbitals for their stabilization. In order to test this, the geometry was reoptimized by use of the 6-311++G** basis set, which includes diffuse functions at all atoms, and which should give an improved description of the lone pairs. The calculated bond length increased somewhat to 1.326 Å, which is still much smaller than the C-O bond length in methanol calculated with the same basis set (1.401 Å). The origin of the change in C-O bond length has been discussed elsewhere[8] and may be related to the marked stabilization (in terms of proton affinities)[9] of methoxide ion over hydroxide ion in the gas phase. Lithium methoxide was calculated to have a considerably longer C-O bond length, 1.358 Å, presumably resulting from the electrostatic stabilization of the oxygen, thus requiring less internal stabilization. With the larger basis set, the bond length increased slightly to 1.361 Å.

In considering structures of organic compounds, it is frequently difficult to distinguish between electronic interactions and steric effects. Consider the series methane, methyl fluoride, and methoxide ion. Symmetry forces the bond angles in methane to be 109.5°. The H-C-F angle in methyl fluoride is similar (108.9°),[10] whereas it might be expected to be considerably smaller. An electron-withdrawing atom should prefer a carbon orbital with increased p character,[11] and the resulting increased s character in the CH bonds would lead to a decrease in the H-C-F angle. The H-C-O angle in methoxide ion has increased to 116.5°. This could be the result of O^- preferring a carbon orbital with increased s character, or it might be due to a steric interaction between the O^- and the hydrogens.

An examination of the angles between bond paths at a given nucleus is useful in studying this problem. The bond path[12] is the path of maximum charge density between a pair of bonded atoms, and in the absence of unsymmetrical steric interaction, it is collinear with a line drawn between a pair of nuclei. However, if the bond is deformed, as in a bending vibration, a bent bond is formed as a result of limited orbital following.[13] Similarly, if the bond is deformed as a result of the formation of a small ring, or an unsymmetrical steric interaction, a bent bond will be formed,[14] and the angle between the bond paths will differ from the conventional bond angle. Thus, any external force on an atom not associated with its bonds may lead to a bent bond.

The two angles are compared for a number of methyl derivatives in Table II. With methoxide ion, the bond path angle is essentially the same as the conventional angle, showing that the deviation from tetrahedral results from an electronic interaction rather than a steric interaction. With the larger and more diffuse S^- group as in MeS^-, both of the angles are slightly larger than tetrahedral, indicating a small electronic effect. The conventional angle is the larger of the two, and the 1° difference suggests a small steric interaction between S^- and H.

The methyl halides are quite different. With both methyl fluoride and methyl chloride, the bond path H-C-X angle is significantly smaller than tetrahedral, indicating that the expected increase in s character in the C-H bonds is found. The conventional angles are larger by ~2.5°, indicating that a steric repulsion between the H and F or Cl also is operative. Among the conventional substituents, the smallest H-C-X bond path angle is found with X = NH_3^+, which should have the largest electronegativity. The bonds angles in Table II are arranged in order of increasing values, and it can be seen that there is a reasonable correlation with the electronegativity of the substituent group. A remarkably small H-C-X bond path angle was found with X = N_2^+. The methyldiazonium ion has some special characteristics, which will be noted below.

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[1] For recent reviews of substituent effects, see: Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1. Topsom, R. D. *Ibid.* **1987**, *16*, 85, 125. Charton, M. *Ibid.* **1987**, *16*, 287.

[2] For an earlier and less detailed examination of some of these compounds, see: Wiberg, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 1229; *Ibid.* **1979**, *101*, 2204.

[3] Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

[4] The 6-31G* structures of some of these compounds may be found in the Carnegie Mellon University Quantum Chemistry Archive.

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[8] Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.*, in press.

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Table I. Energies and Structures of Methyl Derivatives with Threefold Symmetry Axes[a]

X	6-31G*[b]	6-31G**[b]	r_{CH}[c]	∠HCX[d]	r_{CX}[c]	others[c]	
H	-40.195 17	-40.201 70	1.0838	109.47	1.0838		
			(1.094)	(109.47)	(1.094)		
Li	-47.015 54	-47.020 99	1.0934	112.56	2.0013		
BeH	-54.816 01	-54.822 14	1.0898	112.07	1.6988		
					(1.698)		
CH_3	-79.228 75	-79.238 23	1.0856	111.20	1.5273		
			(1.102)	(111.5)	(1.530)		
C≡CH	-115.864 32	-115.871 25	1.0841	110.61	1.4860	C≡C 1.1869	CH 1.0568
			(1.112)	(110.5)	(1.458)	(1.207)	(1.060)
NC	-131.894 36	-131.899 03	1.0813	109.62	1.1533	NC 1.4212	
			(1.094)	(109.3)	(1.166)	(1.414)	
CN	-131.927 53	-131.932 49	1.0825	109.79	1.4683	CN 1.1348	
			(1.104)	(109.5)	(1.458)	(1.157)	
F	-139.034 61	-139.039 73	1.0819	109.09	1.3647		
			(1.095)	(109.0)	(1.382)		
Na	-201.399 85	-201.405 38	1.0910	111.69	2.3236		
CNO	-206.679 95	-206.684 89	1.0822	109.92	1.4709	CN 1.1296	NO 1.2135
					(1.441)	(1.167)	(1.219)
MgH	-239.754 43	-239.760 33	1.0895	112.13	2.1057	MgH 1.7246	
SiH_3	-330.272 41	-330.281 87	1.0861	111.12	1.8879	SiH 1.4783	CSiH 110.60
			(1.093)	(111.2)	(1.867)	(1.455)	(110.6)
CF_3	-375.820 37	-375.825 42	1.0815	109.40	1.4994	CF 1.3249	CCF 111.64
			(1.081)	(112)	(1.494)	(1.340)	(111.9)
Cl	-499.093 15	-499.097 90	1.0779	108.45	1.7846		
			(1.090)	(108.2)	(1.785)		
NH_3^+	-95.573 49	-95.588 86	1.0782	108.10	1.5072	NH 1.0114	CNH 111.59
N_2^+	-148.216 06	-148.221 28	1.0782	104.98	1.0596	NN 1.0728	
O^-	-114.384 47	-114.389 53	1.1331	116.52	1.3106		
		-114.443 95[e]	1.1236	115.21	1.3260		
O^-Li^+	-121.931 55	-121.936 25	1.0959	112.55	1.3584	OLi 1.6008	
		-121.974 04[e]	1.0963	112.35	1.3606	OLi 1.5903	
S^-	-437.114 86	-437.119 70	1.0907	112.12	1.8316		
SO_3^-	-661.693 28	-661.698 22	1.0828	109.17	1.7870	SO 1.4548	CSO 104.45

[a] Observed values (ref 8) are given in parentheses. The 6-31G** energies were calculated at the 6-31G* geometries. [b] In hartrees. [c] In angstroms. [d] In degrees. [e] Calculated by using the 6-311++G** basis set.

Table II. Bond Path Angles for Compounds with C_{3v} Symmetry[a]

compd	angle	bond path[b]	convent.[b]	Δα
MeN_2^+	HCN	101.17	104.98	3.81
$MeNH_3^+$	HCN	104.71	108.10	3.39
	HNC	110.83	111.59	0.76
MeCl	HCCl	105.73	108.45	2.72
MeF	HCF	106.68	109.17	2.49
MeNC	HCN	107.42	109.62	2.20
MeCN	HCC	108.26	109.79	1.53
MeC≡CH	HCC	109.43	110.61	1.18
MeMe	HCC	110.25	111.20	0.95
$MeCF_3$	HCC	110.41	109.40	-1.01
	CCF	110.91	111.64	0.73
$MeSiH_3$	HCSi	110.54	111.12	0.76
	HSiC	110.44	110.60	0.35
MeNa	HCNa	110.82	111.69	0.87
MeS^-	HCS	111.11	112.07	1.01
MeO^-Li^+	HCO	111.20	112.55	1.35
MeMgH	HCMg	111.64	112.13	0.49
MeBeH	HCBe	112.77	112.07	-0.70
MeLi	HCLi	113.37	112.56	-1.81
MeO^-	HCO	116.77	116.52	-0.25

[a] The compounds are listed in order of increasing bond path angle. [b] In degrees.

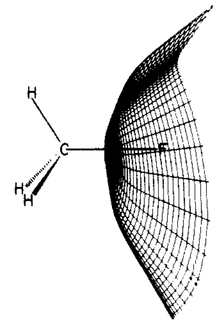

Figure 1. Example of a zero-flux surface separating the C and F of methyl fluoride.

Our main interest is in the distribution of electron population among the atoms in these molecules. It is now clear that the Mulliken population analysis[15] leads to the wrong sign for the charge distribution in most CH bonds.[16] The problem arises from the arbitrary division of electron density in the overlap region between the atoms. The only procedure that leads to a unique definition of population at an atom is Bader's theory of atoms in molecules.[17]

Between each pair of bonded atoms there exists a bond path that is the path of maximum charge density (ρ) connecting the atoms. Along this path, there is a point of minimum charge density known as a bond critical point. It has the characteristic that it is a minimum in ρ along the bond path, but a maximum in ρ in all directions perpendicular to the bond path. If one starts at the bond critical point and develops a series of paths for which ρ decreases most rapidly, they will define a surface that will separate the two atoms. The rate of change of ρ across the surface is zero, and it is known as a zero-flux surface. An example of such a surface is shown in Figure 1.

It has been shown that a set of these surfaces, one for each bonded pair of atoms, will separate a molecule into volume elements that may uniquely be assigned to the atoms they contain. In particular, the integral of $(\hbar^2/4m)\nabla^2\rho$ (where $\nabla^2\rho$ is the

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(15) Mulliken, R. S. *J. Chem. Phys.* **1962**, *36*, 3428. See, however: Mulliken, R. S.; Politzer, P. *J. Chem. Phys.* **1971**, *55*, 5135. Grier, D. D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3556.

(16) (a) Wiberg, K. B.; Wendoloski, J. J. *Phys. Chem.* **1984**, *88*, 586. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1986**, *84*, 2428. (c) Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.

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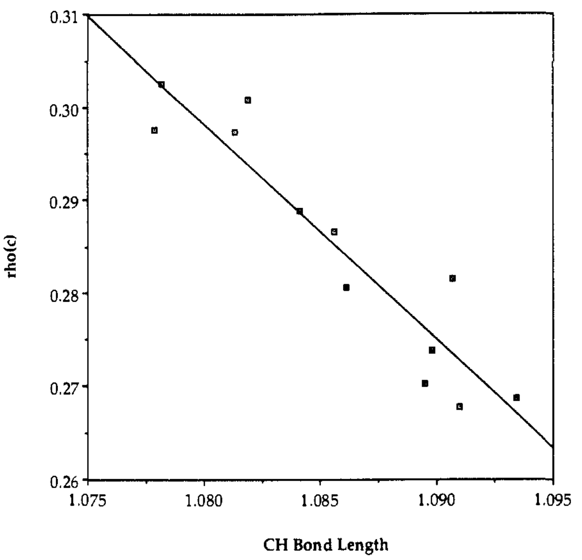

Figure 2. Relationship between the charge density at the bond critical point (ρ_c) and the CH bond length.

Laplacian of ρ, or the sum of the second derivatives of ρ with respect to the coordinates) will be zero within each of these volume elements, and the virial theorem will be locally satisfied for each atom, Ω. Since $V_\Omega = -2T_\Omega$ and $E_\Omega = V_\Omega + T_\Omega$ it can be seen that $E_\Omega = -T_\Omega$. Both the electron population and the kinetic energy of the electrons associated with a given atom may be obtained via numerical integration over the volume element.

With this introduction, we may examine Table III, which shows the bond properties of the methyl derivatives with C_{3v} symmetry. The distances from the atoms to the bond critical points (r_A and r_B) and the ratio of these distances (*R*) are given. These data are related to the relative electronegativities of the two atoms forming the bond. With a symmetrically substituted bond, such as the C–C bond of ethane, the bond critical point is at the center of the bond. If the electronegativity of one of the atoms is increased, the charge density in its vicinity increases, causing the bond critical point to move toward the atom having the lower electronegativity.

The other quantities in the table are the charge density at the bond critical point (ρ_c) and the components of the Laplacian of ρ (λ_1, λ_2, and λ_3). They are the curvatures of ρ at the bond critical point. Finally, there is the ellipticity (ϵ) defined as $\lambda_1/\lambda_2 - 1.0$. With a symmetrically substituted single bond such as the C–C bond in ethane, $\lambda_1 = \lambda_2$ and $\epsilon = 0$.

It can be seen that ρ_c for the CH bonds changes considerably as the substituent is varied (Table III). It may be noted that larger values of ρ_c are generally associated with the shorter CH bonds. Leaving out X = O^- or O^-Li^+, which appear to have special characteristics, the relationship between ρ_c and the calculated CH bond length is shown in Figure 2. It is clear that a large part of the variation in ρ_c is associated with the change in bond length. This should be expected since a shorter bond would lead to increased overlap and a larger value of ρ_c.

Short CH bonds are generally associated with the more electronegative substituents. This is in accord with the expected hybridization changes. An electronegative substituent should lead to increased s character in the CH bonds and it is well recognized that this leads to shorter bonds.[18] As noted above, the ratio, *R*, of the distances from the atoms to the bond critical point is one measure of electronegativity. The correlation between r_{CH} and *R* (correlation coefficient of 0.96) is given in Figure 3 and clearly shows that the CH bond length is related to the electronegativity of the substituent. Since both the bond path angle and the CH bond length are related to hybridization, they should be related to each other. This is examined in Figure 4, and a reasonably good correlation again is found (correlation coefficient of 0.96). It can be seen that most of the structural variation in these compounds may be accounted for by simple hybridization considerations.

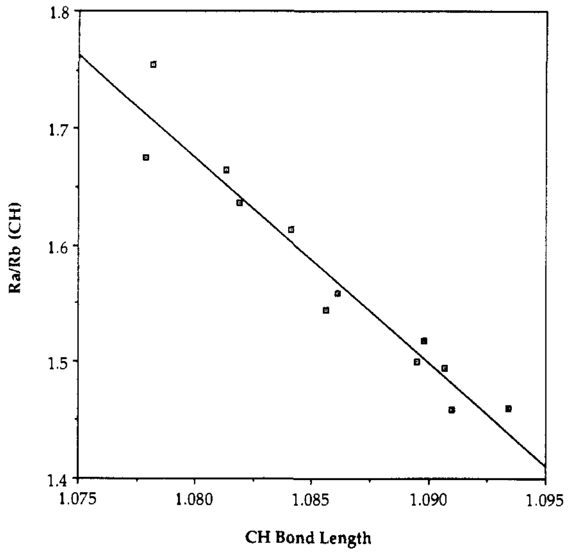

Figure 3. Relationship between the C–H bond length and the ratio (*R*) of the distances from the carbon and hydrogen to the bond critical point.

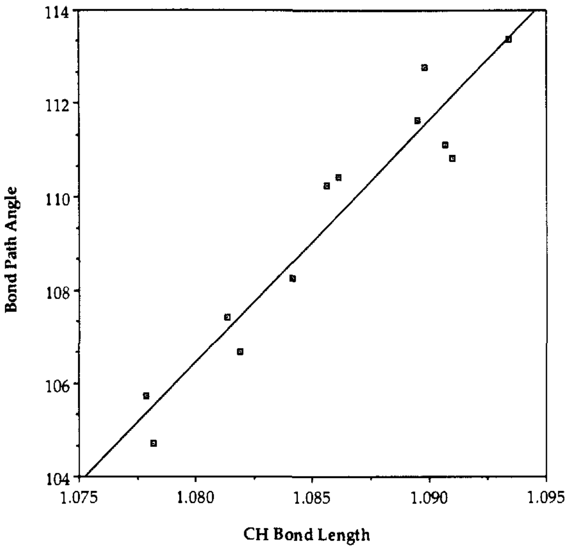

Figure 4. Relationship between the H–C–X bond angle and the C–H bond length.

The variation in ρ_c for the CX bonds also is of interest. With C–C single bonds, a typical value is 0.25 e/B^3. The C–Li bond in methyllithium has a markedly smaller value, 0.04 e/B^3, and with the other extreme of electronegativity, the C–N bond of methyldiazonium ion has ρ_c of 0.17 e/B^3. Bonds with a high degree of ionic character typically have reduced values of ρ_c. In the case of methyllithium, the electronegativity difference also leads to a positive value of $\nabla^2\rho$ (the sum of the three λ in Table III), whereas covalent bonds with little ionic character normally have negative values of $\nabla^2\rho$.

As noted above, the main concern of this investigation is an examination of the changes in charge distribution that result from changes in substituents. We obtain the electron populations by numerical integration of the 6-31G** wave functions, making use of the zero-flux boundary surfaces to define volume elements that may be attributed to individual atoms. The results of these calculations are summarized in Table IV. Here, *n* is the population, *L* is the value of $(\hbar^2/4m)\nabla^2\rho$, which should be zero if the integration of the kinetic energy were exact, and *T* is the kinetic energy, which has been corrected for the virial defect in the ab initio calculations so that the sum of the *T*'s for the atoms will

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[18] Coulson, C. A. *Valence*; Oxford University Press: London, 1952; p 200.

Table III. Bond Properties of Methyl Derivatives with Threefold Symmetry[a]

X	bond	r_A	r_B	R	ρ_c	λ_1	λ_2	λ_3	ϵ
N_2^+	C−H	0.7096	0.3688	1.924	0.3051	−0.8969	−0.8540	0.4399	0.050
	C−N	0.4574	1.0522	2.301	0.1720	−0.0918	−0.0918	0.7468	0.000
	N−N	0.5860	0.4868	1.204	0.6901	−1.5614	−1.5614	0.4892	0.000
NH_3^+	C−H	0.6869	0.3914	1.755	0.3026	−0.8503	−0.8134	0.4363	0.045
	C−N	0.4793	1.0278	2.144	0.2210	−0.3237	−0.3237	0.4027	0.000
	N−H	0.7871	0.2243	3.510	0.3536	−1.4684	−1.4679	0.8867	0.001
F	C−H	0.6721	0.4107	1.636	0.3010	−0.8415	−0.7928	0.4442	0.061
	C−F	0.4316	0.9331	2.162	0.2371	−0.4243	−0.4243	1.3335	0.000
Cl	C−H	0.6750	0.4030	1.675	0.2977	−0.8209	−0.7941	0.4321	0.034
	C−Cl	0.7364	1.0482	1.423	0.1840	−0.2936	−0.2936	0.2865	0.000
NC	C−H	0.6755	0.4058	1.665	0.2974	−0.8177	−0.7826	0.4356	0.045
	C−N	0.4486	0.9726	2.171	0.2558	−0.4555	−0.4555	0.7805	0.000
	N−C	0.7671	0.3862	1.986	0.4404	−1.2308	−1.2308	3.2615	0.000
CNO	C−H	0.6759	0.4063	1.663	0.2992	−0.7829	−0.7641	0.4265	0.025
	C−C	0.6115	0.8594	1.164	0.2595	−0.4800	−0.4800	0.1747	0.000
	C−N	0.3826	0.7469	1.952	0.4343	−0.7823	−0.7823	3.4668	0.000
	N−O	0.6232	0.5903	1.056	0.4967	−1.0797	−1.0797	1.2680	0.000
CN	C−H	0.6751	0.4075	1.657	0.2910	−0.7744	−0.7592	0.4239	0.020
	C−C	0.6263	0.8421	1.344	0.2685	−0.5137	−0.5137	0.1989	0.000
	C≡N	0.3848	0.7501	1.949	0.4902	−1.0480	−1.0480	2.8737	0.000
CF_3	C−H	0.6676	0.4140	1.612	0.2909	−0.7599	−0.7546	0.4159	0.007
	C−C	0.6708	0.8286	1.235	0.2871	−0.2032	−0.2032	0.0606	0.000
	C−F	0.4220	0.9029	2.139	0.2775	−0.7388	−0.6245	1.6210	0.183
CH_3	C−H	0.6589	0.4267	1.544	0.2867	−0.7324	−0.7324	0.4017	0.008
	C−C	0.7637	0.7637	1.000	0.2528	−0.4808	−0.4808	0.2967	0.000
O^{-+}	C−H	0.6610	0.4349	1.520	0.2856	−0.7537	0.7176	0.4165	0.050
	C−O	0.4378	0.9206	2.102	0.2940	−0.6433	−0.6433	0.9988	0.000
	O−Li	0.9780	0.6227	1.571	0.0632	−0.1293	−0.1293	0.9269	0.000
H	C−H	0.6605	0.4233	1.560	0.2855	−0.7273	−0.7273	0.4010	0.000
S^-	C−H	0.6534	0.4373	1.494	0.2815	−0.7037	−0.7019	0.3920	0.003
	C−S	0.9843	0.8473	1.162	0.1714	−0.2127	−0.2127	0.1079	0.000
SiH_3	C−H	0.6616	0.4245	1.559	0.2806	−0.7087	−0.6898	0.3936	0.027
	C−Si	1.1779	0.7096	1.660	0.1174	−0.1708	−0.1708	0.6564	0.000
	Si−H	0.7088	0.7695	1.086	0.1174	−0.1881	−0.1877	0.6633	0.002
BcJ	C−H	0.6570	0.4328	1.518	0.2738	−0.6797	0.6462	0.3802	0.052
	C−Be	1.1421	0.5566	2.052	0.1030	−0.2075	−0.2075	0.7615	0.000
	Be−H	0.5715	0.7659	1.340	0.0935	−0.1934	−0.1934	0.6134	0.000
C≡CH	C−H	0.6692	0.4149	1.613	0.2889	−0.7580	−0.7447	0.4186	0.018
	C−C	0.8067	0.6613	1.220	0.2729	−0.5293	−0.5293	0.2420	0.000
	C≡C	0.5654	0.6215	1.099	0.4164	−0.5814	−0.5814	−0.1028	0.000
	C−H	0.6760	0.3808	1.775	0.3012	−0.8256	−0.8056	0.3842	0.000
MgH	C−H	0.6537	0.4359	1.500	0.2703	−0.6606	−0.6219	0.3789	0.062
	C−Mg	1.2439	0.8618	1.443	0.0543	−0.0639	−0.0639	0.4071	0.000
	Mg−H	0.8780	0.3541	2.480	0.0491	−0.0623	−0.0623	0.3438	0.000
Li	C−H	0.6489	0.4444	1.460	0.2686	−0.6538	−0.6076	0.3610	0.076
	C−Li	1.2988	0.7025	1.849	0.0422	−0.0607	−0.0607	0.3291	0.000
Na	C−H	0.6473	0.4438	1.459	0.2677	−0.6475	−0.6004	0.3676	0.078
	C−Na	1.3383	0.9853	1.358	0.0347	−0.0357	−0.0357	0.2383	0.000
O^-	C−H	0.6640	0.4692	1.415	0.2560	−0.6227	−0.6022	0.3893	0.034
	C−O	0.4339	0.8767	2.021	0.3487	−0.8366	−0.8366	0.9657	0.000
				6-311++G** Data					
O^-	C−H	0.6642	0.4587	1.448	0.2631	−0.6550	−0.6310	0.3984	0.038
	C−O	0.4417	0.878	2.010	0.3343	−0.7819	−0.7819	0.8203	0.000
O^-Li^+	C−H	0.6792	0.4172	1.628	0.2817	−0.7251	−0.6907	0.3935	0.050
	C−O	0.4425	0.9181	0.482	0.2872	−0.5983	−0.5983	1.0016	0.000
	C−Li	0.9753	0.6150	1.586	0.0670	−0.1383	−0.1383	0.9507	0.000

[a] The compounds are listed in order of decreasing charge density at the C−H bond critical point. r_A is the distance (angstroms) from the first atom forming the bond to the critical point, r_B is the distance from the second atom, and R is the ratio of the two distances always taken to be unity or larger. ρ_c is the charge density at the bond critical point, the λ's are the components of the Laplacian of ρ, and ϵ is the ellipticity.

sum to minus the total energy. The integration for a methyl group is generally more precise than that for its carbon atom, but the sum of the carbon and hydrogen populations or kinetic energies usually agreed satisfactorily with that of the methyl group.

The compounds in Table IV are arranged in order of increasing electron population at the methyl group. The methyldiazonium ion has a remarkably small methyl population, close to that of CH_3^+ (8.00e). The nitrogen adjacent to the methyl group has a relatively large population corresponding to a charge of −0.40 e, whereas the terminal nitrogen has a small population (q = +0.66e). These data, along with the relatively small ρ_c for the C−N bond suggests that the ion might best be described as a methyl cation coordinated to a highly polarized N_2. The populations are not in accord with the Lewis structure, $CH_3N^+{\equiv}N$:, commonly written for diazonium ion.

The methyl population for methyl fluoride also is low, corresponding to a charge of +0.74e, with a corresponding negative charge on fluorine. This high ionic character for the C−F bond may at first seem surprising. However, a methyl group and a hydrogen have very similar electronegativities, and it is generally recognized that HF has a large ionic character. Methyl fluoride cannot be much different. It also must be recognized that the atoms defined by the theory of atoms in molecules are not spherical (see below). As a result, the center of charge density for a given atom usually does not coincide with the nuclear position. Thus, the charges represent the first term in a multipole expansion. The dipole, quadrupole, and higher terms may also be obtained via the integration of the appropriate function of the charge density.

Table IV. Atom Properties of Methyl Derivatives with C_{3v}

compound	atom	n_T	L	$T = -E$
$CH_3N_2^+$	CH_3	8.1603	−0.0002	39.3340
$-V/T = 2.002\,803$	C	5.6100	−0.0014	37.6310
$E = -148.2213$	H	0.8504	0.0001	0.5676
$\Delta E = -0.09$	N	7.3967	0.0001	54.8810
	N	6.4429	0.0000	54.0062
sum		21.9999		148.2212
CH_3F	CH_3	8.2573	0.0000	39.2465
$-V/T = 2.001\,369$	C	5.1333	−0.0002	37.2698
$E = -139.0397$	H	1.0413	0.0001	0.6589
$\Delta E = 0.06$	F	9.7427	0.0000	99.7933
sum		18.0000		139.0398
CH_3NC	CH_3	8.3025	−0.0006	39.2686
$-V/T = 2.001\,18$	C	5.2837	−0.0004	37.3525
$E = -131.8990$	H	1.0063	0.0001	0.6389
$\Delta E = 0.64$	N	8.8796	0.0021	55.7449
	C	4.8176	0.0001	36.8865
sum		21.9997		131.9001
$CH_3NH_3^+$	CH_3	8.3369	−0.0005	39.3656
$-V/T = 2.001\,56$	C	5.4961	−0.0011	37.5278
$E + -95.5889$	H	0.9471	0.0001	0.6127
$\Delta E = -0.84$	N	8.2438	−0.0006	55.0501
	H	0.4730	0.0001	0.3906
sum		17.9997		95.5875
CH_3OLi	CH_3	8.3819	−0.0006	39.2458
$-V/T = 2.001\,69$	C	5.0049	0.0001	37.1783
$E = -121.9362$	H	1.1256	0.0001	0.6893
$\Delta E = -0.19$	O	9.5530	−0.0001	75.3057
	Li	2.0649	0.0003	7.3844
sum		19.9998		121.9359
CH_3O^-	CH_3	8.5259	−0.0010	39.0892
$-V/T = 2.000\,48$	C	4.7938	0.0005	36.9415
$E = -114.3895$	H	1.2437	0.0000	0.7159
$\Delta E = -0.32$	O	9.4748	−0.0004	75.2998
sum		18.0007		114.3890
CH_3CNO	CH_3	8.5928	0.0003	39.4777
$-V/T = 2.001\,816\,6$	C	5.6153	−0.0018	37.5974
$E = -206.6849$	H	0.9930	0.0001	0.6265
$\Delta E = 0.31$	C	4.9948	−0.0001	37.1668
	N	7.9033	−0.0005	55.1650
	O	8.5090	−0.0003	74.8749
sum		29.9999		206.6844
CH_3CN	CH_3	8.6377	0.0001	39.4977
$-V/T = 2.001\,54$	C	5.6565	−0.0007	37.6216
$E = -131.9325$	H	0.9938	0.0001	0.6253
$\Delta E = -0.06$	C	4.8299	0.0002	37.1473
	N	8.5322	−0.0001	55.2875
sum		21.9998		131.9324
CH_3Cl	CH_3	8.6839	−0.0006	39.4803
$-V/T = 2.000\,40$	C	5.6731	0.0003	37.5688
$E = -499.0979$	H	1.0032	0.0001	0.6373
$\Delta E = 0.19$	Cl	17.3161	0.0009	459.6179
sum		26.0000		499.0982
$CH_3C{\equiv}CH$	CH_3	8.7427	0.0000	39.5156
$-V/T = 2.000\,89$	C	5.6664	0.0001	37.5990
$E = -115.8713$	H	1.0253	0.0001	0.6389
$\Delta E = -0.12$	C	6.0858	0.0001	37.8633
	C	6.2773	−0.0002	37.9176
	H	0.8943	0.0001	0.5746
sum		22.0001		115.8710
CH_3CF_3	CH_3	8.7758	0.0000	39.6542
$-V/T = 2.001\,704$	C	5.7177	−0.0060	37.7399
$E = -375.8254$	H	1.0211	0.0001	0.6377
$\Delta E - 0.61$	C	3.9748	0.0003	36.3502
	F	9.7497	−0.0005	99.9400
sum		41.9997		375.8244
CH_4	CH_3	8.9387	−0.0001	39.5539
$-V/T = 2.000\,53$	C	5.7541	0.0004	37.6105
$E = -40.2017$	H	1.0613	0.0001	0.6478
$\Delta E = 0.00$				
sum		10.0000		40.2017
CH_3CH_3	CH_3	9.0000	−0.0003	39.6188
$-V/T = 2.000\,48$	C	5.7627	0.0001	37.6326
$E = -79.2382$	H	1.0791	0.0001	0.6621
$\Delta E = -0.28$				
sum		18.0000		79.2376
$CH_3SO_3^-$	CH_3	9.1163	−0.0001	39.7691
$-V/T = 2.001\,497$	C	5.9324	−0.0004	37.8084
$E = -661.6982$	H	1.0613	0.0001	0.6536
$\Delta E = 0.38$	S	12.1700	0.0071	395.0667
	O	9.5694	0.0000	75.6210
sum		49.9945		661.6988
CH_3S^-	CH_3	9.2871	0.0008	39.6483
$-V/T = 2.000\,45$	C	5.8959	0.0004	37.5977
$E = -437.1197$	H	1.1307	0.0001	0.6836
$\Delta E = 0.50$	S	16.7129	0.0002	397.4722
sum		26.0001		437.1205
CH_3SiH_3	CH_3	9.7462	0.0000	39.8510
$-V/T = 2.000\,24$	C	6.6008	−0.0001	37.9311
$E = -330.2819$	H	1.0484	0.0001	0.6400
$\Delta E = 0.44$	Si	10.9941	−0.0035	287.9623
	H	1.7517	0.0001	0.8231
sum		25.9955		330.2826
CH_3BeH	CH_3	9.8749	0.0000	39.7853
$-V/T = 1.999\,53$	C	6.6688	−0.0001	37.8589
$E = -54.8221$	H	1.0685	0.0001	0.6424
$\Delta E = -0.13$	Be	2.2536	0.0004	14.2610
	H	1.8723	0.0007	0.7756
sum		13.9988		54.8219
CH_3Li	CH_3	9.9019	−0.0003	39.6214
$-V/T = 1.999\,78$	C	6.5059	−0.0008	37.6308
$E = -47.0210$	H	1.1320	0.0001	0.6635
$\Delta E = -0.06$	Li	2.0968	0.0002	7.3995
sum		11.9987		47.0209
CH_3Na	CH_3	9.7869	−0.0006	39.6082
$-V/T = 2.000\,578$	C	6.3882	−0.0002	37.6079
$E = -201.4054$	H	1.1329	0.0001	0.6669
$\Delta E = 0.56$	Na	10.2132	0.0001	161.7963
sum		20.0000		201.4045
CH_3MgH	CH_3	9.8112	0.0001	39.6708
$-V/T = 2.000\,081$	C	6.5500	−0.0008	37.7206
$E = -239.7603$	H	1.0873	0.0001	0.6501
$\Delta E = 0.13$	Mg	10.3697	0.0002	199.4387
	H	1.8192	−0.0002	0.6510
sum		22.0001		239.7605
	6-311++G** Basis			
CH_3O^-	CH_3	8.5609	−0.0005	39.1573
$-V/T = 2.000\,181$	C	4.9568	−0.0023	37.0820
$E = -114.4440$	H	1.2020	0.0001	0.6915
$\Delta H = 0.19$	O	9.4389	0.0001	75.2870
sum		17.9998		114.4443
$CH_3O^-Li^+$	CH_3	8.4019	−0.0020	39.2135
$-V/T = 2.000\,453$	C	5.1068	−0.0003	37.2110
$E = -121.9740$	H	1.0984	0.0001	0.6680
$\Delta E = 0.82$	O	9.5263	0.0001	75.4150
	Li	2.0714	0.0002	7.3442
sum		19.9996		121.9727

[a] In the right-hand column are given the virial defect ($-V/T$) found in the SCF calculation, the calculated total energy (E), and the difference between $-E$ and the sum of the T's (ΔE) in kilocalories per mole. L is the integral of $(\hbar^2/4m)\nabla^2\rho$ over a given atom and would be zero if the integration for the kinetic energy were exact.

The use of these terms in studying infrared intensities has been reported,[19] and the electrostatic potentials for a molecule may be reported by using the set of terms derived from the theory.[20]

At the other extreme, the organometallic compounds such as methyllithium have a very large electron population at the methyl group, and almost a full positive charge at Li. The value of ρ_c for the C–Li bond is very small. These data indicate that the C–Li

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(20) Wiberg, K. B.; Breneman, C. M., unpublished results.

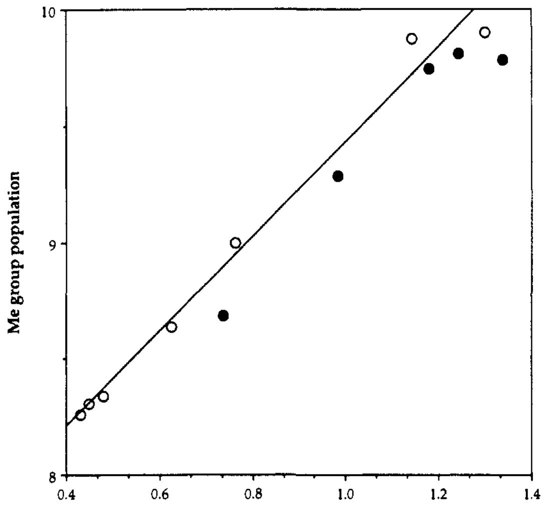


Figure 5. Relationship between the electron population at the methyl group and the distance from the methyl carbon to the C–X bond critical point (r_A).

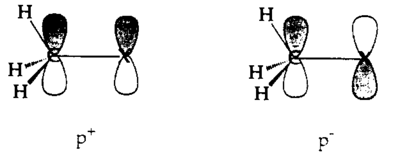
bond is essentially ionic. This now appears to be the consensus concerning these bonds.[21]

One might think that the methyl populations would be related to the electronegativity of the substituent. With the C–X bonds, we cannot use the ratio of the distances from the atoms to the bond critical point as a measure of electronegativity since the intrinsic size of X varies considerably (i.e., a Cl is much larger than F). However, we may use the distance from the carbon to the bond critical point (r_A), and it should increase as the electronegativity of X decreases. The relationship between the methyl populations and r_A for first-row substituents is shown in Figure 5 (open circles). Again, a reasonable correlation is found, with a correlation coefficient of 0.99. The second-row groups (closed circles) fall close to the correlation line.

An examination of the electron populations at the methyl hydrogens shows some interesting trends. For example, the electron populations at the hydrogens of methyl fluoride are greater than that for methyl chloride, despite the greater electronegativity of fluorine. Since the electron populations at the methyl groups are in the expected order for the relative electronegativities of F and Cl, one explanation would be back-bonding by the lone-pair electrons of F, transferring charge density to the methyl hydrogens. This would be less effective with Cl because of the mismatch of the valence orbital sizes between carbon and chlorine. An interaction of this type may be described as transfer of charge from the lone pairs on fluorine to the antibonding σ^* orbitals of the C–H bonds. Although this is a common explanation, it has the problem that the energy difference between the lone pair and σ^* orbitals is large, and the interaction is inversely proportional to the energy difference. An alternate view[8] considers the repulsive interaction between the backsides of the C–H bond orbitals and the lone-pair orbitals. Such a purely Coulombic interaction will serve to transfer charge from carbon to the hydrogen trans to the lone pair. It will be affected by the spatial proximity of the filled orbitals that are involved, and since the chlorine lone-pair orbitals will on the average be farther from the nucleus than those of fluorine, the interaction of the chlorine lone pairs with the backside of the C–H bond orbitals will be relatively small. This type of interaction also conveniently accounts for the charge shift from carbon to hydrogen in methoxide ion.

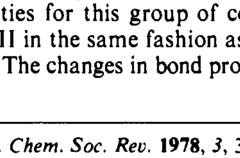
The changes in population for hydrogens attached to saturated, olefinic and acetylenic carbons also might be noted. In ethane the hydrogen population is 1.079, the vinyl hydrogens of propene have smaller populations, 1.046–1.056, and with propyne the acetylenic hydrogen has a much reduced population, 0.894. This corresponds to the change in s character, with an sp-hybridized carbon becoming more electronegative than hydrogen. The reversal of the C–H bond dipole on going to the acetylene corresponds to the change in the sign of the induced dipole for the C–H stretching vibrations on going from ethane or ethylene to acetylene.[16a]

It is often useful to divide the populations into components for the axial (σ) and perpendicular (π) orbitals as given in Table V. The core orbitals are the 1s orbitals for the first-row elements, and the 1s, 2s, and 2p orbitals for the second-row elements. The s terms arise from the s valence orbitals, and p_z is the axial p orbital. The perpendicular (p_x and p_y) orbitals at C and X may take positive (p^+) and negative (p^-) linear combinations, and each is degenerate.



The most interesting changes for the hydrogens are seen with the p^+ and p^- orbitals. The two sets of MOs have similar hydrogen populations with X = CH_3, and with most of the other substituents, the p^+ population is considerably larger than that for p^-. However, with the strongly electronegative groups, N_2^+, F, and NH_3^+, the hydrogen population for p^- is considerably greater than for p^+. In all cases, p^+ has a lower energy than p^-. Normally, the hydrogens would prefer the more strongly bonding molecular orbitals, and it is only the very strongly electronegative groups that can compete with the hydrogens and effectively utilize the more strongly bonding orbitals.

The above discussion has been concerned with the compounds that have C_{3v} symmetry. There is another large group of substituted methanes that have C_s symmetry. The 6-31G*-optimized geometries along with the energies are summarized in Table VI. One interesting feature of these compounds is that the methyl hydrogens which are trans to a lone pair are relatively long, and that the methyl group is tilted toward the lone pairs.[22] These features are well reproduced by the calculations. They may be ascribed to the repulsion between the lone pairs and the backside of the CH orbitals at the adjacent carbon.[8] Evidence for this view is found in the observation that rotation about the C–N bond in methylamine does not lead to significant charge redistribution between C and N, but does lead to charge shifts between C and H.[8]



In the case of nitromethane, both the rotamer with a hydrogen eclipsed with an oxygen and that with the groups staggered were examined. In accord with experimental data,[23] the difference in energy between the two rotamers was essentially zero. The two rotamers of methylaluminum hydride also were examined, and the one having an Al–H eclipsed with a methyl C–H was found to have the lower energy by a small amount.

The bond properties for this group of compounds are summarized in Table VII in the same fashion as for the compounds with C_{3v} symmetry. The changes in bond properties parallel those

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Table V. Components of the Electron Populations for Compounds with C_{3v} Symmetry[a]

X	atom	core	s	p^+	p_z	p^-	sum
N_2^+	C	2.000	1.406	0.549	0.159	1.496	5.610
	H	0.000	0.215	0.131	0.029	0.476	0.850
	CH_3	2.000	2.049	0.940	0.247	2.924	8.160
	N	2.000	2.552	1.985	0.371	0.489	7.397
	N	2.000	1.399	1.075	1.382	0.587	6.443
F	C	1.999	1.032	0.769	0.382	0.951	5.133
	H	0.000	0.211	0.231	0.086	0.514	1.041
	CH_3	1.999	1.665	1.461	0.639	2.494	8.257
	F	2.001	2.335	2.539	1.361	1.506	9.743
NC	C	2.000	1.490	1.452	0.022	0.320	5.284
	H	0.000	0.294	0.516	0.002	0.194	1.006
	CH_3	2.000	2.372	2.996	0.028	0.906	8.303
	N	2.004	3.250	0.928	0.212	2.484	8.880
	C	1.996	0.378	0.076	1.758	0.612	4.818
NH_3^+	C	2.000	1.071	0.230	0.518	1.676	5.496
	H	0.000	0.174	0.048	0.102	0.622	0.947
	CH_3	2.000	1.595	0.374	0.827	3.542	8.337
	N	2.000	2.114	2.735	1.084	0.315	8.244
	H	0.000	0.097	0.297	0.030	0.049	0.473
O^-	C	1.999	1.086	1.267	0.298	0.144	4.794
	H	0.000	0.303	0.601	0.052	0.288	1.244
	CH_3	1.999	1.994	3.071	0.455	1.007	8.256
	O	2.001	2.006	0.930	1.545	2.993	9.475
CN	C	2.000	1.751	1.663	0.075	0.168	5.657
	H	0.000	0.293	0.594	0.008	0.098	0.994
	CH_3	2.000	2.630	3.445	0.100	0.463	8.638
	C	1.996	1.471	0.361	0.144	0.858	4.830
	N	2.004	1.899	0.194	1.756	2.679	8.532
Cl	C	2.000	1.270	1.691	0.529	0.183	5.673
	H	0.000	0.233	0.601	0.062	0.108	1.003
	CH_3	2.000	1.969	3.494	0.715	0.506	8.684
	Cl	10.000	2.031	0.506	1.285	3.494	17.316
C≡CH	C	2.000	1.240	1.682	0.631	0.114	5.666
	H	0.000	0.210	0.634	0.101	0.080	1.025
	CH_3	2.000	1.871	3.584	0.934	0.353	8.743
	C	2.000	1.451	0.345	0.688	1.602	6.086
	C	2.000	1.948	0.070	0.256	2.004	6.277
	H	0.000	0.731	0.000	0.121	0.041	0.894
CH_3	C	2.000	1.266	0.984	0.784	0.765	5.763
	H	0.000	0.245	0.339	0.084	0.412	1.079
	CH_3	2.000	2.000	2.000	1.000	2.000	9.000
S^-	C	2.000	1.420	1.638	0.732	0.105	5.896
	H	0.000	0.286	0.725	0.058	0.061	1.131
	CH_3	2.000	2.277	3.814	0.906	0.289	9.287
	S	10.000	1.723	0.186	1.094	3.711	16.713
SiH_3	C	2.006	1.512	1.719	1.187	0.716	6.601
	H	0.000	0.249	0.645	0.078	0.076	1.048
	CH_3	2.006	2.261	3.650	1.425	0.404	9.746
	Si	9.971	0.463	0.062	0.167	0.329	10.994
	H	0.008	0.423	0.096	0.136	1.089	1.752
BcH	C	2.008	1.668	1.802	1.191		6.669
	H	0.000	0.266	0.728	0.075		1.069
	CH_3	2.008	2.465	3.986	1.416		9.875
	Be	1.986	0.164	0.008	0.095		2.254
	H	0.006	1.371	0.006	0.489		1.872
Li	C	2.011	1.187	1.699	1.609		6.506
	H	0.000	0.270	0.766	0.096		1.132
	CH_3	2.011	1.197	3.997	1.897		9.902
	Li	1.988	0.004	0.004	0.100		2.097
Na	C	2.019	1.177	1.682	1.511		6.388
	H	0.000	0.273	0.771	0.089		1.133
	CH_3	1.019	1.995	3.994	1.779		9.787
	Na	9.981	0.005	0.006	0.221		10.213
MgH	C	2.013	1.222	1.772	1.541		6.550
	H	0.000	0.256	0.738	0.090		1.087
	CH_3	2.013	1.990	3.990	1.816		9.811
	Mg	9.972	0.010	0.009	0.379		10.370
	H	0.014	0.000	0.000	1.806		1.820

[a] The populations p^+ and p^- correspond to the positive and negative linear combinations of the p orbitals (p_x and p_y) perpendicular to the C_3 axis (z direction): p_z is the population for the p component along the z axis and 2s is the population for the 2s orbitals, which do not mix significantly with the p orbitals.

seen with the previous group of compounds. Finally, the electron populations are presented in Table VIII. Again, the compounds are arranged in order of increasing electron population at the methyl group.

A number of interesting comparisons among groups may be made. One concerns acetic acid and methanesulfonic acid. The oxygen populations and the methyl group populations are quite similar for the two acids, and the central atom (C or S, respectively) bears a relatively large positive charge. The ellipticity of a bond is a good indicator of double-bond character since ρ will decrease more slowly in the direction of a π bond than in the direction normal to this bond. As an example, the C=C bond of propene has $\epsilon = 0.467$. The low ellipticity of the C–O and S–O bonds suggests little double-bond character for these bonds, and they might best be considered as ionic single bonds.[24] The same is true for other formal C=O bonds as in acetaldehyde.

As far as the difference in pK_a between the two acids is concerned, it may be noted that the electron population for the acidic hydrogen of the sulfonic acid is smaller than that for acetic acid, and correspondingly, its total energy is less by 10.4 kcal/mol. Since the energy of the hydrogen goes to zero as it is lost as a proton, one factor in the difference in acidity is that the energy change for the proton of the sulfonic acid is less than that for the carboxylic acid. In addition, the negative charge is spread over three oxygens in the sulfonate ion vs two oxygens in the carboxylate ion.

It is difficult to appreciate the relationships between the electronegativity of the substituents and the charge density at the methyl groups by just examining Tables IV and VIII. Therefore, the data for the methyl metal hydrides are presented in a pictorial form in Figure 6. Here, the electron populations have been converted to the equivalent charges by subtracting the population from the atomic number (or the nuclear charge). The charges for each of the atoms are shown along with the net methyl group charges.

In the first row, there is extensive charge transfer from lithium to carbon leading to a species best described as $CH_3^-Li^+$. Both beryllium and boron have similar characteristics. The charges on beryllium and boron are greater than that for lithium because they are attached to a larger number of relatively electronegative atoms. The small charges found with methane show that carbon and hydrogen have about the same electronegativity, with the latter being slightly more electron attracting. This is seen in the above hydrides where the hydrogens bear a somewhat larger negative charge than the carbons.

As one passes to the left of the figure, the first-row elements become more electronegative than carbon. Correspondingly, the methyl carbons now bear positive charges. With methyl fluoride, the charge shift from carbon to fluorine becomes quite large.

The second-row elements are generally considered to be less electronegative than the corresponding first-row elements, and the figure shows that this expectation is borne out. It can be seen that the effects of electronegativity are well demonstrated by the results of this investigation: in the locations of the bond critical points, in the differences between conventional and bond path angles, and in the atomic charges. There are some aspects of the latter that deserve further consideration, and this will be presented below.

The changes in population for the methyl group caused by the substituents may arise from either or both of the following factors. First, the substituent may cause the charge density to be increased or depleted in the vicinity of the methyl group as a result of electronegativity differences. Second, the substituent may cause the bond critical point to move so that the size of the volume element attributed to the methyl group may change, resulting in a change in population. We were interested in gaining information on the relative importance of these two factors.

One way in which to gain a visual picture of the charge distribution for simple molecules is to prepare projection density plots of the type described by Streitwieser.[25] Here, the charge density

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[24] This conclusion concerning S–O bonds in sulfonyl compounds is in accord with the study of: Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

Table VI. Energies and Structures of Methyl Derivatives with C_s Symmetry[a]

X	6-31G*	6-31G**	r_{CH_a}	r_{CH_b}	H_aCX	H_bCX	α	r_{CX}	others	
BH_2	−65.44155	−65.44874	1.0944	1.0855	106.34	113.95	−5.07	1.567	BH 1.1927	CBH 121.02
NH_2	−95.20983	−95.22175	1.0894	1.0840	114.75	109.18	+3.71	1.4531	NH 1.0013	CNH 110.67
			(1.099)		(110.3)		(+2.9)	(1.471)	(1.010)	(110.3)
OH	−115.03542	−115.04669	1.0811	1.0875	107.17	112.05	−3.25	1.3998	OH 0.9463	COH 109.45
		−115.05251[b]	1.0812	1.0872	107.12	110.53		1.4014	OH 0.9423	COH 110.53
			(1.094)				(−3.2)	(1.421)	(0.963)	(108.0)
C_2H_3	−117.07147	−117.08161	1.0843	1.0870	111.43	110.90	+0.35	1.5026	C=C 1.3184	CCC 125.24
			(1.085)	(1.098)	(111.2)			(1.501)	(1.336)	(124.3)
CHO	−152.91596	−152.92258	1.0815	1.0869	110.10	109.88	+0.29	1.5048	C=O 1.1878	CCO 124.47
			(1.086)		(115.3)			(1.501)	(1.216)	(123.9)
OMe	−154.06474	−154.07410	1.0813	1.0889	107.65	111.49	−2.57	1.3912	COC 113.80	
			(1.091)	(1.110)	(107.2)	(110.8)		(1.410)	(111.7)	
NO	−168.82954	−168.83439	1.0819	1.0839	111.21	107.33	+2.58	1.4640	NO 1.1766	CNO 113.83
			(1.084)		(107.2)			(1.489)	(1.224)	(117.4)
NO_2	−243.66198	−243.66689	1.0801	1.0765	106.77	107.93	−0.77	1.4787	NO 1.1916	CNO 117.11
			(1.088)		(107.2)			(1.489)	(1.224)	(117.4)
NO_2	−243.66198	−243.66688	1.0754	1.0789	108.46	107.02	+0.96	1.4787	NO 1.1908, 1.1923	
AlH_2	−282.66296	−282.76012	1.0865	1.0895	112.95	111.18	+1.18	1.9723	AlH 1.5885	CAlH 121.37
PH_2	−381.48626	−381.49543	1.0824	1.8044	113.39	109.10	+2.86	1.8607	PH 1.4042	CPH 98.67
			(1.094)		(109.6)		(+2.0)	(1.858)	(1.423)	(96.5)
SH	−437.70032	−437.70885	1.0803	1.0814	107.58	110.81	−2.15	1.8186	SH 1.3265	CSH 97.65
			(1.092)		(109.2)			(1.814)	(1.335)	(96.5)
CO_2^-	−227.22506	−227.22987	1.0859	1.0887	112.00	109.74	+1.51	1.5541	CO 1.2335, 1.2352	
CO_2H	−227.81065	−227.82215	1.0794	1.0839	109.56	109.66	−0.07	1.5079	C=O 1.187	C-O 1.332
			(1.090)		(109.4)			(1.494)	(1.209)	(1.357)
SO_3H	−662.21811	−662.23013	1.0812	1.0797	106.78	109.03	−1.50	1.7608	SO 1.5905, 1.4244	
dimers										
Li	−94.09892	−94.10903	1.1008	1.0962	116.18	134.37		2.1467		
BeH[c]	−109.66521	−109.67790	1.088	1.091	113.23	111.62		1.7085		
BH_2[c]	−130.90518	−130.92047	1.0872	1.0868	110.50	112.02		1.5911	BH 1.3207, 1.1906	

[a] The energies are given in hartrees, the geometries are given in angstroms and degrees, and α is the methyl tilt angle defined as $2(\alpha_1 - \alpha_2)/3$ where α_1 is the X–C–H angle to the unique hydrogen, and α_2 is the other X–C–H angle. H_a is the unique hydrogen, and H_b is one of a pair of equivalent hydrogens. [b] Calculated by using the 6-311++G** basis set. [c] The angles from carbon to hydrogen are referred to the center of the ring formed by Be and H or B and H.

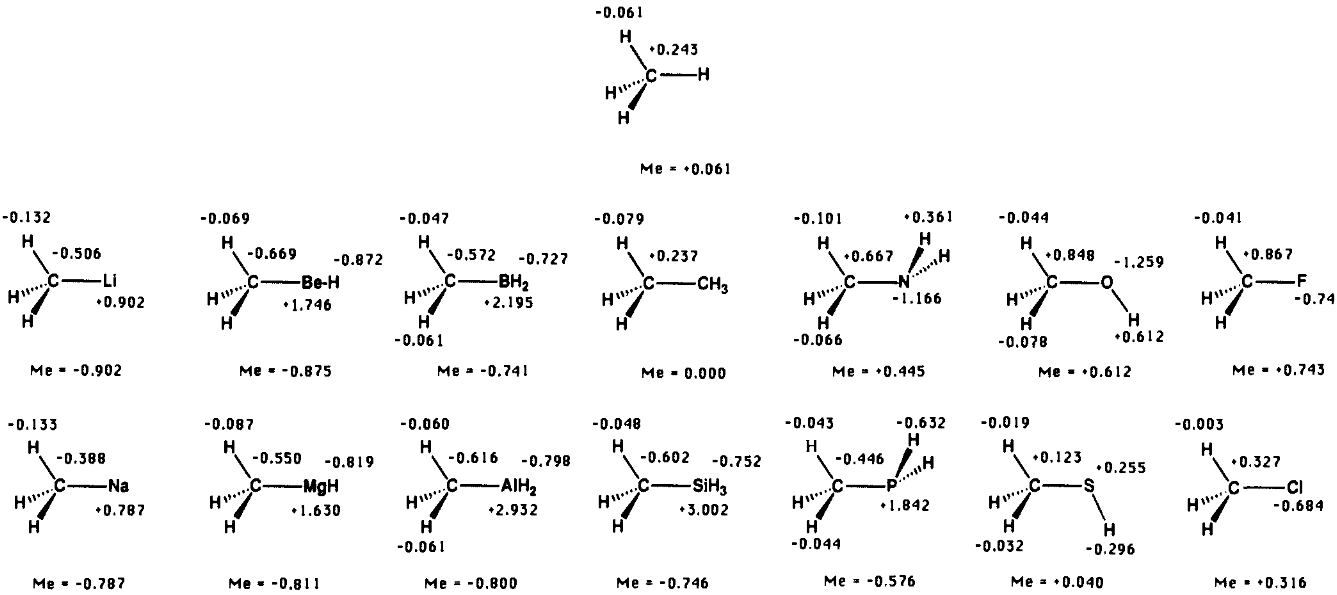

Figure 6. Atomic charges for the methyl metal hydrides.

above and below a given point in a plane containing a HCX group is summed and assigned to that point. Contour plots of the projection density for several substituted methanes are shown in Figure 7. One might first note the remarkable similarity of the methyl groups in the region away from the substituent. In the direction of the substituent, there are marked changes. The bond critical points are marked on the plots, and it can be seen that they appear at intuitively reasonable places. The movement of the bond critical point in response to the electronegativity of the substituent is apparent. It is clear from these data that much of the changes in population results from the movement of the bond critical point, and the corresponding movement of the zero-flux surface, which passes through the critical point.

In order to obtain more quantitative information on the relative roles of charge shifts and bond path shifts, we have chosen to compare a number of the compounds with ethane. Here, all of the compounds were oriented so that the methyl carbons had a common origin, and then the zero-flux surface for the C–C bond of ethane was used to separate the Me and X parts of the molecules. The electron population within the methyl group volume element was obtained by numerical integration of the charge density. The changes in these methyl group populations with a change in substituent (Δn(Me)) would largely be due to the charge

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(25) 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.

Table VII. Bond Properties for Methyl Derivatives with C_s Symmetry, 6-31G**[a]

X	bond	r_A	r_B	R	ρ_c	λ_1	λ_2	λ_3	ϵ
OH	C-H$_a$	0.6685	0.4126	1.620	0.2992	−0.8215	−0.7839	0.4303	0.048
	C-H$_b$	0.6654	0.4220	1.577	0.2937	−0.7937	−0.7537	0.4263	0.053
	C-O	0.4461	0.9541	2.139	0.2643	−0.5213	−0.5182	0.8653	0.006
	OH	0.7622	0.1842	4.139	0.3907	−2.0409	−1.9837	1.6177	0.029
NH$_2$	C-H$_a$	0.6602	0.4292	1.539	0.2885	−0.7557	−0.7285	0.4127	0.037
	C-H$_b$	0.6634	0.4206	1.577	0.2927	−0.7773	−0.7519	0.4163	0.034
	C-N	0.5358	0.9177	1.713	0.2776	−0.5668	−0.5555	0.1686	0.020
	N-H	0.7437	0.2578	2.885	0.3605	−1.3375	−1.2671	0.6594	0.056
OMe	C-H$_a$	0.6687	0.4127	1.620	0.2989	−0.8202	−0.7827	0.4291	0.048
	C-H$_b$	0.6673	0.4216	1.583	0.2925	−0.7888	−0.7505	0.4272	0.051
	C-O	0.4424	0.9494	2.146	0.2695	−0.5384	−0.5305	0.9322	0.015
NO	C-H$_a$	0.6731	0.4088	1.647	0.2950	−0.7928	−0.7741	0.4269	0.024
	C-H$_b$	0.6706	0.4134	1.622	0.2908	−0.7745	−0.7507	0.4190	0.032
	C-N	0.5369	0.9280	1.729	0.2866	−0.6093	−0.5839	0.1934	0.044
	N=O	0.5088	0.6681	1.313	0.5584	−1.4458	−1.3363	0.8711	0.082
NO$_2$	C-H$_a$	0.6779	0.4023	1.685	0.2961	−0.8084	−0.7811	0.4307	0.035
	C-H$_b$	0.6787	0.3978	1.706	0.3017	−0.8370	−0.8063	0.4348	0.038
	C-N	0.4780	1.0007	2.094	0.2581	−0.4819	−0.4475	0.3876	0.077
	N-O	0.5744	0.6172	1.074	0.5511	−1.4396	−1.2655	1.2833	0.138
NO$_2$	C-H$_a$	0.6781	0.3974	1.706	0.3017	−0.8355	−0.8005	0.4382	0.044
	C-H$_b$	0.6756	0.4034	1.675	0.2924	−0.7966	−0.7618	0.4402	0.046
	C-N	0.4787	1.0006	2.093	0.2581	−0.4751	−0.4422	0.3868	0.075
	N-O$_d$	0.5748	0.6160	1.072	0.5311	−1.3479	−1.2890	1.3324	0.046
	N-O$_e$	0.5768	0.6156	1.067	0.5339	−1.3733	−1.2987	1.3260	0.058
CH=CH$_2$	C-H$_a$	0.6613	0.4231	1.563	0.2879	−0.7410	−0.7345	0.4063	0.009
	C-H$_b$	0.6624	0.4245	1.560	0.2852	−0.7304	−0.7228	0.4061	0.011
	C-C	0.7651	0.7375	1.037	0.2662	−0.5248	−0.5104	0.2992	0.028
	C-H	0.6608	0.4183	1.580	0.2947	−0.7742	−0.7662	0.4067	0.010
	C=C	0.6488	0.6697	1.032	0.3637	−0.8211	−0.5599	0.1929	0.467
	C-H$_c$	0.6590	0.4180	1.577	0.2927	−0.7681	−0.7541	0.4012	0.019
	C-H$_d$	0.6590	0.4165	1.582	0.2940	−0.7748	−0.7594	0.4021	0.020
CHO	C-H$_a$	0.6691	0.4123	1.623	0.2910	−0.7603	−0.7567	0.4149	0.005
	C-H$_b$	0.6655	0.4215	1.579	0.2838	−0.7267	−0.7190	0.4055	0.011
	C-C	0.7268	0.7780	1.071	0.2736	−0.5623	−0.5408	0.3167	0.040
	C=O	0.3865	0.8014	2.074	0.4296	−1.2649	−1.1658	0.3186	0.085
	C-H	0.6809	0.4143	1.644	0.2961	−0.8096	−0.8050	0.4494	0.006
BH$_2$	C-H$_a$	0.6625	0.4319	1.534	0.2708	−0.6693	−0.6471	0.3860	0.034
	C-H$_b$	0.6590	0.4265	1.545	0.2820	−0.7144	−0.6968	0.3938	0.025
	C-B	1.0768	0.4975	2.164	0.1866	−0.4456	−0.3546	0.6950	0.257
	B-H	0.5040	0.6887	1.366	0.1811	−0.4595	−0.3551	0.6149	0.294
SH	C-H$_a$	0.6696	0.4107	1.630	0.2928	−0.7737	−0.7621	0.4164	0.015
	C-H$_b$	0.6687	0.4127	1.621	0.2931	−0.7745	−0.7612	0.4197	0.018
	C-S	0.8536	0.9650	1.130	0.1848	−0.2893	−0.2650	0.1941	0.092
	S-H	0.6748	0.6518	1.035	0.2227	−0.3579	−0.2657	0.1008	0.347
PH$_2$	C-H$_a$	0.6640	0.4184	1.587	0.2878	−0.7381	−0.7348	0.4057	0.005
	C-H$_b$	0.6644	0.4200	1.582	0.2858	−0.7299	−0.7240	0.4034	0.008
	C-P	1.1732	0.6878	1.706	0.1536	−0.2087	−0.1822	0.3695	0.146
	P-H	0.6657	0.7394	1.111	0.1630	−0.2567	−0.2239	0.5846	0.147
AlH$_2$	C-H$_a$	0.6590	0.4275	1.541	0.2783	−0.6992	−0.6699	0.3862	0.044
	C-H$_b$	0.6590	0.4305	1.531	0.2746	−0.6826	−0.6521	0.3818	0.047
	C-Al	1.2005	0.7719	1.555	0.0826	−0.1144	−0.1096	0.5777	0.044
	Al-H	0.7811	0.8074	1.034	0.0781	−0.1156	−0.1128	0.5130	0.251
SO$_3$H	C-H$_a$	0.6777	0.4036	1.679	0.2302	−0.7752	−0.7680	0.4216	0.009
	C-H$_b$	0.6774	0.4024	1.683	0.2936	−0.7826	−0.7753	0.4242	0.010
	C-S	0.7613	0.9996	1.313	0.2302	−0.4111	−0.4084	0.2407	0.007
	S-O	0.6001	0.9909	1.651	0.2215	−0.3902	−0.3811	1.2200	0.024
	S=O	0.5518	0.8727	1.582	0.3094	−0.6017	−0.5728	2.7758	0.051
	O-H	0.7807	0.1749	4.458	0.3691	−2.0293	−1.9932	1.6031	0.018
CO$_2^-$	C-H$_a$	0.6521	0.4338	1.503	0.2842	−0.7145	−0.7107	0.3891	0.005
	C-H$_b$	0.6518	0.4369	1.492	0.2797	−0.6983	−0.6844	0.3842	0.020
	C-C	0.8151	0.7389	1.103	0.2511	−0.5135	−0.4864	0.3104	0.056
	C-O$_1$	0.3995	0.8340	2.088	0.3976	−1.1372	−1.0852	2.3163	0.048
	C-O$_2$	0.4001	0.8350	2.087	0.3970	−1.1298	−1.0842	2.2786	0.042
CO$_2$H	C-H$_a$	0.6685	0.4109	1.627	0.2934	−0.7740	−0.7652	0.4174	0.011
	C-H$_b$	0.6681	0.4158	1.607	0.2872	−0.7452	−0.7361	0.4124	0.012
	C-C	0.6943	0.8076	0.860	0.2763	−0.5758	−0.5424	0.2958	0.062
	C=O	0.3878	0.7994	0.485	0.4403	−1.3360	−1.2035	3.0079	0.110
	C-O	0.4232	0.9091	0.465	0.3104	−0.8172	−0.7298	1.4604	0.120
	O-H	0.7754	0.1770	4.382	0.3801	−2.0805	−2.0407	1.6408	0.020
(CH$_3$Li)$_2$	C-H$_a$	0.6530	0.4506	1.443	0.2607	−0.6188	−0.5698	0.3556	0.086
	C-H$_b$	0.6510	0.4452	1.462	0.2660	−0.6418	−0.5957	0.3609	0.077
	C-Li	1.4004	0.7491	1.870	0.0288	−0.0404	−0.0364	0.2207	0.190
(CH$_3$BH$_2$)$_2$	C-H$_a$	0.6588	0.4284	1.539	0.2802	−0.7040	−0.6900	0.3923	0.020
	C-H$_b$	0.6587	0.4281	1.539	0.2801	−0.7034	−0.6900	0.3915	0.020
	C-B	1.0875	0.5040	2.158	0.1826	−0.3859	−0.3576	0.6042	0.079
	B-H$_a$	0.5249	0.8276	1.577	0.1178	−0.1736	−0.1111	0.4810	0.562
	B-H$_b$	0.5045	0.6862	1.360	0.1813	−0.4106	−0.3799	0.6070	0.086

[a] Values as given in Table III.

shift, and the difference between the correct methyl populations and the ones obtained by using the ethyl group volume element (n(Me − T)) could be assigned to the shift of the bond critical point. The results of this analysis are shown in Table IX, and

Table VIII. Atom Properties of Methyl Derivatives with C_s Symmetry[a]

compound	atom	n_T	L	$T = -E$
CH_3NCO	CH_3	8.3469	0.0003	39.3232
$-V/T = 2.002\,084$	C	5.2742	-0.0028	37.3748
$E = -206.7959$	H_a	1.0338	0.0001	0.6525
$\Delta E = 0.25$	H_b	1.0205	0.0001	0.6475
	N	8.7864	0.0000	55.5306
	C	3.4683	0.0001	36.2749
	O	9.3986	0.0000	75.6676
sum		30.0002		206.7963
CH_3OCH_3	CH_3	8.3475	-0.0001	39.8273
$-V/T = 2.001\,25$	C	5.1508	0.0001	37.2917
$E = -154.0741$	H_a	1.0431	0.0001	0.6581
$\Delta E = -0.27$	H_b	1.0768	0.0001	0.6687
	O	9.3046	0.0001	75.4992
sum		29.9996		154.0737
CH_3OH	CH_3	8.3523	0.0000	39.2983
$-V/T = 2.001\,650$	C	5.1519	0.0008	37.2956
$E = -115.0467$	H_a	1.0438	0.0000	0.6595
$\Delta E = 0.10$	H_b	1.0780	0.0001	0.6718
	O	9.2594	-0.0001	75.3960
	H	0.3880	0.0001	0.3522
sum		17.9997		115.0465
CH_3NO_2 (eclipsed)	CH_3	8.3667	-0.0001	39.4387
$-V/T = 2.002\,067$	C	5.4367	-0.0015	37.5604
$E = -243.6669$	H_a	0.9751	0.0001	0.6280
$\Delta E = 0.31$	H_b	0.9778	0.0001	0.6250
	N	6.5358	0.0011	54.0938
	O_1	8.5439	0.0001	75.0657
	O_2	8.5527	0.0001	75.0692
sum		31.9991		243.6674
CH_3NO_2 (staggered)	CH_3	8.3666	0.0001	39.4390
$-V/T = 2.002\,067$	C	5.4377	-0.0047	37.5604
$E = -243.6669$	H_a	0.9797	0.0001	0.6241
$\Delta E = 0.69$	H_b	0.9755	0.0001	0.6269
	N	6.5363	0.0002	54.0932
	O	8.5483	0.0007	75.0679
sum		31.9965		243.6680
CH_3N_3	CH_3	8.4631	0.0001	39.4237
$-V/T = 2.002\,258$	C	5.3470	-0.0042	37.4623
$E = -202.8725$	H_a	1.0201	0.0001	0.6475
$\Delta E = 0.31$	H_b	1.0496	0.0001	0.6565
	N_1	6.6246	0.0000	53.9118
	N_2	7.4843	0.0003	55.0938
	N_3	7.4279	0.0000	54.4437
sum		29.9999		202.8730
CH_3NO	CH_3	8.5154	-0.0001	39.5071
$-V/T = 2.001\,987$	C	5.4612	-0.0021	37.5910
$E = -168.8344$	H_a	1.0172	0.0001	0.6400
$\Delta E = 0.14$	H_b	1.0195	0.0001	0.6380
	N	6.9291	0.0016	54.2277
	O	8.5544	0.0002	75.0998
sum		23.9989		168.8346
CH_3NH_2	CH_3	8.5549	-0.0004	39.4137
$-V/T = 2.001\,195$	C	5.3227	0.0003	37.4095
$E = -95.2219$	H_a	1.1006	0.0001	0.6776
$\Delta E = 0.31$	H_b	1.0657	0.0001	0.6636
	N	8.1660	-0.0001	54.8365
	H	0.6395	0.0001	0.4856
sum		17.9999		95.2214
CH_3SO_3H	CH_3	8.8215	0.0001	39.6601
$-V/T = 2.001\,590$	C	5.8963	0.0006	37.8086
$E = -662.2301$	H_a	0.9752	0.0001	0.6162
$\Delta E = 1.19$	H_b	0.9747	0.0001	0.6177
	S	12.4488	0.0051	395.3737
	O_1	9.3755	0.0001	75.5456
	O_2	9.5151	-0.0001	75.6750
	H	0.3210	0.0000	0.3026
sum		49.9970		662.2320
CH_3CO_2H	CH_3	8.8234	0.0000	39.6541
$-V/T = 2.001\,919$	C	5.7670	-0.0025	37.7454
$E = -227.8222$	H_a	1.0165	0.0001	0.6378
$\Delta E = 0.69$	H_b	1.0212	0.0001	0.6353
	C	4.0911	0.0023	36.5653
	=O	9.4054	0.0002	75.6888
	O	9.3388	-0.0020	75.5959
	H	0.3427	0.0000	0.3192
sum		32.0014		277.8233
CH_3CHO	CH_3	8.9162	-0.0001	39.6749
$-V/T = 2.001\,62$	C	5.8183	-0.0014	37.7584
$E = -152.9226$	H_a	1.0199	0.0001	0.6363
$\Delta E = 0.13$	H_b	1.0399	0.0001	0.6402
	C	4.7069	-0.0023	36.9900
	H	1.0508	0.0000	0.6591
	O	9.3275	0.0000	75.5984
sum		24.0014		152.9224
$CH_3CH{=}CH_2$	CH_3	8.9509	0.0001	39.6150
$-V/T = 2.000\,65$	C	5.7616	-0.0001	37.6528
$E = -117.0816$	H_a	1.0641	0.0001	0.6556
$\Delta E = 0.10$	H_b	1.0626	0.0001	0.6533
	C	5.9756	-0.0001	37.7853
	H	1.0557	0.0001	0.6578
	C	5.9204	0.0002	37.7246
	H_c	1.0512	0.0001	0.6500
	H_d	1.0460	0.0001	0.6490
sum		23.9998		117.0818
CH_3SH	CH_3	8.9598	-0.0004	39.5789
$-V/T = 2.000\,38$	C	5.8769	0.0004	37.6506
$E = -437.7089$	H_a	1.0184	0.0001	0.6371
$\Delta E = 0.25$	H_b	1.0319	0.0001	0.6458
	S	15.7447	-0.0002	397.3840
	H	1.2956	0.0001	0.7456
sum		26.0001		437.7085
$CH_3CO_2^-$	CH_3	9.1718	0.0000	39.7560
$-V/T = 2.001\,370\,4$	C	5.8378	-0.0054	37.7376
$E = -227.2299$	H_a	1.1142	0.0001	0.6756
$\Delta E = 0.06$	H_b	1.1132	0.0001	0.6731
	C	3.8200	-0.0008	36.3276
	-O	9.5011	0.0003	75.5714
	-O	9.5074	0.0003	75.5750
sum		32.0003		227.2300
CH_3PH_2	CH_3	9.5762	-0.0004	39.8415
$-V/T = 2.000\,42$	C	6.4459	-0.0004	37.9101
$E = -381.4854$	H_a	1.0442	0.0001	0.6459
$\Delta E = 1.31$	H_b	1.0430	0.0001	0.6429
	P	13.1573	-0.0008	339.9476
	H	1.6324	0.0002	0.8521
sum		25.9983		381.4933
CH_3BH_2	CH_3	9.7414	-0.0001	39.9291
$-V/T = 1.999\,98$	C	6.5717	0.0000	38.0028
$E = -65.448\,74$	H_a	1.0469	0.0001	0.6315
$\Delta E = 0.01$	H_b	1.0612	0.0001	0.6476
	B	2.8048	0.0000	23.7360
	H	1.7271	0.0000	0.8917
sum		16.0004		65.4488
CH_3AlH_2	CH_3	9.7996	-0.0002	39.7713
$-V/T = 2.000\,241\,4$	H	6.6159	0.0006	37.8488
$E = -282.6701$	H_a	1.0602	0.0001	0.6427
$\Delta E = 0.13$	H_b	1.0613	0.0001	0.6401
	Al	10.6076	-0.0018	241.4135
	H_a	1.7978	0.0000	0.7425
	H_b	1.7984	0.0000	0.7426
sum		24.0027		282.6699
$(CH_3Li)_2$	CH_3	9.9033	-0.0001	39.6633
$-V/T = 1.999\,916$	C	6.5100	0.0010	37.6875
$E = -94.1093$	H_a	1.1385	0.0001	0.6585
$\Delta E = 0.06$	H_b	1.1268	0.0001	0.6587
	Li	2.0965	-0.0001	7.3920
sum		23.9996		94.1094
$(CH_3BH_2)_2$	CH_3	9.7184	-0.0001	39.9044
$-V/T = 1.999\,80$	C	6.5195	0.0001	37.9579
$E = -130.9205$	H_a	1.0649	0.0001	0.6480
$\Delta E = 1.3$	H_b	1.0621	0.0001	0.6461
	H_c	1.0717	0.0001	0.6528
	B	2.8505	-0.0026	23.7146
	H	1.7220	0.0001	0.9550 (bridging H)
	H_d	1.7101	0.0001	0.8852
sum		32.0020		130.9184

[a] Definitions as given in Table IV.

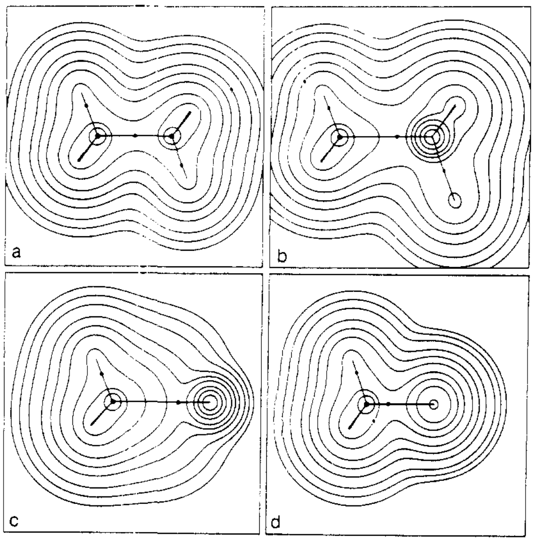

Figure 7. Projection density plots for (a) ethane, (b) methylsilane, (c) methyllithium, and (d) methyl fluoride.

CH_3Li	CH_3BeH	CH_3BH_2	CH_3CH_3	CH_3NH_2	CH_3OH	CH_3F
-0.123	-0.050	-0.030	0.000	0.037	0.102	0.219
-0.779	-0.825	-0.711	0.000	0.408	0.546	0.524

CH_3Na	CH_3MgH	CH_3AlH_2	CH_3SiH_3	CH_3PH_2	CH_3SH	CH_3Cl
-0.074	-0.056	-0.033	0.005	0.059	0.147	0.265
-0.713	-0.755	-0.767	-0.751	-0.635	-0.107	0.051

Figure 8. Changes in methyl group charges. The upper line gives the shift in charge with respect to ethane for a methyl group volume element defined by ethane, and the second line gives the difference between the total charge and the charge density shift component and corresponds to the change produced by the shift of the bond critical point. See text for a comment on the comparison of first- and second-row groups.

for the compounds in Figure 6, the charge shift and bond critical point shift components are shown in Figure 8.

An examination of the figure shows that the charge shift term changes steadily across the periodic table. However, the bond critical point shift term changes very quickly when there is a difference in electronegativity. There is a limit to how large this term may become, because the bond critical point cannot move into the region in which the charge density increases rapidly near the nucleus. The data in the figure suggest that it moves almost as far as possible with any significant difference in electronegativity. The data for the first-row and second-row substituents may not be quite comparable as suggested by the positive value for the charge shift term for SiH_3 when it might have been expected to be negative since it should be less electronegative than carbon. It might have been appropriate to use a slightly larger methyl group size for the second-row elements since the bonds are relatively long and ρ_c is relatively low. However, comparisons across the rows should still be appropriate.

The largest charge shift term was found with methyldiazonium ion (0.576), and as noted above, it might best be considered as a methyl cation coordinated with nitrogen. The charge shifts toward carbon are much smaller, the largest value being found with lithium (0.123e). This should be expected since a methyl group is coordinatively saturated, and so it should be difficult to add much extra charge density. On the other hand, there is nothing preventing a methyl group from transferring charge density to an electronegative substituent.

We close by examining the difference in electron populations between the monomeric and dimeric forms of methyllithium, methylberyllium hydride, and methylborane (Tables VII and VIII). The first two normally exist as higher aggregates,[26] but the dimer should show the nature of the interactions that lead to the aggregates. Methylborane is normally a dimer.[26]

Table IX. Charge Shifts for Methyl Groups with Respect to Ethane[a]

compd	n_T	n(Me)	Δn(Me)	n(Me - T)
$CH_3N_2^+$	8.1603	8.4241	0.5759	0.2638
$CH_3NH_3^+$	8.3369	8.6712	0.3288	0.3343
CH_3Cl	8.6839	8.7348	0.2652	0.0509
CH_3F	8.2573	8.7808	0.2192	0.5235
CH_3NO_2	8.3667	8.7828	0.2172	0.4161
CH_3NC	8.3025	8.8226	0.1774	0.5201
CH_3CNO	8.5928	8.8498	0.1502	0.2570
CH_3SH	8.9598	8.8526	0.1474	-0.1072
CH_3CN	8.6377	8.8638	0.1362	0.2261
CH_3NO	8.5154	8.8960	0.1040	0.3806
CH_3OH	8.3525	8.8979	0.1021	0.5456
$CH_3C{\equiv}CH$	8.7427	8.9253	0.0747	0.1826
CH_3PH_2	9.5762	8.9415	0.0585	-0.6347
CH_3CF_3	8.7758	8.9414	0.0581	0.1661
CH_3NH_2	8.5549	8.9631	0.0369	0.4082
$CH_3SO_3^-$	9.1163	8.9854	0.0146	-0.1309
CH_3SiH_3	9.7463	8.9951	0.0049	-0.7512
CH_3CH_3	9.0000	9.0000	0.0000	0.0000
CH_3BH_2	9.7414	9.0300	-0.0300	-0.7114
CH_3AlH_2	9.7996	9.0326	-0.0326	-0.7670
CH_3S^-	9.2871	9.0483	-0.0483	-0.2388
CH_3BeH	9.8749	9.0500	-0.0500	-0.8249
CH_3MgH	9.8112	9.0560	-0.0560	-0.7552
CH_3Na	9.7869	9.0744	-0.0744	-0.7125
CH_3Li	9.9019	9.1234	-0.1234	-0.7785

[a] The quantities are as follows: n_T, the total electron population for the methyl group; n(Me), the population for the methyl group using the volume element appropriate for the methyl group of ethane; Δn(Me), the change in n(Me) from that found in ethane; and n(Me - T), the difference between n(Me) and n_T.

With methyllithium, the dimer is calculated to be 42.1 kcal/mol more stable than the monomer,[27] but the electron populations are virtually the same as those for the monomer. This is in good accord with the ideas that bonding in alkyllithiums is essentially ionic,[18] and that dimer formation results from a dipole-dipole interaction. The dimer of methylberyllium hydride was found to have a very soft potential energy surface with a considerable variation in structure within a 1 × 10^{-5} hartree energy range. We have been unable to locate the true minimum and therefore the electron populations have not been obtained. The energy of the dimer is 21.1 kcal/mol less than that of two monomers. The structure of methylborane dimer, with bridging hydrogens, was easily located. Except for the bridging hydrogens, the electron populations were quite similar to those of the monomer. Here, the dimer was calculated to be 14.4 kcal/mol more stable than the monomer.

Calculations. The ab initio calculations were carried out by use of GAUSSIAN82[28] and GAUSSIAN86[29] with standard basis sets. The numerical integrations of the charge density was carried out by using PROAIMS.[30]

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(27) The estimate of the binding energy should include a correction for electron correlation. However, since the interaction appear to be largely Coulombic, the HF energy difference should be a reasonable estimate.

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