oretical calculation, could not be ruled out. This is an aspect of the more general problem of demonstrating that a species is actually kinetically stable in its presumed symmetry. Unfortunately, even when structural and spectral data are available, crystal packing forces, the locations of counterions, thermal motions, imprecise positioning of hydrogens in X-ray structures, and incomplete or erroneous assignment of fundamental vibrational frequencies in Raman and infrared spectra can all lead to incorrect or ambiguous conclusions. Similarly, microwave spectroscopy and electron diffraction have limitations in their ranges of utility. Thus, theoretical confirmation by a reliable computational method has become desirable.

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Structures and Charge Distributions in Alkoxide Ions

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Abstract: The structures of methoxide ion, ethoxide ion, *tert*-butoxide ion, fluoromethoxide ion, and trifluoromethoxide ion were obtained via geometry optimizations with the 6-31G* and 6-311++G** basis sets. In all cases, the carbon–oxygen bond shortened about 0.1 Å on going from the alcohol to the alkoxide ion, whereas the bonds attached to the alcohol carbon increased in length. The origin of the changes in bond lengths was studied with use of Bader's theory of atoms in molecules. Two types of interactions were found. With C–H or C–C bonds, the oxygen in the alkoxide ions was found to repel charge from the adjacent carbon, and onto the groups attached to this carbon. This results in a larger volume element for the ion and a decrease in the classical electrostatic energy. The coulombic attraction between the alkoxy oxygen and the carbon leads to a shorter bond. With C–F bonds, the charge polarization is so large that little further polarization can occur on going to the alkoxide ion. Here, charge transfer from the oxygen to the electron-deficient carbon was found. The energy changes in the ionization of the alcohols and of acetic acid were studied. The change in energy of the hydroxy proton on ionization accounts for half of the difference in ionization energy of ethanol and acetic acid.

It has been found from X-ray crystallographic studies that the C–O bond of trifluoromethoxide ion is unusually short and that the C–F bonds are unusually long, compared to those of trifluoromethanol. Ab initio calculations reproduced the experimental result.[1] We should like to report that these structural features are not unique to this alkoxide ion, but they are generally found.

Geometry optimization of methoxide ion with the 6-31G* basis set[2] gave $r(\mathrm{CO}) = 1.311$ Å and $r(\mathrm{CH}) = 1.133$ Å as compared to the values for methyl alcohol of $r(\mathrm{CO}) = 1.400$ and $\mathrm{r(CH)} = 1.085$ Å (av) (Table I).[3] It was possible that the short CO bond length arose from an inadequate basis set in which the oxygen makes use of some of the carbon orbitals in order to describe its relatively diffuse charge distribution. Therefore, the optimizations were repeated with the 6-311++G** basis set which is triple-ζ for the valence electrons and includes both diffuse functions and polarization functions at all atoms. The methanol geometry was essentially unchanged, and the methoxide ion had somewhat less extreme structural changes (Table I). The CO bond length was still 0.074 Å less than that for methanol, and the CH length was 0.038 Å greater.

The geometry changes were clearly due to the charge at oxygen, for lithium methoxide had a calculated structure much closer to that of methanol (Table I). As expected for an ion pair, the C-O-Li geometry was found to be linear.

The structures of ethoxide ion and ethanol, fluoromethoxide ion and fluoromethanol, as well as trifluoromethoxide ion and trifluoromethanol were obtained with both the 6-31G* and 6-311++G** basis sets. The gauche rotamer of fluoromethanol was found to be 4.9 kcal/mol more stable than the trans rotamer[4] with use of the 6-31G* basis. In the case of *tert*-butoxide ion and *tert*-butyl alcohol, it was not possible to use such a large basis set. Here, geometry optimizations were carried out with only the 6-31G* basis.

Before analyzing the origins of the structural changes, it is important to see whether or not key experimental data, the acidity of the alcohols, were satisfactorily reproduced by the calculations. Correction for electron correlation might be important in these cases that involve bond cleavage, and so the energies of methoxide ion and methanol were obtained with the Møller–Plesset perturbation theory through the fourth order (full MP4).[5] The energies are given in Table II and are converted to relative energies in Table III. The energy changes on ionization oscillated with increasing correction for electron correlation and averaged 395 kcal/mol with an uncertainity of about 2 kcal/mol.

Before comparing the result with the experimental value, it was necessary to correct for the loss of one O–H stretching mode and two C–O–H bending modes. Calculations of the vibrational frequencies for methanol and methoxide ion showed that the

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Table I. Calculated Structural Parameters[a]

compd	unit	6-31G*	6-311++G**	compd	unit	6-31G*	6-311++G**	compd	unit	6-31G*	6-311++G**
CH_3O^-	r_{CO}	1.311	1.326	t-BuO$^-$	r_{CO}	1.322		F_3CO^-	rCO	1.218	1.214
	r_{CH}	1.133	1.124		r_{CC}	1.561			rCF	1.386	1.384
	$\angle HCO$	116.52	115.21		r_{CH_a}	1.095			$\angle FCO$	116.61	116.54
CH_3OH	r_{CO}	1.400	1.400		r_{CH_b}	1.089		F_3COH	r_{CO}	1.331	1.328
	r_{CH_a}	1.081	1.082		$\angle CCO$	111.67			r_{CF_a}	1.304	1.301
	r_{CH_b}	1.088	1.088		$\angle H_aCC$	114.80			r_{CF_b}	1.320	1.317
	r_{OH}	0.946	0.940		$\angle H_bCC$	108.94			r_{OH}	0.950	0.945
	$\angle H_aCO$	107.17	107.27	t-BuOH	r_{CO}	1.416			$\angle F_aCO$	108.84	108.91
	$\angle H_bCO$	112.05	111.80		r_{CC_a}	1.523			$\angle F_bCO$	111.90	112.00
	$\angle COH$	109.45	110.01		r_{CC_b}	1.531			$\angle COH$	110.26	110.49
CH_3OLi	r_{CO}	1.358	1.361		r_{CH}	1.085(ave)		$MeCO_2^-$	r_{CO_a}	1.2335	1.2324
	r_{CH}	1.096	1.096		r_{OH}	0.948			r_{CO_b}	1.2351	1.2337
	$\angle HCO$	112.55	112.35		$\angle C_aCO$	105.77			r_{CC}	1.5541	1.5483
	r_{OLi}	1.601	1.590		$\angle C_bCO$	109.33			r_{CH_a}	1.0859	1.0856
$CH_3CH_2O^-$	r_{CO}	1.312	1.325		$\angle COH$	109.44			r_{CH_b}	1.0887	1.0883
	r_{C1H}	1.131	1.123	FCH_2O^-	r_{CO}	1.260	1.258		$\angle CCO_a$	116.02	116.29
	r_{CC}	1.556	1.549		r_{CF}	1.488	1.523		$\angle CCO_b$	114.46	114.832
	r_{C2H_a}	1.097	1.097		r_{CH}	1.116	1.107	$MeCO_2H$	$r_{C=O}$	1.1870	1.1828
	r_{C2H_b}	1.090	1.090		$\angle FCO$	114.80	113.88		r_{C-O}	1.3322	1.3306
	$\angle CCO$	113.69	114.02		$\angle HCO$	117.26	117.29		r_{CC}	1.5019	1.5003
	$\angle HCO$	104.23	105.06	FCH_2OH	r_{CO}	1.364	1.361		r_{CH_a}	1.0794	1.0796
	$\angle H_aC2C1$	113.62	112.36		r_{CF}	1.361	1.363		r_{CH_b}	1.0839	1.0842
	$\angle H_bC2C1$	109.53	109.84		r_{CH_a}	1.077	1.074		r_{OH}	0.9523	0.9460
CH_3CH_2OH	r_{CO}	1.404	1.406		r_{CH_b}	1.083	1.084		$\angle CC{=}O$	125.81	125.74
	r_{C1H}	1.089	1.089		r_{OH}	0.949	0.942		$\angle CC{-}O$	111.83	111.96
	r_{CC}	1.516	1.515		$\angle FCO$	110.75	110.48		$\angle COH$	108.09	108.78
	r_{C2H_a}	1.086	1.086		$\angle H_aCO$	107.48	107.89				
	r_{C2H_b}	1.084	1.085		$\angle H_bCO$	112.41	112.60				
	r_{OH}	0.947	0.940		$\angle COH$	109.89	110.53				
	$\angle HC1O$	109.67	110.17								
	$\angle H_aC2C1$	110.64	110.40								
	$\angle H_bC2C6$	110.30	110.43								
	$\angle CCO$	108.07	108.40								
	$\angle COH$	109.98	110.17								

[a] Angles are given in deg, bond lengths in Å. Ha and Ca are unique atoms, and Hb and Cb are one of a pair of symmetrically related atoms.

Table II. Calculated Energies

	6-31G*	6-311++G**			
compd	RHF	RHF	MP2	MP3	MP4
MeOH	−115.035 42	−115.080 60	−115.449 24	−115.463 84	−115.481 25
MeO$^-$	−114.384 47	−114.443 95	−114.824 95	−114.829 65	−114.855 40
EtOH	−154.075 74	−154.130 41	−154.650 77	−154.675 82	
EtO$^-$	−153.429 57	−153.497 24	−154.033 34	−154.047 37	
FCH_2OH(g)	−213.899 22	−213.976 06	−214.545 10	−214.550 45	
FCH_2O^-	−213.284 50	−213.375 61	−213.961 59	−213.953 92	
F_3COH(a)	−411.647 92	−411.775 64	−412.745 39	−412.431 56	
F_3CO^-	−411.091 49	−411.231 06	−412.215 18	−411.891 24	
t-BuOH	−232.153 35	−232.174 05[a]			
t-BuO$^-$	−231.513 19	−231.527 27[a]			
MeOLi	−121.931 55	−121.974 04	−122.350 17	−122.357 07	
AcOH	−227.810 65	−227.883 94	−228.575 98	−228.583 43	
AcO$^-$	−227.225 06	−227.308 14	−228.010 76	−228.009 01	

[a] 6-31G** at 6-31G* geometry.

Table III. Energy Changes (kcal/mol)

	6-31G*	6-311++G**				ΔE	ΔH	
reaction	RHF	RHF	MP2	MP3	MP4	est	calc	obs[6]
$CH_3OH \rightarrow CH_3O^- + H^+$	408.5	399.5	391.7	398.0	392.7	395	385	381 ± 2
$C_2H_5OH \rightarrow C_2H_5O^- + H^+$	405.5	397.3	387.4	394.4		391	382	378 ± 3
$t\text{-BuOH} \rightarrow t\text{-BuOH}^- + H^+$	401.7					387	378	375 ± 2
$FH_2OH \rightarrow FCH_2O^- + H^+$	385.7	376.8	366.2	374.3		370	361	
$F_3COH \rightarrow F_3CO^- + H^+$	349.1	341.7	332.7	339.1		336	327	
$AcOH \rightarrow AcO\_\ H^+$	367.5	361.3	354.7	360.4		358	349	349 ± 3

zero-point energy change was 9.6 kcal/mol.[6] The estimated ΔH of reaction was then 385 kcal/mol, which may be compared with the observed ΔH of 381 ± 2 kcal/mol.[7] The agreement is quite satisfactory.

The MP3/6-311++G** energies for ethoxide ion, ethanol, fluoromethoxide ion, fluoromethanol, trifluoromethoxide ion, and trifluoromethanol were obtained. Here, it was not practical to obtain the MP4 correction because of the long execution times.

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(6) The vibrational frequencies for methanol and methoxide ion were calculated with the 6-311++G** basis set and were scaled by using the usual factor[2] of 0.90 before calculating the zero-point energy change of 9.6 kcal/mol. The vibrational frequencies for trifluoromethanol and trifluoromethoxide ion were calculated by using the 6-311+G* basis set, and they led to a change in zero-point energy of 8.3 kcal/mol. The calculated frequencies are available as supplementary material. The zero-point energy changes for the other alcohols was assumed to be the same as those for methanol.

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Table IV. Bond Properties of Halomethanes (6-311G** Basis Set)[a]

compd	r_A	r_B	R	ρ_c
methyl fluoride	0.9296	0.4342	2.141	0.2342
difluoromethane	0.9083	0.4276	2.124	0.2579
fluoroform	0.8899	0.4231	2.103	0.2824
carbon tetrafluoride	0.8761	0.4210	2.081	0.3045

[a] r_A is the distance from the fluorine to the bond critical point, r_B is the distance from the carbon to that point, R is the ratio of r_A to r_B, and ρ_c is the charge density (e/au^3) at the bond critical point.

The energy changes on going from RHF to MP2 and MP3 were similar to those for the methanol/methoxide ion pair, and an average value was again taken as the best estimate. After correction for zero-point energy changes,[6] the calculated ionization energy for ethanol was again in good agreement with the observed energy.

The 6-311++G** basis set was too large for practical post-Hartree–Fock calculations for *tert*-butoxide ion and *tert*-butyl alcohol. It was noted that the 6-31G* energy differences were essentially the same as the differences found with the larger basis set and including electron correlation. Therefore, the ionization energy was estimated for *tert*-butyl alcohol assuming that the parallel behavior would include this alcohol. The estimated ΔH was in good agreement with the experimental observations.

Since the calculated energy changes agreed with the experimental results, it is now possible to examine the structural effects in some detail. Before examining the ions, it seems appropriate to consider the effect of fluorine substitution on the C–O bond length in methanol. It can be seen from Table I that the calculated bond lengths decrease from 1.400 Å in methanol to 1.361 Å in fluoromethanol and 1.328 Å in trifluoromethanol. The experimental value for methanol is 1.421 Å.[8] As usual, the calculated bond length is about 1% too short because of neglect of anharmonicity and electron correlation.[9] A similar change in bond lengths (Å) is found with the fluoromethanes: CH_3F; calcd 1.365, obsd 1.383; CH_2F_2, calcd 1.338, obsd 1.360; CHF_3, calcd 1.317, obsd 1.335; and CF_4, calcd 1.302, obsd. 1.319.[7] The fluoromethanol effect has been attributed to the anomeric effect,[4] and that for the fluoromethanes has been attributed to negative hyperconjugation.[10]

However, there is another explanation for all of these bond length changes. In fluoromethane, the electronegative fluorine prefers a carbon orbital with high p-character,[11] and the H–C–F angle determined with the bond paths clearly shows this change in hybridization.[12] As a result, the C–F bond will be relatively long. With difluoromethane, the two fluorines compete for the p-character, leading to less for each, and a shorter C–F bond. The hybridization effect is readily seen in the H–C–H bond angle of 113°. Finally, with CF_4, symmetry requires that each CF bond uses an sp^3 carbon orbital. The increased s-character leads to the shortest C–F bond in the group.

These expectations are realized in examining the wave functions (6-311G**) for the fluoromethanes.[13] Between any pair of bonded atoms there is a point at which the charge density is a minimum along the bond, and a maximum in other directions. This is known as the bond critical point.[14] If the bond is formed by two identical atoms, as with the C–C bond of ethane, the bond critical point will be at the center of the bond. On the other hand, if one of the atoms is more electronegative than the other, there will be a shift in charge density toward the more electronegative atoms, and this will cause the bond critical point to move away from this atom. The data are shown in Table IV. It can be seen that increasing fluorine substitution causes the ratio (R) of the distances from the fluorine (r_A) and the carbon (r_B) to the bond critical point to decrease, showing that the carbon becomes more electronegative with increasing fluorine substitution. The same effect may account for the difference in C–O bond lengths in the alcohols.

There are two interesting aspects to the structures of the ions: the bond angles to the alkoxide oxygen and the bond lengths. Bond angles generally respond to two factors, hybridization changes and electronegativity changes. As noted above, Bent's rule predicts that a less electronegative atom will prefer a bonding orbital with high s-character.[11] This in turn will lead to increased bond angles to the less electronegative atom.

On going from methanol to methoxide ion, the HCO bond angle opens up from 107.3 and 111.8° to 115.2° (Table I). This is just what would be expected from the change in electronegativity at oxygen. The same is seen for ethoxide ion where the CCO angle has increased to 114.0° from 108.4°, and a similar change is found for *tert*-butoxide ion. In this context, the angular change found for trifluoromethoxide ion (116.6° from 108.8° and 111.9° in trifluoromethanol) is not exceptional.

The decreases in C–O bond lengths on ionization were comparable for the series of alcohols that were studied: methanol, 0.07 Å; ethanol, 0.08 Å; *tert*-butyl alcohol, 0.09 Å; fluoromethanol, 0.10 Å; and trifluoromethanol, 0.11 Å. There is a trend toward a greater decrease with increasing acidity, but it is not a marked trend. The α-C–H bond lengths increase by about 0.03 Å, α-C–C bonds increase by 0.03 to 0.04 Å, and in fluoromethanol, the C–F bond lengthens by 0.08 Å. The only unusual change in bond lengths was found with trifluoromethanol where the C–F bonds lengthened by 0.16 Å on ionization.

The bond length changes for trifluoromethoxide ion have been attributed to negative hyperconjugation:[1]

In molecular orbital terms, this would be described as an electron donation from the oxygen lone pair orbitals to the σ* orbitals of the C–F bonds. The similar C–O bond length changes found on going to the other alkoxide ions would then suggest that similar interactions are found with the σ* orbitals of adjacent C–H and C–CH_3 bonds. Is this an appropriate way in which to explain the observations considering the high energy of the σ* orbitals?

In order to explore this problem in more detail, it is helpful to analyze these molecules in terms of Bader's theory of atoms in molecules.[15] Here, one first locates the bond critical points as described above. The data for the bonds in the alcohols and alkoxide ions are summarized in Table V. Here, r_A and r_B are distances from the nuclei to the bond critical point, R is the ratio of r_A to r_B, ρ_c is the charge density at the critical point, and the λ's are the curvatures (second derivatives) of the charge density at the critical point. The Laplacian of ρ ($\nabla^2\rho$) is the sum of the three λ's.

As noted above, the ratio, R, is useful in comparing the electronegativities of two atoms forming a bond. If the electronegativities are the same, the bond critical point will be at the center of the bond, and $R = 1$. When the electronegativities are different, charge transfer will occur toward the more electronegative atom, and the bond critical point will move away from that atom. With the C–O bonds of alcohols as an example, the distance from the bond critical point to the oxygen is about twice as large as the distance to the carbon, leading to $R \sim 0.5$. On going to the alkoxide ion, the distance from the critical point to the carbon is relatively unchanged, but that to the oxygen decreases because of its decreased electronegativity leading to an increase in R. At the same time, the λ values increase, and the value of $\nabla^2\rho$ goes from about zero to a strongly negative value.

Starting at a bond critical point, one may construct a series of rays (gradient paths) for which the charge density decreases

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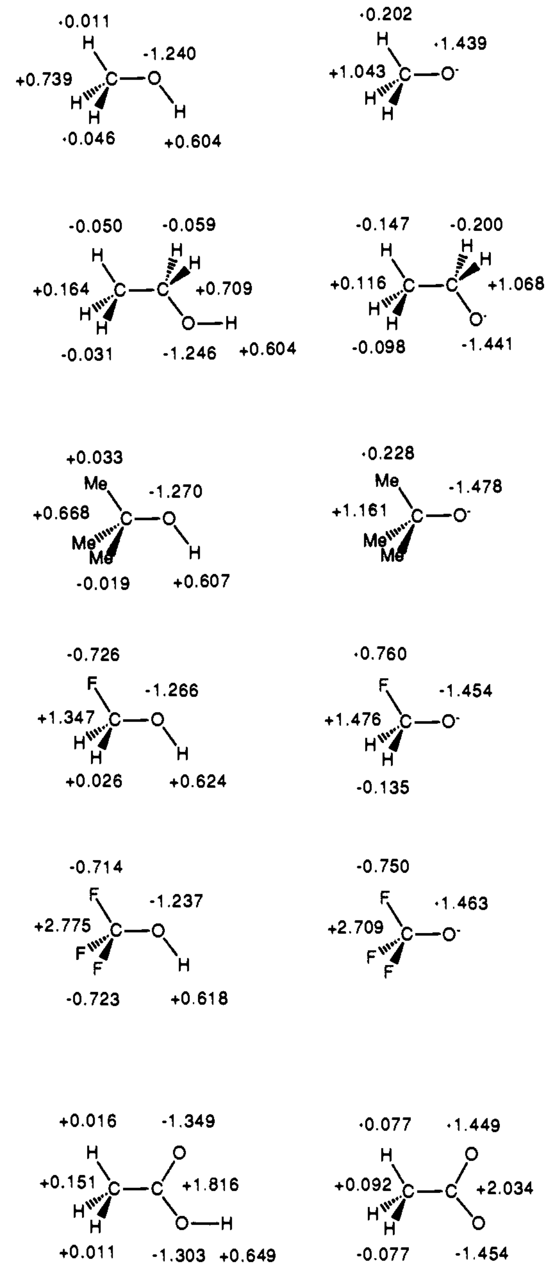

Figure 1. Atomic charges derived from electron populations.

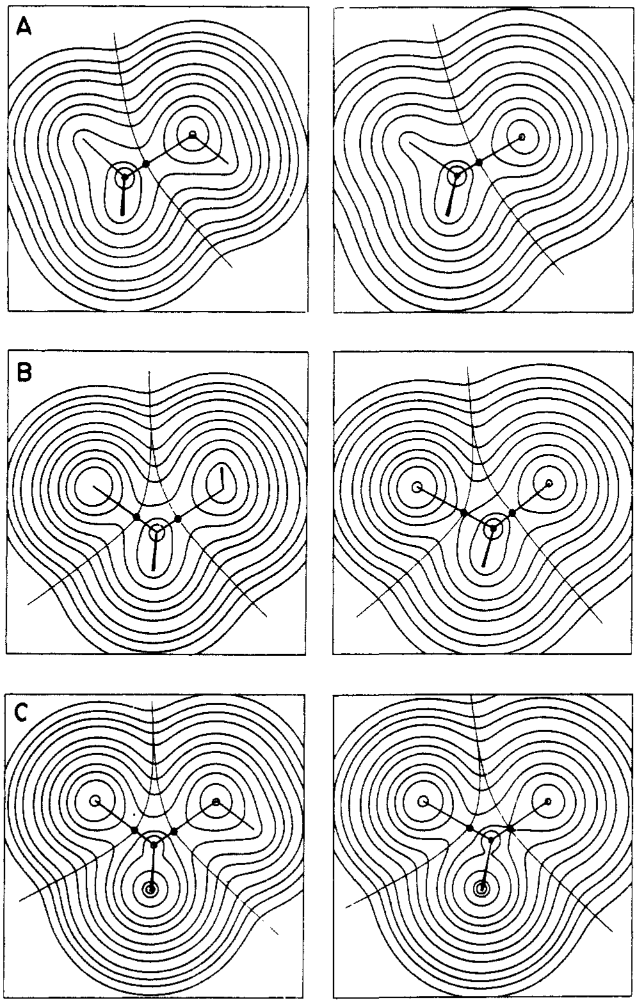

Figure 2. Projection density plots for alcohols (left) and their anions (right). The compounds are (A) methanol, (B) fluoromethanol, and (C) trifluoromethanol. In each case, the hydroxy group or oxygen is at the right, the carbon is in the center, and the other in-plane atom (F in the case of B and C) is at the left. The dark circles show the locations of the bond critical points, and the lines through them show the intersection of the zero-flux surface with the molecular plane.

most rapidly on going outwards from the critical point. A series of such rays would define a surface which separates a given pair of atoms.[16] The set of surfaces for all of the atoms in a molecule leads to a set of volume elements that may be assigned to individual atoms. Within each of these volume elements, the usual quantum mechanical rules, such as the virial theorem, still apply. Numerical integration of the charge density within each of these volume elements gives the electron population for a given atom, and the kinetic energy of the electrons associated with the atom may be obtained in the same fashion. The data that result from these numerical integrations are summarized in Table VI. It should be noted that the virial theorem requires that the total energy of an atom be the negative of its kinetic energy. The kinetic energies have been corrected for the small virial defect found in the SCF calculations and sum to a value that is close to the negative of the calculated total energy.

The changes in population are more easily seen in terms of the equivalent atomic charges, given by the nuclear charge less the electron population. They are shown in Figure 1. Before examining the values, it is appropriate to try to put them in perspective. With methyl fluoride, the charges are found to be -0.75 at fluorine and +0.75 at the methyl group.[17] These charges may at first appear to be rather larger. However, it is generally recognized that hydrogen fluoride is a polar molecule, and since hydrogen and a methyl group have similar electronegativities, hydrogen fluoride and methyl fluoride should have corresponding charge distributions. In the case of bonds to oxygen, the electronegativity of oxygen will be felt by both of the attached atoms leading to a movement of charge toward the oxygen, and a movement of the bond critical points away from the oxygen. Both contribute to yield a large negative atomic charge for oxygen. It is important to recognize that the atoms in molecules are not spherically symmetrical and that bond formation leads to polarization of the charge density.

The charge polarization in these molecules may easily be seen in the projection density plots[18] in which the charge density above and below the plane of the molecule is projected upon the molecular plane. Figure 2 shows contour plots of the projection density for methanol, fluoromethanol, trifluoromethanol, and their anions. The bond critical points are marked with closed circles. The strong charge polarization in the C–O and C–F bonds, with

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Table V. Bond Properties of Alcohols and Alkoxide Ions (6-311++G**)[a]

compd	bond	r_A	r_B	R	ρ_c	λ_1	λ_2	λ_3	$\nabla^2\rho$	ϵ
CH_0OH	$C-H_a$	0.6871	0.3946	1.741	0.2947	−0.7933	−0.7584	0.4429	−1.1089	0.0460
	$C-H_b$	0.6840	0.4038	1.694	0.289	−0.7650	−0.7285	0.4203	−1.0732	0.0502
	C–O	0.4486	0.9520	0.471	0.287	−0.4783	−0.4740	0.9020	−0.0503	0.0090
	O–H	0.7636	0.1756	4.349	0.3937	−2.0945	−2.0434	1.2253	−2.9126	0.0250
CH_3O^-	C–H	0.6771	0.4465	1.516	0.2598	−0.6260	−0.6022	0.3407	−0.8876	0.0396
	C–O	0.4485	0.8775	0.511	0.3324	−0.7563	−0.7563	0.8259	−0.6867	0.0000
CH_3CH_2OH	$C-H_a$	0.6762	0.4102	1.648	0.2819	−0.7045	−0.6991	0.3884	−1.0152	0.0077
	$C-H_b$	0.6803	0.4048	1.681	0.2842	−0.7186	−0.7143	0.4047	−1.0282	0.0066
	C–C	0.7364	0.7782	0.946	0.2647	−0.5260	−0.5052	0.2821	−0.7491	0.0412
	C–H	0.6830	0.4060	1.682	0.2914	−0.7671	−0.7341	0.4174	−1.0838	0.0450
	C–O	0.4496	0.9562	0.470	0.2554	−0.4701	−0.4620	0.8853	−0.0467	0.0175
	O–H	0.7641	0.1758	4.345	0.3932	−2.0089	−2.0388	1.2224	−2.9051	0.0245
$CH_3CH_2O^-$	C–H,a	0.6644	0.4328	1.535	0.2703	−0.6435	−0.6396	0.3368	−0.9464	0.0061
	$C-H_b$	0.6713	0.4188	1.603	0.2775	−0.6830	−0.6749	0.3703	−0.9876	0.0121
	C–C	0.8317	0.7177	1.159	0.2458	−0.4792	−0.4567	0.2810	−0.6548	0.0493
	C–H	0.6776	0.4450	1.523	0.2628	−0.6357	−0.6161	0.3443	−0.9075	0.0319
	C–O	0.4464	0.8785	0.508	0.3337	−0.7715	−0.7606	0.8671	−0.6650	0.0143
FCH_2OH	C–F	0.4356	0.9275	0.470	0.2377	−0.4815	−0.3736	1.3111	0.4560	0.2888
	$C-H_a$	0.6959	0.3777	1.842	0.3130	−0.8889	−0.8626	0.5030	−1.2485	0.0305
	$C-H_b$	0.6968	0.3871	1.800	0.3052	−0.8480	−0.8176	0.4802	−1.1853	0.0372
	C–O	0.4384	0.9237	0.475	0.2903	−0.7149	−0.5683	1.1105	−0.1726	0.2579
	O–H	0.7698	0.1726	4.460	0.388	−2.1008	−2.0562	1.2529	−2.9041	0.0217
FCH_2O^-	C–F	0.5466	0.9825	0.556	0.1581	−0.2052	−0.1784	0.3583	−0.0253	0.1500
	C–H	0.6873	0.4197	1.638	0.2832	−0.7379	−0.7151	0.4097	−1.0433	0.0319
	C–O	0.4196	0.8387	0.500	0.3828	−1.0613	−0.9583	1.5378	−0.4818	0.1074
F_3COH	$C-F_a$	0.4215	0.8791	0.480	0.2998	−0.8015	−0.7734	1.7475	0.1726	0.0363
	$C-F_b$	0.4269	0.8903	0.480	0.2870	−0.7289	−0.6928	1.5639	0.1422	0.0522
	C–O	0.4366	0.8918	0.490	0.3370	−0.8984	−0.8678	1.0915	−0.6747	0.0353
	O–H	0.7776	0.1673	4.649	0.3814	−2.1228	−2.0814	1.3129	−2.8913	0.0199
F_3CO^-	C–F	0.4551	0.9286	0.490	0.2377	−0.5260	−0.4611	0.9670	−0.0201	0.1408
	C–O	0.4079	0.8060	0.506	0.4370	−1.2485	−1.2485	1.8238	−0.6731	0.0000
$MeCO_2H$	C–C	0.6839	0.8165	0.838	0.2744	−0.5574	−0.5231	0.2558	−0.8247	0.0655
	$C-H_a$	0.6866	0.3930	1.747	0.2897	−0.7540	−0.7454	0.4337	−1.0658	0.0115
	$C-H_b$	0.6866	0.3977	1.726	0.2836	−0.7252	−0.7161	0.4181	−1.0232	0.0127
	C=O	0.3947	0.7882	0.501	0.4437	−1.3269	−1.2316	2.6986	0.1401	0.0774
	C–O	0.4301	0.9006	0.478	0.3075	−0.7890	−0.6902	1.3860	−0.0932	0.1432
	O–H	0.7777	0.1683	4.620	0.3828	−2.1235	−2.0871	1.3083	−2.9023	0.0175
$MeCO_2^-$	C–C	0.8025	0.7461	1.076	0.2526	−0.1667	−0.1552	0.0542	−0.6969	0.0597
	$C-H_a$	0.6721	0.4135	1.625	0.2818	−0.6992	−0.6986	0.3831	−1.0147	0.0009
	$C-H_b$	0.6719	0.4165	1.613	0.2774	−0.6837	−0.6723	0.3725	−0.9835	0.0170
	C–O	0.4091	0.8235	0.497	0.3965	−1.0964	−1.0767	2.0188	−0.1543	0.0182
	C–O	0.4095	0.8239	0.497	0.3963	−1.0921	−1.0771	1.9975	−0.1717	0.0139

[a] The distances r_A and r_B are from the critical point to the atom and are given in Å, R is the ratio of r_A to r_B, ρ_c is the charge density at the bond critical point (e/au^3), the λ's are the curvatures of ρ at the bond critical point (e/au^5), $\nabla^2\rho$ is the Laplacian of ρ at the critical point (e/au^5), and ϵ is the ellipticity given by $\lambda_1/\lambda_2 - 1$.

the bond critical points relatively close to the carbons, is readily apparent.

An examination of Figure 1 shows that the conversion of an alcohol to its anion leads to a more negative charge at oxygen and at the atoms attached to the carbon of the C–O bond but a more positive charge at the carbon. The simplest way in which to think of the changes is that the negatively charged oxygen in the anion will repel the charge distribution in the back lobe of the C–H or C–C bond orbitals at the adjacent carbon, causing a shift in charge density from the carbon to the adjacent atom. The greater ionic character of the C–O bond results in a coulombic attraction and a decrease in bond length. Spreading the charge out over a larger volume element leads to a lower classical electrostatic energy for the ion and a decrease in the total energy.

The question of the mechanism of interaction between the lone pairs and the bonds at the adjacent atom may be further examined by considering methylamine and methanol in both the staggered and eclipsed conformations. Some information about these compounds is given in Table VII. It is known that in the staggered conformations, the C–H bond trans to a lone pair is longer than the other C–H bonds,[19] and this is reproduced by the calculations. In addition, we find that the hydrogen trans to the lone pair has a larger electron population than the other methyl hydrogens. This could be attributed either to a charge transfer from the oxygen lone pair to the σ* orbital of the trans C–H bond or to a repulsive interaction between the oxygen lone pair and the backside of the C–H bond orbital. A distinction between these mechanisms is that in the former there should be a charge transfer from oxygen to the C–H bond, and in the second, the charge transfer should be between C and H.

An examination of the electron populations for methylamine shows that there is only a small charge shift between the CH_3 and NH_2 groups, and it is in the opposite direction from that expected for an interaction between the N lone pair and a CH σ* orbital. The major charge shifts are between C and H in the methyl group and between N and H in the amino group. These shifts are in the direction expected for a repulsive interaction. The repulsive interaction between the N lone pair and the CH group trans to it would cause a shift in electron population from C to H, which is the observed direction. The origin of the shift from N to H continues to be studied.

The structure of methanol and the changes in electron population on going from the eclipsed to the staggered form may be accounted for in the same fashion. Again, the charge shift between the CH_3 group and the OH is negligible, and the main shifts are between C and H in the methyl group and between O and H in the hydroxy group. It appears that most of the above observations are better accounted for by lone pair–bond orbital repulsive interactions than by the lone pair–σ* orbital interaction.

The case that does not fit the general pattern is trifluoromethanol. The four electronegative atoms attached to the carbon result in a very low electron population, and the fluorines bear a relatively large negative charge. In this case, the charge polarization in the C–F bonds is so great that little additional po-

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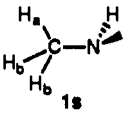
Table VI. Atom Properties of Alcohols and Alkoxide Ions (6-311++G**)[a]

compd	atom	n	T^b	compd	atom	n	T^b	compd	atom	n	T^b
CH_3OH	C	5.2610	37.3271	Me_3COH	Me_a	8.9669	39.6784	F_3COH	C	3.2248	35.8027
	H	1.0110	0.6367		Me_b	9.0186	39.7003		F_a	9.7136	100.0045
	H	1.0460	0.6496		C	5.3320	37.3714		F_b	9.7226	99.9941
	CH_3	8.3643	39.2636		O	9.2700	75.3700		H	0.3823	0.3468
	O	9.2400	75.4553		H	0.3929	0.3529		O	9.2369	75.6318
	H	0.3957	0.3619		sum	41.9990	232.1733		sum	42.0028	411.7740
	sum	18.0000	115.0808				(−232.1741)				(−411.7756)
			(−115.0806)	Me_3CO^-	Me	9.2278	39.7433	F_3CO^-	C	3.2907	35.8494
CH_0O^-	C	4.9568	37.0843		C	4.8386	36.9937		F	9.7504	99.9032
	H	1.2020	0.6914		O	9.4770	75.3027		O	9.4627	75.6701
	CH_3	8.5609	39.1573		sum	41.9990	231.5263		sum	42.0046	411.2291
	O	9.4389	75.2870				(−231.5273)				(−411.2311)
	sum	17.9998	114.4443	FCH_2OH	C	4.6526	36.9250	$MeCO_2H$	C(Me)	5.8493	37.7347
			(−114.4440)		F	9.7257	99.8753		H_a	0.9841	0.6163
CH_3CH_2OH	C(Me)	5.8356	37.7137		Ha	0.9743	0.6388		H_b	0.9894	0.6141
	H_a	1.0499	0.6400		H_b	1.0042	0.6473		Me	8.8124	39.5794
	H_b	1.0307	0.6339		O	9.2656	75.5401		C	4.1842	36.6554
	C	5.2906	37.3513		H	0.3757	0.3474		=O	9.3493	75.6928
	H	1.0593	0.6612		sum	25.9981	213.9739		–O–	9.6026	75.6263
	O	9.2458	75.4710				(−213.9761)		H	0.3506	0.3290
	H	0.3962	0.3618	FCH_2O^-	C	4.5236	36.8168		sum	31.9989	227.8827
	sum	25.9981	154.1280		F	9.7600	99.7091				(−227.8839)
			(−154.1304)		H	1.1351	0.6894	$MeCO_2^-$	C(Me)	5.9075	37.7425
$CH_3CH_2O^-$	C	5.8844	37.7266		O	9.4538	75.4792		H_a	1.0773	0.6510
	H_a	1.1467	0.6685		sum	26.0076	213.3839		H_b	1.0766	0.6469
	H_b	1.0975	0.6544				(−213.3756)		Me	9.1377	39.6878
	C	4.9322	37.0873						C	3.9659	36.4893
	H	1.1996	0.6969						O	9.4486	75.5663
	O	9.4405	75.3101						O	9.4537	75.5669
	sum	25.9980	153.4951						sum	32.0062	227.3098
			(−153.4972)								(−227.3081)

[a] The kinetic energies are given in hartrees and are corrected for the virial defect found in the RHF calculations. [b] The values in parentheses are the total energies obtained from the RHF calculations.

Table VII. Properties of Methylamine and Methanol (6-311++G**)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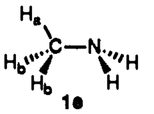
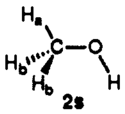

1e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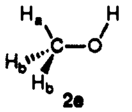
2e

	methylamine		methanol	
property	staggered (**1s**)	eclipsed (**1e**)	staggered (**2s**)	eclipsed (**2e**)
energy, H	−95.24625	−95.24287	−115.08060	−115.07879
ΔE, kcal/mol	2.12		1.14	
r(C–X)	1.454	1.460	1.400	1.404
$r(CH_a)$	1.091	1.086	1.082	1.085
$r(CH_b)$	1.085	1.086	1.088	1.086
r(XH)	1.000	0.997	0.940	0.938
$\angle XCH_a$	114.45	110.67	107.27	111.99
$\angle XCH_b$	109.32	111.64	111.80	109.66
$\angle CXH$	111.36	112.38	110.01	110.61
n(C)	5.3950	5.4024	5.2610	5.2655
$n(H_a)$	1.0710	1.0403	1.0110	1.0475
$n(H_b)$	1.0364	1.0498	1.0460	1.0267
n(X)	8.1579	8.1719	9.2400	9.2450
n(H)	0.6517	0.6429	0.3957	0.3886
$n(CH_3)$	8.5387	8.5422	8.3643	8.3664
$n(XH_n)$	9.4613	9.4577	9.6357	9.6336

larization is possible. As a result, the conversion to the anion leads to charge transfer to the electron-deficient carbon and only a small charge transfer to the fluorines. The considerable difference between trifluoromethanol and the other alcohols may also be seen in the value of $\nabla^2\rho$ for the C–O bonds. Whereas that for methanol is only −0.050, it increases to −0.675 for trifluoromethanol. The component along the bond does not change much, rather the components normal to the bond become more negative with trifluoromethanol. The C–F bond of fluoromethanol behaves in much the same fashion.

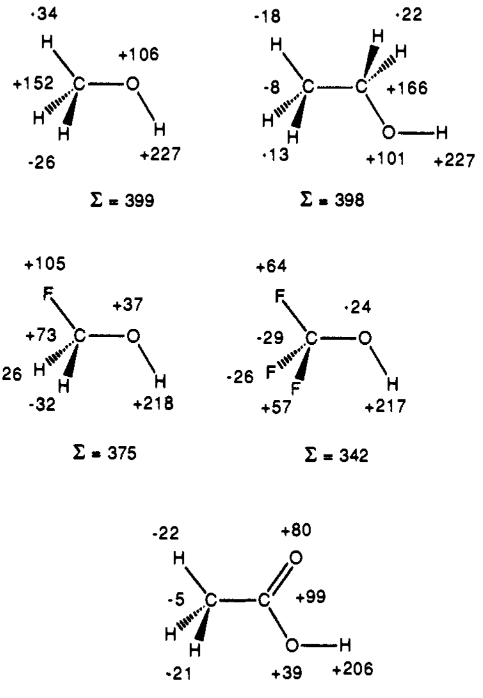

Figure 3. Energy changes (kcal/mol) on ionization.

Although the charges are interesting, the energy changes are of more importance since it is the energies of ionization that are of importance with regard to chemical behavior. The changes in energy on ionization, given in kcal/mol, are shown in Figure 3. The energy of the hydroxy proton in methanol is −227 kcal/mol, and this is lost on dissociation. The change in energy of the proton represents the largest part of the total change in energy. There also is a large increase in energy at the hydroxy oxygen. It was seen in Figure 1 that the electron population at oxygen increases on ionization. If the volume element for oxygen were constant with the increase in electron population, the kinetic energy would increase and the total energy would decrease in a corresponding fashion as required by the virial theorem. This behavior is, for example, found with the carbon bound protons. The decrease in kinetic energy (and increase in total energy) with increasing electron population at oxygen requires that the effective size of the oxygen increases more rapidly than the increase in population.

One question of recent interest has been the origin of the difference in acidity between alcohols and carboxylic acids.[20] The more recent conclusion is that the polarization of the carbonyl group is the major factor, and that carboxylate resonance is at best a minor factor. This question may now be examined in terms of the atom energies. In going from ethanol to acetic acid, one major change in energy is that of the hydroxy proton. Its energy increases by 227 kcal/mol on ionization in ethanol, and it increases by only 206 kcal/mol in acetic acid. Thus, one-half of the total difference in ionization energy of acetic acid vs ethanol is accounted for by the ground-state difference in energy between the two protons that will be lost on ionization. The same trend is found in comparing methanol with fluoromethanol. Trifluoromethanol does not fit this pattern, and as noted above, the bonding and charge distribution for this alcohol is quite different than that for the others.

Conclusions

The change in C–O bond length on going from an alcohol to its alkoxide ion is only to a small extent affected by the nature of the substituents. A hydrogen, methyl group, or fluorine is approximately equally effective. The usual effect on the charge distribution is transfer of charge density from the alcohol carbon to the attached groups, which leads to a reduction in the classical electrostatic energy, and to an internal attractive coulombic interaction, which leads to a short C–O bond in the alkoxide. The charge transfer from carbon to its substituents probably results from a repulsive interaction between the lone pair electrons and the backsides of the C–X bond orbitals. A somewhat different pattern of charge shifts was found with trifluoromethanol, presumably because of the very low electron population at the carbon in the alcohol. A large part of the difference in ionization energies between alcohols and carboxylic acids is found in the difference in hydroxyl proton energies.

Calculations

The calculations were carried out with GAUSSIAN-86[21] and were run on MicroVax and Trace7/200 computers. Standard basis sets were used.[2] The analysis of the wave functions was carried out with the PROAIMS programs.[22]

Acknowledgment. This investigation was supported by the National Science Foundation. The TRACE computer was made available by a NIH instrumentation grant.

Supplementary Material Available: Calculated vibrational frequencies for methanol, methoxide ion, trifluoromethanol, and trifluoromethoxide ion (1 page). Ordering information is given on any current masthead page.

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Measure of Nonplanarity in Conjugated Organic Molecules: Which Structurally Characterized Molecule Displays the Highest Degree of Pyramidalization?

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Abstract: A set of vectors reciprocal to those pointing along the internuclear axes from a conjugated carbon atom are introduced. The resultant of the reciprocal vectors is shown to define the π-orbital axis vector at a nonplanar conjugated atom. The quantities introduced in the transformation are sufficient to define all of the popular measures of pyramidalization in nonplanar conjugated organic molecules and to allow comparisons between the different schemes. The measures of nonplanarity are divided according to isotropy, and it is shown that there is a high degree of correlation between the different scales of pyramidalization, particularly in the case of the isotropic analyses. The compound reported by Greene and co-workers in 1974, 9,9′,10,10′-tetradehydrodianthracene (**2**) is established as possessing the most pyramidalized carbon atoms of all structurally characterized molecules. All measures of pyramidalization concur with this assessment and with the finding that the degree of pyramidalization in this compound surpasses that which is required in icosahedral C_{60}.

The pathways of many organic chemical reactions involve π-electron systems that undergo drastic deviations from planarity, and the same situation prevails in the formation of the carbon spheroids such as icosahedral C_{60}. It is now becoming clear, however, that substantially nonplanar conjugated organic molecules can actually be isolated and subjected to (structural) characterization. When the geometrical features of this diverse class of compounds are examined, it would be useful to identify a simple, easily conceptualized parameter for the measurement of the degree of nonplanarity.

Since interest in these compounds arose in a number of distinct connections, the nonplanarity has been assessed from different standpoints—some of which have depended on local symmetry for their application. Nevertheless, in situations where the different indices overlap in their applicability, it is of some interest to seek relations among these different measures and to enquire as to whether they lead to the same general scale of nonplanarity.

A measure that has found particular favor relates to the degree of pyramidalization, although this term has been used in a number of different connotations. In fact it was a recent paper on

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