Lone Pairs in Carbonyl Compounds and Ethers

Kenneth B. Wiberg,* Manuel Marquez, and Henry Castejon

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

The effective locations of the lone pairs at the oxygens of formaldehyde, acetone, and diethyl ether were examined using several criteria: the minimum in the Laplacian of the charge density (ϱ), the minimum electrostatic potential, the position of hydrogen bonding to water and hydrogen fluoride, and the position of protonation. Whereas the charge density about a carbonyl or ether oxygen is essentially featureless, the Laplacian of ϱ and the electrostatic potential both show minima at locations that correspond to a common picture of the lone pairs. The interaction of a carbonyl oxygen with a lithium cation prefers a 180° C–O–Li angle, whereas protonation prefers a 115° C–O–H angle. Lewis acid bonding to formaldehyde prefers a C–O–M angle of about 120°. Hydrogen bonding leads to a very soft bending potential and C–O⋯H angles of about 120–130°. This suggests that the geometries for hydrogen bonding found in X-ray crystallographic studies may in large measure be determined by crystal forces. The effect of substitution at the carbonyl group on the electrostatic potential also was studied.

1. Introduction.

Both acetone (**1**) and dimethyl ether (**2**) have two lone pairs that can be described in two equivalent ways: they may be taken as two equivalent sp^2 like orbitals (**1A**), or as a p orbital and an orbital with high s-character (**1B**).[1] The charge density (ϱ) at the oxygens of **1** or **2** is devoid of any features that might be ascribed to lone pairs, and so one may wonder why interactions with the lone pairs, such as hydrogen bonding and complex formation with Lewis acids prefer a geometry suggested by formulation **A**.[2] This question is also relevant to the stereoelectronic effects,[3] such as the anomeric effect, that are found with oxygen, and suggest a specific location for the lone pair.
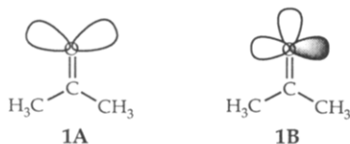
In order to gain more information on this subject, we have studied the properties that may be related to the lone pairs in **1** and **2** and similar compounds via the use of ab initio calculated wave functions. The properties are the following: the Laplacian of the charge density ($\nabla^2\varrho = \partial^2\varrho/\partial x^2 + \partial^2\varrho/\partial y^2 + \partial^2\varrho/\partial z^2$); the electrostatic potential; the geometry of hydrogen bonding with water and with hydrogen fluoride; and the geometry of interaction with a proton. Negative values of $\nabla^2\varrho$ indicate regions of local charge concentration, and it is known that oxygens have two such regions that correspond to the lone pair arrangement in **A**.[4] The electrostatic potential is the energy of a positive test charge at a given location.[5] It shows two regions of negative potential arranged roughly as suggested by formulation **A**. Both hydrogen bonding and protonation at a carbonyl give bond angles of roughly 120°, again in accord with formulation **A**. The first question of interest is the angular relationship between these four quantities.

Table 1. Calculated Structures, MP2/6-31+G*

compound	parameter	calculated	observed[a]
formaldehyde, C_{2v}	r (CO)	1.225	1.208(0.003)
	r (CH)	1.103	1.116(0.007)
	∠HCH	116.61	116.7(0.1)
acetaldehyde	r (CO)	1.227	1.216(0.005)
	r (CH)	1.108	1.111(0.002)
	r (CC)	1.501	1.501(0.005)
	r (CH$_a$)	1.091	1.086(0.005) av
	r (CH$_b$)	1.096	
	∠CCO	124.41	123.9(0.3)
	∠OCH	119.69	120.6(0.3)
	∠CCH$_a$	110.31	115.3(0.3) av
	∠CCH$_b$	109.43	
acetone, C_{2v}	r (CO)	1.232	1.215(0.005)
	r (CC)	1.512	1.515(0.005)
	r (CH$_a$)	1.091	1.086(0.010) av
	r (CH$_b$)	1.096	
	∠CCC	116.73	116.12
	∠CCHa	109.75	110.26 av
	∠CCH$_b$	110.15	
dimethyl ether, C_{2v}	r (CO)	1.420	1.415(0.001)
	r (CH$_a$)	1.090	1.118(0.002) av
	r (CH$_b$)	1.099	
	∠COC	111.42	111.8(0.2)
	∠OCH$_a$	106.78	109.2(0.2) av
	∠OCH$_b$	111.00	
formyl fluoride	r (CO)	1.195	1.188(0.004)
	r (CF)	1.366	1.346(0.003)
	r (CH)	1.093	1.108(0.011)
	∠OCH	128.25	130(4.)
	∠OCF	122.78	122.5(0.2)
carbonyl fluoride	r (CO)	1.187	1.172(0.001)
	r (CF)	1.333	1.316(0.001)
	∠OCF	126.35	126.1(0.1)

[a] The experimental structural data were taken from *Landolt-Bornstein*; New Series; Springer-Verlag: Berlin; Vol. 7 (1976), Vol. 15 (1987), Vol. 21 (1992).

2. Formaldehyde.

Because of its small size, it is computationally convenient to first examine the properties of formaldehyde (**3**). It is known that correction for electron correlation is important in properly describing a carbonyl group.[6] Therefore, we shall make use of wave functions for **3** derived from MP2/6-31+G* geometry optimizations. Diffuse functions (designated by +) are expected to be important in the description of lone pairs,[7] and this level of theory reproduces the experimental geometries quite well (Table 1). Figure 1 shows (a) the

® Abstract published in *Advance ACS Abstracts*, October 1, 1994.

(1) Cf. Liang, M. *J. Chem. Ed.* **1987**, *64*, 124.

(2) LePage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642.

(3) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer: Berlin, 1983.

(4) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

(5) Chirlain, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894.

(6) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley, New York: 1986; p 155 ff.

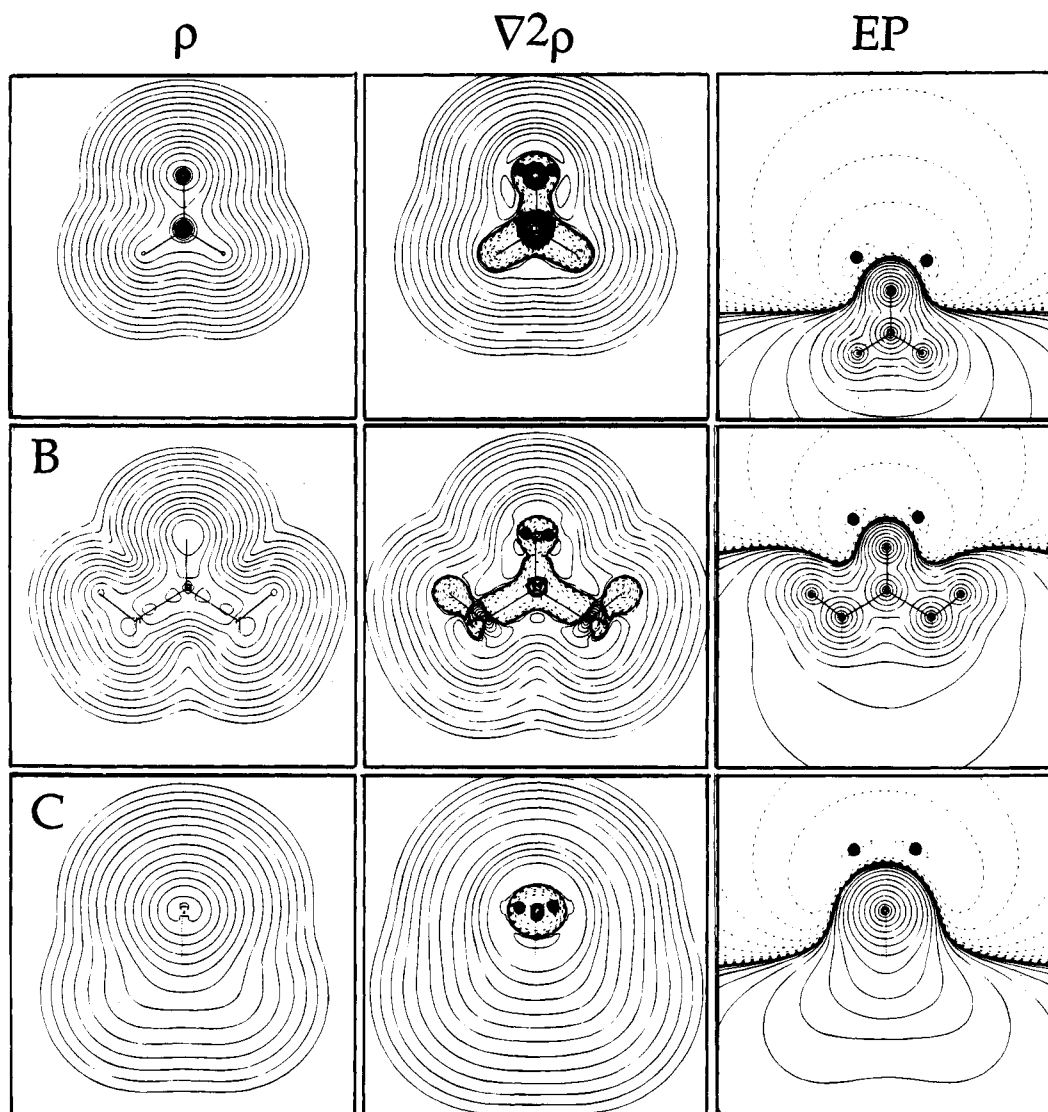$$\rho \qquad\qquad \nabla^2\rho \qquad\qquad EP$$

Figure 1. Contours of the charge density (ϱ), the Laplacian of ϱ ($\nabla^2\varrho$), and the electrostatic potential (EP) for formaldehyde (A), acetone (B), and dimethyl ether (C). For A and B, the plane of the molecule is shown, and for C, the symmetry plane bisecting the C–O–C angle is shown. The minima in $\nabla^2\varrho$ and in the EP are shown as dark circles.

charge distribution in the plane of the formaldehyde molecule, (b) the values of $\nabla^2\varrho$, and (c) the values of the electrostatic potential. It can be seen that the charge distribution is featureless, and gives no indication of discrete lone pairs. Small fluctuations in charge are magnified by examining the Laplacian of ϱ, and it can be seen in Figure 1b that there are regions of negative values of $\nabla^2\varrho$ at the sides of the carbonyl group. The minimum in this quantity was found 0.34 Å from the oxygen and at an angle with respect to the C=O group of 106°. The electrostatic potential also has minima in similar locations. The minima were located 1.31 Å from the oxygen with an angle with respect to the carbonyl group of 128°.

The other way in which to examine lone pairs at the carbonyl oxygen is to introduce a reagent that will interact with the carbonyl group. We have examined several reagents. The lithium cation will interact in a purely electrostatic fashion, but will represent a strong perturbation. A proton also will represent a strong perturbation, but here a covalent bond will be formed.

Weaker interactions may be seen in hydrogen bonding, and here we have examined both hydrogen fluoride and water. The formaldehyde–water complex has been studied many times,[8] and our results for the minimum energy geometry are in good agreement with the more recent study.[9] The energies of the complexes are represented graphically in Figure 2, and are available in tabular form as supplementary material.

The lithium cation interacts via a coulombic interaction, and its energy is minimized when the C=OLi group is linear. In order to calculate a binding energy, one should correct for the basis set superposition error (BSSE) and the change in zero-point energy on forming the complex. It is known that the commonly used counterpoise method for correcting for the BSSE is not entirely satisfactory, and that it is often better to use larger basis sets that minimize this correction.[10] The

(7) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609.

(8) Kumpf, R. A.; Damewood, J. R., Jr. *J. Phys. Chem.* **1989**, *93*, 4478 and references therein.

(9) Ha, T.-K.; Makarewicz, J.; Bauder, A. *J. Phys. Chem.* **1993**, *97*, 11415.

(10) Frisch, M. J.; Del Bene, J. E.; Brinkley, J. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 2279. Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *82*, 2418.
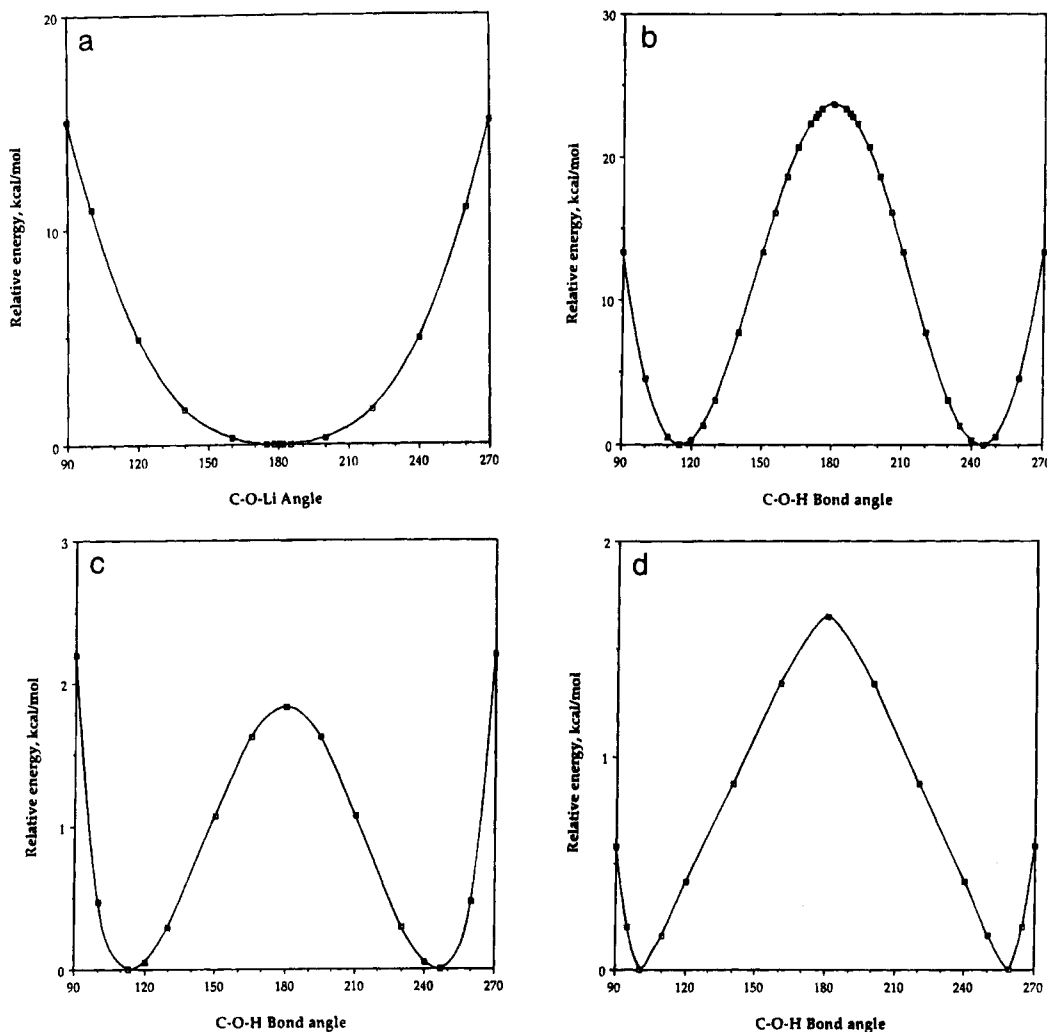
Figure 2. Conformational energy plots for the complexes with Li$^+$ (a), H$^+$ (b), HF (c), and H$_2$O (d).

energy of the complex was calculated at the MP2/6-311++G(2df,p) level of theory at the MP2/6-31+G* geometry. The zero-point energy was estimated via HF/6-31G* calculations and scaling the calculated zero-point energy by 0.893.[11] The data are summarized in Table 2, and leads to a binding energy for the complex of 34.0 kcal/mol (Table 3). The interaction of a proton is quite different because it leads to a covalent bond, and now the equilibrium C=O—H angle is 115.5°. The barrier to inversion is 23.7 kcal/mol and the binding energy is 165.7 kcal/mol, in reasonable agreement with the experimental value of 171.7 kcal/mol.[12] In contrast to these relatively large interactions, hydrogen bonding to HF gives a small barrier to inversion (1.8 kcal/mol), a minimum in energy at 113.2°, and a binding energy of 6.0 kcal/mol. Hydrogen bonding to water also gives a small inversion barrier (1.7 kcal/mol), a minimum in energy at 100.9°, and a binding energy of only 3.6 kcal/mol after correction for the zero-point energy change.[13] In this case, a HF/6-31G* geometry optimization gave a structure with one of the water protons out of the molecular plane, but the MP2/6-31+G*

minimum energy structure had the proton in the molecular plane.

Complexes with Lewis acids also were of interest, and the reaction of formaldehyde with BH$_3$, BF$_3$, and AlH$_3$ were examined. We have previously examined these complexes at a lower theoretical level,[2] and therefore we have just located the minimum energy geometries (Table 3). All three complexes took a C—O—M angle of 121–122° and gave binding energies significantly greater than for hydrogen bonding.

Except for water which gives an unusually small C—O—H angle, and Li$^+$ that interacts differently than the other reagents, the C—O—X angles are in the range of 113–122°, which is significantly smaller than the angle found for the minimum in the electrostatic potential. It should be noted that the hydrogen bonding bending potential is quite soft, and so a range of angles will correspond to only a small change in energy. For example, at the thermal energy ($RT = 0.6$ kcal/mol) the formaldehyde—HF complex can have any C—O—H angle between 100–137°.

3. Acetone and Acetaldehyde. The structural data are shown in Table 1 and the calculated energies are given in Table 2. A contour plot of the values of ϱ for acetone in the plane containing the lone pairs is shown in Figure 1. As observed with formaldehyde, a rather uniform distribution of ϱ is found in the vicinity of the oxygens.

(11) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(12) Lias, S. G.; Liebman, J. F.; Levin, R. D. *Evaluated Gas Phase Basicities and Proton Affinities of Molecules*; *Heats of Formation of Protonated Molecules*. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(13) In the above cases, the MP2/6-31+G* energies gave binding energies of 34.0, 161.6, 6.7 and 4.1 kcal/mol, respectively. Except for the proton affinity, it can be seen that the effect of the BSSE is small.

Table 2. Calculated Energies[a]

compound	total energy, hartrees		ZPE,[b] kcal/mol
	MP2/6-31+G*	MP2/6-311++G(2df,p)	
formaldehyde	−114.17708	−114.29680	16.4
formaldehyde−Li+	−121.46858	−121.58852	17.5
formaldehyde−H+	−114.44774	−114.57370	24.5
formaldehyde−water	−190.39644	−190.61466	31.1
formaldehyde−HF	−214.39436	−214.63119	24.2
formaldehyde−BH₃	−140.66511	−140.82761	35.7
formaldehyde−BF₃	−437.99806	−438.45717	25.1
formaldehyde−AlH₃	−357.87338	−358.05439	30.1
acetaldehyde	−153.35801	−153.52416	33.6
acetaldehyde−H+ (syn)[c]	−153.64842	−153.82193	41.3
acetaldehyde−H+ (anti)	−153.64954	−153.82290	41.3
acetaldehyde−HF (syn)[c]	−253.57718	−253.86062	41.3
acetaldehyde−HF (anti)	−253.57719	−253.86060	41.3
acetone	−192.53670	−192.74960	50.5
acetone−H+	−192.84343	−193.06392	57.9
acetone−water	−268.75819	−269.06966	65.0
acetone−HF	−292.75750	−293.08783	58.1
formyl fluoride	−213.23765	−213.35202	12.3
formyl fluoride−H+ (syn)[d]	−213.01670	−213.61022	20.0
formyl fluoride−H+ (anti)[d]	−213.48164	−213.60872	20.0
formyl fluoride−HF (syn)	−313.45032	−313.63889	20.4
formyl fluoride−HF (anti)	−313.45053	−313.63910	20.3
carbonyl fluoride	−312.27457	−312.44133	8.2
carbonyl fluoride−H+	−312.50438	−312.68480	15.7
carbonyl fluoride−HF	−412.48531	−412.72662	15.9
dimethyl ether	−154.51463	−154.70041	48.3
dimethyl ether−H+	−154.82050	−155.00856	55.9
dimethyl ether−water	−230.73677	−231.01976	62.8
dimethyl ether−HF	−254.73758	−255.03894	55.7
water	−76.20978	−76.30908	12.9
hydronium ion	−76.47778	−76.58107	20.6
hydrogen fluoride	−100.20292	−100.32111	5.6
Li+	−7.23554	−7.23584	0.0
BH₃	−26.46548	−26.50490	15.5
BF₃	−323.80499	−324.14690	7.5
AlH₃	−243.67095	−243.72668	10.9

[a] The frozen core option was used in these calculations. [b] The HF/6-31G* zero point energies were scaled by 0.893 (ref 11). [c] Syn and anti refer to the methyl group. [d] Syn and anti refer to the fluorine.

The values of the Laplacian of ϱ were calculated for the plane containing the lone pair and are shown as a contour plot in Figure 1. The locations of the minima in $\nabla^2\varrho$ are shown as solid circles, and the numerical values are given in Table 3. The electrostatic potentials were calculated for planes containing the lone pairs and are shown as a contour plot in Figure 1. The minima in the potential (i.e. having the largest interaction with the test charge) are shown by the solid circles. The numerical values are included in Table 3.

The interaction of acetone and acetaldehyde with a proton was studied giving the energies summarized in Table 2. The C−O−H angles are given in Table 3. With acetone, the C−O−H angle was 114.0°. In the case of acetaldehyde, the proton may be added either syn to the methyl group (**4a**) or anti (**4b**). The latter was found to have the lower energy by 0.95 kcal/mol. The C−O−H angles were essentially the same (114.6 and 114.8°, respectively). The angle is essentially the same as that found for formaldehyde and acetone. The calculated binding energies are close to the observed proton affinities.

4a   **4b**
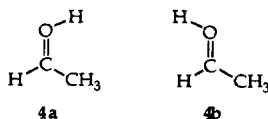
The geometries for hydrogen bonding[14] were, however, quite different than those found with formaldehyde.

With hydrogen fluoride and acetaldehyde, the anti interaction (with respect to the methyl group) occurred at the same angle as for formaldehyde, but the syn interaction occurred at a larger angle (120°). About the same angle was found with acetone. The simplest hypothesis is that there is a small steric interaction when the HF is on the same side as a methyl group, and in view of the soft interaction potential, a small interaction can lead to a significant change in angle.

We also were interested in the effect of electronegative substituents on the electrostatic potential and on the interaction with reagents. Both formyl fluoride and carbonyl fluoride were examined (Tables 2 and 3). The interaction with a proton occurred at essentially the same C−O−H angle as for the other carbonyl compounds (115°). However, the electrostatic potential was significantly decreased and the minima in the EP were found at longer distances than for the other carbonyl compounds.

4. Electrostatic Potentials for Other Carbonyl Compounds. We were interested in examining the effect of substituents on the location and energy associated with the minimum in the electrostatic potential about a carbonyl group. The EP is often taken as a predictor of intermolecular interactions,[15] and it would be helpful if it were possible to make simple predictions

(14) Hydrogen bonding to acetaldehyde and acetone appears to have been studied only at low theoretical levels or via semiempirical methods. Cf. Cai, J.; Topsom, R. D. *Theochem.* **1991**, *74*, 181. Paul, S. O.; Ford, T. A. *S. Afr. J. Chem.* **1988**, *41*, 108.

Table 3. Properties of Compounds and Complexes

compound	property	r (Å)[a]	α[b]	value[c]
formaldehyde	$\nabla^2\varrho$	0.336	105.8	−6.7
	EP	1.310	127.5	−41.9
	H_2O	2.105	100.9	3.6
	HF	1.783	113.2	6.0
	Li^+	1.834	180.0	34.0
	H^+	0.994	115.5	165.7 (172 ± 2)[e]
	BH_3	1.695	120.7	12.5
	BF_3	1.793	120.7	7.2
	AlH_3	2.083	122.3	16.6
acetaldehyde[d]	$\nabla^2\varrho$ (syn)	0.328	106.4	−6.5
	$\nabla^2\varrho$ (anti)	0.330	103.4	−6.6
	EP (syn)	1.276	127.7	−45.2
	EP (anti)	1.269	123.2	−47.0
	HF(syn)	1.742	120.1	7.5
	HF(anti)	1.731	113.1	7.5
	H^+ (syn)	0.991	114.6	179.2
	H^+(anti)	0.990	114.8	179.8 (187 ± 3)[e]
acetone	$\nabla^2\varrho$	0.333	104.8	−6.5
	EP	1.23	133.1	−60.4
	H_2O	1.842	132.9	5.3
	HF	1.712	121.1	8.7
	H^+	0.979	114.0	189.8 (197 ± 3)[e]
formyl fluoride[d]	$\nabla^2\varrho$ (syn)	0.332	111.2	−5.9
	$\nabla^2\varrho$ (anti)	0.333	108.2	−5.9
	EP (syn)	1.371	128.7	−31.0
	EP (anti)	1.434	134.9	−25.1
	HF (syn)	1.880	130.5	19.0
	HF (anti)	1.854	116.5	18.5
	H^+ (syn)	0.997	116.0	154.3
	H^+ (anti)	0.993	115.3	153.4
carbonyl fluoride	$\nabla^2\varrho$	0.333	110.5	−5.7
	EP	1.447	135.2	−20.1
	HF	1.908	133.6	20.3
	H^+	0.995	115.5	145.9 (161 ± 3)[e]
dimethyl ether	$\nabla^2\varrho$	0.334	109.0	−6.9
	EP	1.24	157.2	−58.7
	H_2O	1.865	136.8	4.8
	HF	1.655	135.8	9.1
	H^+	0.976	129.0	185.8 (192 ± 2)[e]
water	$\nabla^2\varrho$	0.342	106.9	−6.2
	EP	1.292	144.1	−54.7
	H^+	0.991	107.7	163.0 (167 ± 2)[e]

[a] Distance from the oxygen to the minimum to $\nabla^2\varrho$ or EP (electrostatic potential), or to the proton or Lewis acid. [b] For the carbonyl compounds, α is the C−O−X angle where X is one of the above. With dimethyl ether and water, the angle is taken with respect to the C−O−C or H−O−H plane. [c] Units: the $\nabla^2\varrho$, e/Bohr;[5] electrostatic potential (EP), kcal/mol; complexes, binding energies (kcal/mol). [d] Syn and anti refer to the methyl group or fluorine. [e] Data were taken from ref 12.

concerning the effect of substituents on the EP's. A number of compounds have been examined at the MP2/6-31+G* level using the MP2/6-31G* geometries,[16] giving the results summarized in Figure 3. Here, the location of the minimum in EP is given in terms of the angle with respect to the C−O bond and the distance from the oxygen. The absolute values of the EP's are given; all have a negative sign.

On going from formaldehyde to acetaldehyde and acetone, there is an increase in the magnitude of the EP, and the minimum moves to shorter distances. The replacement of a methyl with an electronegative atom such as F or Cl decreases the magnitude of the EP and increases the distance from the oxygen. A PH_2 group, with an electronegativity close to that of carbon, leads

(15) Cf. Kahn, S. D.; Pau, C. F.; Obverman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381.

(16) Acetyl derivatives: Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644. Formamide: Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831. The structures of the other compounds in Figure 3 are given in the supplementary material.
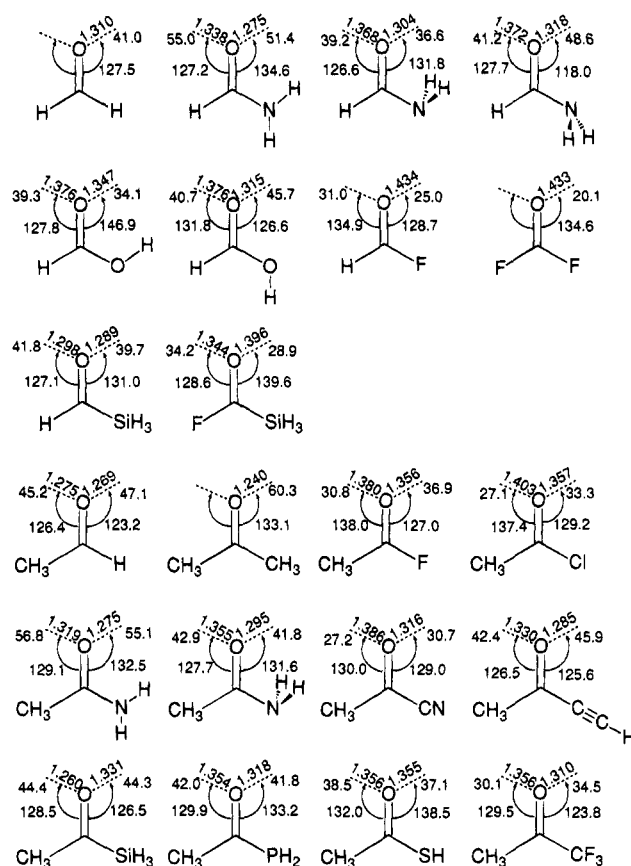

Figure 3. Location of the minima in the electrostatic potential for carbonyl compounds. The angles with respect to the C−O bonds and the distances are given along with the magnitudes of the electrostatic potentials (the latter have negative signs).

to EP's similar to those found with acetaldehyde, but does shift it to a longer distance. A silyl group, which is electropositive with respect to carbon, has about the same effect on the EP as a hydrogen.

The effect of electronegativity is also seen in the series formaldehyde, formyl fluoride, and carbonyl difluoride, where there is a marked increase in the magnitude of the EP and an increase in the distance. In most cases, the main effect of a electronegative atom is seen anti to the substituent. π Donors, such as an amino group, can lead to an increase in the magnitude of the EP, but this is reduced when the amino group is rotated to eliminate the π interaction.

Although there are some trends in the substituent effect on the electrostatic potentials, no clear quantitative relationship has emerged.

5. Dimethyl Ether. The oxygen of dimethyl ether may be significantly different than that for the ketones and aldehydes. Plots of ϱ, $\nabla^2\varrho$, and the electrostatic potential in a plane through the oxygen an bisecting the C−O−C angle are shown in Figure 1. Again, it is seen that the charge density distribution is essentially featureless and does not suggest discrete lone pairs. The Laplacian of ϱ does show minima at a 109° angle from the C−O−C plane, and the electrostatic potential shows minima at a 157° angle (Table 3).

Protonation of dimethyl ether was studied and led to a 129° angle between the O−H vector and the C−O−C plane. The binding energy using the larger basis set and correcting for the change in zero-point energy was 185.8 kcal/mol (obsd 192 kcal/mol).[12] Hydrogen bonding to HF

was studied in the same fashion and gave a binding energy of 10.8 kcal/mol.

6. Summary. Although the charge distribution about a carbonyl oxygen does not show any obvious directionality of the lone pairs, the Laplacian of the charge distribution shows a minimum at 105–110° from the C—O bond and the electrostatic potential shows minima at ~130° from the C—O bond. Interactions that will perturb the charge distribution at a carbonyl group, such as protonation or hydrogen bonding, also lead to similar angles. A strong perturbation, as found with protonation, gives a C—O—H angle of about 115° that is not much affected by substituents attached to the carbonyl carbon. On the other hand, hydrogen bonding leads to a range of angles and very soft bending potentials. Thus, the C—O—H angle is easily distorted with a minimal change in energy, and this suggests that the angles found in X-ray structure determinations are largely a result of crystal forces.

The charge distribution about an ether oxygen also does not show any obvious directionality for the lone pairs. The minimum in the Laplacian of ϱ for dimethyl ether and for water is found at 107–109° from the C—O—C plane, and the minimum in the EP is found at considerably larger angles (144, 152°). Hydrogen bonding prefers an angle of 135–140° which is only slightly larger than that for the carbonyl compounds. Protonation of dimethyl ether gives a relatively large angle (136°) whereas water gives a relatively small angle (106°).

Calculations. The ab initio structures and energies and the electrostatic potentials were obtained using GAUSSIAN-91.[17]

Supplementary Material Available: Tables of energies of formaldehyde complexes, and MP2/6-31G* geometries of some formyl derivatives (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(17) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 91, Development Version (Revision C), Gaussian, Inc., Pittsburgh, PA, 1991.