Barriers to Rotation Adjacent to Double Bonds. 3. The C–O Barrier in Formic Acid, Methyl Formate, Acetic Acid, and Methyl Acetate. The Origin of Ester and Amide "Resonance"

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Abstract: The structures of the rotamers about the C–O bonds of formic acid, methyl formate, acetic acid, and methyl acetate were calculated by using the 6-31G* basis set and complete geometrical relaxation. Large basis sets (6-311+G**) and correction for electron correlation were needed in order to obtain calculated barriers that were in good agreement with the available experimental data. The factors that control the geometry at a carbonyl group are considered, and it is shown that an analysis in terms of bond path angles leads to a direct connection with electronegativity. The nature of the interaction between an amino group and a carbonyl, as in an amide, is examined and shown not to involve charge transfer from the nitrogen to the carbonyl oxygen, but rather it involves charge transfer between carbon and nitrogen. The origin of the rotational barrier in esters and of the difference in energy between the *E* and *Z* conformers is discussed.

We have presented the results of calculations of rotational barriers about C–C bonds adjacent to carbonyl groups.[1,2] It was possible to determine the origin of the barriers and of the differences in energy among the stable rotamers. These data have proven valuable in conformational studies of ketones and have led to improved parameters for modeling of structures via molecular mechanics.[3] Rotation about C–O bonds adjacent to carbonyl groups[4] also is of importance in studying the properties of esters and lactones. Therefore we have carried out a set of calculations for both formic and acetic acids and their methyl esters.

Magnitude of the Rotational Barriers

The *E* conformer of formic acid has been found to be 3900 ± 85 cal/mol less stable than the *Z* isomer,[5] and with methyl formate, two different measurements gave the *E*/*Z* energy difference as 3850 ± 200[6] and 4750 ± 190 cal/mol.[7] In the case of methyl acetate, the *E*/*Z* difference was reported to be ~8.5 ± 1 kcal/mol.[7] The barrier height does not appear to have been measured, but it has been estimated to be "10–15 kcal/mol".[7] The energy difference between the *E* and *Z* conformers of methyl formate which is found in solution appears to be about half as large as that obtained in the gas phase.[8]

Some calculations for these compounds have been reported. The *E*/*Z* energy difference for formic acid was found to be 6.12 kcal/mol with use of the 6-31G* basis set.[9] Some calculations on the methyl esters have been reported, but only with smaller basis sets.[10] Our calculations have shown the importance of including polarization functions in examining the C–C rotational barriers at carbonyl groups,[1,2] and therefore, the 6-31G* basis set has been used throughout. In order to facilitate the geometry optimizations, the 4-31G basis[11] was used in the initial calculations, and for comparison, these values also are given. The 4-31G basis was chosen because it gives geometries closer to 6-31G* than the popular 3-21G basis set.[12]

The results of the calculations for formic acid and methyl formate are given in Table I, and the geometries are compared in Table II. The *E*/*Z* energy difference was calculated to be essentially the same for formic acid and methyl formate with the 6-31G* basis set, and both values are somewhat larger than the observed energy differences. The discrepancy between the calculated and observed energies may be due to an inadequate basis set, electron correlation, experimental error, or some combination of the three. With formic acid, inclusion of polarization functions at hydrogen had only a small effect (*E*/*Z* = 6.00 kcal/mol with the 6-31G** set), and this was reduced by only 0.5 kcal/mol by correcting for electron correlation with the Møller–Plesset method[13] through the third order (MP3). Finally, a calculation was carried out with the much larger 6-311+G** basis set which includes three sets of 2s and 2p orbitals along with diffuse s,p orbitals and a set of d orbitals at carbon and oxygen and three sets of 1s orbitals along with a set of p orbitals at hydrogen. Here, the calculated *E*/*Z* energy difference was reduced to 5.40 kcal/mol. Correction for electron correlation (MP3) further reduced the energy difference to 4.61 kcal/mol. This is still somewhat larger than the experimental value (3.85 kcal/mol), but the difference is not large.

In the case of methyl formate, the 6-31G** calculations gave essentially the same barrier and *E*/*Z* energy difference as found with formic acid, and correction for electron correlation again led to about the same energy differences. The use of the larger 6-311+G** basis set plus correction for electron correlation led to a calculated *E*/*Z* energy difference of 5.59 kcal/mol. This may be compared with the more recent experimental value, 4.75 kcal/mol. The difference between these values, 0.8 kcal/mol, is the same as that found with formic acid. The correction for electron correlation was significantly smaller for methyl formate than for formic acid.

The methyl of the OCH_3 group has two possible orientations. The lower energy rotamer has the methyl hydrogens staggered with respect to the carbonyl group. When the larger basis set was used and corrections made for electron correlation, the calculated energy difference between the two rotamers (1.15 kcal/mol) was in very good agreement with the experimental value (1.19 ± 0.04 kcal/mol).[14]

In examining the results for acetic acid and methyl acetate (Tables III andIV), it is seen that the barriers to rotation were calculated to be essentially the same for the two compounds with

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Table I. Calculated Energies of Formic Acid and Methyl Formate Conformers

		$\frac{\text{4-31G}}{\text{4-31G}}$		$\frac{\text{6-31G*}}{\text{6-31G*}}$		$\frac{\text{6-31G**}}{\text{6-31G*}}$		$\frac{\text{MP3/6-31G**}}{\text{6-31G*}}$		$\frac{\text{6-311+G**}}{\text{6-31G*}}$		$\frac{\text{MP3/6-311+G**}}{\text{6-31G*}}$	
compd	τ[a]	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*
HCO_2H	0 (*Z*)	−188.47561	0.00	−188.76231	0.00	−188.77054	0.00	−189.26038	0.00	−188.82566	0.00	−189.35757	0.00
	45	−188.46634	5.82	−188.75162	6.71	−188.76009	6.55						
	90	−188.45633	12.10	−188.74078	13.51	−188.74955	13.17	−189.23906	13.37	−188.80560	12.59	−189.33783	12.39
	135	−188.45978	9.93	−188.74631	10.04	−188.75495	9.78						
	180 (*E*)	−188.46464	6.88	−188.75255	6.12	−188.76098	6.00	−189.25164	5.48	−188.81705	5.40	−189.35022	4.61
HCO_2Me[b]	0 (*Z*)	−227.44328	0.00	−227.78942	0.00	−227.79579	0.00	−228.43793	0.00	−227.85646	0.00	−228.54570	0.00
	45	−227.43335	6.23	−227.77865	6.76								
	90	−227.42343	12.55	−227.76898	12.83	−227.77536	12.81	−228.41645	13.48	−227.83662	12.45	−228.52526	12.83
	135	−227.42703	10.20	−227.77436	9.45								
	180 (*E*)	−227.43138	7.56	−227.77945	6.30	−227.78594	6.18	−228.42832	6.03	−227.84695	5.97	−228.53679	5.59
HCO_2Me[c]	0	−227.44206	0.86	−227.78734	1.31	−227.79383	1.23	−228.43610	1.15				

[a] O=C—O—H torsional angle. Total energies are given in hartrees, energy differences are given in kcal/mol, and τ are in deg. [b] Methyl hydrogens staggered with respect to C=O. [c] Methyl hydrogen eclipsed with respect to C=O. The Δ*E* is with respect to the above 0° conformer.

Table II. Structures of Formic Acid and Methyl Formate Conformers

unit[a]	0°	45°	90°	135°	180°
	a. Formic Acid, 6-31G*				
$r_{\mathrm{C=O}}$	1.1819	1.1787	1.1747	1.1748	1.1755
$r_{\mathrm{C-O}}$	1.3229	1.3367	1.3507	1.3386	1.3285
$r_{\mathrm{C-H}}$	1.0835	1.0845	1.0870	1.0894	1.0900
$r_{\mathrm{O-H}}$	0.9532	0.9512	0.9593	0.9495	0.9482
∠H—C=O	124.73	123.91	123.02	122.99	123.16
∠H—C—O	110.39	111.20	112.91	113.67	113.82
∠O—C=O	124.88	124.89	124.07	123.34	123.02
∠C—O—H	108.72	110.62	111.87	111.49	111.47
	b. Methyl Formate, 6-31G*				
$r_{\mathrm{C=O}}$	1.1835	1.1804	1.1765	1.1765	1.1776
$r_{\mathrm{C-O}}$	1.3164	1.3291	1.3416	1.3316	1.3229
$r_{\mathrm{H-C}}$	1.0846	1.0857	1.0885	1.0908	1.0907
$r_{\mathrm{O-C}}$	1.4192	1.4191	1.4149	1.4120	1.4117
∠H—C=O	124.21	123.50	122.79	122.91	122.93
∠O—C=O	125.72	125.43	124.16	123.72	123.16
∠H—C—O	110.07	111.07	113.05	113.37	113.91
∠C—O—C	116.83	117.34	115.95	116.49	117.70
r_{CHa}[b]	1.0782	1.0782	1.0782	1.0780	1.0779
r_{CHb}	1.0803	1.0826	1.0854	1.0854	1.0834
r_{CHc}	1.0803	1.0800	1.0825	1.0831	1.0834
∠O—C—Ha	105.85	106.11	106.44	106.48	106.31
∠O—C—Hb	110.44	109.95	110.96	111.24	111.00
∠O—C—Hc	110.44	110.98	110.45	110.64	111.00

[a] Units: bond lengths in Å, angles in deg. [b] Ha is the hydrogen with an O—C—O—H torsional angle of 180°, Hb has a torsional angle of ca. +60°, and Hc has a torsional angle of ca. −60°.

the 6-31G* basis set but that the *E*/*Z* energy difference was predicted to be about 2 kcal/mol greater for methyl acetate than for acetic acid. The use of the larger 6-311+G* basis set again led to a decrease in the *E*/*Z* energy difference for acetic acid, and it was further reduced by inclusion of electron correlation. The *E*/*Z* energy difference for acetic acid was calculated to be about 1 kcal/mol greater than that for formic acid.

In the case of methyl acetate, as with methyl formate, the preferred conformation of the methyl of the OCH_3 group has the hydrogens staggered with respect to the carbonyl. When electron correlation was included, the calculated *E*/*Z* energy difference for methyl acetate (8.6 kcal/mol) was in good agreement with the experimental value (8.5 ± 1 kcal/mol),[7] and the barrier height also was within the experimental range.

It can be seen that the calculations satisfactorally reproduce the available experimental data with respect to the rotational barriers and *E*/*Z* energy differences. It is unusual in conformational problems to require such large basis sets and to have such large corrections for electron correlation. The rotational barrier about the C–C bond at the carbonyl was satisfactorally reproduced with a smaller basis set, and electron correlation had little effect.[1,2]

It is now necessary to determine the origin both of the barriers and the energy differences. It might first be noted that intramolecular hydrogen bonding in the acids cannot be the important factor since the *Z*/*E* energy difference is essentially the same for formic acid and methyl formate. The greater *Z*/*E* difference for methyl acetate than methyl formate is a result of the steric interaction between the two methyl groups in the acetate. This can be seen from the bond angles (Table IV) where the C–C–O bond angle is 7° larger in the *E* than the *Z* rotamer, and the C-O-C angle is 6° larger.

A number of explanations have been proposed for these energy differences,[4] but we shall make use of a different approach that

Table III. Calculated Energies of Acetic Acid and Methyl Acetate Conformers

		$\frac{\text{4-31G}}{\text{4-31G}}$		$\frac{\text{6-31G*}}{\text{6-31G*}}$		$\frac{\text{6-31G**}}{\text{6-31G*}}$		$\frac{\text{MP3/6-31G**}}{\text{6-31G*}}$		$\frac{\text{6-311+G**}}{\text{6-31G*}}$		$\frac{\text{MP3/6-311+G**}}{\text{6-31G*}}$	
compd	τ[a]	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*	*E*	Δ*E*
CH_3CO_2H	0 (*Z*)	−227.47034	0.00	−227.81065	0.00	−227.82215	0.00	−228.46457	0.00	−227.88331	0.00	−228.57466	0.00
	60	−227.45584	9.10	−227.79478	9.96								
	90	−227.44980	12.86	−227.78874	13.75	−227.80078	13.41	−228.44321	13.40	−227.86277	12.88	−228.55466	12.55
	120	−227.45042	12.49	−227.79054	12.62								
	180 (*E*)	−227.45075	8.35	−227.79918	7.20	−227.81080	7.12	−228.45418	6.52	−227.87260	6.72	−228.56533	5.85
CH_3CO_2-Me[b]	0	−266.43691	0.00	−266.83683	0.0	−266.84649	0.00	−267.64167	0.00	−266.90440[d]	0.00	−267.71575[d]	0.00
	60	−266.42232	9.16	−266.82193	9.34								
	90	−266.41627	12.95	−266.81615	12.98	−266.82578	12.99	−267.62065	13.19				
	120	−266.41563	13.35	−266.81610	13.01								
	180	−266.42056	10.25	−266.82181	9.43	−266.83143	9.45	−267.62787	8.66	−266.88951	9.34	−267.70200	8.63
CH_3CO_2-Me[c]	0	−266.43569	0.00	−266.83468									
	60	−266.42108	9.17										
	90	−266.41438	13.37										
	120	−266.41411	13.54										
	180.0	−266.41867	10.68										

[a] O=C—O—R torsional angle. Total energies are given in Hartrees, energy differences are given in kcal/mol, and τ are in deg. [b] Methoxy hydrogens staggered with respect to C—O bond. [c] Methoxy hydrogens eclipsed with respect to C—O bond. [d] 6-311+G* calculations (no polarization functions on hydrogens).

Table IV. Structures of Acetic Acid and Methyl Acetate Conformers

unit	0°	60°	90°	120°	180°
		a. Acetic Acid, 6-31G*			
$r_{C=O}$	1.1869	1.1813	1.1788	1.1787	1.1806
r_{C-O}	1.3323	1.3545	1.3623	1.3548	1.3377
r_{C-C}	1.5019	1.5031	1.5049	1.5078	1.5110
r_{O-H}	0.9523	0.9499	0.9496	0.9490	0.9476
∠C—C=O	125.81	125.20	124.85	124.50	124.29
∠C—C—O	111.82	112.45	113.38	114.34	115.27
∠O—C=O	122.37	122.35	121.77	121.16	120.44
∠C—O—H	108.10	110.73	111.41	111.78	112.17
		b. Methyl Acetate, 6-31G*			
$r_{C=O}$	1.1879	1.1830	1.1807	1.1812	1.1832
r_{C-O}	1.3265	1.3466	1.3534	1.3489	1.3337
r_{C-C}	1.5043	1.5036	1.5060	1.5094	1.5119
r_{O-C}	1.4164	1.4146	1.4115	1.4108	1.4068
∠C—C=O	125.20	124.95	124.54	123.70	123.04
∠C—C—O	111.41	112.37	113.72	115.88	118.08
∠O—C=O	123.39	122.68	121.74	120.42	118.88
∠C—O—C	116.94	116.64	116.73	119.50	122.45

is based on the electron distribution derived from the calculated wave functions. The 6-31G** wave functions should be satisfactory for the following analysis. This basis set gave results that were in reasonable agreement with experiment, and correction for electron correlation, although it leads to a more diffuse electron distribution in the bonding region, does not appear to significantly effect electron populations calculated from the charge densities.[15]

Structural Chemistry of the Carbonyl Group

Before attempting to determine the origin of the rotational barrier in acids and esters, it would appear desirable to examine the nature of the interaction between the carbonyl group and its substituents in the lowest energy conformations. The structures of a variety of disubstituted carbonyl compounds have been calculated with the 6-31G* basis set and are compared with the observed geometries in Table V.[16] As is usually observed, the calculated bond lengths were ~1% shorter than the observed values,[12] and the calculated bond angles were generally in quite good agreement with the experimental values.[17] The latter often have an experimental uncertainty on the order of ±1°, and therefore, in the following comparison the calculated bond angles will be used.

The most striking observation is that the A–C–**B** bond angles are always considerably smaller than 120°, and in many cases they are smaller than the tetrahedral angle. Why are the angles so small and why do they vary with substituents? It is often convenient to consider the interaction between groups in terms of the fraction of p character in the bonds.[18] This may be defined in terms of the bond angles, but the observed angles may not be the appropriate quantities.

The bond path is defined as the path of maximum electron density joining a pair of bonded nuclei.[19] In the absence of a constraint external to the bonds forming the angle, the bond path is expected to be colinear with a line drawn between the nuclei. However, if the bond is distorted as a result of steric interactions between substituents, or the formation of a ring, the bond path will be found to be bent.[19] We propose to use the angle between bond paths at the central angle to indicate the undeformed bond angle. They have been calculated from the 6-31G** wave functions obtained at the 6-31G* geometries and are given in Table VI.

In order to convert the angles to fractional p character, we proceed as follows. The carbon orbitals may be written as

$$\psi_{C=O} = 1/\sqrt{N_1}(s + \lambda p_1)$$

$$\psi_{C-A} = 1/\sqrt{N_2}(s + \delta p_2)$$

$$\psi_{C-B} = 1/\sqrt{N_3}(s + \epsilon p_3)$$

where the p orbitals are aligned with the bond directions. The orthogonality requirement leads to

$$\lambda\delta = -1/\cos\alpha_1$$

$$\lambda\epsilon = -1/\cos\alpha_2$$

$$\delta\epsilon = -1/\cos\alpha_3$$

where α_1, α_2, and α_3 are the three bond angles at the carbon. The equations may be solved for λ, δ, and ϵ, and the carbon orbitals may be obtained via normalizing the ψs (i.e., obtaining the values of N_1, N_2, and N_3). The fractions of p character (p_A, p_B, and p_C) are obtained by squaring the normalized p coefficients. Although there may be some reservation about the form of this treatment in terms of the absolute values of p_A, p_B, and p_C,[20] it is only the changes that are of interest, and they should be satisfactory.

The fractional p-character values thus derived are given in Table VI. It may at first appear surprising that the fractional p character attributed to the carbonyl group in formaldehyde is only 0.58, whereas oxygen is more electronegative than hydrogen. One normally expects that an electronegative atom would prefer a σ orbital having high p character, but this need not be the case with a double bond. In this case, an analysis of the electron populations at each atom on a MO by MO basis is helpful (Table VII). The two carbonyl σ orbitals (MO 3 and 6) are formed by using the carbon 2s and $2p_z$ atomic orbitals, respectively. The carbon contributions to each are about the same, and although it may be coincidental, the fraction of the carbon population in these orbitals derived from $2p_z$ (0.280/(0.280 + 0.204)) is 0.58, the same as the fraction p character derived from the analysis of the bon angles. The large fraction of the hydrogen electron population derived from MO 8 shows the importance of back donation from the oxygen lone pairs into the hydrogens. Protonation of the carbonyl oxygen should considerably increase its electronegativity, and here the σ orbital from the carbon to the oxygen is estimated to have 0.78 p character (Table VI).

The changes in the other fractional *p* characters follow one's expectation based on the electronegativity of the substituents. The angle opposite to the more electronegative atom will have the larger bond angle, and the bond orbital directed toward it will have high p character. This may be examined in the series in which A = B, as well as in the cases where B = H and A is varied. The electronegativity order derived from these structural data is F > Cl > HO > NH_2 > H > CH_3, which is the conventionally accepted order,[21] except for CH_3 and H. However, more recent studies[22] have shown that the bond dipole in methane is, in fact, H_3C^+–H^-, which is in accord with the order found above. It can be seen that structural data are useful for estimating the fractional p character of bonds.

It should be noted that one would not have reached this conclusion using just the conventional bond angles. For example, in formic acid the conventional angles α_1 and α_2 are about equal which does not correspond to the difference in electronegativity

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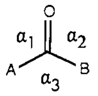
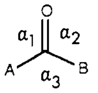
Table V. Comparison of Calculated and Experimental Structures for Carbonyl Derivatives



compd	A	B		$r_{C=O}$	r_{C-A}	r_{C-B}	α_1	α_2	α_3
H_2CO	H	H	calcd	1.184	1.092	1.092	122.1	122.1	115.8
			obsd	1.206*B*	1.108*B*	1.108*B*	121.7*B*	121.7*B*	116.6*B*
FCHO	F	H	calcd	1.164	1.314	1.081	123.03	126.96	110.01
			obsd	1.181*D*	1.228*D*	1.095*C*	122.8*C*	127.3*D*	109.9*D*
ClCHO	Cl	H	calcd	1.165	1.756	1.083	123.21	126.11	110.68
			obsd	1.188*B*	1.760*C*	1.096*B*	123.6*D*	126.5*C*	109.9*D*
HOCHO	HO	H	calcd	1.182	1.323	1.084	124.9	124.7	110.4
			obsd	1.195	1.352	1.105	122.4	123.0	114.6
H_2NCHO	H_2N	H	calcd	1.193	1.349	1.091	124.95	122.39	112.66
			obsd	1.219*D*	1.352*D*	1.098*D*	124.7*C*	122.6*D*	112.7*D*
CH_3CHO	CH_3	H	calcd	1.188	1.505	1.095	124.3	120.3	115.4
			obsd	1.207*B*	1.515*B*	1.106*B*	124.0*C*	121.1*D*	114.9*D*
F_2CO	F	F	calcd	1.157	1.290	1.290	125.86	125.86	108.28
			obsd	1.170*B*	1.317*A*	1.317*A*	126.2*B*	126.2*B*	107.6*B*
ClFCO	Cl	F	calcd	1.158	1.720	1.300	125.78	124.14	110.09
			obsd	1.162*X*	1.751*X*	1.303*X*	117.5*X*	130.5*X*	112.0*X*
CH_3COF	CH_3	F	calcd	1.168	1.496	1.327	128.61	120.56	110.83
			obsd	1.185*C*	1.502*B*	1.343	127.9*D*	121.4*D*	110.7*D*
Cl_2CO	Cl	Cl	calcd	1.159	1.734	1.734	123.43	123.43	113.14
			obsd	1.166*B*	1.746*B*	1.746*B*	124.4*B*	124.4*B*	111.3*B*
CH_3COCl	CH_3	Cl	calcd	1.167	1.503	1.785	127.23	119.88	112.89
			obsd	1.185*B*	1.505*B*	1.796*B*	127.2*B*	121.2*B*	111.6*C*
HOCOOH	HO	OH	calcd	1.188	1.315	1.315	125.14	125.14	109.72
CH_3COOH	CH_3	OH	calcd	1.187	1.502	1.332	125.81	122.36	111.82
			obsd	1.212*B*	1.517*C*	1.361*B*	126.6*D*	123.0*D*	110.6*C*
CH_3COCH_3	CH_3	CH_3	calcd	1.192	1.513	1.513	121.74	121.74	116.51
			obsd	1.222*B*	1.507*B*	1.507*B*	121.4*B*	121.4*B*	117.2
H_2COH^+	H[c]	H[d]	calcd	1.232	1.079	1.076	121.68	116.19	122.13

[a] Units: lengths in Å, angles in deg. [b] The uncertainties in the experimental data use the code given in the following: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. L.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619. For bond lengths, *B* = ±0.002 to ±0.005; *C* = ±0.005 to ±0.010; *D* = ±0.01 to ±0.02. For bond angles, *B* = ±0.2 to ±0.5°; *C* = ±0.5 to ±1.0°; *D* = ±1 to ±2°. In both cases, X = unknown. The experimental data were taken from the above reference unless otherwise noted. [c] Hydrogen on the side of the HO group. [d] Hydrogen opposite to the HO group.

Table VI. Hybridization in Carbonyl Derivatives



compd	A	B	α_1	$\Delta\alpha_1$	α_2	$\Delta\alpha_2$	α_3	$\Delta\alpha_3$	p_O	p_A	p_B
$H_2C{=}O$	H	H	123.00	0.84	123.00	0.84	114.00	-1.72	0.58	0.71	0.71
FCHO	F	H	121.71	-1.32	133.08	6.12	105.21	-4.80	0.42	0.83	0.75
ClCHO	Cl	H	122.40	-0.81	132.46	6.35	105.14	-5.54	0.42	0.83	0.75
HOCHO	HO	H	121.66	-3.22	128.93	4.20	109.41	-0.99	0.50	0.78	0.72
H_2NCHO	H_2N	H	123.92	-1.03	125.53	3.14	110.55	-2.11	0.52	0.75	0.73
CH_3CHO	CH_3	H	124.56	0.29	121.67	1.38	113.76	-1.67	0.57	0.70	0.73
F_2CO	F	F	128.59	2.73	128.59	2.73	102.82	-5.46	0.36	0.82	0.82
Cl_2CO	Cl	Cl	128.19	4.76	128.19	4.76	103.63	-9.51	0.38	0.81	0.81
HOCOOH	HO	OH	125.45	0.31	125.45	0.31	109.10	-0.62	0.49	0.75	0.75
CH_3COCH_3	CH_3	CH_3	122.83	1.09	122.83	1.09	114.34	-2.17	0.58	0.71	0.71
ClFCO	Cl	F	129.71	3.93	126.83	2.60	103.46	-6.62	0.38	0.80	0.82
CH_3COF	CH_3	F	134.74	6.13	119.54	-1.02	105.72	-5.11	0.44	0.72	0.84
CH_3COCl	CH_3	Cl	134.32	7.09	120.00	0.12	105.68	-7.21	0.44	0.73	0.84
CH_3COOH	CH_3	OH	130.13	4.32	119.62	-2.74	110.25	-1.57	0.52	0.69	0.79
H_2COH^+	H	H	121.68	4.65	116.90	-0.71	126.07	-3.93	0.71	0.66	0.59

between hydrogen and hydroxy. The expected difference in angles is found when the bond paths are used. An even more extreme case is formamide. Here, the larger conventional angle is opposite the hydrogen, but the larger bond path angle is found opposite the amino group as expected.

The differences between the conventional and bond path angles ($\Delta\alpha$) may be attributed to a combination of steric and coulombic interactions. A negative value suggests a repulsive interaction between the outer atoms of those forming the bond angle. A positive value could indicate an attractive interaction, but it is more likely that it reflects a smaller repulsion than at other angles. Negative $\Delta\alpha$'s are generally found with small bond path angles that would tend to bring the end atoms close together, and positive $\Delta\alpha$'s are generally found with large angles where the repulsion between the end atoms would be small.

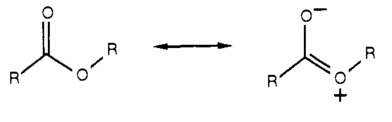
In carbonic acid, with three oxygen substituents, $\Delta\alpha_3$ is essentially zero. In phosgene, the large chlorine substituents will lead to both steric and coulombic repulsion, and a large negative value of $\Delta\alpha_3$ (−9.5°), and in carbonyl fluoride, the somewhat smaller fluorine atoms lead to a correspondingly smaller $\Delta\alpha_3$ (−5.5°). The importance of the coulombic repulsion in these cases is seen by comparing them with acetone. Here, the steric repulsion between the methyls, which are larger than fluorine, leads to $\Delta\alpha_3$ of only −2.2°. It can be seen that an analysis of bond angles in this fashion leads to information on both changes in the electronic interactions (hybridization) and the steric interactions.

Table VII. Electron Populations for Formaldehyde

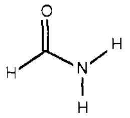
MO	O	C	H	type
1 (A1)	2.000	0.000	0.000	O 1s
2 (A1)	0.004	1.996	0.000	C 1s
3 (A1)	1.776	0.204	0.010	σ CO (2s)
4 (A1)	0.404	0.948	0.324	σ CH_2 ($2p_z$)
5 (B2)	0.776	0.614	0.306	π CH_2 ($2p_y$)
6 (A1)	1.542	0.280	0.088	σ CO ($2p_z$)
7 (B1)	1.560	0.412	0.014	π CO ($2p_x$)
8 (B2)	1.234	0.184	0.290	O 1p ($2p_y$)
total	9.296	4.638	1.032	

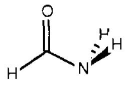
Origin of the Rotational Barrier

We may now examine the origin of the rotational barrier. The simplest explanation would propose significant ester resonance at 0°, which would be lost at ~90°. Such resonance is generally interpreted as charge transfer from the ether oxygen to the acyl oxygen[23] in a fashion similar to the allyl anion:

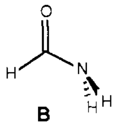


A resonance interaction of this type should be more important with an amide, and here the rotational barrier[24] is much better determined than for the esters. Therefore, formamide appeared to be a good starting point for a study of rotational barriers. The barrier for formamide has been the subject of numerous calculations, with the best calculation using the 4-31G basis set.[25-27] In some cases, the rotational barriers are not well represented with this basis set, and polarization functions are needed.[1,2] We have repeated the calculations with the 6-31G* basis set with complete geometry optimization for the low-energy planar conformer and for the two saddle point conformers having the amide hydrogens toward the carbonyl (A) and having them away from the carbonyl (B). Correction for electron correlation was carried out with MP3/6-31G** at the 6-31G* geometries. The barrier was calculated to be 15.3 kcal/mol (Table VIII). The experimental barrier for formamide is 18–19 kcal/mol.[24] Thus, the barrier is calculated satisfactorally. The optimized geometries are given in Table VIII.





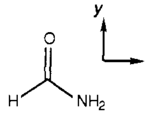
A



B

Boggs et al.[28] have pointed out the importance of the basis set choice in correctly calculating the geometry at amino groups. As a check on the 6-31G* calculations for the planar conformer, we have repeated the optimization using the well-balanced 6-31G** basis set. The planar amino group was again found to have the lower energy, but the potential function for out-of-plane bending was found to be very small. This is in good agreement with the more recent experimental work on formamide.[29] The change in geometry from the 6-31G* basis was insignificant.

Table VIII. Structures and Energies of Formamide Conformers[a]

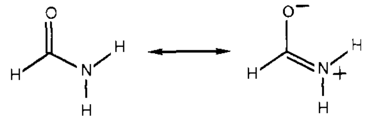


parameter	conformer planar	conformer A	conformer B
energy 6-31G*)	−168.93070	−168.90569	−168.90114
ΔE (kcal/mol)	0.0	15.69	18.55
energy (6-31G**)	−168.94048	−168.91501	−168.91072
ΔE (kcal/mol)	0.0	15.98	18.67
energy (MP3/6-31G**)	−169.42856	−169.40411	−169.40050
ΔE (kcal/mol)	0.0	15.34	17.60
μ (D)	4.095	1.573	4.080
$\mu(y)$	−3.943	−1.285	−3.983
$\mu(x)$	1.102	0.907	−0.883
$r_{C=O}$	1.1927	1.1832	1.1789
r_{CN}	1.3489	1.4273	1.4230
r_{CH}	1.0910	1.0876	1.0943
r_{NH}	0.9957[b] 0.9929[c]	1.0055	1.0046
∠N—C—O	124.95	125.05	123.27
∠H—C—N	112.66	113.48	116.39
∠C—N—H	119.33[b] 121.79[c]	108.48	109.78
∠H—N—H	118.88	105.48	106.36
τ^d	0.0	122.94	58.29

[a] Total energies are given in hartrees, bond lengths are given in Å, and bond angles are given in deg. The structures were obtained by using the 6-31G* basis set. [b] Hydrogen eclipsed with carbonyl. [c] Hydrogen eclipsed with aldehyde proton. [d] H–C–N–H torsional angle.

Before considering the rotational barrier, the 2.3 kcal/mol calculated difference between the two saddle point rotamers, A and B, might be noted. Although one might be tempted to attribute the energy difference to a difference in the interaction of the nitrogen lone pair with the C=O bond orbitals,[30] the explanation may be more simple. The calculated dipole moment of formamide (4.10 D, Table VIII) is in good agreement with the observed value (3.85 D),[31] and so the calculated dipole moments of A and B also should be satisfactory. A large difference in dipole moment between the planar and rotated conformers is predicted (Table VIII), and using a very simple model, it corresponds roughly to a 2.9 D C=O bond moment and a 1.6 D NH_2 group moment (largely an atomic moment derived from the lone pair). Assuming the bond dipoles may be represented by point charges, the difference in coulombic interactions for the two rotamers would be on the order of 2 kcal/mol. Although this is only a very rough estimate, it does suggest that the difference in dipole moments may be sufficient to account for much of the energy difference.

In examining the nature of the interaction between the amide nitrogen and the carbonyl group, it seems reasonable to concentrate on the C=O and C—N bond lengths and the electron populations at the O, C, and N atoms. In the conventional view of amide resonance



it acts to transfer charge from nitrogen to oxygen, reduces the C=O bond order, and increases the C—N bond order. The C-N bond length increases 0.08 Å on going from the planar conformation to A, suggesting that there is some C-N double bond character in the planar conformer. However, the C-O bond length decreases only 0.01 Å. This suggests that the carbonyl is relatively unaffected by the rotation. Acetate ion should be a good model for a species with 50% charge transfer from N to O, and here the

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(23) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955; p 160.

(24) Sunner, B.; Piette, L. H.; Schneider, W. G. *Can. J. Chem.* **1960**, *38*, 681. Kamei, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2269. Drakenberg, T.; Forsen, S. *J. Phys. Chem.* **1970**, *74*, 1.

(25) For a review of early calculations, see: Carlsen, N. R.; Radom, L.; Riggs, N. V.; Rodwell, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2233.

(26) Nalewajski, R. F. *J. Am. Chem. Soc.* **1978**, *100*, 41.

(27) Radom, L.; Riggs, N. V. *Aust. J. Chem.* **1980**, *33*, 249.

(28) Boggs, J. E.; Niu, Z. *J. Comput. Chem.* **1985**, *6*, 46.

(29) Hirota, E.; Sugisaki, R.; Nielsen, C. J.; Sorensen, G. O. *J. Mol. Spectrosc.* **1974**, *49*, 251.

(30) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: New York, 1983.

(31) Costain, C. C.; Dowling, J. M. *J. Chem. Phys.* **1960**, *32*, 158.

calculated C–O bond length is 1.233 Å,[32] which is approximately half-way between that for dimethyl ether (1.400 Å) and propanal (1.188 Å).[12] The values may be compared with 1.193 Å for planar formamide, suggesting that it has a normal C–O double bond. Again, it is seen that there is little evidence for loss of double bond character and for charge transfer of the type indicated above.

Bader has provided a unique way in which to assign volume elements in a molecule which may be attributed to individual atoms.[33] The electron populations were obtained by numerical integration of the charge densities obtained from the 6-31G** wave functions subject to these boundary conditions. The kinetic energies of the electrons within each region also were obtained at the same time. The Virial theorem requires that the potential energy (V) be related to the kinetic energy (T) by $V = -2T$. Since the total energy is $E = V + T$, it can be seen that $E = -T$. As a result, knowing the kinetic energy of the electrons assigned to a given atom, the energy of that atom may be obtained. The sum of the atom energies will equal the energy of the molecule. These data are presented in Table IX.

In examining the electron population at nitrogen, it can be seen to be *larger* in the planar conformer than in the saddle point species, A, just the opposite of what would be expected on the basis of a simple resonance model. The population at oxygen is only slightly affected, and most of the charge transfer occurs between carbon and nitrogen.

There is a marked change in geometry at the nitrogen between the two conformers. In the planar conformer, the bond angles about the nitrogen are all ~120°, corresponding to sp^2 hybridization. This is reasonable since it then places the lone pair in a p orbital which has the appropriate geometry for interacting with the carbonyl π system. In the saddle point structure, A, the angles are ~105°, corresponding roughly to sp^3 hybridization. This is the normal geometry of an amino group, and it places the lone pair in an orbital in the plane of the carbonyl group where it may interact with the carbonyl σ system. The change in geometry is readily understood on this basis. The nitrogen in the planar conformer should, by virtue of its greater s character, be more electronegative than that in the saddle point conformer, and consequently, it withdraws more charge density from carbon. Its higher electronegativitiy also may be seen in the amide hydrogens which have the lower electron populations in the planar conformer. As a result, the C–N bond in the planar conformer has more ionic character, resulting in a shorter and stronger bond.

The changes in the energies of the atoms are interesting (Table VIII). The energy of the oxygen is essentially unchanged in the two conformers. The nitrogen in the planar conformer, having the higher electron population, has a higher electron kinetic energy and, as a consequence, a lower total energy than for the saddle point conformer. The opposite energy change is found for the carbon, along with small changes in the hydrogen energies. The important observation is that the energy of the nitrogen decreases more that the increase in energy of the carbon and the hydrogens on going from the saddle point to the planar conformer. This may be related to the greater electronegativity of nitrogen.

The difference between the two conformers may further be examined by separating the total electron populations into the components for the different types of MOs (Table X). The core orbitals involve just the 1s atomic orbitals on carbon, oxygen, and nitrogen. The π orbitals are those that employ the 2p atomic orbitals perpendicular to the plane of the molecule, and the σ orbitals are those that use the 2s and the 2p orbitals in the plane of the molecule. The N is more effective in acquiring π charge density in the planar conformer than in the saddle point conformers. This is also true for the oxygen, but to a much smaller extent. A major difference between the planar and rotated conformers is that in the latter the amide hydrogens acquire much of their electron populations from the π orbitals, whereas in the former, they are geometrically prevented from achieving much π electron density. (The small amount shown in the table is derived from the p-polarization functions placed on the hydrogens in the 6-31G** basis set.)

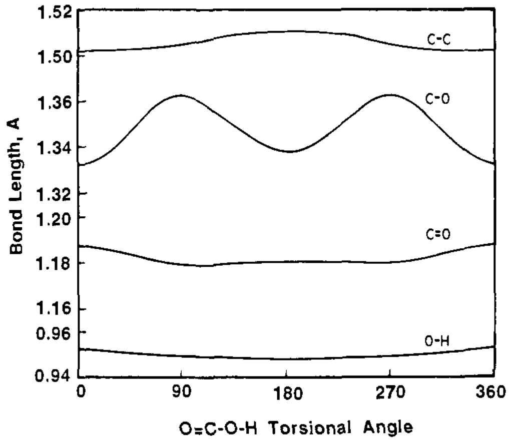

Figure 1. Change in bond lengths (Å) with O=C—O—H torsional angle for acetic acid.

In examining the acids and esters, it is convenient first to examine the bond length changes. They are essentially the same for all four compounds, and those for acetic acid are shown in Figure 1. It can be seen that most of the bond lengths are insensitive to rotation about the C–O bond. Only the C–O single bond length shows significant variation, being ~0.02 Å longer at 90° than at 0°. Thus, as with formamide, there is some gain in double bond character as the bond is rotated from 90° toward the planar conformer. However, the C=O bond is hardly affected.

Further information may be gained by examining the bond path angles (Figure 2). The angles and changes from the conventional angles are essentially the same for formic and acetic acids and are shown in graphical form for acetic acid in Figure 3. The bond path angles are larger than the conventional angles for the H—C=O or CH_3—C=O groups of formic and acetic acids, respectively. This indicates a repulsive interaction between the other groups attached to the central carbon and is expected since the above angles are the largest of the three as a result of the electronegativity of the oxygen opposite the angle.

The conventional and bond path angles tend to move in opposite directions for the O—C=O and C—C—O bonds of acetic acid (Figure 3), with the latter angles changing relatively little. However, with the C—O—H angles, both types of angles increase on going from 0 to 90° and then change at a smaller rate on going to 180°. This strongly suggests a change in hybridization at oxygen on rotation about the C–O bond. The details of the change are not as easily seen as with formamide since the locations and hybridizations of the lone pairs are not as easily determined by symmetry considerations.

We may now proceed to examine the properties of the atoms in these molecules (Table XI). The changes in electron population are not as easily interpreted as in the formamide case. Since the main question relates to the energies of rotamers, it would seem appropriate to concentrate on the atom energies. It can be seen that T' for the carbonyl oxygen is only slightly changed on rotation, whereas T' for the carbonyl carbon and the other oxygen change considerably. These changes parallel those for the geometrical parameters. It is clear that the rotational barrier is mainly concerned with the C–O bond and not with the carbonyl oxygen.

Why does the Z rotamer of formic acid have a lower energy than the E species? One might at first think that it is associated with hydrogen bonding, or at least some attractive coulombic interaction between the carbonyl oxygen and the acid proton in the Z rotamer. However, methyl formate has a similar energy difference, and here this interaction does not exist. It is nevertheless true that the dipole moment of (Z)-methyl formate (calcd 1.98 D) is considerably smaller than that of the E rotamer (calc 4.60 D). Therefore the Z rotamer is stabilized by an attractive interaction between the C=O and O—C dipoles. A comparison

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[32] Unpublished results. The 6-31G* energy was −227.22507 hartrees for the rotamer with a hydrogen eclipsed with an oxygen and −227.22499 hartrees for the 60° rotated species.

[33] Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.

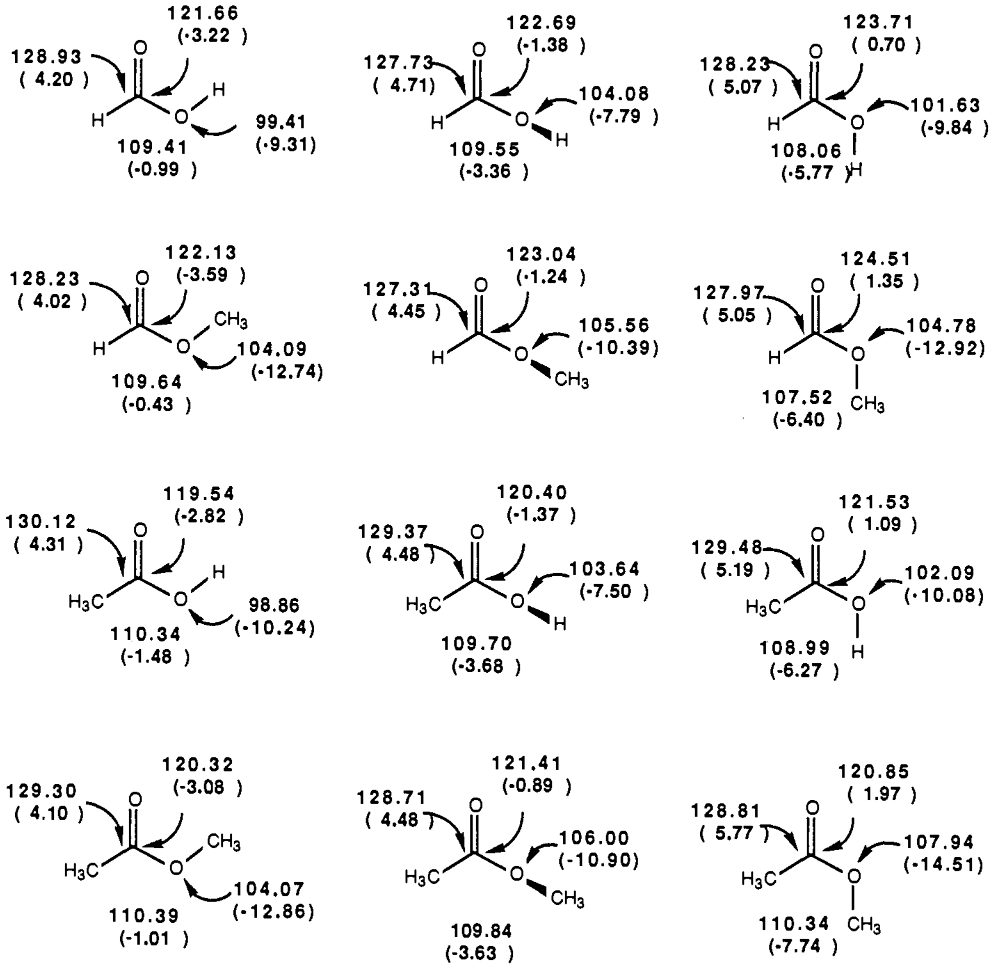

Figure 2. Bond path angles and deviations from bond angles (in parentheses) for formic acid, methyl formate, acetic acid, and methyl acetate.

Table IX. Electron Populations and Atom Energies for Formamide (6-31G**/6-31G*)

conformer	atom	N^a	T^b	L^c	$T' = -E^d$
planar	N	8.476	55.1131	0.0019	55.2279
	C	4.020	36.4747	0.0045	36.5507
	O	9.392	75.4893	-0.0082	75.6466
	H4	1.035	0.6539	0.0001	0.6553
	H5	0.529	0.4203	0.0001	0.4212
	H6	0.544	0.4319	0.0000	0.4328
	sum	23.996			168.9345
A	N	8.222	54.8682	0.0016	54.9785
	C	4.242	36.6454	-0.0050	36.7191
	O	9.343	75.5034	-0.0082	75.6552
	H4	1.005	0.6435	0.0001	0.6448
	H5,6	0.592	0.4548	-0.0001	0.4557
	sum	23.996			168.9090
B	N	8.209	54.8633	0.0020	54.9733
	C	4.226	36.6253	-0.0006	36.6988
	O	9.318	75.4988	-0.0082	75.6502
	H4	1.038	0.6541	0.0000	0.6554
	H5,6	0.604	0.4620	0.0001	0.4629
	sum	23.999			168.9035

[a] Electron populations: units, electrons. [b] Kinetic energy of the electrons associated with each atom: units, hartrees. [c] L is a measure of the accuracy of the numerical integration for T and would be zero if there were no error. L is defined in the Calculation section of the text. [d] Kinetic energy corrected for the virial defect in the MO calculations. $T' = T^*(-1 - V/T)$. The $-V/T$ values are as follows: formamide, 2.002 083 6; A, 2.002 010 0; B, 2.002 005 5.

Table X. Formamide Electron Populations by Orbital Type

conformer	atom	core	σ	π	total
planar	N	2.000	4.626	1.850	8.476
	C	1.996	1.632	0.392	4.020
	O	2.002	5.682	1.710	9.394
	H4	0.000	1.020	0.016	1.036
	H5	0.000	0.512	0.016	0.528
	H6	0.000	0.526	0.016	0.542
A	N	2.000	4.852	1.370	8.222
	C	1.996	1.854	0.390	4.240
	O	2.004	5.736	1.604	9.344
	H4	0.000	0.994	0.016	1.008
	H5,6	0.000	0.280	0.310	0.590
B	N	2.000	4.854	1.356	8.210
	C	1.996	1.824	0.406	4.226
	O	2.004	5.728	1.584	9.316
	H4	0.000	1.026	0.016	1.042
	H5,6	0.000	0.286	0.320	0.606

of the bond path angles (Figure 2) shows that the C–O–H or C–O–C angle in the *Z* rotamer is always smaller than that in the *E* species and that the angle opposite the oxygen is always larger in the *Z* rotamer. This is consistent with the oxygen using a larger degree of s character in its bond to the carbonyl carbon in the *Z* rotamer than in *E*, leading to a lower energy for the former as was found with formamide. The negative Δα values at the oxygen (Figure 2) indicate a repulsive interaction in both the *Z* and *E* rotamers. Although the interactions in the esters are not as easily interpreted as for the amides, it is clear that the same factors must be operative in the two cases.

The rotational barrier for esters has a direct bearing on the energies and conformations of lactones. A smaller ring lactone must adopt the *E* conformation at the ester group, whereas a larger ring lactone may adopt the *Z* conformation. Huisgen has examined the rates of hydrolysis of lactones and from these data estimated an *E*/*Z* energy difference for esters of 3.7 kcal/mol.[34]

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Table XI. Electron Populations and Atom Energies for Acids and Esters (6-31G**/6-31G*)

	atom	N^a	T^b	L^c	$T' = -E^d$		atom	N^a	T^b	L^c	$T' = -E^d$		atom	N^a	T^b	L^c	$T' = -E^d$
a. Formic Acid																	
Z (0°)	C	3.961	36.4143	0.0038	36.4974	Z (90°)	C	3.993	36.4279	0.0032	36.5105	E (180°)	C	3.953	36.4008	−0.0007	36.4828
	=O	9.389	75.5332	0.0001	75.7056		=O	9.345	75.5358	0.0001	75.7070		=O	9.365	75.5378	0.0001	75.7080
	-O-	9.331	75.4449	−0.0010	75.6171		-O-	9.326	75.4050	0.0004	75.5759		-O-	9.311	75.4212	−0.0007	75.5911
	H(0)	0.342	0.3171	0.0001	0.3178		H(O)	0.342	0.3174	0.0001	0.3181		H(O)	0.356	0.3308	0.0001	0.3315
	H(C)	0.975	0.6310	0.0001	0.6324		H(C)	0.992	0.6369	0.0001	0.6383		H(C)	1.015	0.6459	0.0001	0.6474
	sum	23.998			188.7704		sum	23.998			188.7498		sum	24.000			188.7608
					(−188.7705)^e						(−188.7496)^e						(−188.7610)^e
b. Methyl Formate																	
Z (0°)	C(=O)	3.966	36.4213	0.0002	36.4903	Z (90°)	C(=O)	3.984	36.4354	0.0036	36.5034	E (180°)	C(=O)	3.953	36.4194	0.0049	36.4868
	C(Me)	5.242	37.3085	0.0023	37.3792		C(Me)	5.227	37.2862	0.0001	37.3558		C(Me)	5.230	37.2940	−0.0044	37.3630
	=O	9.390	75.5299	0.0002	75.6730		=O	9.348	75.5308	0.0002	75.6718		=O	9.365	75.5305	0.0001	75.6712
	-O-	9.356	75.5212	−0.0062	75.6643		-O-	9.344	75.5030	0.0001	75.6439		-O-	9.339	75.5166	−0.0002	75.6563
	H(ald)	0.984	0.6347	0.0000	0.6359		H(ald)	0.999	0.6389	0.0001	0.6377		H(ald)	1.017	0.6470	0.0000	0.6482
	H(Me)^f	1.026	0.6516	0.0001	0.6528		H(Me)	1.013	0.6460	0.0001	0.6472		H(Me)^f	1.007	0.6428	0.0001	0.6440
	H(Me)	1.020	0.6485	0.0001	0.6497		H(Me)	1.054	0.6602	0.0001	0.6614		H(Me)	1.045	0.6574	0.0001	0.6586
	sum	32.004			227.7949		H(Me)	1.028	0.6511	0.0001	0.6523		sum	32.000			227.7867
					(−227.7958)^e		sum	31.997			227.7735						(−227.7859)^e
											(−227.7754)^e						
c. Acetic Acid																	
Z (0°)	C(=O)	4.083	36.4966	0.0135	36.5666	Z (90°)	C(=O)	4.112	36.5066	0.0030	36.5763	E (180°)	C(=O)	4.071	36.4734	−0.0009	36.5431
	=O	9.405	75.5440	0.0002	75.6889		=O	9.365	75.5498	0.0001	75.6941		=O	9.381	75.5488	0.0012	75.6931
	-O-	9.340	75.4496	−0.0042	75.5943		-O-	9.323	75.3997	0.0001	75.5438		-O-	9.309	75.4182	0.0002	75.5623
	C(Me)	5.778	37.6720	−0.0122	37.7443		C(Me)	5.773	37.6767	−0.0020	37.7487		C(Me)	5.798	37.6888	−0.0008	37.7608
	H(O)	0.343	0.3186	0.0000	0.3192		H(O)	0.347	0.3217	0.0000	0.3223		H(O)	0.362	0.3353	0.0001	0.3359
	H(Me)^f	1.017	0.6366	0.0001	0.6378		H(Me)	1.018	0.6373	0.0001	0.6385		H(Me)^f	1.000	0.6295	0.0001	0.6307
	H(Me)	1.021	0.6341	0.0001	0.6353		H(Me)	1.019	0.6327	0.0001	0.6339		H(Me)	1.039	0.6406	0.0001	0.6418
	sum	32.007			227.8217		H(Me)	1.041	0.6420	0.0001	0.6432		sum	32.001			227.8095
					(−227.8222)^e	sum		31.998			227.8008						(−227.8108)^e
											(−227.8008)^e						
d. Methyl Acetate																	
Z (0°)	C(=O)	4.090	36.4973	0.0010	36.5576	Z (90°)	C(=O)	4.111	36.5095	−0.0064	36.5701	E (180°)	C(=O)	4.096	36.4817	−0.0214	36.5401
	=O	9.406	75.5423	0.0002	75.6671		=O	9.367	75.5419	0.0012	75.6672		=O	9.382	75.5478	0.0002	75.6687
	-O-	9.368	75.5250	−0.0131	75.6498		-O-	9.343	75.4952	−0.0012	75.6205		-O-	9.342	75.5142	0.0002	75.6351
	C(Me)	5.770	37.6716	−0.0065	37.7339		C(Me)	5.776	37.6782	−0.0008	37.7407		C(Me)	5.792	37.6872	−0.0001	37.7475
	H(Me)^a	1.021	0.6384	0.0001	0.6395		H(Me)	1.020	0.6380	0.0001	0.6391		H(Me)^a	1.003	0.6319	0.0001	0.6329
	H(Me)	1.026	0.6362	0.0001	0.6373		H(Me)	1.022	0.6397	0.0001	0.6408		H(Me)	1.039	0.6425	0.0001	0.6435
	C(OMe)	5.233	37.3001	−0.0014	37.3617		H(Me)	1.042	0.6436	0.0001	0.6446		C(OMe)	5.213	37.2837	−0.0063	37.3434
	H(OMe)^a	1.032	0.6543	0.0001	0.6554		C(OMe)	5.213	37.2778	0.0016	37.3397		H(OMe)^a	1.013	0.6463	0.0001	0.6473
	H(OMe)	1.024	0.6502	0.0001	0.6513		H(OMe)	1.017	0.6472	0.0001	0.6483		H(OMe)	1.051	0.6624	0.0001	0.6635
	sum	40.020			266.8422		H(OMe)	1.063	0.6665	0.0010	0.6667		sum	40.021			266.8290
					(−266.8465)^e		H(OMe)	1.031	0.6516	0.0001	0.6527						(−266.8314)^e
							sum	40.005			266.8376						
											(−266.8258)^e						

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[a] Electron population: units, electrons. [b] Kinetic energy of electrons: units, hartrees. [c] L is a measure of the accuracy of the numerical integration for T and would be zero if there were no error. L is defined in the Calculation section of the text. [d] Kinetic energy corrected for the virial defect found in the SCF calculations (i.e., $T^*(-1 - V/T)$). The $-V/T$ values are as follows: formic acid, 2.002 282 9 (0°), 2.002 267 0 (90°), 2.002 252 7 (180°); methyl formate, 2.001 894 5 (0°), 2.001 866 5 (90°), 2.001 849 7 (180°); acetic acid, 2.001 917 9 (0°), 2.001 910 5 (90°), 2.001 910 3 (180°); methyl acetate, 2.001 652 7 (0°), 2.001 659 2 (90°), 2.001 600 8 (180°). [e] RHF calculated total energies (hartrees). If the numerical integration of the kinetic energy were perfect, the sum of T' would equal $-E_T$. [f] Unique hydrogen.

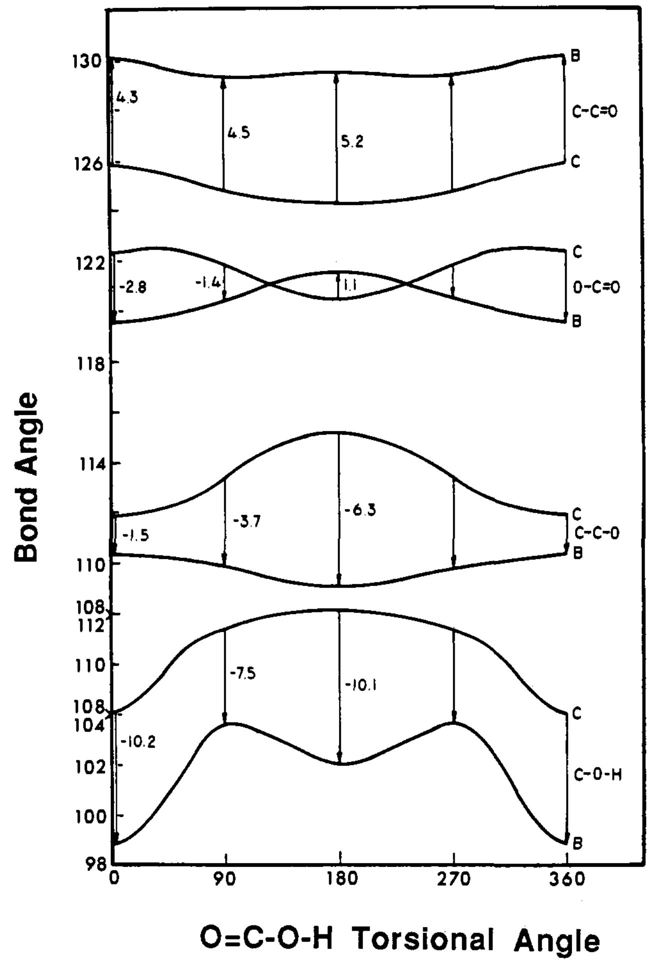

Figure 3. Change in bond angle with O=C—O—H torsional angle for acetic acid (C = conventional bond angle, B = bond path angle).

This is less than half of the difference found for methyl acetate, but the steric interactions in lactones may be less than that in acyclic esters. We are measuring the heats of hydrolysis of lactones in order to gain a better understanding of the interactions in these types of compounds.

Calculations

The molecular orbital calculations were carried out with GAUSSIAN-82.[35] The analysis of the wave functions in terms of the charge distribution was carried out with PROAIMS.[36] This yields the electron populations (N) and the kinetic energies (T) associated with each of the atoms. In the tables, the quantity L is the integrated value of $-(\hbar^2/4m)\nabla^2\rho$. If the numerical integration for T were exact, it would be zero, and its value represents the possible error in T. In order to use T to obtain the energies of the atoms via the virial theorem, it must be corrected for the virial defect found in the MO calculations. The $-V/T$ values are given in the tables, and K is multiplied by $(-V/T) - 1$ to give T'. The sum of T' will be equal to the total energy found in the MO calculation, within the accuracy of the numerical integration.

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Registry No. HCOOH, 64-18-6; $HCOOCH_3$, 107-31-3; CH_3COOH, 64-19-7; CH_3COOCH_3, 79-20-9; H_2NCHO, 75-12-7; H_2CO, 50-00-0; FCHO, 1493-02-3; ClCHO, 2565-30-2; CH_3CHO, 75-07-0; F_2CO, 353-50-4; ClFCO, 353-49-1; CH_3COF, 557-99-3; Cl_2CO, 75-44-5; CH_3COCl, 75-36-5; HOCOOH, 463-79-6; CH_3COCH_3, 67-64-1.

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On the Electronic Structure of Substituted Phthalocyanines: A Hartree–Fock–Slater Study of Octacyano- and Octafluoro-Substituted (Phthalocyaninato)silicon Dihydroxide

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Abstract: The effects of peripheral substitution of strongly electron-withdrawing groups (CN and F) on the electronic properties of $Si(Pc)(OH)_2$ (Pc = phthalocyaninato) are studied via the discrete-variational local exchange (DV–Xα) formalism. Comparisons are made to the electronic structure of the parent molecule, $Si(Pc)(OH)_2$, and the results are discussed in terms of changes in the tight-binding band structure of the corresponding cofacially joined phthalocyaninato polymers. Transition-state calculations yield optical and photoemission spectral energy predictions. The former are in good agreement with experimental data. There is a pronounced lowering of all orbital energies and a substantial increase in ionization potential upon CN and F substitution.

I. Introduction

Phthalocyanine macrocycles form the basis for several extensive families of molecular[1,2] and polymeric[1a,c,3,4] low-dimensional molecular metals.[5] In comparison to other classes of molecular metals, the attractive features of phthalocyanine-based materials include ready availability, chemical stability, low cost, and, in the

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