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Geometrical consequences of intermolecular hydrogen bond formation in the formic acid and acetic acid dimers from ab initio MO calculations

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Abstract

Ab initio molecular orbital calculations on monomer/dimer formic and acetic acids have been performed with the 6-31G* and 6-31G** basis sets, including the electron correlation using second-order Møller–Plesset perturbation theory. Vibrational frequency analyses confirmed the stability of all the computed structures. The computed geometrical changes in dimeric formic and dimeric acetic acids, as compared to their monomers, are in good agreement with the notion of resonance-assisted intermolecular hydrogen bond formation. Trends in the structural changes obtained from electron diffraction were in general confirmed by the calculations, although they failed to predict the difference in the C–C bond length observed in the monomeric and dimeric forms of acetic acid. However, the experimental change in the O–H bond length upon hydrogen bond formation seems definitely exaggerated. Taking into account our previous results on 2-nitroresorcinol and 2-nitrophenol, this change is now expected to be not larger than 0.02 Å.

1. Introduction

In our recent work we have been studying the geometrical consequences of intramolecular hydrogen bond formation in 2-nitroresorcinol [1] and 2-nitrophenol [2]. As 2-nitroresorcinol possesses higher symmetry than 2-nitrophenol, its structural analysis was possible using electron diffraction data alone, while the structure of 2-nitrophenol could be determined only in a concerted ab initio and electron diffraction investigation. Both molecules demonstrate relatively strong intramolecular

hydrogen bonding, assisted by resonance, which is best expressed in terms of the structural changes between these molecules and those of phenol [3] and nitrobenzene [4], in both experimental [1,2] and theoretical [5,2] studies. In view of the generally good agreement between the structural changes determined experimentally and computationally, the rather long O–H bond length and large C–O–H angle found in our electron diffraction investigation of 2-nitroresorcinol [1] are puzzling, even considering the relatively large experimental errors in this study. Initially, the large increase in the O–H bond length was not particularly conspicuous because an analogous

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Table 1
Monomer formic acid: computed geometries^a

Parameter	RHF/6-31G*	RHF/6-31G**	MP2(FC)/ 6-31G*	MP2(FULL)/ 6-31G*	MP2(FULL)/ 6-31G** ^b	MP2(FULL)/ 6-31++G**	MP2(FULL)/ 6-311++G(2D, p)	MP2(FULL)/ 6-311++G(2DF, p)
C–H	1.0834	1.0850	1.0963	1.0960	1.091	1.0908	1.0950	1.0950
C–O	1.3227	1.3216	1.3520	1.3504	1.349	1.3517	1.3476	1.3413
C=O	1.1819	1.1822	1.2133	1.2125	1.212	1.2152	1.2041	1.2013
O–H	0.9533	0.9490	0.9803	0.9801	0.971	0.973	0.9722	0.9710
∠C–O–H	108.71	108.84	105.96	106.10	106.0	107.02	106.78	106.89
∠O–C=O	124.87	124.81	125.08	125.12	125.2	125.08	125.12	125.22
∠O–C–H	110.40	110.46	109.44	109.43	109.4	109.73	109.75	109.67
∠O=C–H	124.73	124.73	125.48	125.45	125.4	125.19	125.13	125.11
Energy (u)	–188.76231	–188.770566	–189.24178	–189.251874	–189.270903 ^c	–189.286628	–189.464289	–189.519820

^a “r_e” equilibrium bond lengths (Å) and angles (deg).

^b From Ref. [8].

^c Calculated from the data of Ref. [8].

large increase in the O–H bond length was reported for dimeric formic acid compared to the monomer [6]. The change of the O–H bond length in monomer/dimer acetic acid was assumed to be approximately the same value in the electron diffraction investigation [7]. However, in view of the good agreement between the electron diffraction and computed O–H bond length change in 2-nitrophenol [2] as compared with phenol [3], which amounts to only 0.01 Å, the early electron diffraction results on formic acid, as well as the O–H bond length and the C–O–H bond angle of 2-nitroresorcinol, reported by us, must be considered suspect. Thus, we decided to investigate the monomers and dimers of formic and acetic acid using the same basis sets and computational levels employed in our studies on phenol [5], nitrobenzene [5], 2-nitrophenol [2], and 2-nitroresorcinol [5]. Our aim in this study, however, is more than just checking the O–H bond length changes that occur on dimer formation. We consider these studies as an extension of our inquiry into the general structural changes that accompany the formation of hydrogen bonds in the gas-phase. We have already alluded to some preliminary results in our recent report on the molecular structure of 2-nitrophenol [2]. The present paper is our complete account of this computational work. There have been other recent computational studies on the structure of the

formic acid dimer [8] and acetic acid dimer [9], the latter of which came to our attention only in the course of our own work. Our interest is somewhat different from that of the other authors in that our study is a part of a general project on the structural consequences of hydrogen bond formation, with at least as much emphasis on the rest of the molecule as on the hydrogen bond itself. The results of the two most recent computational studies [8,9] are used for comparison in our Tables, whereas we only make reference to earlier studies [10].

2. Computational methods

Ab initio molecular orbital calculations were carried out on the monomers and dimers of both formic acid and acetic acid using the GAUSSIAN 92 series of programs [11]. The standard 6-31G basis set [12], augmented by various polarization and diffuse functions, was used throughout. Initially, RHF/6-31G* and RHF/6-31G** optimizations, as well as frequency analyses, were performed on both the monomers and dimers to provide good initial starting geometries for post-Hartree–Fock calculations. These were followed by second-order Møller–Plesset (MP2) optimizations [13] to assess the effect of including electron correlation in the calculations. Specifically, MP2(FC)/6-31G*,

Table 2
Dimer formic acid: computed geometries^a

Parameter	RHF/6-31G*	RHF/6-31G**	MP2(FC)/ 6-31G*	MP2(FULL)/ 6-31G*	MP2(FULL) 6-31G** ^b	MP2(FULL)/ 6-31++G**
C–H	1.0825	1.0842	1.0950	1.0948	1.091	1.0898
C–O	1.2996	1.2981	1.3238	1.3213	1.318	1.3225
C=O	1.1954	1.1960	1.2288	1.2279	1.229	1.2310
O–H	0.9661	0.9625	0.9998	0.9999	0.994	0.9950
∠C–O–H	111.06	111.28	109.32	109.34	109.4	109.65
∠O–C=O	126.03	125.97	126.68	126.71	126.7	126.25
∠O–C–H	111.57	111.71	111.14	111.14	111.3	111.55
∠O=C–H	122.40	122.32	122.18	122.14	122.0	122.20
(C=)O...O(–H)	2.8010	2.7892	2.7561	2.7518	2.699	2.7137
(C=)O...H(–O)	1.8401	1.8307	1.7565	1.7520	1.706	1.7192
∠O–H...O	172.66	173.55	178.56	178.98	178.9	177.67
Energy (u)	–377.548971	–377.548971	–378.512659	–378.533305	–378.57113	–378.598579

^a “*r_e*” equilibrium bond lengths (Å) and angles (deg).

^b From Ref. [8].

Table 3
Monomer acetic acid: computed geometries^a

Parameter	RHF/6-31G*	RHF/6-31G**	MP2(FULL)/ 6-31G*	MP2(FULL)/ 6-31G**	MP2(FULL)/ 6-31G* ^b	MP2(FULL)/ 6-31G**	MP2(FULL)/ 6-31++G** ^b
C-C	1.5019	1.5011	1.5001	1.5016	1.500	1.5016	1.501
C-O	1.3321	1.3309	1.3612	1.3625	1.361	1.3618	1.358
C=O	1.1870	1.1872	1.2170	1.2179	1.217	1.2175	1.210
O-H	0.9523	0.9481	0.9792	0.9794	0.979	0.9708	0.967
C-H ₁	1.0794	1.0795	1.0883	1.0888	1.0883	1.0842	1.0877
C-H ₂	1.0839	1.0840	1.0921	1.0925	1.0921	1.0880	1.0918
C-H ₃	1.0839	1.0840	1.0921	1.0925	1.0921	1.0880	1.0918
∠C-O-H	108.10	108.27	105.45	105.36	105.5	105.34	105.9
∠O-C=O	122.36	122.35	122.60	122.52	122.6	122.67	122.7
∠O-C-C	111.84	111.94	110.98	111.05	111.0	110.97	111.0
∠O=C-C	125.80	125.71	126.42	126.43	126.4	126.36	126.3
∠C-C-H ₁	109.59	109.56	109.30	109.26	-	109.33	-
∠C-C-H ₂	109.63	109.58	109.74	109.73	-	109.64	-
∠C-C-H ₃	109.63	109.58	109.74	109.73	-	109.64	-
Energy (u)	-227.8106479	-227.8221716	-228.4339791	-228.4189369	-228.4339791	-228.453589	-228.6440324

^a r_e, equilibrium bond lengths (Å) and angles (deg).

^b From Ref. [9].

Table 4

Dimer acetic acid: computed geometries^a

Parameter	RHF/6-31G*	RHF/6-31G**	MP2(FC)/ 6-31G*	MP2(FULL)/ 6-31G*	MP2(FULL)/ 6-31G* ^b	MP2(FULL)/ 6-31G**
C–C	1.5014	1.5006	1.5011	1.4995	1.499	1.4992
C–O	1.3081	1.3064	1.3316	1.3301	1.330	1.3269
C=O	1.2007	1.2013	1.2336	1.2327	1.233	1.2334
O–H	0.9658	0.9622	0.9995	0.9998	1.000	0.9944
C–H ₁	1.0794	1.0794	1.0886	1.0882	1.0883	1.0830
C–H ₂	1.0838	1.0839	1.0924	1.0921	1.0921	1.0868
C–H ₃	1.0838	1.0839	1.0924	1.0921	1.0921	1.0868
∠C–O–H	110.80	111.04	109.04	109.12	109.1	109.27
∠O–C=O	123.63	123.62	124.30	124.30	124.3	124.42
∠O–C–C	112.78	112.91	112.36	112.38	112.4	112.53
∠O=C–C	123.60	123.47	123.34	123.32	123.3	123.05
∠C–C–H ₁	109.93	109.91	109.62	109.67	–	109.74
∠C–C–H ₂	109.44	109.36	109.49	109.50	–	109.38
∠C–C–H ₃	109.44	109.36	109.49	109.50	–	109.38
(C=)O···O(–H)	2.7933	2.7793	2.7464	2.7415	2.742	2.6882
(C=)O···H(–O)	1.8291	1.8188	1.7471	1.7421	–	1.6938
∠O–H···O	175.92	175.79	178.56	177.97	–	179.24
Energy (u)	–455.6460755	–455.6690398	–456.8678631	–456.8984318	–456.898396 ^c	–456.968967

^a “r_e” equilibrium bond lengths (Å) and angles (deg).^b From Ref. [9].^c Calculated from the data of Ref. [9].

MP2(FULL)/6-31G*, MP2(FULL)/6-31G** and MP2(FULL)/6-31++G** optimizations were performed to complement and enhance various results which have appeared in the literature [8–10]. MP2(FULL)/6-311++G(2D, p) and MP2(FULL)/

6-311++G(2DF, p) optimizations on formic acid were also performed to provide some insight into the magnitude of changes in the geometrical parameters to be expected in these structures as the basis set becomes more complete.

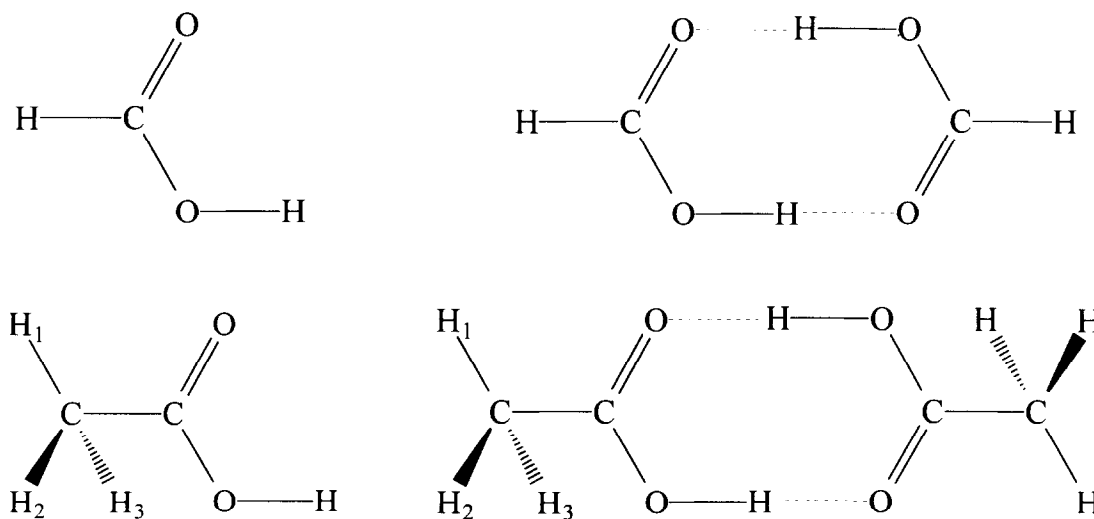


Fig. 1. Monomer formic and acetic acids with the corresponding dimers.

Table 5

Comparison of monomer/dimer formic acid geometrical changes from electron diffraction and MO calculations

Parameter	Electron diffraction ^a			MO calculations ^b MP2(FULL)/6-31G*
	Monomer	Dimer	Difference	Difference
C–H	1.106(24)	1.082(21)	–0.024	–0.001
C–O	1.361(3)	1.323(3)	–0.038	–0.029
C=O	1.217(3)	1.220(3)	+0.003	+0.015
O–H	0.984(24)	1.036(17)	+0.052	+0.020
∠C–O–H	107.3(44)	108.5(4)	+1.2	+3.2
∠O–C=O	123.4(5)	126.2(5)	+2.8	+1.6

^a Bond lengths are r_a values in Ångströms, angles are in degrees; Ref. [6].^b MP2(FULL)/6-31G* ab initio calculations; present work.

3. Results and discussion

The computed equilibrium geometries and total molecular energies of the formic and acetic acid monomers are listed in Tables 1 and 3, and for the corresponding dimers in Tables 2 and 4 (Fig. 1). All these results are reported along with the best computations from the previous works [8,9]. All molecules have a plane of symmetry as confirmed by the calculations. The calculations performed with different basis sets, i.e. RHF/6-31G* and RHF/6-31G**, show a negligible difference between the computed geometries. The introduction of electron correlation appreciably changes the computed values in some cases, while there are only marginal differences between frozen core and full MP2 optimizations.

A comparison of the structural changes in the molecular geometries of formic and acetic acids upon dimer formation from electron diffraction and ab initio calculations is presented in Tables 5 and 6.

In 2-nitroresorcinol [1] and 2-nitrophenol [2] the trends in geometrical changes as compared to phenol and nitrobenzene are in good agreement with those implied by *o*-quinonoid resonance structures. Considering the resonance structures (Fig. 2) describing the electron density redistribution in the formic and acetic acid dimers, several structural consequences of intermolecular hydrogen bond formation may be anticipated. They are described briefly below.

3.1. Monomer/dimer formic acid

For the C–H bond length, any change is hard

Table 6

Comparison of monomer/dimer acetic acid geometrical changes from electron diffraction and MO calculations

Parameter	Electron diffraction ^a			MO calculations ^b MP2(FULL)/6-31G*
	Monomer	Dimer	Difference	Difference
C–C	1.520(5)	1.506(5)	–0.014	–0.001
C–O	1.364(3)	1.334(4)	–0.030	–0.031
C=O	1.214(3)	1.231(3)	+0.017	+0.016
O–H	0.97 ^c	1.03 ^c	+0.06	+0.021
∠C–O–H	107.0 ^c	110.0 ^c	+3.0	+3.7
∠O–C=O	122.8(6)	123.4(8)	+0.6	+1.7

^a Bond lengths are r_a values in Ångströms, angles are in degrees; Ref. [7].^b MP2(FULL)/6-31G* ab initio calculations; present work.^c Assumed in the electron diffraction analysis; Ref. [7].

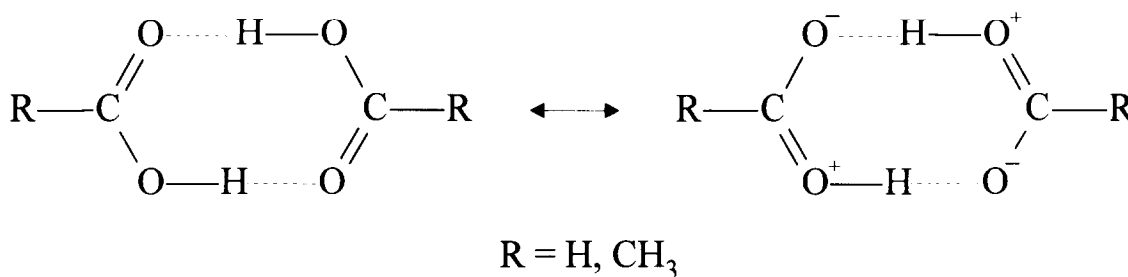


Fig. 2. The resonance structures of the formic and acetic acid dimers.

to predict because of competing effects from the carbonyl bond lengthening and hydroxy C–O bond shortening. The C–H bond shortening seems considerable from the electron diffraction experiment, but it is within the large experimental error. There is virtually no change in the computed C–H bond length.

Considerable shortening of the C–O bond is anticipated by the resonance structure of Fig. 2, and this is confirmed by both experiment and computations.

The C=O bond is expected to be longer on the basis of the resonance structure, providing electron density for the hydrogen bonding. However, the experimental results show only slight lengthening, staying within experimental error. The computed lengthening is more pronounced, amounting to about half of the C–O bond shortening.

The change in the O–H bond length is of primary interest. Formation of the intermolecular hydrogen bond in the formic acid dimer lengthens the O–H bond. The computations show a marked but moderate lengthening, 0.02 Å. The experimental [6] lengthening of 0.05 Å seems exaggerated.

On the basis of the resonance structures one would expect considerable opening of the C–O–H bond angle. The increased double bond character of the C–O bond is achieved at the expense of oxygen lone pairs. The change of the tetrahedral arrangement of the electron pairs around the oxygen is in a direction toward a trigonal planar configuration implying an opening of the C–O–H angle, in accordance with the VSEPR model [14]. Both the experimental and computed structures are in agreement with this prediction, with the computed opening being somewhat larger.

Finally, an opening of the O–C=O angle may be anticipated in agreement with the changes in the C–O bond referred to in the previous paragraph. Again, both the experimental and computed data concur, with the computed structures showing a smaller change in this case.

3.2. Monomer/dimer acetic acid

For the C–C bond length, again, competing effects make any prediction of change difficult, similar to the situation of the C–H bond of formic acid. Some shortening, however, may take place as a consequence of the interaction between the electron-releasing methyl group and the somewhat delocalized π -electron density of the carboxyl group due to hydrogen bond formation. An analogy might be considered between methylcyclohexane ($r_g = 1.536 \pm 0.002$ Å) [15] and monomeric acetic acid on the one hand, and toluene ($r_g = 1.507 \pm 0.004$ Å) [16] and dimeric acetic acid on the other hand. This effect is detected in the experimental data, however, not in the computational results.

The C–O bond shortening and the C=O bond lengthening are predicted by the resonance scheme and are well reflected in both the experimental and the computational results.

Unfortunately, both the O–H bond length and the C–O–H bond angle were assumed in the original electron diffraction study [7]. The assumed opening of the C–O–H bond angle is in good agreement with the calculated results, while the assumed O–H bond lengthening is apparently far too large when compared to the calculated value.

Concerning the O–C=O bond angle, the

Table 7

Dimerization energies (kcal mol⁻¹)

Dimer	Computational level					
	RHF/6-31G*	RHF/6-31G**	MP2(FC)/ 6-31G*	MP2(FULL)/ 6-31G*	MP2(FULL)/ 6-31G**	MP2(FULL)/ 6-31++G**
Formic acid dimer	-15.2	-15.3	-18.3	-18.5	-18.4	-15.9
Acetic acid dimer	-15.5	-15.5	-18.8	-19.1	-19.0	–

experimental results demonstrate a slight opening, within experimental error, in agreement with the expectations mentioned above. The computed change is more pronounced.

4. Conclusions

The trends in the structural changes of formic and acetic acids upon dimerization are in general agreement with those implied by their resonance forms. The experimental data on acetic acid seem to be in closer agreement with the computed structural changes than those on formic acid. The experimentally determined O–H bond length change seems definitely exaggerated and the value of 0.02 Å computed for both compounds appears to us as a realistic and acceptable characterization of this change upon dimerization.

The dimerization energies are given in Table 7. The dimerization energy appears to be slightly more negative for acetic acid than for formic acid at all computational levels. It is interesting to note that the MP2(FULL)/6-31++G**//MP2(FULL)/6-31++G** calculation finds a decrease in the dimerization energy of 2.6 kcal mol⁻¹ compared to that found at the MP2(FULL)/6-31G*//MP2(FULL)/6-31G* level for formic acid. An examination of the two structures shows that the diffuse functions reduce the length of the (C=)O...H(–O) and (C=)O...O(–H) distances in the dimer, bringing the two monomers closer together. The Mulliken charges, based on the SCF density, show that the diffuse functions lower the net negative charge on the oxygen atoms and the net positive charge on the hydrogens, apparently resulting in a less stable dimer.

Acknowledgments

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