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The Strong Hydrogen Bond in the Formic Acid–Formate Anion System

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Abstract: Hydrogen bond energies and geometric structures of several symmetric and asymmetric formic acid–formate anion dimer complexes have been determined. Ab initio gradient optimization at the self-consistent field (SCF) level in a double-ζ + polarization + diffuse Gaussian function basis set was followed by a series of second-order Moller-Plesset (MP2) single-point calculations for the lowest energy structures. The equilibrium asymmetric dimer with the (anti) formic acid–(syn) formate anion conformation has the highest binding energy on both the SCF and MP2 levels at 28.8 and 33.0 kcal/mol, respectively. Experimentally, a gas-phase $\Delta H°_D$ value of 36.8 kcal/mol has been reported for the biformate anion (Meot-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525). The calculated stability of this anti dimer includes a C—H···O interaction that is estimated to contribute ~2.4 (SCF) or ~1.8 (MP2) kcal/mol to the dimer binding energy. The corresponding proton-transferred (syn) formic acid–(anti) formate anion complex is calculated less stable by 5.6 (SCF) or 3.7 (MP2) kcal/mol, even though in the isolated monomer *syn*-formic acid is the lower energy conformer by 5.8 (SCF) or 5.4 (MP2) kcal/mol in the same basis set. The greater stability of the anti dimer can be attributed both to less interfragment exchange repulsion and to more coulomb attraction compared with the syn dimer conformation. The optimized proton transfer curve as a function of one O-H distance shows a (syn dimer) inflection point and an (anti dimer) minimum, while the MP2 curve shows only a single (anti dimer) minimum. However, the proton transfer energy profiles for a series of fixed R(O···O) distances in the strong H-bond region each show two minima, with the anti dimer always lower in energy, except at R_{min} where the minima merge. Two equilibrium symmetric (C_{2h}) structures were also found higher in energy than the asymmetric anti dimer; an anti–anti conformer by 4.1 (SCF) or ~1.0 (MP2) kcal/mol, and a syn–syn conformation by 7.1 (SCF) or 3.8 (MP2) kcal/mol. Experimentally, both symmetric type conformers and both the asymmetric syn–syn and (syn) formic acid–(anti) formate anion type dimers have been observed in bicarboxylic acid crystal structures. Comparison of bond lengths and angles between calculated and observed structures for the respective conformations shows very good agreement. The existence of all these conformer combinations experimentally and the small energy differences calculated between them theoretically show the sensitivity of the specific conformation of this strong H-bond system to molecular structure, environment, and level of theoretical treatment.

Introduction

The hydrogen bond (H bond) is of great interest and importance both as a special type of chemical bond occurring in a wide variety of molecular complexes and because of its pervasive presence in biochemical systems. Aspects of particular interest in hydrogen bonding are the bond strength and the structural–geometrical properties of the combined monomers. Special attention has been paid to the very strong hydrogen bond[1–3] with regard to the characteristic number of minima in the proton transfer energy profile[4] and the overall proton polarizability in the field of the two proton acceptors.[5,6]

Most experimental information on hydrogen bonds comes from condensed phase studies where the crystal structure, solvent, or matrix will affect the H-bond energy, geometry, and characteristic properties mentioned above. Recently developed experimental methods for gas-phase studies such as ion cyclotron resonance,[7] laser spectroscopy–nozzle expansion–molecular beam techniques,[8] and pulsed high-pressure mass spectrometry[9] allow the direct study of "naked" clusters where the ratio of "solvent" to ion or molecule can often be predetermined. Thereby, the intrinsic properties of the hydrogen-bonded system can be studied, either unperturbed by external effects or in a controlled, measured environment.

The results of the gas-phase experiments can be compared with theoretical results. The latter usually describe a wider variety of properties than are available experimentally and allow a more detailed analysis of each result for the purpose of gaining insight, understanding, and predictive ability. Comparison with experiment, where possible, can also be used to test the accuracy of the level of theoretical method used in obtaining properties. For ab initio electronic structure calculations this usually involves deciding on the size basis set and the extent of post-Hartree–Fock (correlation energy) treatment.

Hydrogen bonds in anionic systems involving strong acids (HA) and bases (B^-) are known to have particularly short A···B distances and large binding energies. The energy profile for proton transfer in such cases is expected to have either a double minimum with a low barrier or a single, broad minimum.[2] In a recent ab initio study, an asymmetric equilibrium hydrogen bond structure was found for the prototypical $HOH \cdots OH^-$ system when geometry optimized in the self-consistent field (SCF) approximation with a 6-31G** basis.[10] However, geometry optimization with Moller–Plesset perturbation theory to second order (MP2) gave a single symmetric minimum.[4] This change from a double minimum profile at the SCF level to a symmetric single minimum energy curve for proton transfer when correlation is included demonstrates the sensitivity of this very strong hydrogen bond to the level of theoretical description.

This variability can be attributed to the relative flatness of the energy interaction surface and suggests that small structural effects on the molecular level could also determine the precise final shape of the surface. Recent infrared[11] and NMR studies[12] of such hydrogen-bonded systems in both solution and the solid state have also indicated a not insignificant role for solvent and crystal effects in determining the precise shape of the hydrogen bond curve. The environment sensitivity of the very strong hydrogen bond and its

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Table I. Optimized Geometric Parameters and Energies[a]

geometric parameters							energy, au	
r_1,[b] Å	r_2, Å	ϕ, deg	R, Å	α_1, deg	α_2, deg	ρ, Å	SCF	MP2[d]
0.955	100			108.7			−75.548 072	−76.444 712
1.025	1.462	190	2.477	116	125	3.082	−75.584 879	−76.489 432
1.0498[c]	1.415	190	2.456	116	124	3.020	−75.585 053	−76.490 757
1.075	1.358	189	2.425	117	122	2.925	−75.858 096	−76.491 881
1.100	1.309	189	2.402	118	121	2.870	−75.585 145	−76.492 701
1.150	1.227	188	2.371	119	118	2.776	−75.585 597	−76.493 990
1.200	1.167	188	2.360	120	116	2.719	−75.586 617	−76.494 972
1.250	1.118	187	2.364	122	115	2.681	−75.588 006	−76.495 770
1.300	1.083	186	2.381	123	113	2.656	−75.589 488	−76.496 423
1.350	1.058	185	2.406	123	112	2.634	−75.590 863	−76.496 917
1.400	1.039	184	2.437	123	112	2.615	−75.592 019	−76.497 213
1.450	1.023	183	2.473	123	111	2.588	−75.592 907	−76.497 348
1.450[e]							−75.589 540	−76.494 400
1.500	1.012	182	2.511	122	111	2.559	−75.593 513	−76.497 274
1.550	1.002	181	2.552	122	111	2.535	−75.593 856	−76.497 025
1.5971[c]	0.995	181	2.592	121	111	2.507	−75.593 965	−76.496 669
1.5971[e]							−75.590 119	−76.493 254
1.650	0.989	179	2.639	120	110	2.482	−75.593 863	−76.496 102
1.700	0.984	179	2.683	119	110	2.457	−75.593 604	−76.495 459
1.750	0.979	177	2.729	117	110	2.424	−75.593 202	−76.494 759
100	0.951				111.		−75.538 768	−76.436 077

[a] See Figure 1. All geometry optimizations are at the SCF level in the CEP basis set. [b] Frozen distance with other geometric parameters gradient optimized; except as noted. [c] Not frozen; complete gradient optimization of all geometric parameters. [d] At the SCF optimized geometry. [e] Geometry as on previous line except with a C7–O6–H5–O4 dihedral angle of 90° (instead of planar).

intrinsic "softness" complicates an attempt at a general theoretical description based on calculations appropriate to isolated, gas-phase systems.

Emsely et al.[3] carried out ab initio SCF calculations on the formate ion–formic acid (biformate anion) system in a small basis set with limited geometry optimization. A symmetric, single-minimum planar structure was predicted to be most stable. Recently, the enthalpy of dissociation of the biformate anion in the gas phase has been measured at 36.8 kcal/mol.[13] This value is considered to be unexpectedly large, even for strong acid–base anionic systems, requiring some unusual structural feature for its explanation.[13]

In order to explore this important chemical and prototypical strong H-bond system and its properties in more detail with regard to structural and energetic aspects, we have carried out ab initio SCF and MP2 calculations in a large basis set with extensive geometry optimizations on several conformers of the biformate anion.

Calculational Details and Results

All calculations were carried out with use of the published compact effective potentials (CEP) that replace the K-shell core electrons and the atom valence double-ζ (4 primitive Gaussians split 3-1) sp-type basis functions for the carbon and oxygen atoms.[14] The hydrogen atom valence basis set was the standard 3-1 Gaussian function distribution used in the GAUSSIAN82 set of computer programs.[15] The oxygen atom basis (only) was augmented by a set of diffuse sp-type functions (Gaussian exponent = 0.1000) to better describe the extra negative charge that is expected to concentrate on the more electronegative oxygen atoms. A set of single primitive polarization d-type functions (5 angular momentum components) was added to each carbon and oxygen atom basis set (Gaussian exponents of 0.7500 and 0.8000, respectively). Finally, the valence basis functions for the hydrogen atom involved in the (O—H···O) hydrogen bonding (only) were augmented by a set of p-type Gaussians (primitive exponent = 1.000). Altogether, the basis set consists of 103 functions contracted from 157 Gaussian primitives and is denoted CEP-DZPD.

The main geometric conformer studied here is shown in Figure 1. This conformer does not allow a rigorously symmetric hydrogen bond (with inversion symmetry) between formate anion fragments since the two possible formic acids are in different conformation, syn (S) and anti (A).[16] However, this asymmetric structure does allow the auxiliary

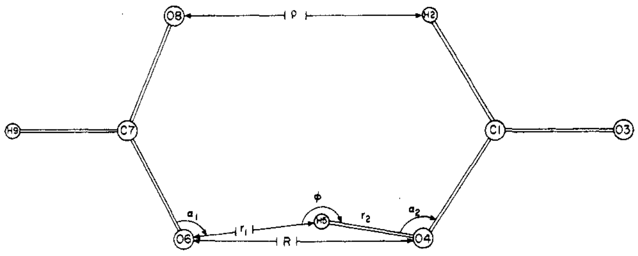

Figure 1. The asymmetric *anti*-formic acid–*syn*-formate anion complex.

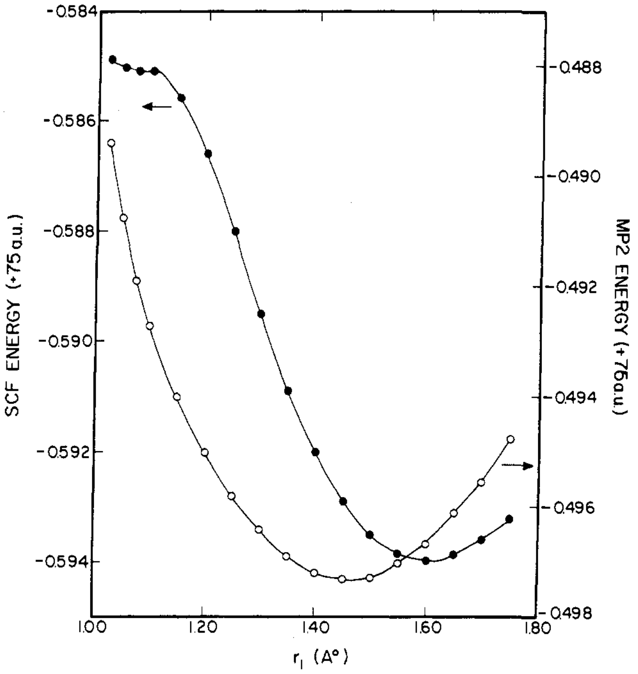

Figure 2. SCF (left side scale) and MP2 (right side scale) energies as a function of H-bond distance (r_1) in the (asymmetric) formic acid–formate anion complex.

H2···O8 interaction which we find to be a stabilizing factor, as will be discussed later. In this geometry, with planarity strictly enforced in all the calculations, the O6···H5 distance (r_1) was stepped in units of 0.025 or 0.050 Å. At each fixed value of r_1 all the other geometric parameters of the planar dimer were gradient optimized at the SCF level. At the

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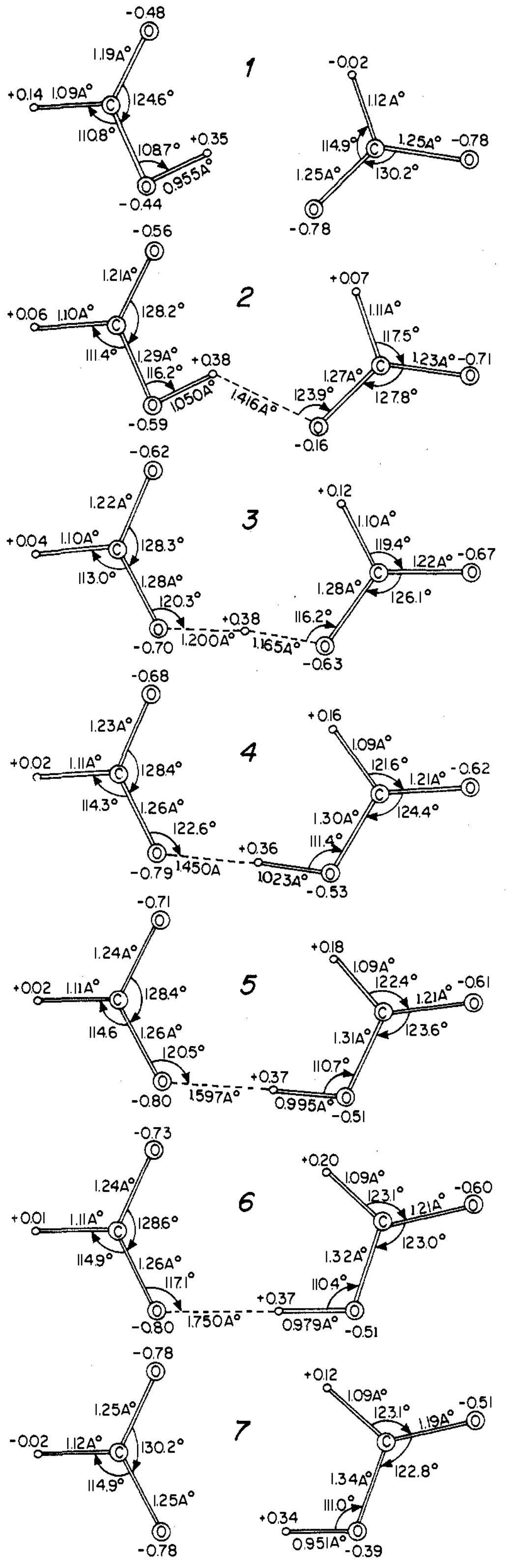

Figure 3. Snapshot sequence of SCF gradient optimized geometric parameters as a function of r_1 (Figure 1) for the asymmetric dimer, from *syn*-formic acid–formate anion (**1**) to formate anion–*anti*-formic acid (**7**). The numbers on the atoms are the Mulliken atomic charges in the CEP-DZPD basis. Structures **1** and **7** are for the dissociated fragments.

two points corresponding to the two expected equilibrium hydrogen bonded structures and which seemed to give minima in the proton transfer energy curve (S—H···A⁻ and S⁻···H—A), the geometry gradient optimization was unrestricted (except for the planarity constraint). At each fixed or optimized value of r_1 the MP2 energy was also calculated. The resultant energies and selected optimum geometric parameters are shown in Table I. The SCF and MP2 energies are plotted in Figure 2.

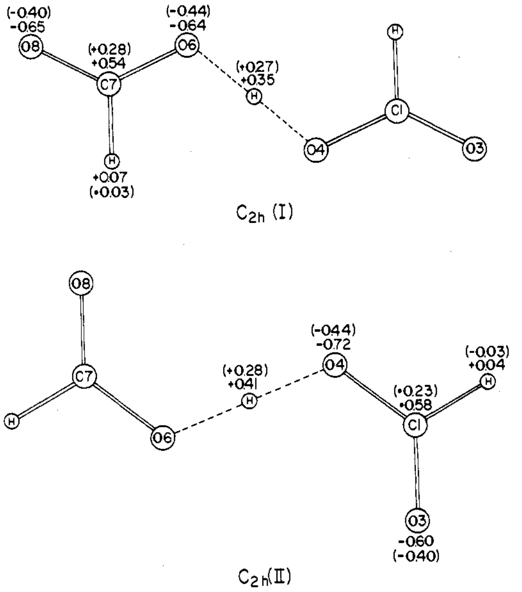

Figure 4. Symmetric formic acid–formate anion complexes. The numbers on the atoms are the Mulliken atomic charge in the CEP-DZPD and STO-3G (parenthesis) basis sets.

Table II. Optimized Geometric Parameters and Energies[a]

structure	r_1, Å	total energy, au: SCF	total energy, au: MP2[d]	H-bond energy,[f] kcal/mol: SCF	H-bond energy,[f] kcal/mol: MP2
C_{2h}(II)	1.1954[b]	−75.582 638	−76.491 222	21.7	29.2
C_{2h}(I)	1.1393[c]	−75.584 400	−76.491 428		
	1.1893[b]	−75.587 358	−76.495 628	24.7	31.9
	1.2392[c]	−75.584 954	−76.494 643		
C_s[e]	1.0498	−75.585 053	−76.490 757	23.2	28.9
	1.5971	−75.593 965	−76.496 669	28.8	32.6
	1.450	−75.592 907	−76.497 348	28.1	33.0

[a] See Figure 4. All geometry optimizations are at the SCF level. [b] Complete gradient optimizations in C_{2h} symmetry. [c] Frozen distance; all other geometric parameters taken from the complete gradient optimization for that structure. [d] At the SCF optimized geometry. [e] From Table I and Figure 1. [f] Relative to optimized (syn) formic acid + formate anion (first line in Table I).

Table III. Comparison of Calculated and Experimental C_{2h} Structures for the Biformate Ion[a]

	calculated		observed	
	C_{2h}(I)	C_{2h}(II)	$KH(HCO_2)_2$[b]	$KH(CF_3CO_2)_2$[c]
		Bond Length (Å)		
H—C	1.103	1.103		
C=O	1.219	1.220	1.22, 1.24	1.22
C—O	1.282	1.278	1.25, 1.26	1.28
O···H	1.189	1.195		
O4···O6	2.38	2.39	2.45	2.43
O4···C7	3.13	3.23	3.16, 3.18[d]	3.18
O4···O8	4.34	3.44	4.38	3.30[e]
		Bond Angle (deg)		
H—C=O	118.7	118.7		
O—C=O	127.0	129.1	124, 125	129.5
H···O—C	114.1	120.3	113, 114[f]	114.1
H—C—O	114.3	112.3		

[a] See Figures 2 and 4. Atom labeling from Figure 1. [b] From ref 18. [c] From ref 19. [d] Twisted 110°. [e] Assuming planarity. [f] Assuming a linear O···H···O alignment.

A snapshot sequence of the geometric parameters in progressing from formate anion–*syn*-formic acid to *anti*-formic acid–formate anion is shown in Figure 3.

Two symmetric structures were also studied and are shown in Figure 4. Here each conformer was gradient optimized on the SCF level in C_{2h} symmetry with a subsequent MP2 calculation at the SCF minimum. The resultant geometric parameters and conformer energies are listed in Table

Table IV. Optimized Geometric Parameters for HCO_2H and HCO_2^-[a]

	HCO_2H[b]		
	syn	anti	HCO_2^-[c]
	Bond Length (Å)		
H—C	1.088	1.094	1.121
C═O	1.194	1.188	1.246
C—O	1.331	1.338	
O—H	0.955	0.951	
	Bond Angle (deg)		
O═C—H	108.7	111.0	
O═C—O	124.6	122.8	130.2
	Energy au		
SCF[d]	−38.058 796	−38.049 491	−37.489 277
MP2[d]	−38.502 298	−38.493 663	−37.942 414

[a] All structures are planar. [b] 54 basis functions. [c] 49 basis functions. [d] SCF optimized geometry.

Table V. Energy Decomposition Analysis for the Asymmetric Biformate Anion[a]

contribution[b]	*syn*-formic acid–formate anion[c]	*anti*-formic acid–formate anion[d]	difference (A − S)
DIST	+8.5	+2.6	−5.9
COUL	−43.7	−46.9	−3.2
EXORT	+44.0	+27.8	−17.2
POL[e]	−14.8	−9.5	+6.3
CT+BSSE[e]	−15.6	−8.0	+7.6
Total	−21.6	−34.0	−12.4
Exact[f]	−23.2	−34.6	−11.4

[a] See Figure 1 and Table I. Energy values in kcal/mol. The analysis is of the SCF wave functions. [b] The contributions are described in the text. [c] $R(O6\cdots O4) = 2.456$ Å. [d] $R(O6\cdots O4) = 2.592$ Å. [e] Sum of contributions from both fragment directions. See ref 25. [f] Using dimer energies from Table I.

II. The SCF optimum C_{2h}(1) structure in Figure 4 was also MP2 optimized only for the r_1 distance with the results also shown in Table II. The optimized geometric parameters for the two C_{2h} structures, as well as a comparison with crystal structures, are found in Table III.

Table IV lists the optimized geometries and energies of the reference formic acids, both anti (O—H "anti" to C═O) and syn conformers, and the formate anion in the CEP-DZPD basis. The combined formic acid (syn or anti) + formate anion SCF and MP2 energies were checked for size extensivity with supermolecule calculations at an interfragment distance of 100 Å. The more stable syn form of the formic acid is used in combination with the formate anion as the combined monomer reference energy in all discussions of H-bond energies (top entry in Table I), except where specified otherwise.

Table V shows an energy decomposition analysis of the two optimized asymmetric biformate anions having $r_1 = 1.0498$ Å (S—H$\cdots$A$^-$) and $r_1 = 1.5971$ Å (S$^-\cdots$H—A), where R is the O$\cdots$O distance involved in the hydrogen bond (Figure 1 and Table I). The former point, although reached by an unrestricted gradient geometry optimization, which at convergence to the equilibrium structure showed only positive eigenvalues of the (iterated) Hessian matrix, actually appears as an inflection point on the SCF proton transfer curve as can be seen in Figure 2. Presumably, an exact second derivative force constant calculation would show this result explicitly. An harmonic frequency calculation at $R = 1.0498$ Å was not carried out, however, due to computer resource limitations.

Discussion

As mentioned above, the only comparable previous study of the hydrogen bond in the biformate anion is that of Emsley et al.,[3] where the two C_{2h} structures displayed in Figure 4 were SCF geometry optimized in a STO-3G basis. The lowest energy conformer (I) was then recalculated in an all-electron double-ζ (AE-DZ) Gaussian basis set. The basis set used here is much more extensive, incorporating both diffuse and polarization functions, and the geometries were directly (SCF) optimized in the larger basis set. Nonetheless, both studies at the SCF level find the C_{2h}(I) structure more stable than C_{2h}(II), by 4.1 (STO-3G) and 3.0 (CEP-DZPD, Table II) kcal/mol, respectively. The SCF hydrogen bond energy for C_{2h}(I), uncorrected for basis set superposition error (BSSE) or zero-point vibrational energy differences (ZPE), is 32.1 (AE-DZ) and 24.7 (CEP-DZPD) kcal/mol. Again, the former result is not at a geometry optimized in that basis set. The large difference in calculated H-bond energy with size basis set in a counter-intuitive direction is surprising in light of the estimate[3] that only 2.8 kcal/mol of the AE-DZ binding energy could be attributed to BSSE.

The STO-3G calculated[3] equilibrium O$\cdots$H distance was found to be 1.17 Å for the C_{2h}(I) conformer on the SCF level compared to the present (Table II) CEP-DZPD result of 1.19 Å; this is not much of a difference considering the substantial improvement in basis set. This perhaps demonstrates the narrow range of possible O$\cdots$H bond distances in very short (O$\cdots$O distances ≤2.50 Å) symmetric hydrogen bonds. The pointwise MP2 optimization of O$\cdots$H with the CEP-DZDP basis (Table II), leaving all the other geometrical parameters the same as at the SCF minimum, shows the equilibrium symmetric O$\cdots$H distance increasing from 1.19 to almost 1.21 Å, with an MP2 binding energy 7.2 kcal/mol larger than the 24.7-kcal/mol SCF value. Thus correlation is seen to play an important role in the bonding energy calculation of symmetric hydrogen bonded structures with their stretched O$\cdots$H distances.

The symmetric hydrogen bond in the smaller water–hydroxide anion dimer has been studied by several groups.[4,17] Rohlfing et al.[4] also found an increase in the MP2 geometry optimized equilibrium O$\cdots$H bond length relative to SCF. Gao et al.[17] calculated (6-31+G*) a 4.7-kcal/mol increase (from 21.8 to 26.5 kcal/mol) in binding energy from SCF to MP2 at an SCF 6-31G* optimized geometry. However, the change in SCF calculated H-bond energy from the 6-31G* to 6-31+G* basis was a substantial decrease from 34.0 to 21.8 kcal/mol for the symmetric form.[17] Thus diffuse functions are critical for an accurate calculation of the H-bond energy in anionic systems and are naturally more important to the description of the smaller monomer anion than for the dimer. This type bias in basis set explains the large binding energy calculated by Emsley et al.[3] for the symmetric biformate anion in a relatively small basis set.

Experimentally, the geometry of the biformate anion is best known from solid-state crystallographic studies[1,2,18,19] where electrostatic forces between the ions can be important in determining the relative orientations and conformations of the carboxylate groups. For example, the geometry of the K^+ salt of the biformate anion is a distorted version of the C_{2h}(I) conformer shown in Figure 4, with the crystallographic inequivalency of the formates caused by interactions with the cations.[18] The crystal structure geometry of $KH(HCO_2)_2$ is compared with the SCF optimized C_{2h}(I) geometry in Table III. Agreement for the monomer groups is seen to be very good, both for the bond lengths (within 0.02 Å) and bond angles (within 3°). In particular, the H-bond heavy atom O4$\cdots$O6 distance (Figure 4) is calculated at 2.38 Å and observed at 2.45 Å. The MP2 (symmetric) one-dimensional optimization of the O4$\cdots$H5 distance (Table II) increases the O4$\cdots$O6 length to 2.41 Å, closer to the observed value. This is probably as good as the comparison can get given the intrinsic differences between the (calculated) gaseous and (observed) crystalline states. The completely nonbonded O4$\cdots$C7 and O4$\cdots$O8 distances are in very good agreement between C_{2h}(I) calculated and the crystal structure.

It should be noted that both possible monomer formic acid conformations in C_{2h}(I) are of the anti form and this dimer structure can therefore be labeled anti–anti. Analogously, the C_{2h}(II) conformer can be called syn–syn. As shown in Table III and observed previously,[16,20] the syn form of formic acid is more stable than the anti form, in the CEP-DZPD basis set, by 5.8 (SCF) or 5.4 (MP2) kcal/mol. It is therefore surprising that the anti–anti conformation, C_{2h}(I), is calculated more stable than syn–syn C_{2h}(II) by 3.0 (SCF) or 2.8 (MP2) kcal/mol. Clearly,

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some effect is present that overcomes the higher energy of the *anti*-formic acid form and gives an additional 3.0 kcal/mol SCF H-bond energy relative to C_{2h}(II).

A possible explanation for the relative stability of the anti–anti conformer lies in purely electrostatic interactions. If we take the Mulliken atomic charges from the CEP-DZPD basis (shown in Figure 4) and calculate the purely Coulomb electrostatic energy classically at the SCF optimized geometries (Table III) for each conformer, then the syn–syn structure comes out ~45 kcal/mol more stable than anti–anti. This is clearly a less than useful result. However, Mulliken populations in an extended and diffuse basis set can be unrealistic because the contribution attributed to a given basis function is allocated to the atom upon which that function is centered, even though that basis orbital may have its maximum charge density located closer to a different center. The possibility of such spatially incorrect partitioning of the charge distribution should be substantially reduced by the use of a minimal basis set.

The energies of both C_{2h} conformers have therefore been SCF recalculated with use of the standard STO-3G basis[21] in the respective SCF optimized geometries of the CEP-DZPD basis set (Table III). The STO-3G energy difference favors the C_{2h}(I) form by 3.1 kcal/mol compared to 3.0 kcal/mol in the CEP-DZPD basis (Table II). This similarity in the energy result gives a measure of credibility to the STO-3G charge distribution even though the dimer system is an anion. That the extra charge is spread symmetrically over both "monomers" mitigates this defect. Using the Mulliken atomic charges calculated from the STO-3G wave function (also shown in Figure 4) to calculate the classical electrostatic energies again gives the C_{2h}(I) conformer more stable by 3.0 kcal/mol. Although the close coincidence of all these conformer energy differences is certainly higher than can be expected, their great similarity seems to be indicative of an important electrostatic contribution to the preferred stability of the C_{2h}(I) conformer.

A different type of dicarboxylate structure is found in $KH(CF_3CO_2)_2$.[19] Here, the X-ray study shows a symmetric hydrogen bond in the C_{2h}(II), syn–syn conformation. The comparison between the crystal structure and the ab initio calculations is also presented in Table III. The O4···O6 distance is seen to be 2.43 Å in the crystal structure, compared to a "gas phase" (SCF) calculated 2.39 Å. The crucial angle is H···O—C, which is calculated larger by ~6° in C_{2h}(II) than in C_{2h}(I) but has the smaller value in $KH(CF_3CO_2)_2$. The CF_3 group replacing the hydrogen atom of the biformate complex may be playing a steric role in determining the specific formic acid conformation in the crystal structure. Infrared and Raman spectra of solid $NaH(HCO_2)_2$ have been interpreted as indicative of a syn–syn biformate anion conformation, although probably with an asymmetric structure.[11b]

Actually, the lowest energy biformate anion calculated here on the SCF level is the asymmetric dimer (Figure 1) with r_1(O···H) = 1.5971 Å (Table I). The SCF hydrogen bond energy associated with this structure is 28.8 kcal/mol, uncorrected for BSSE, ZPE, and the other small thermodynamic correction factors necessary to compare the calculated number to the experimental enthalpy of dissociation.[17] The MP2 calculated energies (at the SCF optimized geometries) predict an equilibrium structure with $r_1 \sim 1.45$ Å and an (uncorrected) calculated binding energy of 33.0 kcal/mol. This number is smaller than the experimental value of 36.8 kcal/mol ($\Delta H°_D$) determined by Meot-Ner and Sieck,[13] and the corrections (BSSE, ZPE, etc.) mentioned above will probably somewhat reduce the ab initio calculated H-bond energy. That the experimentally determined dissociation energy for the biformate anion is unusually large can be deduced from a comparison with the H-bond enthalpy of the biacetate anion which has been determined to be 29.3[13]–30.0[22] kcal/mol, some 7 kcal/mol less than for the biformate anion. The analogous methanol–methoxide H-bond dissociation energy is only ~3 kcal/mol smaller than that for the water–hydroxide system.[23]

Figure 2 dramatically presents the difference between the calculated SCF and MP2 results for the proton transfer energy curve in the asymmetric biformate anion. On the SCF level a minimum (r_1 = 1.5971 Å) and an inflection point (r_1 = 1.0498 Å) separated in energy by 5.6 kcal/mol are found, corresponding to the 2 possible normal hydrogen bonded structures ($S—H···A^-$ and $A^-···H—S$), with R(O···O) = 2.592 and 2.456 Å, respectively. However, the MP2 curve calculated at the SCF optimized geometries shows a single minimum only with the hydrogen atom located at a more symmetric position ($r_1 \sim 1.45$ Å and $R \sim 2.47$ Å). Direct MP2 optimization of the biformate anion might lead to an even more symmetric structure (smaller r_1). The value of R(O···O) would then increase due to the MP2 optimization (by ~0.02 Å, as discussed before),[24] but this could be more than offset by the decrease in R characteristic of the more symmetric structures (Table I).

As indicated above, the conformation shown in Figure 1 is a syn–anti combination dimer which allows an unhindered H2···O8 interaction. It has been suggested that this additional "H bond" gives the asymmetric structure its special stability.[13] The progression from *syn*-formic acid–formate anion to formate anion–*anti*-formic acid in the proton transfer process is shown in Figure 3 in a series of seven dimer structures. Structure **1** (r_1 = 0.955 Å) corresponds to the normal dissociated monomers with formic acid in the lower energy syn form. The second structure (**2**) displays the inflection point (Figure 2) with r_1 = 1.0498 Å obtained by SCF unconstrained geometry optimization, except for assumed planarity. The H2···O8 distance (ρ in Table I and Figure 1) here is a large 3.02 Å, and this H-bond interaction must be weak.

The other SCF minimum, formate anion–*anti*-formic acid (structure **5**), which is (MP2) 3.7 kcal/mol more stable than **1**, has a much shorter ρ value of 2.51 Å, indicative of a stronger H2···O8 interaction. The difference in the H-bond distances between the two "equilibrium" structures can be rationalized in terms of the trends in the electrostatic interaction between these two atoms. Although, as noted above, the Mulliken atomic charges in the extended and diffuse CEP-DZPD basis set probably do not reflect an altogether accurate partitioning of charge density in the geometry space of the dimers, trends in the charges can still be consistent with the structural changes described in the snapshot sequence shown in Figure 3. In **2** the charges on H2 and O8 are calculated to be +0.07 and −0.56, respectively. The small positive charge on the hydrogen atom reflects the formate ion character of that fragment. In **5**, on the other hand, the charges are +0.18 and −0.71, respectively, the former reflecting the charge neutral character of the formic acid monomer and the latter consistent with the formate anion character of that fragment. Thus, on the basis of pure electrostatics, a H2···O8 stabilizing interaction in **5** is expected to be much stronger than in **2**.

In order to assess the importance and strength of the H2···O8 interaction, SCF and MP2 calculations were carried out on two twisted conformations where the C7–O6–H5–O4 dihedral angle was 90°, instead of 0° or 180°, depending on the value of ϕ (Figure 1). Presumably, the major result of such a perpendicular conformation, which maintains the O6–H5–O4 geometry, is to substantially weaken the H2···O8 interaction. The total energies are shown in Table I, where, except for the dihedral twist angle, bond distances and angles from the SCF optimized planar geometry were maintained at each value of the r_1 distance. At the SCF energy minimum for the anti dimer (r_1 = 1.597 Å), where ρ is stretched to 3.71 Å in the twisted conformation, the energy differences between planar and perpendicular configurations are 2.1 (SCF) or 1.8 (MP2) kcal/mol, while at the approximate MP2 minimum (r_1 = 1.450 Å and ρ = 3.92 Å) the energy differences are 2.4 (SCF) or 2.1 (MP2) kcal/mol. Thus the H2···O8 interaction, while stabilizing, cannot wholly explain the 5.6 kcal/mol

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[21] STO-3G basis symmetric biformate anion energies (E): E(I) = −371.748356 au and E(II) = −371.743336 au.

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[24] A similar size increase has been found in the $(HCO_2HOH)^-$ system by: Cybilski, S. M.; Scheiner, S. *J. Am. Chem. Soc.* **1989**, *111*, 23.

(SCF) energy difference between the equilibrium syn (r_1 = 1.050 Å) and anti (r_1 = 1.597 Å) forms of the asymmetric biformate anion, in favor of the latter. Relative to their own separate dissociation limits, which adds the intrinsic stability of the *syn*-formic acid monomer relative to anti, the individual binding energies of the equilibrium syn and anti dimers are 23.2 and 34.6 kcal/mol, respectively; so that the difference between them from this point of view is an even larger 11.4 kcal/mol.

The SCF energy difference between the equilibrium syn and anti dimers can be analyzed by using the reduced variational space (RVS) analysis of Stevens and Fink,[25] based on the energy decomposition analysis of Morokuma et al.[26] This approach resolves the individual dimer total energies into coulomb exchange orthogonality (CEX), polarization (POL), charge transfer (CT), and basis set superposition energy (BSSE) components, relative to the formic acid and formate anion monomers. If the total coulomb energy only (nuclear attraction+electron repulsion) is separately calculated between frozen monomer fragment wave functions (formic acid and formate anion) at the given interfragment distance then the CEX term can be resolved into separate coulomb (COUL) and exchange orthogonality (EXORT) components. The latter is always a repulsive term. In addition, the distortion energy (DIST) necessary to change the optimum monomer bond lengths and angles to their in situ dimer geometry values must be added in order to obtain the true dimer binding energy. For the asymmetric dimer, at hydrogen-bonded distances where the individual monomers can be separately identified, this perturbation theory analysis, which assumes additivity of effects, should be valid.

The results are shown in Table V where a comparison between the energy component totals and the exactly calculated asymmetric dimer binding energies agree, at worst, to within 7% of the total binding energies for the equilibrium syn and anti dimers. Thus, almost perfect additivity is achieved in these cases. Such an energy decomposition analysis would not be appropriate for the C_{2h} dimers since the symmetric placement of the H bond precludes the unambiguous identification of the formic acid and formate anion reference fragments.

Table V shows that the distortion, coulomb, and exchange orthogonality terms favor the anti dimer while the polarization, charge transfer, and BSSE components preferentially stabilize the syn dimer. The outstanding energy difference term in the analysis is clearly the repulsive EXORT term, which is the single largest contribution. Exchange orthogonality is expected to be interfragment distance dependent, behaving like the overlap integral squared.[27] The equilibrium syn dimer has the shorter O6⋯O4 (R) interfragment distance of 2.456 Å (Table II) compared with R = 2.592 Å for the anti dimer, and hence the larger EXORT repulsion value for the former conformer. The stabilizing coulomb interaction is also expected to be distance dependent and, therefore, favor the shorter R syn dimer. However, as noted above, the charge distribution in the equilibrium anti dimer is coulombically inherently more interfragment attractive than in the syn dimer. This result apparently overcomes the distance dependence advantage of the latter for the value of COUL, which, therefore, here also favors the anti dimer. The behavior of the attractive POL term favors, as expected, the syn form, given its (distance)$^{-4}$ dependence.[28] Thus, in summary, the repulsive exchange orthogonality interaction is an important factor in determining the preferred stability of the anti dimer and is reinforced by the H2⋯O8 attractive coulombic interaction.

It is interesting to note the outcome of SCF STO-3G calculations on the two equilibrium asymmetric dimers, as was discussed for the symmetric structures. The STO-3G energy difference[29] between the syn (r_1 = 1.0498 Å) and anti (r_1 = 1.5971 Å) CEP-DZPD basis optimized equilibrium complexes is 2.7 kcal/mol favoring the syn structure, compared to 5.6 kcal/mol in favor of the anti dimer in the CEP-DZPD basis. Using the respective STO-3G SCF Mulliken atomic charges to calculate purely electrostatic energies classically for the two asymmetric dimer configurations gives the syn structure again more stable than anti by 2.2 kcal/mol. Thus, possibly because of the more localized negative charge, the STO-3G basis is here incapable of reproducing the CEP-DZPD basis relative dimer energies, but the atomic charges do seem to faithfully follow the STO-3G SCF charge distribution in a purely Coulombic sense.

The classical view of the hydrogen bond profile traces the one-dimensional energy dependence of the proton transferring (variable r_1) between the two oxygen atoms located at a fixed distance (R) apart. This gives rise to the familiar double well potential separated by a barrier. The latter decreases in height as R decreases until merging into a single minimum at sufficiently small R.[1-3] A family of such double minimum curves can be approximately constructed from the numbers in Table I. Thus, starting at the top of Table I, as r_1 increases R first decreases to a minimum value at ~2.36 Å ($R_{\min}$) for r_1 = ~1.20 Å and then increases again. Thus, except at $R_{\min}$ where there is no barrier, for a given value of R there are two minimum values of r_1, separated by an energy barrier, corresponding to the syn and anti forms of the asymmetric dimer. Since the SCF or MP2 energy values for r_1 larger than ~1.20 Å (out to almost 1.750 Å) are uniformly lower in energy than any of the respective SCF or MP2 energies for r_1 smaller than ~1.20 Å, the anti dimer always has the lower energy of the two minima for any R value in the range (2.36–2.48 Å) covered by Table I having two different r_1 structures. This will probably be true also out to at least the R ~ 2.7 Å shown in Table I. Of course, at larger R values the syn "dimer" has to gradually become the lower energy form. Thus, the gas-phase dimer whose unusually large binding energy was measured by Meot-Ner[9] is identified with the asymmetric *anti*-formic acid–*syn*-formate anion conformation calculated here.

Crystallographically, an asymmetric dicarboxylic acid dimer has been observed[30] in $KH(CH_3CO_2)_2$, which apparently has the *syn*-formic acid structure in a syn–anti combination dimer. The hydrogen atoms are not resolved in the X-ray structure and the formic acid monomer is identified as such from the C–O bond lengths. Here, the biacetate methyl group blocks the additional O⋯H—C hydrogen bond interaction and the acetate anion fragment is rotated away from O8 (Figure 1) about the O4⋯O6 axis by approximately 180°. The observed biacetate anion conformation places every oxygen atom in good electrostatic interaction position with the cations.[30]

The observed biacetate anion can be compared to the r_1 = 1.0498 Å SCF optimized structure having the asymmetric *syn*-formic acid–*anti*-formate anion conformation in Table I and Figure 3. The observed[30] (calculated) values are the following: *d*(O6⋯O4) = 2.476 Å (2.456 Å), *d*(C1–O4) = 1.268 Å (1.269 Å), *d*(C1–O3) = 1.247 Å (1.230 Å), *d*(C7–O6) = 1.290 Å (1.293 Å), *d*(C7–O8) = 1.211 Å (1.210 Å), ∠O8–C7–O6 = 123.5° (128.2°), ∠O3–C1–O4 = 119.3° (127.8°), ∠C1—O4⋯O6 = 115.0° (128.1°), ∠C7—O6⋯O4 = 115.6° (122.0°). The bond distances agree almost exactly. The monomer O–C–O angles differ by 5–7° with the crystal structure values always smaller than calculated, as appropriate to the bulkier methyl group repelling the C–O bonding electrons.[31] Not surprisingly, interfragment angles involving the hydrogen-bonded oxygen atoms show the largest deviations between calculated (isolated gas phase) and observed[30] crystal structure.

Like the biformate anion in $NaH(HCO_2)_2$,[11b] the asymmetric syn–syn biacetate anion is also known and its structure has been determined by X-ray crystallography of the $NH_4H(CH_3CO_2)_2$ crystal.[32] Here again, the asymmetry has been determined by

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the very different (by 0.116 Å) C–O bond lengths on one of the CH_3CO_2 fragments whereas the C–O bond lengths on the other fragment differ by only 0.026 Å. A similar comparison of C–C–O angles shows them to be very different in the assigned acid monomer and similar in the identified acetate anion fragment. It should be remembered that the $KH(CF_3CO_2)_2$ crystal has the symmetric (C_{2h}) syn–syn conformation[19] and that $KH(CH_3CO_2)_2$ has the asymmetric *syn*-acetic acid–*anti*-acetate anion conformation.[30] Thus, both the specific conformation and the number of minima in the proton energy profile in these dicarboxylic anions are strongly dependent on molecular structure and environmental effects.

The progression from structure **1** to **7** (Figure 3) shows some interesting geometrical and electronic structure features. In line with the previous discussion the H2···O8 distance (ρ) decreases, along with the combined C1—O4···H5 and H5···O6—C7 angles, which makes the decrease of ρ possible, as the larger charges on H2 and O8 develop. The calculated charge on the transferring proton actually stays constant at +0.31 within ±0.02 units from the initial (**1**) to the final (**7**) complex, without ever developing the expected near full charge of +1.00. This results corresponds to the charge relay model of H bonding discussed by Zuccarello and Del Re.[33]

Summary

Two symmetric [C_{2h}(I), C_{2h}(II)] and two asymmetric (anti, syn) formic acid–formate anion dimer structures have been determined. The calculated (SCF,MP2) binding energy values are the following: anti (28.8, 33.0) > C_{2h}(I) (24.7, ~32) > syn (23.2, 28.9) ≈ C_{2h}(II) (21.7, 29.2), in kcal/mol. The anti conformer is identified with the biformate anion for which a gas-phase binding energy of 36.8 kcal/mol has been measured by Meot-Ner and Sieck.[19] The other calculated structures, as well as additional conformer types, are found experimentally in crystal structures of bicarboxylic acids. Comparison of bond lengths and angles between calculated and observed crystal structures for the corresponding conformations shows very good agreement. The calculated stability of the anti dimer includes a C—H···O interaction which is estimated to contribute approximately 2.4 (SCF) or 1.8 (MP2) kcal/mol to the dimer energy. The greater stability of the anti dimer relative to the syn conformer can be attributed both to less interfragment exchange repulsion and to more coulomb attraction in the former structure.

The optimized proton transfer curve connecting the two asymmetric dimers as a function of one O–H distance shows a (syn dimer) inflection point and an (anti dimer) minimum, while the MP2 curve shows only a single (anti dimer) minimum. However, the proton transfer energy profiles for a series of fixed R(O···O) distances in the strong H-bond region each show two minima, with the anti dimer always lower in energy, except at R_{min} where the minima merge.

The existence of all these conformer combinations experimentally and the small energy differences calculated between them theoretically shows the sensitivity of the specific conformation of this strong H-bond system to molecular structure, environment, and level of theoretical treatment.

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Second-Moment Equality and the Structural Chemistry of the Main-Group Intermetallic Compounds

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Abstract: We determine electron counting rules for $ZA_{2-x}B_x$ compounds, where Z is an electropositive atom and A and B are main-group atoms. These rules are derived from a Hückel-type theory. Agreement between theory and experiment for all the major $ZA_{2-x}B_x$ families, which include the $MgCu_2$, $MoSi_2$, $CeCd_2$, $CeCu_2$, MgAgAs, $CaIn_2$, AlB_2, $ThSi_2$, and Cu_2Sb structure types, is excellent. The results are interpreted by use of the method of moments.

Introduction

In recent years, research done by several groups has shown that tight-binding band calculations can provide useful insight to the structural preferences of solid-state compounds.[1] General application of the method, however, has generally been hampered by problems related to coordination number.[2] For example, the two forms of carbon, diamond and graphite, are known to have rather similar electronic energies. However, a tight-binding or Hückel calculation on the two structures based on the observed experimental densities shows that diamond is lower in energy by 1 eV/atom. The problem is that diamond contains four-coordinate carbon while graphite contains three-coordinate carbon. As the tight-binding method ignores electron–electron interaction, the higher coordinate geometry is typically the favored one. In this paper, we follow a novel method of removing this coordination number problem.

We demonstrate its utility by studying compounds with the stoichiometry $ZA_{2-x}B_x$, where Z is an electropositive element from the first four columns of the periodic table and A or B are elements from columns 8–16. There are 14 major families. They are the $MgZn_2$, $MgCu_2$, Cu_2Sb, $MoSi_2$, Fe_2P, Co_2Si, $CeCu_2$, MgAgAs, $CdCd_2$, $CaIn_2$, $InNi_2$, AlB_2, $ThSi_2$, and $ZrSi_2$ structure types.[3] (By major we mean structure types with at least two dozen known compounds.) In this paper, we will not discuss the $MgZn_2$, Fe_2P,

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