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Variable hydrogen bond lengths in hydrated complexes of formate and methylammonium ions

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The importance of the full hydrogen bond connectivity pattern on a specific hydrogen bond length has been examined by carrying out theoretical *ab initio* calculations for various hydrated complexes of formate (HCO_2^-) and methylammonium ($MeNH_3^+$) ions, as well as for related complexes in which the water molecules were replaced by HF or NH_3. For the $HCO_2^- \cdots HOH$ interaction substantial cooperative and competitive effects were attained that caused the principal hydrogen bond length to vary between 1.46 and 2.05 Å at the HF/6-311++G(2d,p) level of theory without significant changes to other geometry parameters. A similar range was obtained for the $MeNH_3^+ \cdots OH_2$ hydrogen bond. Increasing H-bond lengths are generally paralleled by decreasing interaction energies. The observed trends, which are relevant for crystallographic studies of H-bond lengths, are essentially independent of basis set size, inclusion of electron correlation effects or correction for basis set superposition error. The effect of hydrogen bonding on the energy potential for $HOO_2^- \cdots {}^+HNH_2Me$ interactions has been investigated.

Introduction

From various spectroscopic studies it is known that the energy potentials for formation of covalent bonds are usually deep and narrow. The nature of the minima is also reflected in the observed ranges for covalent bond lengths in crystal structures, which are typically a modest 0.04–0.08 Å (calculated as the mean value ± two standard deviations).[1] In contrast, hydrogen bonds lengths often have no distinct upper limit, and much larger ranges, from 0.3–0.6 Å for the bulk of the interactions.[2–4] There has been little attempt to explain or elaborate on this difference between the two bond types. The most important observation obviously is the correlation between the hydrogen$\cdots$acceptor distance, $d(H \cdots A)$, and the hydrogen bond angle $\alpha(D\text{–}H \cdots A)$,[3–6] as shown for $-NH_3^+ \cdots {}^-O_2C$-interactions retrieved from the Cambridge Structural Database[7] in Fig. 1. The plot apparently explains part of the large range for hydrogen bond lengths, but it is essential to realize that even if $\alpha(N\text{–}H \cdots O)$ is fixed at some specified value, a 0.2 to 0.4 Å range for $d(O \cdots H)$ remains, *i.e.* much larger than for a covalent bond length. Is it reasonable to attribute such ranges to the weaker nature of the hydrogen bond with presumably broad and shallow energy minima?

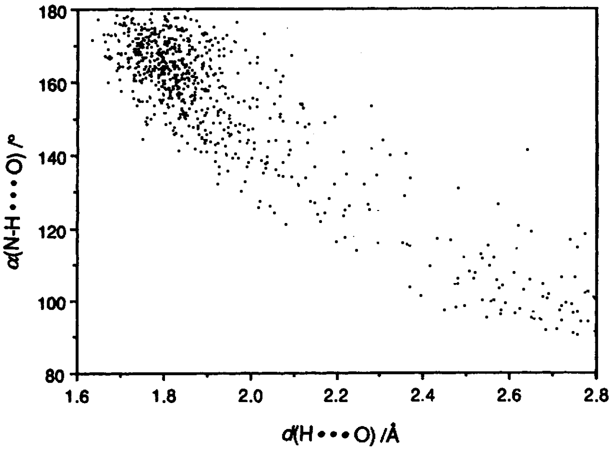
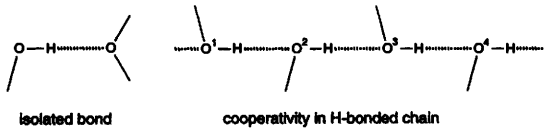


Fig. 1 The hydrogen bond angle $\alpha(N\text{–}H \cdots O)$ as a function of hydrogen bond distance $d(H \cdots O)$ for 752 H-bonds. The H-bonds occur in 356 structures without metal ions retrieved from the Cambridge Structural Database.[7]

Some evidence suggests it is not. The term cooperativity, or cooperative effect,[8,9] has been used to describe the situation where the interaction energy (the negative of the binding energy) of a system with more than one H-bond is nonadditive with $\Delta E_{TOT} > \Delta E^{2\text{-body}}$ where $\Delta E^{2\text{-body}}$ is the sum of two-body interaction energies.[10] This means that H-bonds become stronger when coexisting in a single system than when isolated from each other. In theoretical studies they usually also become shorter, a correlation which is not so easily verified by experimental data. Generally, a cooperative effect is observed when the donor accepts a H-atom from another donor, or the acceptor donates a H-bond to another acceptor.

The effect is particularly evident in chains of H-bonds, of which chains of hydroxy groups (from alcohols or water molecules) are particularly well known. In Scheme 1 δ–$O_2H \cdots O_3$ is thus expected to be shorter than the isolated $O\text{–}H \cdots O$ H-bond.

The cooperative effect gets larger as the chain length increases, but appears to be well converged for more than *ca.* 10 H-bonds.[10,11] The shortening of $O\text{–}H \cdots O\text{–}H$-bonds in infinite chains has been estimated from crystallographic material on carbohydrates to be *ca.* 0.07 Å.[12]

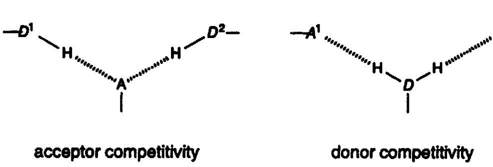


Scheme 1

The opposite effect of cooperativity, or anti-cooperativity,[9] occurs when the interaction energy of a system is nonadditive with $\Delta E_{TOT} < \Delta E^{2\text{-body}}$. It may be appropriate instead to introduce the term competitivity to describe this situation. H-bonds get longer and weaker when the acceptor accepts more than one H-atom, or the donor donates more than one H-bond (Scheme 2).

The effect of H-bonded chains, as described for cooperativity, pertains also to competitivity, although infinite chains may not be so easily formed in crystal structures.

Even with the accumulated knowledge of cooperativity and competitivity, the full impact of these and related effects on



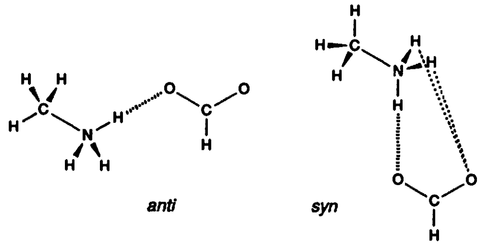
Scheme 2

hydrogen bond lengths in crystal structures has been poorly investigated. The scope of the work presented here was to examine these effects through theoretical calculations. The H-bond donor $MeNH_3^+$ and the H-bond acceptor HCO_2^- were chosen as model compounds, as they contain two of the most common functional groups involved in multiple H-bonds in organic crystal structures. Several complexes have been studied in which the two molecules are hydrogen bonded to a varying number of water, NH_3 and HF molecules, as well as complexes involving direct $MeNH_3^+ \cdots {}^-O_2CH$ interactions. There is a special kind of competitivity in three-centre hydrogen bonds in which one H-atom is shared between two different acceptors. Such interactions are not discussed here.

Method

$MeNH_3^+$ and HCO_2^- ions were used as starting points to which water molecules were successively added. To ease the observation of trends in the variation of hydrogen bond geometries and energies, care was taken to make sure that each water molecule in the hydration shell formed only the single H-bond of interest. This means that none of the optimized structures discussed below corresponds to the global energy minimum for a particular complex. Lower energy isomers always exist which involve water molecules in bridging positions between the two carboxylate oxygen atoms[13] and/or include additional H-bonds between water molecules.

For the complexes with interaction between $MeNH_3^+$ and HCO_2^- the energy potential as a function of $d(H \cdots O)$ was determined by fixing $d(H \cdots O)$ at several different values with optimization of the rest of the structure. The *anti* approach at the carboxylate was always chosen, even if the *syn* position for the proton in HCO_2H is preferred over *anti*. Interactions between $R\text{-}NH_3^+$ and carboxylate in the *syn* position are more difficult to control due to the inevitable formation of additional H-bonds to the distant carboxylate oxygen atom, Scheme 3.



Scheme 3

Several constraints were required to get reasonable potentials, and even then the actual energy contribution from the single H-bond remained elusive.

Ab initio calculations were carried out with the GAUSSIAN92[14] and GAUSSIAN94[15] computer programs running on IBM RS 6000/590 and DEC Alpha 3000/900 computers. Three different basis sets were used for HF optimizations: 6-31+G* (hereafter denoted **1**), 6-311+G** (**2**) and 6-311++G(2d,p) (**3**). MP2 optimizations, with inclusion of second-order electron correlation effects, were carried out with the two smallest basis sets **1** and **2**. The basis set superposition error (BSSE) was estimated by the full counterpoise correction (CP) method of Boys and Bernardi[16] using the MASSAGE keyword of the GAUSSIAN92 and GAUSSIAN94 programs. In the notation used below, HF/**3**//HF/**3** (CP) means the counterpoise corrected interaction energy at the HF/6-311++G(2d,p)//HF/6-311++G(2d,p) level of theory.

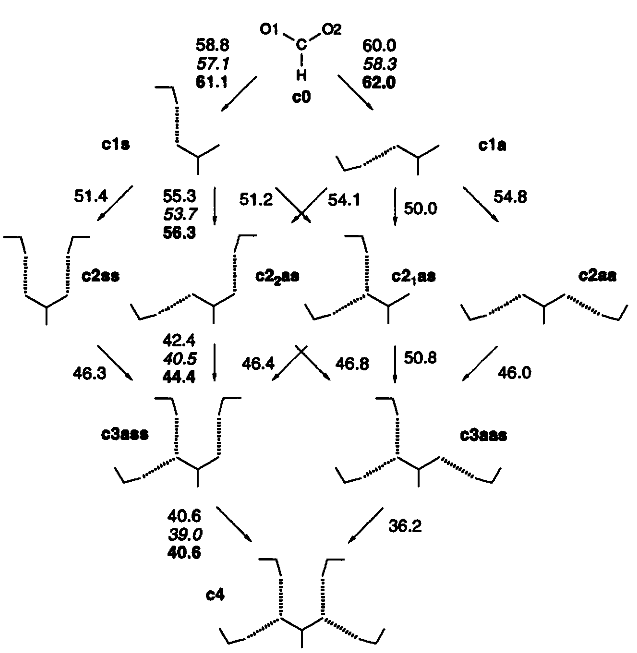


Fig. 2 HF/3//HF/3 interaction energies (kJ mol^{-1}) for the successive addition of water molecules to HCO_2^-. Nomenclature has been indicated. The subscript for the two dihydrated **c2as** complexes gives the number of acceptor atoms. For the first hydration step and for one full path from **c0** to **c4** HF/3//HF/3 (CP) (italic type) and MP2/**2**//MP2/**2** (CP) (bold type) interaction energies are also given.

In the first part of the paper, selected complexes have been optimized at all five levels used (HF/**1**, HF/**2**, HF/**3**, MP2/**1**, MP2/**2**), with correction for BSSE. Other complexes were subject only to HF/**3** optimizations. Throughout, emphasis is put on HF/**3** geometry parameters. In the second part of the paper, energy potentials for H-bonding have been obtained from HF/**1** optimizations, with additional HF/**2** calculations for the energy minima.

All geometry parameters were completely relaxed in most optimizations, but for the largest complexes some peripheral parameters were frozen at values found to be reasonable from calculations on smaller systems. For two complexes it was necessary to constrain certain angles. These parameters have been identified in the Figures.

Results

$HCO_2^- \cdot n\,H_2O$, n = 1–4

The stepwise addition of water molecules to HCO_2^- with formation of hydrogen bonds is shown in Fig. 2, with a total of 12 different routes from the isolated ion **c0** to the tetrahydrated complex **c4**. The interaction energy goes down for each hydration step, with HF/**3**//HF/**3** average values 59.4 for the first, 52.8 for the second, 46.5 for the third and 38.4 kJ mol^{-1} for the fourth. It is clear that the accepting capability of the carboxylate group falls off rapidly as the group is engaged in H-bonding to an increasing number of donors.

Results from the calculations for one selected pathway from **c0** to **c4**, indicated in Fig. 2, are listed in Table 1.† Interaction energies get smaller with larger basis sets, but increase with inclusion of electron correlation. It is furthermore noteworthy that the CP corrections vary little for the various hydration steps, meaning that the CP fraction of the uncorrected

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† Complete listings of calculated absolute energies (hartrees) for all monomers and complexes are available from the author on request.

Table 1 Interaction energies (*IE*) and estimated basis set superposition error BSSE for selected formate–water complexes at each hydration step. Values are given for five different levels of theory: HF/**1**//HF/**1**[a] (top), HF/**2**//HF/**2**, HF/3//HF/3, MP2/**1**//MP2/**1** and MP2/**2**//MP2/**2** (bottom)

Complex	*IE*/kJ mol^{-1}	*IE*^{cp}/kJ mol^{-1}	BSSE/kJ mol^{-1}	%[b]
c1s	63.46	60.16	−3.30	5.20
	61.33	59.34	−1.99	3.25
	58.77	57.09	−1.68	2.86
	71.41	62.87	−8.54	11.96
	68.79	61.06	−7.73	11.23
c2$_2$as	59.59	56.37	−3.22	5.41
	57.23	55.48	−1.75	3.06
	55.28	53.69	−1.60	2.89
	66.98	58.38	−8.61	12.85
	63.91	56.31	−7.60	11.90
c3ass	45.50	42.26	−3.24	7.11
	44.02	41.95	−2.07	4.71
	42.37	40.50	−1.87	4.42
	53.18	44.16	−9.02	16.95
	50.22	44.41	−5.81	11.57
c4	42.80	39.64	−3.17	7.40
	41.14	39.25	−1.88	4.58
	40.62	39.05	−1.57	3.87
	51.54	42.19	−9.36	18.15
	49.05	40.64	−8.42	17.16

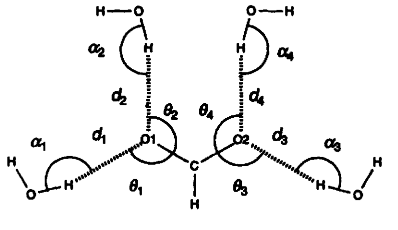
[a] For basis set code, see the text. [b] % BSSE relative to the uncorrected interaction energy for each step.

interaction energies gets larger with increased hydration. At the HF level the CP corrections are always modest, but for the MP2-calculations the BSSE is roughly three times larger (up to 18% at the MP2/1 level), as has also been reported in a previous study on the hydrogen peroxide dimer.[17] The rather substantial differences between uncorrected HF and MP2 calculated energies are thus generally reduced when the BSSE is taken into account.

The essential result to be extracted from Table 1 is that the falling trend in interaction energies with increased hydration is uniformly reproduced at all levels of theory considered. It seems unlikely that inclusion of even higher order electron correlation effects or more sophisticated estimation of the BSSE should have a significant influence on this observation.

A more careful inspection of Fig. 2 reveals more detailed information on the interaction energies. Overall, *anti* H-bonds are lower in energy (and shorter) than *syn* H-bonds, and there is some steric conflict when H-atoms simultaneously occupy both *syn* positions. Two donors prefer two different acceptor atoms rather than a single acceptor, but still the carboxylate group behaves very much like a single acceptor unit and not two independent oxygen acceptors. These observations cause the interaction energy for the second hydration step from **c1a** to **c2$_1$as** to be as low as 50.0 kJ mol^{-1}, while the energy for the third hydration step from **c2$_1$as** to **c3aas** in fact is higher, 50.8 kJ mol^{-1}.

The hydrogen bond parameters defined in Scheme 4 are listed in Table 2.



Scheme 4

It can be seen that declining energies are closely paralleled by longer H-bond distances. *d*(H···O) for *anti* H-bonds goes from 1.780 in **c1a** to 1.880 Å in **c4**. Hereafter, such a hydrogen bond range is indicated as [1.780, 1.880 Å]. The range for *syn* H-bonds is [1.862, 1.978 Å]. Accordingly, the involvement of the carboxylate group in H-bonds to a variable number of water molecules, considered only moderately strong H-bond donors, gives rise to variations for *d*(H···O) up to 0.116 Å in HF/3 calculations. The largest basis sets (**3**) produced slightly wider ranges than the smallest (**1**). Inclusion of electron correlation effects also had a very modest widening effect relative to the corresponding HF-calculation.

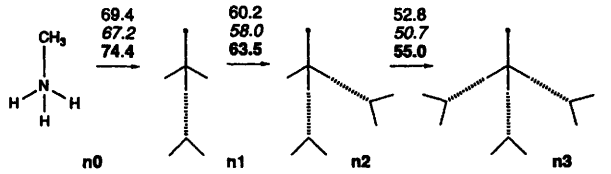
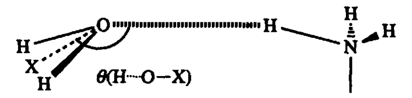


Fig. 3 Nomenclature and HF/3//HF/3, HF/3//HF/3 (CP) (italic type) and MP2/**2**//MP2/**2** (CP) (bold type) interaction energies (kJ mol^{-1}) for hydration of the methylammonium ion

The > C=O bond length of a carbonyl group is known from crystallographic[4] and theoretical work[18] to be sensitive to the number of H-atoms accepted by the group. From the carboxylate geometries given in Table 3 it can be seen that two C–O bonds of different length result from the asymmetric H-bonding in the **c2$_1$as** structure. In the symmetric structures, however, *d*(C–O) is almost unchanged, even when each O-atom accepts two H-atoms.

$MeNH_3^+ \cdot n\,H_2O$, *n* = 1–3

Interaction energies for hydrated complexes of $MeNH_3^+$, illustrated in Fig. 3, are listed in Table 4. As for the carboxylate group, the interaction energies decrease with increased hydration, showing that the potency of the $MeNH_3^+$ donor decreases with increased hydration. Again, these observations are essentially independent of basis set size, inclusion of electron correlation effects and correction for BSSE. Similar results have been obtained experimentally[19] and theoretically[20] for hydration of the ammonium ion, NH_4^+. Covalent and hydrogen bond data (see also Scheme 5) are given in Table 3.



Scheme 5

In all complexes the H-bonds are almost linear with the H-atom being accepted almost exactly on the top of the water O-atom. Rotation of the water molecule around the H-bond axis is virtually unhindered; a $MeNH_3^+ \cdot H_2O$ structure with the water molecule located in the C–N–H plane has only 0.10 kJ mol^{-1} more energy than the minimum structure. The total range for *d*(H···O) in Table 5 is 0.105 Å. This is another example of competitivity, but in this case we are dealing with donor competitivity (Scheme 2). In crystal structures this kind of cooperativity is less easily studied, since H-bond donors invariably participate in hydrogen bonds. Acceptor competitivity, on the other hand, is abundant, since potential H-bond acceptors outnumber the donors in most crystal structures. Hydrogen bonding to $MeNH_3^+$ gives a significant reduction in the C–N bond length from 1.503 for **n0** to 1.485 Å for **n3**.

Other complexes with $HCO_2^- \cdots HOH$ and $MeNH_3^+ \cdots OH_2$ hydrogen bonds

The hydrogen bond length variations observed thus far stem from simple competitivity at the acceptor (HCO_2^-) or at the donor ($MeNH_3^+$). A still shorter H-bond would result if one could: (*i*) eliminate competitivity at the donor or acceptor. (*ii*) Introduce cooperativity at the water molecule. *Vice versa*, a long H-bond would result if one could (*i*) increase competitivity

Table 2 Hydrogen bond distances (Å) and angles (°) for $HCO_2^-\cdot nH_2O$ complexes, n = 1–4. The key to symbols is given in Scheme 4

Structure	d_1(O···H)	d_2(O···H)	d_3(O···H)	d_4(O···H)	θ_1(C–O···H)	θ_2(C–O···H)	θ_3(C–O···H)	θ_4(C–O···H)	α_1(O–H···O)	α_2(O–H···O)	α_3(O–H···O)	α_4(O–H···O)
c1s		1.862				133.4				158.2		
c1a	1.780				131.9				167.3			
c2ss		1.903		1.903		144.5		144.5		156.1		156.1
c2$_2$as		1.889	1.828			133.2	132.6			158.4	167.2	
c2$_1$as	1.826	1.949			123.5	119.8			170.7	157.6		
c2aa	1.829		1.829		134.3		134.3		166.7		166.7	
c3aas	1.852	1.959	1.860		122.7	119.0	136.1		171.2	158.3	166.6	
c3ass	1.849	1.942		1.952	119.9	126.5		156.5	172.5	159.1		154.2
c4	1.880	1.978	1.880	1.978	118.1	134.2	118.1	134.2	173.9	157.1	173.9	157.1

Table 3 Covalent carboxylate geometry and Mulliken charges for selected $HCO_2^-\cdot nH_2O$ complexes with n = 0,2,4 from HF/6-311++G(2d,p) optimizations

Structure	C–O(1)/Å	C–O(2)/Å	H–C–O(1)/°	H–C–O(2)/°	H	C	O(1)	O(2)	H_{anti}[a]	H_{syn}[b]
c0	1.229	1.229	114.8	114.8	−0.06	0.52	−0.73	−0.73		
c1a	1.238	1.221	114.7	115.7	−0.02	0.53	−0.79	−0.71	0.43	
c2₁as	1.246	1.215	114.5	116.6	0.02	0.59	−0.92	−0.71	0.45	0.45
c2aa	1.230	1.230	115.6	115.6	0.01	0.55	−0.78	−0.78	0.43	
c4	1.231	1.231	115.8	115.8	0.09	0.65	−0.88	−0.88	0.42	0.43

[a] H-atom of water molecule in *anti* position. [b] H-atom of water molecule in *syn* position.

Table 4 Interaction energies (IE) and estimated basis set superposition error BSSE for methylammonium–water complexes. Values are given for five different levels of theory: HF/**1**//HF/**1**[a] (top), HF/**2**//HF/**2**, HF/**3**//HF/**3**, MP2/**1**//MP2/**1** and MP2/**2**//MP2/**2** (bottom)

Complex	*IE*/kJ mol⁻¹	*IE*^{cp}/kJ mol⁻¹	BSSE/kJ mol⁻¹	%[b]
n1	75.36	70.61	−4.75	6.30
	73.06	70.05	−3.01	4.12
	69.45	67.16	−2.29	3.30
	86.19	75.37	−10.83	12.56
	82.61	74.39	−8.22	9.95
n2	65.48	61.21	−4.28	6.53
	63.32	60.51	−2.81	4.44
	60.19	58.01	−2.18	3.62
	74.97	64.83	−10.14	13.53
	70.94	63.50	−7.44	10.49
n3	57.36	53.29	−4.08	7.11
	55.39	52.78	−2.62	4.73
	52.76	50.67	−2.09	3.96
	66.11	56.05	−10.06	15.21
	62.09	54.97	−7.13	11.48

[a] For basis set code, see the text. [b] % BSSE relative to the ucorrected interaction energy for each step.

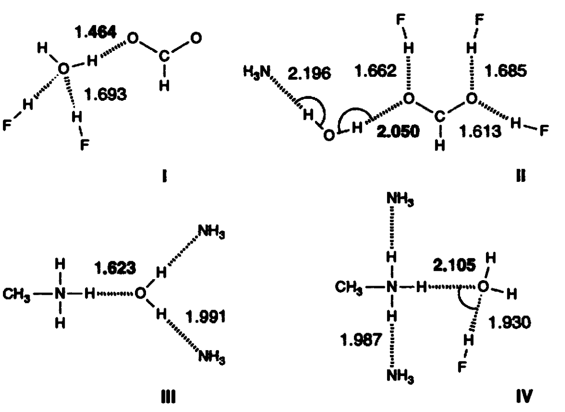


Fig. 4 Selected complexes with $HCOO^-\cdots HOH$ (**I**, **II**) and $MeNH_3^+\cdots OH_2$ (**III**, **IV**) hydrogen bonds. HF/**3** hydrogen bond lengths (Å) have been given in bold type for the principal interaction. The angles indicated with arcs were kept fixed during the optimization. For **II** a free optimization resulted in formation of additional H-bonds between NH_3 and the closest HF, while in **IV** a $MeNH_3^+\cdots FH$ bond was formed that displaced the desired H-bond.

at the donor or acceptor. (*ii*) Introduce competitivity for the water molecule.

The four complexes **I–IV** in Fig. 4 were designed to investigate the extended $d(H\cdots O)$ ranges and optimized at the HF/**3** level. NH_3-molecules have been used as H-bond acceptors, while HF-molecules have been used as H-bond donors. No extra charged species were included in these calculations, as the added electrostatic attraction or repulsion between the charged groups could easily obscure the observation of structural trends. Fig. 4 shows that even when the added donors and acceptors are neutral molecules, the effect on $d(H\cdots O)$ is dramatic. The range for *anti* H-bonds in hydrated carboxylate complexes is extended to [1.464, 2.050 Å], with only negligible changes to $\alpha(O–H\cdots O)$. The new range for the hydrated $MeNH_3^+$ complexes is [1.623, 2.105 Å]. This means that H-bond ranges larger than 0.5 Å can be explained by changes to the secondary H-bond patterns at the acceptor and the donor. It should be noted that the complexes studied here are not extreme; even wider ranges could be obtained with the use of more neutral donors and acceptors in secondary H-bonded shells to enhance cooperative and competitive effects, and additional charged acceptors and donors that form even stronger H-bonds.

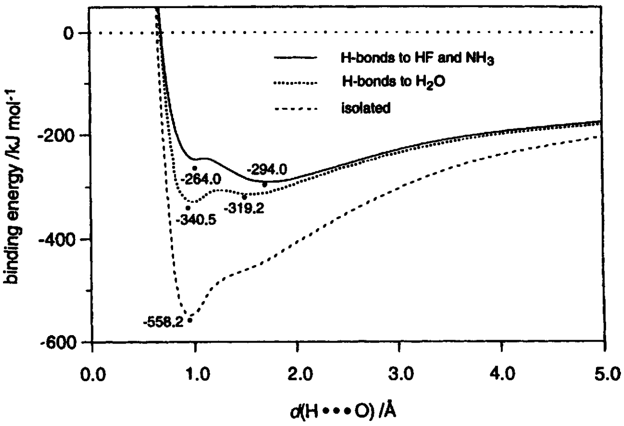
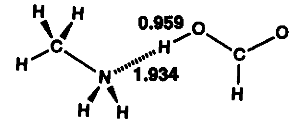


Fig. 5 The three HF/**1**//HF/**1** potentials for interaction between $MeNH_3^+$ and HCO_2^- obtained as described in the text. Bonding energies for the HF/**2**//HF/**2** minima, indicated by bullets, are given.

$HCO_2^-\cdots{}^+H_3NMe$

The HF/**1** potential for $d(H\cdots O)$ has been calculated and is shown in Fig. 5. The HF/**2** energy minimum occurs for $d(H\cdots O)$ = 0.959 Å, meaning that proton transfer takes place, yielding the $MeNH_2\cdots HO_2CH$ dimer **V**, Scheme 6.



V

Scheme 6

There are no local minima elsewhere, and an isolated ion pair is not stable. The total HF/**2**//HF/**2** interaction energy is substantial, 558.2 kJ mol⁻¹, but a modest 40.9 kJ mol⁻¹ when starting with the neutral species $MeNH_2$ and HCO_2H, indicating that the H-bond formed is actually rather weak. This is also reflected by a comparatively long $d(H\cdots N)$ = 1.934 Å. The calculated CP correction is very modest at −2.7 kJ mol⁻¹. CP corrections have not been carried out for the larger complexes described below.

$3H_2O\cdot HCO_2^-\cdots{}^+H_3NMe\cdot 2H_2O$

The inclusion of water molecules around HCO_2^- and $MeNH_3^+$ modifies the H-bond accepting and donating abilities of

Table 5 Covalent and hydrogen bond geometry for the structures $MeNH_3^+ \cdot nH_2O$, n = 0–3, from HF/6-311++G(2d,p) optimizations

Structure	d(C–N)/Å	d(N–H)/Å[a]	d(N–H)/Å[b]	d(H···O)/°	α(N–H···O)/°	θ(H···O–X)/°[c]
n0	1.503	—	1.009	—	—	—
n1	1.495	1.022	1.008	1.826	178.0	177.1
n2	1.489	1.017	1.006	1.882	175.5	176.6
n3	1.485	1.014	—	1.931	173.6	176.3

[a] H-bonded. [b] Not H-bonded. [c] Defined in Scheme 5.

the two ions, as has been shown in the previous sections. To see how hydration affects the potential obtained for the $HCO_2^- \cdots {}^+H_3NMe$ pair, similar calculations were carried out for formation of complex VI between $HCO_2^- \cdot 3H_2O$ and $MeNH_3^+ \cdot 2H_2O$, Fig. 6. There is one local minimum corresponding to the hydrated ion pair (VI/ ±) and a global energy minimum 21.4 kJ mol^{-1} lower for the neutral complex $HCO_2H \cdot 3H_2O \cdots H_2NMe \cdot 2H_2O$, **VI/n**. Fig. 5 clearly reveals the profound effects of hydration. The interaction energy for the neutral dimer has been reduced by 39% from 558 to 340 kJ mol^{-1}. The charged complex has been stabilized relative to the neutral complex. The magnitude of the stabilization can be estimated from Fig. 5 to be *ca.* 100 kJ mol^{-1} at the HF/1 level. The effect of hydration is essential only at relatively short distances. At separations above 5.0 Å hydration of the two ions involved has little bearing on the potential curve, which is determined mainly by the long-range electrostatic attraction energy.

From the pK_a values it is easy to show that an aqueous solution mixture of $MeNH_2$ and HCO_2H is dominated by the ionic species. It is thus clear that VI/ ±, which includes water molecules in the first hydration shell only, is too small to model the bulk effect of water. It is reasonable to assume that one could correctly predict the ionic interaction to be the most stable if additional hydration shells had been included. In a recent related *ab inito* study on glycine,[21] it was found that as few as two water molecules can stabilize the glycine zwitterion in the gas phase.

$3HF \cdot HCO_2^- \cdots {}^+H_3NMe \cdot 2NH_3$

The five hydrogen bonds to water molecules in VI/ ± are rather weak and the 1.492 Å principal H-bond is exceptionally short compared to similar interactions encountered in crystal structures. In order to investigate how stronger hydrogen bonds affect the relative stability of the two energy minima and the hydrogen bond length, the water molecules acting as donors and acceptors in VI were replaced by HF and NH_3, respectively, to yield complex VII, Fig. 6. As for VI the potential has two minima, but the neutral dimer is now barely a minimum. The charged complex VII/ ± is the global energy minimum, which is also the situation that prevails in aqueous solution and in crystal structures. The H-bond distance, 1.688 Å, is inside the range usually observed for interactions between $-NH_3^+$ and $-CO_2^-$ in crystal structures of amino acids and peptides, Fig. 1. It thus seems as if cooperative effects from the second and further hydration shells in solution, or the full hydrogen-bond network in crystal structures, in effect turns a water molecule into at least as good an acceptor as an isolated NH_3-molecule, and as good a donor as an isolated HF-molecule.

It is interesting that upon proton transfer between HCO_2^- and ${}^+H_3NMe$ cooperative and competitive roles of donors and acceptors in secondary H-bonds are switched; that is cooperative effects for $HCO_2^- \cdots {}^+H_3NMe$ become competitive for $HCO_2H \cdots H_2NMe$, and *vice versa.* Accordingly, the isolated neutral dimer V has a rather long hydrogen bond, 1.934 Å, while the combined cooperative effect of the five molecules added in **VI/n** and **VII/n** gives much shorter H-bonds, 1.765 and 1.610 Å, respectively. At the same time the principal H-bond in VI/ ± is very short, 1.492, but 1.688 Å in VII/ ± due to larger competitive effects.

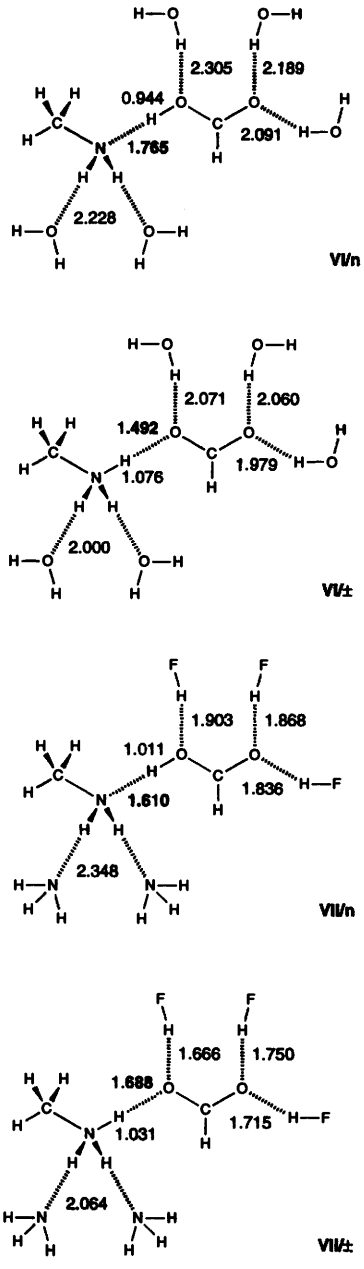


Fig. 6 HF/2 hydrogen bond lengths for the hydrated $MeNH_3^+ \cdots {}^-OOCH$ complex VI (top) and for complex VII with hydrogen bonds to HF and NH_3 (bottom). An ion pair is indicated by ± and a neutral dimer by *n*.

Conclusions

The lengths of $HCO_2^- \cdots HOH$ hydrogen bonds, with closely similar H-bond geometries, vary within a 0.59 Å range between 1.46 and 2.05 Å in various complexes studied by *ab initio* methods at the HF/6–311++G(2d,p) level. The results are relevant for crystal structures, for which it can be inferred that a substantial range for d(O···H) in $RCO_2^- \cdots HOH$ interactions may be explained by the variable nature of the full

H-bond network in which the H-bond of interest constitutes but a single element. A similar conclusion can be derived for $R\text{–}NH_3^+ \cdots OH_2$ interactions. Generally, for a reliable estimation of the relative strength of a hydrogen bond, it is not sufficient to consider just the covalent structures of the donor and the acceptor. When possible, one should also carefully assess how other nearby H-bonds may influence and modify their donating and accepting capabilities. Variations in the number and strength of H-bonds even have a significant effect on covalent bond lengths to the acceptor and donor atoms.

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