The Strongest Hydrogen-bond? *Ab initio*-LCAO-MO-SCF Calculations

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Summary *Ab initio* LCAO–MO–SCF calculations indicate that the hydrogen-bond between the fluoride anion and formic acid, $HCO_2H \cdots F^-$, is stronger than that in the bifluoride anion, $F{-}H \cdots F^-$, previously believed to be the upper limit of H-bond strength.

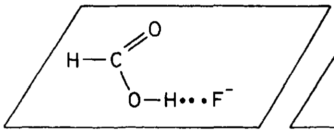
Experimental studies on the carboxylic acid–metal fluoride systems indicate that a very strong H-bond is formed between the hydroxy-group and the fluoride anion.[1] This is reflected in the spectroscopic behaviour[2,3] and chemical reactivity[4] of these solutions. In an attempt to obtain a theoretical estimate of the strength of this linkage in formic acid, a series of *ab initio* LCAO–MO–SCF calculations has been performed on the formic acid–fluoride anion system using the GAUSSIAN70[5] and ATMOL3[6] programs.

The reliability of a single determinant SCF wavefunction for the calculation of the binding energy between two closed-shell systems has been thoroughly investigated by Clementi *et al.*[7] They studied the complexes formed between F^- and H_2O (among others), and calculated the contribution of the molecular extra correlation energy to the total binding energy of the complex to be *ca.* 5%. They therefore concluded that Hartree–Fock binding energies are essentially correct in these systems.

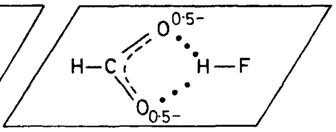
Initially the experimental geometry of formic acid was taken[8] and, using a minimal STO-6G basis set,[9] the value of r(OH) in HCO_2H was optimized to 98 pm and the values of r(OH) and r(HF) in $HCO_2H \cdots F^-$ were optimized to 138 and 99 pm, respectively. The equilibrium orientation of the $H \cdots F$ bond axis was found to be colinear with the O–H bond axis in the molecular plane (**1**). The energy of the $HCO_2H \cdots F^-$ bond was then calculated using the extended ($4s,2p/2s,1p$) Gaussian basis set of Dunning[10] with an s-orbital scaling factor of $\sqrt{2}$ and a p-orbital exponent of 0·7 for the acidic proton.[11] The scaling factor and p-exponent for the other proton were both set at unity.

The energy of the H-bond in $HCO_2H \cdots F^-$ is calculated to be 250 kJ mol^{-1}. This value is to be compared with that of 220 kJ mol^{-1} which we obtain for the H-bond of the bifluoride ion, $F{-}H \cdots F^-$, using the same basis set. Our value for the H-bond in the bifluoride ion is in good agreement with that calculated by Kollman and Allen[11] (217 kJ mol^{-1}) and Neckel, Kuzmany, and Vinek[12] (234 kJ mol^{-1}). Experimentally measured values for $F{-}H \cdots F^-$ give only approximate results ranging from 155[13] to 252 kJ mol^{-1}.[14] Assumptions regarding the lattice energies of the H-bonding species are responsible for this spread of values.[15]

Our results indicate that the H-bond in $HCO_2H \cdots F^-$ is *ca.* 30 kJ mol^{-1} stronger than that in $F–H \cdots F^-$. This estimate of the difference between the two H-bonds is believed to be reliable owing to the fundamental similarity between the two H-bonded systems.



(1)



(2)

In a previous paper[3] we postulated the H-bond between the carboxylic acid group and the fluoride anion as having contributions from the bifurcated structure (**2**). This possibility has been examined theoretically by optimizing the values of *r*(OH) and *r*(HF) in (**2**) with the STO-6G basis, keeping the other geometical parameters fixed: *r*(CH), 108·5 and *r*(CO), 127·9 pm; ∠OCO, 124·4 and ∠HCO, 117·8°. Using the optimized values of *r*(OH), 213 and *r*(HF), 97 pm, with the [4*s*, 2*p*/2*s*,1*p*] basis set, the bifurcated structure is found to be highly unstable with respect to the isolated formic acid and fluoride, in contrast to the results for the cyclic and bifurcated water dimers.[16]

In order to check the stability of the calculated H-bond energies to improvements in the basis set, we have repeated the calculations on $F–H \cdots F^-$ and $HCO_2H \cdots F^-$ with the [5*s*,3*p*/3*s*,1*p*] basis set[10] and we find the binding energies now become 217 and 245 kJ mol^{-1}, respectively. The difference between them remains at *ca.* 30 kJ mol^{-1}. This, and the stability of the results, lead us to conclude that our basis set is sufficiently complete for the reliable calculation of H-bond energies.

A similar system, $HCO_2H \cdots Cl^-$, has been studied by Rode[17] using the CNDO/2 method. From the published graphs a value for the energy of this bond can be estimated as *ca.* 155 kJ mol^{-1}.

The authors thank Dr. M. F. Guest of the Rutherford Computer Laboratory and Dr. P. D. Mallinson of the University of London Computer Centre for their assistance.

(*Received, 6th December* 1976; *Com.* 1327.)

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