

Ab Initio Calculations on the Very Strong Hydrogen Bond of the Biformate Anion and Comparative Esterification Studies

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Abstract: Ab initio LCAO-MO-SCF calculations have been performed on the model biformate anion, $[\text{HCO}_2\cdots\text{H}\cdots\text{O}_2\text{CH}]^-$, and its equilibrium structure and the strength of the H bond has been determined. The resulting H-bond energy of 135 kJ mol^{-1} is found not to be significantly decreased by the inclusion of "ghost orbitals" in the calculations. Esterification experiments using the comparable biacetate anion in the acid solution show this to be capable of converting simple alkyl halides into acetate esters. The very strong H bonding is seen as the reason for the enhanced nucleophilicity of the carboxylic acid group, just as in the case of fluoride-acetic acid.

In a series of ab initio calculations,^{2,3} we have recently shown that the H bond in carboxylic acid-fluoride anion systems, $[\text{RCO}_2\cdots\text{H}\cdots\text{F}]^-$, is predicted to be stronger than that in the bifluoride anion $[\text{F}\cdots\text{H}\cdots\text{F}]^-$, hitherto believed to represent the upper limit of H-bond strength. In addition, we have been able to explain the ready esterification of dihaloalkanes by carboxylic acids in the presence of fluoride ions,⁴ in terms of the formation of a very strong H bond between the fluoride ion and the acid which enhances the nucleophilicity of the hydroxy oxygen atom.

The effects of fluoride on several organic reactions have recently been reported to produce results that were unforeseen but that could be explained in terms of the very strong H bonding that the fluoride ion can produce with OH, SH, and NH groups.⁵⁻⁷

However, the fluoride ion is not unique in forming a very strong H bond to carboxylic acids. It has been known for many years that acid salts of the type $\text{RCO}_2\text{M}\cdot\text{RCO}_2\text{H}$ can contain a bicarboxylate anion held together by a very short, and by implication, very strong H bond.⁸ It was therefore of considerable theoretical interest to extend our studies to the $[\text{RCO}_2\cdots\text{H}\cdots\text{O}_2\text{CR}]^-$ systems so that comparison could be made with the $[\text{F}\cdots\text{H}\cdots\text{F}]^-$ and $[\text{RCO}_2\cdots\text{H}\cdots\text{F}]^-$ systems. Consequently the model biformate system $[\text{HCO}_2\cdots\text{H}\cdots\text{O}_2\text{CH}]^-$ has been studied by means of ab initio calculations employing the refinement of "ghost orbitals".

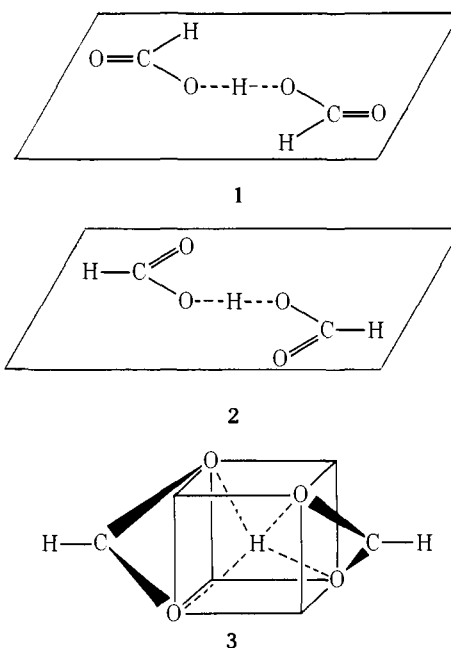
This theoretical work has been supplemented by some esterification studies. In these, the addition of potassium fluoride or potassium acetate to the inactive combination of acetic acid and alkyl halide results in the formation of acetate esters. The enhanced nucleophilicity of the carboxylic acid group by either of these salts is attributed to the formation of very strong H bonds.

Details of the Calculations

Ab initio LCAO-MO-SCF calculations have been performed on the biformate anion complex, using a version of the program GAUSSIAN 70⁹ which has been extensively modified¹⁰ to accommodate 75 contracted basis functions, "ghost orbitals", and level shifters to guarantee the convergence of the SCF calculations. Recent SCF-CI studies of $\text{FH}\cdots\text{F}^-$ ¹¹ and $\text{HOH}\cdots\text{F}^-$ ¹² have demonstrated that the contribution of the molecular extra correlation energy to the energies of these strong H bonds between closed-shell molecules amounts to only ca. 5%. Zero-point vibrational effects are of a similar magnitude.^{12,13} It is therefore to be expected that single determinant SCF wave functions will yield reliable H-bond energies provided that the basis set employed is sufficiently complete.

Initially, assuming the H bond to be linear and the geometry

about both carbon atoms to be the same as in formic acid,¹⁴ the value of R_{OH} in the complex was optimized to 117 pm for the symmetrically H-bonded *trans*³⁵ conformation **1**, using a minimal STO-3G basis set.¹⁵ The effects of asymmetric distortion upon the linear H bond of **1**, and of rotation about the



H bond through possible *cis* and perpendicular conformations (*gauche*), were investigated. The corresponding rotamers of the alternative *trans* conformation **2** were also studied. All of these structures were calculated to be of substantially higher energy than *trans*-**1** which was $-371.752\ 131$ hartrees. With the same geometrical parameters the following energies were obtained for the other conformers: *cis*-**1**, $-371.739\ 504$, and *gauche*-**1**, $-371.751\ 544$ hartrees. For the conformers of structure **2** the values follow: *trans*-**2**, $-371.745\ 521$; *cis*-**2**, $-371.309\ 891$; and *gauche*-**2**, $-371.745\ 194$ hartrees.

In addition to the structures involving a linear H bond, a "double bifurcated" structure **3** was also examined, since it has recently been found that the "bifurcated" H bond in the formic acid-fluoride system is only 35 kJ mol^{-1} weaker than the linear H bond.³ Calculations were performed using a minimal STO-3G basis set for values of $R_{\text{CO}} = 127.9 \text{ pm}$ (as in the formate anion) and 131.2 pm (as in formic acid), keeping the remaining geometrical parameters fixed ($R_{\text{CH}} = 108.5 \text{ pm}$, $\angle\text{OCO} = 124.4^\circ$, $\angle\text{HCO} = 117.8^\circ$ ¹⁴). In both calculations, however, the energy of the "double bifurcated" structure was

found to be substantially higher than that of **1**, i.e., $-371.499\ 401$ hartrees for $R_{CO} = 131.2$ pm and $-371.487\ 847$ hartrees for $R_{CO} = 127.9$ pm.

The H-bond energy of the $[\text{HCO}_2\text{H}\cdots\text{O}_2\text{CH}]^-$ complex in conformation **1** was then evaluated using the $[4s,2p/2s,1p]$ extended Gaussian basis set of Dunning¹⁶ with an s-orbital scaling factor of $\sqrt{2}$ and a p-orbital exponent of 0.7 for the acidic proton, while the scaling factors and p exponents for the other proton were all set to unity. This basis set has previously been shown to yield H-bond energies for $\text{HCO}_2\text{H}\cdots\text{F}^-$ and $\text{FH}\cdots\text{F}^-$ which are stable against further basis set extensions.^{2,3} The total molecular energies of formic acid and the formate anion in this basis set were reported in a previous paper,³ and the conventional H-bond energy is given by the energy difference between the complex and the two isolated molecules.

Attention has recently been drawn to the problem of "basis set extension effects" or "basis superposition errors" in conventional "supermolecule" calculations of intermolecular interactions,^{17,18} and its correction by means of "ghost orbitals" or the "function counterpoise method". The problem was first examined by Boys and Bernardi,¹⁹ who pointed out that "supermolecule" calculations will result in an overestimation of the magnitude of intermolecular energies. This is essentially due to the fact that a less complete basis set is being used for the two isolated molecules than for the complex, where the orbitals of each component molecule overlap and result in a formal extension of the basis set with a concomitant stabilization of the complex. To compensate for this effect, the "function counterpoise method" was proposed in which the calculation on each of the isolated molecules includes the "ghost orbitals" (the orbitals without the electrons or nuclear charges) of the other molecule, located at the same intermolecular configuration as in the complex. The interaction energy is then a function of the intermolecular configuration, and it may also be necessary to take account of intramolecular reorientations which arise from the fact that the equilibrium geometry of each isolated molecule is perturbed upon formation of the complex. This may be accomplished approximately by assuming that the "ghost orbitals" will stabilize the isolated molecule at its equilibrium geometry and at its geometry in the complex to the same extent. Thus a further calculation on each isolated molecule at its geometry in the complex but *without* the inclusion of "ghost orbitals" in the basis set is also required.

Experimental Section

No special precautions, beyond drying the reactants and acetic acid, were taken and the materials were the best commercial grades available.

Esterification Reaction. The brominated hydrocarbon was added to a solution of potassium acetate in acetic acid or potassium fluoride in acetic acid. The halogen:salt ratio was roughly 1:1 with the acetic acid being in excess. The mixture was heated until refluxing and maintained under these conditions for up to 30 h. After cooling, diethyl ether was added and the solution filtered to remove potassium salts. Distilled water was then added to dilute the filtrate and the whole neutralized with NaHCO_3 . The ether layer was separated and the aqueous layer extracted several times with ether. The ether solution was dried (MgSO_4) and stripped of solvent, and the product ester was distilled under reduced pressure.

Reaction of 1-Bromohexane with Acetic Acid-Potassium Acetate. 1-Bromohexane (26.7 g, 0.16 mol), acetic acid (19.4 g, 0.30 mol), and potassium acetate (18.6 g, 0.19 mol) were heated together under reflux conditions for 30 h. The mixture was separated and gave *n*-hexyl acetate (19.0 g, 0.13 mol, 82% yield): δ (Me_4Si) 0.89 (t, 3 H, CH_3), 1.35 (m, 8 H, $(\text{CH}_2)_4$), 1.99 (s, 3 H, CH_3CO), and 4.02 (t, 2 H, CH_2O).

Reaction of 1-Bromohexane with Acetic Acid-Potassium Fluoride. 1-Bromohexane (26.6 g, 0.16 mol), acetic acid (18.6 g, 0.31 mol), and potassium fluoride (11.0 g, 0.19 mol) were heated together under

reflux conditions for 10 h. The mixture was separated and gave *n*-hexyl acetate (17.3 g, 0.12 mol, 75% yield). This reaction with 1-chloro-, 1-bromo-, and 1-iodoheptane gave yields of *n*-heptyl acetate of 85, 100, and 67%, respectively. In general the higher boiling alkyl halides give yields approaching 100% with carboxylic acids and potassium fluoride.

Reaction of 1,6-Dibromohexane with Acetic Acid-Potassium Acetate. 1,6-Dibromohexane (20.6 g, 0.08 mol), acetic acid (19.7 g, 0.3 mol), and potassium acetate (18.4 g, 0.19 mol) were heated together under reflux conditions for 30 h. The mixture was separated and gave 1,6-diacetoxylhexane (11.5 g, 0.067 mol, 84% yield): δ (Me_4Si) 1.47 (m, 8 H, $(\text{CH}_2)_4$), 2.04 (s, 6 H, CH_3), and 4.08 (t, 4 H, CH_2CO).

Reaction of 1,6-Dibromohexane with Acetic Acid-Potassium Fluoride. 1,6-Dibromohexane (20.5 g, 0.08 mol), acetic acid (19.6 g, 0.3 mol), and potassium fluoride (9.2 g, 0.16 mol) were heated together under reflux conditions for 10 h. The mixture was separated and gave 1,6-diacetoxylhexane (13.6 g, 0.08 mol, 100% yield).

Results and Discussion

The results of our calculations for the energy of the H bond between formic acid and the formate anion using the $[4s,2p/2s,1p]$ basis set are presented in Table I. No previous *ab initio* calculations have, to our knowledge, been reported on the biformate anion $[\text{HCO}_2\cdots\text{H}\cdots\text{O}_2\text{CH}]^-$. However, our wave functions for the isolated formic acid and formate anion molecules near their respective equilibrium geometries yield total energies which are lower than those from several previous *ab initio* calculations.²⁰⁻²⁵

The H-bond energy of the biformate anion, evaluated in the conventional way, is found to be $135\ \text{kJ mol}^{-1}$. With the inclusion of "ghost orbitals" in the calculations on the isolated molecules and allowing for the effects of geometry changes associated with H-bond formation (see above), the strength of the H bond is decreased to $123\ \text{kJ mol}^{-1}$. These values are roughly half those determined recently for the formic acid-fluoride ($250\ \text{kJ mol}^{-1}$) acetic acid-fluoride ($249\ \text{kJ mol}^{-1}$), and bifluoride ($220\ \text{kJ mol}^{-1}$) systems.^{2,3} They are, however, close to the results of a recent *ab initio* SCF study on the bichloride anion ($121\ \text{kJ mol}^{-1}$).²⁶ Furthermore, a recent extensive SCF-CI study of the directly comparable system $[\text{HOH}\cdots\text{OH}]^-$ resulted in a value of ca. $105\ \text{kJ mol}^{-1}$ for the energy of the linear, nearly symmetric H bond, after allowing for vibrational corrections.²⁷ The bond lengths characterizing the H bond in this species were calculated to be $R_{\text{OH}} = 109.2$ pm and $R_{\text{OO}} = 246.5$ pm, compared with the value of $R_{\text{OO}} = 234$ pm found for the symmetric H bond in the present work.

It is clear from the total molecular energies presented in Table I that the use of the "function counterpoise method" has a very small effect on the calculated H-bond energy of the biformate anion. This finding is not altogether unexpected since (1) the basis set used for the calculations on each isolated molecule is reasonably complete (as indicated earlier) so that no significant additional stabilization by the "ghost orbitals" of the other molecule is possible, and (2) the intermolecular distance in the equilibrium structure of the H-bonded complex may be sufficiently great to prevent significant overlap between the orbital sets of the two component molecules. "Ghost orbitals" have previously been used in calculations on small H-bonded dimers with minimal basis sets by Johansson et al.,²⁸ and resulted in an improved description of the H-bonding process.

Table I also shows that the increase in R_{OH} , from 98 pm in formic acid to 117 pm in the biformate anion, is most important energetically, and cannot be neglected in the calculation of the H-bond energy. It is interesting to compare this increase in the O-H bond length with that resulting from the formation of the cyclic formic acid dimer as calculated using a minimal STO-3G basis set.²⁹ In the latter system the O-H bond length only increases from 99 to 101 pm upon dimerization, reflecting the

Table I. Numerical Results of the H-Bond Calculation on the Formic Acid-Formate Anion System

Species	Geometry	Total energy hartrees
Formic acid-formate anion complex	Conformation 1 , $R_{OH} = 117$ pm	-376.912 483
Formic acid ^a	Experimental, $R_{OH} = 98$ pm	-188.715 599
Formate anion ^a	Experimental	-188.145 664
	Conventional H-bond energy	135 kJ mol ⁻¹
Formic acid with formate anion "ghost orbitals"	Conformation 1 , $R_{OH} = 117$ pm	-188.673 356
Formate anion with formic acid "ghost orbitals"	Conformation 1	-188.147 060
Formic acid without formate anion "ghost orbitals"	Conformation 1 , $R_{OH} = 117$ pm	-188.672 447
Formate anion without formic acid "ghost orbitals"	Conformation 1	-188.143 545
	Counterpoise H-bond energy	123 kJ mol ⁻¹

^a See ref 3.

formation of two relatively weak hydrogen bonds. Furthermore, the overall hydrogen-bond distance of 254 pm calculated for the dimer is rather longer than the value of 234 pm calculated here for the biformate anion using the same basis set.

Our calculated value of $R_{OO} = 234$ pm is close to the experimental value of $R_{OO} = 244.7$ pm, measured in a crystal of potassium biformate ($\text{KH}(\text{O}_2\text{CH})_2$).³⁰ The difference of 10 pm can be attributed partly to crystal forces and partly to the use of a minimal basis set in determining the structure. This basis set will tend to yield a bond length slightly shorter than would be obtained using a more complete basis set.

The structure of the biformate anion in this crystal is a rotamer of **1** in which the planes through the formate groups make an angle of about 110° with each other. Such distortions of bicarboxylate anions, in those crystals that have been examined, are the rule rather than the exception. Crystal forces may play the key role in determining this conformation of the biformate anion. Similar considerations also apply in the case of sodium biacetate. Here there is a sixfold arrangement of oxygen atoms about each sodium ion and this would seem to be the dominating influence in the lattice.³¹ The biacetate anion in this crystal adopts a conformation that is roughly a 90° rotamer of **2**. So too with $\text{K}^+[\text{HCO}_2\cdots\text{H}\cdots\text{O}_2\text{CH}]^-$ where an eightfold coordination of oxygen atoms around each potassium ion is likely to be the determining factor in the overall lattice arrangement.³⁰

On the other hand, intramolecular forces within the H-bonded anion itself may be important in determining the configuration. For instance, the crystal structure of potassium bisphenylacetate reveals a type **2** planar arrangement^{32,33} which implies that the steric requirements of the bulky phenyl groups are predominant.

The H-bond energy of the biformate anion, although large for an H bond, is only about half that of $[\text{RCO}_2\cdots\text{H}\cdots\text{F}]^-$. It might therefore be expected that this would manifest itself in differences in the chemical reactivity of the two species. The use of potassium acetate-acetic acid in place of potassium fluoride-acetic acid in the esterification of simple alkyl halides appears to bear this out.⁴

Just as KF will cause a reaction to occur between acetic acid and 1-bromohexane and 1,6-dibromohexane, so also will $\text{CH}_3\text{CO}_2\text{K}$. But whereas the KF-promoted reaction gives yields of 75 and 100% of the acetate and diacetate esters, respectively, in 10 h, the use of $\text{CH}_3\text{CO}_2\text{K}$ requires 30 h to reach comparable yields of 82 and 84%, respectively. These observations may reflect the difference in H-bond energy and may be related to the calculated Mulliken charges on the hydroxy oxygen atom of the H-bonded species, which is presumably the attacking nucleophile. The charge is -0.4 e in the case of

formic acid, -0.6 e in the formate anion, -0.6 e in the biformate anion, and -0.7 e in the formic acid-fluoride complex.

Whatever the explanation, these methods of forming esters from halides are to be preferred over the older methods which used metal or quaternary ammonium salts of the carboxylic acid, by themselves or in dipolar aprotic solvents.^{33,34}

As our previous studies have revealed, there is no significant change in the H-bond strength on going from $[\text{HCO}_2\cdots\text{H}\cdots\text{F}]^-$ to $[\text{CH}_3\text{CO}_2\cdots\text{H}\cdots\text{F}]^-$. Similarly we believe that the higher bicarboxylate homologues, $[\text{RCO}_2\cdots\text{H}\cdots\text{O}_2\text{CR}]^-$, will not differ appreciably in H-bond strength from the 135 kJ mol⁻¹ that we calculate for the biformate anion. At present such systems are well beyond our reach.

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Prototypes for Aliphatic and Aromatic Diazonium Ions. An ab Initio Study of the Methane- and Benzenediazonium Ions

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Abstract: Ab initio molecular orbital calculations with minimal (STO-3G) and split-valence (4-31G) basis sets have been carried out for open and bridged structures of the methanediazonium (MDI) and benzenediazonium (BDI) ions. Theoretical geometries and relative energies are reported. Open structures are preferred for both MDI and BDI with N≡N lengths in both cases similar to that in molecular nitrogen. Although the C-N bond is considerably shorter in BDI than in MDI, binding energies calculated with respect to the appropriate parent cation + nitrogen are in the reverse order. The N_αN_β rearrangement in open MDI is predicted to proceed via a symmetric bridged transition state. In contrast, the N_αN_β rearrangement in BDI is predicted to proceed via an asymmetric transition state in which one of the nitrogens is weakly bound to a ring carbon and the other not at all. A symmetric bridged structure is predicted to be a metastable intermediate in this rearrangement, lying in a high-energy shallow potential well. The N₂⁺ substituent is found to be a powerful σ-electron acceptor and π-electron acceptor.

Introduction

It is more than a century since diazonium ions were first discovered,¹ and in the intervening period their reactions have been studied in great detail.²⁻⁴ In contrast, our knowledge of some of their fundamental physical properties, notably their structures and energies, is fragmentary. Thus no experimental structural data have been reported for any simple aliphatic diazonium salt, and the only simple diazonium cation, aliphatic or aromatic, for which an experimental heat of formation appears to be available is the methanediazonium ion.⁵ As a result, there are many questions about diazonium ions that remain to be answered. Of particular interest is the relationship between structure and stability in the various diazonium ions. In addition, there are certain aspects of diazonium ion chemistry which have been extensively studied experimentally, for which it would be desirable to have more direct information. The precise nature of the transition state for the N_αN_β rearrangement in the benzenediazonium ion is one such example.

A promising source of such information is ab initio molecular orbital theory. This has been used extensively in previous structural and energetic studies of organic systems⁶ and, in particular, for studying organic cations.⁷ In this paper, we use such a theoretical procedure to study the structures and stabilities of the methane- and benzenediazonium ions.

Previous theoretical work on diazonium ions has generally been limited to semiempirical treatments, usually on the benzenediazonium ion.^{8,9} Of these, we note particularly the interesting paper by Van Dine and Hoffmann⁹ on rearrangements in diazonium ions (and related systems). Recently, a detailed study of the protonation of diazomethane has been reported.¹⁰ This work included CNDO/2 and MINDO/3 optimizations of the methanediazonium ion together with single calculations at the STO-3G and 4-31G levels. The main point of the study, however, was to compare C- vs. N-proton-

ation in diazomethane. Finally, STO-3G calculations on substituted benzenediazonium ions have recently been reported¹¹ in which the effect of substituents on the stabilities of phenyl cations and benzenediazonium ions is compared.

Method and Results

Standard ab initio LCAO SCF molecular orbital calculations were carried out using a modified version of the Gaussian 70 system of programs.¹²

Open (**1**) and bridged (**2a**, **2b**) structures of the methanediazonium ion were fully optimized, except for specified symmetry constraints, using a gradient optimization procedure¹³ and the minimal STO-3G¹⁴ and split-valence 4-31G¹⁵ basis sets. Optimized geometries are shown in Figure 1 together with previously reported^{16,17} data for CH₃⁺ (**3**, STO-3G and 4-31G) and N₂ (**4**, STO-3G) included for reference. Corresponding energies are listed in Table I. In order to determine the activation energy for a possible N_α-N_β rearrangement in **1**, direct transition state calculations¹⁸ were carried out yielding the structure (**2c**) shown in Figure 4. In this procedure,¹⁸ the transition state is characterized as having near-zero values (within a specified tolerance) of the first derivatives of energy, and one negative eigenvalue for the second derivative energy matrix. Charge distributions with the STO-3G basis derived using the Mulliken approach¹⁹ are given in Figure 5.

For the open (**5**) and bridged (**6**) structures of the benzenediazonium ion, full STO-3G optimization was carried out, subject only to specified symmetry constraints and the assumption of 1.083 Å (the optimized value in benzene²⁰) for the length of the C-H bonds. An optimization of the phenyl cation (**7**) with the same assumption concerning C-H lengths was also carried out. Our structure (**7**) has an energy 3 kcal mol⁻¹ lower than that of a recently reported²¹ STO-3G structure, reflecting a more complete geometry optimization. Optimized structures for the aryl systems are displayed in Figure 7 and corre-