in energy than $^2A_1$ states, whereas in the borohydrides the ordering is reversed (Figure 5). In this respect the $CaBH_4$ and $SrBH_4$ molecules resemble the formate derivatives,[11] CaO_2CH and SrO_2CH (as well as the formamidate[16] derivatives). The $^2A_1$ states of the formates[11] lie lower in energy than the $^2B_1$, $^2B_2$ pair of states which correlate to the ^2E or $^2\Pi$ states of a high symmetry axial ligand.

The alkaline earth borohydride and formate molecules share one striking similarity. In each one bonding occurs off the metal-ligand axis with bridging ligand atoms (three hydrogens for the borohydrides and two oxygens for the formates). The bridging atoms have a partial negative charge. When they point towards the off-axis Ca^+ and Sr^+ p- and d-orbitals containing the excited electron, the π-like orbitals are destabilized relative to the on-axis σ-like orbitals.

In the cases of the methyl and methoxy derivatives, bonding occurs on the metal-ligand axis so the negative charge of the ligand points to the on-axis orbitals of the cation. When containing the excited extra electron, the resulting σ-like molecular orbitals are destabilized relative to the π-like orbitals.

Figure 5 is a correlation diagram of the energy levels resulting from ligand and alkaline earth cation interactions. The BH_4^- ligand only partially lifts the p- and d-orbital degeneracy of the Ca^+ or Sr^+ atom. In addition, the BH_4^- ligand mixes the p and d character of the atomic orbitals so that the $\tilde{A}^2A_1$ state is a $p\sigma$–$d\sigma$ mixture while the $\tilde{B}^2E$ state is a $p\pi$–$d\pi$ mixture. The location of the $^2\Delta$ state is uncertain, but we suspect (contrary to Figure 5) that the $^2\Delta$ state lies above the $\tilde{A}$ and $\tilde{B}$ states for $CaBH_4$ and $SrBH_4$.

Conclusion

We have discovered the $CaBH_4$ and $SrBH_4$ molecules by the reaction of Ca and Sr vapors with diborane. The low-resolution spectra are consistent with a tridentate molecular structure of C_{3v} symmetry with three bridging hydrogens. No evidence of fluxional behavior has been found yet, but the possibility cannot be ruled out. Some ab initio calculations on the alkaline earth monoborohydrides would be most welcome.

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Methyl Chloride/Formic Acid van der Waals Complex: A Model for Carbon as a Hydrogen Bond Donor

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Abstract: AM1 and MP2/6-31+G*//6-31G** + ZPE calculations are reported for the van der Waals complex of formic acid and methyl chloride. Both theoretical approaches predict the formation of a relatively strong C–H···O hydrogen bond. Four minima were located for the formic acid/methyl chloride van der Waals complex, with hydrogen bond strengths ranging from 2.12 to 5.03 kcal/mol. The strength of this interaction argues that carbon may act as a hydrogen bond donor more readily than is generally assumed. Additionally, the computed formic acid/methyl chloride hydrogen bond has significant implications for polymer compatibility by providing support for the hypothesis that compatibility of PVC/acrylate polymer blends is attributable to the formation of C–H···O hydrogen bonds.

Introduction

Interest in carbon as a hydrogen bond donor stems from the role this type of hydrogen bond is increasingly thought to play in diverse areas of chemistry.[1] The C–H···X hydrogen bond has been implicated as a factor in determining crystal-packing structures for a variety of molecules,[2,3] particularly biomolecules,[4,5] in the anaesthetic mode of action[6] for certain halogenated compounds such as chloroform; and in polymer miscibility.[7] The latter is a topic of special importance due to burgeoning commercial interest in polymer blends.

Carbon as a hydrogen bond donor has been the subject of three extensive surveys of the crystallographic literature,[3,8,9] all of which concluded that carbon can indeed act as a hydrogen bond donor under certain circumstances. Theoretical[10-16] and experimental[1,17] studies aimed at determining the magnitude of C–H···X hydrogen bonds are limited, but those that are available indicate interaction energies as large as −5.4 kcal/mol for systems such as malononitrile and water.[11] This certainly constitutes a respectable hydrogen

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Table I. Calculated AM1 Heats of Formation (kcal/mol) and ab Initio Total Energies (au)

structure	AM1	HF/6-31G*	HF/6-31G**	MP2/6-31G**[a]	MP2/6-31+G*[a]
1	−118.77	−687.862 663 1	−687.875 697 4	−688.645 009 6	−688.619 335 0
2	−118.25	−687.859 706 4	−687.872 850 7	−688.641 031 5	−688.615 291 4
3	−117.96	−687.857 883 8	−687.870 940 7	−688.639 176 1	−688.613 985 7
4	−117.71	−687.859 001 3	−687.871 963 1	−688.640 581 5	−688.615 887 4
9	−117.76	−687.858 691 7	−687.871 809 1	−688.639 756 0	
10	−116.90	−687.856 658 3	−687.869 676 8	−688.637 657 1	
11	−117.22	−687.856 893 3	−687.869 935 9	−688.638 125 4	
12	−117.20	−687.858 700 4	−687.871 639 2	−688.640 265 8	
13	−129.76	−844.009 996 1			
HCOH	−97.38	−188.762 309 7	−188.770 566	−189.257 208 3	
CH_3Cl	−18.95	−499.093 152 5	−499.097 898 9	−499.378 089 3	
$CH_3CHClCH_3$	−31.32	−577.169 293 5			
CH_3COOCH_3	−96.41	−266.836 829 6			

[a] Calculated at the HF/6-31G** geometry.

Table II. Calculated Stabilization Energies for the van der Waals Complexes (kcal/mol)

method	**1**	**2**	**3**	**4**	**9**
AM1	−2.44	−1.92	−1.63	−1.38	−1.43
6-31G*	−4.52	−2.66	−1.52	−2.22	−2.03
6-31G**	−4.54	−2.75	−1.55	−2.20	−2.10
6-31+G*[a]	−3.99	−2.28	−1.31	−2.04	
6-31+G**[a]	−4.02				
6-311G*[a]	−4.42				
6-311+G*[a]	−3.96				
6-311+G**[a]	−3.89	−2.35	−1.39	−2.01	
MP2/6-31G**[a]	−6.09	−3.60	−2.43	−3.32	−2.80
+ZPE	−5.14	−2.92	−1.92	−2.75	−2.29
MP2/6-31+G*[a]	−5.98	−3.45	−2.63	−3.82	
+ZPE	−5.03	−2.77	−2.12	−3.25	
BSSE[b]	0.40	0.19	0.18	0.24	

method	**10**	**11**	**12**	**13**
AM1	−0.57	−0.89	−0.87	−2.03
6-31G*	−0.75	−0.90	−2.03	−2.43
6-31G**	−0.76	−0.92	−1.99	
MP2/6-31G**[a]	−1.48	−1.77	−3.12	
+ZPE	−1.06	−1.35	−2.57	

[a] Calculated at the HF/6-31G** geometry. [b] Counterpoise correction to the association energies calculated at the HF/6-31+G* level.

bond. Another molecule long known to be a C–H hydrogen bond donor is chloroform.[1] It has also been estimated to form hydrogen bonds with good acceptors in the range of 5 kcal/mol.[18] In both malononitrile and chloroform, the C–H bond is activated by the presence of very strongly electron-withdrawing substituents.

In order to better understand the ability of carbon activated by a single chlorine substituent to act as a hydrogen bond donor, calculations were carried out for methyl chloride and formic acid. They were chosen because methyl chloride is the simplest chlorine-substituted alkane and formic acid is the simplest analogue of a carboxylic acid or ester, both of which are common hydrogen bond acceptors.

Computational Procedure

The MOLY[19] molecular graphics/modeling package was used to graphically input the MOPAC[20] and GAUSSIAN88[21] data files, as well as display the resulting geometries. Calculations were carried out with the AM1[22] Hamiltonian, as implemented in the MOPAC computer program, and ab initio with a variety of basis sets, as implemented in the GAUSSIAN88 program. The AM1 and ab initio HF/6-31G** geometries were fully optimized, and all stationary points were characterized with calculation of force constants. The initial searches of the potential surface were done with AM1 in order to save computer time. The AM1 stationary points were used as starting points for subsequent ab initio calculations.

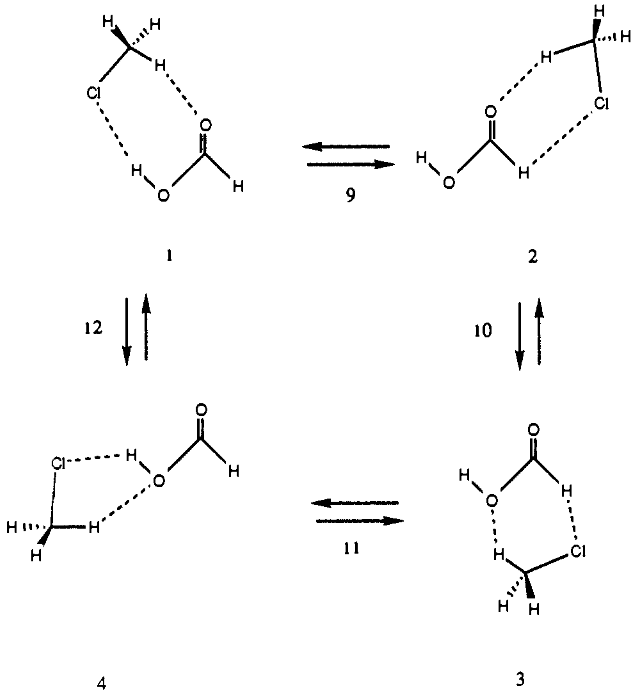

Figure 1. Potential surface for the formic acid/methyl chloride van der Waals complex.

AM1 was chosen for initial survey of the potential surface because, unlike its predecessor MNDO,[23] it has been shown to be capable of reproducing hydrogen bonds.[22] Further, recent studies of a variety of van der Waals complexes by Dannenberg and Vinson[24-26] have shown that AM1 gives geometries and energies that are consistent with both high-level ab initio calculations and experimental results.

AM1 Potential Surface

Four minima, **1**–**4**, which correspond to van der Waals complexes of formic acid and methyl chloride, were found with AM1 (Figure 1). The AM1-calculated heats of formation and energies of association for these complexes are given in Tables I and II, respectively. Attempts to locate stationary points corresponding to **5** and **6** failed. Likewise, structures **7** and **8**, where the hydrogen bond angle (O···H–C) is equal to 180°, are not minima but will spontaneously optimize to **1** and **2** if allowed. This is due to a

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[18] A table of hydrogen bond strengths for chloroform and various acceptors is given in ref 1. See for example: Lambert, J. D.; Clarke, J. S.; Duke, J. F.; Hicks, C. L.; Lawrence, S. D.; Morris, D. M.; Shone, M. G. T. *Proc. R Soc. London, A* **1959**, *249*, 414.

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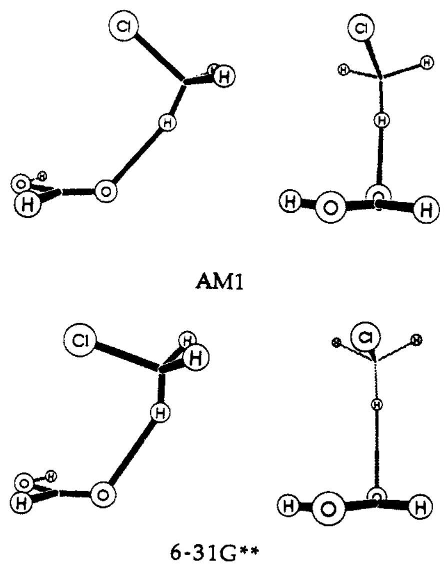
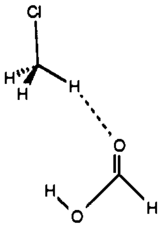


Figure 2. Two views of the AM1- and 6-31G**-calculated transition state for interconversion between **1** and **2**, **9**.

second stabilizing interaction between chlorine and the formic acid acyl or hydroxyl hydrogen. The secondary hydrogen bond, which is present in all four minima (**1**–**4**), disfavors structures where the chlorine is rotated away from formic acid, such as **5** and **6**. It is also responsible for the significant distortion of the O···H–C bond angle away from 180° (Table III).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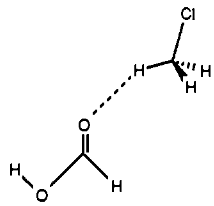
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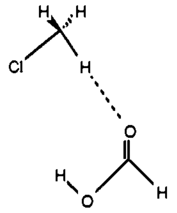
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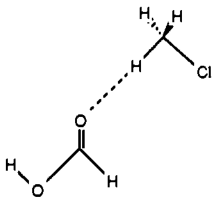
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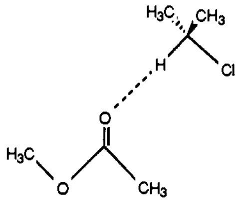
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Although the hydrogen bond strengths are not as large as is typical for more traditional donors, they are significant, ranging from 1.4 to 2.4 kcal/mol. The most stable complex is calculated to be **1**. This is likely due to the larger interaction between chlorine and the hydroxyl hydrogen, as compared to the acyl hydrogen, and synergism between the carbonyl as an acceptor and the hydroxyl group as a donor. The hydrogen bonds that involve the hydroxyl oxygen as proton acceptor are both significantly weaker than those where the carbonyl acts as the acceptor.

Further exploration of the potential energy surface showed that the four minima, **1**–**4**, are separated by transition states **9**–**12** (Figure 1). Each step involves rotation of methyl chloride out of the formic acid plane to break one hydrogen bond while the other is maintained. For example, conversion of **1** to **2** entails rotation about the axis of the carbonyl double bond so that, in the transition state, the H···O–C bond is maintained but rotated almost 90° out of the plane (Figure 2). In this way, methyl chloride can roll about the formic acid structure without ever completely disassociating. Because of this, even the transition-state geometries exhibit a negative enthalpy of association. As can be seen from Table II, the potential surface is calculated to be very flat, indicating that interconversion between the four stable van der Waals complexes should occur freely.

Ab Initio Potential Surface

The methyl chloride/formic acid potential surface was recomputed with the ab initio HF/6-31G* and HF/6-31G** basis sets (Table I). The AM1 stationary points were taken as starting points for the ab initio calculations, but some additional exploration was done in an attempt to guarantee that no minima were missed. The AM1 and ab initio surfaces are virtually identical qualitatively. The only differences are in the magnitudes of the stabilities of the van der Waals complexes, with the ab initio hydrogen bond strengths being generally greater (Table II). At the 6-31G** level, the van der Waals complexes range in stability from −1.6 to −4.5 kcal/mol. As is the case with AM1, **1** is the most stable complex. The stabilities of **3** and **4** are reversed, however, by the ab initio calculations. Both the 6-31G* and 6-31G** calculations predict that **4** is more stable than **3**, in contrast to the AM1 results. The ab initio ordering seems intuitively more reasonable since one would certainly expect the hydroxyl proton to be more acidic than the acyl proton. It is also true, however, that the six-membered ring, **3**, should be less strained than the five-membered ring, **4**. This second factor may account for the AM1 ordering.

Comparison of the computed geometries for **1**–**4** (Figure 3) shows that the AM1 and 6-31G** geometries are very similar.[27] The most significant deviations are between the AM1 and ab initio calculated O···H hydrogen bond distances (Table III). The AM1 O···H distances are systematically smaller than the ab initio values on average by 0.32 Å. Similarly, the Cl···H distances are approximately 0.23 Å shorter for the AM1-calculated geometries than for the ab initio calculated geometries. Otherwise, the close correspondence[27] between the AM1 and ab initio geometries (Figure 3) lends credence to the practice of using AM1 to scout the potential surface.

MP2/6-31G** calculations were carried out at the HF/6-31G** geometries. These are also reported in Table I. The MP2 stabilization energies are consistently more negative (Table II) than the corresponding HF energies. This is not surprising since electron correlation generally lowers the energy of partial or delocalized bonds preferentially. Similar trends have been found in other hydrogen bond studies.[28] Zero-point energies calculated at the HF/6-31G** level have the opposite effect, in part compensating for the extra stabilization due to MP2. The MP2/6-31G**//HF/6-31G** + ZPE calculations give hydrogen bond strengths ranging from 1.92 kcal/mol for **3** to 5.14 kcal/mol for **1**.

In order to obtain a better estimate of basis set effects, a series of single-point calculations were carried out for **1** using successively larger basis sets. The relative energies in Table II show that addition of polarization functions to hydrogen has no effect on **1**. The difference for going from 6-311+G* to 6-311+G** is only 0.07 kcal/mol. For the other two examples of this addition, the difference is even smaller. Given the presence of a third-row element, expansion of the basis set to triple ζ in the valence region might be expected to have a significant effect on the stabilities. This was not the case, however, since the 6-31G* and 6-311G*

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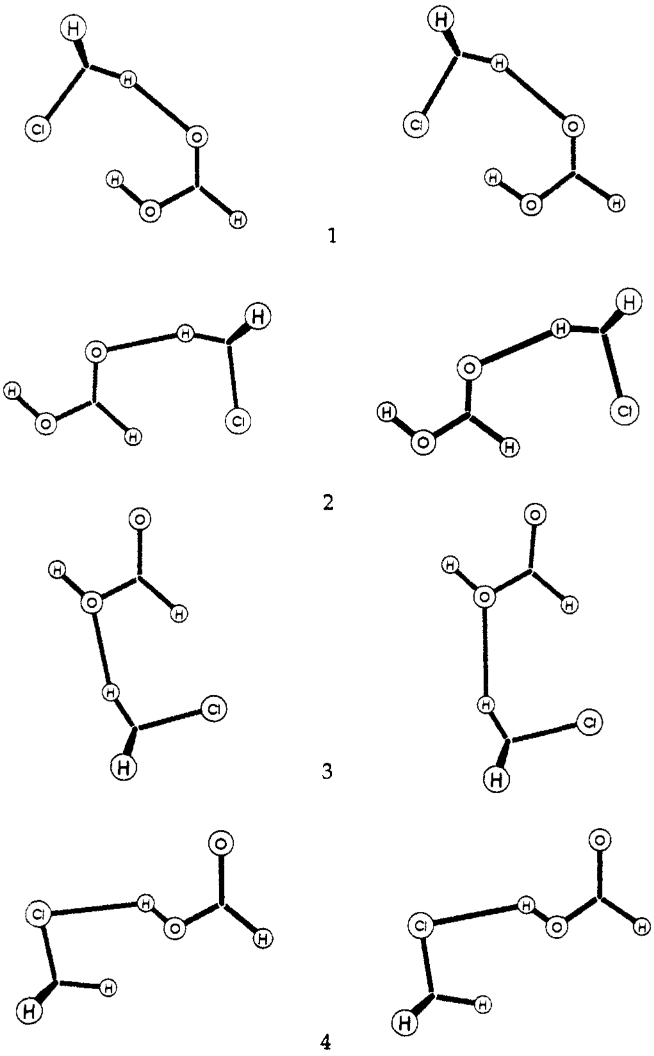

Figure 3. Plots of the AM1- (left column) and 6-31G**- (right column) calculated geometries for **1–4**.

results differ by only 0.1 kcal/mol. Similarly, going from 6-31+G* to 6-311+G* or from 6-31+G** to 6-311+G** had even smaller effects. By contrast, addition of diffuse functions did have a significant effect on the stability of **1**. For example, addition of diffuse functions to the 6-31G* basis set led to a decrease in the stability of **1** of approximately 0.5 kcal/mol. Almost identical changes were observed for addition of diffuse functions to the 6-31G** and 6-311G* basis sets. Thus, it seems that diffuse functions are necessary to properly reproduce the energy of **1**. This leads to the conclusion that the 6-31+G* basis set represents the best compromise of efficiency and completeness for the study of complexes such as **1–4**. To confirm this, single-point calculations were done for **1–4** at the 6-311+G** level. The energies calculated with this very extensive valence triple-ζ basis set with diffuse functions and polarization functions on carbon and hydrogen agreed with the 6-31+G* energies to within 0.1 kcal/mol or better. Since the 6-31+G* and 6-311+G** basis sets give virtually identical results for the hydrogen bond strengths of **1–4** (Table II), it seems likely that basis set effects have converged at the smaller basis set. Therefore, further calculations for the energies of **1–4** were carried out with the 6-31+G* basis set.

A special concern whenever van der Waals complexes are studied is the effect of basis set superposition error. This problem has been described by Boys,[29] along with a procedure for minimizing it. The Boys procedure is referred to as the counterpoise correction and has been widely applied. Counterpoise-corrected energies were computed for **1–4** at the HF/6-31+G* level (Table II). They resulted in only modest corrections to the stabilization energies ranging from 0.18 to 0.40 kcal/mol. A significant body of evidence suggests[30–32] that the counterpoise procedure leads to no improvement in the energies of complexes such as **1–4**. Indeed, the systematic studies cited above[30–32] indicate that inclusion of the counterpoise correction may actually have a negative impact on the accuracy of calculated association energies. This view is not universally accepted, however. The case for including the counterpoise correction in studies of van der Waals complexes can be found in a recent review article by Hobza and Zahradnik.[33] The best procedure is simply to use a sufficiently large basis set so that basis set superposition errors are kept to a minimum. On the basis of the systematic examination of basis sets described above, it appears that the 6-31+G* basis set is sufficiently large. In view of the doubt increasingly cast on the counterpoise procedure, and since their effects are small, the counterpoise corrections have not been applied to the final energies.

Allowance for electron correlation was found to have a large effect on the 6-31G** energies, so additional MP2 calculations were carried out with the 6-31+G* basis set. The MP2/6-31+G*//HF/6-31G** results, corrected for zero-point energies at the HF/6-31G** level, constitute the best estimates of the stabilities of **1–4** (Table II) computed in this study. The hydrogen bond strengths for these complexes range from 5.03 to 2.12 kcal/mol. Calculations by Del Bene[28] for a variety of van der Waals complexes indicated that the Møller–Plesset second-order (MP2) perturbation term is dominant in calculating correlation energies for hydrogen-bonded systems. Inclusion of correlation at the MP3 or MP4 level had a negligible effect on the calculated stabilization energy of the water dimer.[28] Taken together with the basis set studies discussed above, one can reasonably conclude that the use of larger basis sets or higher order Møller–Plesset perturbation theory would be unlikely to provide significant improvement in the calculated properties of **1–4**.

As a final check that the hydrogen bonds calculated in this study are not artifacts of the level of theory, the formic acid/methane complex was examined. The energy of association at the 6-31G** level is much smaller at −0.6 kcal/mol (−0.5 kcal/mol for AM1). This is a strong indication that the stabilities of the formic acid/methyl chloride complexes are a direct result of the electronic effect of the chlorine. In light of all of these factors, a very good case can be made for concluding that methyl chloride forms a strong C–H···O hydrogen bond with formic acid.

Discussion

The strategy of using AM1 to initially explore a potential energy surface has been used profitably before[34] and is also found to be useful in this study. With AM1, it was possible to explore the potential surface much more thoroughly and efficiently than would have been possible with ab initio methods alone. The AM1 calculations not only provided an accurate overall picture of the potential surface, but the AM1 critical points provided excellent starting points for the HF/6-31G** optimizations. In fact, the AM1 and HF/6-31G** geometries were mostly very similar. The close correspondence between the AM1 and HF/6-31G** potential surfaces found in this study is consistent with other reports,[35,36] which indicate that AM1 gives geometries for minima and transition states that agree closely with high-level ab initio results. Thus, it appears that the use of AM1 as a scout in combination with high-level ab initio methods is a generally succesful strategy. AM1 is much faster and more accurate than

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Table III. Selected[a] AM1 and ab Initio Calculated Bond Distances (Å) and Angles (deg)

parameter	AM1	6-31G*	6-31G**
	Structure **1**		
O···H	2.27	2.48	2.46
H···Cl	2.52	2.57	2.59
O···H–C	158	151	152
O–H···Cl	180	174	174
C–Cl···H	94	101	101
C–O···H	130	130	131
	Structure **2**		
O···H	2.31	2.54	2.51
H···Cl	2.82	3.19	3.18
O···H–C	157	153	153
C–H···Cl	128	124	124
C–Cl···H	93	94	94
C–O···H	104	116	116
	Structure **3**		
O···H	2.32	2.74	2.71
H···Cl	2.72	3.20	3.17
O···H–C	159	149	149
C–H···Cl	147	137	136
C–Cl···H	90	97	97
C–O···H	105	118	119
	Structure **4**		
O···H	2.41	2.87	2.82
H···Cl	2.68	2.71	2.72
O···H–C	137	128	129
O–H···Cl	132	135	133
C–Cl···H	84	92	92
C–O···H	170	174	172

[a] These geometric parameters were selected because they are most relevant to the hydrogen bond. They also tend to be the geometric parameters exhibiting the greatest variation between AM1 and ab initio values.

the more typically used STO-3G and 3-21G methods.[37,38]

The significant hydrogen bond predicted by this theoretical study between formic acid and methyl chloride provides new insight into the prevalence of C–H···O hydrogen bonds. If a single chlorine can provide sufficient activation to allow carbon to act as a hydrogen bond donor, then many other common electron-withdrawing groups should also be capable. The ability of a molecule as simple as methyl chloride to act as a hydrogen bond donor certainly helps explain the large number of such bonds found in the crystallographic literature.[8,9] It also supports the conclusion of several of these studies that C–H···X hydrogen bonds are widespread and can have a significant effect on crystal packing.

The hydrogen bond calculated for methyl chloride and formic acid also has direct bearing on the issue of C–H···X hydrogen bonding as a driving force for polymer compatibility. It is widely held that in most cases compatibility between two different homopolymers depends on the existence of some specific interaction between the two polymers.[7,39–41] such as a hydrogen bond.[42,43] An example of this is poly(vinyl chloride) and certain acrylate polymers such as poly(methyl methacrylate). The miscibility of PVC in PMMA has been ascribed to a favorable enthalpy of mixing brought about by C–H···O hydrogen bonding. Polymer miscibility is a subject of intense interest due to the growing importance of polymer blends in many commercial applications, particularly plastics. Therefore, it is useful to examine the degree to which the calculations undertaken in this study can serve as a model for the role of carbon as a hydrogen bond donor in halogenated polymers, such as poly(vinyl chloride).

Admittedly, methyl chloride and formic acid are not reasonable polymer models. Indeed, in terms of size and complexity, they are as far away from polymers as any molecules could be. They do, however, contain the essential elements of the proposed C–H···O hydrogen bond between PVC and PMMA. As such, the relatively strong C–H···O hydrogen bond found for formic acid and methyl chloride is relevant and provides considerable support for hydrogen bonding between PVC and acrylate polymers, such as PMMA. This in turn is consistent with the hypothesis that specific intermolecular interactions are responsible for determining whether two polymers are miscible in each other.[7]

The weaker van der Waals complex, **2**, is probably most applicable to the polymers of interest, PMMA and PVC, because the acidic hydroxyl group is absent in PMMA. Secondary contributions from interaction of the acyl hydrogen and chlorine are relatively small. This has been tested by enforcing a 180° O···H–C bond angle in **2**. While this structure is not a stationary point on the potential surface, it is only slightly (0.2 kcal/mol for AM1, 0.5 kcal/mol for 6-31G**) less stable than **2**. Even the relatively weak intermolecular attraction found in **2** (MP2/6-31+G*//HF/6-31G** + ZPE, $\Delta E = -2.8$ kcal/mol) is more than sufficient, however, to account for a negative enthalpy of mixing when the large number of such potential interactions in a polymeric mixture is considered. Therefore, it is reasonable to conclude that C–H···O hydrogen bonds of the type found in PVC/acrylate polymer mixtures are more than strong enough to provide the primary driving force for compatibility.

In order to conclusively determine that the acid functionality in complexes **1**–**4** is not somehow completely responsible for their stability and to better approximate the polymer system, the van der Waals complex of methyl acetate and isopropyl chloride was examined. The best conformation located with AM1 (**13**) has a stabilization energy of −2.03 kcal/mol. This is almost identical with the change in energy (−1.92 kcal/mol) found by AM1 for the corresponding formic acid/methyl chloride model, **2**. Similarly, the 6-31G* stabilization energy of −2.43 kcal/mol is consistent with the 6-31G* stabilization energy for **2** of −2.66 kcal/mol. This close correspondence between the formic acid/methyl chloride and methyl acetate/isopropyl chloride complex energies is reassuring since it means that the magnitude of the C–H···O bond calculated for the simple model is transferable to larger systems, and probably even to polymers.

Conclusion

AM1 and ab initio calculations for the van der Waals complexes of formic acid and methyl chloride provide strong evidence for significant hydrogen bonding between these molecules. These calculations agree with previous work[11–17] in showing that carbon can be a relatively good hydrogen bond donor if it is activated by an electron-withdrawing group. In this case, there are four distinct minima that represent stable hydrogen-bonded complexes of formic acid and methyl chloride. These four minima are predicted to be separated by small energy barriers leading to facile interconversion. It is interesting to see that even a single chlorine is electron-withdrawing enough to make carbon a reasonable hydrogen bond donor. This observation argues that carbon may act as a hydrogen bond donor more readily than commonly imagined.

Further, this work provides strong evidence that hydrogen bonds between halogenated polymers, such as PVC, and acrylate polymers, such as PMMA, can lead to the observed negative enthalpies of mixing for these and related polymers. Similar studies for other model systems representing additional interpolymer interactions could be very valuable in quantifying the forces responsible for rendering polymers compatible. Such studies are currently underway in this lab.

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Registry No. PMMA, 9011-14-7; PVC, 9002-86-2; methyl chloride, 74-87-3; formic acid, 64-18-6; methane, 74-82-8; methyl acetate, 79-20-9; isopropyl chloride, 75-29-6.

Supplementary Material Available: A listing of AM1 and 6-31G** z matrices and interatomic distances for **1–4** and **9–12** (12 pages). Ordering information is given on any current masthead page.

Balanced Geometries and Structural Trends in Covalent, Ionic, and van der Waals Clusters

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Abstract: Leech's defintion of a balanced structure is refined and extended with use of a simple group theoretical proof. Hence the conditions for a given molecular structure to be in tangential equilibrium under an arbitrary force law are deduced, and the possible orbits are enumerated. The conclusions are verified for a variety of different covalent, ionic, and van der Waals clusters by direct calculation, including stationary points of order 0 to 24. A systematic set of results is also presented for argon clusters including more than 50 stationary points that have been studied with both a Lennard-Jones and a much more accurate potential function involving three-body interactions. The influence of the form of the potential upon the order of the stationary points and upon the geometries of minima and transition states in particular is then discussed.

I. Introduction

Recent investigations of potential energy surfaces[1,2] have revealed some very interesting trends and similarities in the shapes of different kinds of clusters. Furthermore, the relationships between the different systems are not confined to shape alone; similarities in topology of potential energy surfaces also imply relationships in the dynamical processes that the systems exhibit. For example, it was found that most of the low-energy rearrangements exhibited by argon and "trapped ion" clusters can be described in terms of Lipscomb's diamond-square-diamond mechanism[3] (both systems) or Johnson's edge-bridging mechanism[4] (argon clusters only). Such results are of great importance in developing a detailed understanding[5] of the liquid/solid coexistence behavior of small argon clusters,[6] which draws a pleasing parallel with the rationalization of rearrangement rates in *closo*-boranes and carboranes. For the latter systems a topological analysis[7] must be augmented by considerations of orbital symmetry[8] to obtain a complete picture.

Since part of the purpose of this paper is to discuss the similarities and common features of the stationary structures exhibited by different clusters, it will serve us well to introduce some nomenclature. We divide clusters into three classes: (1) covalent clusters (those taken to be such species as boranes, carboranes, and transition-metal clusters); (2) van der Waals clusters (those that include clusters of inert gas atoms such as argon as well as benzene clusters and any other systems in which the binding energy is primarily due to dispersion forces); and (3) ionic clusters (those that include binary alkali halides such as $(KCL)_n$ as well as "trapped ion" clusters; the latter species consist of identical ions held in an attractive well potential[9], which for the present calculations is isotropic and harmonic in form).[1] This scheme may not always be unambiguous, but it will generally be helpful in distinguishing different types of systems in the present work.

In 1957 Leech deduced the conditions for a set of particles confined to the surface of a sphere to be in equilibrium under any pairwise law of force;[10] his geometrical proof enabled all such "balanced" structures to be identified. The necessary and sufficient condition for a structure to be balanced in this sense is that every particle must lie on a rotational axis of the appropriate point group.[10] Balanced structures fall into two classes: (1) all particles equally spaced on a great circle with or without two identical particles at the poles; (2) the particles define the vertices, centers of faces, or mid-points of edges of a regular polyhedron, or any of the three sets taken together. In this report the concept of a balanced structure is extended to systems with arbitrary force laws (which need not be pairwise additive) and to the tangential equilibrium (i.e. the shape) of molecules where the atoms describe more than one orbit of the point group. An orbit of a point group is a complete set of equivalent points that is mapped onto itself (aside from permutations) under all the point group operations. The conclusions are investigated by a series of calculations on a wide variety of different clusters, including a comprehensive survey of stationary points for argon clusters containing 4 to 55 atoms with use of two different potential functions. These results are of interest in dynamical studies of argon clusters where the simpler Lennard-Jones potential is usually employed. The trends that emerge for the two potential functions are discussed in terms of the two-body and three-body contributions; the use of the Lennard-Jones potential should be generally justifiable for dynamical studies as it does not misrepresent the important features of the potential energy surface in any of the cases studied. Finally, the

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