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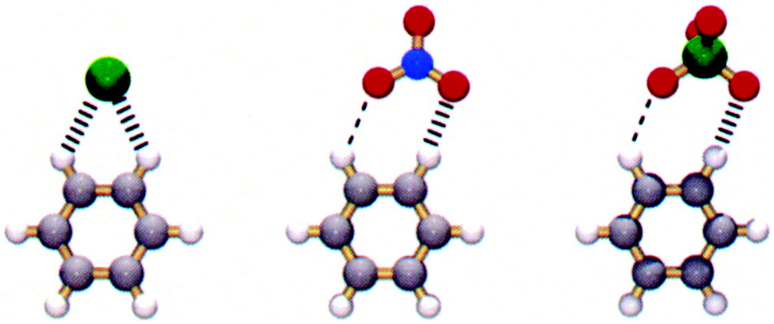

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# Are C−H Groups Significant Hydrogen Bonding Sites in Anion Receptors? Benzene Complexes with $Cl^-$, $NO_3^-$, and $ClO_4^-$

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Charge-neutral anion receptors can be constructed by decorating organic scaffolds with hydrogen bond donor groups, X−H, where X is typically an oxygen or nitrogen atom. As the study of this class of receptors intensifies,[1] there is increasing evidence that C−H groups within the receptors also interact with the anion. This evidence comes in the form of direct observation of close contacts in both crystallographic[2] and theoretical structures,[3] as well as chemical shifts in NMR spectra.[2a,b,4] It is generally assumed that although these C−H contacts serve to provide increased stability, their contribution to the overall bonding is much weaker than that provided by X−H contacts. In what follows, we show that this is not necessarily true.

Electronic binding energies, $\Delta E$, computed for complexes formed between hydrogen bond donors and acceptors provide a useful scale to assess the relative strengths of these interactions. For monoanions, such as $Cl^-$ and $NO_3^-$, the $\Delta E$ values for single hydrogen bonds formed with X−H donors range between 10 and 30 kcal/mol.[5,6] For example, $\Delta E = -19.0$ kcal/mol for a pyrrole−$Cl^-$ complex[5c] and $\Delta E = -16.0$ for a $CH_3OH$−$NO_3^-$ complex.[6] Much lower $\Delta E$ values of −2.7 and −3.1 kcal/mol have been reported for $CH_4$−$Cl^-$ and $CH_4$−$NO_3^-$, respectively.[6,7]

Although this comparison of $\Delta E$ values supports the notion that C−H is a weak donor, providing ≤20% of X−H's binding power, it must be noted that $CH_4$ is one of the weakest members of this class of donors. The strength of the C−H hydrogen bond depends on the acidity of the hydrogen.[6,8] In aliphatic systems, the C−H acidity is appreciably enhanced by the presence of substituents that would stabilize the conjugate anion through inductive or resonance effects. As illustrated by the $C^{\alpha}$−H proton in peptides, when both effects are present, the C−H group becomes a much stronger donor, yielding $C^{\alpha}$−H···O═C interactions that are more than half the strength of N−H···O═C hydrogen bonds.[8]

Aryl C−H groups, such as those in $C_6H_6$, are appreciably more acidic than those in alkanes. This is evident on comparison of gas-phase proton affinities: $CH_3^- + H^+ \rightarrow CH_4$, −418 kcal/mol;[9a] $C_6H_5^- + H^+ \rightarrow C_6H_6$, −401 kcal/mol.[9b] It follows that $C_6H_6$ should form stronger anion complexes than those observed for $CH_4$. This hypothesis is consistent with prior theoretical and experimental studies of $C_6H_6$−halide complexes that yield $C_6H_6$−$Cl^-$ complex $\Delta E$ values of 7.9−10.4 kcal/mol.[10] To further probe the nature of such interactions, the geometries and $\Delta E$ values for 1:1 complexes between $C_6H_6$ and differently shaped anions, $Cl^-$, $NO_3^-$, and $ClO_4^-$, were obtained via MP2/aug-cc-pVTZ calculations.[11] For comparison, $\Delta E$ values for 1:1 $H_2O$−anion complexes[5,6] were obtained at the same level of theory.

The results, Figure 1 and Table 1, confirm that $C_6H_6$ forms stable complexes with these anions through hydrogen-bonding interactions. In the global minima **1**−**3** two C−H groups contact each anion. The halide complex **1** is symmetric with bent C−H···Cl angles. The oxyanion complexes **2** and **3** are both asymmetric with one short linear C−H···O bond and one long bent C−H···O bond. In both cases the shorter, and by inference stronger, hydrogen bond also exhibits a more optimal H···O−A angle, where A = N or Cl.[12] Complexes **4**−**6** are less stable geometries in which $C_6H_6$ interacts with the anion via a single C−H donor. The $Cl^-$ complex **4** is a local minimum. The oxyanion complexes **5** and **6**, which are not stable points on the potential surface, were obtained by imposing $C_{2v}$ symmetry during the optimizations.

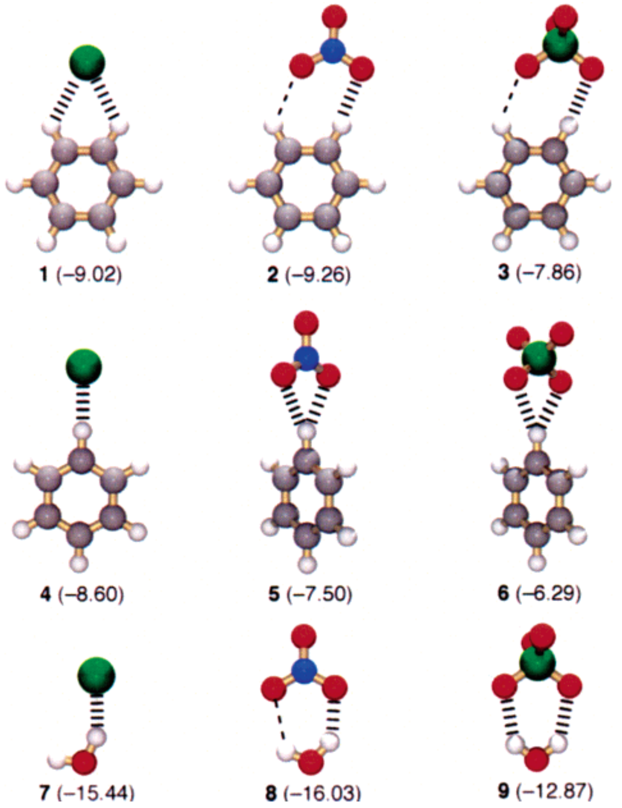

***Figure 1.*** Structures and $\Delta E$ values (kcal/mol) obtained after geometry optimization at the MP2/aug-cc-pVTZ level of theory. When the two hydrogen bonds are not equivalent, **2**, **3**, and **8**, the weaker interaction is indicated by the thinner dashed line.

***Table 1.*** Geometric Parameters for **1**−**9**

| structure | H···X, Å | D···X, Å | D–H···X, deg | H···O–A, deg |
|---|---|---|---|---|
| **1** | 2.69 | 3.45 | 126.8 | |
| **2** | 2.20, 2.40 | 3.28, 3.18 | 171.4, 127.5 | 103.0, 142.0 |
| **3** | 2.27, 2.38 | 3.35, 3.17 | 173.8, 128.5 | 105.2, 146.0 |
| **4** | 2.35 | 3.45 | 180.0 | |
| **5** | 2.33 | 3.33 | 152.3 | 92.4 |
| **6** | 2.37 | 3.36 | 151.8 | 96.2 |
| **7** | 2.12 | 3.09 | 168.8 | |
| **8** | 1.86, 2.32 | 2.80, 2.97 | 161.2, 124.0 | 108.4, 109.7 |
| **9** | 2.11 | 2.94 | 143.6 | 112.8 |

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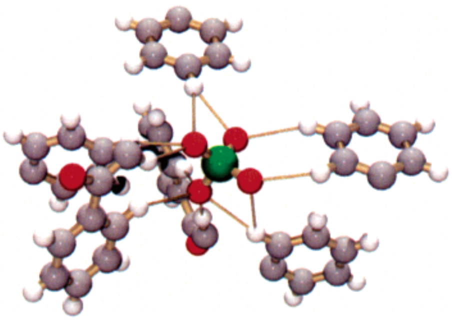

***Figure 2.*** Example of hydrogen bonding in a crystal where the only contacts with the $ClO_4^-$ anion involve C−H donor groups. In this case, there are 11 H···O contacts ≤3.0 Å.[14a]

The results verify that $C_6H_6$ is a significantly stronger C−H donor than $CH_4$. The latter donor forms complexes with a single C−H group, and direct comparison of C−H···anion bond strength is possible only for **4**. In this case, a simple aryl C−H donor gives a $Cl^-$ complex, −8.6 kcal/mol, that is over 3 times more stable than a simple alkyl C−H donor, −2.7 kcal/mol.[7a] Comparison of $\Delta E$ values for **2** and **5**, −9.26 and −7.50 kcal/mol, with the $CH_4$−$NO_3^-$ value, −3.1 kcal/mol,[6] also suggests a factor of 2 to 3 increase in strength for the more acidic C−H···O contact. Finally, comparison of $\Delta E$ values for **1**−**3** with those obtained for **7**−**9** show that C−H hydrogen-bonding interactions with $C_6H_6$ produce 1:1 complexes that are 58−61% as stable as the corresponding $H_2O$ complexes.

When compared with normal X−H donors, the relative strength of these interactions suggests that aryl C−H···anion hydrogen bonds must play an important role in supramolecular chemistry. A search of the Cambridge Structural Database[13] for aryl C−H···anion contacts between charge-neutral benzene rings bearing only hydrogen or carbon substituents and the anions examined herein corroborates that such interactions are common. With the constraints of H···anion distances ≤3.0 Å and C−H···anion angles ≥150°, the search located 220 $Cl^-$ examples, 62 $NO_3^-$ examples, and 256 $ClO_4^-$ examples. In several instances, such as that shown in Figure 2, C−H donor groups provide the only hydrogen bond-to-anion contacts.[14]

In summary, theoretical calculations,[6,7a,10c] examination of crystallographic data, and experimental binding energies,[7b,10a,b] suggest that even in the absence of electron-withdrawing substituents, simple arenes form hydrogen bonds with anions that can exceed 50% of the strength of those formed by O−H and N−H groups. Thus, when present in a receptor, even moderately acidic C−H groups could considerably enhance anion binding affinity and they should be considered as additional binding sites within the host cavity.

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**Supporting Information Available:** Complete ref 11a, Cartesian coordinates and absolute energies for optimized structures **1**−**9** at the MP2/aug-cc-pVTZ level of theory (in text format). This material is available free of charge via the Internet at http://pubs.acs.org.

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