Communication

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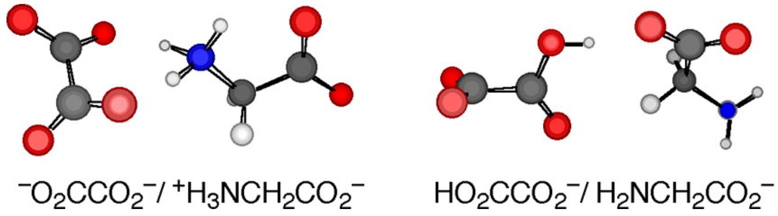

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Zwitterion−Dianion Complexes and Anion−Anion Clusters with Negative Dissociation Energies

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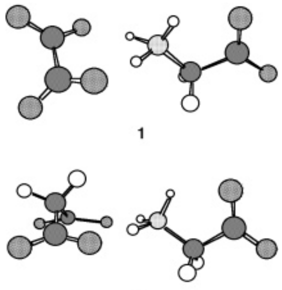
Zwitterions are important species in a wide variety of areas, none more obvious than biological processes.[1−6] To gain insights and probe their stability, computations were carried out on zwitterion−dianion complexes. Remarkably, the dianions of oxalic and malonic acids ($^{-}O_2CCO_2^{-}$ and $^{-}O_2CCH_2CO_2^{-}$, respectively) were found to form clusters with glycine in its zwitterionic form (**1**−**2**, Chart 1). These structures are minima on the potential energy surface at the HF, MP2, and B3LYP levels of theory using the aug-cc-pvdz basis set.[7−10] These findings are surprising for the following reasons: (1) Neither the dianions nor zwitterionic glycine exists independently in the gas phase. More specifically, $^{+}H_3NCH_2CO_2^{-}$ isomerizes without a barrier to $H_2NCH_2CO_2H$,[11] and both oxalate and malonate dianions spontaneously lose an electron since they have negative electron binding energies.[12−14] The electron binding energy for $CH_2(CO_2^{-})_2{\cdot}^{+}H_3NCH_2CO_2^{-}$, however, is predicted to be positive by 1.25 eV (VDE) and 0.77 eV (ADE). (2) Oxalate and malonate dianions are very strong bases because of the large repulsive Coulombic interactions and have predicted proton affinities of 444.4 and 444.5 kcal mol^{-1}, respectively; these values are larger than for methyl anion (416.9 ± 0.7 kcal mol^{-1}), the strongest known base in the gas phase.[15] Zwitterionic glycine is quite acidic ($\Delta H^{\circ}_{\text{acid}} = \sim 321$ kcal mol^{-1});[16] consequently, proton transfer followed by dissociation of the resulting anion−anion pair is predicted to be exothermic by 44.1 and 46.0 kcal mol^{-1}, respectively (eq 1). Separation of the cluster to the dianion and neutral glycine on the other hand is very endothermic.

$$
\begin{aligned}
&^{-}O_2C(CH_2)_nCO_2^{-}\cdot{}^{+}H_3NCH_2CO_2^{-}\\
&\qquad\rightarrow {}^{-}O_2C(CH_2)_nCO_2H + H_2NCH_2CO_2^{-} \qquad (1a)\\
&n = 0 \text{ or } 1 \qquad \Delta H^{\circ} = -44.1 \text{ kcal mol}^{-1}\ (n = 0)\\
&\qquad\qquad\qquad\qquad = -46.0 \text{ kcal mol}^{-1}\ (n = 1)\\
&\qquad\rightarrow {}^{-}O_2C(CH_2)_nCO_2^{-} + H_2NCH_2CO_2H \qquad (1b)\\
&\qquad\qquad\qquad \Delta H^{\circ} = 59.8 \text{ kcal mol}^{-1}\ (n = 0)\\
&\qquad\qquad\qquad\qquad = 58.0 \text{ kcal mol}^{-1}\ (n = 1)
\end{aligned}
$$

A Coulombic barrier retards the former process (eq 1a), but once the proton is transferred, one would expect the resulting anions to spontaneously separate from each other. Therefore, it was surprising that these anion−anion clusters can be located as stationary points and are minima on the potential surfaces at the HF, MP2, and B3LYP levels (**3**−**4**, Chart 2).

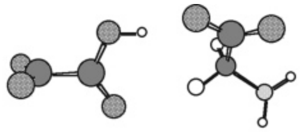
Chart 1. B3LYP Computed Structures of Oxalate (top) and Malonate (bottom) Dianions with Zwitterionic Glycine



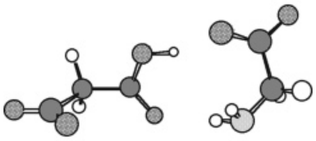
1

2

Chart 2. B3LYP Computed Structures of Monodeprotonated Oxalic (top) and Malonic (bottom) Acids with the Conjugate Base of Glycine



3 (ΔE(**3** − **1**) = 1.1 kcal mol^{-1})



4 (ΔE(**4** − **1**) = 4.0 kcal mol^{-1})

To probe the generality of these findings, monodeprotonated dicarboxylic acid-chloride clusters (X^{-}/Y^{-}) were explored for the following diacids: oxalic, malonic, phthalic (1,2-$C_6H_4(CO_2H)_2$), terphthalic (1,4-$C_6H_4(CO_2H)_2$), 2,6-naphthalenedicarboxylic acid (2,6-$C_{10}H_6(CO_2H)_2$ (**5**)), and 2,6-anthracenedicarboxylic acid (2,6-$C_{14}H_8(CO_2H)_2$, (**6**)) (Chart 3).[17] In each case except for oxalic acid, which dissociated, an anion−anion complex was located and found to be less stable than its separated components (Table 1). While all of these complexes have negative dissociation energies, they appear to be bound with respect to electron loss in that the smallest and least favorable cluster (malonate/Cl^{-}) has computed vertical and adiabatic dissociation energies of +1.16 and +0.88 eV, respectively. This differentiates these ions from anions with negative electron binding energies, the first example of which was recently reported in a landmark study by Wang and Wang.[18]

The barrier for the separation of these dianion complexes to a pair of negative ions is a critical factor in determining how robust these species will be and how readily they might be prepared. Therefore, dissociation barriers for some of these clusters were computed and found to range from virtually nothing to 10 kcal mol^{-1}. All but possibly the smallest value (0.2 kcal mol^{-1}) should be sufficient for these species to be produced using conventional techniques, given that anions with electron binding energies of ≥0.5 kcal mol^{-1} are known and can readily be formed.[15] As for the presence of a barrier and the reason these ions stay together, it is due to the different distance dependencies of hydrogen bonds (short range) and charge−charge (long range) interactions. Consequently,

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Chart 3. Selected Examples of Anion−Anion Clusters

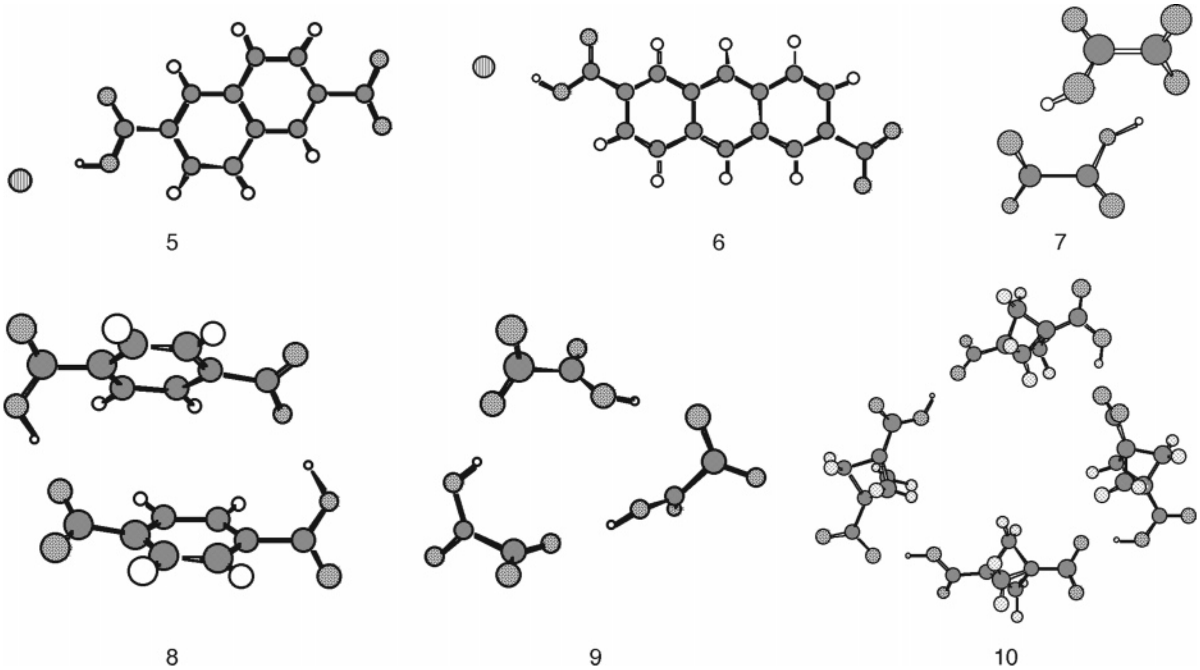

Table 1. Anion−Anion Dissociation Energies and Barriers[a]

cluster (X^-/Y^-)	$\Delta H^\circ_{\text{dissociation}}$	$\Delta H^\ddagger_{\text{dissociation}}$
$Cl^-/CH_2(CO_2H)CO_2^-$	−55.5	0.2
$Cl^-/1,2\text{-}C_6H_4(CO_2H)\ CO_2^-$	−55.4	
$Cl^-[Br^-]/1,4\text{-}C_6H_4(CO_2H)\ CO_2^-$	−22.4[−24.8]	4.9
$Cl^-/2,6\text{-}C_{10}H_6(CO_2H)\ CO_2^-$ (**5**)	−14.9	7.4
$Cl^-/2,6\text{-}C_{14}H_8(CO_2H)\ CO_2^-$ (**6**)	−9.7	9.5
$(HO_2CCO_2^-)_2$ (**7**)	−54.3	
$(1,4\text{-}C_6H_4(CO_2H)\ CO_2^-)_2$ (**8**)	−18.9	8.1
$(HO_2CCO_2^-)_3$ (**9**)	−140.9	
$(C_5H_6(CO_2H)CO_2^-)_4$ (**10**)	−128.7	

[a] All values in kcal mol^{-1}.

even though the Coulombic repulsion between the two anions is larger than the attraction resulting from the hydrogen bond, the energy of the system rises as X^-/Y^- separate before the energetic benefit is realized (i.e. the hydrogen bond is quickly lost over a small distance, but the reduction in the electrostatic repulsion is less).[19]

Dimers, trimers, tetramers and more can easily be envisioned with myriads of possible structures, three-dimensional networks, and magic numbers.[20] In this regard, dimers of monodeprotonated oxalic and terphthalic acid (**7** and **8**, respectively), an oxalate trimer (**9**), and a tetramer derived from 1,3-bicyclo[1.1.1]pentanedicarboxylic acid (**10**) were briefly explored (Chart 3). Structures were easily located despite the fact that dissociation of these di-, tri-, and tetra-anions is exothermic by 19−141 kcal mol^{-1}.

Given the charged nature of amino acids and proteins, these anion−anion interactions could provide a heretofore unrecognized control element in biological processes. This work also provides a new and intriguing opportunity for exploring electrostatic effects and novel clusters. Experimental efforts aimed at producing and characterizing these ions are underway.

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Supporting Information Available: Computed *xyz* coordinates and energies and complete ref 7a. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) This is based on a computed acidity for glycine ($\Delta H^\circ_{\text{acid}} = 340.5$ kcal mol^{-1}) and a CCSD(T)/6-31+G(d,p)//HF/6-31+G(d) zwitterion − neutral energy difference of 19.5 kcal mol^{-1}.
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