Bond Theory

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Anti-Electrostatic Hydrogen Bonds

Frank Weinhold and Roger A. Klein*

Abstract: *Ab initio and hybrid density functional techniques were employed to characterize a surprising new class of H-bonded complexes between ions of like charge. Representative H-bonded complexes of both anion–anion and cation–cation type exhibit appreciable kinetic stability and the characteristic theoretical, structural, and spectroscopic signatures of hydrogen bonding, despite the powerful opposition of Coulomb electrostatic forces. All such "anti-electrostatic" H-bond (AEHB) species confirm the dominance of resonance-type covalency ("charge transfer") interactions over the inessential (secondary or opposing) "ionic" or "dipole–dipole" forces that are often presumed to be essential for numerical modeling or conceptual explanation of the H-bonding phenomenon.*

Contentious disputes over the electronic origin of hydrogen bonding can be traced back to earliest recognition of the H-bonding phenomenon in the 1920s.[1] However, current introductory textbooks,[2] the online Wikipedia compendium,[3] and the (still posted) online "Gold Book" definition[4] of the International Union of Pure and Applied Chemistry (IUPAC) are all essentially unanimous in attributing H-bonding to "dipole–dipole forces" or other manifestations of "essentially electrostatic" character, "not to be confused" with covalent bonding, and so forth. Contemporary molecular dynamics methods for "simulating" H-bonding phenomena are similarly uniform in their dependence on empirical force fields of point charge, distributed multipole, and related "electrostatic potential" forms.[5] Electrostatic conceptions of H-bonding therefore remain the persistent paradigm for many educators, numerical modelers, and other researchers in the chemical, biochemical, and materials sciences.

Despite such apparent consensus, a broad variety of experimental and theoretical evidence challenges plausible rationalization in classical electrostatic terms and supports the alternative "charge transfer", "partial covalency", or "fractional chemical bonding" conception of H-bonding.[6] Such evidence recently prompted the adoption of a significantly revised IUPAC definition of H-bonding[7] that explicitly acknowledges the important role of covalency factors, based on operational criteria of mutually consistent correlations with established experimental signatures. More direct application of such regression-based criteria,[8,9] has further established the primacy of quantum mechanical covalency over classical-type electrostatic factors in characterizing the H-bonding phenomenon. Herein, we present still stronger evidence for the essential irrelevance of electrostatic contributions to H-bonding by documenting a previously unknown class of H-bond complexes between closed-shell ions of like charge, where dominant "electrostatic factors" must be strongly antagonistic to H-bond formation.

In the simplest classical perspective, attempted formation of a hydrogen bonded $[B\cdots H{-}A]^{2\pm}$ complex between closed-shell ions of like charge would confront an insurmountable Coulombic barrier to any stable form of association. Indeed, for typical $R_{A\cdots B}$ separations of main-group H-bonded complexes (i.e., $R_{O\cdots O} \approx 2.9$ Å in the water dimer), the Coulombic e^2/R potential barrier might be expected to range up to 100 kcal mol^{-1} or more, well beyond the strength of even the strongest known H-bonds.[10] However, deeper quantum mechanical considerations suggest that the long-range opposition of classical-type electrostatic forces may still be overcome by the exponential onset of exchange-type covalency effects (intermolecular "resonance" or "charge transfer" forces). Herein, we characterize a variety of such H-bonded anion–anion and cation–cation complexes that explicitly demonstrate how the short-range donor–acceptor covalency forces overcome the powerful long-range electrostatic opposition to be expected between ions of like charge. Characteristic covalency features of H-bonding can be readily recognized and quantified in the framework of natural bond orbital (NBO) analysis[11] as the distinctive $n_B \rightarrow \sigma^*_{AH}$ donor–acceptor interactions (or associated $b_{B\cdots H}$ fractional bond orders) that appear common to B···H–A hydrogen bonding in all known species.[12]

Detection of such experimentally unknown "anti-electrostatic" H-bond (AEHB) complexes may be complicated by the long-range Coulomb barrier, which practically forces thermodynamic instability with respect to dissociated ions. Nevertheless, kinetic trapping in a sufficiently deep H-bonded well should allow such species to be experimentally detected and characterized, with help from predicted theoretical properties to be described below. For this purpose, we primarily employed B3LYP/aug-cc-pVTZ calculations (hybrid density functional theory in augmented correlation-consistent triple-zeta basis level) performed with the Gaussian 09 program[13] and analyzed with the NBO 6.0 program.[14] However, the salient properties of AEHB complexes seem to be robustly calculated with both higher and lower levels of ab initio and density functional theory, in accordance with experience on other H-bonded species.

As a simple prototype of possible H-bonding between familiar inorganic ions, we first considered the interaction of fluoride (F^-) and bicarbonate (HCO_3^-) anions. As shown in Figure 1, the calculated B3LYP/aug-cc-pVTZ potential curve

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[*] Prof. F. Weinhold
Theoretical Chemistry Institute and Department of Chemistry
University of Wisconsin
Madison WI 53706 (USA)
E-mail: weinhold@chem.wisc.edu

Dr. R. A. Klein
30 Kimberley Road, Chesterton, Cambridge CB4 1HH (UK)

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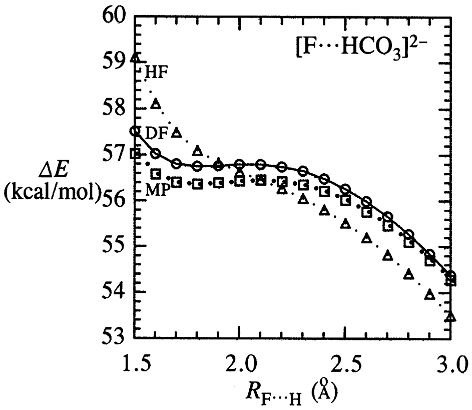

Figure 1. Relaxed-scan potential energy curves for $[F\cdots HCO_3]^{2-}$ H-bonding (all at aug-cc-pVTZ basis level), as calculated with ab initio MP2 (heavy dots; squares), hybrid density functional B3LYP (solid line; circles), and uncorrelated HF (light dots; triangles) methods.

for $[F\cdots HCO_3]^{2-}$ (solid line; circles) exhibits the expected Coulombic repulsion barrier at long-range $R_{F\cdots H}$ separation, but then undergoes pronounced downward curvature that leads to a shallow attractive well at $R_{F\cdots H} = 1.81$ Å. The calculated positive harmonic frequencies (71, 91, 152, … cm^{-1}) establish the local-minimum character of the equilibrium species, and the short $R_{F\cdots H}$ equilibrium distance, near-linear F···HO geometry, and pronounced ν_{OH} vibrational red-shift are recognizable signatures of H-bonding. [For comparison, the corresponding MP2/aug-cc-pVTZ level treatment (heavy dots; squares) gives similar energetics ($\Delta E^{\ddagger}_{HB} = 0.08$ kcal mol^{-1}, $\Delta G^{(0)\ddagger}_{HB} = 0.59$ kcal mol^{-1}) and geometry ($R_{F\cdots H} = 1.79$ Å), whereas uncorrelated HF/aug-cc-pVTZ level (light dots; triangles) gives only a strong inflection feature in this region.]

As shown in Figure 2, the NBO $n_F \rightarrow \sigma^*_{OH}$ donor–acceptor interaction is also of expected form,[15] with estimated second-order interaction energy $E^{(2)}_{n\text{-}\sigma^*} = 13.25$ kcal mol^{-1}. The associated charge transfer (CT) from formal F^- to $HOCO_2^-$ ($Q_{CT} = 0.038e$, similar to that in neutral species such as $H_2O\cdots HF$) is of the expected magnitude, as is the reduced Natural Resonance Theory (NRT) bond order for the covalent OH bond ($b_{OH} = 0.972$). However, the "missing" b_{OH} valency of the three-center F···H–O bonding triad is partitioned rather surprisingly into the usual hydrogen bond component ($b_{F\cdots H} = 0.011$) and an unexpectedly large "long bond"[16] component ($b_{F\cdots O} = 0.014$), presumably reflecting the altered relative electronegativities in the highly ionic A–H···B triad. Aside from this feature, the shallow minimum of Figure 1 ($\Delta E^{\ddagger}_{HB} = 0.05$ kcal mol^{-1}, $\Delta G^{(0)\ddagger}_{HB} = 0.61$ kcal mol^{-1}) appears in all significant respects to represent a rather typical hydrogen bond that can be adequately characterized with simple density functional methods as employed below.

Other popular theoretical signatures of H-bonding based on Bader's "quantum theory of atoms in molecules" (QTAIM)[17] descriptors are also exhibited by this species. The F···H interaction exhibits a typical QTAIM-type bond path and bond critical point (BCP) with associated density $\rho_{BCP} = 0.0314$ and Laplacian density $\nabla^2\rho_{BCP} = 0.0928$, in sensible proximity to the corresponding natural bond critical point (NBCP)[18] properties ($\rho_{NBCP} = 0.0361$, $\nabla^2\rho_{NBCP} = 0.0970$) as typically found for H-bonded species. Thus, the weak $[F\cdots HCO_3]^{2-}$ complex and stronger AEHB species to be described below apparently satisfy all commonly accepted theoretical criteria for authentic H-bonding, despite the paradoxically "anti-electrostatic" charge characteristics.

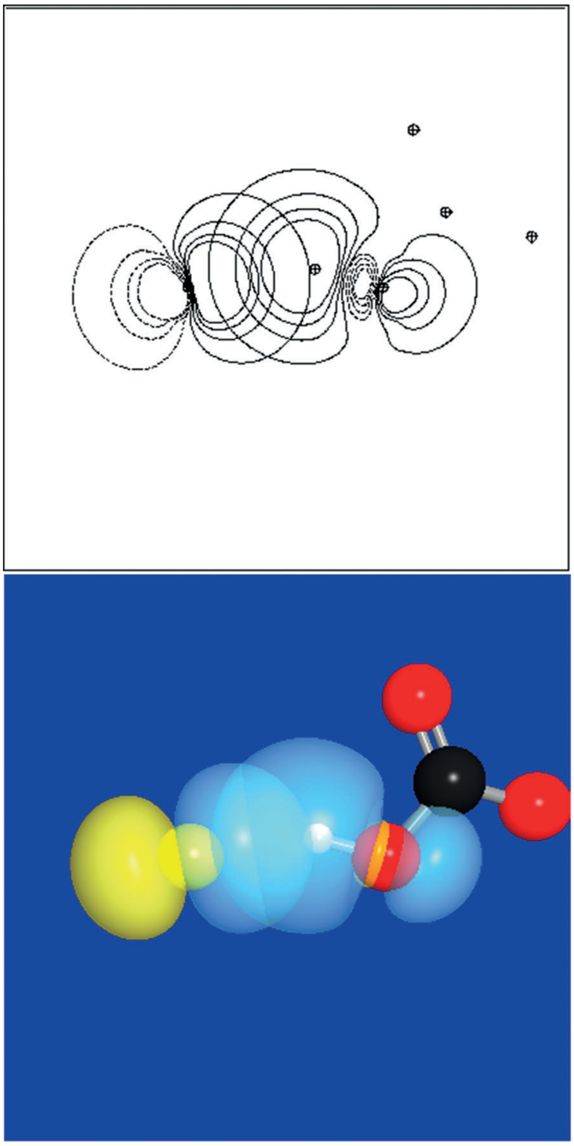

Figure 2. NBO 2d contour and 3d overlap diagrams for $n_F \rightarrow \sigma^*_{OH}$ donor–acceptor interaction in $[F\cdots HCO_3]^{2-}$ equilibrium geometry, with estimated second-order $E_{n\sigma^*}{}^{(2)} = 13.25$ kcal mol^{-1} interaction.

Although only a small well depth remains in this case, the ability of the underlying H-bonding forces to overcome the substantial repulsive penalty at equilibrium geometry ($\Delta E_{HB} = +56.75$ kcal mol^{-1}, $\Delta G^{(0)}_{HB} = +63.39$ kcal mol^{-1}) is quite impressive. Important in this respect is evidently the resonance-assisted H-bond (RAHB)[19] coupling to the carboxylate group, which cooperatively strengthens $n_F \rightarrow \sigma^*_{OH}$ interaction while efficiently redistributing charge to minimize Coulombic and steric repulsions in the challenged H-bond geometry.

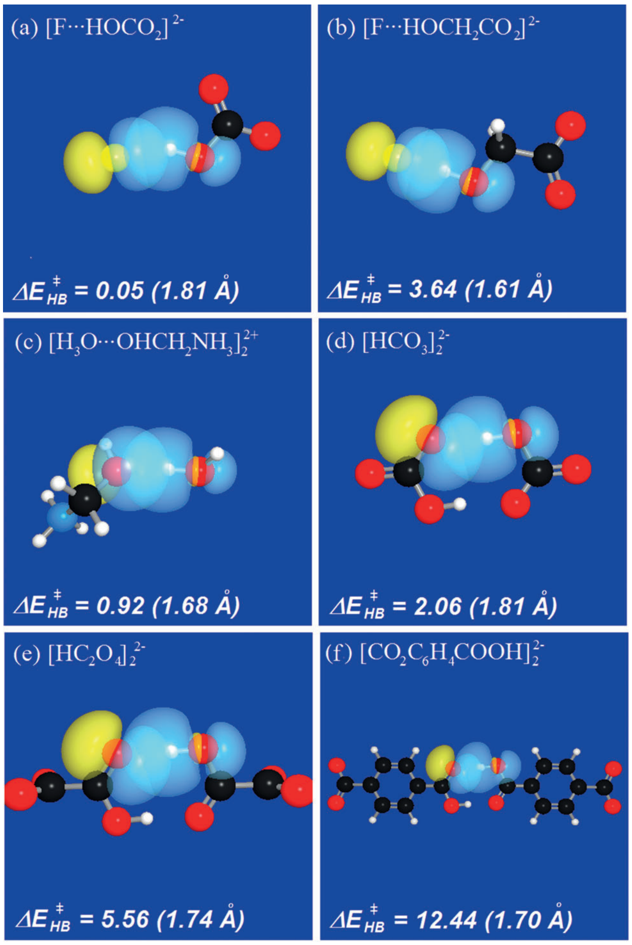

Figure 3. Optimized structures (with leading $n_B \rightarrow \sigma^*_{AH}$ NBO interaction), H-bond well depths ($\Delta E^{\ddagger}_{HB}$, kcal mol^{-1}), and equilibrium $R_{B\cdots H}$ separations (in parentheses) for each AEHB species (a)–(f) discussed in the text.

More robust variants of the $F^{-}\cdots HOCO_2^{-}$ complex are easily envisioned (Figure 3). For example, bicarbonate can be replaced by the analogous $HOCH_2CO_2^{-}$ (glycolate) anion that includes an alkyl "spacer" to better insulate the H-bonded F···H–O triad from the anionic carboxylate group, yielding the $[F\cdots HOCH_2CO_2]^{2-}$ complex with $\Delta E^{\ddagger}_{HB} = 3.64$ kcal mol^{-1}, as shown in Figure 3b. Cation–cation H-bonded complexes are also feasible, such as the hydronium complex with protonated aminomethanol ($[H_2OH\cdots OHCH_2NH_3]^{2+}$, $\Delta E^{\ddagger}_{HB} = 0.92$ kcal mol^{-1}) of Figure 3c. However, the contracted distribution of cationic charge tends to increase Coulombic opposition and reduce H-bond well-depth relative to diffuse anionic species. A more productive anion–anion motif is to pair two carboxylate groups in self-complementary C_2-symmetric interaction geometry to give antiparallel-bridging H-bonds that benefit from the powerful cooperativity of coupled donor–acceptor interactions,[20] as shown in the bicarbonate dimer complex ($[HCO_3]_2^{2-}$, $\Delta E^{\ddagger}_{HB} = 2.06$ kcal mol^{-1}) of Figure 3d or bioxalate dimer complex ($[HC_2O_4]^{2-}$, $\Delta E^{\ddagger}_{HB} = 5.56$ kcal mol^{-1}) of Figure 3e. Such cooperativity and RAHB coupling effects have no counterpart in the classical electrostatic framework of pairwise-additive Coulombic interactions, but are ubiquitous features of intra- and intermolecular resonance phenomena including H-bonding.[15]

Still stronger anion–anion H-bonding is exhibited in the dimer of *p*-biphthalate (mono acid of terephthalic acid, *p*-$HOOCC_6H_4COO^{-}$), where the phenyl spacer maintains RAHB enhancement and disperses excess charge to the conjugatively coupled *p*-carboxylate groups (Figure 3f). In this case, the smaller 6-31+G* Pople-style basis was employed[21] to perform relaxed forward and backward scans with respect to one of the two H-bonded R_{OO} distances (equivalent in the lowest-energy C_{2h} equilibrium geometry), leading to prospective stationary points HB1, HB2 (minima) and TS1, TS2 (first-order transition states) that were subsequently fully optimized to give the energetic and structural features shown in Figures 3f and 4.

As shown in Figure 4, the HB2 species is calculated to be kinetically trapped by 12.44 kcal mol^{-1} with respect to the final TS1 dissociation to anions, significantly surpassing the binding energy of the water dimer and many other well-

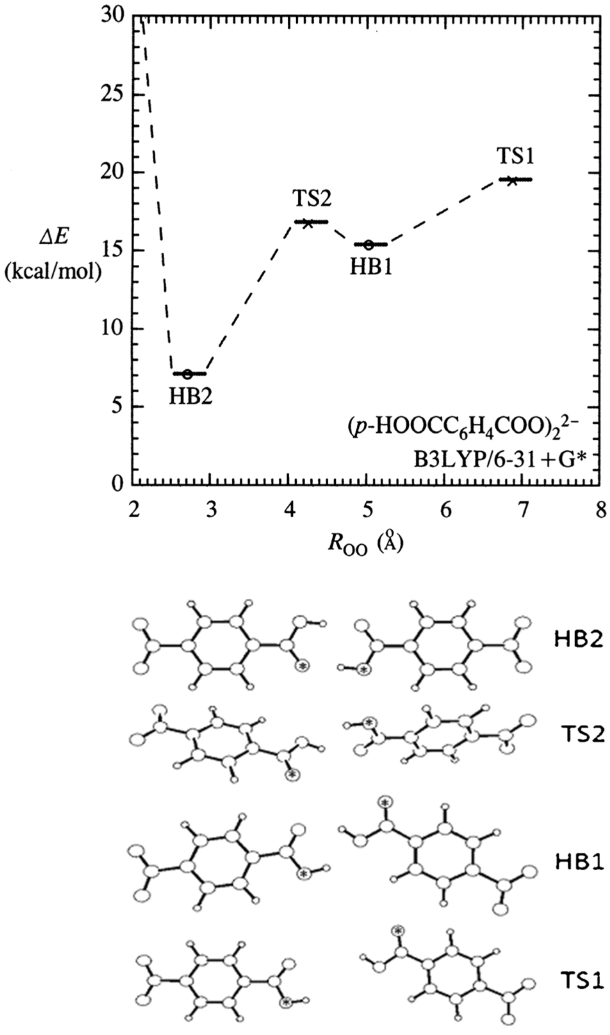

Figure 4. Stationary points of H-bonded biphthalate dimer potential energy surface (B3LYP/6-31+G* level, relative to anions at infinite separation), corresponding to the equilibrium (HB1, HB2) and transition state (TS1, TS2) structures at the right (with asterisks marking atoms of the R_{OO} separation coordinate).

known neutral or singly ionic H-bond complexes. Each H-bond of HB2 exhibits typical strong $n_{O}\rightarrow\sigma^{*}_{OH}$ donor–acceptor interaction, corresponding to estimated total charge transfer of 0.067e and second-order stabilization $E^{(2)}_{n\sigma^{*}}=33.13\,\mathrm{kcal\,mol^{-1}}$, and local NRT analysis of each O–H···O triad gives bond orders ($b_{OH}=0.851$, $b_{O\cdots H}=0.128$,, $b_{O\cdots O}=0.021$) that similarly reflect strong resonance mixing, in line with the trend of previous species.

It is noteworthy that "hydrogen-bond-like" inter-anion arrangements have been recognized[22] in the crystal structures of KHC_2O_4 and other bioxalates, but with chain-like $O_2CCOOH\cdots O_2CCOOH\cdots$ linkages rather than the cyclic dibridged topology of the bioxalate dimer studied here. Note that both patterns have the distinctive Grotthuss-ordering that is expected to confer high cooperativity.[20] Braga and coworkers discussed the paradoxical $O{-}H^{-}\cdots O^{-}$ interaction from molecular electrostatic potential (MEP) considerations and concluded that it is a "tugboat interaction" that "cannot be considered a bond because the ionic chains (or dimers) would 'fall apart' if the cations were removed", but instead is merely "conferring directionality to anion–anion electrostatic interactions".[22] We believe the present results call such conclusions into question.

The long failure to recognize the important AEHB class of H-bond complexes bears testimony to the subtle leverage exerted by a widely accepted paradigm to sway inquiry into self-fulfilling directions. Full recognition of the AEHB phenomenon should therefore prompt critical re-examination and reform of many aspects of current pedagogy[9] and numerical modeling of intermolecular forces,[5] including skeptical reassessment of many varieties of "energy decomposition analysis" methods[23] that have offered apparent theoretical support for electrostatics-based conceptions of H-bonding. Beyond arcane discussions of mathematical overlap artifacts[24] or the trail of experimental evidence[6] that eventually proved persuasive to IUPAC,[7] AEHB complexes may finally put to rest the superficial quasi-classical conceptions of H-bonding and other resonance-type phenomena that have too long held sway in the molecular and supramolecular sciences.

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[2] For samples and further discussion of current "textbook definitions" of H-bonding, see Refs. [8,9].

[3] The current Wikipedia entry for "hydrogen bond" (accessed April 16, 2014) includes firm statements such as: "The hydrogen bond is the electromagnetic attractive interaction between polar molecules… it is not a true bond but a particularly strong dipole–dipole attraction, and should not be confused with a covalent bond."

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