Published in final edited form as:

J Am Chem Soc. 2019 May 29; 141(21): 8550–8556. doi:10.1021/jacs.9b02288.

Hydrogen Bonding to a Dinitrogen Complex at Room Temperature: Impacts on N₂ Activation

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Abstract

We report an experimental and computational analysis of the effects of hydrogen bonding to a metal dinitrogen complex. A series of H-bond donors over a wide pK_a range (> 20) interact with the nitrogen unit of a Re^I-(N₂) complex at room temperature. Analysis by ¹⁵N NMR, IR spectroscopy, association equilibria, and DFT studies indicates that the H-bonding interaction polarizes and weakens the N–N bond. These results provide insight into the role of the secondary sphere residues in nitrogenase enzymes.

Graphical Abstract

INTRODUCTION

The activation and cleavage of N₂ is a fundamentally important global process to sustain life and is accomplished in the biosphere by nitrogenases.¹ N₂ fixation is an energetically demanding process requiring 16 ATP per N₂ by nitrogenases² or high temperatures and pressures (~500 °C, >100 atm) industrially.^{3–5} Despite extensive effort to mimic the mild operative redox potential, atmospheric pressure, and room temperature (RT) conditions

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b02288.

X-ray data for compounds (CIF)

X-ray data for compounds (CIF)

Synthetic details, characterization, and computational details (PDF)

The authors declare no competing financial interest.

required biologically of nitrogenases, all homogeneous synthetic systems that reduce N₂ operate under highly reducing conditions.^{6–14} One chemical principle that has been proposed to explain how nitrogenase efficiently promotes N₂ reduction has been dubbed the “push-pull” mechanism, wherein a “push” of electron density from a reduced metal center is facilitated by a concomitant “pull” from an acidic site. The “push-pull” mechanism, traditionally rationalized through bimetallic activation¹⁵ and later refined to include hydrogen bond (H-bond) activation in nitrogenases,^{2,16} postulates a cooperative activation mode to enable N₂ reduction under mild conditions (Figure 1). The recent isolation of a H-bond-stabilized N₂H₁ nitrogenase intermediate and revised proposals for secondary-sphere interactions along the reduction pathway¹⁷ provide evidence for their participation, yet key aspects regarding their role in N₂ activation are not known.

Despite the role that Brønsted acidic sites are proposed to serve in biological N₂ reduction, examination of these interactions in model systems has not been possible. When not constrained by a protein matrix, most moderately activated dinitrogen complexes ($\nu_{\text{NN}} < 2090 \text{ cm}^{-1}$) undergo protonation at the metal or dinitrogen with weak proton donors, rather than forming an isolable H-bond donor/acceptor adduct.^{18,19} Due to the inherent incompatibility of reduced metal complexes with Brønsted acidic groups (H-bond donors), previous efforts in our group used Lewis acids (LA) as H-bond donor surrogates to examine acid-mediated activation of an Fe-(N₂) complex.²⁰ Unfortunately, the direct translation of this approach to biologically relevant H-bond donors was not possible because of competitive oxidation of the Fe⁰-(N₂) to form Fe^{II}-(H) products, even with mild acids.²¹ Due to these limitations, the role of H-bonding in N₂ activation is largely unexplored.

The general incompatibility of proton donors with activated M-N₂ complexes can be highlighted with examples where secondary sphere groups (incorporated as either H-bond donors or proton relays) afford oxidized metal products.^{22–26} The only report to overcome the acid incompatibility uses low temperature (190–220 K) to arrest intermolecular proton transfer and bias association,²⁷ weakly activating W-(N₂)₂(dppe)₂ ($\nu_{\text{NN}} = -20 \text{ cm}^{-1}$). To clarify the extent to which the push-pull mechanism of N₂ activation can be generally adapted to H-bond donors, we sought to evaluate a complex compatible with a broad range of H-bond donors at RT.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Lewis Acid and Hydrogen Bond Adducts.

To target a N₂ complex compatible with H-bond donors, we initially selected Re(N₂)-Cl(PMe₂Ph)₄ (**1**),¹⁵ because it satisfies the following requirements: (1) high degree of activation of the N₂ ligand²⁸ ($\nu_{\text{NN}} = 1925 \text{ cm}^{-1}$), (2) stability to alcohol solvents, and (3) mild reduction potential^{29–32} to limit M-H formation. To assess the extent that acidic groups induce N₂ activation, we first evaluated adducts with boranes and alkali cations.³³ Addition of 1 equiv of B(C₆F₅)₃ to **1** in fluorobenzene at RT (25–30 °C) resulted in a shift of ν_{NN} from 1925 to 1866 cm⁻¹ ($\nu_{\text{NN}} = -59 \text{ cm}^{-1}$) (Figure 2B).³⁴ Addition of 1 equiv of alkali cation salts, [Li][BAr^F₄] or [Na][BAr^F₄], afforded distinct results: two ν_{NN} shifts (Li: -52 and +19 cm⁻¹; Na: -43 and +18 cm⁻¹). The positive and negative ν_{NN} shifts are consistent with two competitive Lewis basic sites: Re-Cl or Re-NN _{β} , respectively (Figure 2A).³⁵

Despite the evidence for **1** to interact with weak Lewis acids, the competitive basic site (N₂ and Cl) rendered analysis challenging because each donor/acceptor pair has opposing effects on N₂ activation. Using **1** as a starting point, we further optimized the other primary sphere ligands to address three limitations: (1) competitive H-bonding to the –Cl ligand, (2) PMe₂Ph ligand substitution with nucleophilic H-bond donors (alcohols, carboxylic acids), and (3) sterically limited donor/acceptor interactions. To address (1), we prepared a –Br variant because H-bond acceptor ability decreases down a group.³⁶ To address (2) and (3), we targeted 1,2-bis-(diethylphosphino)ethane (depe) as a donating bis-(phosphine) ligand that features a reduced steric profile (solid cone angle (Θ) for two depe = 434° vs four PMe₂Ph = 611.6°).³⁷ *trans*-Re(N₂)Br(depe)₂ (**2**) was prepared in analogy to *trans*-Re(N₂)Cl(depe)₂³⁰ and structurally characterized (see SI). A voltammetry experiment revealed that the reversible Re^I/Re^{II} redox events of **1** and **2** differ by 105 mV (*E*_{1/2}: **1** –0.555 V; **2** –0.660 V vs Fc/Fc⁺, 0.1 M [ⁿBu₄N][BAR^F₄], PhF), reflecting a small electronic perturbation at the metal center. The solution IR spectrum of **2** (ν_{NN}(PhF) = 1940 cm^{–1}; ν_{15N15N} = 1875 cm^{–1}) affords a new ν_{NN} of 1850 cm^{–1} (ν_{NN} = –90 cm^{–1}) upon addition of B(C₆F₅)₃.³⁸ Importantly, the addition of 1 equiv of [Li⁺][BAR^F₄] to **2** resulted in *only* a single shift of –52 cm^{–1}, indicating that the LA/Br interaction is diminished for hard Lewis acids (Figure 2C).

To assess a H-bond interaction to the coordinated N₂ unit, we first examined phenol donors. The addition of 1–5 equiv of phenol to **2** afforded a –29 cm^{–1} shift and a modest +4 cm^{–1} shift (Figure 2D). The intensity of the new peaks increased with additional equivalents of phenol (10, 20), consistent with a weak H-bonding interaction.

To interrogate the role of H-bond donor strength and steric profile on the activation of the dinitrogen ligand, we evaluated a series of H-bond donors (Figure 3). The H-bond donor strength was quantified as a measure of their Lewis acidity (acceptor number^{39,40}).⁴¹ Many of these H-bond donor molecules induce a shift of the ν_{NN} that tracks with the measured Lewis acidity (Figure 3). Weak H-bond donors (aniline, imidazole, *p*-methylthiophenol, and water)⁴² did not interact with the N₂ ligand at RT. In contrast, stronger H-bond donors (alcohols, benzoic acids, and the protonated N-heterocycles; p*K*_a(dmsO)⁴³ > 20) afforded ν_{NN} shifts of increasing magnitude (–25 to –69 cm^{–1}) with their H-bond donor strength (Table 1).⁴⁴ Phenols with 2,6-substitution exhibited less N₂ activation than their H-bond donor strength would predict, which is consistent with a steric limitation for adduct formation with **2**, i.e., perfluorophenol ν_{NN} = –25 cm^{–1} and no observed interaction for 2,6-dimethylphenol.⁴⁵ In addition to changes to the H-bond acceptor, the H-bond donor ν_{EH} vibration is expected to undergo a shift for H-bond formation.⁴⁶ The alcohol adducts of **2** feature a new broad ν_{OH} peak consistent with H-bond formation.⁴⁷ Using experimentally derived vibration analysis,⁴⁶ the ν_{OH} corresponds to H-bond strengths ranging from –4.3 ± 0.1 to –5.8 ± 0.1 kcal/mol. To confirm the vibrational assignment of the H-bond adducts, we examined ¹⁵N-labeled **2** upon addition of Lewis acids and H-bond donor molecules. The addition of B(C₆F₅)₃, phenol, and [imidazolium][BAR^F₄] to **2**-¹⁵N exhibited the ν_{NN} shifts of the adducts **2**-LA offset by 61–65 cm^{–1}, in good agreement with the predicted isotopic shifts for the compounds (Figure S34). Taken together the data support H-bond activation of

the $-\text{N}_2$ ligand of **2** that can exceed the activation by common alkali metal promoters (Li^+ or Na^+).^{3,48}

To assess conditions required to form H-bonding interactions to $\text{M}-(\text{N}_2)$ complexes, we evaluated association constants for representative H-bond donors. Variable solubility, vastly different binding constants observed for Lewis acids, and solvent absorption errors for the high loadings of additives precluded the use of titration methods for the entire series of adducts. Thus, transmission IR spectroscopic measurements were used to determine the binding constants of **2** to H-bond donors at a single concentration of **2** and additive in triplicate.⁴⁹ The neutral H-bond donors (phenols, $\text{C}_6\text{F}_5\text{COOH}$) have low association constants of $\sim 1\text{--}8\text{ M}^{-1}$, while the charged N-H donors bind more strongly, $>45\text{ M}^{-1}$.⁵⁰ The association constant for **2**- $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$ ($2.6 \pm 0.2\text{ M}^{-1}$; CH_2Cl_2 25 °C) is lower than for pyridine- $\text{C}_6\text{H}_5\text{OH}$ (17 M^{-1} ; CH_2Cl_2 20 °C),⁵¹ indicating a weaker H-bond acceptor strength of the $-\text{N}_2$ ligand than pyridine. The low association constants highlight the importance of intramolecular design approaches for H-bond activation with weak H-bond donors.

The large chemical shift range of ^{15}N NMR spectroscopy translates to high sensitivity that provides complementary analysis of Lewis acid and H-bonding interactions to $-\text{N}_2$.^{20,52–55} Upon addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **2**- ^{15}N , the ^{15}N chemical shift of N_β shifts upfield from -61.3 ppm to -173.3 ppm, while N_α undergoes a modest shift from -91.1 ppm to -93.8 ppm (Figure 4).⁵⁶ The upfield shift of N_β is consistent with the increased electron density at the atom: an effect of the push-pull mechanism.²⁰ The addition of 1, 5, 10, and 100 equiv of phenol to **2**- ^{15}N resulted in a gradual upfield shift of the N_β resonance to -68.8 ppm with increasing concentration of phenol (Figure 4). The δN_β for **2** vs **2**- $\text{C}_6\text{H}_5\text{OH}$ is 7.4 ppm and is consistent with interactions at the terminal nitrogen by an electropositive donor/acceptor interaction, i.e., a H-bond. We propose that H-bonding promotes charge transfer via increased π -backbonding, to localize electron density at the terminal nitrogen atom, which affords an upfield shift. The weaker ν_{NN} and binding energy of **2**- $\text{C}_6\text{H}_5\text{OH}$ than **2**- $\text{B}(\text{C}_6\text{F}_5)_3$ result in decreased push-pull charge transfer and dynamism on the NMR time scale, respectively. Decreased charge transfer and a time-averaged configuration response between unbound and bound phenol contribute to poor localization of electron density at N_β and contribute to the modest upfield shift.

Importantly the induced upfield shift of N_β corroborates the proposed H-bond to N_2 . The ^{15}N NMR analysis of H-bonding to **2** demonstrates association at $-\text{N}_\beta$ and induced N_2 polarization by acidic groups.

Electronic Structure Perturbation and Predicted H-Bond Strengths.

To determine the effect of H-bond donors on $\text{M}-\text{N}_2$ activation, we used density functional theory (DFT) analyses. Geometry optimization of **2** using the PBE0 functional⁵⁷ and a combination of 6-311++G(2d,p)⁵⁸ and def2tzvp⁵⁹ basis sets with empirical dispersion⁶⁰ resulted in an $\text{N}-\text{N}$ bond length of $1.132\text{ \AA}$, in good agreement with our crystallographic data ($\text{N}-\text{N} = 1.137(17)\text{ \AA}$). A frequency analysis of the phenol H-bond interactions to either the $-\text{Br}$ or $-\text{N}_2$ of **2** reproduces the relative magnitude of the ν_{NN} shifts ($-\text{Br}$: $\nu_{\text{NN}} = +9\text{ cm}^{-1}$; N_2 : $\nu_{\text{NN}} = -52\text{ cm}^{-1}$). The computationally modeled donors (aniline, thiophenol,

imidazole, H₂O, phenol, imidazolium, and 4-trifluoromethylpyridinium) corroborate a ν_{NN} shift dependence on H-bond donor strength.⁶¹ Noncovalent interaction (NCI) analysis offers a computational methodology to visualize and study weak molecular interactions from calculated electron density.⁶² The NCI analysis of the H-bond adducts of **2** feature a stabilizing interaction between N_β and the H-bond donor (Figure 5A). Together the computational analysis supports the experimental evidence for H-bond interactions between N_β and H-bond donors.

The quantitative analysis of the H-bond interaction provides insight into the energetics and bond metrics associated with the adducts. Biologically relevant H-bond donors (water, amines, thiols) also align with experimentally validated donors. The frequency analysis, *vide supra*, implies that the N–N bond is activated through the H-bond interaction (Table 2). This activation was reflected in an elongation of the N–N bond across the series of H-bond donors ranging from 1.132 Å (**2**) to the strongest H-bond donor, 1.151 Å (**2-CF₃C₅H₄NH⁺**; N–N = 0.019 Å). The calculated free energy and enthalpy of formation of the H-bond adduct track with donor strength (G = 3.5 to –1.2 kcal/mol; H = –1.4 to –10.6 kcal/mol). Due to multiple contacts between the phenyl-containing donors and **2**, the H for H-bond formation was determined using a vibrational analysis of the $\nu_{\text{E-H}}$ bond.^{27,63} The protonation of imidazole to imidazolium provides a 2.3-fold enhancement in the N–N elongation (N–N = 0.0066 vs 0.0150 Å) and a 2-fold stronger H-bond (H = –4.7 vs –9.3 kcal/mol). The calculated binding enthalpy between the –Br and the N_2 ligand of **2-C₆H₅OH** favors N_2 H-bonding by –0.45 kcal/mol. The small difference in energy accounts for the simultaneous formation of positive and negative ν_{NN} shifts in the solution IR measurements.⁶⁴ For the H-bond adducts of **2**, the degree of activation and H-bond strength are dependent on the H-bond donor.

After validating the computational approach, we evaluated the H-bond-induced changes to the electronic structure of the Re-(N₂) unit. We assessed H-bond-induced changes to the N_α – N_β and Re– N_α bond order via a Wiberg bond index analysis.⁶⁵ The N_α – N_β bond index decreases (2.44 to 2.22) while the Re– N_α bond index increases (1.12 to 1.30) with increasing H-bond donor strength (Figure 5B), consistent with H-bond-enhanced π -backbonding. The augmented π -back-donation is enabled by H-bond stabilization of the HOMO π -back-bonding orbital combination ($\text{d}_{\text{xz}} + \text{N}_2 (\pi^*)$) by –0.84 eV for the representative H-bond donor, **2-CF₃C₅H₄NH⁺**.

Examination of the electronic structure of **2** provided insight into the orientation of the acidic interactions to the Re-(N₂) unit. Optimization of the H-bond interaction consistently resulted in H-bond formation oriented toward the HOMO N₂ (π^*) π -backbonding orbital at N_β ($\angle \text{NNH}$ = 125–132°). A constrained end-on linear binding optimization for the phenol H-bond was found to be higher in energy (G = 3.0 kcal/mol), provide a decreased degree of activation (ν_{NN} = –25 cm^{–1}), and have a lower binding enthalpy (H = –5.0 kcal/mol) in comparison to the bent geometry. These effects are consistent with decreased facilitated backbonding from the linear acidic interaction relative to the bent configuration and decreased H-bond accepting strength of the N₂ σ orbital. The bent binding geometry imparts greater HOMO stabilization and identifies the frontier orbitals as the likely site of reactivity, which is consistent with borane,²⁰ silyl cation,⁶⁶ and alkyl⁶⁷ functionalization of other M–N₂

complexes. The electronic structure of the complex informs the geometric preference of acidic interactions to the N₂ ligands.

To evaluate the influence of increased N₂ (π^*) population on N₂ polarization, we analyzed the natural bond orbital (NBO) charge of N _{α} and N _{β} as a function of H-bond donor strength (Figure 5C). H-bonding to the N₂ unit increased the negative charge on the N _{β} atom from -0.234 to a maximum at -0.384 ($e^- = -0.150$) for 4-trifluoromethylpyridinium with a modest increase in the positive charge of N _{α} ($e^- < 0.023$). The charge localization on N _{β} tracks with the difference in charge at Re for each acid (**2**-CF₃C₅H₄NH⁺: $e^- = 0.126$), supporting our analysis as a push-pull charge transfer mechanism.⁶⁸ The induced negative charge on -N _{β} with the donor/acceptor interaction implicates increased basicity²⁰ and corroborates the observed ¹⁵N NMR shielding of -N _{β} . The electronic structure description reflects the “push-pull” mechanism of activation induced by H-bond donors. By this model, acidic H-bond donors serve to pull electron density from the metal d orbitals into a π^* antibonding N₂ orbital to build up negative charge at -N _{β} . Overall, the computational analysis of H-bonding to **2** demonstrates that H-bonding activates the N–N bond by promoting π -backbonding.

■ CONCLUSION

Through a series of experimental and computational studies, we have demonstrated that **2** forms donor/acceptor adducts with a wide variety of acid additives, including H-bond donors at room temperature. The acid tolerance permitted an in-depth study to examine the effects of the H-bonding interaction with the N₂ unit. We used a series of H-bond donors to quantify (1) the extent of -N₂ activation, (2) enthalpy of H-bond formation, (3) association constants, and (4) imparted N₂ polarization. Our study demonstrates that H-bonding to a N₂ ligand has important consequences of increasing N–N bond activation by enhancing π -backbonding and also increasing polarization into the N₂ unit. These effects may facilitate N₂ activation in nitrogenases, and we are working to adapt these principles to synthetic N₂ reduction schemes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

This work was supported by the NIH (Grant No. 1R01GM111486–01A1) and the NSF (Grant No. CHE0840456) for X-ray instrumentation. N.K.S. is a Camille Dreyfus Teacher-Scholar and an Alfred P. Sloan Research Fellow. We thank Dr. Jeff Kampf for crystallographic assistance and Dr. John J. Kiernicki for fruitful discussions.

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Secondary Sphere Interactions in Nitrogenase FeMo cofactor

Evaluating Hydrogen Bonding to N₂ with Synthetic Models

Figure 1.

Nitrogenase FeMo-co active site with proposed acidic sites (top left); orbital diagram of push-pull hypothesis (top right); M-(N₂) reactivity toward H-bond donors (bottom).

Figure 2.

(A) Competitive interactions for complexes **1** and **2**. Solution IR (PhF) of (B) **1** and (C) **2** with Lewis acids [M][BAR^F₄] or (D) phenol.

Figure 3.

Dependence of ν_{NN} in **2** on Lewis acids and H-bond donors as quantified by acceptor number (AN) in PhF; H-bond donors ■ (left to right): 4-CH₃C₆H₅SH, C₆H₅NH₂, H₂O, imidazole, CF₃CH₂OH, 1,2-C₆H₄(OH)₂, 2,6-(CH₃)₂-C₆H₃OH, C₆H₅OH, 4-BrC₆H₄OH, 4-CF₃C₆H₄OH, C₆F₅COOH, C₆F₅OH, 4-NO₂C₆H₄OH, [imidazolium][BAr^F₄], 1,2-C₆H₄(OH)₂, [C₆H₅NH⁺][BAr^F₄], [4-CF₃C₆H₅NH⁺][BAr^F₄]; BR₃ ● (left to right): B(2,6-C₆H₃F₂)₃, B(2,4,6-C₆H₂F₃)₃, B(C₆F₅)₃, BF₃; M⁺ ▲ (left to right): [Na][BAr^F₄], [Li][BAr^F₄]

Figure 4.
 ^{15}N NMR of **2** (top), **2-B(C₆F₅)₃** (middle), and **2-C₆H₅OH** 100 equiv (bottom) in C_6D_6 .

Figure 5.

(A) Noncovalent interaction between the N_β of **2** and imidazolium (NCI analysis; supporting ligands omitted for clarity). (B) Re–N and N–N Wiberg bond indices and (C) NBO N_α (red) and N_β (blue) charges of adducts of **2**.

Table 1.

Summary of Lewis Acidities of H-Bond Donors, Activation of 2, Association Constants, and H-Bond Strength

	H-Bond Donor	AN	$\Delta\nu_{\text{NN}}$ (cm^{-1})	$\Delta\nu_{\text{NN}}$ (cm^{-1})	K_{eq} (M^{-1})	$\Delta\text{H}(\Delta\nu_{\text{EH}})$ (kcal mol^{-1})
R₂N-H	4-CH ₃ C ₆ H ₄ SH	14.4	0	0	< 0.2	nd
	C ₆ H ₅ NH ₂	15.2	0	0	nd	-1.4 ^a
	Imidazole	22.4	0	0	< 0.2	-4.7 ^a
RO-H	H ₂ O	21.2	0	0	nd	-4.2 ^a
	CF ₃ CH ₂ OH	23.4	-25	3	nd	-4.3 ± 0.1
	4- <i>t</i> -C ₄ H ₉ C ₆ H ₄ OH	28.5	-25	1	nd	-4.3 ± 0.1
	C ₆ H ₅ OH	29.9	-29	4	nd	-4.9 ± 0.1; -6.2 ^a
	4-BrC ₆ H ₄ OH	30.2	-32	4	nd	-4.9 ± 0.1
4-CF ₃ C ₆ H ₄ OH	30.4	-34	4	2.6 ± 0.3	-5.4 ± 0.1
	4-NO ₂ C ₆ H ₄ OH	34.8	-36	4	nd	-5.8 ± 0.1
	2,6(CH ₃) ₂ C ₆ H ₃ OH	24.8	0	0	< 0.2	nd
	1,2 C ₆ H ₄ (OH) ₂	37.7	-31	2	nd	-8.2 ^a
C ₆ F ₅ OH	33	-25	2	nd	nd
	R-COOH	32	-38	4	1.2 ± 0.3	nd
Imidazolium	37.5	-53	11	110 ± 10	-9.3 ^a
C ₅ H ₅ NH ⁺	42.2	-57	18	49 ± 10	nd
	4-CF ₃ C ₅ H ₄ NH ⁺	50.2	-69 ^b	15 ^b	nd	-10.6 ^a

^aMeasured in CH₂Cl₂.

Table 2.

Calculated Parameters for 2 and Adducts

compound	N-N (Å)	$\nu_{\text{NN}}(\text{cm}^{-1})$	HOMO (eV)	$H(\nu_{\text{E-H}})$ (kcal/mol)	NBO Re (e ⁻)	NBO N _a (e ⁻)	NBO N _β (e ⁻)	Wiberg B.I. Re-N	Wiberg B.I. N-N
2	1.132		-4.753		-1.672	0.066	-0.234	1.12	2.44
2-C₆H₅SH	1.135	-25	-4.811	-2.5	-1.644	0.072	-0.265	1.15	2.40
2-C₆H₅NH₂	1.135	-18	-4.808	-1.4	-1.649	0.072	-0.270	1.15	2.40
2-imidazole	1.139	-44	-4.945	-4.7	-1.624	0.077	-0.302	1.18	2.36
2-H₂O	1.138	-38	-4.899	-4.2	-1.629	0.074	-0.300	1.18	2.37
2-C₆H₅OH	1.140	-52	-4.964	-6.2	-1.612	0.083	-0.320	1.20	2.34
2-C₆H₅OH⁺	1.131	+9	-4.888	-5.8	-1.658	0.691	-0.223	1.12	2.45
2-C₆H₅OH linear	1.137	-25	-4.957	-5.1	-1.622	0.087	-0.317	1.19	2.36
2-catechol	1.141	-57	-4.984	-8.2	-1.604	0.086	-0.325	1.21	2.33
2-imidazolium	1.148	-104	-5.486	-9.3	-1.572	0.086	-0.365	1.26	2.27
2-CF₃C₃H₄NH⁺	1.151	-138	-5.597	-10.6	-1.545	0.089	-0.384	1.30	2.22
2-BF₃	1.174	-188	-5.654		-1.386	0.132	-0.411	1.51	1.95