High energy density materials: an amphoteric N-rich bistriazole and salts of its cationic and anionic species

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Supporting Information (SI)

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Synthetic Scheme of 1

Scheme S1. Synthesis of 1.
Fig. S1. $^1$H-NMR spectrum of 1 in DMSO-d$_6$ at 25 °C. The signals at 2.51 ppm and at 3.35 ppm are due to the solvent and water, respectively.
Fig. S2. $^{13}$C-NMR spectrum of 1 in DMSO-d6, at 25 °C. The signals nearly 40 ppm are due to the solvent.
Fig. S3. ESI mass spectrum of 1.
Acid-base equilibria, UV-VIS spectra, and UV-VIS titrations

In this section, 1 will also be indicated as $HL$, the singly protonated form of 1 as $H_2L^+$, the doubly protonated form as $H_3L^{++}$, and the deprotonated form as $L^-$. The protolytic equilibria of 1 were studied by UV-VIS absorption spectroscopy in 0.5 M NaCl, as the ionic medium. The 1 stock solutions were prepared starting from the solid. Deionized and doubly distilled water was used to prepare all aqueous solutions. NaCl (Fluka, dried overnight at 120 °C) was used to prepare the ionic medium solutions. Stock solutions of HCl (Carlo Erba p.a.) were standardized against KHCO$_3$ using methyl red as indicator, with a reproducibility of 0.1 %. NaOH (Baker p.a.) stock solutions were standardized against standardized HCl solutions. The experiments were performed as acid-base titrations at constant total concentration of 1 ($C= 5.01 \cdot 10^{-5}$ M). The investigated pH spans between 0.7 and 10. For each experimental point at 2.5<pH<10, the equilibrium free proton concentration was evaluated from the measured electromotive force at the ends of the galvanic cell GE/TS/RE, where TS indicates the Test solution, GE is the glass electrode and RE is a reference electrode (0.5 M NaCl$|Hg_2Cl_2|Hg$) placed outside but electrically connected to TS through a salt bridge. The Nernst potential of the cell, E(mV), can be written as $E= E_0 + 59.16 \log [H^+] + E_j$ where $E_j$= liquid junction potential due to the replacement of Na$^+$ with H$^+$. The evaluation of the constant of the glass electrode, $E_0$, was performed in the first stage of each experiment by a coulometric titration, using the Gran method. The test solutions at 0.3<pH<2 were obtained analytically. All the experiments were carried out in air in a thermostat, at 25.00 ± 0.03 °C. Potentiometric experimental data were collected by means of an automatic data acquisition system based on Hewlett-Packard (HP) instrumentation. The glass membrane electrodes reversible to protons were supplied by Metrohm. Highly precise (± 0.02 mV) emf measurements were made by adapting the impedance of the glass electrode through operational amplifiers. Coulometric variations of the solution composition were carried out using a Hewlett Packard “DC Power Supply”. The intensity of the current in the electrolysis circuit was measured from the potential drop at the ends of a calibrated resistance; the current density was set at about 1 mA/cm$^2$. Absorption spectra were recorded with a Varian Cary 50 UV-Vis spectrophotometer using 1 cm cell. The primary spectrophotometric data (Absorbance, pH, $\lambda$) were elaborated both graphically and numerically, by the HYPERQUAD program. In Figure S5, the continuous curves were obtained by fitting the experimental points with an equation that relates the Absorbance of the solution (at a given wavelength) with the pH, the analytical concentration of 1, and the equilibrium constants, by assuming the law of additivity of absorbances (Bouger-Lambert-Beer equation). The Bouger-Lambert-Beer equation is now explicitly derived for the system 1 (HL).

From the Lambert-Beer law, assuming additivity of the absorbances, it is
in which \( b \) is the optical path of the cell (1 cm) and \( \varepsilon_i^j \) is the molar extinction coefficient of the species \( i \) at the given wavelength. The analytical concentration of \( 1 (HL) \), \( C \), is given by

\[
C = [H_3L^{++}] + [H_2L^+] + [HL] + [L^-] \quad (2)
\]

The acid-base conditional equilibrium constants are

\[
K_{a1} = \frac{[H_3L^{++}] \cdot [H_3O^+]}{[H_3L^+]}, \quad K_{a2} = \frac{[HL] \cdot [H_3O^+]}{[H_2L^+]}, \quad K_{a3} = \frac{[L^-] \cdot [H_3O^+]}{[HL]} \quad (3)
\]

From these, it is possible to express the concentration of all species but one (e. g. the neutral one), as a function of the equilibrium constants and the concentration of \( H_3O^+ \):

\[
[H_3L^{++}] = \frac{[HL] \cdot [H_3O^+]^2}{K_{a1} \cdot K_{a2}}, \quad [H_2L^+] = \frac{[HL] \cdot [H_3O^+]}{K_{a2}}, \quad [L^-] = \frac{[HL] \cdot K_{a3}}{[H_3O^+]} \quad (4)
\]

Putting (4) in (2) it is

\[
C = \frac{[HL] \cdot [H_3O^+]^2}{K_{a1} \cdot K_{a2}} + \frac{[HL] \cdot [H_3O^+]}{K_{a2}} + [HL] + \frac{[HL] \cdot K_{a3}}{[H_3O^+]} \quad (5)
\]

So, it is

\[
[HL] = \frac{CK_{a1}K_{a2}[H_3O^+]}{[H_3O^+]^3 + K_{a1}[H_3O^+]^2 + K_{a1}K_{a2}[H_3O^+] + K_{a1}K_{a2}K_{a3}} \quad (6)
\]

Putting (4) and (6) in (1) yields

\[
A = b \cdot \left( \varepsilon_1^j \frac{[HL] \cdot [H_3O^+]^2}{K_{a1}K_{a2}} + \varepsilon_2^j \frac{[HL] \cdot [H_3O^+]}{K_{a2}} + \varepsilon_3^j [HL] + \varepsilon_4^j \frac{[HL] \cdot K_{a3}}{[H_3O^+]} \right)^{\lambda} \quad (7)
\]

\[
A = b \cdot [HL] \left( \varepsilon_1^j \frac{[H_3O^+]^2}{K_{a1}K_{a2}} + \varepsilon_2^j \frac{[H_3O^+]}{K_{a2}} + \varepsilon_3^j + \varepsilon_4^j \frac{K_{a3}}{[H_3O^+]} \right) \quad (8)
\]
\[ A = b \cdot \frac{C K_{a1} K_{a2} [H_3O^+]}{[H_3O^+]^3 + K_{a1} [H_3O^+]^2 + K_{a1} K_{a2} [H_3O^+] + K_{a1} K_{a2} K_{a3}} \left( \epsilon_1^3 \frac{[H_3O^+]}{K_{a1} K_{a2}} + \epsilon_2^3 \frac{[H_3O^+]}{K_{a2}} + \epsilon_3^3 + \frac{K_{a3}}{[H_3O^+]} \right) \] (9)

\[ A = b \cdot \frac{C}{[H_3O^+]^3 + K_{a1} [H_3O^+]^2 + K_{a1} K_{a2} [H_3O^+] + K_{a1} K_{a2} K_{a3}} \left( \epsilon_1^3 [H_3O^+]^3 + \epsilon_2^3 K_{a1} [H_3O^+]^2 + \epsilon_3^3 K_{a1} K_{a2} [H_3O^+] + \epsilon_4^3 K_{a1} K_{a2} K_{a3} \right) \] (10)

and, finally, the Bouger-Lambert-Beer equation

\[ A = b \cdot \frac{C}{10^{-3pH} + 10^{-2pH - pK_{a1}} + 10^{-pH - pK_{a1} - pK_{a2}} + 10^{-pK_{a1} - pK_{a2} - pK_{a3}}} \left( \epsilon_1^4 10^{-3pH} + \epsilon_2^4 10^{-2pH - pK_{a1}} + \epsilon_3^4 10^{-pH - pK_{a1} - pK_{a2}} + \epsilon_4^4 10^{-pK_{a1} - pK_{a2} - pK_{a3}} \right) \]

The UV-VIS spectra, at constant total concentration and different pH, are reported in Fig. S4 for 1.
Fig. S4. UV–VIS absorption spectra of 1 at constant total concentration, $C = 5.01 \times 10^{-5}$ M, in NaCl 0.5 M recorded at $0.6 \leq \text{pH} \leq 9.9$. The spectra have been grouped in three set of curves for easier lecture.

The plots of Absorbance $\text{vs}$ pH at fixed wavelength and the fitting of the points using the Bouger-Lambert-Beer equation are reported in Fig. S5.
Fig. S5. UV-VIS titration curves of 1, at two different wavelengths. The continuous curves have been constructed by fitting the experimental points (absorbance vs pH data taken from Fig. S4) with the Bouger-Lambert-Beer equation.

Based on the distribution diagram (Fig. 2 of the typescript), the isosbestic points at $\lambda=282$ nm in Fig. S4(a), at 244 nm in Fig. S4(b), and at 259 nm in Fig. S4(c), are related, respectively, with the three equilibria

\[
\begin{align*}
H_3L^2+ + H_2O & \rightleftharpoons H_3O^+ + H_2L^+ \\
H_2L^+ + H_2O & \rightleftharpoons H_3O^+ + HL \\
HL + H_2O & \rightleftharpoons H_3O^+ + L^-
\end{align*}
\]
Tab. S1. Crystal, collection, and refinement data for the structures described in the paper.

| Chemical formula | 1                  | 2                  | 3                  | 4                  |
|------------------|--------------------|--------------------|--------------------|--------------------|
|                  | C₄H₇N₉·0.5(H₂O)    | C₄H₈N₉(N₃O₄)     | (C₄H₉N₉)Br₂·2H₂O  | (C₄H₉N₉)(ClO₄)₂·H₂O |
| Mr               | 190.19             | 288.22             | 379.05             | 400.12             |
| System           | Triclinic          | Triclinic          | Triclinic          | Triclinic          |
| Space group      | P-1                | P-1                | P-1                | P1                 |
| Temp. (K)        | 173                | 173                | 173                | 173                |
| a (Å)            | 7.1560(7)          | 7.722(2)           | 6.5350(15)         | 5.2730(8)          |
| b (Å)            | 11.6750(16)        | 8.773(2)           | 7.0520(19)         | 7.239(3)           |
| c (Å)            | 19.209(3)          | 9.442(4)           | 14.486(6)          | 9.730(3)           |
| α (°)            | 85.50(2)           | 64.22(15)          | 96.67(4)           | 100.17(3)          |
| β (°)            | 85.093(14)         | 66.67(2)           | 100.35(3)          | 95.68(2)           |
| γ (°)            | 76.354(11)         | 71.33(3)           | 106.565(16)        | 105.38(3)          |
| V (Å³)           | 1551.0(4)          | 521.1(3)           | 619.5(4)           | 348.29(18)         |
| Z                | 8                  | 2                  | 2                  | 1                  |
| λ, µ (mm⁻¹)      | Mo Kα, 0.13        | Mo Kα, 0.16        | Mo Kα, 6.55        | Mo Kα, 0.54        |
| Cryst. size (mm) | 0.45 × 0.40 × 0.30 | 0.20 × 0.15 × 0.15 | 0.50 × 0.40 × 0.30 | 0.40 × 0.25 × 0.15 |
| Meas., ind. reflns | 22895, 7082       | 6676, 2386         | 8954, 2789         | 4548, 2585         |
| R(int)           | 0.045              | 0.078              | 0.035              | 0.026              |
| (sin θ/λ)max (Å⁻¹) | 0.650             | 0.650              | 0.650              | 0.649              |
| R[I > 2σ(I)], wR(all), S | 0.046, 0.123, 1.05 | 0.059, 0.162, 1.04 | 0.026, 0.062, 1.10 | 0.025, 0.067, 1.06 |
| Data             | 7082               | 2386               | 2789               | 2585               |
| Parameters       | 593                | 205                | 193                | 250                |
| Restraints       | 6                  | 0                  | 0                  | 3                  |
| Δρ_max, Δρ_min (e Å⁻³) | 0.64, −0.30 | 0.34, −0.32 | 0.45, −0.64 | 0.22, −0.41 |
| CCDC             | 2092331            | 2092333            | 2092335            | 2092337            |
Tab. S2. Crystal, collection, and refinement data for the structures described in the paper.

| Chemical formula | System       | Space group | Temperature (K) | a (Å)     | b (Å)     | c (Å)     | α (°)    | β (°)    | γ (°)    | V (Å³)   | Z      | λ       | μ (mm⁻¹) | Cryst. size (mm) | Meas., ind. reflns | Rint | (sin θ/λ)max (Å⁻¹) | R[I > 2σ(I)], wR(all), S | Reflections | Parameters | Restraints | Δρ max, Δρ min (e Å⁻³) | CCDC  |
|------------------|--------------|-------------|----------------|-----------|-----------|-----------|---------|---------|---------|---------|--------|--------|---------|-----------------|----------------------|------|-------------------|----------------------|-------------|------------|------------|----------------------|--------|
| 5                | (C₄H₉N₉)(NO₃)₂·H₂O | Triclinic   | 173            | 6.690(5)  | 7.290(4)  | 13.985(5) | 75.21(10)| 81.90(10)| 67.68(9)| 609.3(8) | 2      | Mo Kα  | 0.16     | 0.45 × 0.35 × 0.30 | 7338, 2778            | 0.036 | 0.649              | 0.038, 0.097, 1.07    | 2778        | 232        | 0          | 0.29, −0.30          | 2092339 |
| 6                | (C₄H₉N₉)ZnCl₄·2H₂O  | Monoclinic  | 173            | 9.0580(15)| 21.642(3)| 8.4120(19)| 90      | 90      | 90      | 1540.7(5)| 4      | Mo Kα  | 2.30     | 0.20 × 0.20 × 0.20 | 13171, 3507           | 0.021 | 0.650              | 0.024, 0.052, 1.14    | 3507        | 200        | 10         | 0.29, −0.33          | 2092341 |
| 7                | K(C₄H₆N₉)·2H₂O     | Monoclinic  | 173            | 4.230(3)  | 17.330(5)| 13.579(4)| 90      | 90      | 90      | 995.3(8) | 4      | Mo Kα  | 0.54     | 0.45 × 0.20 × 0.20 | 6339, 2241           | 0.029 | 0.650              | 0.031, 0.078, 1.06    | 2241        | 175        | 0          | 0.28, −0.27          | 2092342 |
The DSC curves of energetic compounds 1, 2, 4 and 5 are reported in Fig. S6.

From the TGA analysis reported in the typescript, decomposition temperatures (onset) of 347 °C, 230 °C, 270 °C, 210 °C were determined for 1, 2, 4 and 5 respectively. The DSC curves reported in Fig. S10 basically confirm the decomposition temperatures.
In order to be able to calculate the detonation parameters of 1 and of the corresponding salts, the enthalpy \((H)\) was calculated quantum chemically with the CBS-4M method.\(^5\) The CBS method begins with a HF/3–21G(d) calculation to optimize the structure and for the calculations of the zero-point energy. Then, using a larger basis set, the so-called base-energy is calculated. A MP2 /6 – 31 + G calculation with a CBS extrapolation gives the perturbation-theory correct energy, which takes the electron correlation into account. A MP4 (SDQ) /6 – 31 + (d,p) calculation is used, to estimate the correlation contributions of a higher order. The most widely used CBS–4M version today is a re-parametrization of the original CBS-4 version, which contains additional empirical correction terms (M stands for “minimal population localization” here).

The enthalpies of the gaseous species \(M\) can then be calculated using the method of the atomization energies:\(^6\)–\(^8\)

\[
\Delta H^0_f(g,M) = H^0_M - \sum H^0_{atoms} + \sum \Delta H^0_f(\text{atoms})
\]

The calculated enthalpies \((H)\) for neutral 1 and the corresponding ions as well as the relevant atoms H, C, N, O and Cl using the CBS–4M method, are summarized in Table S3.

| Symmetry | NIMAG | \(-H^{298} / \text{a. u.}\) |
|----------|-------|-----------------------------|
| \(1\text{H-C}_4\text{H}_2\text{N}_9\) | \(C_4\) | 648.458350 |
| \([\text{C}_4\text{H}_8\text{N}_9]^+\) | \(C_4\) | 648.839050 |
| \([\text{C}_4\text{H}_9\text{N}_9]^{2+}\) | \(C_4\) | 649.075205 |
| \([\text{C}_4\text{H}_6\text{N}_9]^\cdot\) | \(C_4\) | 647.936052 |
| \(\text{N(NO}_2)^2^-\) | \(C_2\) | 464.499541 |
| \(\text{ClO}_4^-\) | \(T_d\) | 760.171204 |
| \(\text{NO}_3^-\) | \(D_{3h}\) | 280.080429 |
| \(\text{K}^+\) | \(\) | 599.035967 |
| \(\text{H}\) | \(\) | 0.500991 |
| \(\text{C}\) | \(\) | 37.786156 |
| \(\text{N}\) | \(\) | 54.522462 |
| \(\text{O}\) | \(\) | 74.991202 |
| \(\text{Cl}\) | \(\) | 459.678255 |
| \(\text{K}\) | \(\) | 599.187712 |

Therefore, in Table S3 we already have the \(H^o_{(\text{molecules})}\) and \(H^o_{(\text{atom})}\) values (given in a. u. = atomic units; \(1 \text{ a. u.} = 1 \text{H} = 627.089 \text{kcal mol}^{-1}\)). The values for \(\Delta H^0_f(\text{atoms})\) are easily obtained from the literature and are summarized in Table S4.
Tab. S4. Literature values for $\Delta H^0_f (\text{atoms})$ (in kcal mol$^{-1}$).

|          | NIST$^9$ |
|----------|----------|
| H        | 52.1     |
| C        | 171.3    |
| N        | 113.0    |
| O        | 59.6     |
| Cl       | 29.0     |
| K        | 21.3     |

According to the equation given above, we can now easily calculate the standard enthalpies of formation $\Delta H^0_f (g)$ for the gas phase (Tab. S5).

Tab. S5. Calculated standard enthalpies of formation $\Delta H^0_f (g)$ for the gas-phase.

| gas-phase species       | formula                  | $\Delta H^0_f (g) / \text{kcal mol}^{-1}$ | $\Delta H^0_f (g) / \text{kJ mol}^{-1}$ |
|-------------------------|--------------------------|------------------------------------------|----------------------------------------|
| 1                       | C$_4$H$_7$N$_9$          | 120.0                                    | 502.2                                  |
| 1-cation                | [C$_4$H$_8$N$_9$]$^+$    | 247.6                                    | 1035.8                                 |
| 1-dication              | [C$_4$H$_9$N$_9$]$^{2+}$ | 465.7                                    | 1948.6                                 |
| 1-anion                 | [C$_4$H$_6$N$_9$]$^-$    | 81.3                                     | 340.1                                  |
| Dinitramide anion       | [N(NO$_2$)$_2$]$^-$      | -29.2                                    | -122.2                                 |
| Perchlorate anion       | [ClO$_4$]$^-$            | -66.1                                    | -276.6                                 |
| Nitrate anion           | [NO$_3$]$^-$             | -74.6                                    | -312.3                                 |
| K$^+$                   | K$^+$                    | 116.4                                    | 487.1                                  |

To be able to convert the standard enthalpies of formation $\Delta H^0_f (g)$ for the gas-phase into values for the condensed phase, for covalent molecules (NG) we additionally require the enthalpy of sublimation $\Delta H_{\text{sub.}}$ (for solids) or the enthalpy of vaporization $\Delta H_{\text{vap.}}$ (for liquids). Both values can be estimated using the Trouton’s rule, in which $T_m$ is the melting point of the solid and $T_b$ is the boiling point of the liquid:$^{10}$

$$\Delta H_{\text{sub.}} [\text{J mol}^{-1}] = 188 \ T_m [\text{K}]$$

$$\Delta H_{\text{vap.}} [\text{J mol}^{-1}] = 90 \ T_b [\text{K}]$$

Neutral triamine (compound 1 of the typescript) is a solid and has a m.p. of 351 °C (= 624 K). Therefore, the enthalpy of sublimation is calculated to be $\Delta H_{\text{sub.}}(1) = 117$ kJ mol$^{-1}$ (28.0 kcal mol$^{-1}$).

In the case of ionic solids of the type AB, AB$_2$ or A$_2$B, the lattice energy ($\Delta U_L$) and lattice enthalpy ($\Delta H_L$) can be calculated by using the Jenkin’s method.$^{11-14}$ Only the molecular volumes of the ions are required. These can be most easily obtained from single crystal X-ray diffraction data:

$$\Delta U_L = \left| z_+ \right| \left| z_- \right| \sqrt{\frac{a}{3V_M} + \beta}$$

$$\Delta H_L = \left| z_+ \right| \left| z_- \right| \left[ \frac{a}{\sqrt{3V_M}} + \beta \right]$$

Here $|z_+|$ and $|z_-|$ are the dimensionless charges of the cations and anions and $v$ is the number of ions per ‘molecule’ (2 for [1-cation][N$_3$O$_4$] and [K][1-anion], 3 for [1-dication][ClO$_4$]$_2$ and [1-dication][NO$_3$]$_2$. $V_M$ is the volume in nm$^3$ of a formula unit (e.g. for all anhydrous: $V_M([1\text{-cation}][N_3O_4]) = 0.256$ nm$^3$, $V([1\text{-dication}][\text{ClO}_4]_2) = 0.324$ nm$^3$, $V_M([1\text{-dication}][\text{NO}_3]_2) = 0.280$ nm$^3$. The lattice parameters were obtained by the Full-Matrix Least-Squares Refinement technique and refined using the program MOPAC. The lattice parameter of unit cell of (I) is $a = 8.289$ Å.
nm$^3$, $V_M([\text{K}][\text{1-anion}]) = 0.200$ nm$^3$). The constants $\alpha$ and $\beta$ are dependent on the composition of the salt and are summarized in Table S6.

Tab. S6. The values for the constants $\alpha$ and $\beta$ for calculating the lattice energy by using the Jenkin’s method.

| salt type | $\alpha$ / kJ mol$^{-1}$ | $\beta$ / kJ mol$^{-1}$ |
|-----------|--------------------------|--------------------------|
| AB        | 117.3                    | 51.9                     |
| AB$_2$    | 133.5                    | 60.9                     |
| A$_2$B    | 165.3                    | -29.8                    |

The lattice energy $\Delta U_L$ can easily be converted into the corresponding lattice enthalpy $\Delta H_L$:

$$\Delta H_L (A_p B_q) = \Delta U_L + \left[ p \left( \frac{n_A}{2} - 2 \right) + q \left( \frac{n_B}{2} - 2 \right) \right] RT$$

$n_A, n_B = 3$ for monoatomic ions, $5$ for linear polyatomic ions, $6$ for non-linear, polyatomic ions.

Therefore, the following values for the lattice energies and enthalpies can be written for the anhydrous salts (Tab. S7):

Tab. S7. Lattice energies and enthalpies.

| Salt | Salt name from Chart 3 | $\Delta U_L$ / kJ mol$^{-1}$ | $\Delta H_L$ / kJ mol$^{-1}$ |
|------|-------------------------|-----------------------------|-------------------------------|
| [1-cation][N$_3$O$_4$] | 2                        | 473.3                       | 478.3                         |
| [1-dication][ClO$_4$]$_2$ | 4                        | 1531.6                      | 1539.0                        |
| [1-dication][NO$_3$]$_2$ | 5                        | 1589.8                      | 1597.2                        |
| [K]$^+$[1-anion] | 7                        | 505.0                       | 506.2                         |

The final solid-state enthalpies of formation $\Delta H^\circ_f$ for all compounds in this study are summarized in Tab. S8.
Tab. S8. Enthalpies of formation of triamine compounds.

| Compound | Formula       | $\Delta H^0 / \text{kJ mol}^{-1}$ | $\rho / \text{g cm}^{-3}$ |
|----------|---------------|-----------------------------------|---------------------------|
| 1        | C$_4$H$_7$N$_9$ | +385.2                           | 1.629                     |
| [1-cation][N$_3$O$_4$] | C$_4$H$_8$N$_{12}$O$_4$ | +435.3                           | 1.837                     |
| [1-dication][ClO$_4$]$_2$ | C$_4$H$_9$N$_9$O$_8$Cl$_2$ | -143.6                           | 1.908                     |
| [1-dication][NO$_3$]$_2$ | C$_4$H$_9$N$_{11}$O$_6$ | -273.2                           | 1.773                     |
| [K][1-anion] | C$_4$H$_6$N$_9$K | +321.0                           | 1.704                     |

The detonation and combustion parameters of the triamine compounds were computed using the EXPLO5 code (version V6.05.02)$^{15-16}$ (Tab. S9).

Tab. S9. Detonation parameters.

| Compound | Formula       | $\rho / \text{g cm}^{-3}$ | $V_{\text{ad}} / \text{m s}^{-1}$ | $p_{C/J} / \text{kbar}$ | $Q_{\text{ex}} / \text{kJ kg}^{-1}$ |
|----------|---------------|---------------------------|-----------------------------------|------------------------|-----------------------------------|
| 1        | C$_4$H$_7$N$_9$ | 1.629                     | 7681                              | 194                    | -2378                             |
| [1-cation][N$_3$O$_4$] | C$_4$H$_8$N$_{12}$O$_4$ | 1.837                     | 8948                              | 311                    | -4496                             |
| [1-dication][ClO$_4$]$_2$ | C$_4$H$_9$N$_9$O$_8$Cl$_2$ | 1.908                     | 7033                              | 191                    | -1711                             |
| [1-dication][NO$_3$]$_2$ | C$_4$H$_9$N$_{11}$O$_6$ | 1.773                     | 8092                              | 246                    | -3289                             |
| [K][1-anion] | C$_4$H$_6$N$_9$K | 1.704                     | 6788                              | 146                    | -1245                             |

The sensitivities are listed in Tab. S10.
Tab. S10. Sensitivities of triamine compounds (grain size 100 – 500 μm)

| Compound          | IS / J | FS / N | ESD / J |
|-------------------|--------|--------|---------|
| 1                 | > 40   | > 360  | 1       |
| [1-cation][N₃O₄] | 4      | > 360  | 0.1     |
| [1-dication][ClO₄]₂ | 4      | 192    | 0.1     |
| [1-dication][NO₃]₂ | > 25   | > 360  | 0.6     |
| [K][1-anion]      | n.d.   | n.d.   | n.d.    |

n.d. = not determined
Optimized Structures of tautomers/conformers

In the following we report the optimized geometries (xyz format) for the conformers of all tautomers computed both in gas and water.

**1H cis GAS**

| Atom | X  | Y  | Z   |
|------|----|----|-----|
| N    | -0.262924 | -2.703204 | -1.435773 |
| N    | -0.448205  | -2.389924  | -0.114407  |
| C    | -0.114495  | -1.109664  | -0.088401  |
| N    | 0.251206   | -0.580325  | -1.311119  |
| C    | 0.149491   | -1.616626  | -2.129135  |
| C    | -0.101072  | -0.307976  | 1.126432   |
| N    | -0.066650  | 1.084860   | 1.120800   |
| C    | 0.018189   | 1.434791   | 2.438215   |
| N    | 0.032333   | 0.360000   | 3.202922   |
| N    | 0.031836   | -0.737213  | 2.364640   |
| N    | 0.000509   | 2.746197   | 2.849071   |
| N    | 0.479458   | -1.629647  | -3.467018  |
| H    | -0.384855  | -3.656309  | -1.742853  |
| N    | -0.111456  | 2.018462   | 0.070777   |
| H    | 0.379614   | 3.401808   | 2.176440   |
| H    | 0.331278   | 2.874214   | 3.796000   |
| H    | -0.086768  | -2.211932  | -4.069552  |
| H    | 0.637924   | -0.705554  | -3.845818  |
| H    | 0.408732   | 1.615202   | -0.707437  |
| H    | -1.080471  | 2.112842   | -0.233788  |

**1H cis WATER**

| Atom | X  | Y  | Z   |
|------|----|----|-----|
| N    | -0.317680 | -2.679146 | -1.450515 |
| N    | -0.505471 | -2.355662 | -0.132437 |
| C    | -0.099834 | -1.094312 | -0.101159 |
| N    | 0.320416  | -0.586695 | -1.304254 |
| C    | 0.167439  | -1.617178 | -2.135509 |
| C    | -0.069113 | -0.301320 | 1.121791  |
| N    | -0.064529 | 1.085287  | 1.134352  |
| C    | 0.032409  | 1.432295  | 2.452291  |
| N    | 0.079695  | 0.347519  | 3.208589  |
| N    | 0.028772  | -0.746517 | 2.353844  |
| N    | -0.005712 | 2.735567  | 2.869421  |
| N    | 0.518192  | -1.638327 | -3.455106 |
| H    | -0.551655 | 3.602757  | -1.787100 |
| N    | -0.150493 | 2.024228  | 0.093466  |
| H    | 0.291346  | 3.407599  | 2.170791  |
| H    | 0.390369  | 2.894525  | 3.786971  |
| H    | 0.065489  | -2.322838 | -4.046107 |
| H    | 0.609580  | -0.726445 | -3.883135 |
| H    | 0.384713  | 1.656240  | -0.691963 |
| H    | -1.123931 | 2.087938  | -0.204234 |
### 1H trans GAS

| Atom | x | y | z |
|------|---|---|---|
| N    | 0.189794 | -1.328091 | -2.335911 |
| N    | 0.175443 | -0.226172 | -1.518321 |
| C    | 0.028601 | -0.778522 | -0.314194 |
| N    | -0.056738 | -2.144883 | -0.311377 |
| C    | 0.054536 | -2.454375 | -1.590386 |
| C    | -0.033070 | 0.022653 | 0.897544 |
| N    | -0.046230 | 1.417178 | 0.909555 |
| C    | -0.056841 | 1.751433 | 2.234782 |
| N    | -0.051383 | 0.667362 | 2.986401 |
| N    | -0.031075 | -0.419791 | 2.132746 |
| N    | -0.143761 | 3.053500 | 2.659497 |
| N    | 0.097629 | -3.730337 | -2.106995 |
| H    | 0.371101 | -1.221920 | -3.322116 |
| N    | -0.039724 | 2.365689 | -0.125921 |
| H    | 0.213989 | 3.738217 | 2.005282 |
| H    | 0.138030 | 3.188857 | 3.620674 |
| H    | -0.144472 | -4.431674 | -1.418438 |
| H    | -0.359978 | -3.876866 | -2.996960 |
| H    | 0.642514 | 2.063471 | -0.818338 |
| H    | -0.948367 | 2.344269 | -0.587522 |

### 1H trans WATER

| Atom | x | y | z |
|------|---|---|---|
| N    | 0.148741 | -1.344581 | -2.333491 |
| N    | 0.133502 | -0.237384 | -1.529044 |
| C    | 0.025359 | -0.775880 | -0.318792 |
| N    | -0.032021 | -2.143393 | -0.294963 |
| C    | 0.048903 | -2.468696 | -1.583106 |
| C    | -0.021964 | 0.032109 | 0.891956 |
| N    | -0.041762 | 1.420795 | 0.917686 |
| C    | -0.062903 | 1.754243 | 2.243991 |
| N    | -0.058694 | 0.663161 | 2.991304 |
| N    | -0.028089 | -0.422156 | 2.124507 |
| N    | -0.156156 | 3.050446 | 2.669387 |
| N    | 0.100606 | -3.739931 | -2.081664 |
| H    | 0.233011 | -1.246273 | -3.335749 |
| N    | -0.025780 | 2.377950 | -0.106589 |
| H    | 0.159036 | 3.738611 | 1.995562 |
| H    | 0.170142 | 3.211905 | 3.613255 |
| H    | -0.236825 | -4.451810 | -1.447067 |
| H    | -0.194935 | -3.878016 | -3.039120 |
| H    | 0.734449 | 2.152386 | -0.744459 |
| H    | -0.894621 | 2.306514 | -0.633604 |
2H cis GAS

N  0.009528  -2.878240  -1.511246
N  0.065217  -2.396133  -0.233630
C  0.021846  -1.051499  -0.235964
N  -0.050016  -0.602587  -1.492320
C  -0.051071  -1.757355  -2.225309
C  0.028497  -0.250989  0.966215
N  0.100766   1.133618  0.987294
C  0.017243   1.461774  2.312525
N  -0.091220   0.373121  3.054888
N  -0.092222  -0.704367  2.192849
N  0.120298   2.754821  2.751528
N  -0.054086  -1.748317  -3.604956
N  0.224364   2.072329  -0.050048
H  0.099890  -3.016992   0.562050
H  -0.212656   2.899175  3.694776
H  -0.159481   3.459237  2.080342
H  -0.335505  -2.621223  -4.029947
H  -0.488079  -0.934145  -4.016646
H  1.191416   2.065788  -0.374226
H  -0.344728   1.741983  -0.828176

2H cis WATER

N  0.018116  -2.886266  -1.507417
N  0.058298  -2.399794  -0.230318
C  0.016628  -1.055231  -0.241186
N  -0.041212  -0.612681  -1.500090
C  -0.037220  -1.767369  -2.230769
C  0.012546  -0.249073   0.961240
N  0.097416   1.133147  0.993134
C  0.026685   1.460425  2.319238
N  -0.089932   0.365099  3.057504
N  -0.105822  -0.709965  2.185945
N  0.145046   2.745460  2.761546
N  -0.022051  -1.761827  -3.609946
N  0.220670   2.085440  -0.027887
H  0.096760  -3.023273   0.564256
H  -0.232535   2.918591  3.683821
H  -0.077151   3.456077  2.074210
H  -0.333977  -2.624678  -4.037673
H  -0.453139  -0.944969  -4.023814
H  1.152247   2.011117  -0.433775
H  -0.451374   1.859769  -0.758019
### 2H \textit{trans} GAS

| Atom | X    | Y    | Z    |
|------|------|------|------|
| N    | -0.131296 | -1.540815 | -2.544013 |
| N    | -0.126473  | -0.503342  | -1.659812  |
| C    | -0.088111  | -0.965922  | -0.388437  |
| N    | -0.067454  | -2.295813  | -0.394952  |
| C    | -0.099045  | -2.593234  | -1.723726  |
| C    | -0.078805  | -0.114188  | 0.790689   |
| N    | 0.026695   | 1.272358   | 0.757381   |
| C    | 0.011213   | 1.654853   | 2.078503   |
| N    | -0.084279  | 0.602476   | 2.854713   |
| N    | -0.143976  | -0.514114  | 2.039446   |
| N    | -0.025313  | 2.989800   | 2.460075   |
| N    | -0.147542  | -3.894713  | -2.177056  |
| N    | -0.003859  | 2.091033   | -0.381465  |
| H    | -0.164529  | 0.459007   | -1.964386  |
| H    | -0.174345  | 3.062704   | 3.461227   |
| H    | 0.788679   | 3.533230   | 2.188515   |
| H    | 0.162372   | -4.028671  | -3.129220  |
| H    | 0.214041   | -4.573224  | -1.521550  |
| H    | -0.750706  | 2.775736   | -0.270065  |
| H    | 0.882732   | 2.582841   | -0.475867  |

### 2H \textit{trans} WATER

| Atom | X    | Y    | Z    |
|------|------|------|------|
| N    | -0.078957  | -1.526891  | -2.535085  |
| N    | -0.065484  | -0.490961  | -1.647221  |
| C    | -0.080717  | -0.954659  | -0.383276  |
| N    | -0.109494  | -2.290948  | -0.392360  |
| C    | -0.107635  | -2.586794  | -1.722816  |
| C    | -0.071978  | -0.114197  | 0.802094   |
| N    | -0.005901  | 1.269393   | 0.784996   |
| C    | -0.016149  | 1.644131   | 2.105478   |
| N    | -0.080539  | 0.571937   | 2.876819   |
| N    | -0.118264  | -0.535588  | 2.045144   |
| N    | -0.058215  | 2.948692   | 2.516698   |
| N    | -0.198043  | -3.883557  | -2.187588  |
| N    | 0.027084   | 2.068937   | -0.363694  |
| H    | -0.042920  | 0.480276   | -1.936503  |
| H    | 0.091624   | 3.063950   | 3.511597   |
| H    | 0.459120   | 3.623176   | 1.965519   |
| H    | 0.134801   | -4.014298  | -3.134634  |
| H    | 0.171627   | -4.575602  | -1.548167  |
| H    | -0.755118  | 2.720724   | -0.350232  |
| H    | 0.905155   | 2.582279   | -0.406767  |
### 4H cis GAS

|  | X       | Y       | Z         |
|---|---------|---------|------------|
| C | 0.224423| 0.875040| 3.262369   |
| N | 0.435079| -0.419415| 1.996689  |
| C | 0.318121| 0.375493 | 1.148096   |
| H | 0.718487| 5.187320 | 5.690269   |
| N | 0.144119| 3.032491 | 4.546114   |
| C | -0.035153| 3.335222| 5.876884   |
| N | -0.207975| 2.238188| 6.570896   |
| N | -0.153173| 1.170923| 5.690269   |
| N | -0.14208| 4.650015| 6.321804   |
| C | 0.392597| 0.507363|-0.230650   |
| N | 0.23518| 0.926597| 3.466102   |
| H | 0.088356| 2.421625| 1.799246   |
| C | 0.229518| 3.926597| 3.466102   |
| N | 0.086046| 3.015240| 4.563814   |
| C | -0.031862| 3.319819| 5.898570   |
| N | -0.119007| 2.209858| 6.607247   |
| N | -0.063270| 1.143874| 5.718918   |
| N | -0.144559| 4.604100| 6.364922   |
| N | 0.484281| 0.488394|-0.192321   |
| N | 0.163733| 3.881174| 3.465860   |
| H | 0.237773| 2.416434| 1.837709   |
| H | -0.087761| 4.668459| 7.374240   |
| H | 0.423819| 5.305370| 5.904292   |
| H | 0.317567| -0.373326|-0.697544   |
| H | 0.025102| 1.282082|-0.622181   |
| H | -0.641027| 4.505062| 3.464222   |
| H | 1.022711| 4.425566| 3.508588   |

### 4H cis WATER

|  | X       | Y       | Z         |
|---|---------|---------|------------|
| C | 0.177157| 0.858979| 3.279605   |
| N | 0.241553| 1.417843| 2.022663   |
| C | 0.323804| 0.361776| 1.165971   |
| C | 0.062298| 1.630403| 4.505369   |
| N | 0.086046| 3.015240| 4.563814   |
| C | -0.031862| 3.319819| 5.898570   |
| N | -0.119007| 2.209858| 6.607247   |
| N | -0.063270| 1.143874| 5.718918   |
| N | -0.144559| 4.604100| 6.364922   |
| N | 0.484281| 0.488394|-0.192321   |
| N | 0.163733| 3.881174| 3.465860   |
| H | 0.237773| 2.416434| 1.837709   |
| H | -0.087761| 4.668459| 7.374240   |
| H | 0.423819| 5.305370| 5.904292   |
| H | 0.317567| -0.373326|-0.697544   |
| H | 0.025102| 1.282082|-0.622181   |
| H | -0.641027| 4.505062| 3.464222   |
| H | 1.022711| 4.425566| 3.508588   |
|        | 4H trans GAS          |        | 4H trans WATER          |
|--------|-----------------------|--------|-------------------------|
|        | N        | -1.285696 | -1.280767 |
|        | N        | -0.194019 | -0.189022 |
|        | C        | -0.651554 | -0.648326 |
|        | N        | -2.027154 | -2.024451 |
|        | C        | -2.365696 | -2.368909 |
|        | C        | 0.117436  | 0.120147  |
|        | N        | 1.501125  | 1.502691  |
|        | C        | 1.789903  | 1.785329  |
|        | N        | 0.680301  | 0.666222  |
|        | N        | -0.376121 | -0.385053 |
|        | N        | 3.076578  | 3.063341  |
|        | N        | -3.66453  | -3.66222  |
|        | N        | 2.468307  | -0.385053 |
|        | H        | -2.618386 | -2.634408 |
|        | H        | 3.780324  | 3.783897  |
|        | H        | 3.183897  | -3.712797 |
|        | H        | -4.339263 | -4.360676 |
|        | H        | 2.154312  | 2.482251  |
|        | H        | 2.482628  | 2.427334  |
|        |        |        |        |
|------|------|------|------|
| 1H-1'H cis GAS | 1H-1'H cis WATER |
| N    | -0.101063 | -0.173830 |
| N    | -0.195131 | -0.303416 |
| C    | -0.026298 | -0.020815 |
| N    | 0.160912  | -0.082529 |
| C    | 0.112961  | 0.038428  |
| C    | -0.003523 | -0.271599 |
| N    | -0.069943 | 0.165862  |
| C    | 0.028228  | 0.012031  |
| N    | 0.127042  | -0.02853  |
| N    | 0.123932  | -0.215898 |
| N    | -0.001084 | -0.172937 |
| N    | 0.302853  | 0.221145  |
| H    | -0.172937 | -0.015158 |
| N    | -0.215898 | 0.143356  |
| C    | 0.028228  | 0.012769  |
| H    | -0.046802 | 0.319407  |
| H    | 0.307793  | 0.037230  |
| H    | -1.158230 | 1.919290  |

|        |        |        |        |
|------|------|------|------|
| N    | -0.101063 | -0.173830 |
| N    | -0.195131 | -0.303416 |
| C    | -0.026298 | -0.020815 |
| N    | 0.160912  | -0.082529 |
| C    | 0.112961  | 0.038428  |
| C    | -0.003523 | -0.271599 |
| N    | -0.069943 | 0.165862  |
| C    | 0.028228  | 0.012031  |
| N    | 0.127042  | -0.02853  |
| N    | 0.123932  | -0.215898 |
| N    | -0.001084 | -0.172937 |
| N    | 0.302853  | 0.221145  |
| H    | -0.172937 | -0.015158 |
| N    | -0.215898 | 0.143356  |
| C    | 0.028228  | 0.012769  |
| H    | -0.046802 | 0.319407  |
| H    | 0.307793  | 0.037230  |
| H    | -1.158230 | 1.919290  |
### 1H-1'H trans GAS

|     | X       | Y       | Z       |
|-----|---------|---------|---------|
| N   | -0.006673 | -1.281320 | -2.532924 |
| N   | -0.040256 | -0.216775 | -1.684282 |
| C   | 0.026246  | -0.821232 | -0.501534 |
| N   | 0.103502  | -2.176099 | -0.524447 |
| C   | 0.078084  | -2.446291 | -1.825614 |
| C   | 0.021128  | -0.051054 | 0.731856  |
| N   | -0.070163 | 1.350469  | 0.777330  |
| C   | -0.044787 | 1.710672  | 2.085656  |
| N   | 0.056805  | 0.564012  | 2.767131  |
| N   | 0.099187  | -0.537928 | 1.938504  |
| N   | -0.112315 | 2.967934  | 2.516819  |
| N   | 0.076590  | -3.685037 | -2.375435 |
| H   | -0.074752 | -1.131761 | -3.530009 |
| N   | -0.175097 | 2.324359  | -0.223068 |
| H   | 0.103033  | 0.426548  | 3.767686  |
| H   | -0.186261 | 3.700188  | 1.820223  |
| H   | -0.091352 | 3.207316  | 3.496307  |
| H   | 0.353317  | -3.818677 | -3.336313 |
| H   | 0.268368  | -4.450564 | -1.744621 |
| H   | 0.625177  | 2.233355  | -0.847698 |
| H   | -1.009781 | 2.131886  | -0.775567 |

### 1H-1'H trans WATER

|     | X       | Y       | Z       |
|-----|---------|---------|---------|
| N   | -0.038819 | -1.308465 | -2.540725 |
| N   | -0.071808 | -0.231024 | -1.708615 |
| C   | 0.009445  | -0.807077 | -0.516021 |
| N   | 0.094369  | -2.168470 | -0.521713 |
| C   | 0.060900  | -2.457844 | -1.821830 |
| C   | 0.009118  | -0.028963 | 0.713285 |
| N   | -0.066648 | 1.365097  | 0.770715 |
| C   | -0.042131 | 1.713323  | 2.085323 |
| N   | 0.045140  | 0.559039  | 2.756632 |
| N   | 0.077430  | -0.530481 | 1.916570 |
| N   | -0.091943 | 2.959160  | 2.532020 |
| N   | 0.053290  | -3.708414 | -2.358628 |
| H   | -0.093330 | -1.179839 | -3.542312 |
| N   | -0.155492 | 2.343523  | -0.222787 |
| H   | 0.087272  | 0.424693  | 3.758129 |
| H   | -0.172727 | 3.704216  | 1.851426 |
| H   | -0.096534 | 3.176027  | 3.517562 |
| H   | 0.351970  | -3.817441 | -3.318436 |
| H   | 0.368604  | -4.442534 | -1.738721 |
| H   | 0.658952  | 2.269133  | -0.829167 |
| H   | -0.987057 | 2.166343  | -0.782707 |
### 2H-1'H *cis* GAS

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| N    | -0.33313 | -2.932961 | -1.589852 |
| N    | -0.200382 | -2.462415 | -0.329703 |
| C    | -0.090761 | -1.120195 | -0.345778 |
| N    | -0.152222 | -0.665412 | -1.597849 |
| C    | -0.303825 | -1.812725 | -2.327436 |
| C    | 0.080760  | -0.292950 | 0.824488 |
| N    | 0.087227  | 1.107384 | 0.779774 |
| C    | 0.28203   | 1.545128 | 2.051230 |
| N    | 0.375269  | 0.438713 | 2.800272 |
| N    | 0.259189  | -0.711556 | 2.048597 |
| N    | 0.347895  | 2.826742 | 2.396388 |
| N    | -0.467011 | -1.815550 | -3.678114 |
| N    | -0.070276 | 2.018100 | -0.271966 |
| H    | 0.526544  | 0.362954 | 3.797301 |
| H    | -0.187190 | -3.102189 | 0.454206 |
| H    | 0.266548  | 3.516461 | 1.657605 |
| H    | 0.508191  | 3.126914 | 3.346222 |
| H    | -0.159830 | -1.001169 | -4.187300 |
| H    | -0.377677 | -2.701977 | -4.153024 |
| H    | 0.606255  | 1.787366 | -0.998810 |
| H    | -0.997594 | 1.889336 | -0.676253 |

### 2H-1'H *cis* WATER

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| N    | -0.281741 | -2.951341 | -1.582128 |
| N    | -0.120038 | -2.449455 | -0.328738 |
| C    | -0.095315 | -1.105992 | -0.370141 |
| N    | -0.240938 | -0.679169 | -1.623855 |
| C    | -0.351526 | -1.843567 | -2.328322 |
| C    | 0.070603  | -0.266023 | 0.799113 |
| N    | 0.094607  | 1.127488 | 0.769155 |
| C    | 0.267265  | 1.546890 | 2.052545 |
| N    | 0.338936  | 0.428327 | 2.787202 |
| N    | 0.218358  | -0.703492 | 2.019791 |
| N    | 0.340177  | 2.814349 | 2.422992 |
| N    | -0.584243 | -1.864664 | -3.682525 |
| N    | -0.021122 | 2.048391 | -0.274773 |
| H    | 0.465062  | 0.349851 | 3.788081 |
| H    | -0.031513 | -3.065672 | 0.468818 |
| H    | 0.261898  | 3.525233 | 1.706203 |
| H    | 0.468254  | 3.083367 | 3.387217 |
| H    | -0.256562 | -1.045890 | -4.178327 |
| H    | -0.345416 | -2.732158 | -4.145561 |
| H    | 0.720682  | 1.874038 | -0.949746 |
| H    | -0.917428 | 1.909490 | -0.737006 |


### 2H-1'H trans WATER

| At. | x    | y    | z    |
|-----|------|------|------|
| N   | 0.188610 | -2.292776 | -2.111761 |
| N   | 0.557995  | -1.328498  | -1.227319  |
| C   | -0.488793  | -0.984418  | -0.450342  |
| N   | -1.562632  | -1.693159  | -0.794684  |
| C   | -1.100820  | -2.478617  | -1.808807  |
| C   | -0.482571  | -0.002630  | 0.626454   |
| N   | 0.330332  | 1.133742   | 0.713866   |
| C   | -1.30045   | -0.054262  | 1.641647   |
| N   | 0.513693   | 2.924585   | 2.264116   |
| N   | -1.885619  | -3.422998  | -2.425163  |
| N   | 1.306530   | 1.664240   | -0.121541  |
| H   | -1.517764  | 1.234046   | 3.249051   |
| H   | 1.523328   | -1.031018  | -1.196568  |
| H   | 0.198699   | 3.396205   | 3.099314   |
| H   | 1.227142   | 3.349774   | 1.684743   |
| H   | -1.568211  | -3.716017  | -3.340189  |
| H   | -2.878827  | -3.233932  | -2.389156  |
| H   | 2.153851   | 1.104512   | -0.104967  |
| H   | 0.949791   | 1.803332   | -1.062519  |

### 4H-1'H cis GAS

| At. | x    | y    | z    |
|-----|------|------|------|
| N   | -2.440882 | -0.184444 | -1.950797 |
| N   | -2.018580 | -0.213140 | -0.664637 |
| C   | -0.708305  | -0.054385  | -0.657201  |
| N   | -0.244948  | 0.082025   | -1.958720  |
| C   | -1.369945  | -0.011956  | -2.726210  |
| C   | 0.077357   | -0.006197  | 0.547238   |
| N   | 1.488331   | 0.030010   | 0.595178   |
| C   | 1.846934   | 0.033448   | 1.912827   |
| N   | 0.700025   | 0.000777   | 2.585785   |
| N   | -0.406816  | -0.015425  | 1.763936   |
| N   | 3.099203   | 0.091112   | 2.384023   |
| N   | -1.386411  | -0.010850  | -4.087173  |
| N   | 2.334634   | 0.062602   | -0.509042  |
| H   | 0.719690   | 0.138088   | -2.252928  |
| H   | 0.559047   | -0.000173  | 3.588048   |
| H   | 3.283121   | 0.056469   | 3.376694   |
| H   | 3.890941   | -0.004769  | 1.764902   |
| H   | -2.315894  | -0.011042  | -4.488343  |
| H   | -0.712844  | 0.551373   | -4.587777  |
| H   | 2.898999   | 0.908785   | -0.526695  |
| H   | 2.892711   | -0.784696  | -0.584999  |
### 4H-1'H trans WATER

| Atom | \( x \)  | \( y \)  | \( z \)  |
|------|----------|----------|----------|
| N    | -1.317993| 0.104682 | -2.751067|  
| N    | -0.245919| 0.118421 | -1.892580|  
| C    | -0.714044| 0.042474 | -0.684508|  
| N    | -2.088246| -0.018248| -0.684508|  
| C    | -2.419771| 0.023233 | -2.006634|  
| C    | 0.070382 | 0.010706 | 0.545014  |  
| N    | 1.463802 | 0.054517 | 0.582577  |  
| C    | 1.826977 | -0.005165| 1.893129  |  
| N    | 0.680230 | -0.078660| 2.579573  |  
| N    | -0.420835| 0.069971 | 1.533115  |  
| N    | 3.078412 | 0.019388 | 2.323628  |  
| N    | -3.697267| 0.054313 | -2.478434 |  
| N    | 2.425437 | 0.137857 | 0.426297  |  
| H    | 2.710588 | 0.067544 | 0.112332  |  
| H    | 0.558089 | 0.128943 | 3.582392  |  
| H    | 3.309695 | 0.076602 | 3.301211  |  
| H    | 3.817514 | 0.051682 | 1.632370  |  
| H    | -3.783556| 0.125072 | -3.470608 |  
| H    | -4.413137| 0.390979 | -1.919558 |  
| H    | 2.306918 | 0.651862 | 1.057811  |  
| H    | 2.273900 | 0.995773 | -0.953299 |  

### 1H-4H cis GAS

| Atom | \( x \)  | \( y \)  | \( z \)  |
|------|----------|----------|----------|
| N    | -2.740950| -0.163835| -1.492315|  
| N    | -2.483483| -0.159803| -0.139435|  
| C    | -1.181813| -0.060284| -0.065052|  
| N    | -0.616422| -0.009787| -1.341390|  
| C    | -1.628343| -0.077238| -2.233369|  
| C    | -0.391527| 0.018694 | 1.140599  |  
| N    | 1.000221 | 0.008223 | 1.176104  |  
| C    | 1.303907 | 0.095049 | 2.515621  |  
| N    | 0.190608 | 0.138031 | 3.228319  |  
| N    | -0.865499| 0.093703 | 2.362025  |  
| N    | 2.581492 | 0.240429 | 2.986603  |  
| N    | -1.529854| -0.069764| -3.568722 |  
| N    | 1.860082 | 0.077739 | 0.065836  |  
| H    | 0.390047 | 0.070486 | -1.491265 |  
| H    | -3.700177| -0.234789| -1.806193 |  
| H    | 2.610803 | 0.348244 | 3.994819  |  
| H    | 3.283287 | -0.408253| 2.649960  |  
| H    | -2.352221| -0.104545| -4.153378 |  
| H    | -0.638232| 0.043847 | -4.027328 |  
| H    | 2.453253 | 0.903683 | 0.159284  |  
| H    | 2.454823 | -0.749829| 0.039275  |  

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1H-4H *cis* WATER

|    |    |    |    |
|----|----|----|----|
| N  | -2.735604 | -0.125601 | -1.493566 |
| N  | -2.481527 | -0.096569 | -0.143167 |
| C  | -1.176902 | -0.030974 | -0.068199 |
| N  | -0.605775 | -0.019543 | -1.329220 |
| C  | -1.612632 | -0.080983 | -2.229298 |
| C  | -0.400489 | 0.029183  | 1.154350  |
| N  | 0.983174  | 0.065745  | 1.197055  |
| C  | 1.292332  | 0.109281  | 2.533542  |
| N  | 0.176981  | 0.097184  | 3.252044  |
| N  | -0.884332 | 0.049437  | 2.373735  |
| N  | 2.561334  | 0.242217  | 3.012508  |
| N  | -1.506714 | -0.095713 | -3.553837 |
| N  | 1.828532  | 0.088774  | 0.080381  |
| H  | 0.402075  | 0.031062  | -1.483719 |
| H  | -3.688917 | -0.179428 | -1.826731 |
| H  | 2.643722  | 0.102748  | 4.011834  |
| H  | 3.312469  | -0.186045 | 2.485955  |
| H  | -2.328184 | -0.134574 | -4.140097 |
| H  | -0.603048 | -0.052385 | -4.002092 |
| H  | 2.405739  | 0.927612  | 0.100756  |
| H  | 2.417768  | -0.741426 | 0.067764  |

1H-4H *trans* GAS

|    |    |    |    |
|----|----|----|----|
| N  | -1.497076 | -0.163844 | -2.446868 |
| N  | -0.263910 | -0.129989 | -1.821999 |
| C  | -0.559511 | -0.038266 | -0.552213 |
| N  | -1.943248 | -0.013084 | -0.363801 |
| C  | -2.518403 | -0.094202 | -1.579697 |
| C  | 0.273484  | 0.034524  | 0.617583  |
| N  | 1.649930  | 0.049235  | 0.723212  |
| C  | 1.877810  | 0.107050  | 2.080126  |
| N  | 0.726708  | 0.116315  | 2.743694  |
| N  | -0.270131 | 0.071534  | 1.816092  |
| N  | 3.115192  | 0.237279  | 2.628228  |
| N  | -3.827332 | -0.103090 | -1.853271 |
| N  | 2.551584  | 0.116914  | -0.336583 |
| H  | -2.378090 | 0.045799  | 0.552948  |
| H  | -1.534702 | -0.229439 | -3.455146 |
| H  | 3.899431  | -0.216032 | 2.179641  |
| H  | 3.131656  | 0.207187  | 3.639859  |
| H  | -4.164712 | -0.167159 | -2.802551 |
| H  | -4.515410 | -0.038752 | -1.117215 |
| H  | 3.141460  | 0.940803  | -0.248741 |
| H  | 3.105270  | -0.732781 | -0.403298 |
1H-4H trans WATER

|  |  |  |  |
|---|---|---|---|
| N | -1.461952 | -0.203404 | -2.412550 |
| N | -0.262482 | -0.179328 | -1.739555 |
| C | -0.603798 | -0.047852 | -0.484959 |
| N | -1.984175 | 0.009971 | -0.349848 |
| C | -2.516628 | -0.089924 | -1.588769 |
| C | 0.235617 | 0.024648 | 0.689685 |
| N | 1.613059 | 0.071896 | 0.747535 |
| C | 1.900070 | 0.111614 | 2.090553 |
| N | 0.778354 | 0.087608 | 2.799909 |
| N | -0.265327 | 0.032708 | 1.904762 |
| N | 3.163534 | 0.255618 | 2.580052 |
| N | -3.802955 | -0.067361 | -1.917791 |
| N | 2.486059 | 0.151768 | -0.338473 |
| H | -2.483027 | 0.107190 | 0.527365 |
| H | -1.473585 | -0.302086 | -3.419036 |
| H | 3.918160 | -0.171368 | 2.057196 |
| H | 3.240759 | 0.117898 | 3.579900 |
| H | -4.093011 | -0.175626 | -2.879257 |
| H | -4.521253 | -0.007744 | -1.210812 |
| H | 3.084809 | 0.967858 | -0.234872 |
| H | 3.047770 | -0.694082 | -0.401036 |
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