# Supporting information for:

# New hydrogen-bond-aided supramolecular synthon: a case study of 2,4,6-trinitroaniline

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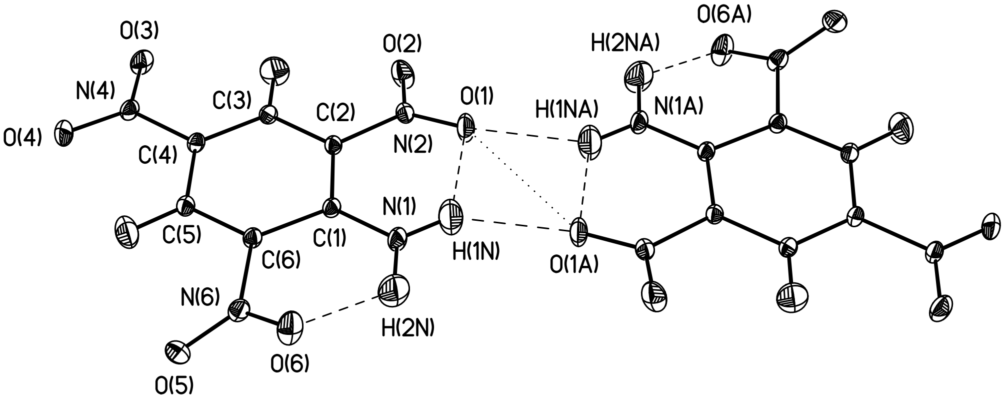

Figure S1: Numbering scheme of the TNA molecule and general view of centrisymmetric dimer in crystal

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# Multipole refinement

Refinement was performed in the following sequence:

1. Multipole populations $P_{lm}$ and expansion/contraction coefficients $\kappa$ and $\kappa'$ were constrained to be the same for chemically-equivalent atoms (the so-called "chemical constraints"). The highest possible symmetry constraints was imposed on $P_{lm}$ of particular molecular fragments: **mm2** for all heavy atoms except C(2) and C(6); **m** for C(2) and C(6). Multipole populations, monopole populations, $\kappa$, $\kappa'$ and coordinates together with ADPs were refined consecutively until full convergence. Scale factor was refined between each step with all data.

2. The same sequence of refinement steps was used but with the chemical constraints removed.

3. Refinement was performed without symmetry constraints on oxygen and nitrogen atoms, and constaints for **m** symmetry for carbon atoms.

4. All symmetry constraints were removed, multipole population were refined together with $\kappa'$ coefficient and monopole populations together with $\kappa$ coefficients.

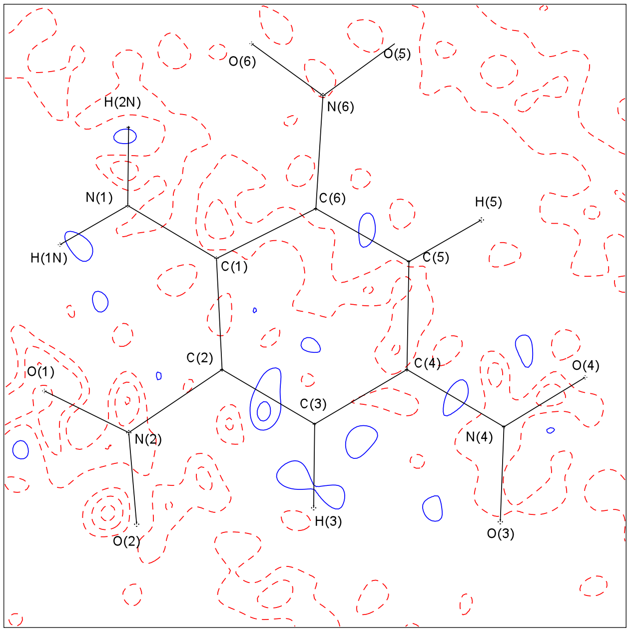

Figure S2: Residual electron density map in the average molecular plane for reflection data with $\sin\theta/\lambda \leq 0.904$ Å$^{-1}$. Contours step is 0.05 $e$Å$^{-3}$, positive countours are drawn with a solid blue line and negative with a dashed red line.

# Molecular geometry

Table S1: Bond lengths in TNA and its dimer

| | X-ray | B3LYP | | B3LYP-D3 | | MP2 | |
|---|---|---|---|---|---|---|---|
| | | mon | dim | mon | dim | mon | dim |
| O1-N2 | 1.2412(2) | 1.233 | 1.235 | 1.233 | 1.235 | 1.236 | 1.237 |
| O2-N2 | 1.2192(2) | 1.216 | 1.216 | 1.216 | 1.216 | 1.223 | 1.224 |
| O3-N4 | 1.2273(2) | 1.221 | 1.221 | 1.221 | 1.221 | 1.227 | 1.227 |
| O4-N4 | 1.2293(2) | 1.221 | 1.220 | 1.221 | 1.220 | 1.227 | 1.227 |
| O5-N6 | 1.2281(2) | 1.216 | 1.216 | 1.216 | 1.216 | 1.223 | 1.223 |
| O6-N6 | 1.2288(2) | 1.233 | 1.232 | 1.233 | 1.232 | 1.236 | 1.235 |
| N1-C1 | 1.3327(2) | 1.328 | 1.326 | 1.328 | 1.325 | 1.339 | 1.336 |
| N1-H1N | 1.010 | 1.009 | 1.009 | 1.009 | 1.009 | 1.009 | 1.009 |
| N1-H2N | 1.010 | 1.009 | 1.010 | 1.009 | 1.010 | 1.009 | 1.010 |
| N2-C2 | 1.4531(2) | 1.468 | 1.461 | 1.465 | 1.458 | 1.470 | 1.464 |
| N4-C4 | 1.4523(2) | 1.467 | 1.467 | 1.465 | 1.465 | 1.466 | 1.466 |
| N6-C6 | 1.4598(2) | 1.468 | 1.470 | 1.465 | 1.467 | 1.470 | 1.472 |
| C1-C2 | 1.4328(2) | 1.437 | 1.440 | 1.436 | 1.439 | 1.428 | 1.430 |
| C1-C6 | 1.4353(3) | 1.437 | 1.441 | 1.436 | 1.440 | 1.428 | 1.431 |
| C2-C3 | 1.3852(2) | 1.380 | 1.382 | 1.379 | 1.381 | 1.382 | 1.383 |
| C3-C4 | 1.3828(3) | 1.382 | 1.380 | 1.381 | 1.379 | 1.379 | 1.378 |
| C4-C5 | 1.3906(3) | 1.382 | 1.384 | 1.381 | 1.383 | 1.379 | 1.380 |
| C5-C6 | 1.3812(3) | 1.380 | 1.379 | 1.379 | 1.378 | 1.382 | 1.380 |
| O1...H1N | 1.900 | 1.854 | 1.904 | 1.850 | 1.905 | 1.850 | 1.897 |
| O6...H2N | 1.961 | 1.854 | 1.849 | 1.850 | 1.845 | 1.850 | 1.839 |

Bond lenghts from ab-initio methods that are longer by more than 0.01 Å compared to experimental values are highlighted blue, and shorter by more than 0.01 Å are highlithed red, except for H-bonds.

# CSD analysis

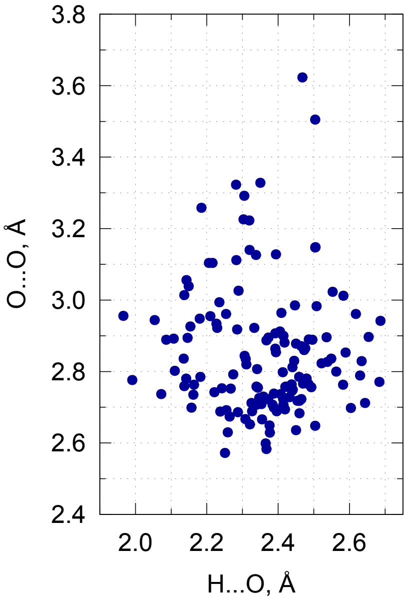

Figure S3: Plot of N-H...O vs. O...O distance in 135 crystal structures of 1-amino-2-nitrocompounds where H-bonded dimer is formed

# Charge density descriptors

Table S2: Topological characteristics of intramolecular bond critical points in TNA and its dimer. The first line is $\rho(\mathbf{r})$, e Å$^{-3}$, the second is $\nabla^2\rho(\mathbf{r})$, e Å$^{-5}$, and the third is ellepticity.

| | X-ray | | | B3LYP | | B3LYP-D3 | | MP2 | |
|---|---|---|---|---|---|---|---|---|---|
| | shade | isot | kap | mon | dim | mon | dim | mon | dim |
| O(1)-N(2) | **3.20** | **3.21** | **3.21** | **3.37** | **3.35** | **3.37** | **3.35** | **3.30** | **3.29** |
| | -5.5 | -5.5 | -5.5 | -28.0 | -27.8 | -28.0 | -27.9 | -26.1 | -26.1 |
| | 0.19 | 0.19 | 0.19 | 0.12 | 0.12 | 0.12 | 0.12 | 0.13 | 0.13 |
| O(2)-N(2) | **3.43** | **3.43** | **3.44** | **3.52** | **3.51** | **3.52** | **3.52** | **3.41** | **3.41** |
| | -10.8 | -10.6 | -10.6 | -30.7 | -30.6 | -30.7 | -30.7 | -27.8 | -27.7 |
| | 0.12 | 0.12 | 0.12 | 0.11 | 0.11 | 0.11 | 0.11 | 0.12 | 0.12 |
| O(3)-N(4) | **3.35** | **3.35** | **3.35** | **3.48** | **3.47** | **3.48** | **3.47** | **3.38** | **3.38** |
| | -10.8 | -10.8 | -10.7 | -29.9 | -29.8 | -29.9 | -29.8 | -27.3 | -27.3 |
| | 0.10 | 0.10 | 0.10 | 0.12 | 0.12 | 0.12 | 0.12 | 0.13 | 0.13 |
| O(4)-N(4) | **3.31** | **3.31** | **3.31** | **3.48** | **3.48** | **3.48** | **3.48** | **3.38** | **3.38** |
| | -7.5 | -7.6 | -7.4 | -29.9 | -29.9 | -29.9 | -29.9 | -27.3 | -27.3 |
| | 0.10 | 0.10 | 0.10 | 0.12 | 0.12 | 0.12 | 0.12 | 0.13 | 0.13 |
| O(5)-N(6) | **3.36** | **3.36** | **3.36** | **3.52** | **3.52** | **3.52** | **3.52** | **3.41** | **3.41** |
| | -11.0 | -10.9 | -10.8 | -30.7 | -30.7 | -30.7 | -30.7 | -27.8 | -27.8 |
| | 0.10 | 0.10 | 0.10 | 0.11 | 0.11 | 0.11 | 0.11 | 0.12 | 0.12 |
| O(6)-N(6) | **3.35** | **3.36** | **3.36** | **3.37** | **3.38** | **3.37** | **3.38** | **3.30** | **3.31** |
| | -8.9 | -9.1 | -8.7 | -28.0 | -28.1 | -28.0 | -28.2 | -26.1 | -26.1 |
| | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.13 | 0.13 |
| N(1)-C(1) | **2.37** | **2.37** | **2.37** | **2.39** | **2.40** | **2.39** | **2.41** | **2.30** | **2.32** |
| | -22.7 | -23.0 | -23.0 | -29.4 | -29.6 | -29.5 | -29.7 | -27.5 | -27.7 |
| | 0.22 | 0.22 | 0.22 | 0.17 | 0.18 | 0.17 | 0.17 | 0.17 | 0.18 |
| N(1)-H(1N) | **2.13** | **2.16** | **2.06** | **2.29** | **2.29** | **2.29** | **2.29** | **2.25** | **2.25** |
| | -27.3 | -28.1 | -27.2 | -47.7 | -48.5 | -47.8 | -48.8 | -48.8 | -49.4 |
| | 0.06 | 0.07 | 0.06 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |

Table S2: $\rho(\mathbf{r})$ characteristics in BCPs (continued)

| | shade | isot | kap | mon | dim | mon | dim | mon | dim |
|---|---|---|---|---|---|---|---|---|---|
| N(1)-H(2N) | **2.10** | **2.12** | **2.02** | **2.29** | **2.29** | **2.29** | **2.29** | **2.25** | **2.25** |
| | -28.1 | -28.8 | -28.1 | -47.7 | -47.8 | -47.8 | -47.9 | -48.8 | -48.7 |
| | 0.05 | 0.06 | 0.05 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| N(2)-C(2) | **1.80** | **1.81** | **1.80** | **1.79** | **1.81** | **1.80** | **1.82** | **1.78** | **1.79** |
| | -12.6 | -12.7 | -12.6 | -16.1 | -16.5 | -16.3 | -16.7 | -16.7 | -17.0 |
| | 0.27 | 0.26 | 0.27 | 0.21 | 0.22 | 0.21 | 0.22 | 0.15 | 0.16 |
| N(4)-C(4) | **1.80** | **1.80** | **1.79** | **1.81** | **1.81** | **1.82** | **1.82** | **1.81** | **1.82** |
| | -12.4 | -12.5 | -12.1 | -16.7 | -16.7 | -16.8 | -16.9 | -17.6 | -17.6 |
| | 0.20 | 0.20 | 0.20 | 0.17 | 0.17 | 0.17 | 0.17 | 0.12 | 0.13 |
| N(6)-C(6) | **1.82** | **1.83** | **1.82** | **1.79** | **1.78** | **1.80** | **1.79** | **1.78** | **1.78** |
| | -13.3 | -13.4 | -13.1 | -16.1 | -15.9 | -16.3 | -16.1 | -16.7 | -16.5 |
| | 0.20 | 0.20 | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 | 0.15 | 0.15 |
| C(1)-C(2) | **1.99** | **1.99** | **1.98** | **1.99** | **1.98** | **2.00** | **1.99** | **2.01** | **2.00** |
| | -15.8 | -15.7 | -15.6 | -20.1 | -19.9 | -20.2 | -20.0 | -20.6 | -20.4 |
| | 0.23 | 0.23 | 0.23 | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 |
| C(1)-C(6) | **1.97** | **1.97** | **1.96** | **1.99** | **1.98** | **2.00** | **1.99** | **2.01** | **2.00** |
| | -15.6 | -15.6 | -15.4 | -20.1 | -19.9 | -20.2 | -20.0 | -20.6 | -20.4 |
| | 0.21 | 0.21 | 0.21 | 0.21 | 0.20 | 0.21 | 0.20 | 0.21 | 0.20 |
| C(2)-C(3) | **2.19** | **2.19** | **2.19** | **2.21** | **2.20** | **2.21** | **2.21** | **2.18** | **2.18** |
| | -18.6 | -18.7 | -18.8 | -23.6 | -23.5 | -23.7 | -23.6 | -23.4 | -23.3 |
| | 0.24 | 0.24 | 0.25 | 0.23 | 0.22 | 0.23 | 0.22 | 0.22 | 0.22 |
| C(3)-C(4) | **2.17** | **2.17** | **2.17** | **2.21** | **2.22** | **2.21** | **2.22** | **2.20** | **2.21** |
| | -19.1 | -19.0 | -19.1 | -23.8 | -24.0 | -23.9 | -24.1 | -24.0 | -24.1 |
| | 0.23 | 0.22 | 0.23 | 0.20 | 0.21 | 0.20 | 0.21 | 0.20 | 0.21 |
| C(3)-H(3) | **1.88** | **1.93** | **1.85** | **1.99** | **1.99** | **1.99** | **1.99** | **1.95** | **1.95** |
| | -18.2 | -18.9 | -18.0 | -26.7 | -26.7 | -26.8 | -26.8 | -26.1 | -26.0 |
| | 0.03 | 0.04 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 |
| C(4)-C(5) | **2.16** | **2.16** | **2.16** | **2.21** | **2.20** | **2.21** | **2.20** | **2.20** | **2.20** |
| | -18.5 | -18.4 | -18.5 | -23.8 | -23.8 | -23.9 | -23.9 | -24.0 | -24.0 |
| | 0.23 | 0.23 | 0.23 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |

Table S2: $\rho(\mathbf{r})$ characteristics in BCPs (continued)

| | shade | isot | kap | mon | dim | mon | dim | mon | dim |
|---|---|---|---|---|---|---|---|---|---|
| C(5)-C(6) | **2.20** | **2.20** | **2.20** | **2.21** | **2.21** | **2.21** | **2.22** | **2.18** | **2.19** |
| | -18.5 | -18.6 | -18.7 | -23.6 | -23.7 | -23.7 | -23.8 | -23.4 | -23.4 |
| | 0.25 | 0.25 | 0.26 | 0.23 | 0.23 | 0.23 | 0.23 | 0.22 | 0.22 |
| C(5)-H(5) | **1.83** | **1.85** | **1.80** | **1.99** | **1.99** | **1.99** | **1.99** | **1.95** | **1.95** |
| | -17.0 | -17.5 | -16.9 | -26.7 | -26.8 | -26.8 | -26.8 | -26.1 | -26.1 |
| | 0.03 | 0.03 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 |
| H(1N)...O(1) | **0.20** | **0.19** | **0.20** | **0.24** | **0.21** | **0.24** | **0.21** | **0.24** | **0.22** |
| | 3.2 | 3.2 | 3.2 | 3.1 | 3.0 | 3.2 | 3.0 | 3.2 | 3.1 |
| | 0.04 | 0.12 | 0.04 | 0.02 | 0.04 | 0.02 | 0.04 | 0.03 | 0.06 |
| H(2N)...O(6) | **0.17** | **0.17** | **0.17** | **0.24** | **0.24** | **0.24** | **0.24** | **0.24** | **0.24** |
| | 2.8 | 2.7 | 2.8 | 3.1 | 3.1 | 3.2 | 3.2 | 3.2 | 3.3 |
| | 0.04 | 0.12 | 0.05 | 0.02 | 0.02 | 0.02 | 0.01 | 0.03 | 0.03 |

The following shorthands are used in Table S2:
**shade** — anisotropic model was used for hydrogen atoms, ADPs were calculated with SHADE server ;
**isot** — isotropic model with $U_{\mathrm{iso}} = 0.03$ Å$^{-1}$ was used for hydrogen atoms ;
**kap** — the same as *shade*, but with $\kappa = 1.16$ and $\kappa' = 1.0$ instead of the default XD2006 values of $\kappa = \kappa' = 1.2$.

Table S3: Integrated AIM charges of TNA

| | X-ray | | | B3LYP | | B3LYP-D3 | | MP2 | |
|---|---|---|---|---|---|---|---|---|---|
| | shade | isot | kap | mon | dim | mon | dim | mon | dim |
| O(1) | -0.424 | -0.426 | -0.398 | -0.505 | -0.530 | -0.505 | -0.532 | -0.493 | -0.517 |
| O(2) | -0.388 | -0.389 | -0.395 | -0.457 | -0.459 | -0.457 | -0.459 | -0.443 | -0.444 |
| O(3) | -0.376 | -0.374 | -0.364 | -0.471 | -0.471 | -0.471 | -0.471 | -0.458 | -0.459 |
| O(4) | -0.384 | -0.387 | -0.379 | -0.471 | -0.470 | -0.471 | -0.470 | -0.458 | -0.457 |
| O(5) | -0.390 | -0.392 | -0.383 | -0.457 | -0.457 | -0.457 | -0.457 | -0.443 | -0.443 |
| O(6) | -0.431 | -0.436 | -0.412 | -0.505 | -0.501 | -0.505 | -0.501 | -0.493 | -0.489 |
| N(1) | -1.127 | -1.096 | -1.232 | -1.183 | -1.180 | -1.185 | -1.183 | -1.286 | -1.283 |
| N(2) | 0.342 | 0.332 | 0.336 | 0.435 | 0.425 | 0.433 | 0.422 | 0.434 | 0.423 |
| N(4) | 0.355 | 0.350 | 0.355 | 0.446 | 0.446 | 0.444 | 0.444 | 0.437 | 0.436 |
| N(6) | 0.329 | 0.318 | 0.322 | 0.435 | 0.438 | 0.433 | 0.436 | 0.433 | 0.435 |
| C(1) | 0.526 | 0.506 | 0.526 | 0.589 | 0.599 | 0.591 | 0.602 | 0.611 | 0.622 |
| C(2) | 0.145 | 0.140 | 0.146 | 0.236 | 0.242 | 0.238 | 0.245 | 0.225 | 0.230 |
| C(3) | -0.104 | -0.030 | -0.156 | 0.053 | 0.052 | 0.053 | 0.052 | 0.037 | 0.037 |
| C(4) | 0.339 | 0.322 | 0.348 | 0.249 | 0.249 | 0.250 | 0.251 | 0.241 | 0.242 |
| C(5) | -0.094 | -0.023 | -0.140 | 0.053 | 0.053 | 0.053 | 0.053 | 0.037 | 0.038 |
| C(6) | 0.148 | 0.145 | 0.144 | 0.236 | 0.233 | 0.238 | 0.235 | 0.225 | 0.222 |
| H(1N) | 0.507 | 0.510 | 0.543 | 0.493 | 0.504 | 0.494 | 0.506 | 0.520 | 0.531 |
| H(2N) | 0.538 | 0.537 | 0.577 | 0.493 | 0.494 | 0.494 | 0.495 | 0.520 | 0.521 |
| H(3) | 0.248 | 0.194 | 0.288 | 0.166 | 0.165 | 0.166 | 0.165 | 0.177 | 0.176 |
| H(5) | 0.248 | 0.208 | 0.283 | 0.166 | 0.167 | 0.166 | 0.167 | 0.177 | 0.179 |
| Tolal | 0.007 | 0.007 | 0.007 | 0.001 | 0.000 | 0.001 | -0.001 | 0.001 | -0.003 |

The following shorthands are used:

**shade** — anisotropic model was used for hydrogen atoms, ADPs were calculated with SHADE server;

**isot** — isotropic model with $U_{\mathrm{iso}} = 0.03$ Å$^{-1}$ was used for hydrogen atoms;

**kap** — the same as *shade*, but with $\kappa = 1.16$ and $\kappa' = 1.0$ instead of the default XD2006 values of $\kappa = \kappa' = 1.2$.

Total values given at the bottom indicate the so-called “charge leakage” due to the inaccuracy in determination of atomic bassin boundaries.

Table S4: The difference of AIM atomic charges in the monomer and the dimer of TNA, data of ab-initio calculations

| | B3LYP | B3LYP-D3 | MP2 |
|---|---|---|---|
| O(1) | -0.025 | -0.027 | -0.024 |
| O(2) | -0.002 | -0.002 | -0.001 |
| O(3) | 0.000 | 0.000 | -0.001 |
| O(4) | 0.001 | 0.001 | 0.001 |
| O(5) | 0.000 | 0.000 | 0.000 |
| O(6) | 0.004 | 0.004 | 0.004 |
| N(1) | 0.002 | 0.002 | 0.002 |
| N(2) | -0.010 | -0.010 | -0.011 |
| N(4) | -0.001 | -0.001 | -0.001 |
| N(6) | 0.003 | 0.003 | 0.002 |
| C(1) | 0.010 | 0.011 | 0.011 |
| C(2) | 0.006 | 0.007 | 0.005 |
| C(3) | 0.000 | -0.001 | 0.000 |
| C(4) | 0.001 | 0.001 | 0.001 |
| C(5) | 0.000 | 0.000 | 0.000 |
| C(6) | -0.003 | -0.003 | -0.003 |
| H(1N) | 0.010 | 0.012 | 0.011 |
| H(2N) | 0.001 | 0.001 | 0.001 |
| H(3) | -0.001 | -0.001 | -0.001 |
| H(5) | 0.001 | 0.001 | 0.001 |

Values are calculated as $\Delta q = q_{dim} - q_{mon}$, difference higher than 0.01 a.u. are highlighted blue (q is higher in dimer) and red (q is higher in isolated molecule).

Table S5: The difference of scaled AIM atomic energies (in kcal/mol) in the monomer and the dimer of TNA. Values given with small font for B3LYP-D3 calculation indicate energy variations due to conformational change. Neative values correspond to stabilization in dimer

| | B3LYP | B3LYP-D3 | | MP2 |
|---|---|---|---|---|
| O(1) | -8.68 | -11.42 | 2.16 | -12.01 |
| O(2) | 0.31 | 0.56 | 0.19 | 1.33 |
| O(3) | 0.03 | 0.05 | -0.28 | -0.08 |
| O(4) | 0.13 | 0.20 | -0.67 | 0.17 |
| O(5) | -0.34 | -0.19 | -0.54 | -0.34 |
| O(6) | -0.17 | -0.09 | -1.72 | 0.18 |
| N(1) | -2.15 | -3.26 | -3.45 | -2.45 |
| N(2) | -5.46 | -5.86 | -6.32 | -5.51 |
| N(4) | -0.23 | -0.16 | -0.60 | -0.43 |
| N(6) | 1.60 | 1.86 | 1.52 | 1.41 |
| C(1) | 7.39 | 8.06 | 9.17 | 7.58 |
| C(2) | 4.54 | 5.00 | 4.64 | 4.36 |
| C(3) | -1.05 | -0.75 | -1.15 | -0.34 |
| C(4) | -0.67 | -0.35 | -0.90 | -0.05 |
| C(5) | -0.52 | -0.41 | -0.37 | -0.39 |
| C(6) | -0.07 | -0.05 | 0.20 | -0.03 |
| H(1N) | 3.52 | 3.91 | -0.40 | 3.58 |
| H(2N) | 0.11 | -0.03 | -1.13 | 0.04 |
| H(3) | -0.32 | -0.30 | 0.07 | -0.29 |
| H(5) | 0.23 | 0.29 | 0.00 | 0.29 |

Energy difference is calculated as from scaled electronic energy, $K_{scaled} = (1 + \mathrm{V/T}) \cdot K$, where V/T is a *molecular* virial ratio and $K$ is the value of the kinetic energy integrated over an atomic basin. The use of $K_{scaled}$ is reasonable as the difference of the virial ratio of systems is negligible (see Table S6).

Values given with small font for B3LYP-D3 calculation are obtained from K values of an isolated TNA molecule in dimer geometry. Differencies higher by magnitude than 1.0 kcal/mol are highlited blue (negative, stabilization in dimer) and red (positive, destabilization in dimer).

Table S6: Molecular virial values (V/T) in calculations of TNA

| | monomer | dimer | $\Delta \cdot 10^6$ |
|---|---|---|---|
| B3LYP | -2.0042385826 | -2.0042400178 | -1.4352 |
| B3LYP-D3 | -2.0042438104 | -2.0042421022 | 1.7082 |
| MP2 | -2.0003549948 | -2.0003554532 | -0.4584 |

Table S7: Symmetry-independent bonding intermolecular contacts in crystal of the TNA

| Atom 1 | Atom 2 | $R_{ij}$, Å | $R_{ij} - \sum vdW_{ij}$, Å | $\rho(\mathbf{r})$, $e\text{Å}^{-3}$ | $\nabla^2\rho(\mathbf{r})$, $e\text{Å}^{-5}$ | $E_{cont}$, kcal/mol |
|---|---|---|---|---|---|---|
| O(3) | H(2N) | 2.198 | -0.522 | 0.076 | 1.46 | -2.60 |
| O(1) | H(1N) | 2.180 | -0.540 | 0.070 | 1.46 | -2.45 |
| O(6) | H(3) | 2.417 | -0.303 | 0.057 | 0.96 | -1.67 |
| O(1) | O(1) | 2.820 | -0.220 | 0.053 | 0.98 | -1.61 |
| O(4) | H(3) | 2.483 | -0.237 | 0.057 | 0.87 | -1.58 |
| O(5) | O(5) | 2.864 | -0.176 | 0.052 | 0.93 | -1.54 |
| O(2) | C(4) | 2.957 | -0.263 | 0.055 | 0.87 | -1.52 |
| O(5) | N(6) | 3.000 | -0.070 | 0.050 | 0.75 | -1.32 |
| O(5) | H(5) | 2.418 | -0.302 | 0.039 | 0.83 | -1.23 |
| C(5) | C(6) | 3.113 | -0.107 | 0.049 | 0.65 | -1.21 |
| O(3) | O(6) | 3.068 | 0.028 | 0.036 | 0.63 | -0.96 |
| O(2) | O(3) | 3.175 | 0.135 | 0.037 | 0.58 | -0.93 |
| N(1) | C(1) | 3.348 | 0.098 | 0.035 | 0.45 | -0.76 |
| O(1) | C(6) | 3.253 | 0.033 | 0.034 | 0.45 | -0.75 |
| O(4) | C(2) | 3.355 | 0.135 | 0.029 | 0.41 | -0.65 |
| O(4) | O(6) | 3.241 | 0.201 | 0.022 | 0.39 | -0.55 |
| O(3) | H(5) | 2.819 | 0.099 | 0.022 | 0.36 | -0.51 |
| O(3) | O(5) | 3.527 | 0.487 | 0.011 | 0.20 | -0.26 |

Data correspond to the refinement with ADPs on hydrogen atoms and $\kappa = \kappa' = 1.2$

Only independent contacts (e.g. one from O1...C1A and C1...O1A) are shown.

Intermolecular contacts are sorted by energy calculated with Espinosa-Mollins-Lecomte correlation$^{\#1}$

$$E_{cont} = k \cdot v(\mathbf{r});\ k = -0.5a_0^3$$

where $v(\mathbf{r})$ is a potential energy density in CP(3,-1) of the contact and $a_0$ is the Bohr radius. As $v(\mathbf{r})$ is not directly avaliable from multipole refinement data, it is calculated with the so-called gradient expansion$^{\#2}$

$$v(\mathbf{r}) = -\frac{3}{5}(3\pi^2)^{\frac{2}{3}}\rho(\mathbf{r})^{\frac{5}{3}} - \frac{1}{36}\frac{[\nabla\rho(\mathbf{r})]^2}{\rho(\mathbf{r})} - \frac{1}{12}\nabla^2\rho(\mathbf{r})$$

#1 E. Espinosa et al. Chem. Phys. Lett., 1998, 285, 170;
E. Espinosa et al., Chem. Phys. Lett., 1999, 300, 745

#2 D. Kirzhnits et al., Sov. Phys. Usp., 1975, 18, 649

Table S8: Atomic coordiantes (Å) of the optimized TNA molecule from B3LYP-D3/def2-TZVP calculation

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.0000000000 | 2.5973126731 | 2.4034195416 |
| O | 8.0 | 0.0000000000 | -2.5973126731 | 2.4034195416 |
| O | 8.0 | 0.0000000000 | 3.5089327079 | 0.4503379591 |
| O | 8.0 | 0.0000000000 | -3.5089327079 | 0.4503379591 |
| O | 8.0 | 0.0000000000 | 1.0841056179 | -3.5444173625 |
| O | 8.0 | 0.0000000000 | -1.0841056179 | -3.5444173625 |
| N | 7.0 | 0.0000000000 | 0.0000000000 | 2.6452361940 |
| N | 7.0 | 0.0000000000 | 2.5308198518 | 1.1724029916 |
| N | 7.0 | 0.0000000000 | -2.5308198518 | 1.1724029916 |
| N | 7.0 | 0.0000000000 | 0.0000000000 | -2.9837796797 |
| C | 6.0 | 0.0000000000 | 0.0000000000 | 1.3176495945 |
| C | 6.0 | 0.0000000000 | 1.2083099481 | 0.5417007071 |
| C | 6.0 | 0.0000000000 | -1.2083099481 | 0.5417007071 |
| C | 6.0 | 0.0000000000 | 1.2016478786 | -0.8374631173 |
| C | 6.0 | 0.0000000000 | -1.2016478786 | -0.8374631173 |
| C | 6.0 | 0.0000000000 | 0.0000000000 | -1.5187755257 |
| H | 1.0 | 0.0000000000 | 0.8914139798 | 3.1179818448 |
| H | 1.0 | 0.0000000000 | -0.8914139798 | 3.1179818448 |
| H | 1.0 | 0.0000000000 | 2.1361373456 | -1.3755863430 |
| H | 1.0 | 0.0000000000 | -2.1361373456 | -1.3755863430 |

Table S9: Atomic coordiantes (Å) of the optimized TNA dimer from B3LYP-D3/def2-TZVP calculation

| | | | | |
|---|---|---|---|---|
| O | 8.0 | 0.9829445973 | 0.9755740939 | 0.0000000000 |
| O | 8.0 | -0.9829445973 | -0.9755740939 | 0.0000000000 |
| O | 8.0 | 2.1770814665 | 2.7698133069 | 0.0000000000 |
| O | 8.0 | -2.1770814665 | -2.7698133069 | 0.0000000000 |
| O | 8.0 | 6.8468098550 | 2.7554415800 | 0.0000000000 |
| O | 8.0 | -6.8468098550 | -2.7554415800 | 0.0000000000 |
| O | 8.0 | 7.9672335732 | 0.8989519053 | 0.0000000000 |
| O | 8.0 | -7.9672335732 | -0.8989519053 | 0.0000000000 |
| O | 8.0 | 5.8119898523 | -3.2368470024 | 0.0000000000 |
| O | 8.0 | -5.8119898523 | 3.2368470024 | 0.0000000000 |
| O | 8.0 | 3.6708126671 | -3.4788913456 | 0.0000000000 |
| O | 8.0 | -3.6708126671 | 3.4788913456 | 0.0000000000 |
| N | 7.0 | 2.1130180489 | -1.3849140395 | 0.0000000000 |
| N | 7.0 | -2.1130180489 | 1.3849140395 | 0.0000000000 |
| N | 7.0 | 2.0714617862 | 1.5583085973 | 0.0000000000 |
| N | 7.0 | -2.0714617862 | -1.5583085973 | 0.0000000000 |
| N | 7.0 | 6.9273204586 | 1.5375113304 | 0.0000000000 |
| N | 7.0 | -6.9273204586 | -1.5375113304 | 0.0000000000 |
| N | 7.0 | 4.6852482198 | -2.7799962253 | 0.0000000000 |
| N | 7.0 | -4.6852482198 | 2.7799962253 | 0.0000000000 |
| C | 6.0 | 3.2404283552 | -0.6893779135 | 0.0000000000 |
| C | 6.0 | -3.2404283552 | 0.6893779135 | 0.0000000000 |
| C | 6.0 | 3.2846140084 | 0.7492672917 | 0.0000000000 |
| C | 6.0 | -3.2846140084 | -0.7492672917 | 0.0000000000 |
| C | 6.0 | 4.4709612379 | 1.4560642952 | 0.0000000000 |
| C | 6.0 | -4.4709612379 | -1.4560642952 | 0.0000000000 |
| C | 6.0 | 5.6734772369 | 0.7805737959 | 0.0000000000 |
| C | 6.0 | -5.6734772369 | -0.7805737959 | 0.0000000000 |
| C | 6.0 | 5.7096707207 | -0.6016862556 | 0.0000000000 |
| C | 6.0 | -5.7096707207 | 0.6016862556 | 0.0000000000 |
| C | 6.0 | 4.5342770067 | -1.3203538862 | 0.0000000000 |
| C | 6.0 | -4.5342770067 | 1.3203538862 | 0.0000000000 |
| H | 1.0 | 1.2226579522 | -0.9109963343 | 0.0000000000 |
| H | 1.0 | -1.2226579522 | 0.9109963343 | 0.0000000000 |
| H | 1.0 | 2.1830225952 | -2.3921383707 | 0.0000000000 |
| H | 1.0 | -2.1830225952 | 2.3921383707 | 0.0000000000 |
| H | 1.0 | 4.4503344367 | 2.5342391856 | 0.0000000000 |
| H | 1.0 | -4.4503344367 | -2.5342391856 | 0.0000000000 |
| H | 1.0 | 6.6536204996 | -1.1232042869 | 0.0000000000 |
| H | 1.0 | -6.6536204996 | 1.1232042869 | 0.0000000000 |

We have performed a single-point B3LYP-D3/def2-TZVP calculation of the dimer with another configuration (figure Figure S4 below), in which TNA molecules were displaced to prevent the oxygen atom O(1) from H-bonding. The parameters of the O...O interactions (O...O 2.775 Å, -N=O...O 155.3°) were approximately the same as in the dimer discussed in the paper (O...O 2.770 Å, -N=O...O 163.3°). This was made to dismiss all doubts about the bonding nature and the reliability of O...O interaction energy estimated from EML correlation. Only one BCP corresponding to the bonding O...O interaction was found in the intermolecular space. The energy of this interaction from EML correlation is equal to 2.1 kcal/mol (compare with 2.3 kcal/mol in the dimer concerned in the paper); the value calculated from the energy difference between the TNA dimer and two monomers is equal to 1.8 kcal/mol.

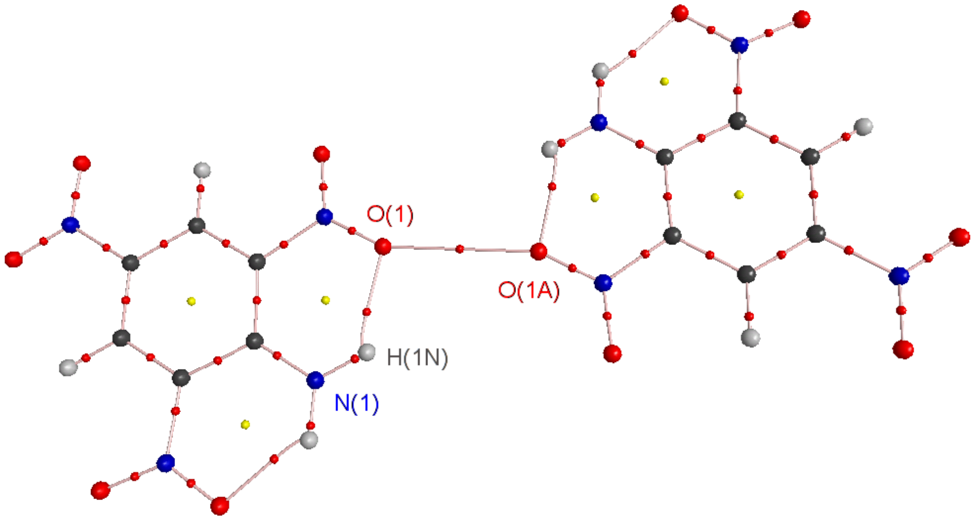

Figure S4: Tested confuguration of TNA molecules connected only by O...O bond