Supplementary Materials for

Full-nitro-nitroamino cooperative action: Climbing the energy peak of benzenes with enhanced chemical stability

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The PDF file includes:

Sections S1 to S9
Figs. S1 to S21
Tables S1 to S17
Scheme S1 and S2
Legends for CIF files
References

Other Supplementary Material for this manuscript includes the following:

CIF files
Section S1. Failed direct nitration and single crystal preparation

The details of failed direct nitration and single crystal preparation of compounds in this study are provided in this section.

Section S1.1 Failed direct nitration
The direct nitration of TATB failed in the following nitration systems:
TATB (400 mg) was slowly added in the mixture H$_2$SO$_4$ (3 mL) and HNO$_3$ (1 mL) at -10 °C, which was then stirred at -10 to 0 °C for another 2 h. The reaction system was poured into ice water, the precipitate was filtered to get the starting material TATB. For the nitration systems Ac$_2$O/HNO$_3$, CH$_3$COOH/HNO$_3$, and TFA/HNO$_3$, the amounts and experimental steps were the same as the above H$_2$SO$_4$/HNO$_3$ system. The precipitates were turned out to be the starting material TATB.

Section S1.2 Single crystal preparation
**Compound 1:** The crystal of 1 suitable for single-crystal XRD was obtained from slow evaporation of its acetonitrile solution at room temperature;
**TNTNB:** The crystal of TNTNB suitable for single-crystal XRD was obtained in situ from the reaction system in the refrigerator at -20 °C;
**TNTNB·5H$_2$O·EtOH:** The crystal of TNTNB·5H$_2$O·EtOH suitable for single-crystal XRD was obtained through slow evaporation of its ethanol solution in air;
**TNTNB·2H$_2$O:** The crystal of TNTNB·2H$_2$O suitable for single-crystal XRD was obtained from the cooling crystallization of its chlorofrom solution;
**Salt 3:** The crystal of 3 suitable for single-crystal XRD was obtained from slow evaporation of its methanol solution at room temperature;
**Salt 4:** The crystal of 4 suitable for single-crystal XRD was obtained from slow evaporation of its methanol solution at room temperature.
Section S2. Spectrum Analysis

$^1$H, $^{13}$C NMR, $^{15}$N NMR, mass, and IR spectra of compounds in this study are provided in this section.
Fig. S1. $^1$H and $^{13}$C NMR of compounds in this work. (A) $^1$H and $^{13}$C NMR of compound 1; (B) $^1$H and $^{13}$C NMR of TNTNB; (C) $^1$H and $^{13}$C NMR of salt 3; (D) $^1$H and $^{13}$C NMR of salt 4.
Fig. S2. $^{15}$N NMR of compounds in this work. (A) $^{15}$N NMR of compound TNTNB in MeOD-d$_4$, δ 357.00, 348.34, 180.74 ppm; (B) $^{15}$N NMR of salt 3 in DMSO-d$_6$, δ 368.21, 364.11, 239.39, 22.16 ppm; (C) $^{15}$N NMR of salt 4 in DMSO-d$_6$, δ 369.24, 364.61, 240.25, 49.24 ppm.

Fig. S3. Mass spectrum of TNTNB.
Fig. S4. IR spectra of compounds in this work. (A) IR spectrum of compound 1; (B) IR spectrum of TNTNB; (C) IR spectrum of salt 3; (D) IR spectrum of salt 4.
Section S3. X-ray crystallography details

Crystallographic data, bond lengths, bond angles, and hydrogen bonds of compounds in this study are provided in this section.
| Compound            | TNTNB | TNTNB·5H₂O·EtOH | TNTNB·2H₂O |
|---------------------|-------|----------------|------------|
| Formula             | C₆H₃N₉O₁₂ | C₆H₃N₉O₁₂·5H₂O·C₂H₅OH | C₆H₃N₉O₁₂·2H₂O |
| Mw                  | 393.17 | 529.32         | 429.21     |
| Crystal system      | Monoclinic | Triclinic | Orthorhombic |
| Space group         | P2₁/c  | P-1            | P2ac2ab    |
| a [Å]               | 10.8254(17) | 11.3859(16) | 6.0676(5) |
| b [Å]               | 7.0752(11) | 12.8408(19) | 11.1609(9) |
| c [Å]               | 17.673(3) | 16.841(2)     | 22.1885(16) |
| α[°]                | 90      | 93.665(5)     | 90         |
| β[°]                | 104.747(5) | 109.509(5) | 90         |
| γ[°]                | 90      | 104.939(5)    | 90         |
| V [Å³]              | 1309(4) | 2211.8(5)     | 1502.6(2)  |
| Z                   | 4       | 4              | 4          |
| T [K]               | 173     | 150            | 153        |
| λ [Å]               | 0.71073 | 1.34139       | 0.71073    |
| Pcalcd [g cm⁻³]     | 1.995   | 1.590          | 1.897      |
| μ [mm⁻¹]            | 0.195   | 0.893          | 0.188      |
| F(000)              | 792     | 1096           | 872        |
| θ range[°]          | 2.38-27.09 | 3.66-52.98 | 2.59-25.52 |
| Index ranges        | -14 ≤ h ≤ 13 | -13 ≤ h ≤ 13 | -7 ≤ h ≤ 7 |
|                     | -9 ≤ k ≤ 9   | -15 ≤ k ≤ 15  | -12 ≤ k ≤ 14 |
|                     | -22 ≤ l ≤ 20 | -20 ≤ l ≤ 20  | -28 ≤ l ≤ 24 |
| Data/restraints/parameters | 2991/0/244 | 7734/14/652 | 3429/4/268 |
| GOF on F2           | 1.027   | 1.151          | 1.037      |
| R[F²> 2σ(F²)]       | 0.0463  | 0.0910         | 0.0426     |
| wR(F²)              | 0.1063  | 0.2408         | 0.0853     |
| Compound | 1 | 3·3H₂O | 4·H₂O |
|----------|-----------------|-----------------|-----------------|
| Formula  | C₁₂H₁₂N₆O₉     | C₆H₁₈N₁₂O₁₅    | C₆H₁₇N₁₅O₁₃    |
| Mw       | 384.28          | 498.32          | 507.35          |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | P-1    | P-1          | P-1            |
| a [Å]    | 8.341(5)        | 9.4159(19)      | 10.7758(14)     |
| b [Å]    | 9.879(6)        | 10.208(2)       | 13.1812(18)     |
| c [Å]    | 11.002(7)       | 10.950(2)       | 14.3688(19)     |
| α[°]     | 75.806(14)      | 72.909(3)       | 90.074(4)       |
| β[°]     | 68.235(14)      | 83.273(3)       | 107.040(4)      |
| γ[°]     | 78.927(14)      | 80.560(3)       | 103.732(4)      |
| V [Å³]   | 811.1(9)        | 948.9(5)        | 1890.0(4)       |
| Z        | 2               | 2              | 4               |
| T [K]    | 296             | 196            | 150             |
| λ [Å]    | 0.71073         | 0.71073        | 1.34139         |
| d(calcd) [g cm⁻³] | 1.573        | 1.672          | 1.783          |
| μ [mm⁻¹] | 0.137            | 0.162          | 0.956          |
| F(000)   | 396             | 516            | 1048            |
| θ range[°] | 2.65-23.10    | 2.44-27.13     | 3.96-53.16     |
| Index ranges | -9 ≤ h ≤ 9   | -11 ≤ h ≤ 12  | -12 ≤ h ≤ 12  |
|           | -11 ≤ k ≤ 11  | -12 ≤ k ≤ 13  | -15 ≤ k ≤ 15  |
|           | -13 ≤ l ≤ 13  | -14 ≤ l ≤ 13  | -17 ≤ l ≤ 17  |
| Data/restraints/parameters | 2872/0/247 | 4439/9/298 | 6623/421/664 |
| GOF on F2 | 0.992          | 1.100          | 1.053          |
| R[F²>2σ(F²)] | 0.0486     | 0.0493        | 0.0569         |
| wR(F²)    | 0.1434         | 0.1618         | 0.1672         |
Table S3. Bond lengths (Å) and bond angles (°) for TNTNB.

| Bond lengths          | C1 C6 1.387(3) | C5 N7 1.474(3) | N5 N6 1.372(2) |
|-----------------------|----------------|----------------|-----------------|
| C1 C2 1.400(3)        | C6 N8 1.408(3) | N5 H5 0.8800   |                 |
| C1 N1 1.471(3)        | N1 O1 1.212(2) | N6 O8 1.214(2) |                 |
| C2 C3 1.395(3)        | N1 O2 1.223(2) | N6 O7 1.223(2) |                 |
| C2 N2 1.405(3)        | N2 N3 1.378(2) | N7 O9 1.213(2) |                 |
| C3 C4 1.399(3)        | N2 H2 0.8800  | N7 O10 1.216(2)|                 |
| C3 N4 1.473(3)        | N3 O3 1.215(2) | N8 N9 1.361(3) |                 |
| C4 C5 1.389(3)        | N3 O4 1.228(2) | N8 H8 0.8800   |                 |
| C4 N5 1.408(3)        | N4 O5 1.217(2) | N9 O12 1.216(2)|                 |
| C5 C6 1.389(3)        | N4 O6 1.229(2) | N9 O11 1.217(2)|                 |

| Bond angles           | C6 C1 C2 122.88(19) | C1 C6 C5 117.75(18) | N6 N5 C4 121.26(17) |
|-----------------------|----------------------|----------------------|----------------------|
| C6 C1 N1 117.49(18)  | C1 C6 N8 121.09(19)  | N6 N5 H5 119.4       | C4 N5 H5 119.4       |
| C2 C1 N1 119.63(18)  | C5 C6 N8 121.15(19)  | C4 N5 H5 119.4       |                     |
| C3 C2 C1 116.81(19)  | O1 N1 O2 125.61(19)  | O8 N6 O7 127.22(19)  |                     |
| C3 C2 N2 122.95(18)  | O1 N1 C1 118.43(19)  | O8 N6 N5 115.66(18)  |                     |
| C1 C2 N2 120.18(19)  | O2 N1 C1 115.94(18)  | O7 N6 N5 117.11(18)  |                     |
| C2 C3 C4 122.45(19)  | N3 N2 C2 120.87(17)  | O9 N7 O10 125.4(2)   |                     |
| C2 C3 N4 119.06(18)  | N3 N2 H2 119.6       | O9 N7 C5 118.08(18)  |                     |
| C4 C3 N4 118.49(18)  | C2 N2 H2 119.6       | O10 N7 C5 116.54(19) |                     |
| C5 C4 C3 117.75(19)  | O3 N3 O4 126.33(18)  | N9 N8 C6 118.85(17)  |                     |
| C5 C4 N5 118.20(19)  | O3 N3 N2 116.40(19)  | N9 N8 H8 120.6       |                     |
| C3 C4 N5 124.04(18)  | O4 N3 N2 117.27(18)  | C6 N8 H8 120.6       |                     |
| C4 C5 C6 122.29(19)  | O5 N4 O6 125.99(18)  | O12 N9 O11 127.0(2)  |                     |
| C4 C5 N7 118.93(19)  | O5 N4 C3 117.37(18)  | O12 N9 N8 116.25(18) |                     |
| C6 C5 N7 118.70(18)  | O6 N4 C3 116.64(18)  | O11 N9 N8 116.75(18) |                     |
Table S4. Bond lengths (Å) and bond angles (°) for TNTNB·5H₂O·EtOH.

| Bond lengths          | Bond angles          |
|-----------------------|----------------------|
| O1 N2 1.295(4)        | H13D O13 H13E 109.4  |
| O2 N3 1.247(5)        | H19A O19 H19B 104.5  |
| O3 N5 1.223(5)        | O8 N1 N4 123.6(3)    |
| O4 N7 1.230(4)        | O8 N1 O7 117.9(4)    |
| O5 N6 1.226(5)        | N14 N1 O7 118.5(4)   |
| O6 N2 1.262(5)        | O6 N2 N4 124.8(3)    |
| O7 N1 1.296(4)        | O6 N2 O1 118.2(4)    |
| O8 N1 1.265(5)        | N4 N2 O1 117.0(4)    |
| O9 N6 1.253(5)        | O2 N3 O12 120.2(4)   |
| O10 N10 1.238(5)      | O2 N3 N5 123.6(3)    |
| O11 N8 1.249(5)       | O12 N3 N5 116.2(4)   |
| O12 N3 1.256(4)       | H26A O26 H26B 104.5  |
| O23 N8 1.250(5)       | N2 N4 C10 112.8(4)   |
| O30 H30B 0.8700       | N2 N4 H4 123.6       |
| O31 H31A 0.8700       | N3 N5 H5 121.6       |
| O31 H31B 0.8699       | O15 N6 O5 124.0(3)   |
| O32 C14 1.438(7)      | C10 C1 C4 122.9(3)   |
| O32 H32 0.8400        | C10 C1 N6 118.0(3)   |
|                       | C4 C1 N6 118.6(4)    |
|                       | C5 C2 C6 118.1(4)    |
|                       | C5 C2 N14 119.8(3)   |
|                       | C6 C2 N14 121.5(4)   |
|                       | C8 C3 N5 115.2(4)    |
|                       | C8 C3 C6 115.6(4)    |
|                       | N5 C3 C6 129.0(4)    |
| C1 C10 1.397(6)       | C1 C4 1.400(5)       |
| C2 C5 1.396(6)        | C2 C6 1.397(6)       |
| C2 C6 1.397(6)        | C3 C8 1.390(6)       |
| C3 C6 1.404(5)        | C4 C7 1.399(6)       |
| C5 C11 1.397(6)       | C7 C12 1.388(6)      |
| C8 C11 1.400(6)       | C9 C10 1.401(6)      |
| C9 C12 1.403(6)       | C13 C14 1.477(8)     |
| C13 H13A 0.9800       | O2W H2WB 0.8700      |
| O3W H3WA 0.9586       | O3W H3WB 0.8700      |
| N17 C4 C7 116.4(3)    | N17 C4 C1 127.7(3)   |
| C7 C4 C1 115.5(4)     | C2 C5 C11 123.1(4)   |
| C2 C5 N15 117.7(3)    | C11 C5 N15 118.9(4)  |
| C2 C6 C3 122.3(4)     | C1 C4 C7 116.9(3)    |
| C2 C6 N7 117.1(3)     | C2 C5 N8 123.7(4)    |
| O16 N7 C6 116.9(3)    | O4 N7 C6 118.7(4)    |
| O11 N8 O23 120.7(4)   | O11 N8 C13 123.2(3)  |
| O11 N8 O23 120.7(4)   | O11 N8 C13 122.3(3)  |
| O4 N7 C6 118.7(4)     | O23 N8 N13 117.0(4)  |
| O11 N8 O23 120.7(4)   | O27 N9 O21 124.6(4)  |
| C5 C11 C8 115.0(4)    | O10 N10 O17 120.2(4) |
| C7 C12 N13 116.5(4)   | O10 N10 O17 120.2(4) |
| C7 C12 N13 116.5(4)   | C7 C12 N13 116.5(4)  |
| C7 C12 N9 112.0(4)    | C14 C13 H13B 109.5   |
| C14 C13 H13B 109.5    | H13A C13 H13B 109.5  |
| H13B C13 H13C 109.5   | C14 C13 H13C 109.5   |
| H13B C13 H13C 109.5   | C13 C2S H2SA 106.5   |
| C13 C2S H2SA 106.5    | C13 C2S H2SA 106.5   |
| C13 C2S H2SA 106.5    | C13 C2S H2SB 106.5   |
| C13 C2S H2SB 106.5    | C13 C2S H2SB 106.5   |
| C13 C2S H2SB 106.5    | C2S O1S H1S 109.5    |
| C2S O1S H1S 109.5     | H2WA O2W H2WB 104.5  |
| H2WA O2W H2WB 104.5   | H3WA O3W H3WB 104.5  |
### Table S5. Bond lengths (Å) and bond angles (°) for TNTNB·2H₂O.

| Bond lengths | Bond angles |
|--------------|-------------|
| C1 C6 1.390(5) | N3 O4 1.208(3) N7 H7 0.8800 |
| C1 C2 1.393(5) | N3 O3 1.222(3) N8 O9 1.229(4) |
| C1 N1 1.409(4) | N4 N5 1.378(4) N8 O10 1.230(4) |
| C2 C3 1.396(4) | N4 H4 0.8800 N9 O12 1.216(3) |
| C2 N3 1.465(4) | N5 O5 1.219(4) N9 O11 1.230(3) |
| C3 C4 1.396(4) | N5 O6 1.225(3) O13 H13A 0.87(2) |
| C3 N4 1.398(4) | N6 O8 1.215(3) O13 H13B 0.84(2) |
| C4 C5 1.389(4) | N6 O7 1.223(3) O14 H14A 0.8700 |
| C4 N6 1.479(4) | N7 N8 1.358(4) O14 H14B 0.8700 |
| C5 C6 1.398(4) | N2 O1 1.220(4) N1 N2 1.355(4) |
| C5 N7 1.419(4) | N2 O2 1.232(4) N1 H1 0.8800 |
| C6 N9 1.471(4) | N2 O1 1.220(4) N1 N2 1.355(4) |

C6 C1 C2 117.4(3) N2 N1 H1 118.8 O5 N5 N4 117.0(3)
C6 C1 N1 125.1(3) C1 N1 H1 118.8 O6 N5 N4 115.7(3)
C2 C1 N1 117.4(3) O1 N2 O2 126.7(3) O8 N6 O7 124.9(3)
C1 C2 C3 123.8(3) O1 N2 N1 118.8(3) O8 N6 C4 116.6(3)
C1 C2 N3 118.2(3) O2 N2 N1 114.5(3) O7 N6 C4 118.5(3)
C3 C2 N3 118.0(3) O4 N3 O3 125.5(3) N8 N7 C5 118.1(3)
C4 C3 C2 115.9(3) O4 N3 C2 116.6(3) N8 N7 H7 121.0
C4 C3 N4 123.6(3) O3 N3 C2 118.0(3) C5 N7 H7 121.0
C2 C3 N4 120.4(3) N5 N4 C3 120.7(3) O9 N8 O10 126.0(3)
C5 C4 C3 122.6(3) N5 N4 H4 119.6 O9 N8 N7 116.1(3)
C5 C4 N6 117.9(3) C3 N4 H4 119.6 O10 N8 N7 117.9(3)
C3 C4 N6 119.5(3) O5 N5 O6 127.4(3) O12 N9 O11 125.3(3)
C4 C5 C6 118.4(3) O12 N9 C6 117.7(3) C5 C6 N9 119.1(3)
C4 C5 N7 118.0(3) O11 N9 C6 116.9(3) N2 N1 C1 122.5(3)
C6 C5 N7 123.5(3) H13A O13 H13B 108(3) H14A O14 H14B 104.5
C1 C6 C5 121.4(3) C1 C6 N9 119.5(3)
Table S6. Bond lengths (Å) and bond angles (°) for 1.

| Bond lengths       | Bond angles       |
|--------------------|-------------------|
| C1 C2 1.383(3)     | C2 C1 C6 116.3(2) |
| C1 C6 1.388(3)     | C2 C1 N1 119.6(2) |
| C1 N1 1.404(3)     | C6 C1 N1 124.2(2) |
| C2 C3 1.390(3)     | C1 C2 C3 124.0(2) |
| C2 N2 1.466(3)     | C1 C2 N2 117.8(2) |
| C3 C4 1.388(3)     | C3 C2 N2 118.1(2) |
| C3 N3 1.411(3)     | C4 C3 C2 116.9(2) |
| C4 C5 1.397(3)     | C4 C3 N3 123.7(2) |
| C4 N4 1.459(3)     | C2 C3 N3 119.3(2) |
| C5 C6 1.388(3)     | C3 C4 C5 122.2(2) |
| C5 N5 1.413(3)     | C3 C4 N4 118.7(2) |
| C6 N6 1.468(3)     | C5 C4 N4 119.2(2) |
| C7 O1 1.213(3)     | C6 C5 C4 117.4(2) |
| C7 N1 1.366(3)     | C7 C8 1.492(4)    |
| C8 O1 1.214(3)     | C9 O4 1.214(3)    |
| C9 N3 1.365(3)     | C9 N3 1.365(3)    |
| C10 O4 1.491(4)    | C10 O4 1.491(4)   |
| C11 O7 1.219(3)    | C11 O7 1.219(3)   |
| C11 N5 1.354(3)    | C11 N5 1.354(3)   |
| C11 C12 1.488(4)   | C11 C12 1.488(4)  |
| N2 O2 1.196(3)     | N2 O2 1.196(3)    |
| N2 O3 1.198(3)     | N2 O3 1.198(3)    |
| N4 O5 1.218(3)     | N4 O5 1.218(3)    |
| N4 O6 1.221(3)     | N4 O6 1.221(3)    |
| N6 O8 1.209(2)     | N6 O8 1.209(2)    |
| C7 N1 C1 123.3(2)  | C7 N1 C1 123.3(2) |
| C7 N1 C1 123.3(2)  | C7 N1 C1 123.3(2) |
| O2 N2 O3 124.2(3)  | O2 N2 O3 124.2(3) |
| O2 N2 C2 118.5(2)  | O2 N2 C2 118.5(2) |
| O3 N2 C2 117.3(2)  | O3 N2 C2 117.3(2) |
| C9 N3 C3 120.46(19)| C9 N3 C3 120.46(19)|
| O5 N4 O6 125.3(2)  | O5 N4 O6 125.3(2) |
| O5 N4 C4 116.8(2)  | O5 N4 C4 116.8(2) |
| O6 N4 C4 117.8(2)  | O6 N4 C4 117.8(2) |
| C11 N5 C5 122.5(2) | C11 N5 C5 122.5(2) |
| O8 N6 O9 125.8(2)  | O8 N6 O9 125.8(2) |
| O8 N6 C6 117.6(2)  | O8 N6 C6 117.6(2) |
| O9 N6 C6 116.6(2)  | O9 N6 C6 116.6(2) |
Table S7. Bond lengths (Å) and bond angles (°) for 3·3H₂O.

| Bond lengths                  |   | Bond angles                  |   |
|-------------------------------|---|-------------------------------|---|
| O1 N1 1.260(2)                |   | O11 N8 O12 123.85(17)        |   |
| O2 N1 1.283(2)                |   | H12 N12 H12B 110.9           |   |
| O3 N2 1.222(2)                |   | H12A N12 H12D 107.6          |   |
| O4 N2 1.224(2)                |   | O11 N9 O12 118.06(16)        |   |
| O5 N4 1.257(2)                |   | N3 C2 C3 116.48(15)          |   |
| O6 N4 1.250(2)                |   | N1 C9 O12 114.67(15)         |   |
| O7 N5 1.210(2)                |   | H10C N10 H10B 92.9           |   |
| O8 N5 1.211(2)                |   | N3 C2 C10 128.35(16)         |   |
| O9 N7 1.264(2)                |   | C3 C2 C10 115.06(15)         |   |
| O10 N7 1.252(2)               |   | C4 C3 C2 125.80(15)          |   |
| O11 N8 1.225(2)               |   | O10 N9 O12 107.0             |   |
| O12 N8 1.227(2)               |   | C4 C3 C2 115.38(15)          |   |
| O13 H13A 0.8564               |   | N4 C2 C10 118.31(15)         |   |
| O13 H13B 0.8758               |   | C12 C9 C10 112.81(15)        |   |
| O14 H14B 0.8856               |   | O11 N9 O12 106.0             |   |
|                               |   | C12 C9 N9 120.70(15)         |   |
|                               |   | O6 N4 C3 123.93(16)          |   |
|                               |   | C10 N9 H11B 103.0            |   |
|                               |   | O5 N4 C3 115.68(16)          |   |
|                               |   | H11C N11 H11A 118.8          |   |
|                               |   | O7 N5 C3 117.33(15)          |   |
|                               |   | H11C N11 H11A 119.2          |   |
|                               |   | O8 N5 C3 118.20(16)          |   |
|                               |   | H11B N11 H11A 96.4           |   |
|                               |   | N7 N6 C4 115.84(15)          |   |
|                               |   | H12C N12 H12B 118.1          |   |
|                               |   | O10 N7 O9 120.40(17)         |   |
|                               |   | H12C N12 H12A 115.6          |   |
|                               |   | O10 N7 N6 123.30(16)         |   |
|                               |   | H12B N12 H12A 100.3          |   |
|                               |   | O9 N7 N6 116.30(18)          |   |
|                               |   | C4 C3 C5 117.28(15)          |   |

Bond lengths (Å):
- O1 N1: 1.260(2)
- O2 N1: 1.283(2)
- O3 N2: 1.222(2)
- O4 N2: 1.224(2)
- O5 N4: 1.257(2)
- O6 N4: 1.250(2)
- O7 N5: 1.210(2)
- O8 N5: 1.211(2)
- O9 N7: 1.264(2)
- O10 N7: 1.252(2)
- O11 N8: 1.225(2)
- O12 N8: 1.227(2)
- O13 H13A: 0.8564
- O13 H13B: 0.8758
- O14 H14B: 0.8856

Bond angles (°):
- H13A O13 H13B: 105.6
Table S8. Bond lengths (Å) and bond angles (°) for 4·H₂O.

| Bond lengths | Bond angles |
|--------------|-------------|
| C1 N1 N2 1.438(4) | N2 H2B 0.9100 |
| C2 C3 1.402(3) | N1 H1B 0.9100 |
| C2 N3 1.458(3) | N1 H1C 0.9100 |
| C3 C4 1.388(3) | N2 H2A 0.9100 |
| C3 N4 1.394(3) | N2 H2C 0.9100 |
| N5 O9 1.252(3) | O2 H2A 0.9386 |
| N6 O4 1.213(3) | N2 H2B 0.9100 |
| N6 O10 1.223(3) | N1 H1B 0.9100 |
| N8 O11 1.258(3) | N2 H2C 0.9100 |
| N9 O6 1.221(3) | N1 H1B 0.9100 |
| N9 O12 1.235(3) | N1 H1C 0.9100 |
| C1 C6 1.393(3) | N2 H2C 0.9100 |
| C2 N3 1.459(3) | N1 H1C 0.9100 |
| C3 C4 1.389(3) | N2 H2C 0.9100 |
| C3 N4 1.389(3) | N1 H1C 0.9100 |
| C4 C5 1.395(3) | N1 H1C 0.9100 |
| C4 N6 1.471(3) | N2 H2B 0.9100 |

| Bond lengths | Bond angles |
|--------------|-------------|
| C6 C1 C2 118.2(2) | N7 C5 C4 115.2(2) |
| C6 C1 N1 121.0(2) | N7 C5 C6 129.5(2) |
| C2 C1 N1 119.6(2) | C4 C5 C6 114.9(2) |
| C3 C2 C1 122.8(2) | C1 C6 C5 122.6(2) |
| C3 C2 N3 118.9(2) | C1 C6 N9 117.7(2) |
| C1 C2 N3 118.0(2) | C5 C6 N9 119.5(2) |
| C4 C3 N4 115.1(2) | N2 N1 C1 112.64(19) |
| C4 C3 C2 114.5(2) | O1 N2 O7 119.1(2) |
| N4 C3 C2 130.0(2) | O1 N2 N1 123.4(2) |
| O4 N6 O10 124.5(2) | O7 N2 N1 117.5(2) |
| O4 N6 C4 117.6(2) | O2 N3 O8 123.6(2) |
| O10 N6 C4 117.9(2) | O2 N3 C2 118.8(2) |
| N8 N7 C5 118.0(2) | O8 N3 C2 117.6(2) |
| O11 N8 N7 115.3(2) | N5 N4 C3 118.4(2) |
| O12 N9 C6 116.8(2) | H2A N2 H2B 109.5 |
| C6 C1 C2 118.8(2) | N2 H2C 109.5 |
| C6 C1 N1 119.4(2) | H2A N2 H2C 109.5 |
| C2 C1 N1 120.7(2) | H2B N2 H2C 109.5 |
| C1 C2 C3 121.8(2) | N2 H2A 109.5 |
| C4 C3 N4 115.5(2) | H1A H1C 109.5 |
| C3 C4 C5 126.5(2) | N2 H1C 109.5 |
| C3 C4 N6 117.51(19) | H1A H1C 109.5 |
| C5 C4 N6 116.0(2) | H1B H1C 109.5 |
Table S9. Hydrogen bonds for TNTNB.

|        | D-H\cdot\cdot\cdot A | D-H Å | H\cdot\cdot\cdot A Å | D\cdot\cdot\cdot A Å | D-H\cdot\cdot\cdot A ° |
|--------|------------------------|--------|-----------------------|----------------------|------------------------|
| N(2)-H(2)...O(8)#1 | 0.88 | 0.88 | 2.30 | 3.031(2) | 140.5 |
| N(2)-H(2)...O(11)#2 | 0.88 | 0.88 | 2.29 | 2.845(2) | 120.9 |
| N(5)-H(5)...O(6)#3 | 0.88 | 0.88 | 2.20 | 2.933(2) | 140.1 |
| N(8)-H(8)...O(2)#4 | 0.88 | 0.88 | 2.34 | 2.997(2) | 131.9 |
| N(8)-H(8)...O(7)#5 | 0.88 | 0.88 | 2.44 | 3.113(2) | 133.5 |

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z-1/2  #2 x,y-1,z  #3 -x+1,y+1/2,-z+3/2
#4 -x+2,-y+1,-z+1  #5 -x+2,y+1/2,-z+3/2
### Table S10. Hydrogen bonds for TNTNB·5H₂O·EtOH.

| D-H···A     | D-H/Å | H···A/Å | D···A/Å | D-H···A/° |
|-------------|-------|---------|---------|-----------|
| O(3W)-H(3WB)...O(18)#1 | 0.87  | 2.61    | 3.09(18)| 116.5     |
| O(3W)-H(3WB)...O(17)    | 0.87  | 2.64    | 3.49(15)| 168.5     |
| O(2W)-H(2WB)...O(2W)#2 | 0.87  | 2.32    | 2.80(16)| 115.3     |
| O(2W)-H(2WA)...O(25)#3 | 0.87  | 2.64    | 3.39(9) | 145.2     |
| O(1S)-H(1S)...O(26)#4  | 0.84  | 2.04    | 2.82(6) | 155.5     |
| O(1W)-H(1WB)...O(2)    | 0.87  | 2.13    | 2.85(4) | 140.1     |
| O(1W)-H(1WA)...O(1)    | 0.87  | 2.03    | 2.85(4) | 159.3     |
| O(33)-H(33A)...O(23)   | 0.87  | 2.56    | 3.15(5) | 126.0     |
| O(32)-H(32)...O(31)    | 0.84  | 2.29    | 3.09(5) | 159.6     |
| N(18)-H(18)...O(23)    | 0.88  | 2.38    | 3.09(4) | 138.2     |
| N(18)-H(18)...O(25)    | 0.88  | 2.57    | 3.06(5) | 116.6     |
| O(31)-H(31B)...O(26)   | 0.87  | 1.98    | 2.85(4) | 176.4     |
| O(31)-H(31A)...O(19)#5 | 0.87  | 1.95    | 2.81(4) | 172.9     |
| O(30)-H(30B)...O(15)#4 | 0.87  | 2.35    | 3.21(4) | 171.9     |
| O(30)-H(30A)...O(7)    | 0.87  | 2.14    | 2.88(3) | 142.5     |
| O(29)-H(29B)...N(1)    | 0.87  | 2.67    | 3.47(4) | 153.2     |
| O(29)-H(29B)...O(7)    | 0.87  | 2.00    | 2.83(4) | 160.4     |
| O(29)-H(29A)...O(22)#6 | 0.87  | 2.58    | 3.01(4) | 111.2     |
| O(29)-H(29A)...O(12)#6 | 0.87  | 2.56    | 3.04(4) | 116.1     |
| O(28)-H(28B)...O(28)#3 | 0.87  | 2.44    | 2.87(6) | 110.9     |
| O(28)-H(28A)...O(31)#5 | 0.87  | 2.08    | 2.94(7) | 175.7     |
| N(17)-H(17)...O(28)#3  | 0.88  | 2.24    | 2.88(5) | 130.0     |
| N(13)-H(13)...O(33)    | 0.88  | 2.17    | 2.88(5) | 137.9     |
| N(5)-H(5)...O(32)#7    | 0.88  | 2.60    | 3.22(5) | 128.4     |
| O(26)-H(26B)...O(1)    | 0.87  | 1.93    | 2.76(5) | 159.4     |
| O(26)-H(26A)...O(33)#8 | 0.87  | 2.37    | 2.82(5) | 112.7     |
| O(19)-H(19B)...N(1)#5  | 0.87  | 2.56    | 3.32(5) | 146.6     |
| O(19)-H(19B)...O(8)#5  | 0.87  | 2.19    | 2.87(4) | 134.9     |
| O(19)-H(19B)...O(7)#5  | 0.87  | 2.31    | 3.09(5) | 149.4     |
| O(19)-H(19A)...N(10)   | 0.87  | 2.57    | 3.40(4) | 161.4     |
| O(19)-H(19A)...O(17)   | 0.87  | 1.98    | 2.81(4) | 161.0     |
| O(13)-H(13E)...O(19)#5 | 0.87  | 2.12    | 2.93(4) | 156.5     |
| O(13)-H(13D)...O(1)    | 0.87  | 2.17    | 2.88(4) | 139.5     |
| O(3W)-H(3WB)...O(18)#1 | 0.87  | 2.61    | 3.09(18)| 116.5     |

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z    #2 -x+2,-y,-z+1   #3 -x+1,-y,-z+1   #4 x-1,y,z   #5 -x+1,-y+1,-z+1
#6 -x+1,-y+1,-z+2   #7 x,y-1,z   #8 x,y+1,z
Table S11. Hydrogen bonds for TNTNB·2H₂O.

| D-H⋯A | D-H/Å | H⋯A/Å | D⋯A/Å  | D-H⋯A/°  |
|--------|--------|--------|--------|--------|
| N(1)-H(1)...O(14)#1 | 0.88  | 1.89  | 2.722(4) | 156.6 |
| N(4)-H(4)...O(13)   | 0.88  | 1.99  | 2.844(4) | 163.6 |
| N(7)-H(7)...O(4)#2  | 0.88  | 2.31  | 2.917(3) | 126.0 |
| N(7)-H(7)...O(13)#2 | 0.88  | 2.12  | 2.846(4) | 139.8 |
| O(13)-H(13A)...O(14)#3 | 0.87(2) | 1.91(2) | 2.770(4) | 173(4) |
| O(13)-H(13B)...O(9)#4 | 0.84(2) | 2.32(3) | 3.026(4) | 141(3) |
| O(14)-H(14A)...O(10)#5 | 0.87  | 2.41  | 2.926(3) | 118.8 |
| O(14)-H(14A)...O(11)#6 | 0.87  | 2.13  | 2.966(3) | 159.7 |
| O(14)-H(14B)...O(2)#7 | 0.87  | 2.17  | 2.927(4) | 145.1 |
| O(14)-H(14B)...O(6)#8 | 0.87  | 2.47  | 3.038(3) | 123.2 |
| N(1)-H(1)...O(14)#1 | 0.88  | 1.89  | 2.722(4) | 156.6 |
| N(4)-H(4)...O(13)   | 0.88  | 1.99  | 2.844(4) | 163.6 |
| N(7)-H(7)...O(4)#2  | 0.88  | 2.31  | 2.917(3) | 126.0 |
| N(7)-H(7)...O(13)#2 | 0.88  | 2.12  | 2.846(4) | 139.8 |

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z   #2 -x+1,y-1/2,-z+1/2   #3 -x+1,y+1/2,-z+1/2
#4 -x+1/2,-y+1,z-1/2   #5 x+1/2,-y+1/2,-z+1   #6 x-1/2,-y+1/2,-z+1
#7 x-1,y-1,z   #8 -x,y-1/2,-z+1/2
| D-H···A     | D-H/Å | H···A/Å | D···A/Å | D-H···A/° |
|------------|-------|---------|---------|---------|
| N(12)-H(12D)...N(4) | 0.99  | 2.54    | 3.436(3) | 149.9   |
| N(12)-H(12D)...N(3)  | 0.99  | 1.94    | 2.929(2) | 179.1   |
| N(12)-H(12D)...O(5)  | 0.99  | 2.38    | 3.013(3) | 121.0   |
| N(12)-H(12A)...N(9)#1 | 0.81  | 2.48    | 3.031(3) | 126.1   |
| N(12)-H(12A)...O(2)#1 | 0.81  | 2.31    | 3.115(3) | 178.2   |
| N(12)-H(12B)...O(12)#2 | 0.79  | 2.33    | 3.097(2) | 164.0   |
| N(12)-H(12B)...O(10)#2 | 0.79  | 2.60    | 3.081(2) | 120.9   |
| N(10)-H(10A)...O(3)#1 | 0.92  | 2.63    | 3.151(3) | 116.1   |
| N(10)-H(10A)...O(2)#1 | 0.92  | 2.19    | 3.063(3) | 157.0   |
| N(10)-H(10C)...O(8)#3 | 0.80  | 2.54    | 3.174(3) | 137.1   |
| N(10)-H(10C)...O(6)#4 | 0.80  | 2.64    | 3.123(3) | 120.3   |
| O(14)-H(14A)...O(1)  | 0.85  | 2.00    | 2.834(2) | 165.8   |
| O(14)-H(14B)...N(2)#5 | 0.89  | 2.66    | 3.463(2) | 151.7   |
| O(14)-H(14B)...O(4)#5 | 0.89  | 2.05    | 2.932(2) | 173.9   |
| N(11)-H(11A)...O(14) | 0.87  | 1.91    | 2.752(2) | 162.1   |
| N(11)-H(11B)...O(9)#6 | 0.89  | 2.06    | 2.938(3) | 168.6   |
| N(11)-H(11C)...N(4)#7 | 0.87  | 2.62    | 3.479(2) | 169.1   |
| N(11)-H(11C)...O(6)#7 | 0.87  | 2.17    | 2.985(2) | 156.3   |
| N(11)-H(11C)...O(5)#7 | 0.87  | 2.38    | 3.129(3) | 144.1   |
| N(11)-H(11D)...O(2)#8 | 0.82  | 2.08    | 2.866(2) | 160.5   |
| N(12)-H(12D)...N(4)  | 0.99  | 2.54    | 3.436(3) | 149.9   |
| N(12)-H(12D)...N(3)  | 0.99  | 1.94    | 2.929(2) | 179.1   |
| N(12)-H(12D)...O(5)  | 0.99  | 2.38    | 3.013(3) | 121.0   |
| N(12)-H(12A)...N(9)#1 | 0.81  | 2.48    | 3.031(3) | 126.1   |
| N(12)-H(12A)...O(2)#1 | 0.81  | 2.31    | 3.115(3) | 178.2   |
| N(12)-H(12B)...O(12)#2 | 0.79  | 2.33    | 3.097(2) | 164.0   |
| N(12)-H(12B)...O(10)#2 | 0.79  | 2.60    | 3.081(2) | 120.9   |
| N(10)-H(10A)...O(3)#3 | 0.92  | 2.63    | 3.151(3) | 116.1   |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1  #2 x,y,z+1  #3 -x,-y+2,-z+1
#4 x,y+1,z  #5 -x+1,-y,-z+1  #6 x,y-1,z  #7 x,y,z-1
#8 -x+1,-y,-z
Section S4. Chemical stability

The chemical stability details of TNTNB with water, acids, and bases are provided in this section.

Section S4.1 Water stability
TNTNB exhibits better water stability than HNB, the results have been discussed in the main article, TNTNB can coexist with water in the forms of TNTNB·5H2O·EtOH and TNTNB·2H2O. The crystal structures of both hydrates have been shown in the main article. In addition, $^{13}$C NMR of TNTNB in 50%CD$_3$OD+50%H$_2$O and D$_2$O were respectively tested. As can be seen in Fig. S5, two obvious singles can be observed, which indicates there is no decomposition happened when TNTNB meets water.

In addition, TNTNB was dissolved in CD$_3$OD aqueous solution and monitored over time. $^{13}$C NMR spectroscopy (Fig. S6) indicated that TNTNB remained intact even after one month.

Section S4.2 Acid stability
HPLC-MS and $^{13}$C NMR were used to prove that there is no reaction happened between TNTNB and halogen acids (HCl, HBr, and HI) at room temperature. HCl (g), HBr (g) and HI (g) were respectively added into the methanol solution of TNTNB. According to HPLC-MS results (Fig. S7, S8, S9, S10), it was found that the peak time of the liquid chromatography of the reaction solution and the peak signal of the mass spectrum are consistent with the spectrum of TNTNB, indicating TNTNB is stable with halogen acids (HCl, HBr, and HI).

In addition, the reaction products of TNTNB and halogen acids were also test by $^{13}$C NMR. TNTNB (about 100 mg) was dissolved in CD$_3$OD-d4 (0.5 mL), HCl (g), HBr (g) and HI (g) were respectively added into the CD$_3$OD solution of TNTNB. The results are shown Fig. S11, the $^{13}$C NMR peak of TNTNB did not change when meeting halogen acids, thus indicating its stability with halogen acids.

Section S4.3 Base stability
The stability of TNTNB with bases has been discussed in the main article. TNTNB can react with bases (NH$_3$·H$_2$O and N$_2$H$_4$·H$_2$O) to generate ionic salts without the decomposition of the benzene skeleton and the loss of the nitro groups. The structures of these salts were fully characterized.
Fig. S5. $^{13}$C NMR of TNTNB in 50%CD$_3$OD+50%H$_2$O and D$_2$O.

Fig. S6. $^{13}$C NMR of TNTNB in CD$_3$OD-d$_4$ for one month.
Fig. S7. HPLC-MS results of TNTNB.

Fig. S8. HPLC-MS results of TNTNB and HCl.
Fig. S9. HPLC-MS results of TNTNB and HBr.

Fig. S10. HPLC-MS results of TNTNB and HI.
Fig. S11. $^{13}$C NMR of TNTNB, TNTNB-HCl, TNTNB-HBr, and TNTNB-HI, respectively.
Section S5. Theoretical simulations on the reactivities of HNB and TNTNB toward water

The calculation details of the theoretical simulations on the reactivities of HNB and TNTNB toward water are provided in this section.

The reactivities of HNB and TNTNB toward water were studied by means of DLPNO-CCSD(T) at the cc-PVDZ level using the ORCA program. In the calculated reaction process, several isomeric structures were found to be minima on the potential energy surface. In addition, some other structures were characterized as transition states for the interconversion among the located minima. Geometries for these, obtained after energy minimization procedures, are shown in the following reaction processes (Fig. S12, S13, and S14).

Section 5.1 The reaction process of HNB and H$_2$O
The reaction process for HNB and H$_2$O is shown in Fig. S12. The hydrolysis starts after a nucleophilic attack of water on the C atom of benzene (1). The C atom expands two substituents, and the benzene ring forms a seven-substituted structure (2). The next step is followed by the intramolecular proton transfer from the water (3) toward the neighboring nitro group (4). In the last step, intermolecular proton transfer occurs from the neighboring nitro group to the departing nitro group, which yields the hydrolysis product 5 and HNO$_2$.

Section 5.2 The reaction process of TNTNB and H$_2$O
For TNTNB, we investigated two possible reaction routes of H$_2$O to nitroamino and nitro groups, respectively.

Route 1: (H$_2$O to C-NHNO$_2$):
Route 1 shown in Fig. S13 is similar to the process of the reaction of HNB and H$_2$O. The hydrolysis starts after a nucleophilic attack of water on the C atom connected nitroamino group (6). The C atom expands two substituents, and the benzene ring forms a seven-substituted structure (7). The next step is followed by the intramolecular proton transfer from the water (8) toward the neighboring nitro group (9). In the last step, intermolecular proton transfer occurs from the neighboring nitro group to the departing nitroamino group, which yields the hydrolysis product 10 and NH$_2$NO$_2$.

Route 2: (H$_2$O to C-NO$_2$):
Route 2 shown in Fig. S14 is different from route 1. The hydrolysis starts after a nucleophilic attack of water on the C atom connected nitro group (11). The C atom expands two substituents, and the benzene ring forms a seven-substituted structure (12). The next step is the transfer of intramolecular protons from water (13) to the oxygen atom on the neighboring nitroamino groups (14). Then, intermolecular proton transfer from the nitrogen of the adjacent nitroamino group (15) to the leaving nitro group (16). In the last step, intramolecular transfer of protons from the O atom of the nitroamino group to the N atom, which yields the hydrolysis product 17 and HNO$_2$.

Section 5.3 Energy analysis for the reaction of HNB and TNTNB to H$_2$O
With the proposed reaction process, the energy changes of these structures were calculated and shown in Table S13. The energy barriers of these reactions were also provided in Fig. S15, S16, and S17, the results indicated that the Gibbs free energies of TNTNB reacting with water are 44.45 kcal mol$^{-1}$ for route 1 and 39.36 kcal mol$^{-1}$ for route 2, which are both significantly higher.
than that of HNB (26.63 kcal mol\(^{-1}\)), thus further confirming the higher water stability of TNTNB.
Fig. S12. Geometries for products 1-5 of H$_2$O/HNB obtained with energy minimization procedures by means of DLPNO-CCSD(T) at cc-PVDZ level using ORCA program.

Fig. S13. Geometries for products 6-10 of H$_2$O/TNTNB (Route 1: H$_2$O to C-NHNO$_2$) obtained with energy minimization procedures by means of DLPNO-CCSD(T) at cc-PVDZ level using ORCA program.
Fig. S14. Geometries for products 11-17 of H₂O/TNTNB (Route 2: H₂O to C-NO₂) obtained with energy minimization procedures by means of DLPNO-CCSD(T) at cc-PVDZ level using ORCA program.
Table S13. Calculated (TightDLPNO-CCSD(T)-F12/cc-pVDZ-F12) total energy (E), zero-point energy (ZPE), values of the correction (E(Corr)), and relative energy (E(Rel)) for these structures.

| Pieces          | E        | ZPE     | E(Corr)  | E(Rel)  |
|-----------------|----------|---------|----------|---------|
|                 | a.u.     | a.u.    | a.u.     | kcal mol\(^{-1}\) |
| HNB+H\(_2\)O   | -1533.75437 | 0.137024 | -1533.617342 | 0.00       |
| 1               | -1533.76755 | 0.139007 | -1533.628546 | -7.03      |
| 2               | -1533.72757 | 0.14147  | -1533.586101 | 19.60      |
| 3               | -1533.75042 | 0.143762 | -1533.606656 | 6.70       |
| 4               | -1533.73103 | 0.137907 | -1533.593125 | 15.20      |
| 5               | -1533.80418 | 0.141019 | -1533.663162 | -28.75     |
| TNTNB+H\(_2\)O-route-1 | -1699.60184 | 0.18981  | -1699.412033 | 0.00       |
| 6               | -1699.61458 | 0.19247  | -1699.422112 | -6.33      |
| 7               | -1699.54371 | 0.192257 | -1699.351448 | 38.02      |
| 8               | -1699.57035 | 0.196208 | -1699.374138 | 23.78      |
| 9               | -1699.55951 | 0.192308 | -1699.367203 | 28.13      |
| 10              | -1699.62528 | 0.195481 | -1699.429797 | -11.15     |
| TNTNB+H\(_2\)O-route-2 | -1699.60184 | 0.18981  | -1699.412033 | 0.00       |
| 11              | -1699.61892 | 0.19356  | -1699.425355 | -8.36      |
| 12              | -1699.55399 | 0.191355 | -1699.36263  | 31.00      |
| 13              | -1699.55273 | 0.191156 | -1699.361569 | 31.66      |
| 14              | -1699.55295 | 0.193092 | -1699.359854 | 32.74      |
| 15              | -1699.53755 | 0.19149  | -1699.34606  | 41.40      |
| 16              | -1699.61496 | 0.192745 | -1699.42221  | -6.39      |
| 17              | -1699.65893 | 0.193394 | -1699.465534 | -33.57     |
Fig. S15. The energy changes of the reaction process of HNB and H$_2$O.

Fig. S16. The energy changes of the reaction process of TNTNB and H$_2$O (route 1).

Fig. S17. The energy changes of the reaction process of TNTNB and H$_2$O (route 2).
Section S6. Heat of formation

The calculation details of heat of formation are provided in this section.

The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1). The enthalpy of reaction is obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction ($H_{corr}$), and other thermal factors (Table S14). The solid-state heats of formation were calculated with Trouton’s rule according to the following equation (T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition):

$$\Delta H_{sub} = 188 / \text{J mol}^{-1} \cdot \text{K}^{-1} \cdot T$$

For energetic salts, the solid-phase heat of formation is calculated on basis of a Born-Haber energy cycle (Scheme S2). The number is simplified by equation 1:

$$\Delta H_{f}(\text{salt, 298 K}) = \Delta H_{f}(\text{cation, 298K}) + \Delta H_{f}(\text{anion, 298K}) - \Delta H_L$$  \hspace{1cm} (1)

in which $\Delta H_L$ can be predicted by using the formula suggested by Jenkins, etal.(equation 2):

$$\Delta H_L = U_{pot} + [p(nM/2 - 2) + q(nX/2 - 2)]RT$$  \hspace{1cm} (2)

In this equation, $n_M$ and $n_X$ depend on the nature of the ions $M^+$ and $X_q^-$, respectively. The equation for lattice potential energy $U_{pot}$(equation 3) has the form:

$$U_{POT} [\text{kJ mol}^{-1}] = \gamma (\rho_m/M_m)^{1/3} + \delta$$  \hspace{1cm} (3)

where $\rho_m$ [g cm$^{-3}$] is the density of the salt, $M_m$ is the chemical formula mass of the ionic material, and values for $\gamma$ and the coefficients $\gamma$ (kJmol$^{-1}$cm) and $\delta$ (kJmol$^{-1}$) are assigned literature values.

The gas state heat of formation of TNTNB is 456.15 kJ mol$^{-1}$, and its solid state heat of formation is $456.15 - 0.188 \cdot (273+65) = 392.61$ kJ mol$^{-1}$ (Table S15).

The gas state heat of formation of HNB is 176.12 kJ mol$^{-1}$, and its solid state heat of formation is $176.12 - 0.188 \cdot (273+258) = 76.29$ kJ mol$^{-1}$.
Scheme S1. Isodesmic reactions for calculating heats of formation for TNTNB, its anion (TNTNB$^{3-}$), and HNB, respectively.

Table S14. Calculated Total Energy ($E_0$), Zero Point Energy (ZPE) and values of Thermal Correction ($H_{corr}$) of the compounds.

| Compound   | ZPE/a.u.  | $H_{corr}$/a.u. | $E_0$/a.u.    |
|------------|-----------|-----------------|---------------|
| TNTNB      | 0.166062  | 0.186304        | -1621.715559  |
| TNTNB$^{3-}$| 0.123723  | 0.147274        | -1620.00445   |
| HNB        | 0.111460  | 0.130390        | -1456.1091563 |
| CH$_4$     | 0.044793  | 0.048605        | -40.3796224   |
| NH$_3$     | 0.034252  | 0.03807         | -56.544652    |
| Benzene    | 0.100437  | 0.105785        | -231.584238   |
| NH$_2$NO$_2$ | 0.038103  | 0.042549        | -260.4883392  |
| CH$_3$NH$_2$ | 0.064027  | 0.067452        | -95.5938501   |
| CH$_3$NO$_2$ | 0.049842  | 0.05513         | -244.4784832  |
Scheme S2. Born–Haber Cycle for the formation of energetic salts.

|        | TNTNB | Salt 3 | Salt 4 | HNB |
|--------|-------|--------|--------|-----|
| \( \Delta H_f^0 \) (kJ mol\(^{-1}\)) | 392.61 | -184.38 | 300.27 | 76.29 |
| \( \Delta H_f^0 \) (kJ g\(^{-1}\))  | 1.00   | -0.42  | 0.61   | 0.22 |
Section S7. Detonation performance

The details of calculation methods, heat of detonation, detonation velocity, and detonation pressure are provided in this section.

Section S7.1 Calculation methods
Because the presented compounds in this work belong to traditional CHON explosives, K-J equation is more suitable to calculate the detonation performance of the presented compounds. And the equation is as followed:

$$D = 1.01(N\sqrt{\frac{M}{2}}Q)^{1/2}(1+1.3d)$$

$$P = 1.558d^2N\sqrt{\frac{M}{2}}Q^{1/2}$$

where \(D\) is detonation velocity (km s\(^{-1}\)), \(P\) is detonation pressure (GPa), \(N\) is the number of moles of the gas generated per gram (mol g\(^{-1}\)), \(\bar{M}\) is the average molecular weight of the gaseous product (g mol\(^{-1}\)), \(Q\) is the heat of detonation (cal g\(^{-1}\)), and \(d\) is the density of explosive (g cm\(^3\)). For explosives whose molecular formula is \(C_aH_bO_cN_d\), the calculation method of \(N\), \(\bar{M}\), and \(Q\) is shown in Table S16.

Section S7.2 Heat of detonation
For CL-20 (\(C_6H_6O_{12}N_{12}\)), it has the characteristic of \(2a+b/2>c\geq b/2\), the calculation method of \(Q\) is:

\[
Q\times 10^3 = \left[28.9b+94.05\left(c-2b/4\right)+0.239H_f\right]/M
\]

\[
= (28.9\cdot 6+94.05\cdot (12-6/4)+0.239\cdot 365.4)/438.2
\]

\[
= (173.4+423.2+87.3)/438.2
\]

\[
= 1.561\text{ cal g}^{-1}
\]

Thus \(Q = 1561\text{ kcal kg}^{-1} = 6534\text{ kJ kg}^{-1}\)

where \(H_f = 365.4\text{ kJ mol}^{-1}\), \(M = 438.2\text{ g mol}^{-1}\).

It should be noted that the heat of detonation of CL-20 calculated using K-J equation is very close to the value (6406 kJ mol\(^{-1}\), the difference is only 1.9\%) from the following reference, indicating the calculated result is trustable.

Fischer, N.; Fischer, D.; Klappótké, T. M.; Piercey, D. G.; Stierstorfer, J. J. Mater. Chem., 2012, 22, 20418-20422.

For HNB (\(C_6O_{12}N_6\)), it has the characteristic of \(c\geq 2a+b/2\), the calculation method of \(Q\) is:

\[
Q\times 10^3 = (28.9b+94.05a+0.239H_f)/M
\]

\[
= (28.9\cdot 0+94.05\cdot 6+0.239\cdot 76.3)/348.1
\]

\[
= (0+564.3+18.2)/348.1
\]

\[
= 1.673\text{ cal g}^{-1}
\]

Thus \(Q = 1673\text{ kcal kg}^{-1} = 6993\text{ kJ kg}^{-1}\)

In the above calculation, \(H_f = 76.3\text{ kJ mol}^{-1}\), \(M = 348.1\text{ g mol}^{-1}\).

For TNTNB (\(C_6H_3O_{12}N_9\)), it has the characteristic of \(2a+b/2>c\geq b/2\), the calculation method of \(Q\) is:

\[
Q\times 10^3 = (28.9b+94.05(c-2b/4)+0.239H_f)/M
\]

\[
= (28.9\cdot 3+94.05\cdot (12-3/4)+0.239\cdot 392.6)/393.1
\]

\[
= (86.7+493.8+93.8)/393.1
\]
Thus \( Q = 1715 \text{ kcal kg}^{-1} = 7179 \text{ kJ kg}^{-1} \)
In the above calculation, \( H_f = 392.6 \text{ kJ mol}^{-1}, M = 393.1 \text{ g mol}^{-1} \),

For \( \text{TNTNB}^{3^-3\text{NH}_4^+} (\text{C}_6\text{H}_{12}\text{O}_{12}\text{N}_{12}) \), it has the characteristic of \( 2a+b/2 > c \geq b/2 \), the calculation method of \( Q \) is:
\[
Q \cdot 10^3 = \frac{[28.9b + 94.05(c/2 - b/4) + 0.239H_f]}{M}
\]
\[
= \frac{[28.9 \times 12 + 94.05 \times (12/2 - 12/4) + 0.239 \times (-184.4)]}{444.2}
\]
\[
= 1.317 \text{ cal g}^{-1}
\]
Thus \( Q = 1317 \text{ kcal kg}^{-1} = 5513 \text{ kJ kg}^{-1} \)
In the above calculation, \( H_f = -184.4 \text{ kJ mol}^{-1}, M = 444.2 \text{ g mol}^{-1} \),

For \( \text{TNTNB}^{3^-3\text{N}_2\text{H}_5^+} (\text{C}_6\text{H}_{15}\text{O}_{12}\text{N}_{15}) \), it has the characteristic of \( 2a+b/2 > c \geq b/2 \), the calculation method of \( Q \) is:
\[
Q \cdot 10^3 = \frac{[28.9b + 94.05(c/2 - b/4) + 0.239H_f]}{M}
\]
\[
= \frac{[28.9 \times 15 + 94.05 \times (12/2 - 15/4) + 0.239 \times 300.3]}{489.3}
\]
\[
= 1.465 \text{ cal g}^{-1}
\]
Thus \( Q = 1465 \text{ kcal kg}^{-1} = 6120 \text{ kJ kg}^{-1} \)
In the above calculation, \( H_f = 292.5 \text{ kJ mol}^{-1}, M = 489.2 \text{ g mol}^{-1} \),

Section S7.3 Detonation velocity and detonation pressure
The detonation velocity and detonation pressure of these compounds were then calculated.
The \( N \) and \( \bar{M} \) were first calculated using the methods in Table S13:
For \( \text{HNB} \), \( N = 0.026 \text{ mol g}^{-1}; \bar{M} = 38.68 \text{ g mol}^{-1} \);
For \( \text{TNTNB} \), \( N = 0.029 \text{ mol g}^{-1}; \bar{M} = 34.14 \text{ g mol}^{-1} \);
For \( \text{TNTNB}^{3^-3\text{NH}_4^+} \), \( N = 0.034 \text{ mol g}^{-1}; \bar{M} = 27.20 \text{ g mol}^{-1} \);
For \( \text{TNTNB}^{3^-3\text{N}_2\text{H}_5^+} \), \( N = 0.036 \text{ mol g}^{-1}; \bar{M} = 25.74 \text{ g mol}^{-1} \);

With values of \( N \), \( \bar{M} \), and \( Q \), the detonation velocity and detonation pressure of \( \text{HNB} \), \( \text{TNTNB} \), \( \text{TNTNB}^{3^-3\text{NH}_4^+} \), and \( \text{TNTNB}^{3^-3\text{N}_2\text{H}_5^+} \) were calculated using K-J equation.
For \( \text{HNB} \), \( N\bar{M}^{1/2}Q^{1/2} = 6.61, (N\bar{M}^{1/2}Q^{1/2})^{1/2} = 2.57 \)
\[
D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1+1.3d)
\]
\[
= 1.01 \times 2.57 \times (1+1.3 \times 1.980)
\]
\[
= 9.277 \text{ km s}^{-1}
\]
\[
= 9277 \text{ m s}^{-1}
\]
\[
P = 1.558d^2N\bar{M}^{1/2}Q^{1/2}
\]
\[
= 1.558 \times 1.98^2 \times 6.61
\]
\[
= 40.4 \text{ GPa}
\]

For \( \text{TNTNB} \), \( N\bar{M}^{1/2}Q^{1/2} = 7.02, (N\bar{M}^{1/2}Q^{1/2})^{1/2} = 2.65 \)
\[
D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1+1.3d)
\]
\[
= 1.01 \times 2.65 \times (1+1.3 \times 1.964)
\]
\[
= 9.510 \text{ km s}^{-1}
\]
\[
= 9510 \text{ m s}^{-1}
\]
\[
P = 1.558d^2N\bar{M}^{1/2}Q^{1/2} \\
= 1.558 \times 1.964^2 \times 7.02 \\
= 42.2 \text{ GPa}
\]

For TNTNB₃⁺·3NH₄⁺, \(N\bar{M}^{1/2}Q^{1/2} = 6.44, (N\bar{M}^{1/2}Q^{1/2})^{1/2} = 2.54\)
\[
D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.3d) \\
= 1.01 \times 2.54 \times (1 + 1.3 \times 1.821) \\
= 8.645 \text{ km s}^{-1} \\
= 8645 \text{ m s}^{-1} \\
P = 1.558d^2N\bar{M}^{1/2}Q^{1/2} \\
= 1.558 \times 1.821^2 \times 6.44 \\
= 33.3 \text{ GPa}
\]

For TNTNB₃⁺·3N₂H₅⁺, \(N\bar{M}^{1/2}Q^{1/2} = 6.99, (N\bar{M}^{1/2}Q^{1/2})^{1/2} = 2.65\)
\[
D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.3d) \\
= 1.01 \times 2.65 \times (1 + 1.3 \times 1.885) \\
= 9.235 \text{ km s}^{-1} \\
= 9235 \text{ m s}^{-1} \\
P = 1.558d^2N\bar{M}^{1/2}Q^{1/2} \\
= 1.558 \times 1.885^2 \times 6.99 \\
= 38.7 \text{ GPa}
\]
Table S16. The calculation method of $N$, $\bar{M}$, and $Q$ for C$_a$H$_b$O$_c$N$_d$ explosive.

| Condition | $N$ | $M$ | $Q \times 10^{-3}$ |
|-----------|-----|-----|---------------------|
| $c \geq 2a+b/2$ | $(b+2c+2d)/4M$ | $4M/(b+2c+2d)$ | $(28.9b+94.05a+0.239H_f)/M$ |
| $2a+b/2 > c \geq b/2$ | $(b+2c+2d)/4M$ | $(56d+88c-8b)/(b+2c+2d)$ | $[28.9b+94.05(c/2-b/4)+0.239H_f]/M$ |
| $b/2 > c$ | $(b+d)/2M$ | $(2b+28d+32c)/(b+d)$ | $(57.8c+0.239H_f)/M$ |

where $M$ is the mole weight of explosives (g/mol); $H_f$ is the heat of formation (kJ/mol).
**Section S8. Thermal Stability and bond dissociation energy (BDE)**

The details of thermal stability and bond dissociation energy (BDE) calculation are provided in this section.

**Section S8.1 The test of thermal stability**

The thermal stability of these new compounds was tested using differential scanning calorimeter (DSC) method and the DSC plots are shown in Fig. S18.

**Section S8.2 Bond dissociation energy**

The bond dissociation energy (BDE) in this work was given in terms of $\text{BDE}=E(A)+E(B)−E(AB)$ in which the total energy $E$ of each species includes the electronic energy ($E_e$) and the ZPE generated from a vibrational frequency calculation (B3LYP/6-311G**). NH$_2$NO$_2$, MeNHNO$_2$, and CH$_3$NO$_2$ were adopted to verify our revised calculation method, where NH$_2$NO$_2$ and CH$_3$NH$_2$NO$_2$ were referenced for N-NO$_2$ bond and CH$_3$NO$_2$ was referenced for C-NO$_2$ bond.

As shown in Table S17, the trigger bond for TNTNB is N-NO$_2$ with BDE of 153.01 kJ mol$^{-1}$, and the trigger bonds for salts 3 and 4 are both C-NO$_2$ with BDEs of 202.51 and 211.69 kJ mol$^{-1}$, respectively. The salt formation effectively increases the BDEs of trigger bonds. In addition, the BDEs of N-NO$_2$ for salts 3 and 4 are even up to 308.89 and 371.38 kJ mol$^{-1}$, respectively.
Fig. S18. DSC plots for TNTNB, salt 3, and salt 4, respectively.
Table S17. The BDEs of trigger bonds for NH$_2$NO$_2$, MeNHNO$_2$, CH$_3$NO$_2$, TNTNB, salt 3, and salt 4, respectively.

| Compd | Bond | H a.u. | $\Delta_{\text{rxn}}$H a.u. | BDE$^{298K}$ kJ mol$^{-1}$ | Experimental data kJ mol$^{-1}$ |
|-------|------|--------|------------------|-----------------|-------------------------------|
| NH$_2$NO$_2$ | H$_2$N-NO$_2$ | -261.071487 | 0.086716 | 227.672836 | 230$^a$ |
| | H$_2$N- | -55.867609 |
| | NO$_2$ | -205.117162 |
| MeNHNO$_2$ | NH$_2$-NO$_2$ | -300.365135 | 0.08526 | 204.3006374 | 209$^a$ |
| | CH$_3$NH- | -95.163418 |
| | NO$_2$ | -205.116457 |
| CH$_3$NO$_2$ | CH$_3$-NO$_2$ | -245.029167 | 0.101937 | 267.6355678 | 263$^b$ |
| | H$_3$C- | -39.811397 |
| | NO$_2$ | -205.115833 |

-the comparison of calculated data with experimental data

-the BDEs of N-NO$_2$

| Compd | Bond | H a.u. | $\Delta_{\text{rxn}}$H a.u. | BDE$^{298K}$ kJ mol$^{-1}$ |
|-------|------|--------|------------------|-----------------|
| TNTNB | PhN-NO$_2$ | -1624.85146 | 0.058278 | 153.0088743 |
| | PhN- | -1419.74996 |
| | NO$_2$ | -205.043217 |
| Salt 3 | PhN-NO$_2$ | -1623.328014 | 0.1176503 | 308.8909538 |
| | PhN- | -1418.162039 |
| | NO$_2$ | -205.0483246 |
| Salt 4 | PhN-NO$_2$ | -1623.332894 | 0.1414505 | 371.3784385 |
| | PhN- | -1418.141978 |
| | NO$_2$ | -205.0494662 |

-the BDEs of C-NO$_2$

| Compd | Bond | H a.u. | $\Delta_{\text{rxn}}$H a.u. | BDE$^{298K}$ kJ mol$^{-1}$ |
|-------|------|--------|------------------|-----------------|
| TNTNB | Ph-NO$_2$ | -1624.85146 | 0.076512 | 200.8822367 |
| | Ph- | -1419.731727 |
| | NO$_2$ | -205.043217 |
| Salt 3 | Ph-NO$_2$ | -1623.328014 | 0.07713312 | 202.5129871 |
| | Ph- | -1418.199629 |
| | NO$_2$ | -205.0512519 |
| Salt 4 | Ph-NO$_2$ | -1623.332894 | 0.08062912 | 211.6917342 |
| | Ph- | -1418.199821 |
| | NO$_2$ | -205.0560441 |
| HNB | Ph-NO$_2$ | -1459.02369 | 0.0967817 | 254.100329 | (✔) |
| | Ph- | -1253.870805 |
| | NO$_2$ | -205.0561033 |

Note: [a] (50); [b] (51). References 50 and 51 are shown in the main Reference list.
Section S9. Other quantum computing analysis

The details of other quantum computing analysis, including nucleus independent chemical shift, 2D fingerprints and Hirshfeld surfaces, are provided in this section.

Section S9.1 Nucleus independent chemical shift
The nucleus independent chemical shift (NICS) is a useful tool to describe the compound aromaticity or magnetic properties of a structure. The original definition of the NICS is the negative value of the absolute magnetic shielding computed at ring centers. The NICS(1) concept is more practical for illustration of \(\pi\)-electron structure characteristics because it is defined as an NICS of 1 Å above the ring plane. However, the NICS(1) is still based on the total isotropic shielding value. The NICS(1)\(_{zz}\) was therefore proposed to reflect contributions arising from the \(zz\) component of the shielding tensor. Larger negative values imply stronger molecule aromaticity. NICS(1)\(_{zz}\) is believed to offer an improved interpretation of aromaticity with fewer errors.

The NICS(1)\(_{zz}\) values of HNB and TNTNB were calculated using GIAO/B3LYP/6-31+G(d,p) method, and the values are -19.8 and -22.1 ppm, respectively, which indicates that TNTNB exhibits a stronger magnetic field shielding. In addition, the shielding maps were presented as Fig. S19. A darker red color in the ring means that the structure has better aromaticity. It is clear than the benzene ring in TNTNB is much redder than that of HNB, thus indicating a better aromaticity.

Section S9.2 2D fingerprints and Hirshfeld surfaces of salts
The 2D-fingerprints and Hirshfeld surfaces of two salts (3 and 4) were performed and compared with HNB and TNTNB (Fig. S20 and S21). The formation of ionic salt further reduces the contents of O···O to 14.3% and 13.1%, and increases the content of O···H to 59.1% and 59.6%, respectively. In addition, the ionic salt also promotes the generation of N···H-type hydrogen bonding, and accounts for 7.5% and 8.6%, respectively, so that the hydrogen bonding of the ionic salt even reaches 66.6% and 68.2%, respectively, which will lead to the better stability of these ionic salts.
Fig. S19. Magnetic field shielding maps for (A) HNB and (B) TNTNB based on NICS method.
Fig. S20. 2D-fingerprint plots, Hirshfeld surfaces (inside) and contributions of the individual atomic contacts in crystal stacking for compounds in this work. (A) and (B) HNB; (C) and (D) TNTNB; (E) and (F) salt 3; and (G) and (H) salt 4.

Fig. S21. The comparison of O⋯O and N/O⋯H contacts in compounds HNB, TNTNB, 3, and 4.
CIF files. Crystallographic data (in CIF format) and CHECKCIF (in PDF format) for crystal structures of presented benzene materials.
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