

Supporting Information

## All-nitrogen ions based compounds as energetic oxidizers: A theoretical study on $[\text{N}_5^+][\text{NO}_3^-]$ , $[\text{N}_5^+][\text{N}(\text{NO}_2)_2^-]$ , $[\text{NO}_2^+][\text{N}_5^-]$ and $\text{NO}_2\text{-N}_3$

Qi Sun, Pengcheng Wang, Qiuhan Lin, Ming Lu\*<sup>a</sup>

A: School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

Table s1 Calculated heat of formation of four ions and the lattice energy of  $[\text{NO}_2^+][\text{N}_5^-]$  and  $[\text{N}_5^+][\text{NO}_3^-]$

| Compd                                       | $\Delta H_{\text{cation}}^{\text{a}}$<br>[kJ mol <sup>-1</sup> ] | $\Delta H_{\text{anion}}^{\text{b}}$<br>[kJ mol <sup>-1</sup> ] | $\Delta H_{\text{L}}^{\text{c}}$<br>[kJ mol <sup>-1</sup> ] |
|---|--|---|---|
| $[\text{NO}_2^+][\text{N}_5^-]$             | 980.3  | 258.7   | 607.0   |
| $[\text{NO}_3^-][\text{N}_5^+]$             | 1471.7   | -307.9  | 581.7   |
| $[\text{N}_5^+][\text{N}(\text{NO}_2)_2^-]$ | 1471.7   | -190.1  | 543.8   |

<sup>a</sup> heats of formation of cations; <sup>b</sup> heats of formation of anions; <sup>c</sup> the lattice energy

### Distributions of electrostatic potentials

| Begin    | End      | Center   | Area     | %        |
|----------|----------|----------|----------|----------|
| -40.0000 | -35.0000 | -37.5000 | 3.6620   | 2.5454   |
| -35.0000 | -30.0000 | -32.5000 | 14.5226  | 10.0943  |
| -30.0000 | -25.0000 | -27.5000 | 10.9467  | 7.6088   |
| -25.0000 | -20.0000 | -22.5000 | 7.9799   | 5.5467   |
| -20.0000 | -15.0000 | -17.5000 | 5.9355   | 4.1256   |
| -15.0000 | -10.0000 | -12.5000 | 5.6653   | 3.9378   |
| -10.0000 | -5.0000  | -7.5000  | 5.9265   | 4.1193   |
| -5.0000  | 0.0000   | -2.5000  | 6.5790   | 4.5729   |
| 0.0000   | 5.0000   | 2.5000   | 6.9441   | 4.8267   |
| 5.0000   | 10.0000  | 7.5000   | 7.8200   | 5.4355   |
| 10.0000  | 15.0000  | 12.5000  | 13.7570  | 9.5621   |
| 15.0000  | 20.0000  | 17.5000  | 11.5903  | 8.0562   |
| 20.0000  | 25.0000  | 22.5000  | 9.9659   | 6.9270   |
| 25.0000  | 30.0000  | 27.5000  | 8.8882   | 6.1780   |
| 30.0000  | 35.0000  | 32.5000  | 9.2091   | 6.4010   |
| 35.0000  | 40.0000  | 37.5000  | 6.6890   | 4.6494   |
| 40.0000  | 45.0000  | 42.5000  | 5.1383   | 3.5715   |
| 45.0000  | 50.0000  | 47.5000  | 2.6497   | 1.8418   |
| um:      |          |          | 143.8691 | 100.0000 |

Figure s1 . Distributions of electrostatic potentials of  $[\text{N}_5^+][\text{NO}_3^-]$

| Begin    | End      | Center   | Area    | %       |
|----------|----------|----------|---------|---------|
| -40.0000 | -35.0000 | -37.5000 | 1.3326  | 0.7624  |
| -35.0000 | -30.0000 | -32.5000 | 8.9478  | 5.1188  |
| -30.0000 | -25.0000 | -27.5000 | 22.5496 | 12.9000 |
| -25.0000 | -20.0000 | -22.5000 | 11.9280 | 6.8236  |
| -20.0000 | -15.0000 | -17.5000 | 9.8591  | 5.6401  |
| -15.0000 | -10.0000 | -12.5000 | 8.4139  | 4.8134  |
| -10.0000 | -5.0000  | -7.5000  | 7.1274  | 4.0774  |
| -5.0000  | 0.0000   | -2.5000  | 5.7570  | 3.2934  |
| 0.0000   | 5.0000   | 2.5000   | 4.7123  | 2.6958  |
| 5.0000   | 10.0000  | 7.5000   | 4.2461  | 2.4291  |
| 10.0000  | 15.0000  | 12.5000  | 10.3182 | 5.9028  |
| 15.0000  | 20.0000  | 17.5000  | 17.4149 | 9.9626  |
| 20.0000  | 25.0000  | 22.5000  | 21.3787 | 12.2302 |
| 25.0000  | 30.0000  | 27.5000  | 13.5481 | 7.7505  |
| 30.0000  | 35.0000  | 32.5000  | 8.4247  | 4.8196  |
| 35.0000  | 40.0000  | 37.5000  | 6.7878  | 3.8831  |
| 40.0000  | 45.0000  | 42.5000  | 5.9606  | 3.4099  |
| 45.0000  | 50.0000  | 47.5000  | 5.3564  | 3.0642  |

Figure s2. Distributions of electrostatic potentials of [N5+][N(NO2)2-]

| Begin    | End      | Center   | Area     | %        |
|----------|----------|----------|----------|----------|
| -40.0000 | -35.0000 | -37.5000 | 0.0000   | 0.0000   |
| -35.0000 | -30.0000 | -32.5000 | 0.0000   | 0.0000   |
| -30.0000 | -25.0000 | -27.5000 | 0.0000   | 0.0000   |
| -25.0000 | -20.0000 | -22.5000 | 0.8491   | 0.6925   |
| -20.0000 | -15.0000 | -17.5000 | 6.8364   | 5.5757   |
| -15.0000 | -10.0000 | -12.5000 | 10.3083  | 8.4074   |
| -10.0000 | -5.0000  | -7.5000  | 15.8050  | 12.8904  |
| -5.0000  | 0.0000   | -2.5000  | 27.2180  | 22.1987  |
| 0.0000   | 5.0000   | 2.5000   | 16.6301  | 13.5634  |
| 5.0000   | 10.0000  | 7.5000   | 10.4498  | 8.5227   |
| 10.0000  | 15.0000  | 12.5000  | 7.4615   | 6.0855   |
| 15.0000  | 20.0000  | 17.5000  | 5.7256   | 4.6697   |
| 20.0000  | 25.0000  | 22.5000  | 4.6978   | 3.8315   |
| 25.0000  | 30.0000  | 27.5000  | 4.2584   | 3.4731   |
| 30.0000  | 35.0000  | 32.5000  | 5.0662   | 4.1319   |
| 35.0000  | 40.0000  | 37.5000  | 4.0097   | 3.2703   |
| 40.0000  | 45.0000  | 42.5000  | 2.2499   | 1.8350   |
| 45.0000  | 50.0000  | 47.5000  | 1.0449   | 0.8522   |
| um:      |          |          | 122.6106 | 100.0000 |

Figure s3. Distributions of electrostatic potentials of [NO2+][N5-].

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Note: Area unit is in Angstrom<sup>2</sup>

| Begin    | End      | Center   | Area     | %        |
|----------|----------|----------|----------|----------|
| -40.0000 | -35.0000 | -37.5000 | 0.0000   | 0.0000   |
| -35.0000 | -30.0000 | -32.5000 | 0.0000   | 0.0000   |
| -30.0000 | -25.0000 | -27.5000 | 0.0000   | 0.0000   |
| -25.0000 | -20.0000 | -22.5000 | 0.0000   | 0.0000   |
| -20.0000 | -15.0000 | -17.5000 | 9.9342   | 9.3938   |
| -15.0000 | -10.0000 | -12.5000 | 15.6436  | 14.7928  |
| -10.0000 | -5.0000  | -7.5000  | 12.2124  | 11.5482  |
| -5.0000  | 0.0000   | -2.5000  | 7.7741   | 7.3512   |
| 0.0000   | 5.0000   | 2.5000   | 12.4493  | 11.7722  |
| 5.0000   | 10.0000  | 7.5000   | 11.0341  | 10.4339  |
| 10.0000  | 15.0000  | 12.5000  | 10.0869  | 9.5383   |
| 15.0000  | 20.0000  | 17.5000  | 7.6175   | 7.2032   |
| 20.0000  | 25.0000  | 22.5000  | 6.7251   | 6.3593   |
| 25.0000  | 30.0000  | 27.5000  | 8.5203   | 8.0569   |
| 30.0000  | 35.0000  | 32.5000  | 3.7542   | 3.5500   |
| 35.0000  | 40.0000  | 37.5000  | 0.0000   | 0.0000   |
| 40.0000  | 45.0000  | 42.5000  | 0.0000   | 0.0000   |
| 45.0000  | 50.0000  | 47.5000  | 0.0000   | 0.0000   |
| Sum:     |          |          | 105.7517 | 100.0000 |

Figure s4. Distributions of electrostatic potentials of NO2-N3 (N4O2).

| Begin    | End      | Center   | Area     | %        |
|----------|----------|----------|----------|----------|
| -40.0000 | -35.0000 | -37.5000 | 0.0000   | 0.0000   |
| -35.0000 | -30.0000 | -32.5000 | 0.0000   | 0.0000   |
| -30.0000 | -25.0000 | -27.5000 | 0.0000   | 0.0000   |
| -25.0000 | -20.0000 | -22.5000 | 0.0000   | 0.0000   |
| -20.0000 | -15.0000 | -17.5000 | 0.0000   | 0.0000   |
| -15.0000 | -10.0000 | -12.5000 | 0.1732   | 0.1522   |
| -10.0000 | -5.0000  | -7.5000  | 28.5648  | 25.1099  |
| -5.0000  | 0.0000   | -2.5000  | 33.1091  | 29.1046  |
| 0.0000   | 5.0000   | 2.5000   | 14.8749  | 13.0758  |
| 5.0000   | 10.0000  | 7.5000   | 9.2337   | 8.1169   |
| 10.0000  | 15.0000  | 12.5000  | 6.9760   | 6.1322   |
| 15.0000  | 20.0000  | 17.5000  | 5.4911   | 4.8270   |
| 20.0000  | 25.0000  | 22.5000  | 4.7634   | 4.1872   |
| 25.0000  | 30.0000  | 27.5000  | 4.5678   | 4.0154   |
| 30.0000  | 35.0000  | 32.5000  | 5.3126   | 4.6701   |
| 35.0000  | 40.0000  | 37.5000  | 0.6923   | 0.6085   |
| 40.0000  | 45.0000  | 42.5000  | 0.0000   | 0.0000   |
| 45.0000  | 50.0000  | 47.5000  | 0.0000   | 0.0000   |
| Sum:     |          |          | 113.7588 | 100.0000 |

Figure s5. Distributions of electrostatic potentials of N2O5.

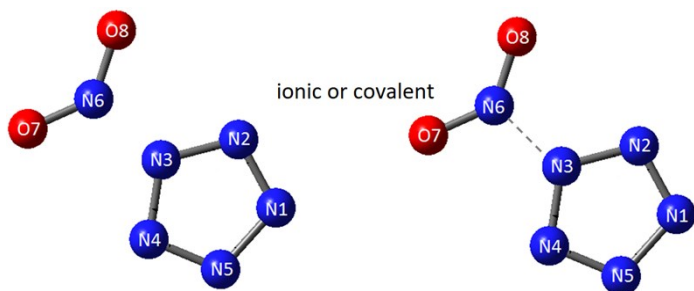
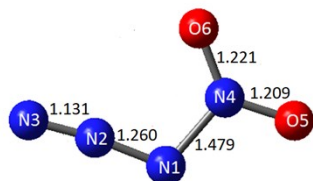


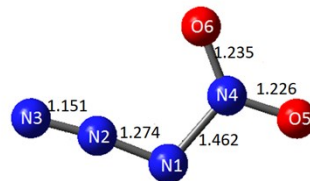
Figure s6 Ionic  $[\text{NO}_2^+][\text{N}_5^-]$  or covalent  $\text{NO}_2\text{-N}_5$

This work



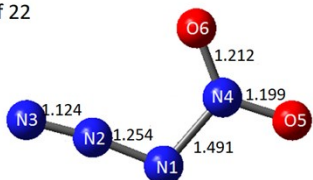
N3-N2-N1: 173.4°  
 N2-N1-N4: 109.3°  
 N1-N4-O6: 118.4°  
 N1-N4-O5: 112.5°  
 O5-N4-O6: 129.1°

Ref 15



N3-N2-N1: 172.7°  
 N2-N1-N4: Not provided  
 N1-N4-O6: 118.5°  
 N1-N4-O5: 112.5°  
 O5-N4-O6: 129.0°

Ref 22



No bond angle data provided

Figure s7 Comparison of the  $\text{NO}_2\text{-N}_3$  structures.