## Supporting Information (SI) for:

### Synthesis and stability of 2-tetrazenium salts

by Carles Miró Sabaté and Henri Delalou

**Table 1** Calculated, scaled and measured infrared (IR) and Raman (Ra) frequencies (>600 cm\(^{-1}\)) with intensity (IR) and activity (Ra) values for N\(_4\)Me\(_4\) (I).

<table>
<thead>
<tr>
<th></th>
<th>(v_{\text{unscl}}) (cm(^{-1})) (^a)</th>
<th>(v_{\text{scl}}) (cm(^{-1})) (^b)</th>
<th>(I_{\text{calc}}/A_{\text{calc}}) IR/Ra (^c)</th>
<th>(v_{\text{meas}}) (IR, cm(^{-1})) (^d)</th>
<th>(v_{\text{meas}}) (Ra, cm(^{-1})) (^e)</th>
<th>Assignment (^f)</th>
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<td>all C: (v(C-N) + v(N-N))</td>
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<tr>
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<td>(v(N2-N3) + \text{all C: } \delta(C-H))</td>
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<td>C2/C3: (v(C-H))</td>
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<td>C2/C3: (v(C-H))</td>
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<td>C1/C4: (v(C-H))</td>
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<td>C3: (v(C-H))</td>
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<td>C2: (v(C-H))</td>
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<td>3025</td>
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<td>2999(22)</td>
<td>(v_{\text{as}}(C-H))</td>
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<td>(v_{\text{as}}(C-H))</td>
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<td>(v_{\text{as}}(C-H))</td>
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<td>1/187</td>
<td>3088(13)</td>
<td>(v_{\text{as}}(C-H))</td>
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</tbody>
</table>

\(^a\) Calculated (unscaled) frequencies (B3LYP/6-311+G(d,p)); \(^b\) Calculated frequencies (B3LYP/6-311+G(d,p)) scaled by 0.9613; \(^c\) Calculated IR intensities and Raman activities; \(^d\) Experimental IR frequencies and intensities in () brackets; \(^e\) Experimental Raman frequencies and activities in () brackets; \(^f\) Approximate description of vibrational modes: \(v\) = stretching, \(\delta\) = in-plane bending, \(\gamma\) = out-of-plane bending, \(\omega\) = in-plane rocking, \(\tau\) = torsion; as = asymmetric and s = symmetric.
Table 2 Calculated, scaled and measured (averaged values for compounds 2 and 3) infrared (IR) and Raman (Ra) frequencies (>600 cm⁻¹) with intensity (IR) and activity (Ra) values for the N₄Me₂H⁺ cation.

|   | v_unscal (cm⁻¹) a | v_scal (cm⁻¹) b | I_cal/cm calc | ν_m (IR, cm⁻¹) c | ν_RA (Ra, cm⁻¹) d | Mode Assignment /
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<td>619</td>
<td>595</td>
<td>35/2</td>
<td>620 (s)</td>
<td>620 (1)</td>
<td>γ(N(2–N3))</td>
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<td>774</td>
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<td>675 (w)</td>
<td>ν(C–N) + ν(N–N)</td>
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<td>861</td>
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<td>815 (w)</td>
<td>820 (3)</td>
<td>ν(C–N) + ν(N–N)</td>
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<td>902</td>
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<td>900 (w)</td>
<td>900 (15)</td>
<td>ν(N3–N4) + ν(N1–C2)</td>
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<td>945 (w)</td>
<td>950 (2)</td>
<td>C3/C4: ν(C–N) + τ(C–H)</td>
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<td>4/1</td>
<td>1000 (w)</td>
<td>1005 (3)</td>
<td>C3/C4: γ(C–H)</td>
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<td>C1/C2: γ(C–H)</td>
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<td>1050 (w)</td>
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<td>C1/C2: τ(C–H)</td>
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<td>1092</td>
<td>7/17</td>
<td>1070 (w)</td>
<td>1070 (1)</td>
<td>C1/C2: γ(C–H)</td>
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<td>1156</td>
<td>1111</td>
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<td>1105 (w)</td>
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<td>1160 (m)</td>
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<td>ν(N1–N2) + C3/C4: γ(C–H)</td>
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<td>3080 (w)</td>
<td>ν(N4–H)</td>
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a Calculated (unscaled) frequencies (B3LYP/6-311+G(d,p)); b Calculated frequencies (B3LYP/6-311+G(d,p)) scaled by 0.9613; c Calculated IR intensities and Raman activities; d Experimental IR frequencies and intensities in () brackets; e Experimental Raman frequencies and activities in () brackets; f Approximate description of vibrational modes: ν = stretching, δ = in-plane bending, γ = out-of-plane bending, ω = in-plane rocking, τ = torsion; as = asymmetric and s = symmetric.
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<table>
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<th>(v) unscal (cm(^{-1})) (a)</th>
<th>(\nu) scal (cm(^{-1})) (b)</th>
<th>(I_{\text{calc}}/A_{\text{calc}}) IR/Ra (c)</th>
<th>(v) meas (IR, cm(^{-1})) (d)</th>
<th>(v) meas (Ra, cm(^{-1})) (e)</th>
<th>Mode Assignment (f)</th>
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\(a\) Calculated (unscaled) frequencies (B3LYP/6-311+G(d,p)); \(b\) Calculated frequencies (B3LYP/6-311+G(d,p)) scaled by 0.9613; \(c\) Calculated IR intensities and Raman activities; \(d\) Experimental IR frequencies and intensities in ( ) brackets; \(e\) Experimental Raman frequencies and activities in ( ) brackets; \(f\) Approximate description of vibrational modes: \(\nu\) = stretching, \(\delta\) = in-plane bending, \(\gamma\) = out-of-plane bending, \(\omega\) = in-plane rocking, \(\tau\) = torsion; \(s\) = asymmetric and \(s\) = symmetric.
**Table 4** Geometry of medium to strong hydrogen bonds in the crystal structure of dimethylammonium picrate.

<table>
<thead>
<tr>
<th>D–H•••A</th>
<th>D–H (Å)</th>
<th>H•••A (Å)</th>
<th>D•••A (Å)</th>
<th>D–H•••A (°)</th>
</tr>
</thead>
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<tr>
<td>N7–H5•••O8</td>
<td>0.798(4)</td>
<td>2.018(5)</td>
<td>2.776(5)</td>
<td>158.6(5)</td>
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<tr>
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<td>0.798(4)</td>
<td>2.550(5)</td>
<td>3.096(7)</td>
<td>127.0(7)</td>
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<tr>
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<td>2.058(8)</td>
<td>2.886(5)</td>
<td>153.6(5)</td>
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<tr>
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<td>2.227(7)</td>
<td>2.832(6)</td>
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<tr>
<td>N8–H13•••O1i</td>
<td>0.881(6)</td>
<td>1.877(5)</td>
<td>2.862(5)</td>
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<tr>
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<td>2.900(8)</td>
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<tr>
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<td>2.767(7)</td>
<td>160.4(4)</td>
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<td>126.4(4)</td>
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</table>

Symmetry code: (i) 0.5+x, y, 1-z.

**Table 5** Graph-set matrix for strong to medium hydrogen bonds in dimethylammonium picrate. First level motifs on-diagonal and second level graph-sets off-diagonal.

<table>
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<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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<tr>
<td>N7–H6•••O1 (B)</td>
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<tr>
<td>N8–H13•••O1 (C)</td>
<td>D2,2(5)</td>
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<tr>
<td>N7–H6•••O7 (D)</td>
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<tr>
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<td>D1,1(2)</td>
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Symmetry code: (i) 0.5+x, y, 1-z

**Fig. 1** Optimized geometry and Mulliken charges in N₄Me₄ (1) (B3LYP/6-31+G(d,p)).
Fig. 2 Optimized geometry and Mulliken charges for the N₄Me₄H⁺ cation (B3LYP/6-31+G(d,p)).

Fig. 3 Optimized geometry and Mulliken charges for the N₄Me₅⁺ cation (B3LYP/6-31+G(d,p)).

References (Supporting Information)