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Support Information for:

**Exploring the thermal decomposition and detonation mechanisms of
2,4-dinitroanisole by TG-FTIR-MS and molecular simulations**

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and detonation**

23 **1. Validation of the ReaxFF/lg description**

24 **Table S1** Experiment and computed lattice parameters of DNAN and TNT. The data
 25 outside and in the parenthesis are for DNAN and TNT, respectively.

Parameters	Exp	Reaxff-lg	Deviation/%
a/Å	8.77 (14.91)	8.66 (14.82)	-1.26 (-0.60)
b/Å	12.65 (6.03)	12.48 (6.00)	-1.27 (-0.50)
c/Å	15.43 (19.68)	15.23 (19.57)	-1.27 (-0.56)
$\beta/^\circ$	81.89 (-)	81.89 (-)	0.00 (-)
$\rho/\text{g}\cdot\text{cm}^{-3}$	1.56 (1.70)	1.61 (1.73)	3.21 (1.76)

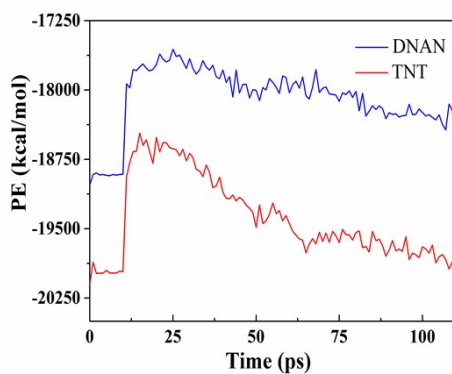
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27 **Table S2** Experiment and computed bond lengths of DNAN and TNT. The data
 28 outside and in the parenthesis are for DNAN and TNT, respectively.

Bond/Å	Exp	Reaxff-lg	DFT
C-N	1.47 (1.41)	1.52 (1.52)	1.48 (1.49)
C-C	1.38 (1.39)	1.36 (1.43)	1.39 (1.39)
C-C _{CH3}	- (1.50)	- (1.53)	- (1.51)
C-O	1.39 (-)	1.44 (-)	1.38 (-)
N-O	1.20 (1.23)	1.28 (1.28)	1.22 (1.22)
C _{ph} -H	1.09 (0.97)	1.13 (1.13)	1.08 (1.08)
C _{CH3} -H	1.09 (0.99)	1.12 (1.12)	1.09 (1.09)

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30 2. Detonation of DNAN and TNT during fast heating

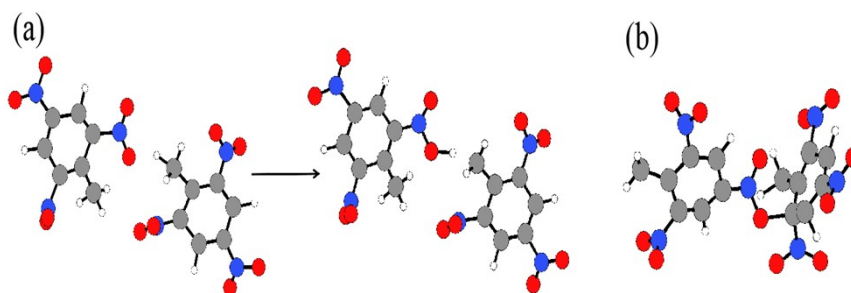


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32 **Fig. S1** The potential energy (PE) evolution of DNAN (blue) and TNT (red) crystals

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upon fast heating from 300 to 2500 K in 2 ps.



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35 **Fig. S2** Snapshots of bimolecular H (a) and O (b) transfer of TNT in condensed

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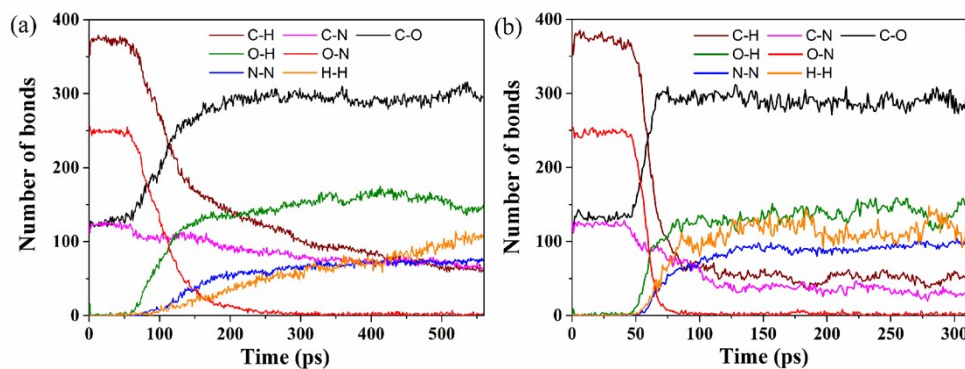
phase. The C, H, O, and N atoms are colored in gray, white, red and blue,

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respectively.

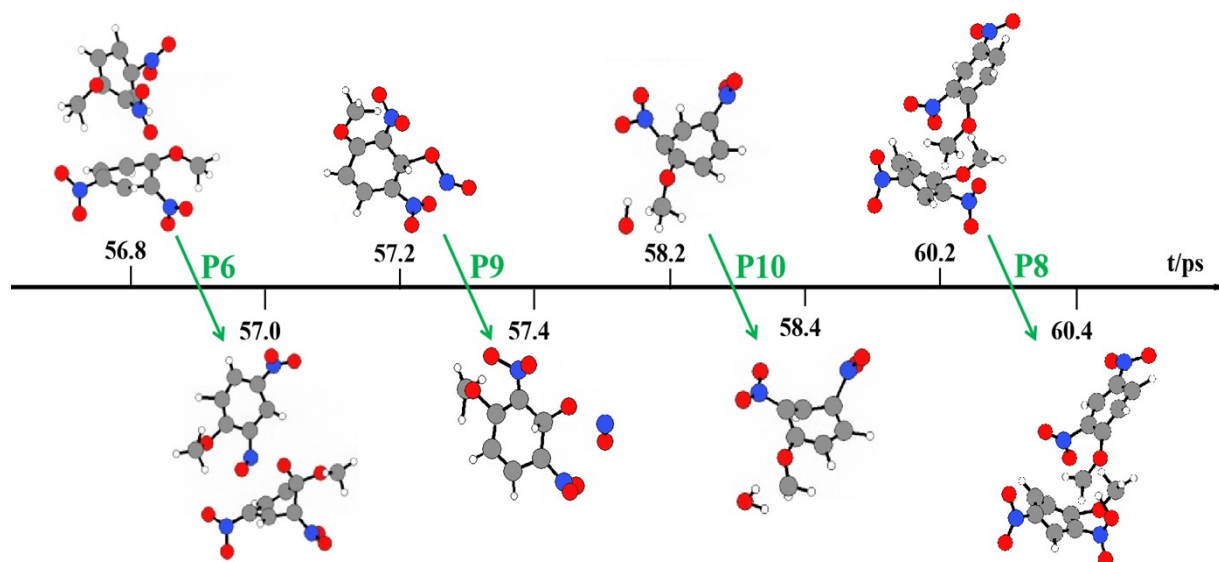
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39 3. Detonation of DNAN during slow heating



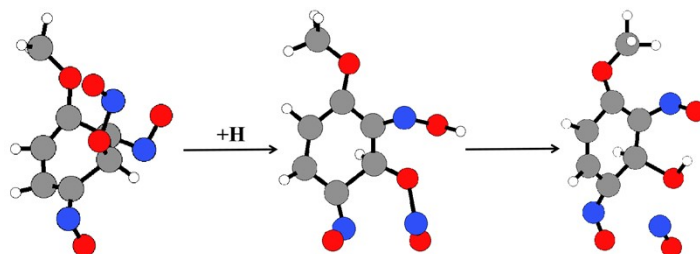
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41 **Fig. S3** The evolution of the numbers of direct bonding between C, H, O and N atoms
42 during the decomposition of DNAN in condensed phase at 2500 K (a) and 3500 K (b).
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45 **Fig. S4** The snapshots and initial time for the four types of bimolecular reactions
46 during the initial decomposition of DNAN in condensed phase at 2500K. P6 and P8
47 are the A+A type oxygen transfers, P9 is the A+B type oxygen transfer, while P10 is
48 the A+B type hydrogen transfer (see Table 2 in the text). The C, H, O, and N atoms
49 are colored in gray, white, red and blue, respectively.

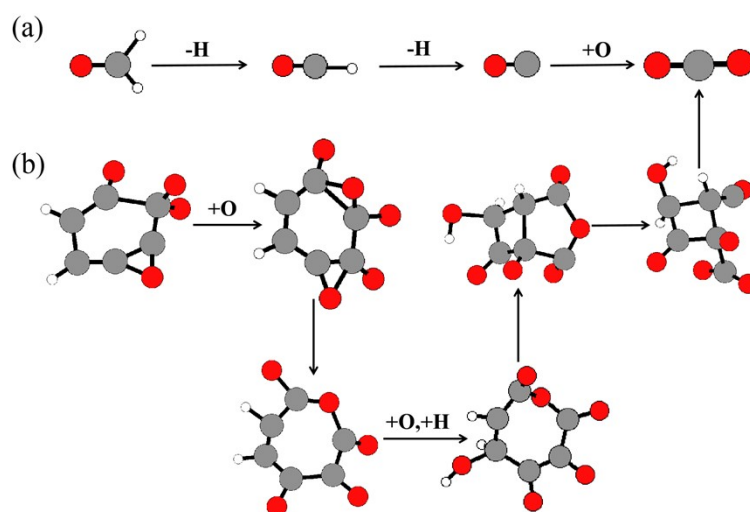
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52 **Fig. S5** The formation of NO from a nucleophilic attack at the phenyl ring by NO₂
53 during the initial decomposition of the DNAN crystal at 2500 K. The C, H, O, and N
54 atoms are colored in gray, white, red and blue, respectively.

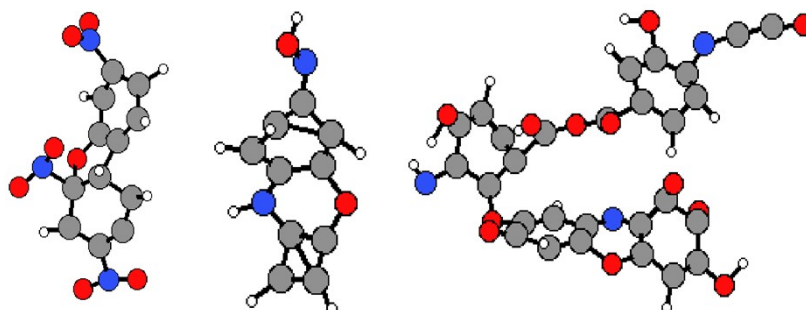
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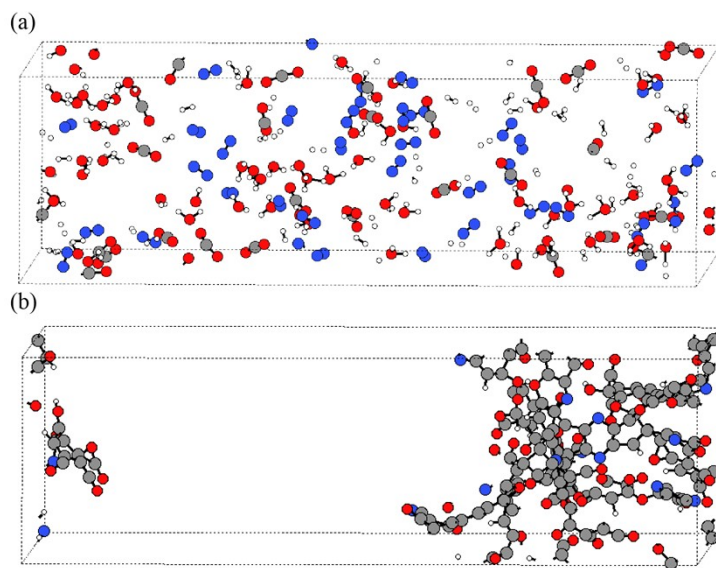
57 **Fig. S6** The formation of CO2 from CH2O (a) and carbon cluster (B) during the
58 intermediate decomposition stage of the DNAN crystal at 2500 K. The C, H, and O
59 atoms are colored in gray, white, red and blue, respectively.

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62 **Fig. S7** Three carbon clusters formed during the intermediate decomposition stage of
63 the DNAN crystal at 2500 K. The C, H, O, and N atoms are colored in gray,
64 red and blue, respectively.



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66 **Fig. S8** The final gas products (a) and carbon clusters (b) formed from the thermal

67 decomposition of the DNAN crystal at 2500 K. The C, H, O, and N atoms are colored

68 in gray, white, red and blue, respectively.

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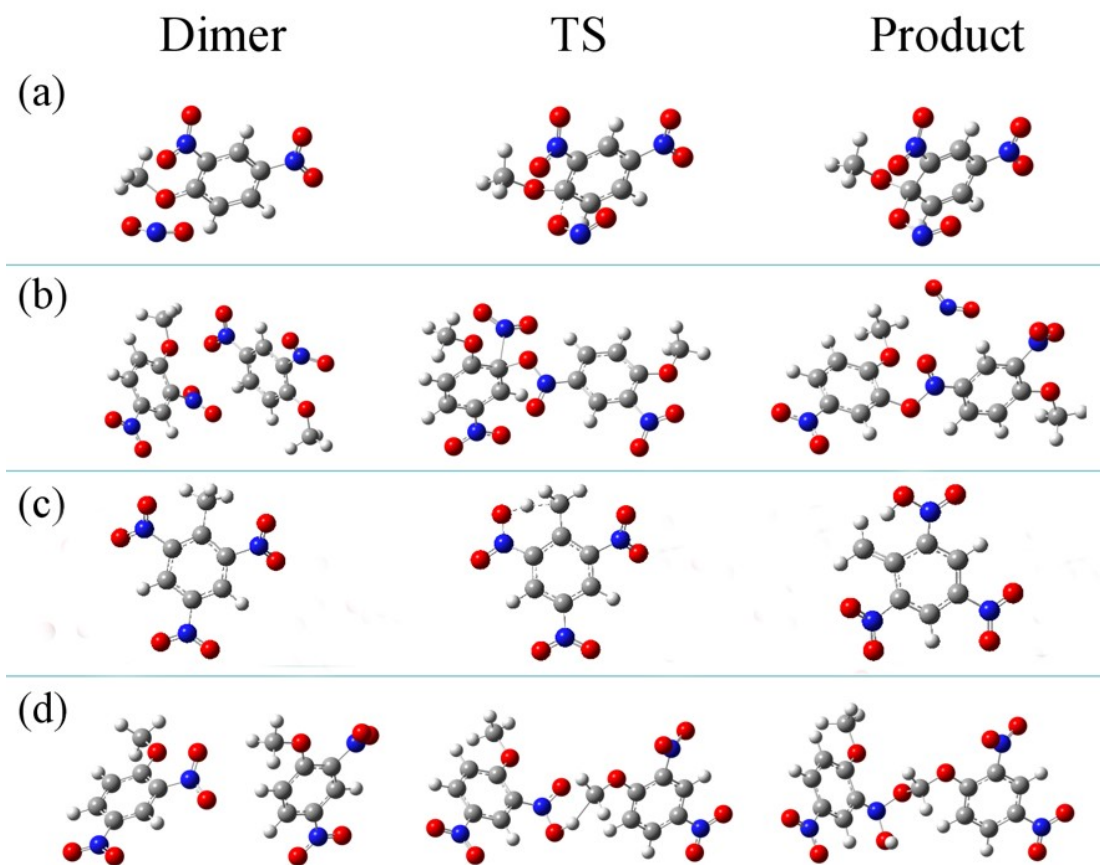
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81 **4. Key reactions of DNAN and TNT during thermal decomposition**
82 **and detonation**



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84 **Fig. S9** The structures of the reactant dimer, transition state and product of the
85 reactions in Fig. 11 (b) of the text: (a) NO₂-O transfer, (b) DNAN-O transfer, (c)
86 TNT- α -H transfer, (d) DNAN-H transfer. The C, H, O, and N atoms are colored in
87 gray, white, red and blue, respectively.