Supporting Information

Exploring the Photochemistry of Solid 1,1-Diamino-2,2-dinitroethylene (FOX-7) Spanning Simple Bond Ruptures, Nitro-to-Nitrite Isomerization, and Non-Adiabatic Dynamics

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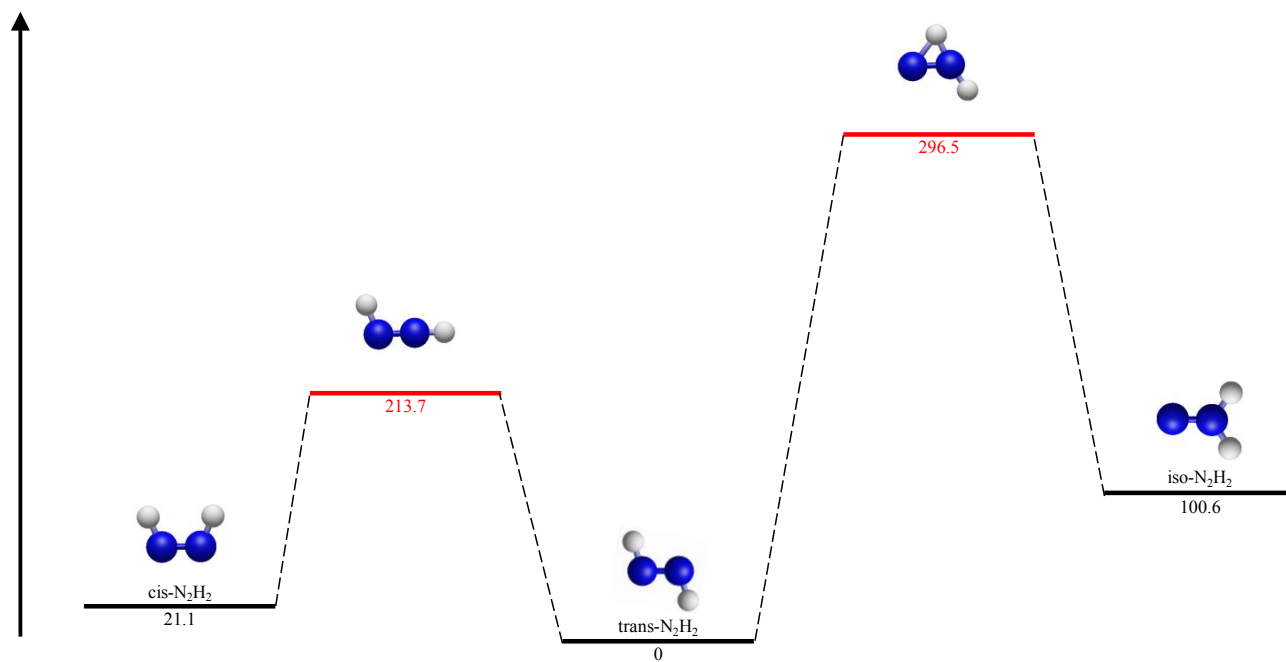†These authors contributed equally

Figure S1. Potential energy surface (MRCI+Q/AVQZ//CASSCF(12,10)/AVQZ + ZPE(CASSCF(12,10)/AVQZ) showing isomerization barriers between N_2H_2 isomers.
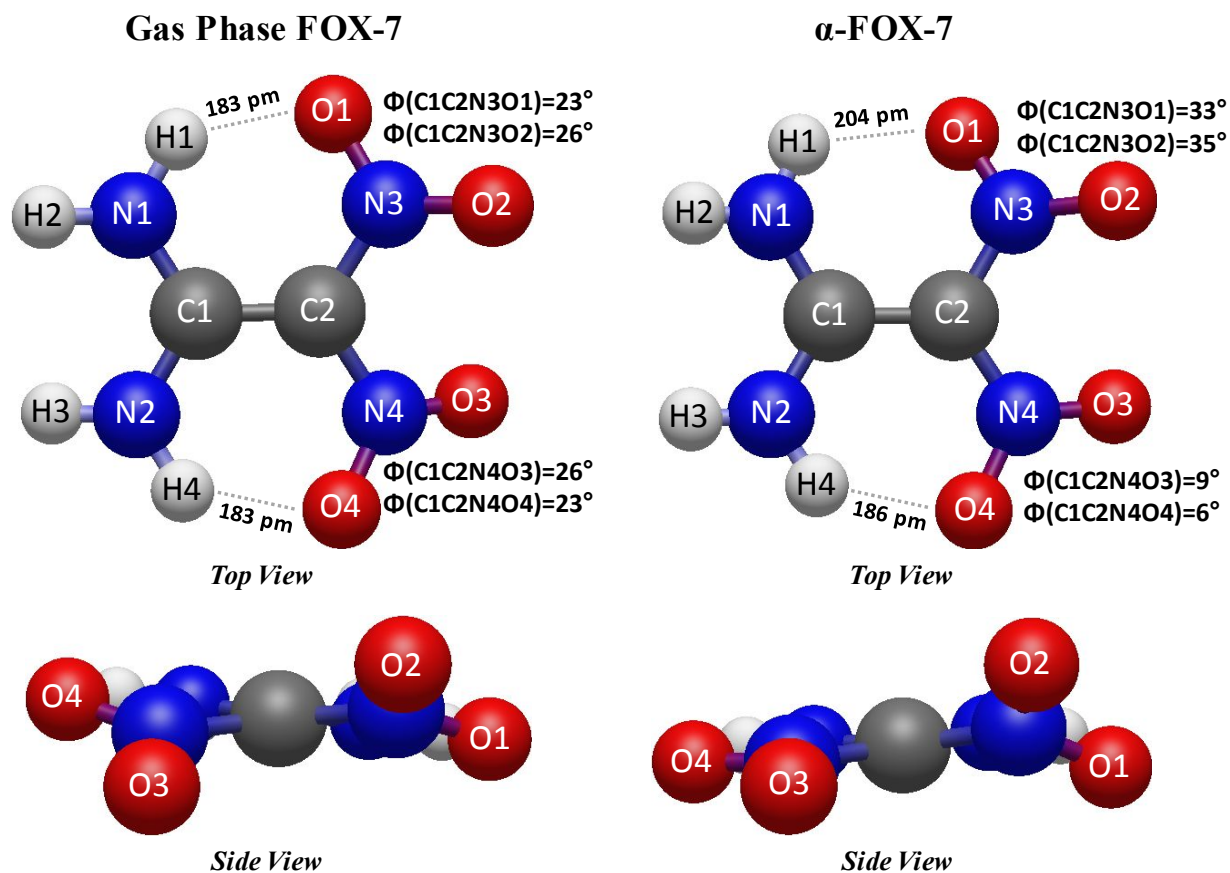
Figure S2. Geometric comparison between gas phase FOX-7 in gas phase and crystalline α-FOX-7.
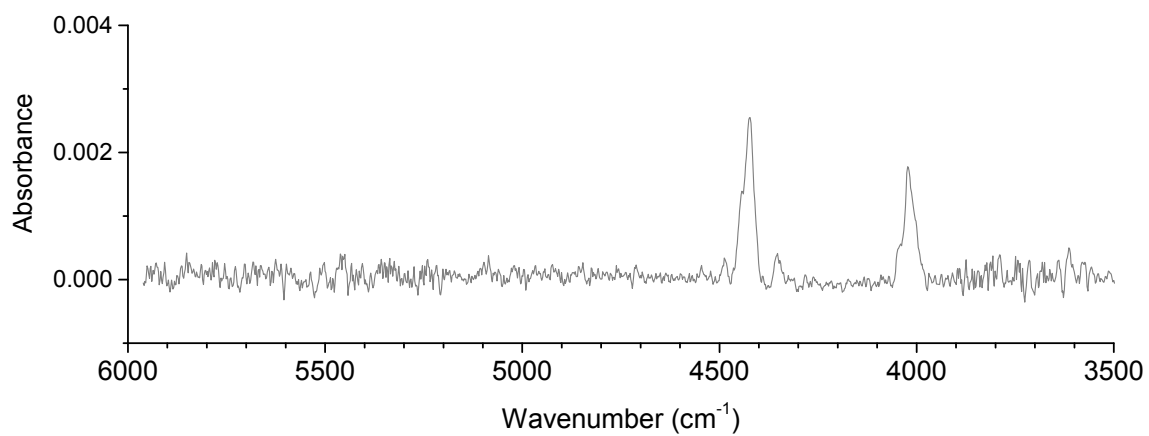
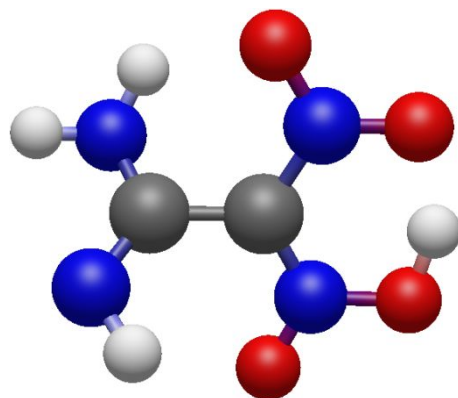Figure S3. Infrared spectrum of FOX-7 taken at 300 K showing the overtone/combination band region.

Figure S4. The zwitterionic form of FOX-7, which exists in equilibrium with the olefinic form in various solvents.

Nitric oxide ($C_{\infty v}$, X $^2\Pi$)
IE = 9.26 ± 0.01 eV

trans-Diazene (C_{2h}, X ^1A_g)
IE = 9.61 ± 0.01 eV
E = 0 kJ mol^{-1}

cis-Diazene (C_{2v}, X $^1A_1$)
IE = 9.64 ± 0.01 eV
E = 21.1 kJ mol^{-1}

iso-Diazene (C_{2v}, X $^1A_1$)
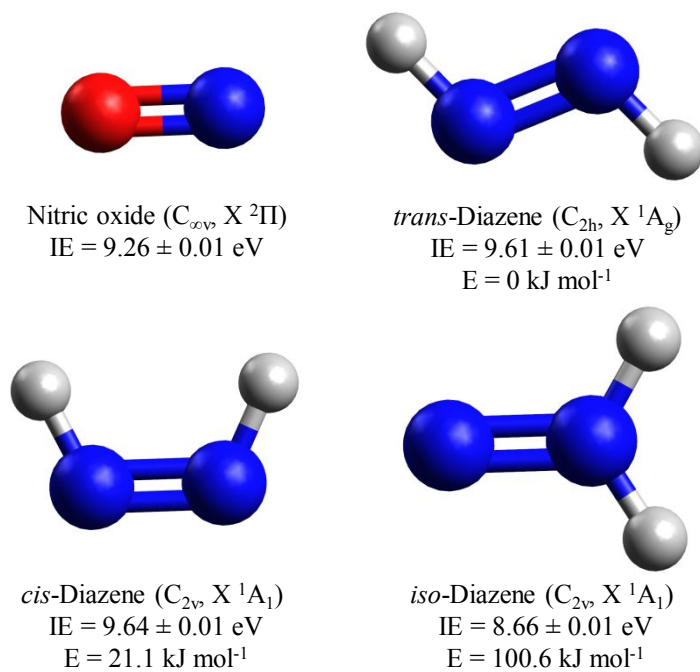IE = 8.66 ± 0.01 eV
E = 100.6 kJ mol^{-1}

Figure S5. Calculated adiabatic ionization energies of nitric oxide (NO) and N_2H_2 isomers along with their relative energies.

Table S1. Infrared fundamental modes of intermediate **i3** from the potential energy surface of Figure 8 calculated at the M06-2X-D3/def2-TZVPP level. An anharmonic scaling factor of 0.983 was applied to the wavenumbers in accordance with Alecu et al.[1]
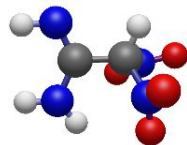
Mode	Wavenumber (cm^{-1})	Intensities (km mol^{-1})
1	3611.7	60.0
2	3524.0	70.3
3	3465.1	16.2
4	3124.0	7.4
5	1766.8	172.0
6	1729.3	293.2
7	1712.3	306.1
8	1624.4	144.4
9	1478.9	49.2
10	1434.4	175.1
11	1412.2	62.7
12	1296.6	9.0
13	1266.2	21.9
14	1124.5	1.7
15	1108.9	56.7
16	1022.8	0.9
17	988.7	4.5
18	965.6	15.0
19	898.2	77.3
20	859.7	9.8
21	807.1	47.5
22	723.1	5.8
23	669.6	43.8
24	634.3	152.4
25	594.6	50.0
26	538.9	42.0
27	457.9	5.8
28	420.7	17.5
29	405.6	16.3
30	373.2	0.7
31	249.6	7.1
32	233.9	3.4
33	222.3	0.9
34	162.1	0.9
35	130.2	0.6
36	114.1	0.8

Calculation of Irradiation Dose

The FOX-7 samples were exposed to photons at 355 nm and 532 nm over an area of 1.0 ± 0.1 cm^2 for 5 hours. While the molecules were *exposed* to photons, only a fraction of them were absorbed, and the radiant *exposure* (H_e, J cm^{-2}) is given by:

$$H_e = E_e \times t \tag{S1}$$

Where E_e is the irradiance (J s^{-1} cm^{-2}) and t is the exposure time. This exposure can be expressed in terms of photons by considering the energy per photon (E_p, J photon^{-1}):

$$E_p = \frac{energy}{photon} = \frac{\frac{hc}{\lambda}}{photon} = \frac{hc}{\lambda \times photon} \tag{S2}$$

Here, h is Planck's constant (6.626×10^{-34} J s), c is the speed of light (2.998×10^8 m s^{-1}), and λ is the wavelength of light (in meters). Further, this exposure can be given in photons per molecule by dividing by the column density, N (molecules cm^{-2}), which is simply the product of density ($\rho = 1.89$ g cm^{-3}) and the sample thickness ($d = 2 \times 10^{-4}$ cm), divided by the molar mass of FOX-7 (M $= 148.1$ g mol^{-1}). Using the the Avogadro constant ($N_A = 6.022 \times 10^{23}$ mol^{-1}) converts this value from moles to molecules:

$$N = \frac{\rho \times d \times N_A}{M} \tag{S3}$$

The numbers of photons per molecule is thus:

$$\frac{Photon}{Molecule} = \frac{H_e}{E_p \times N} = \frac{E_e \times t}{\left(\frac{hc}{\lambda \times photon}\right) \times \left(\frac{\rho \times d \times N_A}{M}\right)} = \frac{E_e \times t \times \lambda \times photon \times M}{h \times c \times \rho \times d \times N_A} \tag{S4}$$

However, because only a fraction of these photons are absorbed, the UV-Vis spectrum must be considered in order to determine the number of photons absorbed by the sample. Utilizing the multiple UV-Vis spectra taken of the samples, the average absorbance value (A_λ) at 355 nm is $A_{355} = 0.17 \pm 0.04$ and for for 532 nm the aborbance is $A_{532} = 0.053 \pm 0.014$. While the irradiation occurred perpendicular to the surface, the UV-Vis spectra were taken at a 30° angle of incidence (θ) with respect to the surface normal. While the beampath (2d) of the irradiation photons through the sample is 4 μm (2 μm into the sample followed by reflection and 2 μm to exit the sample), the pathlenghth (L) of the UV-Vis photons is obtained by:

$$L = \frac{2d}{\cos \theta} \tag{S5}$$

The Beer-Lambert Law relates the absorbance value to the pathlength (l):

$$A_\lambda = \varepsilon_\lambda \times C \times l \tag{S6}$$

In this case, the absorbitivity (ε_λ) and concentration (C) of the sample remain constant for different pathlengths and do not need calculated. To correct for the difference in absorbance for the irradiation beampath compared to the UV-Vis pathlength:

$$\varepsilon_\lambda \times C = \frac{A_\lambda}{l} = \frac{A_{\lambda,irrad.}}{2d} = \frac{A_{\lambda,UVVis}}{L} \tag{S7}$$

Using the above relationship, the corrected absorbance values for the irradiation photons are $A_{355,irrad.} = 0.15 \pm 0.03$ and $A_{532,irrad.} = 0.046 \pm 0.012$. Absorbance is also related to transmittance (T_λ), which is the ratio of light intensity (I) passing through the sample compared to the intensity without the sample (I_o, $T = I/I_o$) by:

$$A_\lambda = - \log_{10} T_\lambda \tag{S8}$$

After solving for T_λ, the transmittance values for the 355 nm and 532 nm irradiations are $T_{355} = 0.71 \pm 0.05$ and $T_{532} = 0.90 \pm 0.02$. Thus, 71 % of the irradiated 355 nm photons and 90 % of the 532 nm photons passed through the sample and were not absorbed, meaning 29 % of the 355 nm photons and 10 % of the 532 nm photons were absorbed. These correction factors ($1 - T_\lambda$) can be applied to equation S4 to obtain the number of absorbed photons per molecule:

$$\frac{\text{Absorbed Photon}}{\text{Molecule}} = \frac{(1 - T_\lambda) \times H_e}{E_p \times N} = \frac{(1 - T_\lambda) \times E_e \times t \times \lambda \times \text{photon} \times M}{h \times c \times \rho \times d \times N_A} \tag{S9}$$

Finally, the dose (D) in eV molecule^{-1} can be calculated by using the energy of a photon in units of eV (E_{eV} = eV photon^{-1}). This works out to be E_{eV} (355 nm) = 3.49 eV and E_{eV} (532 nm) = 2.33 eV.

$$D = \frac{(1 - T_\lambda) \times H_e \times E_{eV}}{E_p \times N} = \frac{(1 - T_\lambda) \times E_e \times t \times \lambda \times \text{photon} \times M \times E_{eV}}{h \times c \times \rho \times d \times N_A}$$

$$\tag{S10}$$

These calculations demonstrate that the irradiation dose is 230 ± 50 eV molecule^{-1} at 355 nm and 80 ± 20 eV molecule^{-1} at 532 nm. For the 355 nm irradiation, each molecule absorbs a photon, on average, every 5 minutes, which is sufficient time to exclude multi-photon processes from occurring.

Synthesis of FOX-7

The synthesis of FOX-7 was performed according to a mixed procedure of Latypov *et al*. and Astrat'ev et al.[2-3]
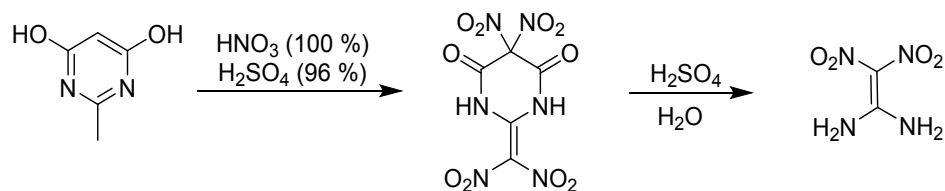
Concentrated sulfuric acid (96%, 42.0 mL) was cooled to 15 °C with an ice bath and 4,6-dihydroxy-2- methylpyrimidine (6.30 g, 0.05 mol, 1 eq) was slowly added in small portions under constant stirring, keeping the temperature between 15 °C and 20 °C the whole time. After all of the solid was dissolved, HNO_3 (100%, 8.87 mL, 0.2125 mol, 4.25 eq) was also added slowly at 15°C and stirring was continued for 6 h at 15 °C. The resulting precipitate was filtered and washed with H_2SO_4 (96%, 15 mL). The acid-wet solid was then directly dissolved in water (50 mL) under ice cooling, and conc. H_2SO_4 was added until a pH of 2 was reached. This mixture was stirred for 2 h at 15 °C. The solid was finally filtered and washed with water until a neutral pH was obtained. It was allowed to dry in air and FOX-7 (5.63 g, 0.038 mol) was obtained as a yellow crystalline solid.

NMR spectroscopy

^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.74 (s, 4H, NH_2).
^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) 128.0 (1C, $C(NO_2)_2$), 158.1 (1C, $C(NH_2)_2$).
^{14}N NMR (28.9 MHz, DMSO-d_6): δ (ppm) −25 (2N, $C(NO_2)_2$).

Elemental analysis

$C_2H_4N_4O_4$ (148.08), calculated (%): C 16.22, H 2.72, N 37.84; found (%): C 16.28, H 2.56, N 37.89.

IR spectroscopy

IR (ATR): ν = 3402 (s), 3329 (s), 3295 (s), 3226 (s), 1632 (s), 1622 (s), 1605 (s), 1520 (s), 1516 (s), 1505 (s), 1470 (s), 1456 (s), 1390 (vs), 1350 (s), 1212 (vs), 1166 (vs), 1140 (vs), 1022 (s), 857 (m), 789 (m), 749 (s), 738 (m), 673 (w), 636 (m), 617 (s), 602 (vs).
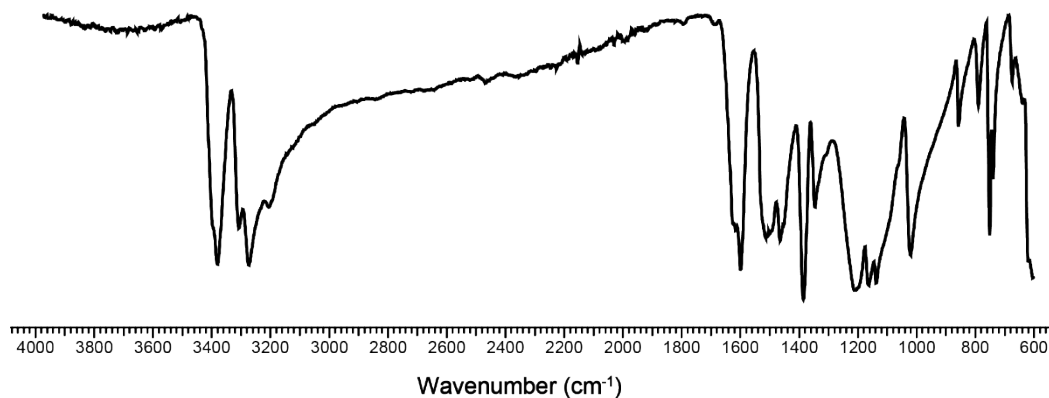

Figure S6. IR spectra of freshly prepared FOX-7 powder.

Differential thermal analysis (DTA)[4-5]

Onset temperatures measured in the range from 25°C to 400°C with a heating rate of 5°C min^{-1}.

T_{endo}: 115 °C, 162 °C (phase transition)
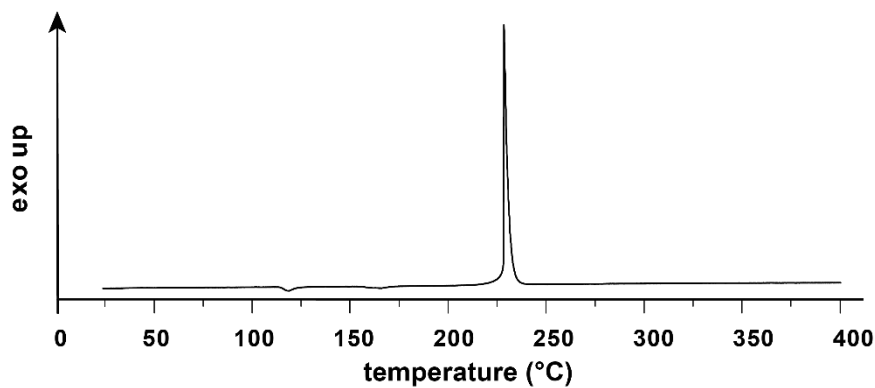
T_{exo}: 228°C (decomposition)

Figure S7. DTA measurement of FOX-7.

(1) Alecu, I. M.; Zheng, J.; Zhao, Y.; Truhlar, D. G., Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries. *Journal of Chemical Theory and Computation* **2010,** *6*, 2872-2887.

(2) Latypov, N. V.; Johansson, M.; Holmgren, E.; Sizova, E. V.; Sizov, V. V.; Bellamy, A. J., On the Synthesis of 1,1-Diamino-2,2-Dinitroethene (FOX-7) by Nitration of 4,6-Dihydroxy-2-Methylpyrimidine. *Organic Process Research & Development* **2007,** *11*, 56-59.

(3) Astrat'ev, A. A.; Dashko, D. V.; Mershin, A. Y.; Stepanov, A. I.; Urazgil'deev, N. A., Some Specific Features of Acid Nitration of 2-Substituted 4,6-Dihydroxypyrimidines. Nucleophilic Cleavage of the Nitration Products. *Russian Journal of Organic Chemistry* **2001,** *37*, 729-733.

(4) Bellamy, A. J., FOX-7 (1,1-Diamino-2,2-Dinitroethene). In *High Energy Density Materials*, Klapötke, T. M., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2007, 1-33.

(5) Klapötke, T. M., *Energetic Materials Encyclopedia*. 5th ed.; de Gruyter: 2021, 707−723.