

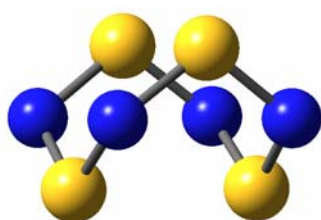
Matrix isolation and computational study of the photochemistry of tetrasulfur tetranitride, S₄N₄

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SUPPORTING INFORMATION

B3LYP/cc-pVTZ optimized geometries, energies, and thermal corrections of all the stationary points discussed in this work

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A1. Tetrasulfur tetranitride (4) - cage structure
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E(RB3LYP) = -1811.818604
nuclear repulsion energy 789.713436
Zero-point correction= 0.022212
Thermal correction to Energy= 0.029447
Thermal correction to Enthalpy= 0.030391
Thermal correction to Gibbs Free Energy= -0.008857

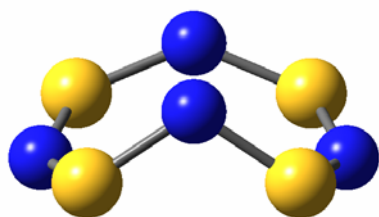
7	1.310090	1.310090	0.000000
7	-1.310090	1.310090	0.000000
7	-1.310090	-1.310090	0.000000
7	1.310090	-1.310090	0.000000
16	0.000000	1.375657	0.975052
16	-1.375657	0.000000	-0.975052
16	0.000000	-1.375657	0.975052
16	1.375657	0.000000	-0.975052

RB3LYP/aug-cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON), T = 0 K
 $\Delta G_{\text{solv}} = -8.07$ kcal/mol

TDB3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON)

λ , nm	f	λ , nm	f	λ , nm	f
437	0.0022	259	0.4616	237	0.0000
398	0.0056	248	0.0000	235	0.0352
320	0.0416	243	0.0000		
286	0.0022	241	0.0011		

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A2. Tetrasulfur tetranitride (9) - boat structure
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E(RB3LYP) = -1811.817142
nuclear repulsion energy 731.041375
Zero-point correction= 0.021386
Thermal correction to Energy= 0.029412
Thermal correction to Enthalpy= 0.030356
Thermal correction to Gibbs Free Energy= -0.012885

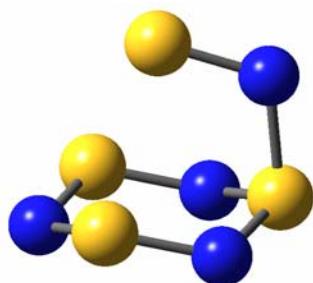
7	0.000000	1.715879	0.000000
7	-1.331095	-1.273193	0.000000
7	0.310268	-0.150470	1.934218
7	0.310268	-0.150470	-1.934218
16	0.844863	1.253260	1.351345
16	0.844863	1.253260	-1.351345
16	-0.689428	-1.284266	-1.485896
16	-0.689428	-1.284266	1.485896

RB3LYP/aug-cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON), T = 0 K
 $\Delta G_{\text{solv}} = -8.06$ kcal/mol

TDB3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON)

λ , nm	f	λ , nm	f	λ , nm	f
656	0.0074	336	0.0039	274	0.0054
478	0.0215	322	0.0093	268	0.0016
439	0.0001	312	0.1897	264	0.0570
371	0.0041	309	0.0153	258	0.1112

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A3. Cyclic N₃S₃-NS (10)
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E(RB3LYP) = -1811.800541
nuclear repulsion energy 788.489643
Zero-point correction= 0.022062
Thermal correction to Energy= 0.029498
Thermal correction to Enthalpy= 0.030442
Thermal correction to Gibbs Free Energy= -0.010536

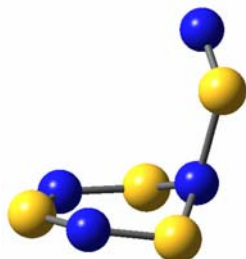
7	-1.636053	0.951605	0.000000
7	1.234316	-1.432456	0.000000
7	0.586586	0.859984	1.366375
7	0.586586	0.859984	-1.366375
16	-1.695149	-0.624101	0.000000
16	0.000000	1.592881	0.000000
16	0.678823	-0.755446	1.371099
16	0.678823	-0.755446	-1.371099

RB3LYP/aug-cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON), T = 0 K
 $\Delta G_{\text{solv}} = -7.59$ kcal/mol

TDB3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON)

λ , nm	f	λ , nm	f	λ , nm	f
579	0.0007	345	0.0137	292	0.0064
428	0.0032	320	0.0114	260	0.0516
370	0.0012	317	0.0058	256	0.0109
366	0.0218	293	0.1279	251	0.0026

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 A4. Cyclic S_3N_3 -SN (**11**)
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E(RB3LYP) = -1811.797607
 nuclear repulsion energy 729.410065
 Zero-point correction= 0.020769
 Thermal correction to Energy= 0.029504
 Thermal correction to Enthalpy= 0.030448
 Thermal correction to Gibbs Free Energy= -0.015127

7	0.668863	0.208950	0.771558
7	-1.250381	-1.475901	-0.129127
7	-1.506368	1.197525	-0.540679
7	2.655603	-0.791647	-1.007348
16	-0.377383	1.576908	0.652668
16	0.018125	-1.354293	0.955698
16	-2.006156	-0.274992	-0.803457
16	2.117038	0.429096	-0.408711

RB3LYP/aug-cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON), T = 0 K
 $\Delta G_{\text{solv}} = -7.96$ kcal/mol

TDB3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ, SCRF=(PCM,SOLVENT=ARGON)

λ , nm	f	λ , nm	f	λ , nm	f	λ , nm	f
668	0.0056	354	0.0050	291	0.0006	267	0.0526
521	0.0036	320	0.0114	288	0.0046	254	0.0045
475	0.0338	335	0.0198	282	0.0043	250	0.0234
361	0.0615	316	0.0061	273	0.0290	249	0.0393

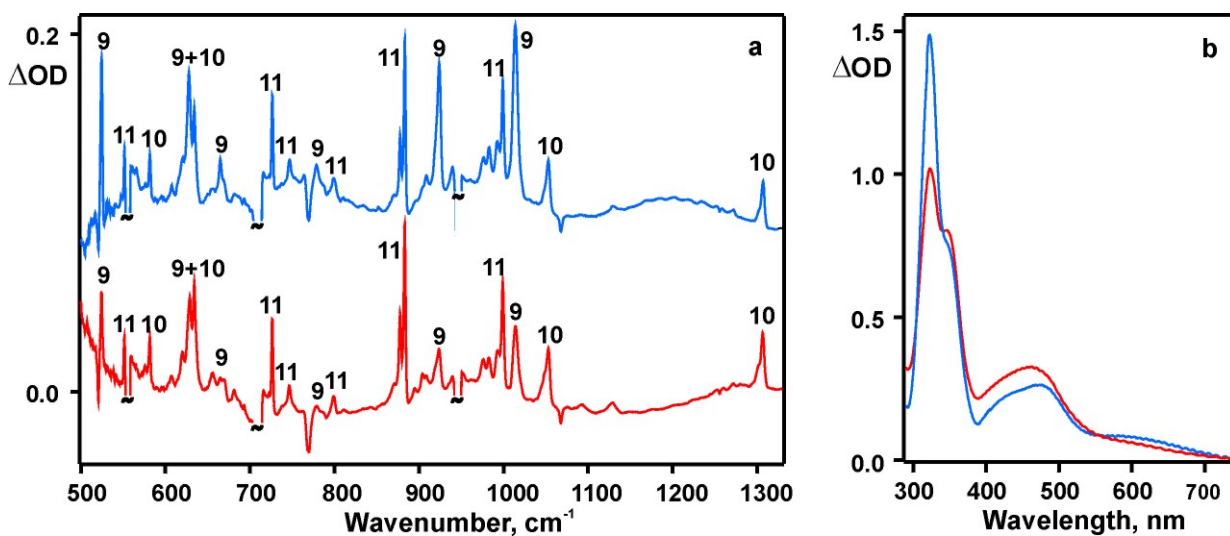


Figure S1. The difference IR (a) and UV-Vis (b) spectra obtained after photolysis of **4** at 254 nm (red trace) and at 365 nm (blue trace) in argon matrix at 12 K. The difference spectra correspond to the equal amount of photolysed **4**. The IR-bands of **4** are clipped. The numbers mark the IR-bands of intermediates (**9-11**) formed upon photolysis of **4**.

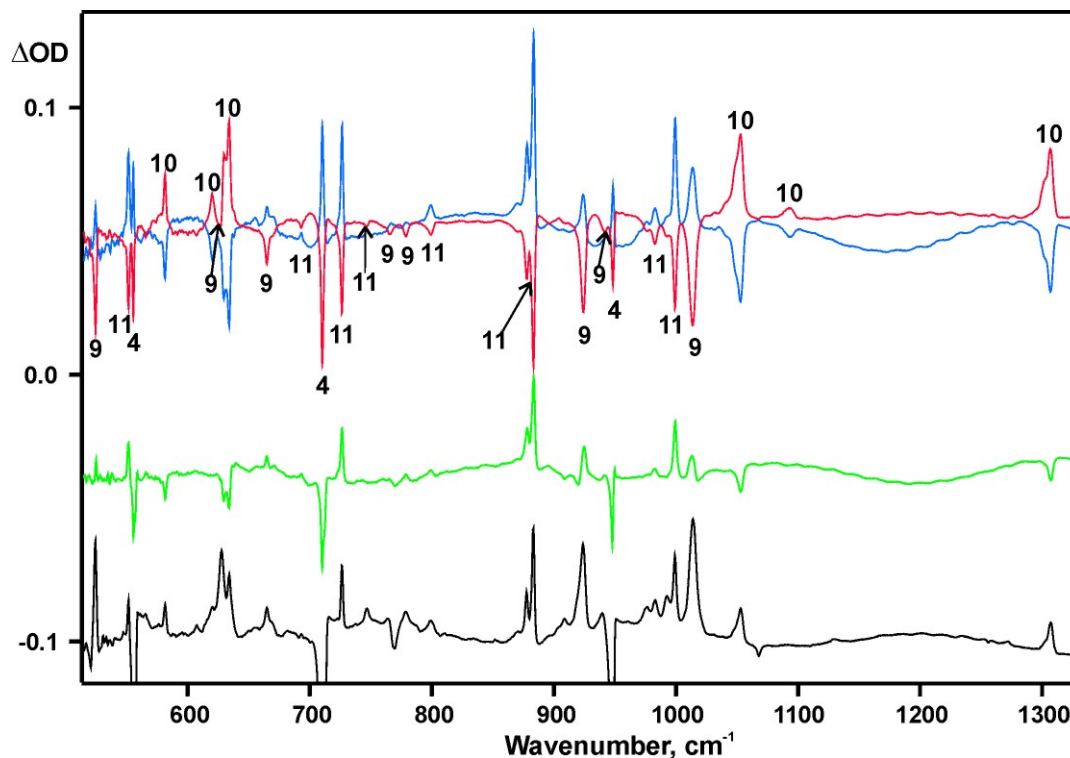


Figure S2. The sequence of difference IR spectra recorded in argon matrix at 12 K after photolysis of **4** at 365 nm for 5 min (black trace) and subsequent irradiations at $\lambda > 405$ nm for 5 min (green trace), at 313 nm for 15 min (red trace) and at $\lambda > 405$ nm for 5 min (blue trace). The numbers mark the IR-bands of intermediates **9-11**.