Photochemical Study on Reactivity of Tetrasulfur Tetranitride, S_4N_4

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SUPPORTING INFORMATION

Full citation for the Gaussian 03 Program (Reference 20):

Frisch, M. J. ; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C. and Pople, J. A. *Gaussian 03, Rev. B.01*, Gaussian, Inc., Pittsburg, **2003**.

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

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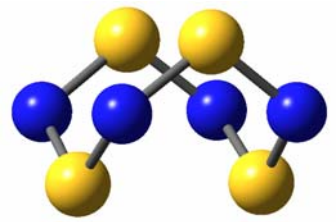
A1. Tetrasulfur tetranitride S_4N_4 (1) – cage structure



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

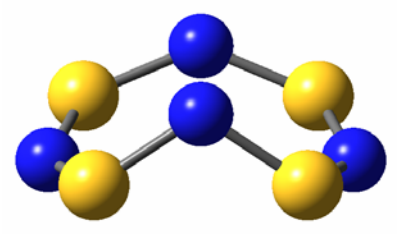
Thermal correction to Gibbs Free Energy = -0.008857

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

Table S1. Positions of electronic transitions (λ) and oscillator strengths (f) of **1** calculated by the B3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ method in 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		

A2. Tetrasulfur tetranitride S_4N_4 (2) – boat structure



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

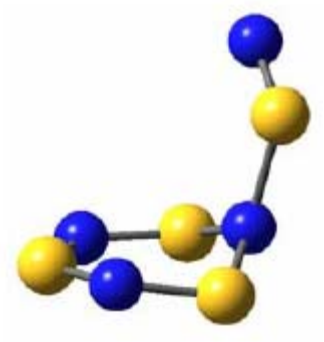
Thermal correction to Gibbs Free Energy = -0.012885

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

Table S2. Positions of electronic transitions (λ) and oscillator strengths (f) of **2** calculated by the B3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ method in 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

A3. Cyclic S_3N_3-S≡N (3)



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

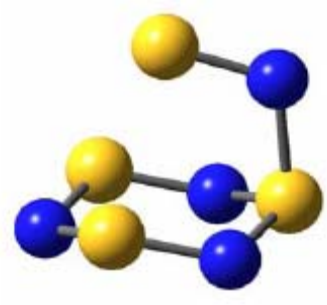
Thermal correction to Gibbs Free Energy= -0.015127

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

Table S3. Positions of electronic transitions (λ) and oscillator strengths (f) of **3** calculated by the B3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ method in 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

A4. Cyclic N_3S_3-N=S (4)



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

Table S4. Positions of electronic transitions (λ) and oscillator strengths (f) of **4** calculated by the B3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ method in 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

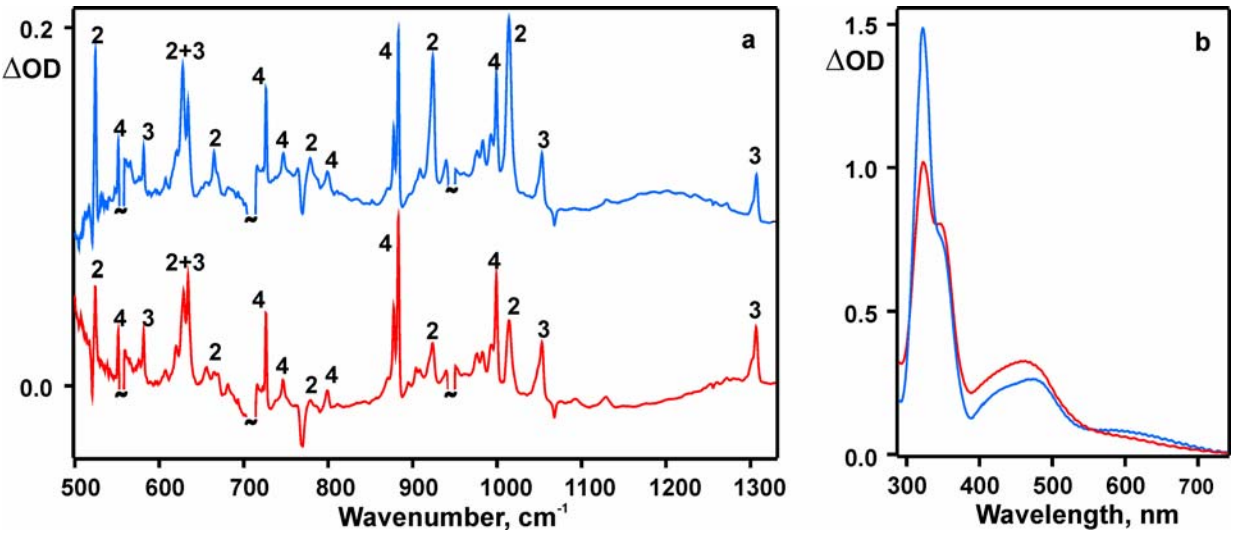


Figure S1. The difference IR (a) and UV-Vis (b) spectra obtained after photolysis of **1** at 254 nm (red trace) and at 365 nm (blue trace) in argon matrix at 12 K. The difference spectra correspond to the equal amount of photolysed **1**. The IR-bands of **1** are clipped. The numbers mark the IR-bands of intermediates (**2**–**4**) formed upon photolysis of **1**.

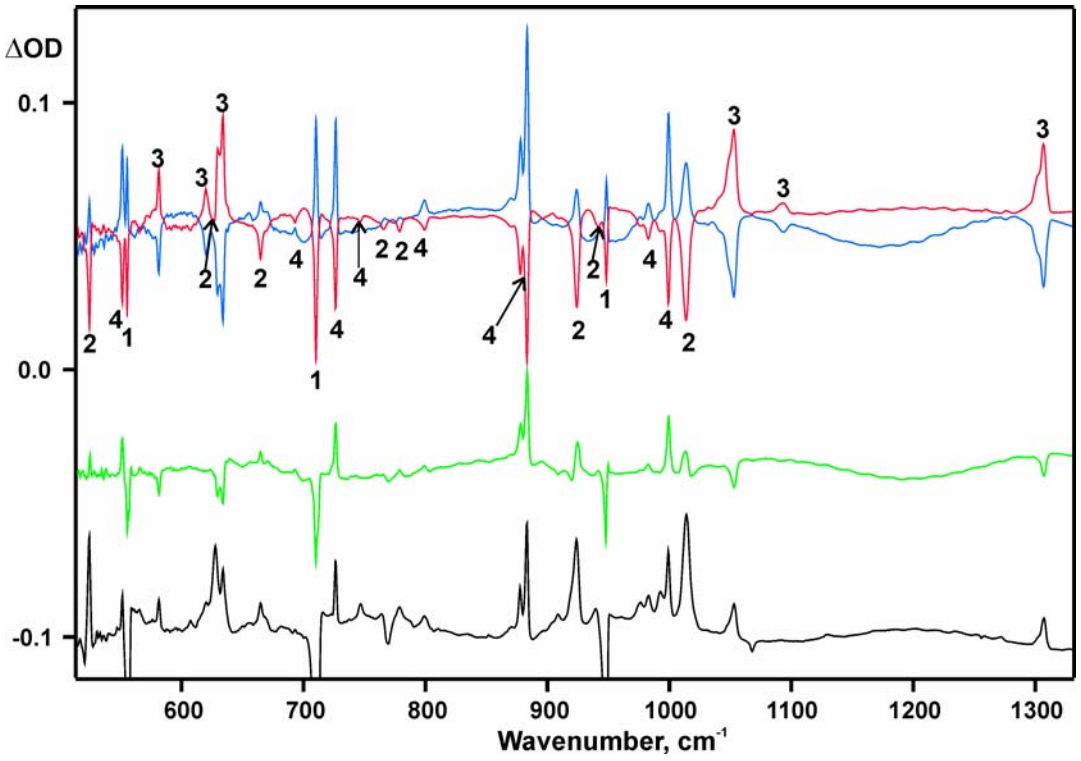


Figure S2. The sequence of difference IR spectra recorded in argon matrix at 12 K after photolysis of **1** at 365 nm for 5 min (black trace) and subsequent irradiations at > 405 nm for 5 min (green trace), at 313 nm for 15 min (red trace) and at > 405 nm for 5 min (blue trace). The numbers mark the IR-bands of compounds **1**, **2**–**4**.

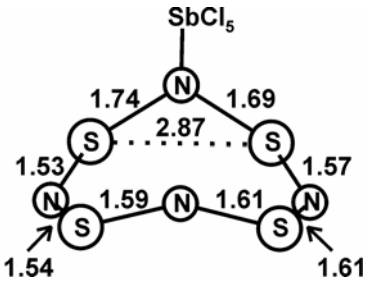


Figure S3. The experimental bond lengths (Å) in the N-bonded adduct of **1** with $SbCl_5$.[27]

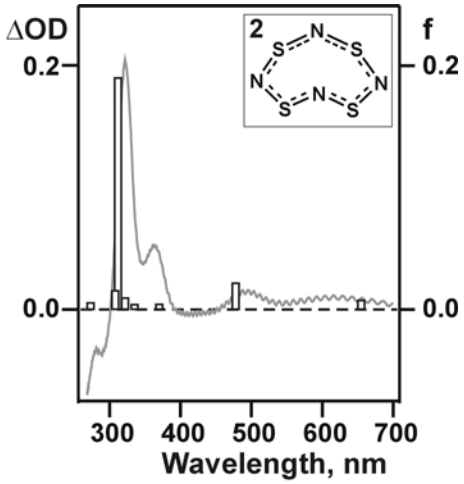


Figure S4. Difference UV-Vis spectrum recorded upon bleaching of species **3**, **4** and **1** at > 405 nm for 10 min in argon matrix at 12 K (corresponds to the difference IR spectrum 2 in Fig. 7b). The vertical black open bars indicate the positions and oscillator strengths of the electronic transitions of boat structure **2** calculated by the TD-B3LYP/aug-cc-pVTZ method at the B3LYP/cc-pVTZ geometry.