Matrix isolation and computational study of the photochemistry of 1,3,2,4-benzodithiadiazine

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Supporting information, part 2

Full citation for the Gaussian 03 Program (Reference 14)

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

Table S1. Vertical excitation energies of 1,3,2,4-dithiadiazine **1** calculated using CASSCF(16,12)/ANO-S/CASPT2 method at B3LYP/6-311G(df,p) geometry.

State	ΔE_{CASSCF}, eV	ΔE_{CASPT2}, eV	ref. weight*	λ nm	f	Major configurations
1^1A	0.0	0.0	0.71			82% of ground configuration
2^1A	2.89	1.75	0.69	707	2.4×10^{-2}	72%: 43a→44a
3^1A	4.17	3.22	0.69	385	6.3×10^{-2}	35%: 2(43a→44a) 18%: 42a→44a
4^1A	4.35	3.31	0.69	375	1.4×10^{-3}	21%: 42a→44a 19%: 2(43a→44a) 12%: 43a →45a
5^1A	5.66	4.04	0.67	307	5.1×10^{-3}	18%: 43a→46a 17%: 41a→44a
6^1A	6.19	4.15	0.67	299	7.5×10^{-2}	17%: 43a →47a 12%: 43a →44a + 43a→45a
7^1A	5.00	4.27	0.69	290	9.3×10^{-3}	55%: 40a →44a 10%: 40a→44a + 43a→44a
8^1A	6.00	4.29	0.68	289	3.4×10^{-1}	19%: 43a →45a 16%: 42a→44a 11%: 39a→44a
9^1A	6.41	4.55	0.67	273	3.3×10^{-2}	14%: 43a→47a 11%: 43a→45a
10^1A	6.73	4.92	0.67	252	2.8×10^{-3}	15%: 43a →44a + 43a→45a 14%: 41a→44a
11^1A	6.62	5.07	0.68	245	1.4×10^{-2}	18%: 42a →45a + 43a→44a

*- with level shift = 0.25 a.u.

Table S2. Vertical excitation energies of thyazil **3** calculated using CASSCF(16,12)/ANO-S/CASPT2 method at B3LYP/6-311G(df,p) geometry

state	ΔE_{CASSCF}, eV	ΔE_{CASPT2}, eV	ref. weight*	λ nm	f	Major configurations
$1^1A'$	0.0	0.0	0.70			83% of ground configuration
$1^1A''$	2.21	2.27	0.70	546	1.2×10^{-5}	81%: 8a" →36a'
$2^1A''$	3.60	3.22	0.69	385	1.7×10^{-4}	77%: 7a" →36a'
$2^1A'$	4.09	3.34	0.69	371	1.0×10^{-2}	46%: 35a' →36a' 21%: 8a" →9a"
$3^1A'$	5.26	4.03	0.68	307	7.5×10^{-2}	35%: 7a" →9a"
$4^1A'$	5.12	4.07	0.68	304	4.5×10^{-1}	37%: 8a" →9a" 16%: 7a" →9a"
$3^1A''$	5.10	4.50	0.69	276	4.5×10^{-5}	83%: 35a' →9a"
$4^1A''$	5.46	4.83	0.69	257	3.7×10^{-3}	64%: 6a" →36a'
$5^1A'$	6.44	4.90	0.67	253	1.6×10^{-1}	16%: 8a" →10a" 14%: 5a" →9a" 10%: 8a" →9a"
$5^1A''$	5.56	4.96	0.69	250	1.8×10^{-4}	61%: 5a" →36a'
$6^1A'$	6.94	5.36	0.67	231	1.9×10^{-2}	32%: 5a" →9a" 13%: 35a' →9a" + 8a" →36a'
$7^1A'$	5.69	5.51	0.69	225	3.4×10^{-2}	46%: 2(8a" →36a') 18%: 8a" →36a' + 7a" →36a'
$8^1A'$	7.14	5.98	0.68	207	1.3×10^{-3}	61%: 8a" →36a' + 35a' →9a"

* - with level shift = 0.25 a.u.

Table S3. Vertical excitation energies of *o*-quinoid acyclic product **6** calculated using CASSCF(16,12)/ANO-S/CASPT2 method at B3LYP/6-311G(df,p) geometry.

State	ΔE_{CASSCF}, eV	ΔE_{CASPT2}, eV	ref. weight*	λ nm	f	Major configurations
1^1A	0.0	0.0	0.70			71% of ground configuration
2^1A	1.18	0.54	0.70	2315	4.0×10^{-4}	56%: 42a→44a
3^1A	1.72	1.02	0.69	1214	4.0×10^{-4}	36%: 41a→44a 13%: 43a→44a
4^1A	2.57	1.77	0.69	701	5.3×10^{-4}	30%: 42a →44a + 43a →44a
5^1A	3.13	2.20	0.69	564	4.6×10^{-3}	12%: 2(42a→44a) 12%: 40a →44a
6^1A	3.01	2.30	0.69	540	7.9×10^{-3}	46%: 42a →45a 11%: 41a →45a
7^1A	3.51	2.55	0.69	487	1.7×10^{-3}	19%: 42a →45a + 43a →44a 11%: 42a →44a + 43a →45a
8^1A	3.83	2.57	0.69	482	3.6×10^{-2}	21%: 43a →44a 13%: 39a →44a
9^1A	4.21	2.91	0.68	426	2.7×10^{-3}	10%: 42a→44a + 43a→44a
10^1A	3.96	2.99	0.69	414	9.1×10^{-3}	20%: 2(43a →44a)
11^1A	4.33	3.01	0.68	412	1.4×10^{-2}	12%: 42a →44a + 42a →45a
12^1A	4.10	3.03	0.69	410	2.2×10^{-3}	8%: 42a →44a + 42a →45a 9%: 41a →44a + 42a →45a 9%: 40a →44a + 42a →44a

13^1A	4.40	3.08	0.68	402	3.0×10^{-3}	6%: 42a →45a + 43a →44a 6%: 41a →44a + 43a →44a 6%: 41a →45a + 2(42a →44a)
14^1A	4.93	3.22	0.68	385	4.8×10^{-3}	7%: 41a →44a + 43a →44a 7%: 42a →47a
15^1A	4.57	3.39	0.68	366	4.2×10^{-4}	10%: 41a →45a + 2(42a →44a)
16^1A	5.43	3.84	0.67	323	3.7×10^{-3}	6%: 42a →44a + 42a →45a 5%: 42a →47a 6%: 40a →44a + 42a →45a
17^1A	5.09	3.88	0.68	320	4.2×10^{-2}	13%: 40a →44a + 43a →44a
18^1A	4.74	3.88	0.69	320	1.4×10^{-3}	8%: 42a →47a 7%: 38a →44a + 42a →44a
19^1A	5.52	3.90	0.67	318	4.5×10^{-3}	12%: 39a →44a + 42a →44a
20^1A	5.24	4.20	0.68	296	4.5×10^{-4}	8%: 43a →44a + 37a →45a

* - wth level shift = 0.25 a.u.

Table S4. Vertical excitation energies of *o*-quinoid acyclic product **7** calculated using CASSCF(16,12)/ANO-S/CASPT2 method at B3LYP/6-311G(df,p) geometry

State	ΔE_{CASSCF}, eV	ΔE_{CASPT2}, eV	ref. weight*	λ nm	f	Major configurations
1^1A	0.0	0.0	0.71			74% of ground configuration
2^1A	1.63	0.69	0.69	1802	3.3×10^{-4}	38%: 41a→44a 16%: 41a →44a + 43a →44a 12%: 41a→45a
3^1A	1.40	1.03	0.69	1203	9.2×10^{-5}	57%: 42a→44a
4^1A	2.08	1.17	0.69	1064	2.2×10^{-6}	52%: 41a →44a + 42a →44a
5^1A	2.70	1.84	0.69	674	3.7×10^{-4}	38%: 41a→45a 13%: 41a→44a + 43a →44a
6^1A	3.59	2.39	0.69	519	3.3×10^{-3}	22%: 38a →44a
7^1A	3.65	2.59	0.69	478	1.2×10^{-4}	53%: 41a →44a + 42a →45a
8^1A	4.05	2.64	0.69	471	8.1×10^{-2}	36%: 43a →44a 11%: 39a →44a
9^1A	3.86	2.83	0.69	438	8.2×10^{-4}	24%: 42a→44a + 43a→44a
10^1A	3.75	2.86	0.70	433	9.9×10^{-3}	29%: 2(43a →44a) 12%: 40a →44a
11^1A	4.20	3.07	0.69	404	5.6×10^{-4}	32%: 41a →44a + 41a →45a
12^1A	4.36	3.15	0.69	394	5.8×10^{-4}	29%: 38a →44a + 42a →44a 20%: 41a →45a + 42a →44a
13^1A	4.46	3.23	0.69	384	4.1×10^{-4}	19%: 40a →44a + 41a →44a
14^1A	5.13	3.27	0.68	379	6.4×10^{-3}	12%: 39a →44a + 41a →44a

15^1A	4.54	3.56	0.69	349	4.1×10^{-3}	24%: 39a →44a + 42a →44a 14%: 42a →45a
16^1A	5.29	3.68	0.68	337	1.9×10^{-4}	25%: 41a →44a + 42a →44a + 43a →45a 10%: 41a →44a + 42a →45a + 43a →44a
17^1A	4.99	3.72	0.69	333	7.1×10^{-2}	7%: 43a →44a 8%: 43a →45a
18^1A	5.48	3.91	0.68	317	1.1×10^{-1}	20%: 39a →44a
19^1A	5.60	4.18	0.68	297	2.1×10^{-2}	17%: 39a →44a + 42a →44a
20^1A	5.39	4.36	0.69	284	2.6×10^{-3}	52%: 2(41a →44a) + 43a →45a

* - with level shift = 0.25 a.u.

Table S5. Vertical excitation energies of thiazabenzocyclobutene **8a** calculated using CASSCF(16,12)/ANO-S/CASPT2 method at B3LYP/6-311G(df,p) geometry.

State	ΔE_{CASSCF}, eV	ΔE_{CASPT2}, eV	ref. weight*	λ nm	f	Major configurations
1^1A	0.0	0.0	0.71			85% of ground configuration
2^1A	2.96	2.49	0.70	499	1.0×10^{-2}	38%: 43a→44a 34%: 40a→44a
3^1A	3.83	2.71	0.69	457	1.2×10^{-2}	23%: 43a→44a 11%: 42a→44a 17%: 43a→45a 16%: 40a→44a
4^1A	4.25	2.79	0.68	444	4.8×10^{-2}	13%: 42a→44a 23%: 42a→45a 17%: 40a →45a
5^1A	4.33	2.89	0.68	430	2.0×10^{-3}	42%: 42a→44a 13%: 43a →45a
6^1A	4.70	3.40	0.69	365	4.8×10^{-2}	42%: 42a →45a 24%: 43a →45a 10%: 40a→45a
7^1A	5.54	3.88	0.68	319	2.4×10^{-2}	19%: 41a →44a
8^1A	5.93	3.92	0.67	316	1.0×10^{-1}	16%: 42a →46a
9^1A	6.43	4.51	0.67	275	4.7×10^{-2}	27%: 41a→44a 18%: 41a→45a
10^1A	6.24	4.53	0.68	274	3.0×10^{-3}	18%: 42a →44a + 43a→44a

* - with level shift = 0.25 a.u.

Table S6. Vertical excitation energies of thiazabenzocyclobutene **8b** calculated using CASSCF(16,12)/ANO-S/ CASPT2 method at B3LYP/6-311G(df,p) geometry

State	ΔE_{CASSCF}, eV	ΔE_{CASPT2}, eV	ref. weight*	λ nm	f	Major configurations
1^1A	0.0	0.0	0.70			85% of ground configuration
2^1A	2.96	2.45	0.70	507	1.3×10^{-2}	43%: 43a→44a 36%: 40a→44a
3^1A	4.02	2.79	0.69	444	2.3×10^{-2}	26%: 42a→44a 14%: 43a→45a 12%: 42a→45a 11%: 40a→44a
4^1A	4.43	2.96	0.68	419	5.6×10^{-2}	11%: 43a→44a 41%: 42a→45a 12%: 40a →44a
5^1A	4.56	3.10	0.68	400	5.6×10^{-3}	37%: 42a→44a
6^1A	5.01	3.56	0.68	348	6.3×10^{-2}	43%: 43a →45a 16%: 42a →45a
7^1A	5.61	3.85	0.67	322	7.6×10^{-3}	13%: 41a →44a
8^1A	5.92	3.95	0.67	314	9.7×10^{-2}	12%: 43a →46a 13%: 42a→46a
9^1A	6.58	4.54	0.67	273	5.5×10^{-2}	23%: 41a→44a
10^1A	6.39	4.59	0.67	270	5.6×10^{-3}	15%: 42a →45a + 43a→44a 13%: 41a→44a

* - with level shift = 0.25 a.u.

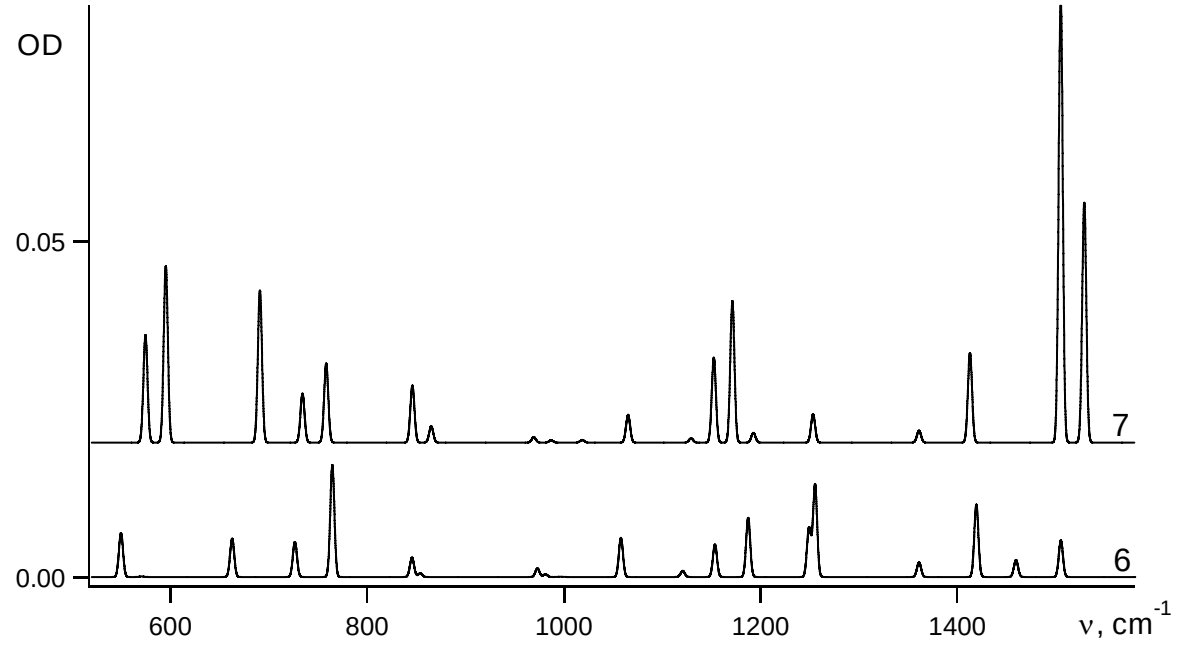

Figure S1. Traces shows the IR spectra of *o*-quinoid acyclic compounds **6** and **7** calculated by B3LYP/6-311G(df,p) (scaling factor 0.97)

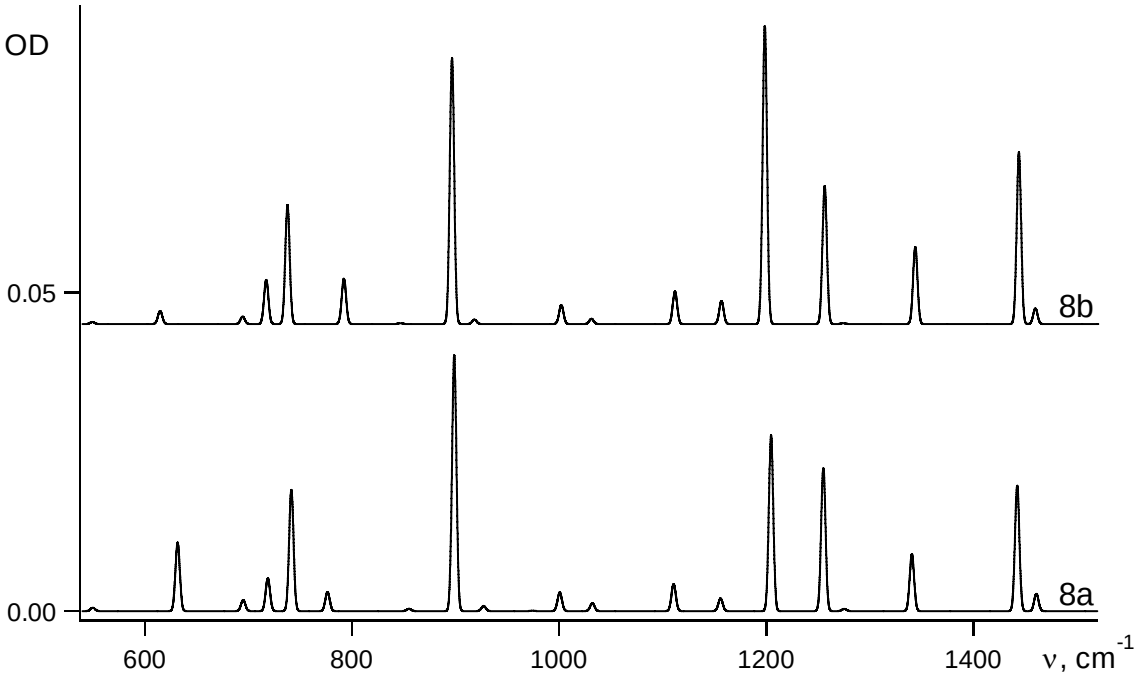

Figure S2. Traces shows the IR spectra of two rotamers of thiazabenzocyclobutene **8** calculated by B3LYP/6-311G(df,p) (scaling factor 0.98)

Table S7. Summary of B3LYP calculations

compound	B3LYP/6-31G(d)		B3LYP/6-311G(df,p)	
	H(0 K), h.	ΔH(0 K), kcal/mol	H(0 K), h.	ΔH(0 K), kcal/mol
1,3,2,4-dithiadiazine **1**	-1136.747288	0.0	-1136.902585	0.0
thyazil **3**	-1136.692164	34.6	-1136.847473	34.6
o-quinoid acyclic **6**	-1136.691544	35.0	-1136.841469	38.4
o-quinoid acyclic **7**	-1136.687894	37.3	-1136.839467	39.6
thiazacyclobutene **8a**	-1136.694988	32.8	-1136.849643	33.2
thiazacyclobutene **8b**	-1136.694618	33.1	-1136.849483	33.3