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Electronic Supplementary Information

Spectroscopic characterization of C-4 substituted 3,5-dichloro-4*H*-1,2,6-thiadiazines

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1. Comparison of IR and resonance Raman spectra of thiadiazines 5a, 5b and 5c

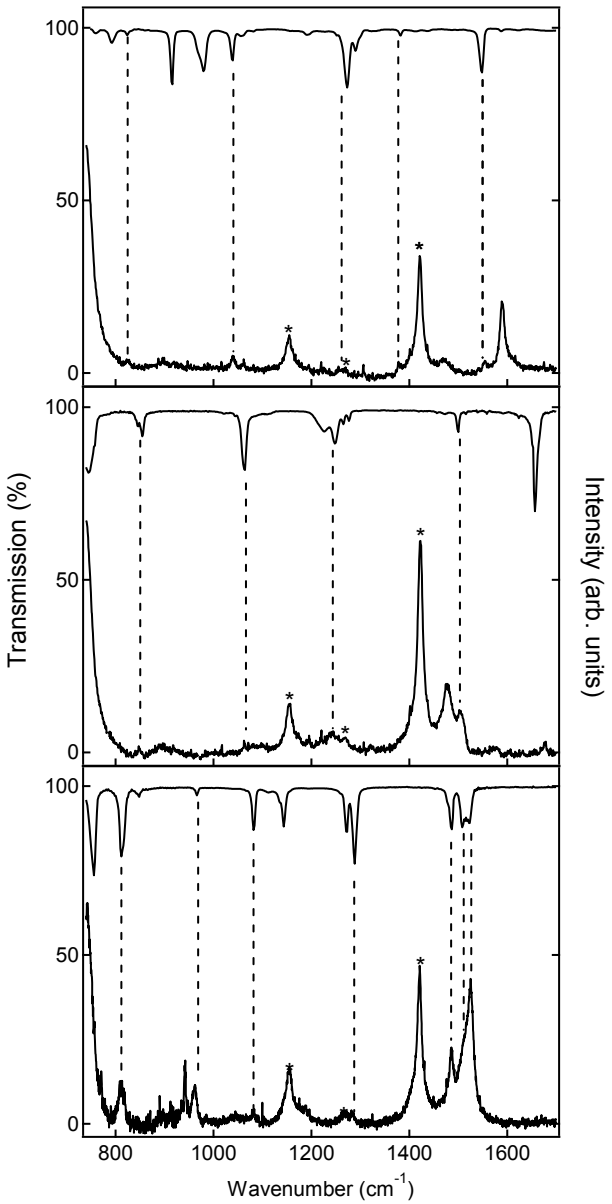
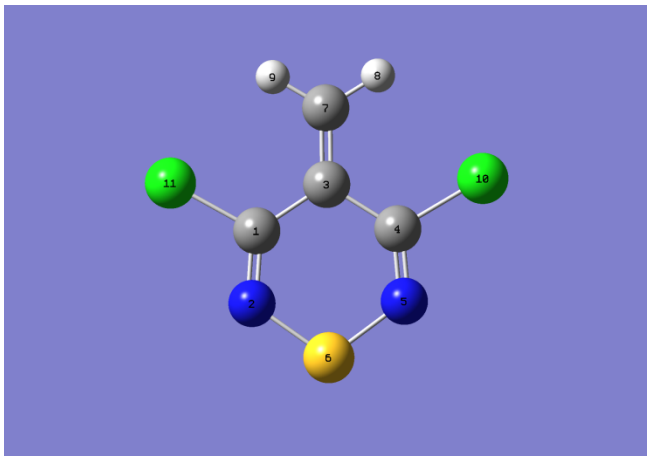


Figure S1. Comparison of IR and Raman spectra of thiadiazine **5a** (top), **5b** (middle) and **5c** (bottom). The IR spectra are shown in transmission (top of each panel). In the case of thiadiazine 5b, the IR spectrum was multiplied by two for clarity.

2. Atomic coordinates of the geometry optimized structures of thiadiazines 5a, 5b and 5c and their H-analogues using MP2/6-311G(d)

*2.1 3,5-Dichloro-4-methylene-4*H*-1,2,6-thiadiazine (**5a**)*

Figure S1 Optimised geometry using MP2/6-311G(d) showing atom labels

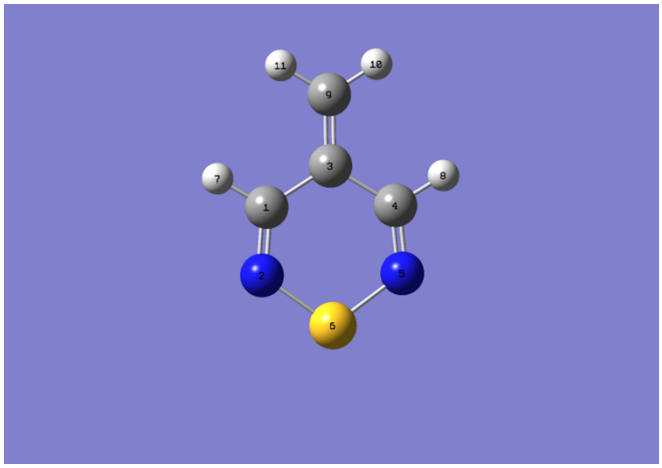


Atomic coordinates

C1	-0.00002	-0.01575	1.241068
N2	-0.00002	1.266697	1.340458
C3	0.000022	-0.81886	0
C4	-0.00002	-0.01575	-1.24107
N5	-0.00002	1.266697	-1.34046
S6	-1E-06	2.243887	0
C7	0.00011	-2.17292	0
H8	0.000148	-2.73159	-0.92553
H9	0.000148	-2.73159	0.925532
Cl10	-1.6E-05	-0.88333	-2.74823
Cl11	-1.6E-05	-0.88333	2.748228

*2.2 4-Methylene-4*H*-1,2,6-thiadiazine (**5a** with Cl substituted with H)*

Figure S2 Optimised geometry using MP2/6-311G(d) showing atom labels

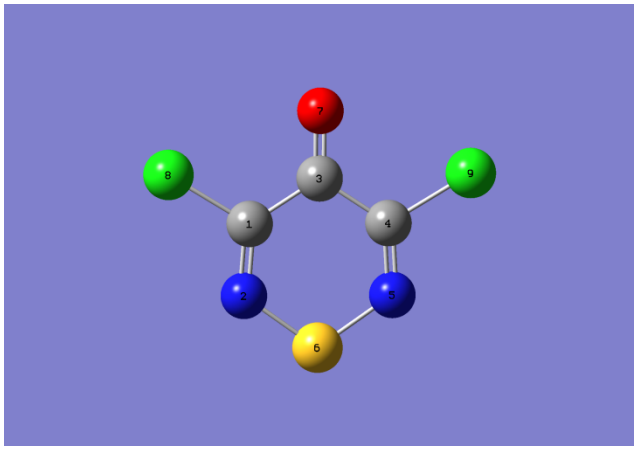


Atomic coordinates

C1	-0.52692	-1.24891	0.000042
N2	0.766276	-1.36086	0.000019
C3	-1.29261	0	0.000004
C4	-0.52692	1.248911	0.000042
N5	0.766276	1.360854	0.000019
S6	1.738807	0	-3.3E-05
H7	-1.07991	-2.19091	0.000079
H8	-1.07991	2.190905	0.000079
C9	-2.64792	0.000001	-4.7E-05
H10	-3.21136	0.928108	-6.9E-05
H11	-3.21136	-0.92811	-6.9E-05

*2.3 3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-one (**5b**)*

Figure S3 Optimised geometry using MP2/6-311G(d) showing atom labels

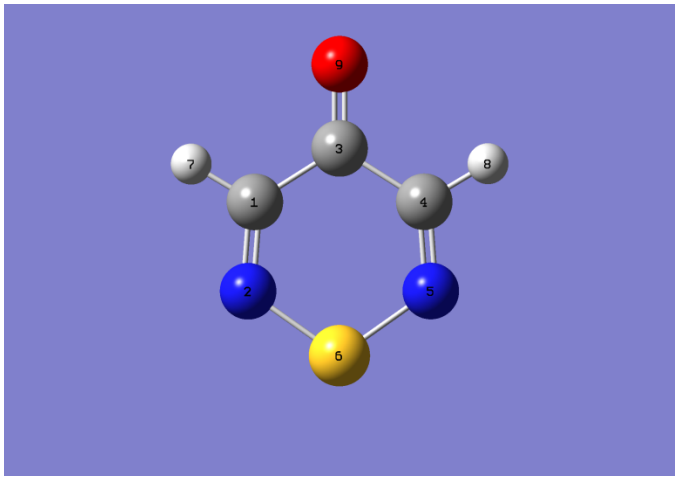


Atomic coordinates

1	-5E-06	-0.02818	1.244174
2	-2.4E-05	1.272124	1.3307
3	0.000057	-0.84314	0
4	-5E-06	-0.02818	-1.24417
5	-2.4E-05	1.272124	-1.3307
6	-1.7E-05	2.217415	0
7	0.000064	-2.06469	0
8	-5E-06	-0.92276	2.710934
9	-5E-06	-0.92276	-2.71093

*2.4 4H-1,2,6-Thiadiazin-4-one (**5b** with Cl substituted with H)*

Figure S4 Optimised geometry using MP2/6-311G(d) showing atom labels

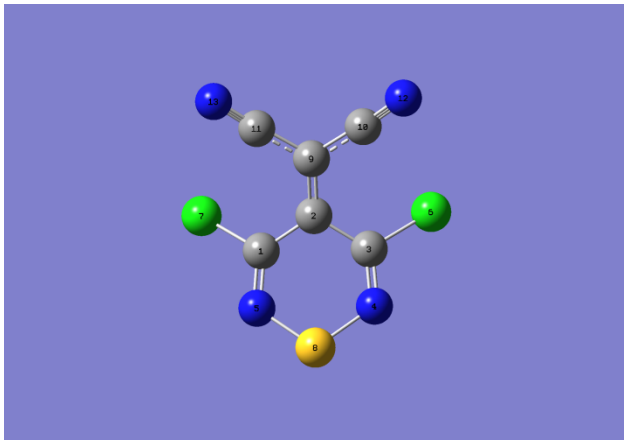


Atomic coordinates

1	-7.7E-05	-0.55866	1.245979
2	-7.7E-05	0.748805	1.343998
3	0.000132	-1.34277	0
4	-7.7E-05	-0.55866	-1.24598
5	-7.7E-05	0.748805	-1.344
6	0.000035	1.694294	0
7	-0.00017	-1.11525	2.183778
8	-0.00017	-1.11525	-2.18378
9	0.000124	-2.57511	0

*2.5 2-(3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile (**5c**)*

Figure S5 Optimised geometry using MP2/6-311G(d) showing atom labels

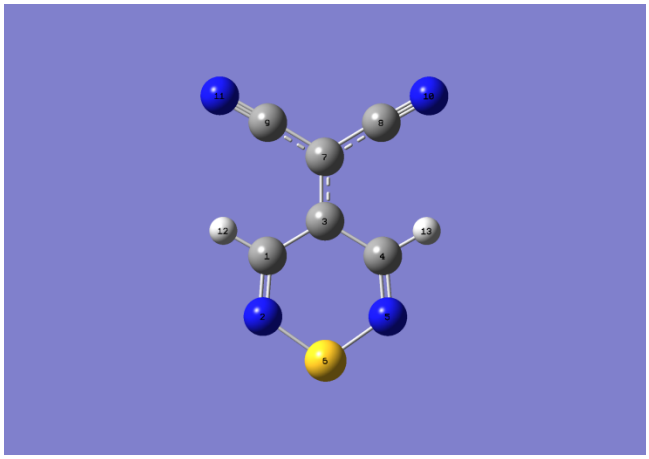


Atomic coordinates

1	0.665807	1.214645	0.146719
2	-0.14228	-0.00033	0.022368
3	0.66954	-1.21283	0.146726
4	1.885151	-1.3181	-0.30634
5	1.881061	1.323695	-0.30642
6	0.01124	-2.58089	0.954535
7	0.002978	2.580878	0.953923
8	2.699092	0.004051	-0.83801
9	-1.4957	-0.0023	-0.24594
10	-2.24703	-1.19949	-0.45983
11	-2.25038	1.192822	-0.4596
12	-2.92494	-2.13762	-0.6895
13	-2.93083	2.129198	-0.68893

*2.6 2-(4*H*-1,2,6-Thiadiazin-4-ylidene)malononitrile (**5c** with Cl substituted with H)*

Figure S7 Optimised geometry using MP2/6-311G(d) showing atom labels



Atomic coordinates

1	0.000283	-0.56937	1.239975
2	0.000092	-1.87703	1.342897
3	0.000054	0.178313	0
4	0.000283	-0.56937	-1.23998
5	0.000092	-1.87703	-1.3429
6	-0.00023	-2.82781	0
7	-4.1E-05	1.565865	0
8	-9.9E-05	2.302998	-1.22105
9	-9.9E-05	2.302998	1.22105
10	-6.9E-05	2.879637	-2.25033
11	-6.9E-05	2.879637	2.250325
12	0.000509	-0.03012	2.18773
13	0.000509	-0.03012	-2.18773

3. Comparison of bond lengths and angles of thiadiazines 5a, 5b and 5c from X-ray crystal structures and geometry optimizations

*3.1 3,5-Dichloro-4-methylene-4*H*-1,2,6-thiadiazine (**5a**)*

Table S1. Experimental and computational bond lengths for 3,5-dichloro-4-methylene-4*H*-1,2,6-thiadiazine (**5a**)

Atom1[a]	Atom2[a]	X-ray length (Å)	MP2/6-311G(d) (Å)
C1	N2	1.273(4)	1.286
C1	C3	1.473(5)	1.478
C1	Cl11	1.743(4)	1.739
N2	S6	1.657(3)	1.659
C3	C4	1.470(5)	1.478
C3	C7	1.341(5)	1.354
C4	N5	1.266(5)	1.286
C4	Cl10	1.745(4)	1.739
N5	S6	1.661(3)	1.659
C7	H8	0.930(4)	1.081
C7	H9	0.930(4)	1.081

[a] Atom labels as in Figure S1.

Table S2 Experimental and computational bond angles for 3,5-dichloro-4-methylene-4*H*-1,2,6-thiadiazine (**5a**)

Atom1[a]	Atom2[a]	Atom3[a]	X-ray angle (º)	MP2/6-311G(d) (º)
N2	C1	C3	128.1(3)	127.3
N2	C1	Cl11	114.8(3)	115.5
C3	C1	Cl11	117.1(3)	117.2
C1	N2	S6	121.4(3)	121.7
C1	C3	C4	113.2(3)	114.2
C1	C3	C7	122.8(3)	122.9
C4	C3	C7	124.0(3)	122.9
C3	C4	N5	128.5(4)	127.3
C3	C4	Cl10	116.4(3)	117.2
N5	C4	Cl10	115.1(3)	115.5
C4	N5	S6	121.3(3)	121.7
N2	S6	N5	107.4(2)	107.8
C3	C7	H8	120.1(4)	121.1
C3	C7	H9	120.0(4)	121.1
H8	C7	H9	120.0(4)	117. 8

[a] Atom labels as in Figure S1.

*3.2 3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-one (**5b**)*

Table S3 Experimental and computational bond lengths for 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**5b**)

Atom1[a]	**Atom2**[a]	**X-ray length (Å)**[b]	**MP2/6-311G(d) (Å)**
C1	N2	1.272	1.303
C1	C3	1.474	1.487
C1	Cl8	1.720	1.718
N2	S6	1.618	1.632
C3	C4	1.477	1.487
C3	O7	1.209	1.222
C4	N5	1.276	1.303
C4	Cl9	1.720	1.718
N5	S6	1.615	1.632

[a] Atom labels as in Figure S3. [b] Bond length error limits not known.

Table S4 Experimental and computational bond angles for 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**5b**)

Atom1[a]	**Atom2**[a]	**Atom3**[a]	**X-ray angle (°)** [b]	**MP2/6-311G(d) (°)**
N2	C1	C3	127.4	127.0
N2	C1	Cl8	117.4	117.6
C3	C1	Cl8	115.3	115.4
C1	N2	S6	121.8	121.6
C1	C3	C4	113.0	113.5
C1	C3	O7	123.5	123.2
C4	C3	O7	123.6	123.2
C3	C4	N5	127.3	127.0
C3	C4	Cl9	114.9	115.4
N5	C4	Cl9	117.8	117.6
C4	N5	S6	121.7	121.6
N2	S6	N5	108.8	109.2

[a] Atom labels as in Figure S3. [b] Bond angle error limits not known.

*3.3 2-(3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile (**5c**)*

Table S5 Experimental and computational bond lengths for 2-(3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile (**5c**)

Atom1[a]	**Atom2**[a]	**X-ray length (Å)**[b]				**MP2/6-311G(d) (Å)**
		A	**B**	**C**	**D**	
C1	C2	1.47(1)	1.44(1)	1.47(1)	1.447(9)	1.465
C1	N5	1.28(1)	1.25(1)	1.27(1)	1.27(1)	1.302
C1	Cl7	1.722(7)	1.719(7)	1.733(7)	1.722(9)	1.720
C2	C3	1.468(9)	1.457(9)	1.433(9)	1.46(1)	1.465
C2	C9	1.36(1)	1.39(1)	1.36(1)	1.35(1)	1.380
C3	N4	1.27(1)	1.27(1)	1.28(1)	1.28(1)	1.302
C3	Cl6	1.703(8)	1.719(8)	1.711(9)	1.711(7)	1.720
N4	S8	1.612(7)	1.618(7)	1.620(8)	1.618(7)	1.641
N5	S8	1.599(7)	1.625(7)	1.597(7)	1.633(8)	1.641
C9	C10	1.46(1)	1.42(1)	1.433(9)	1.422(9)	1.430
C9	C11	1.43(1)	1.42(1)	1.45(1)	1.45(1)	1.430
C10	N12	1.11(1)	1.14(1)	1.14(1)	1.131(9)	1.180
C11	N13	1.14(1)	1.14(1)	1.125(9)	1.16(1)	1.180

[a] Atom labels as in Figure S5. [b] Four independent molecules (**A-D**) per unit cell.

Table S6 Experimental and computational bond angles for 2-(3,5-dichloro-4*H*-1,2,6-thiadiazin-4-ylidene)malononitrile (**5c**)

Atom1[a]	**Atom2**[a]	**Atom3**[a]	**X-ray angle (º)**[b]				**MP2/6-311G(d) (º)**
			A	**B**	**C**	**D**	
C2	C1	N5	126.8(7)	125.3(7)	126.5(7)	127.6(7)	123.7
C2	C1	Cl7	117.3(5)	118.7(5)	118.8(5)	119.0(5)	119.1
N5	C1	Cl7	115.5(6)	115.8(6)	114.5(6)	113.4(6)	117.2
C1	C2	C3	112.1(6)	112.8(6)	112.1(6)	111.4(6)	112.0
C1	C2	C9	123.7(7)	123.4(6)	123.1(6)	124.9(6)	124.0
C3	C2	C9	124.1(6)	123.8(6)	124.8(6)	123.7(6)	124.0
C2	C3	N4	124.7(7)	125.4(7)	126.2(7)	126.3(7)	123.7
C2	C3	Cl6	119.1(5)	118.7(5)	119.3(5)	119.0(6)	119.1
N4	C3	Cl6	116.3(6)	115.8(6)	114.4(6)	114.6(6)	117.2
C3	N4	S8	123.7(6)	121.9(6)	122.3(6)	121.9(6)	120.7
C1	N5	S8	121.8(6)	123.0(6)	122.3(6)	120.6(6)	120.7
N4	S8	N5	107.0(4)	106.3(4)	107.0(4)	107.1(4)	107.2
C2	C9	C10	125.3(7)	126.3(7)	125.0(6)	125.2(7)	123.1
C2	C9	C11	124.0(7)	124.9(7)	125.3(6)	125.0(7)	123.1
C10	C9	C11	110.6(7)	108.6(6)	109.5(6)	109.5(7)	113.6
C9	C11	N13	172(1)	173.8(8)	172.3(8)	172(1)	175.6
C9	C10	N12	170.2(9)	172.7(8)	170.4(8)	170.5(8)	175.6

[a] Atom labels as in Figure S5. [b] Four independent molecules (**A-D**) per unit cell.