Electronic Supporting Information

A Molecular Electron Density Theory Study of the Participation of Tetrazines in Aza-Diels-Alder Reactions

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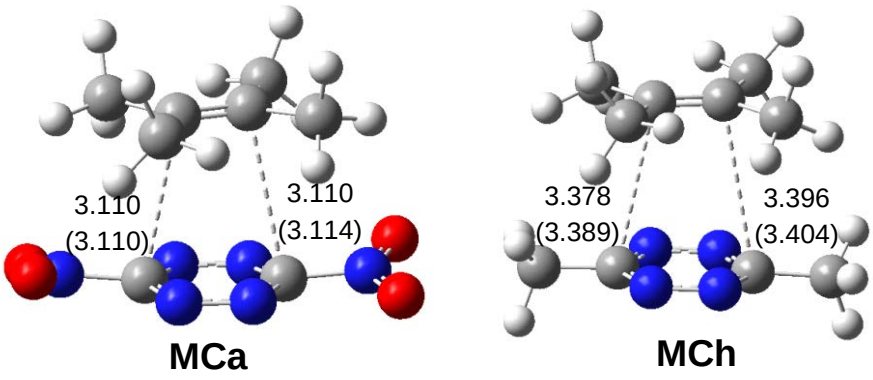

Figure S1. MPMWB95/6-311(d,p) geometries of the MCs **MCa** and **MCh**. The distances are given in Angstroms. Values in DCM are given in parentheses.

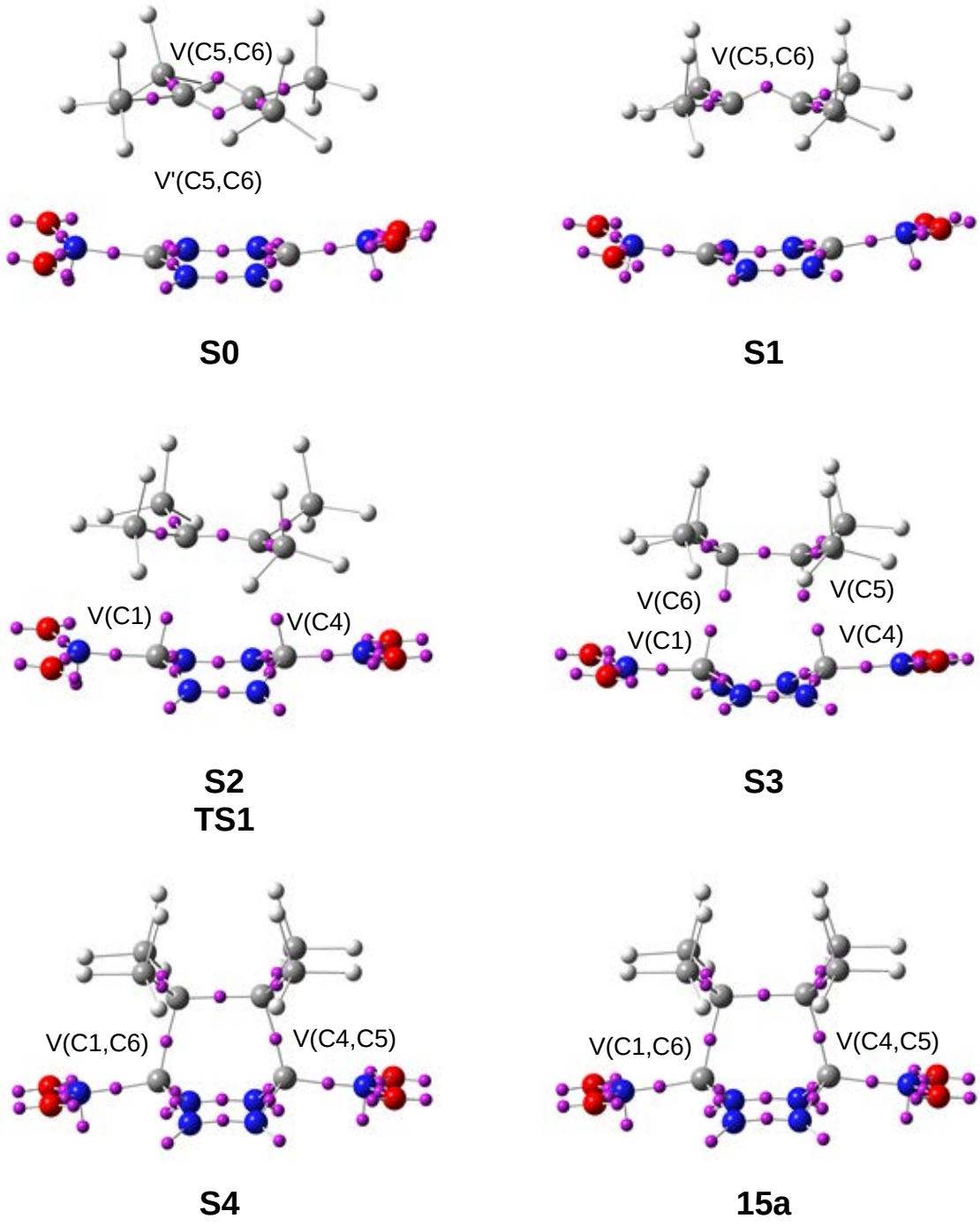

Figure S2. Attractor positions of the ELF valence basins of the IRC structures, **S0** – **S4**, defining the five phases characterizing the molecular mechanism of the polar ADA reaction between dinitro tetrazine **14a** and TME **15**, **TS1a** and **15a** are also included.

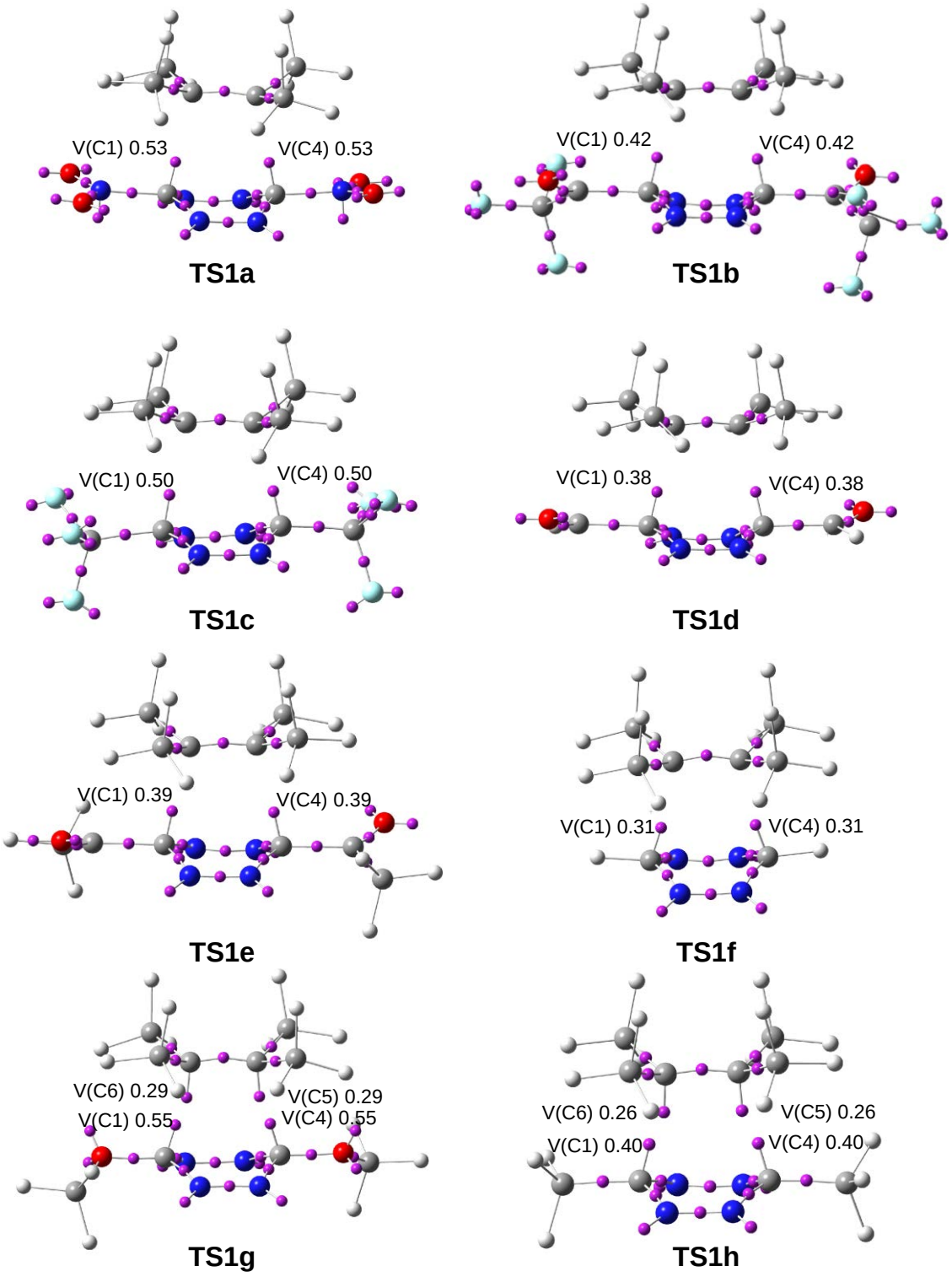

Figure S3. Attractor positions of the ELF valence basins of the **TS1a-h**. The electron populations, in average number of electrons, is given in e.

Table S1. MPW95/6-311G(d,p) electronic chemical potential μ, chemical hardness η, global electrophilicity ω, and global nucleophilicity *N*, in eV, for the studied reagents.

	R	μ	η	ω	*N*
TCE **18**		-7.35	6.09	4.44	0.00
14a	NO_2	-6.92	6.01	3.98	0.47
14b	$COCF_3$	-6.50	5.56	3.80	1.11
14c	CF_3	-6.25	6.03	3.24	1.13
14d	CHO	-5.98	5.74	3.12	1.54
14e	COMe	-5.55	5.85	2.63	1.92
14f	H	-5.17	6.03	2.22	2.21
14g	OMe	-4.94	5.91	2.07	2.50
14h	Me	-4.75	5.90	1.91	2.70
Ethylene **2**		-3.67	9.90	0.68	1.78
TME **15**		-2.64	8.85	0.40	3.33

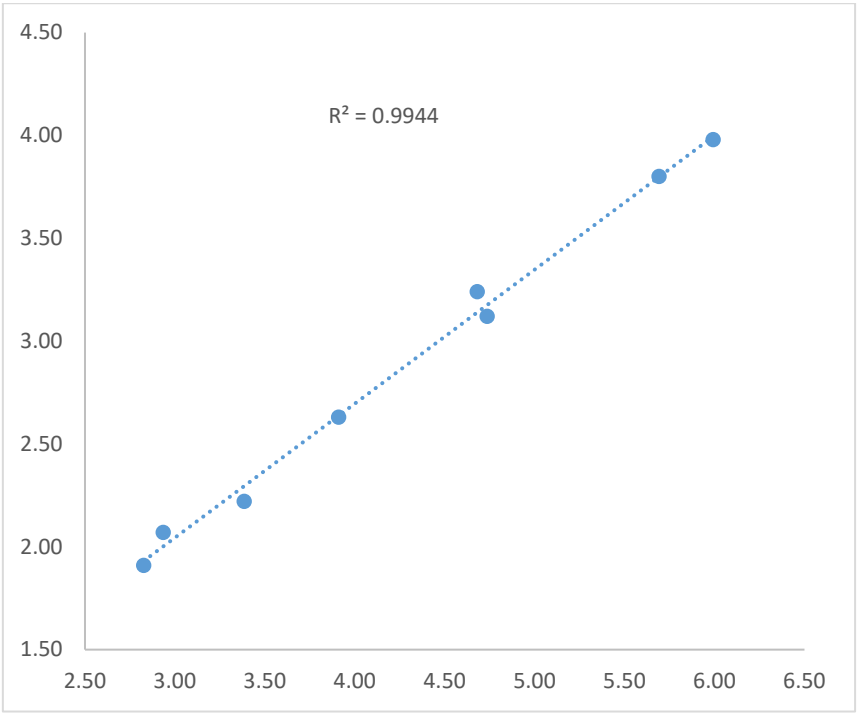

Figure S4. Lineal correlation between the B3LYP/6-31G(d) and the MPW95/6-311G(d,p) global electrophilicity ω indices of tetrazines **14a-h**.

Table S2. MPW95/6-311G(d,p) electronic energies (E, in a.u.), enthalpies (H, in a.u.), entropies (S, in cal/mol.K) and Gibbs free energies (G, in a.u.), computed at 25 ºC and 1 atm in DCM, for the stationary points involved in the domino reactions of the series tetrazine derivatives **14a-d** with TME **15**.

	E	H	S	G
15	-235.762490	-235.587197	83.6	-235.626919
N2	-109.503466	-109.494303	45.7	-109.516020
14a	-705.149383	-705.080595	97.9	-705.127111
Mca	-940.922268	-940.674856	139.2	-940.741013
TS1a	-940.912397	-940.666115	125.2	-940.725597
16a	-940.970454	-940.720548	120.3	-940.777724
TS2a	-940.943065	-940.695819	123.5	-940.754490
17a	-831.529971	-831.292073	121.6	-831.349837
14b	-1196.907292	-1196.808467	127.2	-1196.868915
MCb	-1432.679571	-1432.401999	172.1	-1432.483772
TS1b	-1432.660915	-1432.384802	155.7	-1432.458802
16b	-1432.710327	-1432.430657	147.2	-1432.500576
TS2b	-1432.687818	-1432.410889	152.4	-1432.483282
17b	-1323.276623	-1323.008965	150.5	-1323.080485
14c	-970.314012	-970.239771	106.1	-970.290182
MCc	-1206.086454	-1205.832324	149.2	-1205.903192
TS1c	-1206.062581	-1205.809544	132.8	-1205.872633
16c	-1206.123165	-1205.867072	130.6	-1205.929146
TS2c	-1206.097969	-1205.844381	130.6	-1205.906414
17c	-1096.683435	-1096.439244	128.8	-1096.500435
14d	-522.842940	-522.761816	90.3	-522.804719
MCd	-758.613679	-758.355212	133.1	-758.418447
TS1d	-758.591740	-758.333398	120.8	-758.390792
16d	-758.640010	-758.378397	114.6	-758.432846
TS2d	-758.620460	-758.361296	119.3	-758.417958
17d	-649.199426	-648.949699	117.1	-649.005329

Table S3. MPW95/6-311G(d,p) electronic energies (E, in a.u.), enthalpies (H, in a.u.), entropies (S, in cal/mol.K) and Gibbs free energies (G, in a.u.), computed at 25 ºC and 1 atm in DCM, for the stationary points involved in the domino reactions of the series tetrazine derivatives **14e-h** with TME **15**.

	E	H	S	G
14e	-601.469316	-601.329645	103.5	-601.378816
Mce	-837.241281	-836.923300	150.4	-836.994750
TS1e	-837.216513	-836.898310	133.3	-836.961668
16e	-837.265269	-836.943881	127.4	-837.004412
TS2e	-837.243974	-836.925040	132.5	-836.987995
17e	-727.828883	-727.519393	130.1	-727.581208
14f	-296.250369	-296.191733	68.0	-296.224042
MCf	-532.019808	-531.782661	118.8	-531.839099
TS1f	-531.992498	-531.756747	103.4	-531.805878
16f	-532.050019	-531.810586	98.4	-531.857330
TS2f	-532.023820	-531.787310	99.5	-531.834573
17f	-422.601918	-422.375955	94.6	-422.420890
14g	-525.274277	-525.143621	93.1	-525.187838
MCg	-761.044139	-760.734621	137.7	-760.800025
TS1g	-761.004197	-760.696710	125.1	-760.756165
16g	-761.059871	-760.750670	119.2	-760.807294
TS2g	-761.045961	-760.737557	121.1	-760.795116
17g	-651.638842	-651.339490	117.7	-651.395400
14h	-374.869781	-374.753117	83.8	-374.792915
MCh	-610.638501	-610.344321	125.7	-610.404055
TS1h	-610.602603	-610.307359	114.6	-610.361792
16h	-610.657750	-610.359038	109.8	-610.411208
TS2h	-610.633376	-610.337438	113.1	-610.391199
17h	-501.216475	-500.930536	106.8	-500.981266

Table S4. MPW95/6-311G(d,p) electronic energies (E, in a.u.), enthalpies (H, in a.u.), entropies (S, in cal/mol.K) and Gibbs free energies (G, in a.u.), computed at 25 ºC and 1 atm in DCM, for the stationary points involved in the domino reactions of the series tetrazine derivatives **14f-h** with TCE **18**.

	E	H	S	G
18	-447.412441	-447.353755	93.7	-447.398282
14f	-296.250369	-296.191734	68.0	-296.224044
MCi	-743.671571	-743.552230	129.4	-743.613714
TS1i	-743.609098	-743.492206	112.5	-743.545636
19i	-743.660889	-743.540928	110.0	-743.593187
TS2i	-743.639276	-743.522318	111.7	-743.575377
20i	-634.221429	-634.114355	107.4	-634.165384
14g	-525.274277	-525.143619	93.1	-525.187836
MCj	-972.696831	-972.505410	153.6	-972.578394
TS1j	-972.631587	-972.442820	135.7	-972.507281
19j	-972.667580	-972.477027	136.6	-972.541921
TS2j	-972.657040	-972.468551	136.0	-972.533160
20j	-863.255869	-863.075764	131.7	-863.138355
14h	-374.869781	-374.753117	83.8	-374.792915
MCk	-822.292731	-822.115362	140.6	-822.182181
TS1k	-822.234947	-822.059083	126.8	-822.119334
19k	-822.280144	-822.102589	118.0	-822.158641
TS2k	-822.259275	-822.083558	127.5	-822.144158
20k	-712.845780	-712.679087	120.5	-712.736340

Table S5. MPWB1K/6-311G(d,p) unique imaginary frequency of the TSs **TS1a-k** and **TS2a-k** computed in DCM, in cm^{-1}.

TS1a	-286.2929
TS1b	-337.4865
TS1c	-350.5034
TS1d	-379.2771
TS1e	-389.2782
TS1f	-432.0035
TS1g	-474.5200
TS1h	-473.2847
TS1i	-432.0035
TS1j	-568.1225
TS1k	-548.4563
TS2a	-582.5346
TS2b	-583.5926
TS2c	-576.9181
TS2d	-579.7784
TS2e	-578.0920
TS2f	-616.9326
TS2g	-597.8970
TS2h	-600.4108
TS2i	-619.0927
TS2j	-578.7566
TS2k	-601.7070