

Supporting Information for the paper  
**Electron dynamics with explicit-time density functional theory of the  
[4+2] Diels-Alder reaction**

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### **Computational details**

**QM calculations.** Geometry optimizations were carried out using the M06-2X hybrid meta-GGA density functional<sup>1</sup> as implemented in Gaussian09, Revision D.01<sup>2</sup> on systems **1** and **2**, described in the main text. The performance of DFT in computing geometry, electronic and energetic features of the Diels-Alder reaction has been largely reported in previous studies.<sup>3,4</sup> Houk and co-workers have shown that it is possible to obtain reliable activation energies for pericyclic reactions employing the M06-2X functional.<sup>5,6</sup> The basis set for all computations is a double- $\zeta$  (6-31+G(d)).

Structures of the critical points (minima and saddle points) were fully optimized using the gradient method available in the Gaussian package.<sup>2</sup> Frequency calculations were carried out at the same level of theory to verify the nature of the critical points. All transition states (saddle points) were characterized by the presence of one imaginary frequency. IRC computations were also carried out to establish the structure and the energetics of intermediate points along the energy path.

### **Quantum dynamics. RT-TDDFT wavepacket dynamics**

Wavefunction coefficients and energies of the critical and intermediate geometries computed on the ground-state singlet concerted PES of systems **1** and **2**, as reported in the QM section, were used to set-up the wavepacket dynamics, in vacuum. Initially the diabatic wavefunction,  $\psi(t=0)$ , is constrained on the unperturbed, no interacting, diene (DN) and dienophile (DP), obtained from their geometries at the transition state or on an IRC point, calculated at the M06-2X/6-31+G(d) level of theory.

$$\psi^0 = \begin{pmatrix} \psi_{DN}^0 & 0 \\ 0 & \psi_{DP}^0 \end{pmatrix} \quad (2)$$

$\psi_{DN}^0$  and  $\psi_{DP}^0$  wavefunctions are orthogonal.

We also run electron dynamics on reactants geometries calculated by means of the LC-wPBE<sup>7</sup> long-range corrected functional, as implemented in Gaussian09:<sup>2</sup> the obtained bond order between fragments does not increase above 0.02 during the simulation, demonstrating that the applied local exchange-correlation functional (M06-2X) in the present study is suitable to describe the orbital overlap even on well separated reaction centers. The ground state Hamiltonian of the total interacting system, build up from its own eigenstates calculated at the same level of theory, is applied on the initial diabatic wavefunction as a constrained position-dependent perturbation, representing the electronic coupling interaction driving the electron dynamics. The coefficients of  $\psi(t)$  were updated at each time step, according to the implemented algorithm, and the total density matrix in time  $P(t)$  was calculated as the sum of the diene and dienophile density matrices,  $P_{DN}(t)$  and  $P_{DP}(t)$ , respectively obtained as the product of their total molecular orbital coefficients:

$$P_{DN}(t) = \sum_{i=1}^{n_{occ}(DN)} c_{v,i}^*(t) c_{i,v}(t); \quad P_{DP}(t) = \sum_{k=1}^{n_{occ}(DP)} c_{v,k}^*(t) c_{k,v}(t) \quad (3)$$

During the simulation, the total electron numbers is conserved, and no net charge is transferred between molecular fragments.

The time-dependent inter- and intra-molecular bond order between atoms A and B were calculated from the total density matrix  $P(t)$ , according to the Wiberg definition<sup>8-10</sup>

$$BO_{AB}(t) = \sum_{\mu \in A, \nu \in B} P_{\mu\nu}(t) P_{\nu\mu}(t) \quad (4)$$

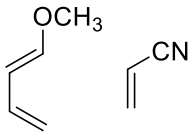
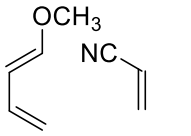
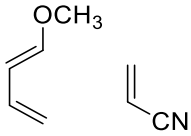
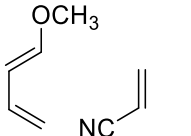
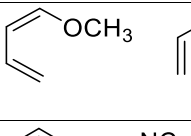
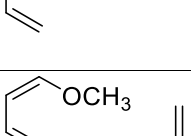
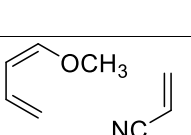

The time-dependent atomic effective charge on atom A, for an atom centered basis set, was estimated by the Lödwin population analysis:

$$q_A(t) = Z_a - \sum_{i \in A} P_{ii}(t) \quad (5)$$

The orbital occupation numbers, determined by projecting the time-dependent density matrix onto the initial orbitals, were also calculated to track the process in terms of orbital symmetry:

$$n_k(t) = \psi_k^*(0) P(t) \psi_k(0) \quad (6)$$

**Table S1.** Energies relative to reactants (kcal mol<sup>-1</sup>), computed at the M06-2X/6-31+G(d) level, of the transition states corresponding to different approaches of 1-methoxy-butadiene and cyano-ethylene. Energy values include ZPE corrections. Approach **a** is the favored orientation discussed in the paper.

	Relative orientation of the two substrate molecules	Energy
<b>a</b>		11.2
<b>b</b>		13.1
<b>c</b>		15.0
<b>d</b>		15.6
<b>e</b>		16.8
<b>f</b>		17.0
<b>g</b>		17.8
<b>h</b>		19.6

**Table S2.** Bond order (BO) values for the bonds of system **1**. Maximum, minimum and average BO's were calculated over 5 fs dynamics on TS<sub>1</sub>. BO's for reactants (products) are obtained from DFT computations.

	C <sub>1</sub> C <sub>2</sub>	C <sub>2</sub> C <sub>3</sub>	C <sub>5</sub> C <sub>6</sub>	C <sub>4</sub> C <sub>5</sub>
<b>Rx<sub>1</sub></b> <b>(Pd<sub>1</sub>)</b>	2.11 (1.15)	1.23 (2.04)	2.23 (1.15)	0.0 (1.13)
<b>Maximum TS<sub>1</sub></b>	2.03	1.80	2.27	0.83
<b>Minimum TS<sub>1</sub></b>	1.31	1.14	1.21	0.0
<b>Average TS<sub>1</sub></b>	1.60	1.42	1.65	0.42

**Table S3.** Energies relative to reactants (kcal mol<sup>-1</sup>) computed for transition state and along the IRC in the reactant direction for system **1** and **2**. Energy values include ZPE corrections.

	IP <sub>1</sub>	IP <sub>2</sub>	IP <sub>3</sub>	IP <sub>4</sub>	IP <sub>5</sub>	Transition state
<b>System 1</b>	8.8	11.3	14.0	16.8	19.2	20.3
<b>System 2</b>	9.0	14.2	16.4	17.3	17.9	18.2

**Table S4.** Löwdin charges for system **1**. Maximum, minimum and average charges Q were calculated over the 5 fs dynamics.

	C <sub>1</sub> (C <sub>4</sub> )	C <sub>2</sub> (C <sub>3</sub> )	C <sub>5</sub> (C <sub>6</sub> )
<b>Rx<sub>1</sub></b> <b>(Pd<sub>1</sub>)</b>	-0.42 (-0.41)	-0.27 (-0.28)	-0.44 (-0.42)
<b>Maximum TS<sub>1</sub></b>	-0.32	-0.03	-0.16
<b>Minimum TS<sub>1</sub></b>	-0.68	-0.51	-0.67
<b>Average TS<sub>1</sub></b>	-0.47	-0.28	-0.42

**Table S5.** Percentages of the dynamics computed for different ranges of Qs at the transition state TS<sub>1</sub> and for various points IP<sub>n</sub> determined along the IRC in the reactant direction.

Charge range	TS <sub>1</sub>	IP <sub>1</sub>	IP <sub>2</sub>	IP <sub>3</sub>	IP <sub>4</sub>	IP <sub>5</sub>
C <sub>4</sub> ]-0.57 ; -0.37[ C <sub>5</sub> ]-0.52 ; -0.32[	51%	69%	84%	91%	94%	96%
C <sub>4</sub> ]-0.57 ; -0.37[ C <sub>5</sub> > -0.32	15%	8%	1%	0%	0%	0%
C <sub>4</sub> ]-0.57 ; -0.37[ C <sub>5</sub> < -0.52	18%	9%	4%	1%	0%	0%

**Comments to Table S5 .** For 51% of dynamics the Q's on C<sub>1</sub> (C<sub>4</sub>) range between -0.57 and -0.37 and the Q's on C<sub>5</sub> (C<sub>6</sub>) range between -0.52 and -0.32. For 15% of dynamics C<sub>5</sub> (C<sub>6</sub>) become more positive (Q > -0.32) and for 18% of dynamics C<sub>5</sub> (C<sub>6</sub>) become more negative (Q < -0.52). These data emphasize the charge transfer occurring between the two fragments (in both directions) and that it is

necessary to invoke ~~also~~ the contribution of structures such as V, VI and VII to provide a more accurate description of the resonance hybrid corresponding to transition state.

Dynamics carried out along the IRC shows that, as the system approaches the reactants, the percentages of points corresponding to charges of  $C_5$  ( $C_6$ )  $> -0.32$  (increase of positive charge on ethene) and  $C_5$  ( $C_6$ )  $< -0.52$  (increase of negative charge) reach rapidly zero. This is consistent with the fact that a significant increase of positive or negative charges on  $C_5$  ( $C_6$ ) indicates an electron transfer between the two fragments, which disappears when they move away from each other.

**Table S6.** Bond order (BO) values for the bonds of system **2**. Maximum, minimum and average BOs were calculated over 5 fs dynamics. BO's for reactants (products) are obtained from DFT computations.

	<b>C<sub>1</sub>C<sub>2</sub></b>	<b>C<sub>2</sub>C<sub>3</sub></b>	<b>C<sub>3</sub>C<sub>4</sub></b>	<b>C<sub>5</sub>C<sub>6</sub></b>	<b>C<sub>1</sub>C<sub>6</sub></b>	<b>C<sub>4</sub>C<sub>5</sub></b>
<b>Rx<sub>2</sub></b> <b>(Pd<sub>2</sub>)</b>	1.89 (1.07)	1.21 (2.01)	2.09 (1.15)	2.10 (1.09)	0.0 (1.01)	0.0 (1.13)
<b>Maximum TS<sub>2</sub></b>	1.74	1.71	1.99	2.05	0.39	0.90
<b>Minimum TS<sub>2</sub></b>	1.22	1.18	1.24	1.18	0.00	0.00
<b>Average TS<sub>2</sub></b>	1.47	1.44	1.51	1.49	0.20	0.55

**Table S7.** Löwdin charges of system **2**. Maximum, minimum and average charges were calculated over the 5 fs of the dynamics.

	<b>C<sub>1</sub></b>	<b>C<sub>2</sub></b>	<b>C<sub>3</sub></b>	<b>C<sub>4</sub></b>	<b>C<sub>6</sub></b>	<b>C<sub>5</sub></b>
<b>Rx<sub>2</sub></b> <b>(Pd<sub>2</sub>)</b>	-0.08 (-0.08)	-0.29 (-0.25)	-0.25 (-0.24)	-0.44 (-0.40)	-0.23 (-0.24)	-0.34 (-0.38)
<b>Maximum TS<sub>2</sub></b>	0.08	-0.10	0.03	-0.24	-0.09	-0.23
<b>Minimum TS<sub>2</sub></b>	-0.24	-0.46	-0.51	-0.66	-0.49	-0.56
<b>Average TS<sub>2</sub></b>	-0.09	-0.28	-0.26	-0.44	-0.27	-0.41

**Table S8.** Mulliken charges for system **1**. Maximum, minimum and average charges were calculated over the 5 fs dynamics.

	<b>C<sub>1</sub> (C<sub>4</sub>)</b>	<b>C<sub>2</sub> (C<sub>3</sub>)</b>	<b>C<sub>5</sub> (C<sub>6</sub>)</b>
<b>Rx<sub>1</sub></b> <b>(Pd<sub>1</sub>)</b>	-0.51 (-0.55)	-0.08 (-0.08)	-0.39 (-0.42)
<b>Maximum TS<sub>1</sub></b>	3.34	3.49	0.96
<b>Minimum TS<sub>1</sub></b>	-3.95	-4.03	-1.74
<b>Average TS<sub>1</sub></b>	-0.31	-0.31	-0.45

**Comments to Table S8** . The Mulliken charges vary greatly and reach values of up to  $\pm 4$  for the butadiene carbons. These values are unphysical and were not further considered for the analysis. Löwdin charges differ greatly from the Mulliken ones. The computation of the Löwdin charges implies the orthogonalization of the density matrix. The computation of the Mulliken charges leaves unchanged the density matrix: for this reason, the charges include inter-fragment contributions that should not be considered.

**Table S9.** Cartesian coordinates (Ångströms) for reactant, products, transition state and the various points along the IRC computed at the M06-2X/6-31+G(d) level for system **1**.

### Butadiene

scf done: -155.9048688787

C	-1.279622	1.708235	0.192623
H	-1.025914	0.833845	-0.401952
H	-2.315981	1.818299	0.497739
C	-0.358423	2.621448	0.517002
H	-0.666400	3.509299	1.068606
C	1.069001	2.533667	0.164030
H	1.584600	3.479896	0.004027
C	1.756224	1.391684	0.055238
H	1.294865	0.428262	0.260552
H	2.804362	1.390706	-0.228041

### Ethylene

scf done: -78.541590926

C	-0.691860	-0.854842	2.676542
H	-0.733978	-1.913143	2.920474
H	-1.559746	-0.430027	2.178143
C	0.368084	-0.107490	2.975315
H	0.405562	0.949037	2.722154
H	1.237254	-0.525531	3.476824

### TS1

scf done = -234.421135364

C	-0.707000	1.385000	-0.015000
H	-1.773000	1.271000	0.161000
H	-0.285000	0.688000	-0.730000
C	-0.085000	2.582000	0.258000
H	-0.655000	3.372000	0.743000
C	1.318000	2.717000	0.192000
H	1.769000	3.606000	0.627000
C	2.128000	1.658000	-0.150000
H	3.208000	1.751000	-0.076000
C	0.237000	0.025000	1.531000
H	-0.255000	-0.830000	1.077000
H	-0.314000	0.516000	2.326000
C	1.610000	0.152000	1.461000
H	2.142000	0.738000	2.200000
H	2.199000	-0.603000	0.948000
H	1.780000	0.888000	-0.831000

### IP1

scf done: -234.422564

C	-1.478035	0.026399	-0.601064
H	-2.541738	-0.094357	-0.415808
H	-1.035783	-0.702822	-1.271003
C	-0.846670	1.196062	-0.302088
H	-1.407571	1.984085	0.196263
C	0.570977	1.332629	-0.369633
H	1.016447	2.217636	0.080088



C	1.382626	0.302381	-0.737927
H	2.462512	0.388311	-0.654665
C	-0.502541	-1.389497	1.004259
H	-1.013514	-2.212317	0.511616
H	-1.071200	-0.864240	1.763663
C	0.850566	-1.265296	0.934300
H	1.390607	-0.640192	1.636859
H	1.448689	-1.985138	0.381989
H	1.026282	-0.503676	-1.369894

## IP2

scf done: -234.426087

C	-1.496077	0.052539	-0.629550
H	-2.559045	-0.068577	-0.441780
H	-1.037474	-0.704887	-1.255112
C	-0.853399	1.196943	-0.303487
H	-1.407701	1.985548	0.201235
C	0.577281	1.334724	-0.371924
H	1.017017	2.219238	0.084351
C	1.392622	0.331135	-0.767929
H	2.472075	0.417241	-0.682167
C	-0.491504	-1.419827	1.035808
H	-1.015253	-2.214500	0.511681
H	-1.072203	-0.862075	1.762198
C	0.848396	-1.297154	0.966328
H	1.391087	-0.637854	1.634709
H	1.450611	-1.986821	0.381194
H	1.030700	-0.505837	-1.354157

## IP3

scf done: -234.430454

C	-1.514285	0.077709	-0.657863
H	-2.578808	-0.036692	-0.475197
H	-1.044353	-0.703533	-1.243836
C	-0.858811	1.199130	-0.304834
H	-1.407859	1.990892	0.200820
C	0.581917	1.337847	-0.373923
H	1.016147	2.224467	0.083719
C	1.403010	0.358946	-0.797595
H	2.482167	0.452512	-0.717037
C	-0.482882	-1.450833	1.067495
H	-1.014715	-2.223705	0.519721
H	-1.071329	-0.865213	1.764950
C	0.848863	-1.328968	0.998159
H	1.391018	-0.641282	1.637539
H	1.452428	-1.996165	0.389190
H	1.038994	-0.503024	-1.344526

## IP4

scf done: -234.434702

C	-1.531623	0.101898	-0.685155
H	-2.599401	0.000464	-0.514202
H	-1.056542	-0.697707	-1.241641
C	-0.862747	1.202923	-0.306838
H	-1.407367	1.999529	0.196261
C	0.584723	1.342243	-0.376309
H	1.013462	2.232732	0.079314

C	1.412878	0.385918	-0.826326
H	2.491545	0.493116	-0.757462
C	-0.476200	-1.482304	1.098955
H	-1.012394	-2.241774	0.536595
H	-1.069077	-0.876231	1.774972
C	0.851282	-1.360923	1.029716
H	1.391699	-0.652408	1.647599
H	1.455086	-2.014937	0.406619
H	1.050589	-0.494658	-1.344292

### IP5

scf done: -234.438371

C	-1.547378	0.125340	-0.711039
H	-2.618960	0.041054	-0.555506
H	-1.072468	-0.687864	-1.248416
C	-0.865677	1.208408	-0.310180
H	-1.406212	2.009981	0.189688
C	0.586117	1.348136	-0.379837
H	1.009491	2.242724	0.073071
C	1.421430	0.411954	-0.853435
H	2.498993	0.536853	-0.799986
C	-0.470782	-1.514275	1.130095
H	-1.008542	-2.267891	0.561133
H	-1.066013	-0.894417	1.791550
C	0.855020	-1.393054	1.060901
H	1.393500	-0.670354	1.664046
H	1.458666	-2.041400	0.431501
H	1.064096	-0.481595	-1.353116

**Table S10.** Cartesian coordinates (Ångstroms) for reactant, products, transition state and the various points along the IRC computed at the M06-2X//6-31+G(d) level for system **2**.

### Cyanoethylene

scf done: -170.759618

C	1.779343	-0.359253	2.106494
H	2.375533	0.528912	1.919474
C	1.383349	-0.698316	3.334917
H	0.787235	-1.587365	3.515156
H	1.651969	-0.086392	4.189280
C	1.441851	-1.147593	0.951621
N	1.177981	-1.771542	0.013024

### 1-Methoxy-butadiene

scf done: -270.386075

C	-1.328065	1.826089	0.052780
H	-2.371330	2.125643	0.037823
H	-1.117421	0.759620	0.033852
C	-0.345113	2.732543	0.114059
H	-0.609908	3.786163	0.201263
C	1.089681	2.430346	0.075342
H	1.772136	3.039703	0.663482
C	1.599300	1.448681	-0.677269
H	0.979233	0.853168	-1.351226

O	2.912708	1.117211	-0.638302
C	3.383142	0.413851	-1.772852
H	4.417085	0.138792	-1.564061
H	2.791826	-0.495312	-1.941326
H	3.345032	1.045386	-2.668277

## TS2

scf done: -441.131252

C	-0.836563	1.293756	0.447337
H	-1.781012	1.088501	0.944877
H	-0.597267	0.592422	-0.348458
C	-0.403393	2.611911	0.371167
H	-0.919423	3.357145	0.973057
C	0.805291	2.999699	-0.227076
H	1.188935	4.004667	-0.072152
C	1.626227	2.104866	-0.872782
H	1.278138	1.150775	-1.262079
C	1.809205	0.475407	1.127020
H	2.575881	1.168619	1.451204
C	0.540213	0.449510	1.703388
H	0.364747	1.073841	2.572841
H	-0.005665	-0.490432	1.702623
O	2.832276	2.503027	-1.292974
C	3.659335	1.514594	-1.900103
H	4.156520	0.916171	-1.131635
H	3.069251	0.853486	-2.543236
H	4.398972	2.054194	-2.491233
C	2.206677	-0.579893	0.258076
N	2.492654	-1.412269	-0.502861

## IP1

scf done: -441.132575

C	-2.365084	0.090924	0.555359
H	-3.301657	-0.121691	1.063676
H	-2.101491	-0.625562	-0.218765
C	-1.917080	1.394661	0.495323
H	-2.425993	2.140020	1.103370
C	-0.701140	1.784530	-0.104772
H	-0.316461	2.787450	0.060353
C	0.113897	0.898569	-0.756601
H	-0.227690	-0.064366	-1.130096
C	0.302402	-0.749087	1.264189
H	1.063563	-0.038046	1.563635
C	-0.951549	-0.777696	1.844888
H	-1.143702	-0.137524	2.698641
H	-1.522199	-1.702320	1.820782
O	1.324880	1.289578	-1.170681
C	2.149738	0.299201	-1.776441
H	2.646737	-0.299696	-1.008055
H	1.559268	-0.361380	-2.419724
H	2.890521	0.836778	-2.368097
C	0.697087	-1.797032	0.383117
N	0.983430	-2.627144	-0.379248

## IP2

scf done: -441.135397

C	-2.384680	0.102555	0.539144
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H	-3.315561	-0.114223	1.055242
H	-2.100598	-0.625733	-0.215106
C	-1.921257	1.394052	0.494833
H	-2.424432	2.139923	1.107121
C	-0.698512	1.785366	-0.106134
H	-0.312558	2.786136	0.068425
C	0.111499	0.907079	-0.764906
H	-0.225364	-0.062136	-1.126192
C	0.306850	-0.758839	1.277007
H	1.061650	-0.032195	1.553178
C	-0.935250	-0.789830	1.863184
H	-1.139952	-0.133828	2.700895
H	-1.524984	-1.700445	1.820746
O	1.327266	1.291710	-1.173054
C	2.149469	0.299004	-1.777502
H	2.645389	-0.300952	-1.009016
H	1.558090	-0.360577	-2.420993
H	2.891981	0.833825	-2.369490
C	0.697243	-1.799878	0.384297
N	0.983703	-2.626793	-0.380629

### IP3

scf done: -441.138721

C	-2.404234	0.114064	0.522757
H	-3.330422	-0.106065	1.045355
H	-2.100394	-0.625928	-0.211677
C	-1.925508	1.393639	0.493906
H	-2.423558	2.140150	1.109772
C	-0.696061	1.786178	-0.107390
H	-0.309126	2.784981	0.075935
C	0.109346	0.915170	-0.772770
H	-0.223421	-0.059589	-1.123307
C	0.311567	-0.768470	1.289768
H	1.060161	-0.027588	1.544550
C	-0.919101	-0.802081	1.881729
H	-1.135809	-0.131022	2.703892
H	-1.527444	-1.698923	1.821125
O	1.329490	1.294095	-1.175664
C	2.149264	0.298947	-1.778534
H	2.644250	-0.301660	-1.009789
H	1.557166	-0.359895	-2.422117
H	2.893429	0.831164	-2.370887
C	0.697562	-1.802772	0.385616
N	0.983965	-2.626521	-0.381931

### IP4

scf done: -441.141996

C	-2.443553	0.136540	0.490000
H	-3.364898	-0.085329	1.019704
H	-2.105598	-0.624166	-0.207614
C	-1.934253	1.394413	0.490625
H	-2.424393	2.143130	1.110487
C	-0.691641	1.788157	-0.108806
H	-0.302546	2.782998	0.091246
C	0.105951	0.930006	-0.787196
H	-0.221491	-0.052266	-1.122708
C	0.322509	-0.787596	1.314596
H	1.060231	-0.024296	1.533847

C	-0.888106	-0.826749	1.919938
H	-1.124185	-0.127519	2.712698
H	-1.528641	-1.698072	1.828028
O	1.333668	1.299600	-1.181719
C	2.148735	0.299177	-1.780976
H	2.640950	-0.302769	-1.011194
H	1.555012	-0.358110	-2.424687
H	2.896733	0.825610	-2.373859
C	0.698991	-1.809796	0.389261
N	0.984462	-2.626153	-0.385107

## IP5

scf done: -441.144851

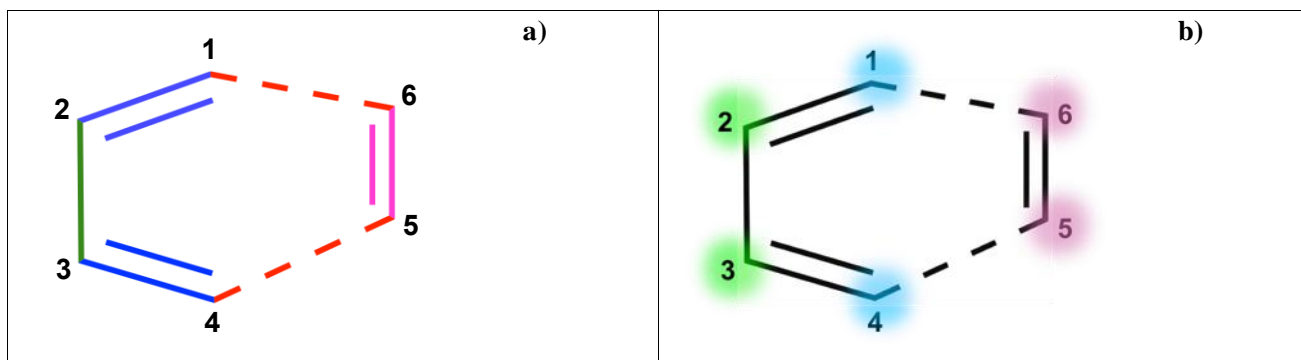
C	-2.535585	0.192163	0.410331
H	-3.472109	-0.007439	0.921791
H	-2.149113	-0.609468	-0.213687
C	-1.958449	1.406881	0.470755
H	-2.443480	2.168653	1.079186
C	-0.682515	1.791670	-0.104539
H	-0.286501	2.775933	0.131342
C	0.101188	0.958534	-0.814769
H	-0.226866	-0.026444	-1.146663
C	0.356963	-0.836826	1.373552
H	1.081561	-0.048421	1.546059
C	-0.817823	-0.887170	2.016362
H	-1.073764	-0.143442	2.761387
H	-1.510002	-1.711228	1.876198
O	1.339892	1.316475	-1.200861
C	2.145894	0.302910	-1.788970
H	2.627116	-0.302226	-1.014192
H	1.549088	-0.350479	-2.433960
H	2.905011	0.815355	-2.380113
C	0.707004	-1.833593	0.404725
N	0.984517	-2.625574	-0.395507

## Pd2

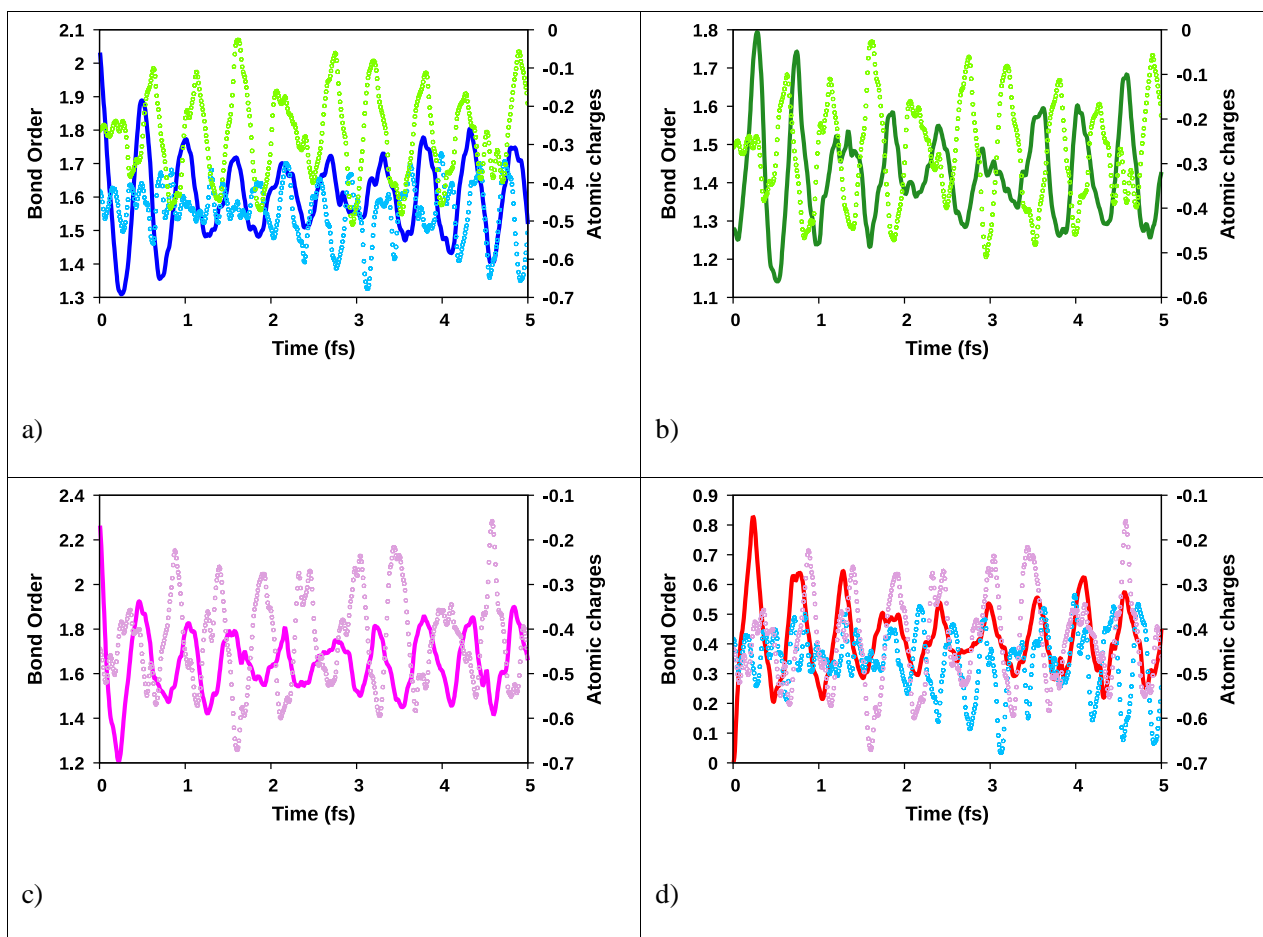
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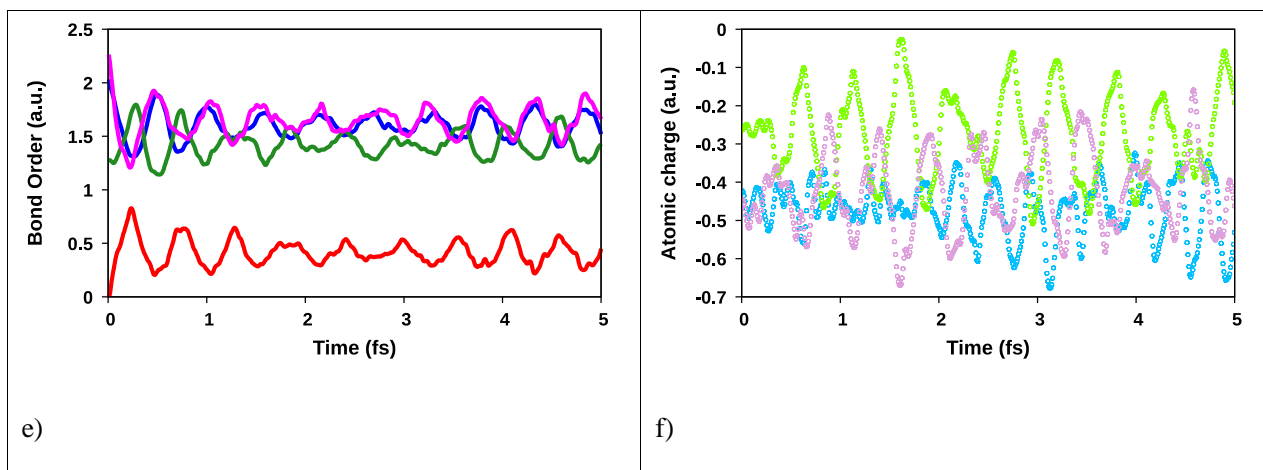
C	-0.547167	1.317343	0.909858
H	-0.898167	1.697816	1.875739
H	-1.268724	0.546262	0.603031
C	-0.548318	2.432306	-0.100251
H	-1.406229	3.101923	-0.100945
C	0.434229	2.636307	-0.979977
H	0.396542	3.479942	-1.664597
C	1.646582	1.753007	-1.096568
H	1.819319	1.516201	-2.158715
C	1.467900	0.429898	-0.312318
H	2.451693	-0.036728	-0.188040
C	0.844952	0.710004	1.064548
H	1.507363	1.419917	1.572731
H	0.809740	-0.207949	1.658629
O	2.762689	2.466414	-0.595655
C	3.998215	2.062180	-1.145658
H	4.224993	1.009573	-0.925885
H	4.008909	2.206356	-2.234630
H	4.766754	2.688936	-0.690885
C	0.638865	-0.510265	-1.082116

N -0.023870 -1.241174 -1.685757

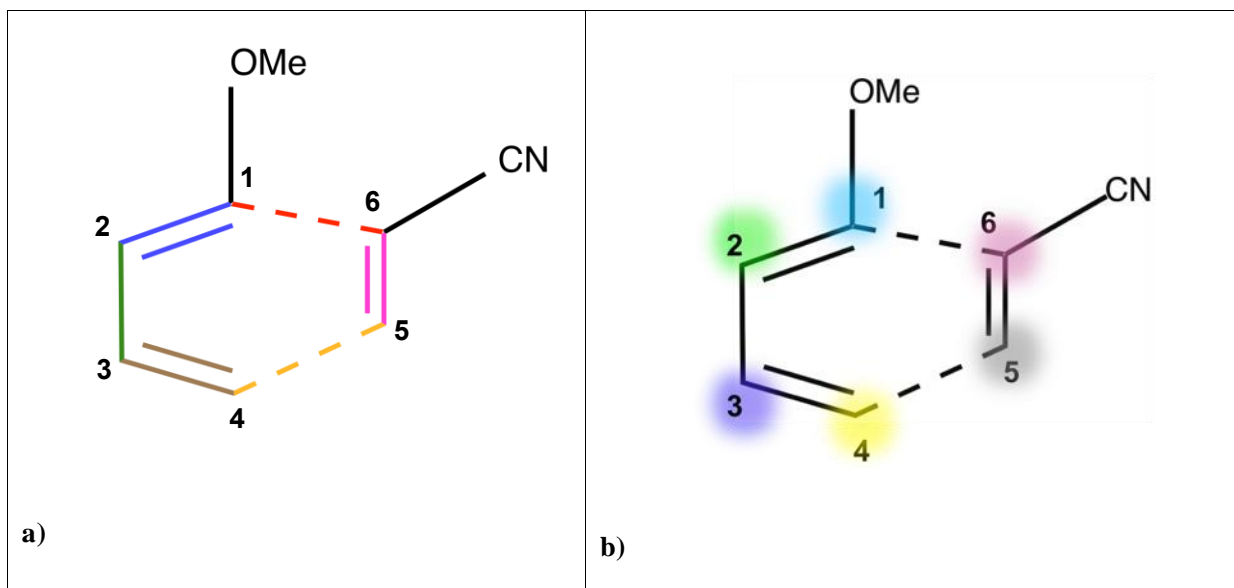


**Scheme S1.** Color code for a) bond orders, b) atomic charges of system 1 used in Figure S1.

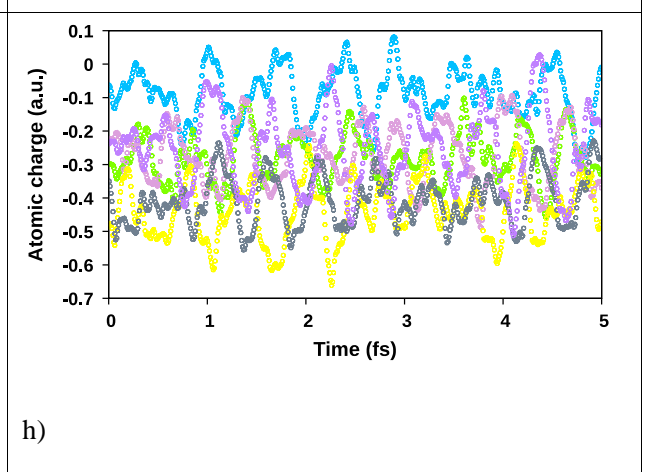
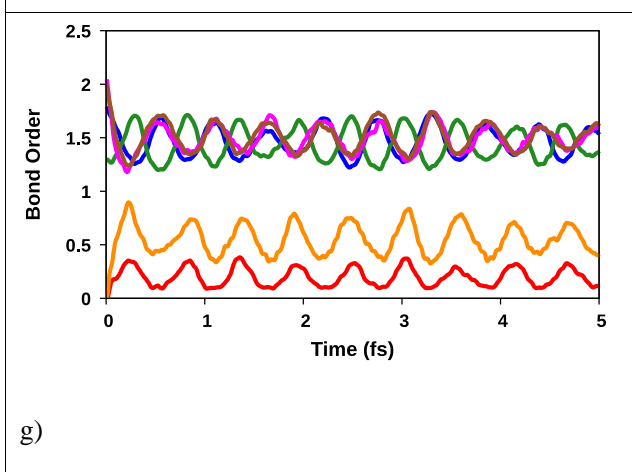
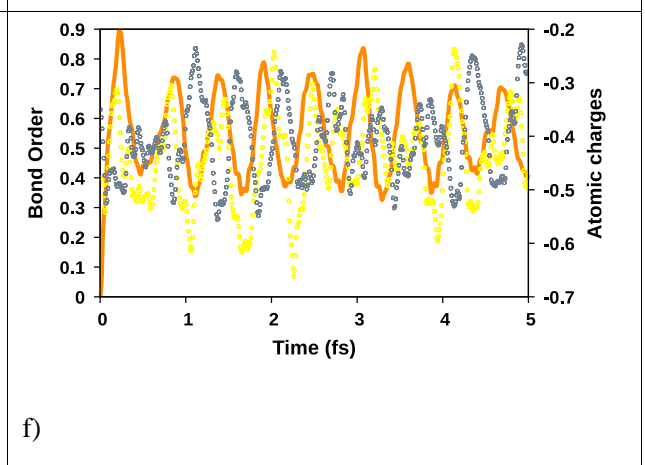
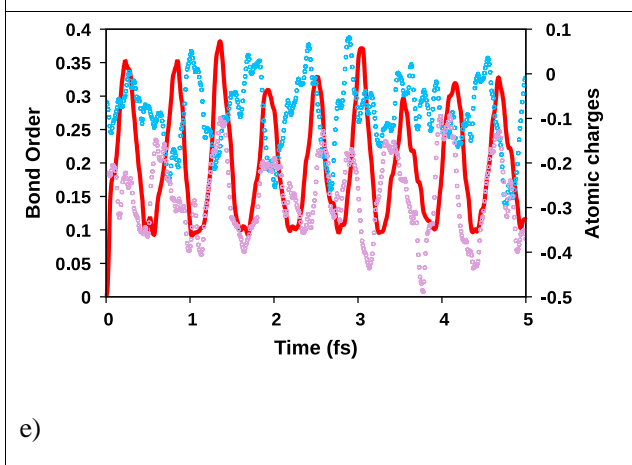
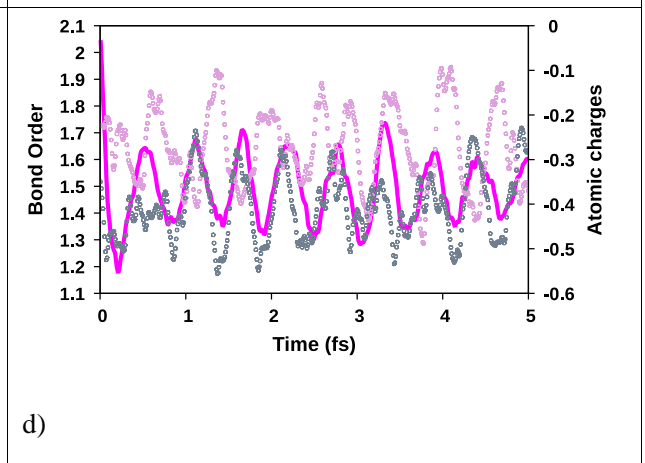
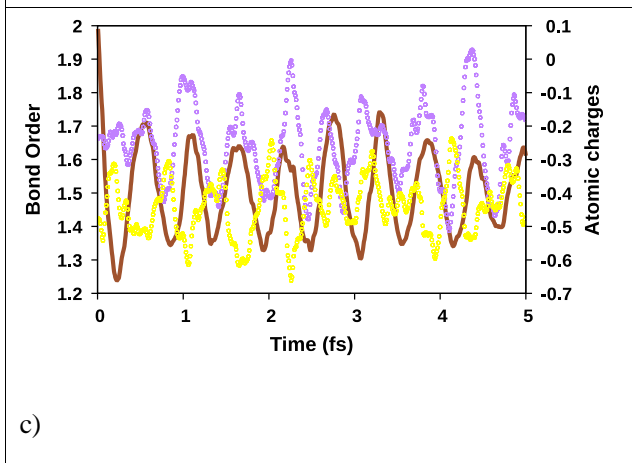
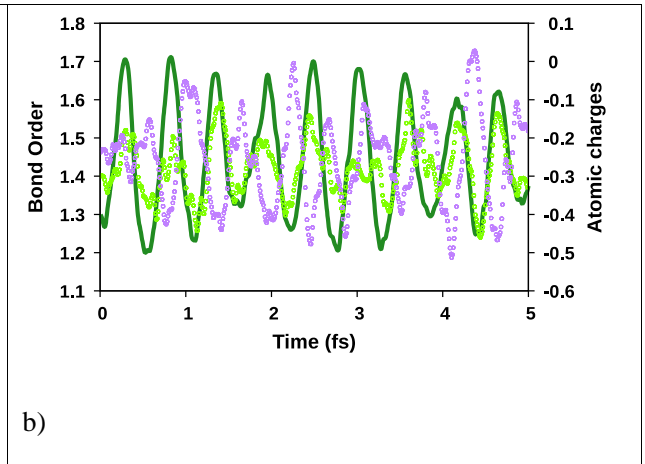
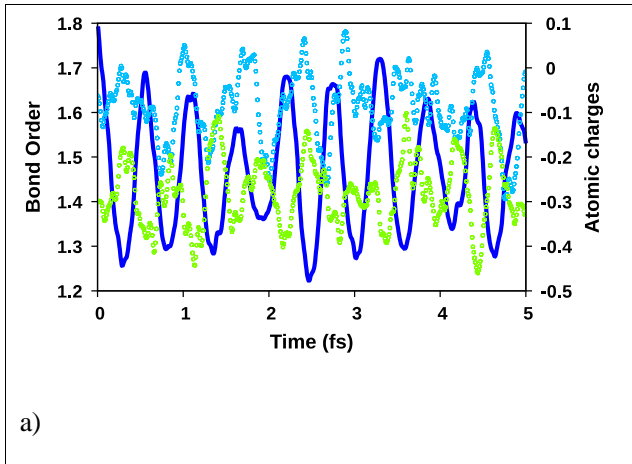




**Figure S1.** System 1. Left axis: bond order (solid lines); Right axis: Löwdin atomic charges of the atoms involved in the bond (dotted lines); a) C<sub>1</sub>-C<sub>2</sub> bond order (blue); C<sub>1</sub> (light blue) and C<sub>2</sub> (light green) charges; b) C<sub>2</sub>-C<sub>3</sub> bond order (dark green); C<sub>2</sub>/C<sub>3</sub> (light green) charges; c) C<sub>5</sub>-C<sub>6</sub> bond order (magenta); C<sub>5</sub>/C<sub>6</sub> (plum) charges; d) C<sub>1</sub>-C<sub>6</sub> bond order (red); C<sub>1</sub> (light blue) and C<sub>6</sub> (plum) charges; e) comparison of the bond orders, color coding as above; f) comparison of the charges, color coding as above.

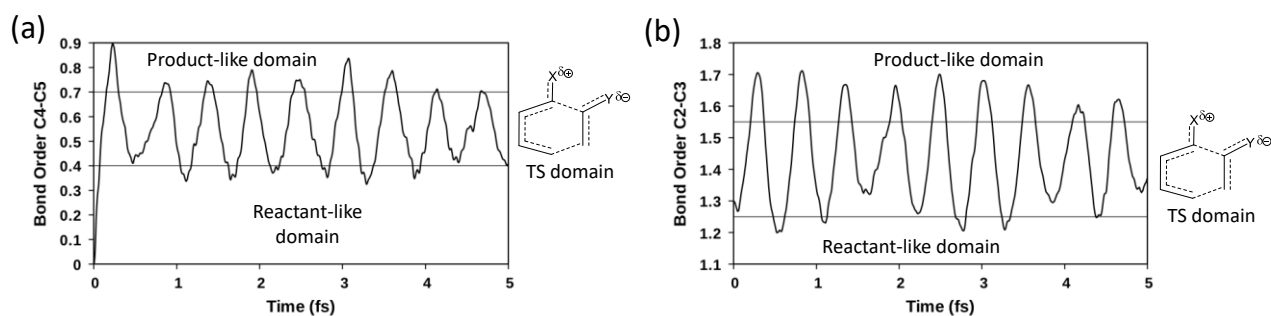


**Scheme S2.** Color code for **a)** bond orders, **b)** atomic charges of system 2 used in Figure S2.





**Figure S2.** System 2. Left axis: bond order (solid lines); Right axis: Lowdin atomic charges of the atoms involved in the bond (dotted lines); a) C<sub>1</sub>-C<sub>2</sub> bond order (blue); C<sub>1</sub> (light blue) and C<sub>2</sub> (light green) charges; b) C<sub>2</sub>-C<sub>3</sub> bond order (dark green); C<sub>2</sub> (light green) and C<sub>3</sub> (violet) charges; c) C<sub>3</sub>-C<sub>4</sub> bond order (brown); C<sub>3</sub> (violet) and C<sub>4</sub> (yellow) charges; d) C<sub>5</sub>-C<sub>6</sub> bond order (magenta); C<sub>6</sub> (plum) and C<sub>5</sub> (gray) charges; e) C<sub>1</sub>-C<sub>6</sub> bond order (red); C<sub>1</sub> (light blue) and C<sub>6</sub> (plum) charges; f) C<sub>4</sub>-C<sub>5</sub> bond order (orange); C<sub>4</sub> (yellow) and C<sub>6</sub> (gray) charges; g) comparison of the bond orders, color coding as above; h) comparison of the charges, color coding as above.



**Figure S3.** Time-dependency of (a) C<sub>4</sub>-C<sub>5</sub> (C<sub>1</sub>-C<sub>6</sub>) BO and (b) C<sub>2</sub>-C<sub>3</sub> BO. The transition state (benzene-like) domain corresponds to the central horizontal zone.

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