Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ab initio molecular dynamics of thiophene: The interplay of internal conversion and intersystem crossing (Electronic Supplementary Information)

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Contents

1 Quantum chemical calculations of thiophene CAS(8/7)

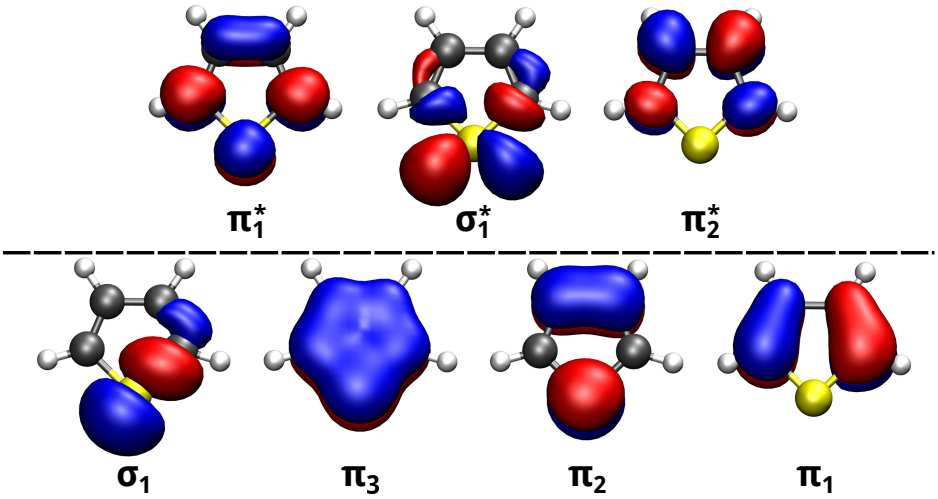

Fig. S1 State-averaged CASSCF molecular orbitals included in the active space CAS(8/7) of thiophene, obtained with the 6-31G* basis set at the SA(2S+3T)-CASSCF optimized ground state equilibrium geometry.

Table S1 Calculated excitation energies (eV) for singlet and triplet states of thiophene at the most relevant geometries. Shown are the CAS(8/7)/6-31G* values of this work and results from previous calculations (references) [1–3] and from CAS(8/7)/6-31G* calculations of this work. All energies are relative to the ground state minimum energy. The energies of the optimized states are given in bold.

	CASSCF(8/7)/6-31G*					references				
Structure	S_0	S_1	T_1	T_2	T_3	S_0	S_1	T_1	T_2	T_3
S_0-Min	**0.00**	6.19	3.72	5.05	6.52	**0.00**[a]	5.58[a]	3.76[a]	4.75 [a]	6.11[a]
S_1-Min-a	0.82	**5.40**	3.23	4.86	6.42	1.49[a]	**5.08**[a]	4.04[a]	4.55[a]	6.09[a]
S_1-TS	1.06	**5.55**	3.65	5.05	5.79	1.64[a]	**5.15**[a]	3.81[a]	4.65[a]	5.47[a]
S_1-Min-b	3.21	**3.38**	3.15	3.56	5.53	3.55[a]	**4.00**[a]	3.64[a]	4.29[a]	5.69[a]
S_1/S_0-CoIn-a	**3.57**	**3.57**	3.44	3.87	6.26	**4.03**[a]	**4.08**[a]	3.80[a]	4.31[a]	5.94[a]
S_1/S_0-CoIn-b	**4.96**	**4.96**	4.88	6.30	7.15	**4.61**[b]	**4.61**[b]	-	-	-
S_1/S_0-CoIn-c	**5.54**	**5.55**	5.42	7.35	7.90	**4.97**[b]	**4.97**[b]	-	-	-
T_1-Min-a	1.10	5.71	**2.90**	5.38	6.45	-	5.11[c]	**3.17**[c]	5.04[c]	-
T_1-Min-b	3.25	3.47	**3.10**	3.70	5.30	2.99[c]	3.77[c]	**3.52**[c]	4.45[c]	-
T_2-Min	0.45	5.71	3.64	**4.61**	6.41	-	-	-	-	-
S_0/T_1-STC	**3.11**	3.46	**3.11**	3.70	5.30	-	-	-	-	-
S_1/T_2-STC	3.35	**3.59**	3.39	**3.59**	5.71	-	-	-	-	-

[a] CASPT2(8/7)/6-31G* [1] [b] CASPT2(10/8)/6-311G* [2] [c] BHLYP/MRCI/TZVPP+R [3]

2 Quantum chemical calculations of thiophene CAS(10/9)

Table S2 Calculated excitation energies (eV) for the most relevant singlet and triplet states of thiophene at different triplet minimum and STC structures. Energies were calculated using CASSCF(10/9)/6-31G*. All energies are relative to the ground state minimum energy. The energies of the optimized states are given in bold.

	CASSCF(10/9)/6-31G*					CASPT2(10/9)/6-31G*					BHLYP/MRCI/TZVPP+R[3]				
Structure	S_0	S_1	T_1	T_2	T_3	S_0	S_1	T_1	T_2	T_3	S_0	S_1	T_1	T_2	T_3
T_1-Min-a	1.14	5.95	**3.09**	5.52	6.37	1.24	5.68	**3.15**	5.19	5.96	-	5.11	**3.17**	5.04	-
T_1-Min-b	3.35	3.54	**3.10**	3.83	5.34	3.27	4.11	**3.63**	4.51	5.59	2.99	3.77	**3.52**	4.45	-
T_2-Min	0.42	5.71	3.69	**4.68**	6.47	0.53	5.45	3.80	**4.63**	6.26	-	-	-	-	-
S_0/T_1-STC	**3.12**	3.54	**3.12**	3.82	5.32	3.58	4.076	3.68	4.33	5.63	-	-	-	-	-
S_1/T_2-STC	3.50	**3.72**	3.49	**3.72**	5.74	4.14	4.42	4.18	4.39	6.11	-	-	-	-	-

Table S3 Calculated excitation energies (eV) for the most relevant singlet and triplet states of all optimized ground state minima. The optimized geometries and energies were obtained using CASSCF(10/9)/6-31G*. The electronic ground state at the S_0-Min geometry has been chosen as the common origin.

Structure	S_0	S_1	T_1	T_2	T_3
thiophene (S_0-Min)	**0.00**	6.18	3.78	5.06	6.25
cyclopropene	**2.59**	5.15	4.98	5.92	7.13
cyclobutene	**1.46**	8.32	5.06	7.32	7.32

Table S4 Spin-orbit coupling (SOC) constants (cm^{-1}) between selected singlet and triplet states at different important geometries. SOC strength can be considered as the length of the spin-orbit-coupling vector.[1,4] Its components corresponds to the spin-orbit coupling matrix elements calculated by an efficient method using the Breit-Pauli-spin-orbit operator[5] implemented in Molpro program[6,7] in combination with the CASSCF(10/9)/6-31G* level of theory.

SOC	S_0-Min	S_1-Min-a	S_1-Min-b	S_1/S_0-CoIn-a	T_1-Min-a	T_1-Min-b	S_0/T_1-STC	S_1/T_2-STC
S_0/T_1	0.62	3.64	115.58	39.48	9.57	104.99	106.19	122.08
S_0/T_2	0.03	13.17	2.06	103.13	6.38	2.19	3.35	0.23
S_0/T_3	58.51	24.39	56.18	19.64	8.26	68.02	66.50	50.08
S_1/T_1	0.52	10.95	0.08	100.43	0.58	0.16	0.20	0.08
S_1/T_2	0.01	0.27	118.43	40.55	0.59	109.90	110.19	125.40
S_1/T_3	20.90	11.83	0.14	49.95	2.29	0.20	0.17	0.14

3 Excited state dynamics of thiophene

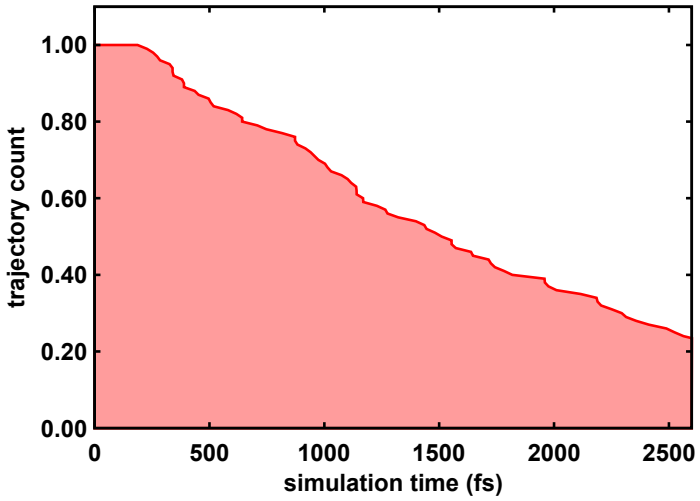

Fig. S2 Percentage of the 100 CAS(8/7)-ST trajectories which have reached at least a given simulation time.

Table S5 Distribution of the CAS(10/9)-ST,CAS(10/9)-S and CAS(8/7)-ST trajectories according to the observed type of dynamics, the final populated state as well as the final geometry. All percentages are given with respect to the total number of analyzed trajectories. Trajectories that only show vibrational dynamics in the S_1 state without any participation of other states are counted as vibrational dynamics.

	CAS(10/9)-ST	CAS(10/9)-S	CAS(8/7)-ST
non-adiabatic dynamics	83.3	83.2	81.0
vibrational dynamics	16.7	16.8	19.0
final state (%)			
S_0	31.8	75.8	39.0
S_1	22.2	24.2	19.0
T_1	43.9	-	39.0
T_2	2.0	-	2.0
T_3	0.0	-	1.0
final geometry(%)			
thiophene	41.4	54.7	49.0
open-ring	53.5	25.3	48.0
cyclopropene	5.1	16.8	3.0
cyclobutene	0.0	3.2	0.0

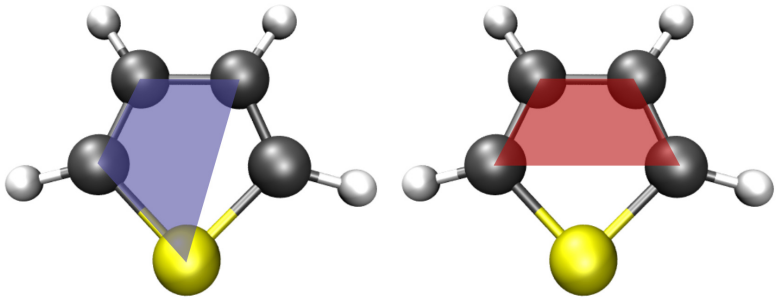

Fig. S3 Definition of the collective variables Φ_{SCCC} (blue) and Φ_{CCCC} (red) shown for the S_0-Min geometry. Both dihedral angles were redefined in the range between 0° and 90°.

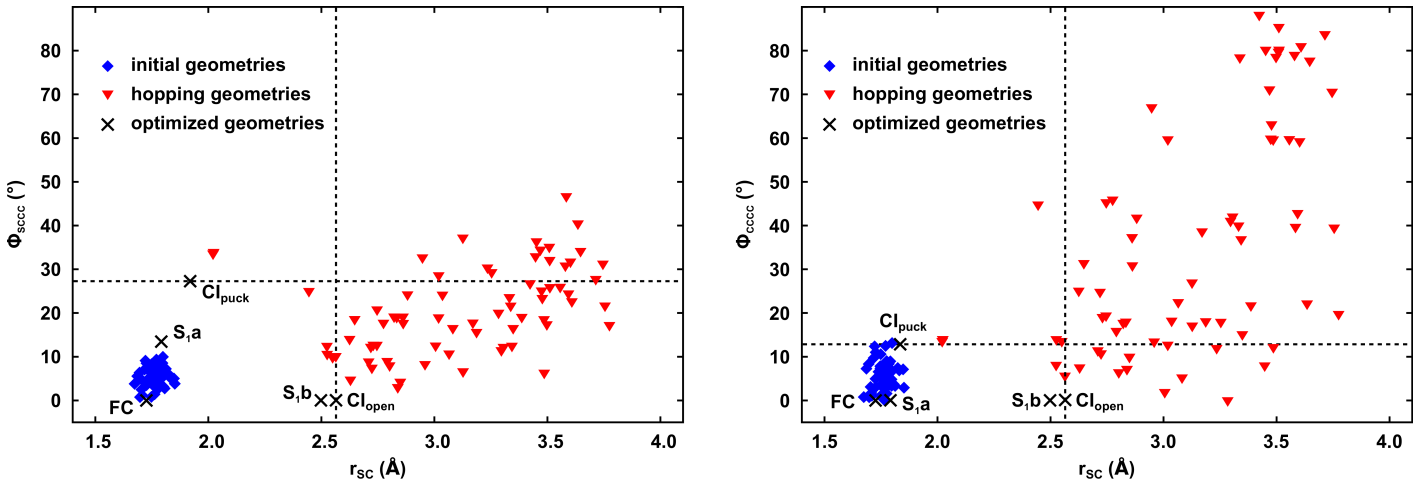

Fig. S4 Location of the initial geometries and the geometries where surface hops from the S_1 state to the S_0 state occurred depending on the averaged CS distance and dihedral angles Φ_{SCCC} (top) and Φ_{CCCC} (bottom). Only trajectories form the CAS(10/9)-S dynamics simulation set are shown. The initial geometries are represented in blue, while the S_1/S_0 hopping geometries are marked in red. Both dihedral angles were redefined in the range between 0° and 90°. Additionally important CASSCF(10/9)/6-31G* optimized geometries are represented in black.

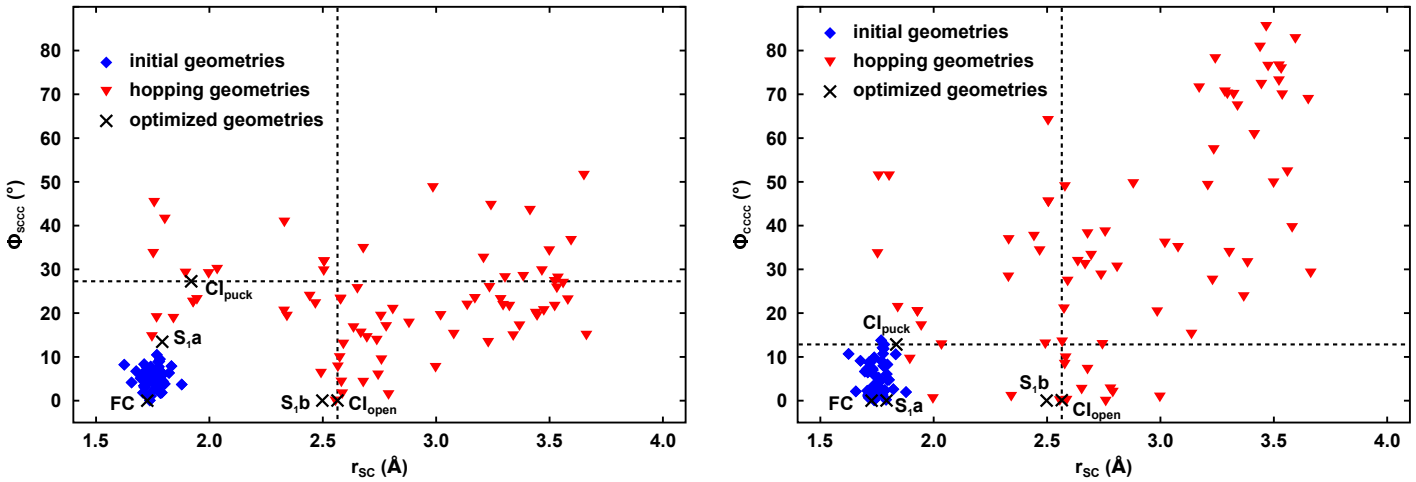

Fig. S5 Location of the initial geometries and the geometries where surface hops from the S_1 state to the S_0 state occurred depending on the averaged CS distance and dihedral angles Φ_{SCCC} (top) and Φ_{CCCC} (bottom). Only trajectories form the CAS(8/7)-ST dynamics simulation set are shown. The initial geometries are represented in blue, while the S_1/S_0 hopping geometries are marked in red. Both dihedral angles were redefined in the range between 0° and 90°. Additionally important CASSCF(8/7)/6-31G* optimized geometries are represented in black.

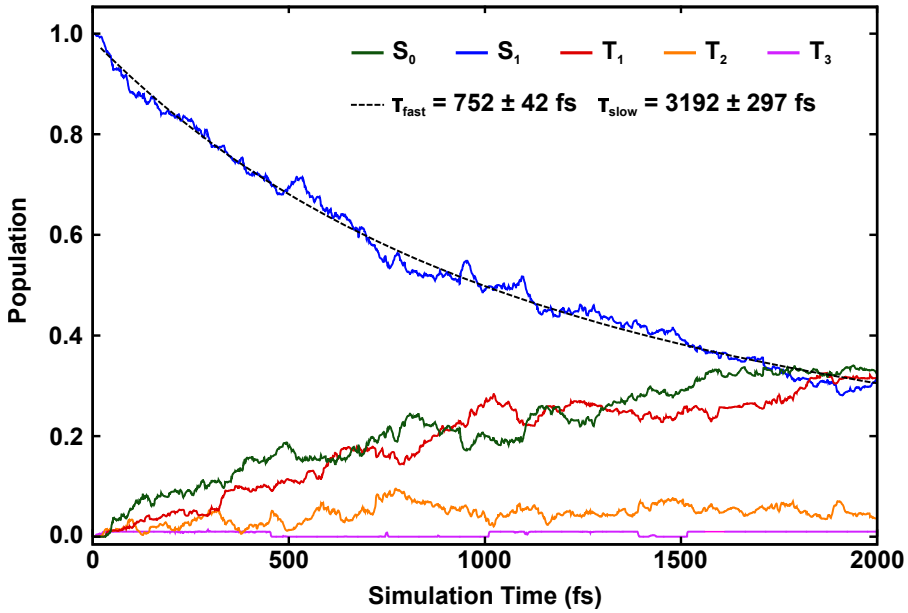

Fig. S6 Time evolution of the average populations of the considered excited states for the CAS(8/7)-ST dynamics simulations. The ground and the four lowest excited states are displayed in color. The fitting function used is $a \cdot exp(-t/\tau_{fast}) + b \cdot exp(-t/\tau_{slow})$ (a =0.479 ± 0.043 and b = 0.508 ± 0.043).

4 Optimized geometries of thiophene

S_0 Minimum (S_0-Min)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	0.013205	-1.252181	0.000100
C	1.266005	-0.716728	-0.000017
C	1.266020	0.716704	-0.000023
C	0.013209	1.252175	0.000098
S	-1.237390	0.000047	0.000124
H	-0.262646	-2.286529	0.000148
H	2.158385	-1.312937	-0.000088
H	2.158397	1.312919	-0.000113
H	-0.262614	2.286529	0.000162

CASPT2(10/9)/6-31G* optimized

C	0.003488	-1.239320	0.000104
C	1.272904	-0.714985	-0.000032
C	1.272915	0.714974	-0.000035
C	0.003508	1.239329	0.000102
S	-1.206340	0.000013	-0.000042
H	-0.286870	-2.280961	0.000268
H	2.169890	-1.324154	-0.000118
H	2.169911	1.324129	-0.000129
H	-0.286834	2.280974	0.000273

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	0.015861	-1.262315	0.000154
C	1.265955	-0.719944	-0.000010
C	1.260649	0.715022	0.000039
C	0.004454	1.246147	0.000072
S	-1.225349	0.031314	0.000298
H	-0.260403	-2.296666	0.000058
H	2.161506	-1.311444	-0.000197
H	2.151017	1.314426	0.000023
H	-0.261119	2.283460	-0.000045

S_1 Minimum a (S_1-Min-a)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.368247	2.269233	-0.483790
C	-1.667507	1.112520	0.079958
C	-0.225354	1.227010	0.014629
C	0.230925	2.475289	-0.602194
S	-1.171957	3.586881	-0.697438
H	1.191734	2.914004	-0.416864
H	-3.365306	2.552766	-0.209072
H	-2.179875	0.271124	0.499788
H	0.448745	0.478358	0.377718

CASPT2(10/9)/6-31G* optimized

C	-2.365424	2.234333	-0.543891
C	-1.666741	1.163869	0.077708
C	-0.234408	1.277315	0.012206
C	0.228144	2.439744	-0.662514
S	-1.156968	3.546405	-0.440181
H	1.210164	2.876146	-0.514314
H	-3.386271	2.512100	-0.304125
H	-2.172299	0.315304	0.528581
H	0.436962	0.521970	0.409265

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.367239	2.270528	-0.465767
C	-1.670076	1.125757	0.145863
C	-0.227486	1.234560	0.052597
C	0.221172	2.486694	-0.590386
S	-1.155818	3.546355	-0.811097
H	1.167422	2.944076	-0.372826
H	-3.348317	2.591709	-0.173425
H	-2.178546	0.231092	0.442672
H	0.452047	0.456415	0.335102

S_1 transition state (S_1-TS)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.401222	2.007129	-0.522510
C	-1.646890	0.948659	0.079641
C	-0.225652	1.143581	-0.064726
C	0.159733	2.467726	-0.507584
S	-1.217249	3.521678	-0.666757
H	1.155476	2.847227	-0.542537
H	-3.414786	2.240660	-0.253946
H	-2.046552	0.228134	0.768351
H	0.504150	0.433455	0.268985

CASPT2(10/9)/6-31G* optimized

C	-2.394864	2.016703	-0.525206
C	-1.631489	1.033599	0.172398
C	-0.207259	1.190806	0.001419
C	0.176412	2.402590	-0.624952
S	-1.262823	3.412875	-0.607578
H	1.146029	2.881320	-0.521900
H	-3.422699	2.291039	-0.292906
H	-2.057106	0.188632	0.708659
H	0.520805	0.420670	0.248982

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.421442	1.987604	-0.529950
C	-1.649183	0.948926	0.074999
C	-0.227942	1.148376	-0.073509
C	0.155278	2.469644	-0.522391
S	-1.182845	3.503150	-0.724749
H	1.149343	2.862060	-0.478227
H	-3.413310	2.248962	-0.203608
H	-2.050279	0.232240	0.766279
H	0.507388	0.437286	0.250072

S_1 Minimum b (S_1-Min-b)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.793069	1.261016	-0.056022
C	-1.633005	0.669431	0.223167
C	-0.271779	1.169422	-0.052255
C	0.136647	2.331945	-0.646736
S	-0.889999	3.598954	-1.270298
H	1.195620	2.489976	-0.744450
H	-3.805764	0.955464	0.115412
H	-1.666488	-0.294008	0.710497
H	0.516383	0.509257	0.268155

CASPT2(10/9)/6-31G* optimized

C	-2.739905	1.296114	-0.074820
C	-1.609923	0.655375	0.229971
C	-0.255332	1.141897	-0.038702
C	0.104894	2.332008	-0.646294
S	-0.978281	3.512430	-1.224833
H	1.169257	2.523767	-0.761152
H	-3.787590	1.059757	0.062260
H	-1.671256	-0.319208	0.723572
H	0.556682	0.489317	0.277468

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.798557	1.259364	-0.055000
C	-1.634762	0.672946	0.221385
C	-0.273820	1.175682	-0.055358
C	0.134927	2.334166	-0.647831
S	-0.875142	3.590425	-1.266342
H	1.195109	2.486924	-0.742865
H	-3.808837	0.947447	0.119587
H	-1.664611	-0.290672	0.708609
H	0.514239	0.515175	0.265284

T_1 Minimum a (T_1-Min-a)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.342175	2.287577	-0.414784
C	-1.620359	1.104853	0.064189
C	-0.271853	1.210981	0.001570
C	0.209312	2.489252	-0.532735
S	-1.184244	3.538916	-1.052460
H	1.120714	2.959443	-0.217698
H	-3.285401	2.610048	-0.018324
H	-2.146518	0.242239	0.425891
H	0.413681	0.443879	0.307086

CASPT2(10/9)/6-31G* optimized

C	-2.317895	2.301319	-0.404216
C	-1.622927	1.094699	0.053173
C	-0.268740	1.201447	-0.009479
C	0.184059	2.499204	-0.519352
S	-1.181823	3.456574	-1.142218
H	1.069221	3.009620	-0.153062
H	-3.236615	2.668394	0.042232
H	-2.166092	0.225472	0.408036
H	0.433971	0.430457	0.287620

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.332442	2.292415	-0.407702
C	-1.617892	1.111235	0.075835
C	-0.267973	1.199991	-0.016352
C	0.206629	2.491791	-0.556315
S	-1.166626	3.509057	-1.071154
H	1.079788	2.979893	-0.163525
H	-3.282081	2.616317	-0.029209
H	-2.145379	0.257153	0.456083
H	0.419135	0.429334	0.275074

T_1 Minimum b (T_1-Min-b)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.768283	1.291852	-0.072107
C	-1.603686	0.663900	0.225507
C	-0.283639	1.141561	-0.038011
C	0.107717	2.344188	-0.652457
S	-0.907384	3.563072	-1.251750
H	1.167838	2.501652	-0.749884
H	-3.781156	0.985610	0.099687
H	-1.662847	-0.297629	0.712439
H	0.519985	0.497252	0.274047

CASPT2(10/9)/6-31G* optimized

C	-2.671060	1.366697	-0.111690
C	-1.573513	0.643152	0.235551
C	-0.248688	1.097413	-0.016346
C	0.061970	2.321009	-0.640038
S	-1.070998	3.430045	-1.181556
H	1.116350	2.554585	-0.775856
H	-3.723752	1.140714	0.020243
H	-1.683420	-0.326654	0.727581
H	0.581658	0.464496	0.289582

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.775153	1.286231	-0.069139
C	-1.609207	0.667418	0.223816
C	-0.284228	1.151203	-0.042871
C	0.108508	2.346234	-0.653503
S	-0.891434	3.556020	-1.248457
H	1.170244	2.497188	-0.747680
H	-3.786689	0.976550	0.104365
H	-1.661443	-0.294562	0.710846
H	0.517948	0.505175	0.270093

T_2 Minimum (T_2-Min)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.356781	2.172954	-0.151519
C	-1.647228	0.992474	0.202656
C	-0.166633	1.149673	0.010833
C	0.162099	2.402578	-0.576398
S	-1.278845	3.445726	-0.814828
H	1.140012	2.820653	-0.687185
H	-3.416672	2.277817	-0.246751
H	-2.123668	0.037786	0.305852
H	0.554724	0.538587	0.516257

CASPT2(10/9)/6-31G* optimized

C	-0.044499	0.066366	1.753763
C	1.284754	-0.013747	2.220546
C	2.266273	0.384170	1.208933
C	1.670025	0.761404	-0.012968
S	0.000606	0.170527	-0.013592
H	-0.912804	-0.382278	2.216808
H	1.550258	-0.297477	3.232259
H	3.333319	0.424368	1.394368
H	2.174566	0.866623	-0.963801

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.350154	2.172401	-0.156380
C	-1.650202	0.990049	0.220607
C	-0.166515	1.144943	0.010391
C	0.148716	2.404706	-0.581230
S	-1.264808	3.428180	-0.824178
H	1.127382	2.822812	-0.687627
H	-3.410371	2.292169	-0.227824
H	-2.128406	0.031548	0.277539
H	0.561366	0.551440	0.527619

S_1/S_0 conical intersection a (S_1/S_0-CoIn-a)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	0.687641	1.054422	0.002396
C	-0.688606	1.055840	0.001948
C	-1.687388	-0.039790	-0.000488
C	-1.499970	-1.357272	-0.001118
S	1.736047	-0.325002	0.000356
H	1.158478	2.021314	0.004045
H	-1.137508	2.035209	0.003255
H	-2.710043	0.308955	-0.001756
H	-2.206291	-2.163472	-0.002609

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	0.666673	1.040594	0.002287
C	-0.707876	1.076256	0.001726
C	-1.694506	-0.025377	-0.000284
C	-1.471061	-1.314826	-0.001543
S	1.675520	-0.370224	0.000916
H	1.175363	1.988107	0.003783
H	-1.145145	2.059979	0.002827
H	-2.724927	0.301589	-0.000707
H	-2.121681	-2.165896	-0.002976

S_1/S_0 conical intersection b (S_1/S_0-CoIn-b)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.412909	2.340219	-0.167328
C	-1.624774	1.073898	0.092575
C	-0.289591	1.148420	-0.046613
C	0.109469	2.476532	-0.558888
S	-1.017326	3.280499	-1.517293
H	1.039147	2.943782	-0.284181
H	-2.124522	3.006821	0.649704
H	-2.149060	0.179405	0.377353
H	0.426138	0.361892	0.108476

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.423473	2.331097	-0.158278
C	-1.624615	1.074959	0.102265
C	-0.292092	1.150114	-0.054097
C	0.106458	2.481703	-0.569968
S	-0.983571	3.278745	-1.524722
H	1.031731	2.944808	-0.271507
H	-2.136692	3.010180	0.649109
H	-2.144340	0.178725	0.390538
H	0.423168	0.361132	0.090465

S_1/S_0 conical intersection c (S_1/S_0-CoIn-c)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.049702	1.798399	-1.012073
C	-1.785966	0.965353	0.144055
C	-0.416978	1.104251	-0.092065
C	0.044912	2.395026	-0.603990
S	-1.464612	3.475926	-0.847795
H	0.705071	2.399491	-1.453232
H	-2.369469	1.427460	-1.971477
H	-2.248154	0.011846	0.299521
H	0.286523	0.288874	-0.051079

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.047800	1.804470	-1.005979
C	-1.796641	0.979536	0.164200
C	-0.425167	1.112289	-0.092832
C	0.049854	2.411534	-0.599002
S	-1.468224	3.447883	-0.851629
H	0.713103	2.404323	-1.446704
H	-2.339819	1.408582	-1.964910
H	-2.245446	0.015972	0.301682
H	0.261764	0.282038	-0.092960

S_0/T_1 singlet-triplet minimum-energy crossing (S_0/T_1-STC)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.729673	1.315001	-0.084510
C	-1.592446	0.655221	0.229728
C	-0.263502	1.124968	-0.029975
C	0.096012	2.325415	-0.642780
S	-0.981905	3.515167	-1.226168
H	1.146767	2.523436	-0.760593
H	-3.757807	1.051982	0.065683
H	-1.673063	-0.304733	0.716256
H	0.544160	0.485004	0.279828

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.748899	1.301932	-0.077564
C	-1.601374	0.661034	0.226931
C	-0.270134	1.139478	-0.037197
C	0.100175	2.333011	-0.646688
S	-0.942052	3.524470	-1.231567
H	1.155718	2.512560	-0.755242
H	-3.771433	1.022316	0.080927
H	-1.668487	-0.299971	0.713755
H	0.535028	0.496631	0.274115

S_1/T_2 singlet-triplet minimum-energy crossing (S_1/T_2-STC)

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-2.785771	1.247035	-0.049268
C	-1.617712	0.642865	0.236447
C	-0.276965	1.134191	-0.034457
C	0.073331	2.277288	-0.618144
S	-0.773861	3.706256	-1.326197
H	1.113609	2.549304	-0.773158
H	-3.802768	0.954140	0.115890
H	-1.675331	-0.319013	0.723597
H	0.534011	0.499394	0.272759

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-2.788537	1.248394	-0.049901
C	-1.620473	0.647373	0.234211
C	-0.278140	1.143530	-0.039157
C	0.079213	2.289515	-0.624418
S	-0.781259	3.676563	-1.311068
H	1.124197	2.539487	-0.768372
H	-3.805238	0.955045	0.115479
H	-1.671939	-0.314745	0.721369
H	0.530719	0.506299	0.269326

S_0 minimum cyclopropene derivate

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	-0.316282	-1.359312	-1.376735
C	0.967549	-1.279998	-1.515098
C	0.310720	-0.088841	-0.878610
C	0.457604	0.139517	0.614583
S	0.446520	1.612200	1.360375
H	-1.240800	-1.874818	-1.509443
H	1.898500	-1.680939	-1.847765
H	0.193893	0.825666	-1.439243
H	0.576953	-0.755132	1.205791

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	-0.318981	-1.355271	-1.374696
C	0.965214	-1.279202	-1.513750
C	0.311720	-0.086646	-0.876108
C	0.459705	0.144553	0.616123
S	0.452578	1.596543	1.346718
H	-1.244042	-1.870551	-1.505055
H	1.894827	-1.684751	-1.844802
H	0.196808	0.827173	-1.438644
H	0.576831	-0.753506	1.204071

S_0 minimum cyclobutene derivate

SA(2S+3T)-CASSCF(10/9)/6-31G* optimized

C	0.411404	-0.763656	0.079073
C	-0.297594	-0.657553	-1.309102
C	-0.068033	0.635086	-1.401958
C	0.668341	0.683145	-0.024855
S	-0.499470	0.242413	1.392583
H	1.111626	-1.513771	0.393374
H	-0.843009	-1.367907	-1.898924
H	-0.351411	1.400273	-2.097773
H	1.590692	1.183805	0.199594

SA(2S+3T)-CASSCF(8/7)/6-31G* optimized

C	0.424867	-0.789369	0.052714
C	-0.268917	-0.688896	-1.324668
C	-0.055217	0.644282	-1.376536
C	0.647829	0.669541	-0.026671
S	-0.476736	0.322650	1.337642
H	1.096936	-1.536459	0.424633
H	-0.834681	-1.383720	-1.913514
H	-0.383769	1.430486	-2.026864
H	1.572234	1.173319	0.185276

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