A. Electronic Supporting Information

In the electronic supporting information we will, in Section A.1, give details of the electronic wavefunction at the structures with more significant multiconfigurational character, in Section A.2 we discuss values of some characteristic coordinates as found in the structures encountered during the reaction. Full structural data of all identified stationary points is given in Section A.3 in the form of cartesian coordinates.

A.1. Electronic wavefunction at selected structures

In this section we will show that a significant multiconfigurational character is present in the wavefunction of certain points on the proposed reaction path thus showing the necessity to consider a multiconfigurational treatment.

Table 1 gives the configurations with absolute contributions ≥ 0.1 in the CI-vectors at the structures with the clearest multiconfigurational character. It shows that multiconfigurational wavefunctions are mostly encountered around structure **4** and that the most important determinants besides the unexcited determinant are doubly excited. Since this is a critical region in the reaction path a multiconfigurational (or multireferential respectively) treatment seems to be advisable. A simple unrestricted treatment to gather the most basic multiconfigurational chracter would not suffice to reach a qualitatively similar wavefunction, since the unrestricted description only contains a single excitation.

Table 1: Most important determinants in the CI-vectors at selected structures along the proposed reaction path.

determinant	**2b4**	**4**	**46**
2222200000	0.8178830	0.8205011	0.8295311
2222020000	-0.3342401	-0.3208726	-0.4023350
2220202000	-0.1227693	-0.1141400	-0.1575986

A.2. Data on specific coordinates

In this section we give a tabular overview on how some significant intramolecular coordinates as depicted in Figure 1 change during the various reaction steps discussed in the main article. We focus on the coordinates most indicative of the various reaction steps.

Firstly, in Figure 1 the two broken bonds of the reaction process are shown, as well as the dihedral angle centered around the C_1'-C_5' bond opposite to the sulfur atom in the thienyl unit on the right side of the molecule. The changes in the C_1-C_2 bond length allow

Table 2: Chosen distances (d, in Å), bond angles (α, in °) and dihedral angles (ω, in °) for the ground state minima of dithienylethene, calculated on the CASSCF(10,10)/6-31G(d) level of theory.

structure	CI	1	2a	2b	3	4	5	6
d(C_1-C_2)	1.452	1.507	4.921	1.548	3.466	2.428	2.517	1.525
d(C_2'-S')	1.792	1.836	1.836	3.342	3.367	4.935	2.743	1.834
α(C_2-C_1-C_0)	130.8	59.5	87.3	117.4	66.4	128.1	127.6	119.8
α(C_1-C_2-S)	113.4	109.4	15.4	109.0	73.9	94.4	92.3	105.9
α(C_1'-C_2'-S')	109.1	105.0	104.5	78.1	77.9	3.5	91.9	105.9
ω(C_0'-C_1'-C_5'-C_4')	-159.7	-144.3	-139.5	-178.8	-179.4	1.0	-163.1	168.1

for a differentiation of the **a** and **b** paths in the proposed reaction scheme. In the local minima **2a**, **3**, **4** and **5** the direct C_1-C_2 bond is broken and thus enlarged. Due to the newly formed six-membered ring in structures **4** and **5** the distance is smaller compared to **2a**, **3** and thus also acts as indicator for this structural element. Similarly the C_2'-S' bond distance can be used to follow the **b** side of the reaction scheme. It changes for the **2b** and **3** ground state minima as the relevant bond is broken and thus the sulfur arm is moved away for the relaxed structure. As pointed out in Sec 3.3 the relaxed ground state structure of **4** moves this sulfur arm even further away and the bond distance increases. In the structure of the byproduct, **5**, both atoms are not directly binding to each other. The shown dihedral angle C_0'-C_1'-C_5'-C_4' emphasizes the aforementioned unusual geometry of the **4** ground state minimum in the reaction process. The angle changes by about 40° in the reaction process, with the exception of the minimum **4** in which the angle has changed by roughly 180°. This also happens in a similar fashion in the structures **2a** and **3** for the dangling arm on the left hand side of the molecule.

The following figure, Figure 2, deals with the three angles of significance in the molecule's reaction process. The first one, C_2-C_1-C_0, shows the formation, movement and opening of the three-membered ring which occurs in **1**, moves in the reaction process toward **2b** and opens following the rest of the reaction path. The low values of **2a** and **3** are misleading as they are a result of the sulfur arms ending with the C_2 atom pointing away from the center of the molecule as discussed before. The second bond angle, C_1-C_2-S, gives some measure the strain of the first thienyl ring that is building up in some minimum structures. The seemingly strange angle in structure **2a** is again caused by the orientation of the free sulfur arm, as it rotates away from the rest of the molecule around the C_1-C_5 bond in the relaxed structure of a broken ring. Analogously the values of the C_1'-C_2'-S' angle for structures **2b**, **3** and **4** can be explained.

The discussed data can be found in Table 2.

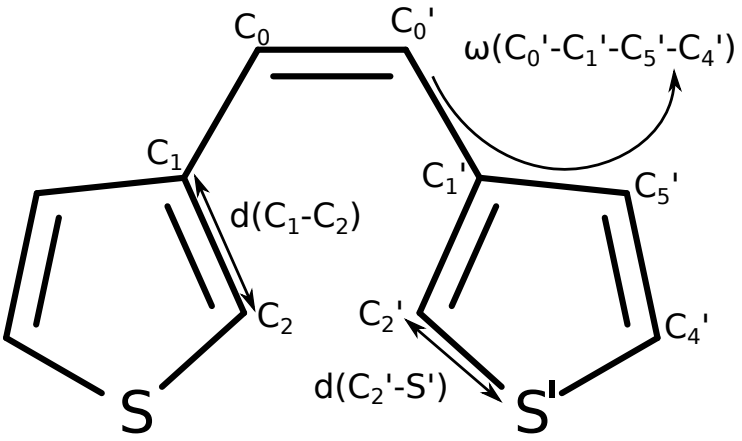

Figure 1: Sketch of the relevant bond distances of dithienylethene for the ground state reaction process toward byproduct and closed-ring product.

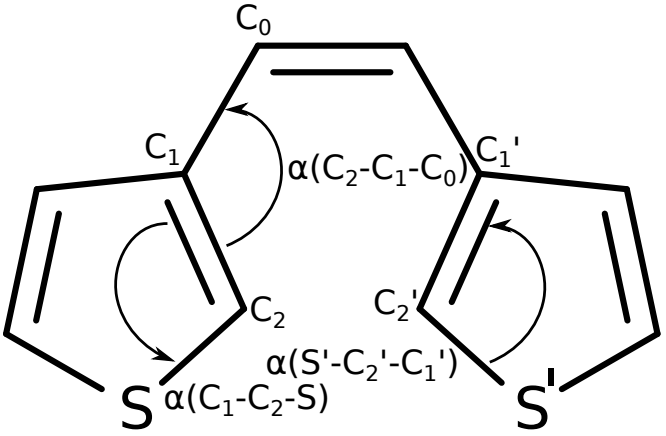

Figure 2: Sketch of the relevant bond angles of dithienylethene for the ground state reaction process toward byproduct and closed-ring product.

A.3. Cartesian coordinates of encountered stationary points

In the following we will list the cartesian coordinates of the structures (**1**, **2a**, **2b**, **3**, **4**, **5**, **6**) and transition states (**12a**, **12b**, **2a3**, **2a4**, **2b3**, **2b4**, **34**, **45**, **46**).

Table 3: Cartesian coordinates (in Å) of the ground state minimum **1**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	0.713783	0.518704	-1.132323
C	-0.714851	-0.241148	0.939316
C	-0.206438	2.052613	0.620752
C	-0.378596	1.477707	-0.751941
C	-0.568702	-0.017958	-0.549804
H	-1.753247	-0.459839	1.168531
H	0.109211	3.064102	0.798138
H	-0.904575	2.010904	-1.523818
S	0.289023	-1.495690	1.828305
C	-0.314953	1.086910	1.551454
C	0.130056	0.928082	2.936047
C	0.480796	-0.343224	3.210141
H	0.888437	-0.705725	4.133228
H	0.246222	1.740230	3.627941
C	-1.290484	-0.822293	-1.573383
C	-0.680343	-0.882977	-2.764657
S	0.867691	-0.021939	-2.841982
H	-1.051653	-1.366712	-3.646273
H	-2.234782	-1.290927	-1.365370
H	1.628453	0.517007	-0.569305

Table 4: Cartesian coordinates (in Å) of the ground state transition state **12a**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	0.671896	-0.256064	-4.821403
C	-0.668022	-0.151698	1.379241
C	-0.015906	2.073405	1.108379
C	-0.313988	1.495090	-0.212293
C	-0.605966	0.171282	-0.096289
H	-1.704699	-0.337815	1.648562
H	0.352120	3.068944	1.265425
H	-0.302508	2.057894	-1.124659
S	0.321657	-1.488622	2.155381
C	-0.180941	1.110485	2.042626
C	0.310389	0.853930	3.395445
C	0.606012	-0.448177	3.576080
H	1.015381	-0.889022	4.463385
H	0.485366	1.614232	4.132310
C	-1.014418	-0.801775	-1.113202
C	-0.670100	-0.869173	-2.411003
S	0.470382	0.263313	-3.271700
H	-1.053599	-1.659882	-3.031373
H	-1.659703	-1.589059	-0.758265
H	0.090166	-1.153297	-5.020970

Table 5: Cartesian coordinates (in Å) of the ground state transition state **12b**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	0.714408	0.516779	-1.132658
C	-0.715834	-0.241153	0.938179
C	-0.204903	2.052565	0.618939
C	-0.377047	1.477037	-0.753544
C	-0.568968	-0.018576	-0.550813
H	-1.754613	-0.460409	1.166713
H	0.112297	3.063591	0.796177
H	-0.901458	2.010419	-1.526290
S	0.288795	-1.485333	1.836844
C	-0.318007	1.087799	1.549529
C	0.130455	0.922671	2.933878
C	0.480058	-0.351190	3.196868
H	0.894016	-0.713296	4.117331
H	0.248488	1.730404	3.630729
C	-1.291211	-0.822226	-1.574834
C	-0.679661	-0.884401	-2.765454
S	0.867981	-0.025216	-2.840306
H	-1.052356	-1.367088	-3.647093
H	-2.236593	-1.288963	-1.367531
H	1.627979	0.513061	-0.567858

Table 6: Cartesian coordinates (in Å) of the ground state minimum **2a**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	0.639732	-0.267270	-4.850520
C	-0.658679	-0.153595	1.374995
C	-0.005183	2.071635	1.111581
C	-0.276563	1.490048	-0.213319
C	-0.569307	0.165955	-0.099950
H	-1.699880	-0.341408	1.625053
H	0.357461	3.068404	1.273458
H	-0.245382	2.051081	-1.126126
S	0.318535	-1.486732	2.173272
C	-0.187054	1.110904	2.044913
C	0.277829	0.858406	3.407829
C	0.572520	-0.442622	3.597211
H	0.964911	-0.880722	4.493501
H	0.436722	1.620661	4.146331
C	-0.957717	-0.813153	-1.119013
C	-0.626900	-0.866555	-2.422636
S	0.437143	0.272574	-3.284946
H	-1.000056	-1.671085	-3.030959
H	-1.578461	-1.619091	-0.762898
H	0.074580	-1.189892	-4.995213

Table 7: Cartesian coordinates (in Å) of the ground state transition state **2a3**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	0.932749	-1.516949	-4.381533
C	-0.527063	0.159211	0.577683
C	0.488944	2.278534	0.693253
C	-0.129505	2.163354	-0.501172
C	-0.767915	0.821012	-0.580175
H	-0.853418	-0.825837	0.831761
H	1.044829	3.119994	1.057550
H	-0.163376	2.895190	-1.284519
S	-0.352725	-1.607644	3.510500
C	0.279856	1.028173	1.454491
C	0.796698	0.815880	2.693455
C	0.708890	-0.361271	3.555687
H	1.453470	-0.375914	4.335473
H	1.407419	1.604422	3.101022
C	-1.552763	0.331468	-1.739860
C	-1.042176	-0.268076	-2.825117
S	0.701675	-0.577324	-3.048109
H	-1.676576	-0.594720	-3.630380
H	-2.619828	0.479369	-1.705729
H	-0.012220	-1.764449	-4.861263

Table 8: Cartesian coordinates (in Å) of the ground state transition state **2a4**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	-0.966257	-1.956609	-2.181720
C	0.467805	0.183473	0.407487
C	-0.572716	2.298295	0.508638
C	0.053483	2.182590	-0.681812
C	0.704001	0.845576	-0.750580
H	0.794673	-0.806594	0.638556
H	-1.134274	3.137432	0.869511
H	0.084921	2.911736	-1.467826
S	0.539854	-1.385885	3.445091
C	-0.334646	1.062395	1.281956
C	-0.830887	0.848659	2.526683
C	-0.657076	-0.318080	3.397735
H	-1.465373	-0.434625	4.104852
H	-1.467268	1.612635	2.942378
C	1.502045	0.373713	-1.906937
C	1.040789	-0.276631	-2.985837
S	-0.662855	-0.712171	-3.271342
H	1.710624	-0.548196	-3.780710
H	2.559183	0.585066	-1.877237
H	-2.014626	-2.205794	-2.375510

Table 9: Cartesian coordinates (in Å) of the ground state minimum **2b**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	-0.182173	-0.818769	-0.961568
C	0.216841	0.283413	-0.023779
C	2.511135	-0.308815	0.252655
C	2.326490	-0.154306	-1.074895
C	0.907403	0.203674	-1.365844
H	-0.500521	1.051363	0.189907
H	3.422349	-0.623003	0.726086
H	3.064935	-0.321291	-1.836106
S	-1.560469	0.244621	2.806563
C	1.265241	-0.056678	0.995075
C	1.173946	-0.131306	2.347966
C	0.017053	0.065297	3.208938
H	0.260929	0.071948	4.259380
H	2.082979	-0.359574	2.879859
C	0.419228	1.013098	-2.512788
C	-0.832613	0.729021	-2.900709
S	-1.622338	-0.585242	-2.008543
H	-1.389663	1.239013	-3.661674
H	1.014351	1.787608	-2.959982
H	0.065041	-1.838398	-0.731221

Table 10: Cartesian coordinates (in Å) of the ground state transition state **2b3**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	1.346270	-0.134299	-1.836652
C	-0.466599	0.259894	0.208084
C	0.378959	2.433164	0.470288
C	0.020454	2.282074	-0.819058
C	-0.481489	0.890632	-1.021555
H	-0.813043	-0.727149	0.418833
H	0.817733	3.301725	0.921363
H	0.121448	2.998540	-1.609759
S	-0.302495	-1.648677	3.043094
C	0.111427	1.170705	1.195000
C	0.373131	1.017797	2.524870
C	0.188856	-0.143245	3.387766
H	0.438837	0.069048	4.416569
H	0.771534	1.878419	3.035089
C	-1.260195	0.470046	-2.219444
C	-0.904838	-0.546295	-3.018193
S	0.568278	-1.461269	-2.611129
H	-1.495268	-0.877778	-3.850213
H	-2.151883	1.031999	-2.441530
H	2.127038	-0.517148	-1.177726

Table 11: Cartesian coordinates (in Å) of the ground state transition state **2b4**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	0.674815	-0.564652	-0.535758
C	-0.399994	0.381306	-0.132163
C	0.306186	2.620774	0.236527
C	0.262260	2.425685	-1.119022
C	-0.130495	1.060105	-1.431298
H	-1.332069	-0.167613	-0.063106
H	0.611234	3.520545	0.734722
H	0.531180	3.158046	-1.856859
S	-0.156136	-1.517440	2.601082
C	-0.097657	1.395202	0.951444
C	-0.011891	1.229580	2.305229
C	-0.082196	0.000866	3.076276
H	0.020347	0.144081	4.139917
H	0.165968	2.120189	2.885221
C	-0.537394	0.503654	-2.699832
C	-0.493771	-0.832494	-2.889815
S	0.350164	-1.814996	-1.715260
H	-0.880405	-1.332679	-3.755985
H	-0.859702	1.156793	-3.491668
H	1.650898	-0.556028	-0.094211

Table 12: Cartesian coordinates (in Å) of the ground state minimum **3**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	-1.424919	0.743015	-3.336608
C	0.278789	-0.402604	0.764025
C	0.401764	1.887778	0.283036
C	0.540037	1.209046	-0.882696
C	0.447277	-0.244502	-0.591800
H	0.189214	-1.342108	1.292750
H	0.434381	2.963356	0.421699
H	0.730567	1.648782	-1.853155
S	-0.368095	-1.134180	3.985816
C	0.217664	0.915364	1.369221
C	0.043481	1.295563	2.673210
C	-0.138372	0.480743	3.861912
H	-0.129216	1.059994	4.789607
H	0.057927	2.369882	2.864444
C	0.570307	-1.364517	-1.504492
C	0.396869	-1.414706	-2.846899
S	-0.161335	-0.104376	-3.930693
H	0.581758	-2.350484	-3.371418
H	0.830972	-2.310743	-1.027029
H	-1.739099	0.354141	-2.354777

Table 13: Cartesian coordinates (in Å) of the ground state transition state **34**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	-2.059019	0.675458	1.818109
C	0.521482	0.080432	-0.151973
C	2.662438	-0.128766	-1.110906
C	2.788923	-0.079168	0.226159
C	1.435602	0.101472	0.825761
H	-0.500125	0.351027	-0.037305
H	3.441986	-0.259871	-1.835314
H	3.701543	-0.121203	0.789168
S	-1.970175	-0.078132	-2.792643
C	1.224285	-0.011285	-1.449115
C	0.786092	0.008383	-2.738872
C	-0.548113	0.075407	-3.346548
H	-0.484697	0.203982	-4.416700
H	1.566581	-0.024103	-3.481057
C	1.313744	0.197840	2.288073
C	0.298464	0.092926	3.167993
S	-1.419261	-0.336161	2.976902
H	0.548467	0.189729	4.209458
H	2.262528	0.387126	2.764149
H	-3.109375	0.383222	1.763196

Table 14: Cartesian coordinates (in Å) of the ground state minimum **4**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	1.192692	0.250234	-1.393816
C	0.146928	-0.531698	-0.660630
C	-1.380923	0.101962	1.073060
C	-2.063408	0.180712	-0.111128
C	-1.200508	-0.117933	-1.217088
H	0.297985	-1.602230	-0.808046
H	-1.788774	0.318481	2.036349
H	-3.095151	0.462561	-0.207638
S	-0.034356	0.220961	4.213487
C	0.011085	-0.254628	0.835203
C	1.063278	-0.365922	1.693861
C	1.132681	-0.181441	3.134657
H	2.122585	-0.340719	3.531468
H	2.008197	-0.639317	1.253757
C	-1.455272	-0.104530	-2.581288
C	-0.425190	-0.119652	-3.521770
S	1.200566	0.245094	-3.101462
H	-0.602830	-0.234471	-4.572471
H	-2.468118	-0.030644	-2.938111
H	1.926515	0.861506	-0.908579

Table 15: Cartesian coordinates (in Å) of the ground state transition state **45**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	-0.586938	-0.791692	-0.535355
C	0.318645	0.304796	-0.111908
C	2.625327	-0.243138	0.236514
C	2.461969	-0.064067	-1.102020
C	1.086714	0.269480	-1.398536
H	-0.189355	1.234191	0.114439
H	3.535897	-0.523951	0.729709
H	3.231380	-0.172865	-1.843033
S	-1.501216	0.410033	2.595432
C	1.350980	-0.067558	0.939782
C	1.196138	-0.251589	2.257074
C	-0.017745	-0.130541	3.049760
H	0.097821	-0.456693	4.071146
H	2.068280	-0.544408	2.818098
C	0.486059	0.687732	-2.623904
C	-0.850962	0.527672	-2.827131
S	-1.772131	-0.494491	-1.761418
H	-1.381348	0.942394	-3.661922
H	1.095416	1.122220	-3.397052
H	-0.508716	-1.787487	-0.147466

Table 16: Cartesian coordinates (in Å) of the ground state transition state **46**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	0.236604	-1.206068	-1.390860
C	-0.542140	-0.154023	-0.661793
C	0.095463	1.384170	1.069052
C	0.178619	2.053163	-0.084850
C	-0.119175	1.189205	-1.216310
H	-1.612108	-0.301486	-0.814490
H	0.298797	1.790217	2.036345
H	0.453779	3.087240	-0.179351
S	0.233063	0.033324	4.208034
C	-0.266949	-0.019782	0.833496
C	-0.377584	-1.065420	1.691979
C	-0.187573	-1.130790	3.135582
H	-0.357111	-2.117656	3.535910
H	-0.655096	-2.011336	1.256425
C	-0.097323	1.453679	-2.560519
C	-0.135175	0.419440	-3.522844
S	0.261451	-1.179145	-3.113526
H	-0.294608	0.602248	-4.566382
H	0.026792	2.463378	-2.912801
H	0.891522	-1.905379	-0.910730

Table 17: Cartesian coordinates (in Å) of the ground state minimum **5**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	-0.104419	1.415485	-1.186808
C	-0.401988	0.531628	-0.001244
C	-0.103796	1.420004	1.180493
C	-0.054306	0.841748	-2.521195
C	-0.053548	0.851796	2.517478
C	0.143604	2.672601	-0.741735
C	0.144038	2.675354	0.730604
C	-0.008026	-0.479559	2.727694
H	-0.010035	1.510921	3.366801
C	-0.008163	-0.490723	-2.725132
H	-0.010194	1.497195	-3.373318
H	0.364981	3.529283	-1.350195
H	0.365878	3.534278	1.335739
C	0.389278	-0.762095	0.001180
H	-1.461164	0.279593	-0.000488
S	-0.000912	-1.752992	-1.481941
H	0.033715	-0.896430	-3.718519
S	-0.001673	-1.749687	1.489440
H	1.449864	-0.551022	0.001360
H	0.032300	-0.881930	3.722489

Table 18: Cartesian coordinates (in Å) of the ground state minimum **6**, calculated on the CASSCF(10,10)/6-31G(d) level of theory

C	-0.027380	-2.290266	-0.731408
C	0.025858	-2.290222	0.732856
C	-0.102978	-1.128446	1.411973
C	0.102706	-1.128902	-1.410825
C	0.385177	0.165062	-0.654140
C	-0.383961	0.165720	0.654313
C	-0.002914	-0.896388	2.848147
C	0.069439	0.404829	3.182342
C	0.004125	-0.898064	-2.847613
C	-0.067997	0.402524	-3.183206
S	-0.027767	1.526698	-1.814791
H	1.448250	0.224940	-0.442073
S	0.026825	1.525739	1.813827
H	-1.447124	0.225440	0.441836
H	-0.043770	-1.698882	-3.561649
H	-0.164287	0.797111	-4.175036
H	-0.175667	-3.219119	-1.252892
H	0.173335	-3.219127	1.254458
H	0.046129	-1.696524	3.562864
H	0.168404	0.799143	4.174084