SUPPLEMENTARY INFORMATION

A Theoretical Investigation of the Non-Ergodicity of Internal Conversion in 1,2-Dithiane Using Non-Adiabatic Multiconfigurational Molecular Dynamics

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Ab Initio Quantum Chemical Calculations

Structures of interest to the contemporary picture of the internal conversion process in 1,2-dithiane were optimised at the triply state-averaged complete active space self-consistent field (SA3-CASSCF) level of theory, as implemented in MOLPRO 2012.1.27,[1] with the state averaging being over the three lowest-energy singlet states and without the imposition of symmetry. A 10-electron, 8-orbital active space (Fig. S1) was chosen, comprising the $\sigma_{S\text{-}S}$ and $\sigma^*_{S\text{-}S}$ orbitals, two sets of $\sigma_{S\text{-}C}$ and $\sigma^*_{S\text{-}C}$ orbitals, and two sulfur-centred orbitals, LP_S, containing lone electron pairs. The successively more complete *def*2-SVP, *def*2-TZVP and *def*2-TZVPP basis sets[2] were used. The character of each stationary point located was verified *via* vibrational frequency analysis.

HOMO -4 ($\sigma_{S\text{-}C}$)   HOMO -3 ($\sigma_{S\text{-}C}$)   HOMO -2 ($\sigma_{S\text{-}S}$)   HOMO -1 (LP_S)   HOMO (LP_S)   LUMO ($\sigma^*_{S\text{-}S}$)   LUMO +1 ($\sigma^*_{S\text{-}C}$)   LUMO +2 ($\sigma^*_{S\text{-}C}$)
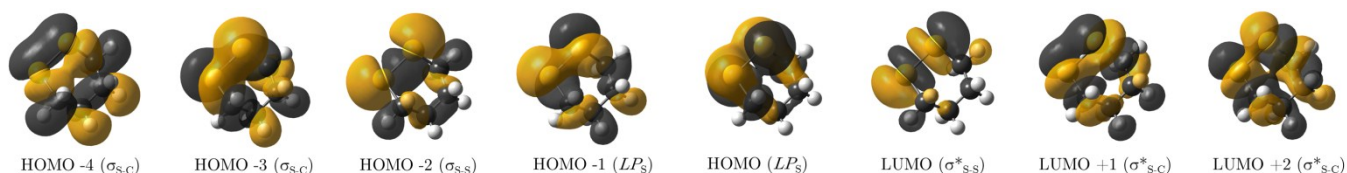
Figure S1: The orbitals included in the 10-electron, 8-orbital SA3-CASSCF active space chosen to optimise structures of interest in MOLPRO 2012.1.27. The same SA3-CASSCF active space was chosen for our non-adiabatic multiconfigurational molecular dynamics simulations.

The Cartesian coordinates in Ångström (Å) and the total electronic energies, E, in atomic units (a.u.) of the optimised structures are reported here.

Table S1: The Cartesian coordinates in Ångström (Å) and the total electronic energies, E, in atomic units (a.u) of the optimised S_0 minimum-energy structure as calculated at the SA3-CASSCF(10,8) level using the *def2*-SVP, *def2*-TZVP and *def2*-TZVPP basis sets.

def2-SVP				*def2*-TZVP				*def2*-TZVPP			
E = -950.872632850095 a.u.				E = -951.318092169631 a.u.				E = -951.321066121261 a.u.			
S	-1.0295852191	0.2989103612	1.0512144853	S	-1.0143030097	0.2883443664	1.0465581941	S	-1.0142472879	0.2884330893	1.0464552740
S	1.0295964160	-0.2989104549	1.0512018705	S	1.0142916919	-0.2883460884	1.0465684710	S	1.0142399000	-0.2884340963	1.0464623810
C	1.5099017556	0.4833157854	-0.5733563428	C	1.5127462318	0.4673382710	-0.5696599375	C	1.5126827253	0.4674368919	-0.5695826683
C	-0.7581596247	0.1129029845	-1.7598239146	C	-0.7552383422	0.1259611770	-1.7529045255	C	-0.7552743834	0.1259426477	-1.7528251093
C	0.7581409989	-0.1129028811	-1.7598324630	C	0.7552618530	-0.1259637063	-1.7528909795	C	0.7552894553	-0.1259444106	-1.7528165871
C	-1.5099079079	-0.4833156276	-0.5733387297	C	-1.5127442618	-0.4673321327	-0.5696826078	C	-1.5126811353	-0.4674330384	-0.5695967927
H	-1.1686944483	-0.3259021630	-2.6735089908	H	-1.1697469340	-0.2986523873	-2.6632247043	H	-1.1694554598	-0.2981399751	-2.6625503701
H	-0.9685077151	1.1845295021	-1.8070876275	H	-0.9451490437	1.1942846331	-1.7913740872	H	-0.9450788233	1.1934546640	-1.7913225282
H	1.1686650511	0.3259017684	-2.6735227435	H	1.1697858962	0.2986417119	-2.6632080981	H	1.1694800904	0.2981331622	-2.6625398295
H	0.9684882238	-1.1845294798	-1.8070986512	H	0.9451733190	-1.1942874673	-1.7913479211	H	0.9450944903	-1.1934565973	-1.7913061193
H	-1.3551756747	-1.5583861082	-0.4879369324	H	-1.3749271411	-1.5381164155	-0.4994126242	H	-1.3744706109	-1.5372948855	-0.4990413953
H	-2.5809236999	-0.2972866555	-0.6646647769	H	-2.5732470424	-0.2629084361	-0.6579238986	H	-2.5725049153	-0.2639330719	-0.6575666410
H	1.3551707267	1.5583863439	-0.4879528156	H	1.3749142651	1.5381208539	-0.4993904583	H	1.3744627019	1.5372975991	-0.4990275951
H	2.5809166591	0.2972866603	-0.6646928269	H	2.5732530327	0.2629292756	-0.6578892269	H	2.5725089679	0.2639462220	-0.6575446814

Table S2: The Cartesian coordinates in Ångström (Å) and the total electronic energies, E, in atomic units (a.u.) of the optimised S_1 minimum-energy structure as calculated at the SA3-CASSCF(10,8) level using the *def2*-SVP, *def2*-TZVP and *def2*-TZVPP basis sets.

def2-SVP				*def2*-TZVP				*def2*-TZVPP			
E = -950.799916740909 a.u.				E = -951.236599792737 a.u.				E = -951.239533538302 a.u.			
S	0.3078611872	0.9930201318	-1.7450039490	S	0.2970682951	0.9928636067	-1.7771709545	S	0.2972198536	0.9921494288	-1.7779230969
S	-0.2960636713	0.9839205105	1.7613475856	S	-0.2846722550	0.9738972581	1.8050917061	S	-0.2846817343	0.9740034372	1.8050772338
C	0.7312838285	-0.5345946746	1.4621157195	C	0.7206032015	-0.5410619826	1.4715769468	C	0.7207811768	-0.5404251621	1.4715135258
C	-0.0177750946	-1.6558266720	-0.7890873900	C	0.0039096811	-1.6386661378	-0.7974374623	C	0.0034965708	-1.6385659572	-0.7970345217
C	0.0311766690	-1.6876786560	0.7418628867	C	0.0119364920	-1.6770964985	0.7332141697	C	0.0124103246	-1.6770364951	0.7336594590
C	-0.7738119314	-0.4968358231	-1.4565593873	C	-0.7675487687	-0.4952488675	-1.4751700787	C	-0.7681302243	-0.4948220498	-1.4742814738
H	-0.5081035478	-2.5788098760	-1.1073452072	H	-0.4536526651	-2.5649833972	-1.1300381988	H	-0.4541832142	-2.5640055362	-1.1293414547
H	0.9966215834	-1.7086914756	-1.1939551547	H	1.0231658786	-1.6621987068	-1.1709014806	H	1.0217606722	-1.6624340983	-1.1709333168
H	0.5558029937	-2.6072444173	1.0169646371	H	0.5110851489	-2.6009063858	1.0140108858	H	0.5118276382	-2.5998662434	1.0141740649
H	-0.9816857238	-1.7872425206	1.1387725073	H	-1.0055279179	-1.7563442691	1.1005902012	H	-1.0040429468	-1.7569671576	1.1014140184
H	-1.6275272404	-0.1842347322	-0.8567679095	H	-1.6150435943	-0.1882379006	-0.8784392559	H	-1.6141313022	-0.1874638220	-0.8770328838
H	-1.1313249760	-0.8106319040	-2.4354616768	H	-1.1202566555	-0.8209209036	-2.4428703737	H	-1.1220727449	-0.8201481706	-2.4407571836
H	1.6416597805	-0.2195442885	0.9506225935	H	1.6255146665	-0.2279378741	0.9665774338	H	1.6248666323	-0.2272336473	0.9667042799
H	1.0263911406	-0.8516242679	2.4638547473	H	1.0110210564	-0.8751377054	2.4611094584	H	1.0118464304	-0.8737931110	2.4602541617

Table S3: The Cartesian coordinates in Ångström (Å) and the total electronic energies, E, in atomic units (a.u.) of the optimised S_1/S_0 minimum-energy conical intersection (MECI) structure as calculated at the SA3-CASSCF(10,8) level using the *def2*-SVP, *def2*-TZVP and *def2*-TZVPP basis sets.

def2-SVP				*def2*-TZVP				*def2*-TZVPP			
E = -950.799775263637 a.u.				E = -951.238639924770 a.u.				E = -951.241641375358 a.u.			
S	0.3121873216	0.9003880758	-1.9469614918	S	0.3033388805	0.9121492253	-1.9488965330	C	-0.0439831038	-1.5874099261	-0.7777776528
S	-0.2707928223	0.9703930908	1.9026461453	S	-0.2688646253	0.9587721295	1.9244754568	C	0.0458777432	-1.6480602957	0.7499749633
C	0.7719431527	-0.4959670096	1.4536774248	C	0.7655887655	-0.4952665482	1.4519760420	C	-0.8514387396	-0.4105132316	-1.3747428914
C	-0.0636812264	-1.5889653202	-0.7702988377	C	-0.0445470551	-1.5866208329	-0.7784622378	H	-0.5199216072	-2.5036651576	-1.1037581984
C	0.0583219232	-1.6554084877	0.7561660846	C	0.0463412152	-1.6479166782	0.7491660548	H	0.9521242139	-1.6065573894	-1.2050397143
C	-0.8674612906	-0.3965564835	-1.3476842914	C	-0.8524213312	-0.4093330609	-1.3744444848	C	0.7651020009	-0.4952412608	1.4526987297
H	-0.5589364806	-2.5057946587	-1.0911183569	H	-0.5212090468	-2.5034472053	-1.1042804904	H	0.5835413171	-2.5605950987	0.9900264955
H	0.9281257119	-1.6223624574	-1.2279719960	H	0.9519902742	-1.6059578097	-1.2067730078	H	-0.9449409888	-1.7545903790	1.1742378324

H	0.6143510247	-2.5691962291	0.9843462100	H	0.5849656969	-2.5611245345	0.9882596912	S	0.3030784216	0.9122785492	-1.9487529586
H	-0.9293546742	-1.7776360229	1.2042608158	H	-0.9448557586	-1.7550547005	1.1744322519	H	-1.5772041426	-0.0418404483	-0.6694860315
H	-1.5877690075	-0.0263272540	-0.6238990107	H	-1.5782367201	-0.0407228925	-0.6679359130	H	-1.3468397289	-0.7499056791	-2.2732955155
H	-1.3767958032	-0.7327021749	-2.2500426358	H	-1.3483564441	-0.7490849786	-2.2735155956	S	-0.2688452482	0.9594692834	1.9234804171
H	1.6445080560	-0.1471147050	0.8964863460	H	1.6173475220	-0.1359036764	0.8862959446	H	1.6164643230	-0.1363610333	0.8877523073
H	1.1513120721	-0.8267863311	2.4228531866	H	1.1551666532	-0.8343925226	2.4054980131	H	1.1541511730	-0.8335847110	2.4057737192

LIIC Pathways

An approximate pathway (Fig. S2) between the S_0 minimum-energy structure/Franck-Condon point and S_1/S_0 MECI was computed at the SA3-CASSCF(10,8)/*def*2-SV(P) level *via* linear interpolation in internal coordinates (LIIC). At each of fifteen linearly-interpolated points, a single-point (SP) energy calculation was carried out at the SA3-CASSCF(10,8)/*def*2-SV(P) level, followed by a level-shifted[3] (0.3 a.u.) extended multi-state CASPT2 (LS-XMS-CASPT2)[4] SP energy calculation to correct for the absence of dynamic correlation under the CASSCF approximation. The fourteen lowest-energy (1s) orbitals were not correlated in our LS-XMS-CASPT2 calculations. The correct ordering of electronic excited states was reproduced in both calculations, as were the general forms of the electronic excited state surfaces. The magnitude of the correction for dynamic correlation at the LS-XMS-CASPT2 level is greater around the Franck-Condon point than in the vicinity of the S_1/S_0 MECI and S_1/S_0 coupling region (CR). The SA3-CASSCF(10,8)/*def*2-SV(P) level was concluded to be suitable for our subsequent NAMMD simulations.

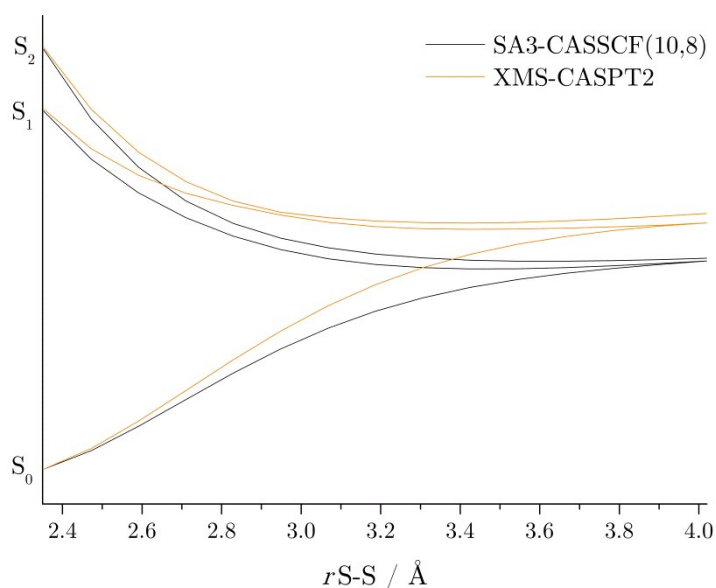Fission of the disulfide bond is confirmed to be without barrier in the S_1 and S_2 states.

Figure S2: LIIC pathways between the S_0 minimum-energy structure/Franck-Condon point and the S_1/S_0 MECI for the S_0, S_1 and S_2 states. The results of calculations at the SA3-CASSCF(10,8)/*def*2-SV(P) and LS-XMS-CASPT2/*def*2-SV(P) level are included.
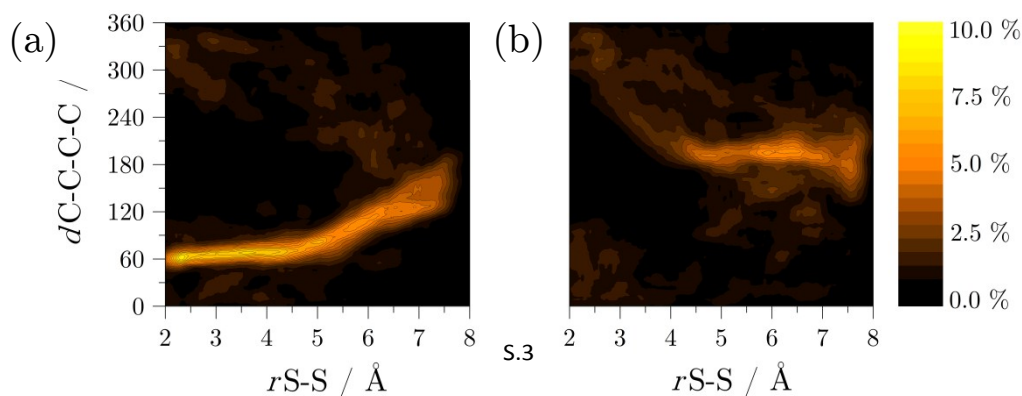

S.3

Figure S3: A heat-density map of the percentage of NAMMD trajectories visiting a given segment of phase space during a) the ring-opening and b) the ring-closing half-periods of our motion. The phase space is sampled to a slightly greater extent during the ring-closing half-periods than during the ring-opening half-periods, a consequence of both a phase shift in the evolution of the rS-S and dC-C-C-C internal coordinates expressed as a function of time and of intramolecular vibrational relaxation (IVR).

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