

The lowest triplet states of bridged
cis-2,2'-bithiophenes
- theory vs. experiment

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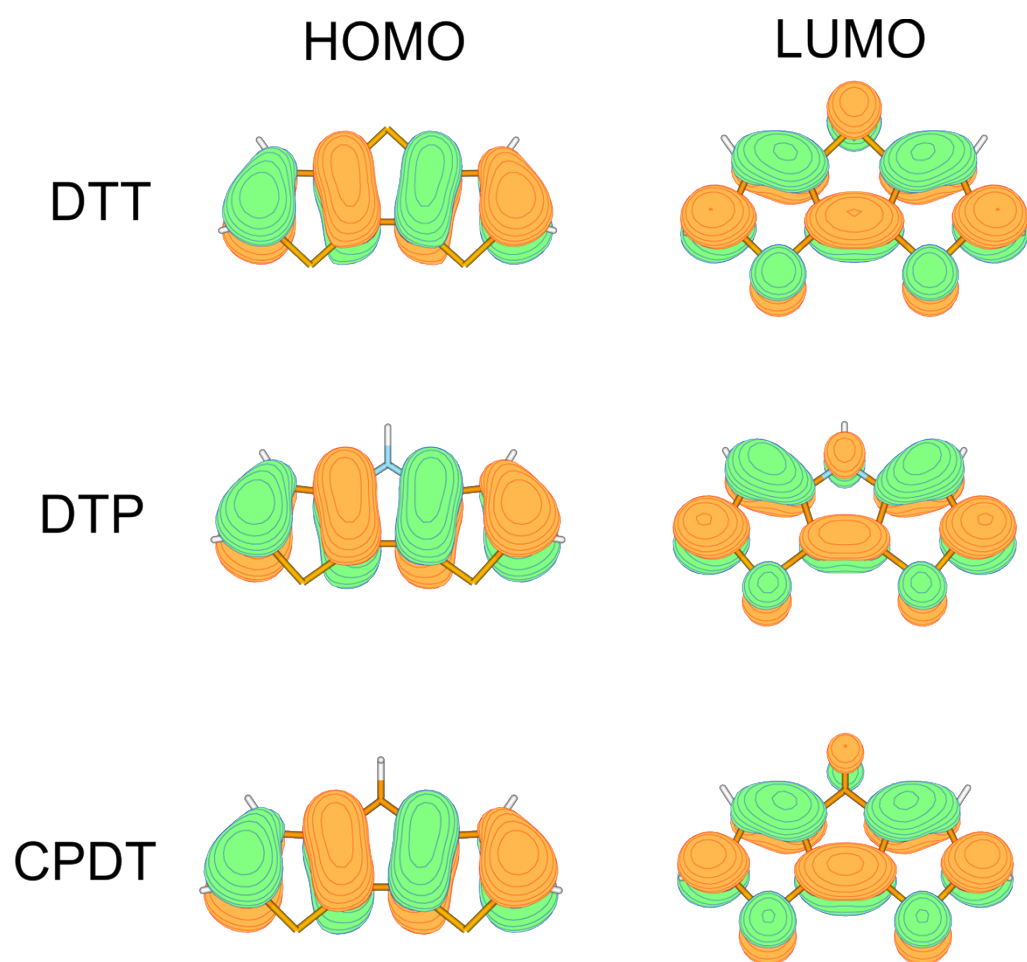


Figure 1S. HOMO and LUMO π -orbitals of the studied bridged bithiophenes.

Table S1. Total populations of delocalized π -electrons calculated by means of the EDDB approach for selected exchange-correlation functionals, using the def2-TZVPP basis set. The molecular geometries were taken from the CC2/aug-cc-pVQZ calculations.

State	Molecule	Terminal ring			Central ring		
		PBE	B3LYP	CAM-B3LYP	PBE	B3LYP	CAM-B3LYP
X^1A_1	<i>cis</i> -2T	1.986	1.836	1.710			
	CPDT	1.960	1.826	1.710	0.454	0.383	0.300
	DTP	1.788	1.675	1.559	1.761	1.643	1.489
	DTT	1.723	1.601	1.486	1.345	1.218	1.063
1^3B_1	<i>cis</i> -2T	1.380	1.312	1.248			
	CPDT	1.400	1.330	1.261	0.484	0.390	0.306
	DTP	1.147	1.052	0.962	1.058	0.937	0.803
	DTT	1.251	1.177	1.113	0.848	0.718	0.599

All DFT calculations have been done using GAMESS package of programs:
M.W.Schmidt, K.K.Baldrige, J.A.Boatz, S.T.Elbert, M.S.Gordon, J.H.Jensen, S.Koseki,
N.Matsunaga, K.A.Nguyen, S.Su, T.L.Windus, M.Dupuis, J.A.Montgomery
J. Comput. Chem., 14, 1347-1363(1993).

Table S2: Ground state and the lowest (T1) triplet state geometries of DTT obtained in the CC2 and CASPT2 calculations with the selected basis sets:

CC2/aug-cc-pVDZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	-0.7127600	0.0000000	-0.6386027	-0.6844117	0.0000000	-0.6491636
C	0.7127600	0.0000000	-0.6386027	0.6844117	0.0000000	-0.6491636
S	-1.9769797	0.0000000	-1.8360270	-1.9572874	0.0000000	-1.8803730
S	1.9769797	0.0000000	-1.8360270	1.9572874	0.0000000	-1.8803730
C	-3.2066721	0.0000000	-0.5834573	-3.1930168	0.0000000	-0.6071000
C	3.2066721	0.0000000	-0.5834573	3.1930168	0.0000000	-0.6071000
C	-2.6777470	0.0000000	0.7025890	-2.6443552	0.0000000	0.7200749
C	2.6777470	0.0000000	0.7025890	2.6443552	0.0000000	0.7200749
C	-1.2504640	0.0000000	0.6708246	-1.2619858	0.0000000	0.7067415
C	1.2504640	0.0000000	0.6708246	1.2619858	0.0000000	0.7067415
S	0.0000000	0.0000000	1.9144648	0.0000000	0.0000000	1.9720624
H	-3.2946879	0.0000000	1.6036218	-3.2766410	0.0000000	1.6108912
H	3.2946879	0.0000000	1.6036218	3.2766410	0.0000000	1.6108912
H	-4.2581384	0.0000000	-0.8761807	-4.2477174	0.0000000	-0.8871023
H	4.2581384	0.0000000	-0.8761807	4.2477174	0.0000000	-0.8871023

CC2/aug-cc-pVTZ

	Ground State			Triplet state (T1)		
	X	y	z	x	y	Z
C	-0.7073411	0.0000000	-0.6355379	-0.6779884	0.0000000	-0.6448466
C	0.7073411	0.0000000	-0.6355379	0.6779884	0.0000000	-0.6448466
S	-1.9622901	0.0000000	-1.8154292	-1.9412141	0.0000000	-1.8610205
S	1.9622901	0.0000000	-1.8154292	1.9412141	0.0000000	-1.8610205
C	-3.1788890	0.0000000	-0.5778464	-3.1627279	0.0000000	-0.6028714
C	3.1788890	0.0000000	-0.5778464	3.1627279	0.0000000	-0.6028714
C	-2.6551770	0.0000000	0.6957814	-2.6201909	0.0000000	0.7138003
C	2.6551770	0.0000000	0.6957814	2.6201909	0.0000000	0.7138003
C	-1.2400161	0.0000000	0.6635465	-1.2513544	0.0000000	0.7008548
C	1.2400161	0.0000000	0.6635465	1.2513544	0.0000000	0.7008548
S	0.0000000	0.0000000	1.8907902	0.0000000	0.0000000	1.9505066
H	-3.2622747	0.0000000	1.5896004	-3.2439146	0.0000000	1.5966435
H	3.2622747	0.0000000	1.5896004	3.2439146	0.0000000	1.5966435
H	-4.2190870	0.0000000	-0.8655098	-4.2060228	0.0000000	-0.8778135
H	4.2190870	0.0000000	-0.8655098	4.2060228	0.0000000	-0.8778135

CC2/aug-cc-pVQZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	-0.7068243	0.0000000	-0.6359223	-0.6772816	0.0000000	-0.6447892
C	0.7068243	0.0000000	-0.6359223	0.6772816	0.0000000	-0.6447892
S	-1.9593705	0.0000000	-1.8092523	-1.9380417	0.0000000	-1.8550094
S	1.9593705	0.0000000	-1.8092523	1.9380417	0.0000000	-1.8550094
C	-3.1717405	0.0000000	-0.5777225	-3.1549680	0.0000000	-0.6030379
C	3.1717405	0.0000000	-0.5777225	3.1549680	0.0000000	-0.6030379
C	-2.6504994	0.0000000	0.6948048	-2.6152113	0.0000000	0.7128430
C	2.6504994	0.0000000	0.6948048	2.6152113	0.0000000	0.7128430
C	-1.2370857	0.0000000	0.6628383	-1.2482977	0.0000000	0.7004798
C	1.2370857	0.0000000	0.6628383	1.2482977	0.0000000	0.7004798
S	0.0000000	0.0000000	1.8841743	0.0000000	0.0000000	1.9442262
H	-3.2578175	0.0000000	1.5874085	-3.2393477	0.0000000	1.5942706
H	3.2578175	0.0000000	1.5874085	3.2393477	0.0000000	1.5942706
H	-4.2113900	0.0000000	-0.8642418	-4.1976015	0.0000000	-0.8768700
H	4.2113900	0.0000000	-0.8642418	4.1976015	0.0000000	-0.8768700

CASPT2/aug-cc-pVDZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.7136255	0.0000000	-0.3835927	0.6867350	0.0000000	-0.3945098
C	-0.7136255	0.0000000	-0.3835927	-0.6867350	0.0000000	-0.3945098
S	1.9719845	0.0000000	-1.5819141	1.9542653	0.0000000	-1.6270414
S	-1.9719845	0.0000000	-1.5819141	-1.9542653	0.0000000	-1.6270414
C	3.1990547	0.0000000	-0.3325500	3.1837509	0.0000000	-0.3553392
C	-3.1990547	0.0000000	-0.3325500	-3.1837509	0.0000000	-0.3553392
C	2.6761136	0.0000000	0.9494787	2.6399164	0.0000000	0.9664119
C	-2.6761136	0.0000000	0.9494787	-2.6399164	0.0000000	0.9664119
C	1.2465096	0.0000000	0.9183673	1.2555399	0.0000000	0.9510616
C	-1.2465096	0.0000000	0.9183673	-1.2555399	0.0000000	0.9510616
S	0.0000000	0.0000000	2.1594470	0.0000000	0.0000000	2.2156959
H	3.2910713	0.0000000	1.8500722	3.2680461	0.0000000	1.8581933
H	-3.2910713	0.0000000	1.8500722	-3.2680461	0.0000000	1.8581933
H	4.2493234	0.0000000	-0.6248218	4.2376262	0.0000000	-0.6318616
H	-4.2493234	0.0000000	-0.6248218	-4.2376262	0.0000000	-0.6318616

CASPT2/aug-cc-pVTZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.7082923	0.0000000	-0.3827743	0.6805557	0.0000000	-0.3897570
C	-0.7082923	0.0000000	-0.3827743	-0.6805557	0.0000000	-0.3897570
S	1.9577838	0.0000000	-1.5637152	1.9372577	0.0000000	-1.6070136
S	-1.9577838	0.0000000	-1.5637152	-1.9372577	0.0000000	-1.6070136
C	3.1716639	0.0000000	-0.3287424	3.1539086	0.0000000	-0.3509628
C	-3.1716639	0.0000000	-0.3287424	-3.1539086	0.0000000	-0.3509628
C	2.6535886	0.0000000	0.9406375	2.6162095	0.0000000	0.9600888
C	-2.6535886	0.0000000	0.9406375	-2.6162095	0.0000000	0.9600888
C	1.2361485	0.0000000	0.9087521	1.2450980	0.0000000	0.9449977
C	-1.2361485	0.0000000	0.9087521	-1.2450980	0.0000000	0.9449977
S	0.0000000	0.0000000	2.1338521	0.0000000	0.0000000	2.1941052
H	3.2586618	0.0000000	1.8340181	3.2356762	0.0000000	1.8438289
H	-3.2586618	0.0000000	1.8340181	-3.2356762	0.0000000	1.8438289
H	4.2104142	0.0000000	-0.6167738	4.1959939	0.0000000	-0.6234715
H	-4.2104142	0.0000000	-0.6167738	-4.1959939	0.0000000	-0.6234715

Table S3: Ground state and the lowest (T1) triplet state geometries of DTP obtained in the CC2 and CASPT2 calculations with the selected basis sets:

CC2/aug-cc-pVDZ						
	Ground State			Planar Triplet state (T1)		
	x	y	z	x	y	Z
C	-0.7129425	0.0000000	-0.9262563	-0.6870171	0.0000000	-0.9269425
C	0.7129425	0.0000000	-0.9262563	0.6870171	0.0000000	-0.9269425
S	-2.0867799	0.0000000	-1.9953361	-2.0572785	0.0000000	-2.0394885
S	2.0867799	0.0000000	-1.9953361	2.0572785	0.0000000	-2.0394885
C	-3.1880779	0.0000000	-0.6247342	-3.1770665	0.0000000	-0.6581831
C	3.1880779	0.0000000	-0.6247342	3.1770665	0.0000000	-0.6581831
C	-2.5439110	0.0000000	0.6096434	-2.5130437	0.0000000	0.6292117
C	2.5439110	0.0000000	0.6096434	2.5130437	0.0000000	0.6292117
C	-1.1287572	0.0000000	0.4336244	-1.1412562	0.0000000	0.4746144
C	1.1287572	0.0000000	0.4336244	1.1412562	0.0000000	0.4746144
N	0.0000000	0.0000000	1.2498891	0.0000000	0.0000000	1.2895978
H	0.0000000	0.0000000	2.2630279	0.0000000	0.0000000	2.3023770
H	-3.0781915	0.0000000	1.5620621	-3.0639238	0.0000000	1.5719370
H	3.0781915	0.0000000	1.5620621	3.0639238	0.0000000	1.5719370
H	-4.2625605	0.0000000	-0.8154618	-4.2513804	0.0000000	-0.8471365
H	4.2625605	0.0000000	-0.8154618	4.2513804	0.0000000	-0.8471365

CC2/aug-cc-pVDZ, cont.			
	Distorted Triplet state (T1)		
	x	y	Z
C	-0.6867213	-0.1311816	-0.9196702
C	0.6867213	-0.1311816	-0.9196702
S	-2.0577979	-0.1668179	-2.0296514
S	2.0577979	-0.1668179	-2.0296514
C	-3.1731732	-0.0099286	-0.6518602
C	3.1731732	-0.0099286	-0.6518602
C	-2.5072283	0.0372184	0.6299335
C	2.5072283	0.0372184	0.6299335
C	-1.1373613	-0.0302409	0.4792309
C	1.1373613	-0.0302409	0.4792309
N	0.0000000	-0.0783289	1.3237480
H	0.0000000	0.4439459	2.1972823
H	-3.0556946	0.1106096	1.5714102
H	3.0556946	0.1106096	1.5714102
H	-4.2475975	0.0070164	-0.8399022
H	4.2475975	0.0070164	-0.8399022

CC2/aug-cc-pVTZ

	Ground State			Triplet state (T1)		
	X	y	z	x	y	Z
C	-0.7079726	0.0000000	-0.9208997	-0.6807296	0.0000000	-0.9203996
C	0.7079726	0.0000000	-0.9208997	0.6807296	0.0000000	-0.9203996
S	-2.0702102	0.0000000	-1.9734240	-2.0396599	0.0000000	-2.0189519
S	2.0702102	0.0000000	-1.9734240	2.0396599	0.0000000	-2.0189519
C	-3.1604381	0.0000000	-0.6196455	-3.1471993	0.0000000	-0.6547228
C	3.1604381	0.0000000	-0.6196455	3.1471993	0.0000000	-0.6547228
C	-2.5218514	0.0000000	0.6029642	-2.4902909	0.0000000	0.6228837
C	2.5218514	0.0000000	0.6029642	2.4902909	0.0000000	0.6228837
C	-1.1197813	0.0000000	0.4277440	-1.1324707	0.0000000	0.4708083
C	1.1197813	0.0000000	0.4277440	1.1324707	0.0000000	0.4708083
N	0.0000000	0.0000000	1.2392694	0.0000000	0.0000000	1.2805232
H	0.0000000	0.0000000	2.2455129	0.0000000	0.0000000	2.2864350
H	-3.0471961	0.0000000	1.5473963	-3.0338719	0.0000000	1.5566475
H	3.0471961	0.0000000	1.5473963	3.0338719	0.0000000	1.5566475
H	-4.2232225	0.0000000	-0.8065264	-4.2096167	0.0000000	-0.8397442
H	4.2232225	0.0000000	-0.8065264	4.2096167	0.0000000	-0.8397442

CC2/aug-cc-pVTZ, cont.

	Distorted Triplet state (T1)		
	x	y	Z
C	-0.6805335	-0.2046637	-0.8990811
C	0.6805335	-0.2046637	-0.8990811
S	-2.0396584	-0.3345397	-1.9888739
S	2.0396584	-0.3345397	-1.9888739
C	-3.1439752	-0.0678464	-0.6469381
C	3.1439752	-0.0678464	-0.6469381
C	-2.4859048	0.0931766	0.6171878
C	2.4859048	0.0931766	0.6171878
C	-1.1298394	0.0134265	0.4755039
C	1.1298394	0.0134265	0.4755039
N	0.0000000	0.0512526	1.3060432
H	0.0000000	0.5785295	2.1666135
H	-3.0278892	0.2490723	1.5389238
H	3.0278892	0.2490723	1.5389238
H	-4.2062295	-0.0630911	-0.8331085
H	4.2062295	-0.0630911	-0.8331085

CC2/aug-cc-pVQZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	-0.7075908	0.0000000	-0.9193688	-0.6799979	0.0000000	-0.9185595
C	0.7075908	0.0000000	-0.9193688	0.6799979	0.0000000	-0.9185595
S	-2.0658471	0.0000000	-1.9667424	-2.0351787	0.0000000	-2.0125898
S	2.0658471	0.0000000	-1.9667424	2.0351787	0.0000000	-2.0125898
C	-3.1536928	0.0000000	-0.6207812	-3.1397696	0.0000000	-0.6561330
C	3.1536928	0.0000000	-0.6207812	3.1397696	0.0000000	-0.6561330
C	-2.5184191	0.0000000	0.6014698	-2.4866892	0.0000000	0.6213548
C	2.5184191	0.0000000	0.6014698	2.4866892	0.0000000	0.6213548
C	-1.1180782	0.0000000	0.4279042	-1.1307234	0.0000000	0.4713791
C	1.1180782	0.0000000	0.4279042	1.1307234	0.0000000	0.4713791
N	0.0000000	0.0000000	1.2384709	0.0000000	0.0000000	1.2800725
H	0.0000000	0.0000000	2.2435554	0.0000000	0.0000000	2.2848285
H	-3.0450406	0.0000000	1.5440440	-3.0319389	0.0000000	1.5530038
H	3.0450406	0.0000000	1.5440440	3.0319389	0.0000000	1.5530038
H	-4.2155572	0.0000000	-0.8075388	-4.2012788	0.0000000	-0.8409058
H	4.2155572	0.0000000	-0.8075388	4.2012788	0.0000000	-0.8409058

CC2/aug-cc-pVQZ, cont.

	Distorted Triplet state (T1)		
	x	y	Z
C	-0.6798194	-0.0928573	-0.9154917
C	0.6798194	-0.0928573	-0.9154917
S	-2.0352667	-0.0947697	-2.0085289
S	2.0352667	-0.0947697	-2.0085289
C	-3.1370056	0.0061751	-0.6522738
C	3.1370056	0.0061751	-0.6522738
C	-2.4827840	0.0190399	0.6222226
C	2.4827840	0.0190399	0.6222226
C	-1.1283556	-0.0390590	0.4738704
C	1.1283556	-0.0390590	0.4738704
N	0.0000000	-0.0936761	1.2998040
H	0.0000000	0.3032310	2.2259740
H	-3.0264933	0.0639816	1.5538151
H	3.0264933	0.0639816	1.5538151
H	-4.1983221	0.0327119	-0.8365027
H	4.1983221	0.0327119	-0.8365027

CASPT2/aug-cc-pVDZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.7132880	0.0000000	-0.2967276	0.6882534	0.0000000	-0.2971766
C	-0.7132880	0.0000000	-0.2967276	-0.6882534	0.0000000	-0.2971766
S	2.0843678	0.0000000	-1.3668975	2.0553539	0.0000000	-1.4100583
S	-2.0843678	0.0000000	-1.3668975	-2.0553539	0.0000000	-1.4100583
C	3.1811368	0.0000000	0.0023222	3.1689974	0.0000000	-0.0305408
C	-3.1811368	0.0000000	0.0023222	-3.1689974	0.0000000	-0.0305408
C	2.5428272	0.0000000	1.2326414	2.5102590	0.0000000	1.2507462
C	-2.5428272	0.0000000	1.2326414	-2.5102590	0.0000000	1.2507462
C	1.1245806	0.0000000	1.0560107	1.1355305	0.0000000	1.0951469
C	-1.1245806	0.0000000	1.0560107	-1.1355305	0.0000000	1.0951469
N	0.0000000	0.0000000	1.8709750	0.0000000	0.0000000	1.9105764
H	0.0000000	0.0000000	2.8816528	0.0000000	0.0000000	2.9204396
H	3.0749358	0.0000000	2.1846960	3.0568696	0.0000000	2.1941146
H	-3.0749358	0.0000000	2.1846960	-3.0568696	0.0000000	2.1941146
H	4.2546069	0.0000000	-0.1867662	4.2422345	0.0000000	-0.2161471
H	-4.2546069	0.0000000	-0.1867662	-4.2422345	0.0000000	-0.2161471

CASPT2/aug-cc-pVDZ, cont.

	Distorted Triplet state (T1)		
	x	y	Z
C	-0.6883959	-0.0450545	-0.2579216
C	0.6883959	-0.0450545	-0.2579216
S	-2.0624987	0.0169432	-1.3630072
S	2.0624987	0.0169432	-1.3630072
C	-3.1694422	0.0418455	0.0249601
C	3.1694422	0.0418455	0.0249601
C	-2.5044658	-0.0225200	1.2956943
C	2.5044658	-0.0225200	1.2956943
C	-1.1322836	-0.0699283	1.1351662
C	1.1322836	-0.0699283	1.1351662
N	0.0000000	-0.1873259	1.9766153
H	0.0000000	0.2835243	2.8764754
H	-3.0452947	-0.0364863	2.2425344
H	3.0452947	-0.0364863	2.2425344
H	-4.2431965	0.0765884	-0.1544189
H	4.2431965	0.0765884	-0.1544189

CASPT2/aug-cc-pVTZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.7082291	0.0000000	-0.2912907	0.6823606	0.0000000	-0.2903630
C	-0.7082291	0.0000000	-0.2912907	-0.6823606	0.0000000	-0.2903630
S	2.0679911	0.0000000	-1.3451909	2.0374876	0.0000000	-1.3891546
S	-2.0679911	0.0000000	-1.3451909	-2.0374876	0.0000000	-1.3891546
C	3.1536084	0.0000000	0.0075641	3.1391702	0.0000000	-0.0267373
C	-3.1536084	0.0000000	0.0075641	-3.1391702	0.0000000	-0.0267373
C	2.5208129	0.0000000	1.2260820	2.4875293	0.0000000	1.2445850
C	-2.5208129	0.0000000	1.2260820	-2.4875293	0.0000000	1.2445850
C	1.1155530	0.0000000	1.0499467	1.1265564	0.0000000	1.0907476
C	-1.1155530	0.0000000	1.0499467	-1.1265564	0.0000000	1.0907476
N	0.0000000	0.0000000	1.8600974	0.0000000	0.0000000	1.9008509
H	0.0000000	0.0000000	2.8638316	0.0000000	0.0000000	2.9037283
H	3.0436704	0.0000000	2.1701930	3.0268023	0.0000000	2.1789277
H	-3.0436704	0.0000000	2.1701930	-3.0268023	0.0000000	2.1789277
H	4.2153316	0.0000000	-0.1776758	4.2004287	0.0000000	-0.2087021
H	-4.2153316	0.0000000	-0.1776758	-4.2004287	0.0000000	-0.2087021

CASPT2/aug-cc-pVTZ, cont.

	Distorted Triplet state (T1)		
	x	y	Z
C	-0.6824707	-0.0462897	-0.2503472
C	0.6824707	-0.0462897	-0.2503472
S	-2.0428961	0.0094271	-1.3430707
S	2.0428961	0.0094271	-1.3430707
C	-3.1393905	0.0387245	0.0255024
C	3.1393905	0.0387245	0.0255024
C	-2.4829261	-0.0147227	1.2888756
C	2.4829261	-0.0147227	1.2888756
C	-1.1245026	-0.0648680	1.1312044
C	1.1245026	-0.0648680	1.1312044
N	0.0000000	-0.1628856	1.9588684
H	0.0000000	0.2255695	2.8875952
H	-3.0173326	-0.0197113	2.2260898
H	3.0173326	-0.0197113	2.2260898
H	-4.2007815	0.0755853	-0.1519335
H	4.2007815	0.0755853	-0.1519335

Table S4 Ground state and the lowest (T1) triplet state geometries of CPDT obtained in the CC2 and CASPT2 calculations with the selected basis sets:

CC2/aug-cc-pVDZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.0000000	0.7243395	-0.9533241	0.0000000	0.6869449	-0.9899744
C	0.0000000	-0.7243395	-0.9533241	0.0000000	-0.6869449	-0.9899744
S	0.0000000	2.0253461	-2.0959317	0.0000000	2.0137157	-2.1532555
S	0.0000000	-2.0253461	-2.0959317	0.0000000	-2.0137157	-2.1532555
C	0.0000000	3.2016973	-0.7955375	0.0000000	3.1813168	-0.8111170
C	0.0000000	-3.2016973	-0.7955375	0.0000000	-3.1813168	-0.8111170
C	0.0000000	2.6029756	0.4664126	0.0000000	2.5625884	0.4757759
C	0.0000000	-2.6029756	0.4664126	0.0000000	-2.5625884	0.4757759
C	0.0000000	1.1827855	0.3784704	0.0000000	1.1786005	0.4064697
C	0.0000000	-1.1827855	0.3784704	0.0000000	-1.1786005	0.4064697
C	0.0000000	0.0000000	1.3345807	0.0000000	0.0000000	1.3747834
H	0.8924825	0.0000000	1.9852575	0.8915117	0.0000000	2.0285372
H	-0.8924825	0.0000000	1.9852575	-0.8915117	0.0000000	2.0285372
H	0.0000000	3.1851885	1.3913208	0.0000000	3.1553345	1.3945999
H	0.0000000	-3.1851885	1.3913208	0.0000000	-3.1553345	1.3945999
H	0.0000000	4.2643693	-1.0439583	0.0000000	4.2489339	-1.0384274
H	0.0000000	-4.2643693	-1.0439583	0.0000000	-4.2489339	-1.0384274

CC2/aug-cc-pVTZ

	Ground State			Triplet state (T1)		
	X	y	z	x	y	Z
C	0.0000000	0.7193135	-0.9470495	0.0000000	0.6805745	-0.9820594
C	0.0000000	-0.7193135	-0.9470495	0.0000000	-0.6805745	-0.9820594
S	0.0000000	2.0093557	-2.0726822	0.0000000	1.9952040	-2.1315553
S	0.0000000	-2.0093557	-2.0726822	0.0000000	-1.9952040	-2.1315553
C	0.0000000	3.1741780	-0.7891826	0.0000000	3.1514867	-0.8062678
C	0.0000000	-3.1741780	-0.7891826	0.0000000	-3.1514867	-0.8062678
C	0.0000000	2.5812502	0.4609751	0.0000000	2.5402645	0.4705394
C	0.0000000	-2.5812502	0.4609751	0.0000000	-2.5402645	0.4705394
C	0.0000000	1.1742384	0.3732623	0.0000000	1.1704094	0.4034434
C	0.0000000	-1.1742384	0.3732623	0.0000000	-1.1704094	0.4034434
C	0.0000000	0.0000000	1.3221960	0.0000000	0.0000000	1.3643529
H	0.8826713	0.0000000	1.9679959	0.8818023	0.0000000	2.0126890
H	-0.8826713	0.0000000	1.9679959	-0.8818023	0.0000000	2.0126890
H	0.0000000	3.1542017	1.3783341	0.0000000	3.1257244	1.3805733
H	0.0000000	-3.1542017	1.3783341	0.0000000	-3.1257244	1.3805733
H	0.0000000	4.2255301	-1.0327510	0.0000000	4.2074145	-1.0295391
H	0.0000000	-4.2255301	-1.0327510	0.0000000	-4.2074145	-1.0295391

CC2/aug-cc-pVQZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.0000000	0.7187912	-0.9457304	-0.0000000	0.6797995	-0.2740981
C	0.0000000	-0.7187912	-0.9457304	-0.0000000	-0.6797995	-0.2740981
S	0.0000000	2.0052527	-2.0659611	-0.0000000	1.9903537	-1.4384916
S	0.0000000	-2.0052527	-2.0659611	-0.0000000	-1.9903537	-1.4384916
C	0.0000000	3.1672777	-0.7901865	-0.0000000	3.1439663	-0.1000945
C	0.0000000	-3.1672777	-0.7901865	-0.0000000	-3.1439663	-0.1000945
C	0.0000000	2.5776351	0.4595070	-0.0000000	2.5366917	1.1822222
C	0.0000000	-2.5776351	0.4595070	-0.0000000	-2.5366917	1.1822222
C	0.0000000	1.1726251	0.3730668	-0.0000000	1.1689111	1.1099617
C	0.0000000	-1.1726251	0.3730668	-0.0000000	-1.1689111	1.1099617
C	0.0000000	0.0000000	1.3214884	0.0000000	0.0000000	2.0807561
H	0.8815202	0.0000000	1.9667258	0.8806564	0.0000000	2.7359982
H	-0.8815202	0.0000000	1.9667258	-0.8806564	0.0000000	2.7359982
H	0.0000000	3.1514793	1.3750994	-0.0000000	3.1235532	2.1016337
H	0.0000000	-3.1514793	1.3750994	-0.0000000	-3.1235532	2.1016337
H	0.0000000	4.2177353	-1.0332652	-0.0000000	4.1989087	-0.3261412
H	0.0000000	-4.2177353	-1.0332652	-0.0000000	-4.1989087	-0.3261412

CASPT2/aug-cc-pVDZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.0000000	0.7261309	-0.2391675	0.0000000	0.6899651	-0.2740981
C	0.0000000	-0.7261309	-0.2391675	0.0000000	-0.6899651	-0.2740981
S	0.0000000	2.0216300	-1.3821729	0.0000000	2.0068737	-1.4384916
S	0.0000000	-2.0216300	-1.3821729	0.0000000	-2.0068737	-1.4384916
C	0.0000000	3.1946752	-0.0849054	0.0000000	3.1733925	-0.1000945
C	0.0000000	-3.1946752	-0.0849054	0.0000000	-3.1733925	-0.1000945
C	0.0000000	2.6024296	1.1731506	0.0000000	2.5622303	1.1822222
C	0.0000000	-2.6024296	1.1731506	0.0000000	-2.5622303	1.1822222
C	0.0000000	1.1803192	1.0842435	0.0000000	1.1758096	1.1099617
C	0.0000000	-1.1803192	1.0842435	0.0000000	-1.1758096	1.1099617
C	0.0000000	0.0000000	2.0424670	0.0000000	0.0000000	2.0807561
H	0.8914033	0.0000000	2.6937988	0.8899073	0.0000000	2.7359982
H	-0.8914033	0.0000000	2.6937988	-0.8899073	0.0000000	2.7359982
H	0.0000000	3.1825389	2.0976826	0.0000000	3.1511960	2.1016337
H	0.0000000	-3.1825389	2.0976826	0.0000000	-3.1511960	2.1016337
H	0.0000000	4.2562072	-0.3324945	0.0000000	4.2395696	-0.3261412
H	0.0000000	-4.2562072	-0.3324945	0.0000000	-4.2395696	-0.3261412

CASPT2/aug-cc-pVTZ

	Ground State			Triplet state (T1)		
	x	y	z	x	y	Z
C	0.0000000	0.7210727	-0.2319029	0.0000000	0.6840137	-0.2667559
C	0.0000000	-0.7210727	-0.2319029	0.0000000	-0.6840137	-0.2667559
S	0.0000000	2.0047267	-1.3588104	0.0000000	1.9885243	-1.4166593
S	0.0000000	-2.0047267	-1.3588104	0.0000000	-1.9885243	-1.4166593
C	0.0000000	3.1671568	-0.0792113	0.0000000	3.1435987	-0.0943017
C	0.0000000	-3.1671568	-0.0792113	0.0000000	-3.1435987	-0.0943017
C	0.0000000	2.5812459	1.1675264	0.0000000	2.5391555	1.1771298
C	0.0000000	-2.5812459	1.1675264	0.0000000	-2.5391555	1.1771298
C	0.0000000	1.1721867	1.0799426	0.0000000	1.1672980	1.1065162
C	0.0000000	-1.1721867	1.0799426	0.0000000	-1.1672980	1.1065162
C	0.0000000	0.0000000	2.0311770	0.0000000	0.0000000	2.0702124
H	0.8815087	0.0000000	2.6772223	0.8803088	0.0000000	2.7194450
H	-0.8815087	0.0000000	2.6772223	-0.8803088	0.0000000	2.7194450
H	0.0000000	3.1528241	2.0838900	0.0000000	3.1205692	2.0877612
H	0.0000000	-3.1528241	2.0838900	0.0000000	-3.1205692	2.0877612
H	0.0000000	4.2170793	-0.3228765	0.0000000	4.1979672	-0.3168732
H	0.0000000	-4.2170793	-0.3228765	0.0000000	-4.1979672	-0.3168732

Table S5

Angles between the NH bond and the CNC plane for the T1 state of DTP, as calculated using selected quantum chemistry methods and basis sets:

Method	Angle [deg]
CC2/aug-cc-pVDZ	34.135
CC2/aug-cc-pVTZ	28.888
CC2/aug-cc-pVQZ	26.989
CASPT2/aug-cc-pVDZ (76)	35.293
CASPT2/aug-cc-pVTZ (76)	30.259

Table S6 Huang-Rhys factors calculated at the CC2/aug-cc-pVDZ level of theory.

[illegible]

Table S8 Huang-Rhys factors calculated at the CASPT2 /aug-cc-pVDZ level of theory.

	CPDT		DTT		DTP pl.	
ν_1	1512	0.013	1514	1.050	1564	0.690
ν_2	1487	0.842	1483	0.034	1498	0.016
ν_3	1436	0.218	1408	0.068	1455	0.074
ν_4	1421	0.099	1334	0.244	1388	0.569
ν_5	1360	0.253	1198	0.003	1266	0.002
ν_6	1236	0.003	1094	0.074	1101	0.038
ν_7	1095	0.005	910	0.000	1047	0.125
ν_8	998	0.110	806	0.018	839	0.058
ν_9	838	0.072	660	0.226	732	0.005
ν_{10}	717	0.002	485	1.302	598	0.820
ν_{11}	602	1.338	445	0.064	480	0.095
ν_{12}	457	0.393	193	0.212	206	0.330
ν_{13}	199	0.073				
ν_{14}						
ν_{15}						
ν_{16}						
ν_{17}						
ν_{18}						
ν_{19}						

Table S9 Huang-Rhys factors calculated at the CASPT2 /aug-cc-pVTZ level of theory.

	CPDT		DTT		DTP pl.	
ν_1	1512	0.001	1512	0.987	1564	0.714
ν_2	1487	0.000	1482	0.103	1498	0.016
ν_3	1436	0.000	1410	0.041	1455	0.084
ν_4	1421	0.014	1336	0.293	1388	0.583
ν_5	1360	0.886	1206	0.006	1266	0.002
ν_6	1236	0.217	1103	0.084	1101	0.043
ν_7	1095	0.101	914	0.000	1047	0.123
ν_8	998	0.253	819	0.015	839	0.050
ν_9	838	0.004	663	0.231	732	0.004
ν_{10}	717	0.006	489	1.307	598	0.869
ν_{11}	602	0.109	448	0.114	480	0.100
ν_{12}	457	0.067	195	0.257	206	0.365
ν_{13}	199	0.002				
ν_{14}						
ν_{15}						
ν_{16}						
ν_{17}						
ν_{18}						
ν_{19}						