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

Supporting information for:

Theoretical Studies on Photo-induced Cycloaddition and (6-4) Reactions of Thymidine:4-Thiothymidine Dimer in a DNA Duplex

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1. Molecular orbitals for the $Tp^{4S}T$.

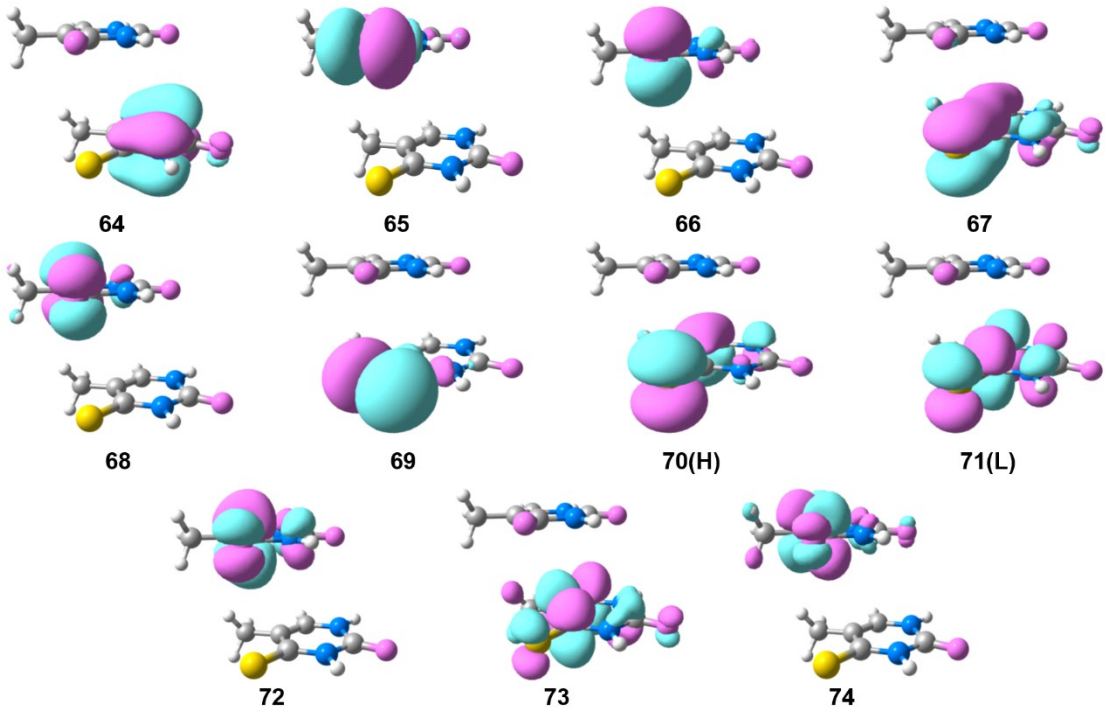

Figure S1. Molecular orbitals used as the active space of the QM(CASSCF)/MM and QM(MS-CASPT2)/MM computations for the $Tp^{4S}T$.

2. The choice of the active spaces.

We have made a comparison for the vertical and adiabatic excitation energies of the minimum and intersection structures of $Tp^{4S}T$ and S^5-thietane with two different active spaces, i.e., (14,11) and (16,12). We found that the increase of the active space to be (16,12) do not improve the calculations apparently. To balance computational accuracy and efficiency, we adopted an active space of 14 electrons in 11 orbitals.

Table S1 QM(MS-CASPT2//CASSCF)/MM computed vertical and adiabatic excitation energies (kcal/mol) of several minimum and intersection structures of $Tp^{4S}T$ and S^5-thietane with two different active spaces. Potential energies of S_0 minima of $Tp^{4S}T$ is taken as reference zero point.

$Tp^{4S}T$	
(14,11)	(16,12)

S_0	^{1}(Root 1) 0.00 ^{1}(Root 2) 72.60 ^{1}(Root 3) 93.20 ^{3}(Root 1) 70.27 ^{3}(Root 2) 70.43 ^{3}(Root 3) 96.36	S_0	^{1}(Root 1) 0.00 ^{1}(Root 2) 72.25 ^{1}(Root 3) 91.79 ^{3}(Root 1) 68.95 ^{3}(Root 2) 69.76 ^{3}(Root 3) 95.60
S_1	68.77	S_1	68.44
S_2	73.84	S_2	73.14
T_1	53.31	T_1	51.69
T_2	55.23	T_2	54.64
S_2/S_1	100.40/101.14	S_2/S_1	99.38/100.32
S_2/T_2	100.91/104.21/98.67/101.40	S_2/T_2	103.84/105.18/98.31/100.28

S^5-thietane

(14,11)		(16,12)	
S_0	13.55	S_0	12.87
T_{1cc}	60.42	T_{1cc}	59.82
T_{1cs}	56.30	T_{1cs}	55.70
T_{1cccs}	82.22	T_{1cccs}	81.70

3. The selection of different initial structures.

To make it clear that whether the selection of the initial structures could affect the results of our QM/MM calculations. We selected another initial condition at 0.9 ns and the corresponding QM/MM calculations were carried out to study the minimum and intersection structures of $Tp^{4S}T$. The calculated results were collected in Table S2, which was also appended in the third section of Supporting Information "the selection of different initial structures". It could be found that the selection of the initial structures does not apparently affect the computational results of $Tp^{4S}T$ and the order of the electronic states does not change. A similar result was obtained in our previous work, where the different initial conditions at 10.0, 15.0 and 20.0 ps were chosen to study the excited-state decay mechanism of 2,4-dithiothymine in the same surroundings (Phys. Chem. Chem. Phys., 2017, 19, 7689).

Table S2 QM(MS-CASPT2//CASSCF)/MM computed vertical and adiabatic excitation energies (kcal/mol) of several minimum and intersection structures of $Tp^{4S}T$ with two different initial conditions at 0.9 and 1.0 ns. Potential energies of S_0 minima is taken as reference zero point.

$Tp^{4S}T$	
1 ns	0.9 ns

S_0	^{1}(Root 1)	0.00	S_0	^{1}(Root 1)	0.00
	^{1}(Root 2)	72.60		^{1}(Root 2)	73.05
	^{1}(Root 3)	93.20		^{1}(Root 3)	95.04
	^{3}(Root 1)	70.27		^{3}(Root 1)	70.63
	^{3}(Root 2)	70.43		^{3}(Root 2)	71.42
	^{3}(Root 3)	96.36		^{3}(Root 3)	96.32
S_1	68.77		S_1	65.56	
S_2	73.84		S_2	76.06	
T_1	53.31		T_1	56.83	
T_2	55.23		T_2	59.65	
S_2/S_1	100.40/101.14		S_2/S_1	103.68/104.26	
S_1/T_2	68.95/65.27		S_1/T_2	63.94/61.30	

4. **The consideration of hydrogen bond interactions with explicit waters in QM region.**

After 1.0 ns equilibrium MD simulations, four waters were found to strongly interact with thymine and 4-thiothymine. The thymine:4-thiothymine dimer with four waters was set as the QM subsystem, while the remaining system, i.e., water environment, the nucleic acids and sodium ions, was viewed as the MM subsystem (see Figure S2). Based on this initial structure, an additional QM(MS-CASPT2//CASSCF(14,11))/MM calculations were carried out to explore the energies and structures of $Tp^{4S}T$ system. The final results are collected in Table S3 and Figure S3. It is clear that the vertical and adiabatic excitation energies are 1.0 ~ 2.0 kcal/mol lower than those of system without waters in QM region, which might result from the hydrogen bond interactions between thymine:4-thiothymine and waters. Moreover, the key bond parameters of the optimized structures have a little difference from those of system without waters in QM region.

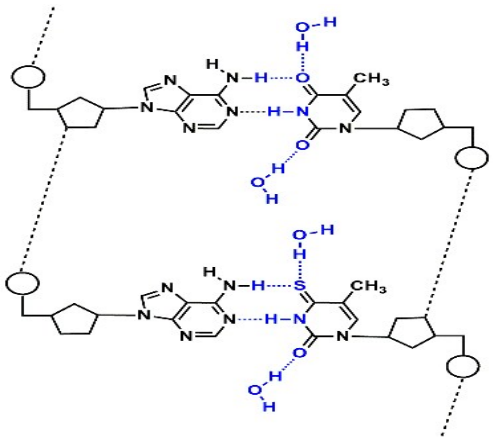

Figure S2. Part of the QM/MM model studied in this work; the hydrogen bonds were highlighted in blue. The thymine:4-thiothymine dimer with four waters was set as the QM region, while the remaining system (water environment, the nucleic acids and sodium ions) was viewed as the MM region.

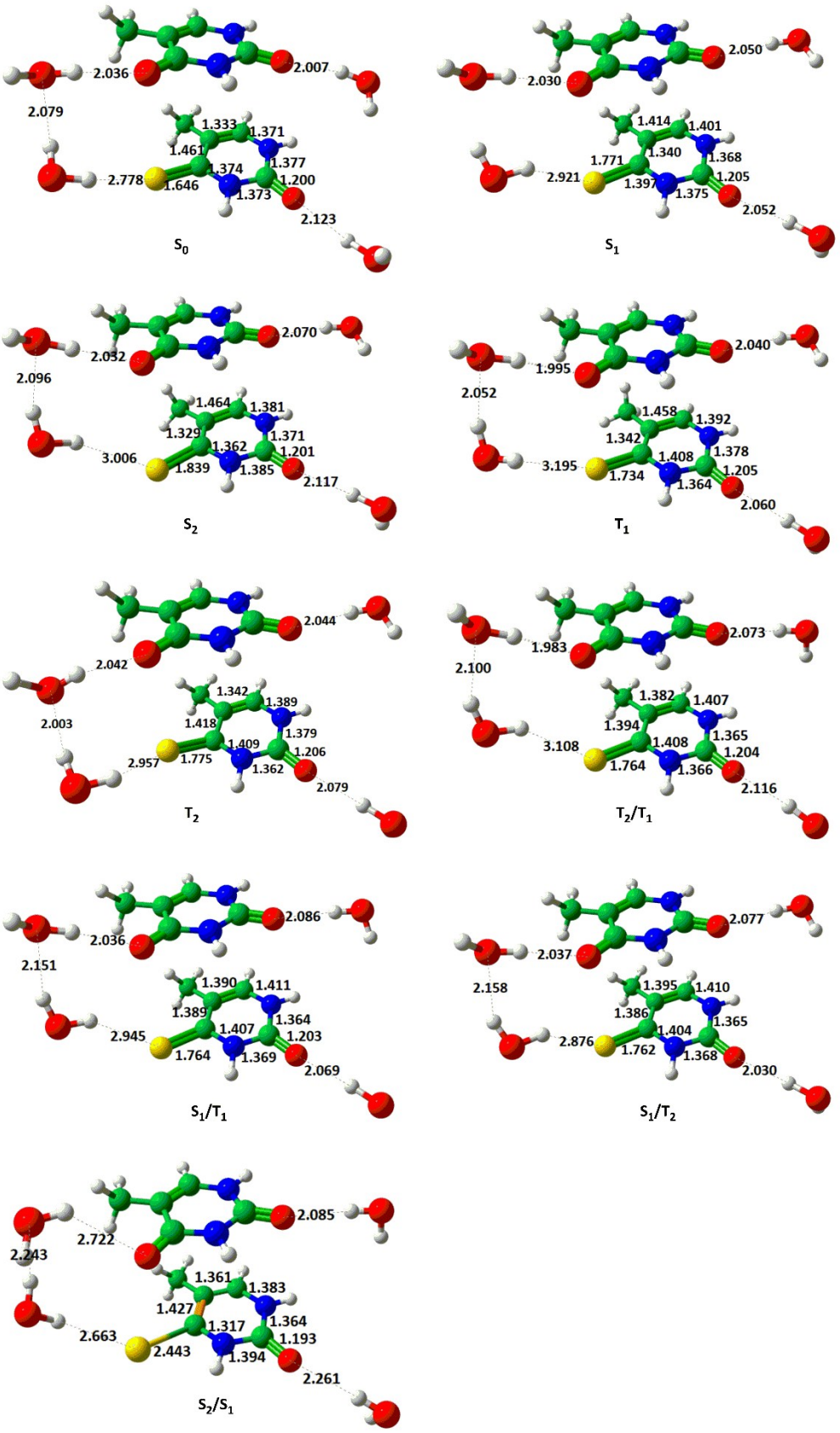

Figure S3. QM(CASSCF)/MM/6-31G* optimized several minimum and intersection structures of Tp^{4S}T with four waters in QM region. Also shown are the selected bond lengths.

Table S3 QM(MS-CASPT2//CASSCF)/MM computed vertical and adiabatic excitation energies (kcal/mol) of several minimum and intersection structures of $Tp^{4S}T$ with four waters in QM region. Potential energies of S_0 minima is taken as reference zero point

$Tp^{4S}T$					
no water in QM region			four waters in QM region		
S_0	^{1}(Root 1)	0.00	S_0	^{1}(Root 1)	0.00
	^{1}(Root 2)	72.60		^{1}(Root 2)	70.86
	^{1}(Root 3)	93.20		^{1}(Root 3)	90.21
	^{3}(Root 1)	70.27		^{3}(Root 1)	68.44
	^{3}(Root 2)	70.43		^{3}(Root 2)	69.06
	^{3}(Root 3)	96.36		^{3}(Root 3)	97.15
S_1	68.77		S_1	67.82	
S_2	73.84		S_2	71.05	
T_1	53.31		T_1	53.09	
T_2	55.23		T_2	55.32	
T_1/T_2	52.85/53.12		T_1/T_2	52.55/52.75	
S_2/S_1	100.40/101.14		S_2/S_1	99.31/100.29	
S_1/T_1	56.19/54.56		S_1/T_1	53.49/50.91	
S_1/T_2	68.95/65.27		S_1/T_2	67.11/65.38	

5. Comparison with several previous works.

(I). Water Solvent and Hydrogen Bonding Interactions: In the current system, the energies of electronic states related to C=O and C=S moieties in 4-thiothymine differ greatly. Consequently, only four excited electronic states including $S_1(n\pi^*)$, $S_2(\pi\pi^*)$, $T_1(\pi\pi^*)$, and $T_2(n\pi^*)$ were involved in the photophysical processes. To consider the water solvent and hydrogen bonding interactions on the energies and structures of $Tp^{4S}T$ system, an additional QM/MM calculations were carried out with four explicit water molecules in the QM region. The calculated results indicated that the explicit water molecules do not affect the vertical and adiabatic excitation energies of $Tp^{4S}T{:}4H_2O$ apparently. Notably, the order of electronic states and the excited-state decay mechanism would remain unchanged. By contrast, in our previous contribution as in Ref. 14, there are two C=S moieties in 2,4-dithiothymine and molecular orbital energies of these two moieties are nearly degenerated. Thus, the lowest several excited singlet and triplet states would become much closer and more electronic states were involved in the photophysical processes, i.e., $^1n_8\pi_8^*$, $^1\pi_7\pi_8^*$, $^1n_7\pi_7^*$, $^3n_8\pi_8^*$, $^3\pi_8\pi_8^*$, $^3\pi_7\pi_7^*$. As the involved energy levels lie close with each other, the water solvent could change the order of the electronic states and finally affect excited-state decay mechanism of 2,4-dithiothymine (see the LIIC paths in Ref. 14), which is different from the system considered herein. (II). Non-covalent Stacking Interactions: Energy decomposition analysis (EDA) was performed to gain better insights on non-covalent stacking interactions of the S_0 and T_1 structures of QM($Tp^{4S}T$) and QM(S^5-thietane) at B3LYP-D3BJ/QZ4P theoretical level using the Amsterdam Density Functional (ADF2016) program. As listed in Table S4, the interaction energies between thymine and 4-thiothymine, i.e., QM($Tp^{4S}T$), are

estimated to be -4.26 kcal/mol (in the S_0 state) and -37.29 kcal/mol (in the T_1 state), which indicates that the stacking effect makes the complex more stable. Specifically, in the T_1 state, the orbital interaction is mainly responsible for the facile complexation of thymine and 4-thiothymine, which might be benefit for the subsequent formation of S^5-thietane. In addition, we also explored the stacking interactions of QM(S^5-thietane), i.e., S_{0cccs}, T_{1cc}, and T_{1cs}. The interaction energies of these three systems decrease significantly in comparison to those of $Tp^{4S}T$ and are calculated to be -147.0, -91.5, and -99.4 kcal/mol, respectively. The orbital and electrostatic interactions take the major responsibility of the facile formation of C-C and C-S bonds in the T_1 state or the generation of cycloaddition product in the S_0 state.

Table S4 Energy decomposition analysis (EDA) on non-covalent stacking interactions of the S_0 and T_1 structures of QM($Tp^{4S}T$) and QM(S^5-thietane) by using B3LYP-D3BJ/QZ4P method.

$Tp^{4S}T$					
S_0	ΔE_{elstat}	2.45	T_1	ΔE_{elstat}	-0.57
	ΔE_{Pauli}	0.12		ΔE_{Pauli}	3.92
	ΔE_{oi}	-0.90		ΔE_{oi}	-34.31
	ΔE_{disp}	-5.93		ΔE_{disp}	-6.33
	ΔE_{int}	-4.26		ΔE_{int}	-37.29
S^5-thietane					
S_{0cccs}	ΔE_{elstat}	-276.95	T_{1cc}	ΔE_{elstat}	-178.14
	ΔE_{Pauli}	527.44		ΔE_{Pauli}	327.33
	ΔE_{oi}	-384.96		ΔE_{oi}	-228.46
	ΔE_{disp}	-12.55		ΔE_{disp}	-12.24
	ΔE_{int}	-147.02		ΔE_{int}	-91.51
T_{1cs}	ΔE_{elstat}	-94.13			
	ΔE_{Pauli}	169.36			
	ΔE_{oi}	-163.05			
	ΔE_{disp}	-11.54			
	ΔE_{int}	-99.36			

6. Cartesian coordinates of critical structures at QM(CASSCF)/MM level

2.1 Critical structures of $Tp^{4S}T$

S_0

N	31.805358286	26.895680933	24.622201770
C	30.584631200	26.274367893	24.722903777
O	29.537518126	26.801642929	24.481853761
N	30.648181207	24.970309799	25.138132807
C	31.777653286	24.237954744	25.495787834
O	31.683681281	23.098611663	25.863342863
C	33.046248381	24.967838795	25.366813824

C	34.318419470	24.260969748	25.737255853
C	32.999451374	26.237625888	24.932828794
H	29.765626144	24.511838764	25.220052816
H	34.314433469	23.988025726	26.785820926
H	34.433805479	23.345511681	25.172003813
H	35.176504531	24.893973790	25.549336836
H	33.893279437	26.813637928	24.800738786
N	28.782930070	27.430960972	27.980500014
C	27.979907013	26.414461902	28.418946045
O	26.784732927	26.418481903	28.396591042
N	28.678066062	25.334029822	28.907997080
C	30.036161159	25.190285813	29.070913091
S	30.679353208	23.795299711	29.644186135
C	30.815586218	26.376781899	28.705064066
C	32.299217325	26.423049903	28.940662080
C	30.156564171	27.418453973	28.175215027
H	28.097800020	24.572900770	29.190743099
H	32.692892352	27.387429973	28.642146061
H	32.524129340	26.269682891	29.987993160
H	32.813644362	25.652030846	28.383432045
H	30.670500205	28.307798037	27.872289008
H	31.800751291	27.824564004	24.267667745
H	28.340862037	28.215353031	27.560246985

S_1

N	31.794321290	26.889993934	24.593375770
C	30.568234199	26.277381890	24.699691777
O	29.526433127	26.796598928	24.426096756
N	30.627267202	24.982673798	25.152272810
C	31.747024284	24.261489744	25.545700838
O	31.647858278	23.138001665	25.957958866
C	33.023263376	24.980525799	25.392808825
C	34.296259469	24.275053747	25.765066853
C	32.980984374	26.237956889	24.929367794
H	29.741153141	24.536083766	25.260117815
H	34.304531467	24.019434730	26.817644932
H	34.405278476	23.350174680	25.214102816
H	35.155114531	24.901491790	25.558219838
H	33.878588439	26.804386930	24.780820782
N	28.804923073	27.428947976	27.972212014
C	28.017459018	26.404580898	28.425080046
O	26.819180932	26.402810900	28.406815043
N	28.711521066	25.330140824	28.918419083
C	30.105080167	25.275340821	29.080922092

S	30.754673213	23.739804708	29.655685136
C	30.860689223	26.393244900	28.748166067
C	32.346377326	26.459094902	28.990898088
C	30.190853174	27.481636980	28.200324027
H	28.126218024	24.620521769	29.297107107
H	32.740881357	27.403066970	28.637970059
H	32.573914346	26.379750896	30.047028163
H	32.876568368	25.666710848	28.474959050
H	30.684564207	28.394807043	27.944879008
H	31.794970288	27.826085003	24.258895743
H	28.337984038	28.204930028	27.566427982

S_2

N	31.813214288	26.897145934	24.620988774
C	30.592176204	26.282534891	24.742283782
O	29.542411126	26.800509929	24.495896765
N	30.661977207	24.985789800	25.192213812
C	31.782713289	24.257792747	25.548688837
O	31.689389283	23.139570665	25.950316869
C	33.056238379	24.976971797	25.372819827
C	34.332373472	24.269893745	25.729896850
C	33.007158375	26.236348888	24.913638794
H	29.782319141	24.522152767	25.285720818
H	34.331384472	23.982172724	26.773910925
H	34.452968480	23.363648681	25.151137809
H	35.185042531	24.913042793	25.549659841
H	33.902343439	26.801680929	24.748019783
N	28.833159077	27.434476974	27.970540015
C	28.046114019	26.403327901	28.403990046
O	26.852064933	26.388406897	28.398974044
N	28.773085071	25.318137820	28.865628075
C	30.119421167	25.285542819	29.025942090
S	30.684846211	23.582580697	29.779017143
C	30.890294224	26.362663895	28.705099066
C	32.378766329	26.396754901	28.924123079
C	30.211529171	27.465979975	28.115714025
H	28.233438034	24.527762766	29.147189097
H	32.749938358	27.412908974	28.852736074
H	32.627205348	26.011387872	29.902743150
H	32.904265367	25.791780858	28.195997029
H	30.714682208	28.348075040	27.786676998
H	31.806122291	27.825040005	24.263571744
H	28.352554039	28.204739032	27.563356981

T_1

N	31.776944289	26.865416932	24.560995769
C	30.541648196	26.276501890	24.691349779
O	29.506387125	26.799974931	24.403749755
N	30.582844200	24.996455801	25.188748812
C	31.689416281	24.279747745	25.617782844
O	31.572685273	23.184047669	26.099109881
C	32.975921375	24.963284796	25.423193828
C	34.234226465	24.245703746	25.819215857
C	32.952941372	26.208663885	24.918677795
H	29.689266137	24.570558769	25.318866819
H	34.231018466	24.021829728	26.879021936
H	34.325297467	23.303794675	25.293875821
H	35.105326524	24.849657788	25.597067841
H	33.859323435	26.755076924	24.750630781
N	28.821556072	27.437780976	27.966786010
C	28.036983018	26.376889899	28.346164038
O	26.838969933	26.369373899	28.299995038
N	28.738294069	25.290618819	28.787400072
C	30.120973170	25.250341816	29.023116087
S	30.757876211	23.716187707	29.583003127
C	30.869093219	26.373914896	28.777904071
C	32.353352327	26.484077905	29.015254090
C	30.199825173	27.500404982	28.198157030
H	28.172664027	24.532999763	29.097219095
H	32.600544345	27.486762977	29.343328110
H	32.691365353	25.789212857	29.768470143
H	32.909229368	26.290018892	28.105670024
H	30.631874203	28.479353052	28.233068033
H	31.788376290	27.807785000	24.244096746
H	28.339309039	28.211166033	27.570326986

T_2

N	31.796345287	26.879624933	24.599451768
C	30.572878200	26.269186893	24.745755783
O	29.524048125	26.790946929	24.505830766
N	30.643887204	24.976722798	25.201797815
C	31.774964287	24.243116746	25.531646837
O	31.688489279	23.113012661	25.930393865
C	33.046234379	24.956237796	25.336860825
C	34.326327469	24.238633742	25.661883846
C	32.991741372	26.221686884	24.887137788
H	29.761353143	24.526157766	25.323267823
H	34.387963473	24.016025728	26.720458921

H	34.385813474	23.294739674	25.135941807
H	35.183767531	24.840615790	25.388616826
H	33.884769436	26.790046925	24.720759778
N	28.829287076	27.436979977	28.008913017
C	28.068662018	26.394050900	28.465784048
O	26.869679936	26.368467895	28.458260047
N	28.789007072	25.330987825	28.947032083
C	30.186468173	25.317300820	29.118606096
S	30.886019223	23.799155715	29.695695137
C	30.920468223	26.440952901	28.737713070
C	32.417544332	26.517479906	28.905743081
C	30.222146176	27.498254977	28.185724027
H	28.220855030	24.638183774	29.380373115
H	32.777852358	27.499431978	28.625501060
H	32.709529352	26.340801894	29.933895153
H	32.929843372	25.790683858	28.285609037
H	30.698801207	28.409926045	27.893583005
H	31.786971287	27.814368002	24.260066744
H	28.340313037	28.187814028	27.579059983

S_1/S_0

N	31.817553287	26.890479936	24.556231766
C	30.604943203	26.252530891	24.651177775
O	29.552735125	26.746069925	24.378279755
N	30.692198208	24.951391797	25.093177808
C	31.816888291	24.242980743	25.455946831
O	31.746934287	23.109839661	25.828748858
C	33.077586379	24.995037797	25.331145822
C	34.356192470	24.301633749	25.703273852
C	33.013232377	26.261974889	24.892722794
H	29.818242148	24.473717761	25.165751811
H	34.356940473	24.029964727	26.752244926
H	34.477376479	23.384763684	25.141941809
H	35.208716535	24.941423796	25.512253835
H	33.898968442	26.852100932	24.763714783
N	28.792525074	27.508956978	27.994036014
C	28.020172014	26.481334904	28.493106051
O	26.834041933	26.404126901	28.337771039
N	28.675742064	25.493550833	29.219223101
C	30.074835163	25.565922839	29.269617105
S	31.176553244	24.062005732	29.913122152
C	30.840226219	26.477943904	28.789119073
C	32.302715324	26.121865878	28.867813080
C	30.208136172	27.655075988	28.077793019

H	28.252400032	24.599649770	29.071220093
H	32.891371366	26.529820907	28.060301017
H	32.753546358	26.398726901	29.812738143
H	32.480275337	25.035545802	28.657340063
H	30.514962195	28.631362058	28.426792045
H	31.797537290	27.837381005	24.255996746
H	28.264181036	28.212813028	27.529722983

S_2/S_1

N	31.808138287	26.926470937	24.665422776
C	30.573381199	26.356863895	24.837742786
O	29.538129124	26.858222931	24.509100764
N	30.607278203	25.132348810	25.460384834
C	31.705098280	24.457483762	25.958144867
O	31.572115270	23.456173688	26.593620913
C	33.002210377	25.076115805	25.638963846
C	34.257605463	24.355203753	26.041067873
C	32.986783373	26.266282890	25.020135801
H	29.717331137	24.701133779	25.603185844
H	34.235612465	24.104796735	27.093423951
H	34.364098474	23.426499687	25.494824832
H	35.126677530	24.970598799	25.844097861
H	33.894799440	26.775274927	24.765683783
N	28.868307077	27.459108979	27.975246014
C	28.161400024	26.378177901	28.412409045
O	26.980199943	26.250328889	28.391447043
N	28.992973088	25.364148824	28.925714083
C	30.277655176	25.427785827	29.166394098
S	30.720334213	23.006360654	29.455565117
C	30.973243229	26.602363916	28.731871069
C	32.450634336	26.741197923	28.979463087
C	30.232219176	27.589122987	28.168383026
H	28.542426053	24.502758765	29.183584098
H	32.830587363	27.659570989	28.547926052
H	32.659418351	26.751096924	30.040480161
H	32.990888376	25.906538866	28.555806057
H	30.653825205	28.526897051	27.867620003
H	31.826527292	27.812834002	24.214938741
H	28.339443038	28.187368027	27.547145980

T_2/T_1

N	31.832562289	26.890188936	24.597323771
C	30.612017202	26.268891892	24.725405780
O	29.564228125	26.781525928	24.463086759

N	30.686868208	24.978894795	25.186720814
C	31.819352289	24.260455747	25.546503838
O	31.738682286	23.131644664	25.949890866
C	33.086193384	24.986674796	25.372824827
C	34.370149473	24.288671748	25.721657851
C	33.028593377	26.246125888	24.908875792
H	29.806344147	24.524482766	25.308653820
H	34.388944473	24.010154728	26.768744927
H	34.488381482	23.378213681	25.148976808
H	35.217847536	24.932588796	25.523381835
H	33.921017442	26.816546931	24.745058782
N	28.790358072	27.414788971	27.973526014
C	27.974921015	26.421164900	28.440605048
O	26.775777925	26.460064905	28.431553048
N	28.628569061	25.320598822	28.933410082
C	30.025948160	25.244083819	29.105236094
S	30.688331208	23.772878709	29.766199142
C	30.817120218	26.355906899	28.748158071
C	32.301292324	26.328630897	28.993347089
C	30.184999172	27.417824972	28.184259026
H	28.007247014	24.666468775	29.352041113
H	32.752372357	27.288358964	28.778896072
H	32.511643339	26.089302877	30.032274162
H	32.798690363	25.592016844	28.370203042
H	30.699410211	28.312983037	27.906120008
H	31.813796288	27.823509000	24.254589743
H	28.339862040	28.197329027	27.562471985

S_0/T_1

N	31.806223290	26.887826937	24.548048765
C	30.584576203	26.271045892	24.648297775
O	29.535743127	26.805938928	24.434002760
N	30.649910204	24.951821796	25.020441803
C	31.765841287	24.202924740	25.337932822
O	31.680001282	23.042534660	25.596087841
C	33.031679380	24.956586794	25.297207822
C	34.289691469	24.243261746	25.698665851
C	32.991707373	26.234932890	24.891049789
H	29.770024141	24.482454763	25.069350803
H	34.245701462	23.959054722	26.743371926
H	34.420840478	23.334111679	25.126571808
H	35.155747532	24.876853789	25.551678837
H	33.885055440	26.819705929	24.800503784
N	28.800043074	27.402370970	27.939691013

C	28.108705024	26.423768902	28.578036057
O	26.924383936	26.262106887	28.537867054
N	28.898833080	25.579683839	29.352453110
C	30.260016180	25.746721855	29.680624138
S	30.647814207	23.931274721	29.116635096
C	30.925025228	26.786336927	28.880499078
C	32.410523330	26.961210942	29.024056086
C	30.190662173	27.546899982	28.081434023
H	28.346624042	25.018659798	29.969929155
H	32.750985357	27.844950002	28.496181052
H	32.687472350	27.068706950	30.065701162
H	32.943828373	26.104304877	28.624753058
H	30.624775205	28.329802037	27.492976979
H	31.808431288	27.827996005	24.223673742
H	28.291950036	27.962884010	27.296104965

S_1/T_1

N	31.835008289	26.886310935	24.585988768
C	30.614284203	26.266631893	24.723849782
O	29.567500128	26.783081926	24.464467759
N	30.690155208	24.978078798	25.187094810
C	31.828762288	24.264112748	25.539360839
O	31.754255285	23.133267666	25.934417866
C	33.092296379	24.996885800	25.364716827
C	34.378471473	24.304753751	25.705919850
C	33.031608375	26.249270889	24.898172790
H	29.811891147	24.522400766	25.320123822
H	34.408117475	24.031369730	26.754279925
H	34.490819481	23.389848686	25.139263807
H	35.224674536	24.947048797	25.494864833
H	33.921263441	26.819110927	24.727861781
N	28.791975074	27.422610973	27.962522011
C	27.996879013	26.427439900	28.449233045
O	26.798470930	26.449243902	28.469165051
N	28.654679063	25.317757823	28.939706085
C	30.043141161	25.271164819	29.108251097
S	30.709288209	23.794077714	29.805685147
C	30.821157216	26.379779900	28.735754066
C	32.296423322	26.276803891	29.002657090
C	30.198358172	27.440951976	28.169433025
H	28.026815015	24.705848780	29.412199116
H	32.826449361	27.184738957	28.751445071
H	32.465311337	26.071606877	30.060234163
H	32.745883358	25.474695835	28.419598045

H	30.709079211	28.338969038	27.873852007
H	31.816835289	27.819605000	24.245629746
H	28.321906040	28.199721029	27.560702983

S_1/T_2

N	31.794818287	26.889980938	24.593871768
C	30.567949200	26.277702889	24.699948777
O	29.526834127	26.797562930	24.425425760
N	30.627250204	24.983803798	25.153349812
C	31.747878286	24.263686745	25.547074836
O	31.648370278	23.140006665	25.958903866
C	33.022726378	24.985246801	25.393928829
C	34.295442467	24.280369745	25.767504852
C	32.980089371	26.238663891	24.930825794
H	29.741537138	24.536404765	25.260667816
H	34.303240471	24.023905727	26.819952928
H	34.405443473	23.354943683	25.217791816
H	35.154432532	24.906605791	25.560621837
H	33.877149437	26.806540930	24.781982781
N	28.806164073	27.430722974	27.972330015
C	28.022081016	26.405023898	28.425223045
O	26.825257930	26.399793902	28.407780046
N	28.718296064	25.329598825	28.918853083
C	30.108837167	25.274649816	29.082454092
S	30.756513215	23.739013709	29.659452137
C	30.860528221	26.391200900	28.751503069
C	32.345643326	26.455251905	28.993309089
C	30.192382173	27.490447977	28.200863031
H	28.133972026	24.619477771	29.298583109
H	32.740575355	27.399166971	28.640452059
H	32.572964346	26.374363898	30.049524160
H	32.870311365	25.659049848	28.477447051
H	30.685805207	28.403533044	27.947771010
H	31.795039288	27.826067000	24.258874745
H	28.337699039	28.205257028	27.566328984

S_2/T_2

N	31.803883290	26.905334936	24.618900772
C	30.573581201	26.296574890	24.700197776
O	29.544360128	26.813219930	24.382777756
N	30.610959202	25.018778800	25.198499813
C	31.718280281	24.296915747	25.620270845
O	31.601160275	23.190436669	26.073263874
C	33.004895375	24.994816796	25.453425830

C	34.264359463	24.273201748	25.837314857
C	32.982576372	26.244731887	24.967417798
H	29.718978137	24.577879767	25.283740817
H	34.260348464	24.023263729	26.891486934
H	34.361160471	23.344209677	25.290394819
H	35.133106530	24.885750788	25.631485846
H	33.887249441	26.796196928	24.805985785
N	28.729681069	27.472980979	28.051079019
C	27.806503000	26.484986904	28.759307068
O	26.669605919	26.302886895	28.318123037
N	28.677596063	25.263679818	28.851599078
C	29.955235157	25.296328822	29.130108096
S	30.758400213	23.851553719	29.738754142
C	30.691114209	26.475281905	28.926514082
C	32.168990313	26.582387914	29.189379102
C	30.001135161	27.503491979	28.293884036
H	28.147588027	24.429514760	28.992231086
H	32.546248341	27.526392982	28.814328071
H	32.408849331	26.542225912	30.246041175
H	32.720879357	25.787111854	28.698804064
H	30.564963201	28.349433041	27.940121012
H	31.817060290	27.826747003	24.247130746
H	28.304768037	28.212485028	27.531361983

2.2 Critical structures of S^5-thietane

S_{0cccs}

N	31.515144270	26.621774916	25.299059821
C	30.702019208	25.674174845	24.726247780
O	29.947715157	25.876968860	23.826109712
N	30.840289218	24.396592754	25.241604814
C	31.844042292	23.928377724	26.072128874
O	32.084028307	22.757017636	26.156734880
C	32.585479346	24.983863796	26.852645932
C	34.088862454	24.797046785	26.706974924
C	32.042487306	26.397906898	26.619404916
H	30.331082181	23.704226708	24.732756782
H	34.621990492	25.514500838	27.316206964
H	34.377326476	23.799000713	27.009816946
H	34.380825476	24.933786795	25.669737847
H	32.865064367	27.070824950	26.787893925
N	28.923555082	28.337264039	27.746995997
C	28.617037061	27.005393945	27.590648986
O	27.501338979	26.589650914	27.468626978
N	29.701712137	26.181456883	27.578415985

C	31.071461236	26.526205907	27.832363003
S	31.948932298	25.035206800	28.659681063
C	31.153237240	27.860948004	28.524270051
C	32.397030331	28.251480031	29.278035109
C	30.115042167	28.696014066	28.397241041
H	29.458870120	25.220134817	27.494210978
H	32.364812327	29.299214111	29.543985127
H	32.493902339	27.676929992	30.191510174
H	33.301711396	28.088990023	28.702387064
H	30.144370170	29.684785138	28.807735073
H	31.310196255	27.555644985	25.016568802
H	28.131244022	28.932805084	27.828569003

T_{1cc}

N	31.383366260	26.678446920	25.506559835
C	30.506966194	25.747784850	24.983300799
O	29.572445126	26.023197875	24.295188751
N	30.808817216	24.431360758	25.262406819
C	31.966994302	23.968397727	25.860539859
O	32.267527323	22.801020640	25.834941857
C	32.750077357	24.995963799	26.531388907
C	34.191388461	24.744864781	26.841711929
C	32.131065312	26.357471899	26.713774920
H	30.232962173	23.762658709	24.796380784
H	34.486873480	25.206176815	27.777280001
H	34.390965475	23.684111702	26.894270935
H	34.819039505	25.168361809	26.059566878
H	32.953009371	27.047879946	26.803105930
N	28.920385082	28.215619033	27.787686002
C	28.724896069	26.852015931	27.835287003
O	27.643449990	26.337142893	27.877586004
N	29.879394151	26.105721876	27.810863002
C	31.236453246	26.549258910	28.029085016
S	31.954628298	25.497660836	29.366553112
C	31.249569248	28.023079018	28.423125043
C	32.498893338	28.645090059	28.996531085
C	30.123552168	28.749224067	28.269511036
H	29.697368137	25.132595809	27.917491011
H	32.388264330	29.721006140	29.052857092
H	32.699446355	28.274646035	29.994249157
H	33.382573400	28.439777044	28.402671046
H	30.109660164	29.802760146	28.468370047
H	31.026410233	27.606029988	25.423551827
H	28.092393019	28.750082069	27.933732011

T_{1cs}

N	31.578662272	26.655964920	25.171100809
C	30.614480205	25.745072854	24.803365786
O	29.612327130	26.016048870	24.208744742
N	30.897820225	24.426955759	25.137363807
C	31.923026298	23.933033722	25.896788866
O	32.123692311	22.764143638	25.996864872
C	32.733634354	24.984054797	26.617057914
C	34.161936461	24.522794765	26.877836933
C	32.672483351	26.285098893	25.947374866
H	30.277868181	23.754406708	24.736759780
H	34.705914496	25.285330820	27.417594970
H	34.173000462	23.612560699	27.456084974
H	34.665052492	24.334948753	25.938005868
H	33.332126399	27.064046946	26.257652887
N	28.844415074	28.280391037	27.834584002
C	28.435876045	26.967886941	27.815571002
O	27.299088964	26.619274918	27.684906990
N	29.460341122	26.066937878	27.935826008
C	30.765116213	26.368754899	28.343262041
S	31.887513293	25.036060802	28.466324047
C	31.076360237	27.720357997	28.591251058
C	32.405888330	28.139078026	29.170234099
C	30.105434166	28.656404065	28.325264040
H	29.164770101	25.115629809	27.956919013
H	32.431572334	29.209174104	29.322779109
H	32.570401345	27.664737992	30.129648168
H	33.237530393	27.873214005	28.530457053
H	30.255770178	29.701695140	28.495284049
H	31.358660255	27.613754986	25.014174799
H	28.107126023	28.947444085	27.789453999

T_{1cccs}

N	31.505701266	26.654631917	25.337804824
C	30.713402208	25.673371845	24.792421787
O	29.922700154	25.846563859	23.917636723
N	30.930888226	24.402236757	25.291161819
C	31.956339297	23.980477727	26.112520878
O	32.218569321	22.817506644	26.231656885
C	32.694083350	25.076347802	26.854118934
C	34.191211462	24.955722795	26.603961915
C	32.081294307	26.467664906	26.645052920
H	30.428317189	23.687721707	24.806958783

H	34.737764500	25.676653850	27.198432958
H	34.539347484	23.962090723	26.852681932
H	34.403504478	25.137067811	25.553917839
H	32.877723366	27.178596956	26.792325928
N	28.899297078	28.265002034	27.835426002
C	28.675538066	26.904647937	27.822032002
O	27.580540986	26.423501900	27.873572004
N	29.792211146	26.123128881	27.689915991
C	31.156650242	26.529385907	27.906771007
S	32.154019311	25.095469807	28.669556061
C	31.147291240	27.804903001	28.692786064
C	32.331864328	28.290729033	29.473627122
C	30.112688170	28.817638075	28.272211036
H	29.575847127	25.151615810	27.710612992
H	32.429410333	29.367728113	29.398400115
H	32.235708319	28.045697017	30.529472198
H	33.259222395	27.848555006	29.129557096
H	30.451564194	29.681415136	27.717331992
H	31.261066248	27.573120984	25.043064802
H	28.071052021	28.815295074	27.884311005

S_0/T_{1cc}

N	31.370998255	26.691433919	25.505443838
C	30.496739193	25.759280856	24.982753799
O	29.558593128	26.031758873	24.298449747
N	30.801013217	24.443940761	25.264271820
C	31.962020301	23.979022728	25.856434862
O	32.257776322	22.810344643	25.830414856
C	32.748876358	25.007950801	26.519046911
C	34.182075460	24.749563779	26.858081932
C	32.127613314	26.366472897	26.707668924
H	30.221017177	23.774677711	24.804572786
H	34.464290481	25.221153817	27.793378002
H	34.371180474	23.687815705	26.928982936
H	34.827142505	25.157145812	26.082129879
H	32.945713371	27.060539946	26.794425931
N	28.931189083	28.212611030	27.787465001
C	28.735663069	26.851236934	27.834417004
O	27.653748991	26.344830897	27.874415004
N	29.884591153	26.107343879	27.823790003
C	31.240917248	26.560757911	28.022836014
S	31.970628300	25.517997837	29.428991116
C	31.254136249	28.027007016	28.420058043
C	32.504757341	28.651053061	28.988891088

C	30.131661169	28.752848068	28.269432036
H	29.706460137	25.133414811	27.936231009
H	32.397170331	29.727630138	29.031422091
H	32.701760352	28.291342037	29.990419157
H	33.388191405	28.434703044	28.398813042
H	30.106957164	29.799618146	28.500041051
H	31.016403232	27.620254987	25.424253829
H	28.095003022	28.734589066	27.929313011

S_0/T_{1cs}

N	31.564537272	26.654503920	25.180465812
C	30.613251201	25.747475853	24.790571783
O	29.627186131	26.019226871	24.175680742
N	30.881429225	24.439271756	25.136703806
C	31.911798295	23.940629723	25.906576867
O	32.116795311	22.763092639	25.984002870
C	32.703126355	24.977988796	26.668959920
C	34.149216458	24.529483767	26.865938933
C	32.637387348	26.298464894	26.000620871
H	30.251171178	23.774029712	24.740722778
H	34.692512495	25.283194817	27.422066973
H	34.189802458	23.594621696	27.406381974
H	34.630552490	24.390611755	25.904054866
H	33.296597396	27.075614946	26.309900891
N	28.851319075	28.284707033	27.829145002
C	28.458787049	26.969046940	27.794476002
O	27.324151968	26.608496916	27.684619991
N	29.496342124	26.076916875	27.882517004
C	30.802326216	26.388226897	28.284411038
S	31.913777296	25.040949802	28.448522048
C	31.094652238	27.738072994	28.577130058
C	32.420880334	28.162738027	29.159843101
C	30.107589166	28.663624064	28.332639041
H	29.208870103	25.123330809	27.895749007
H	32.440271336	29.230585103	29.327203110
H	32.594892345	27.678663989	30.112463169
H	33.250799391	27.913211010	28.511611051
H	30.249798175	29.707037136	28.517886051
H	31.349933254	27.612142985	25.016166802
H	28.110355020	28.948024084	27.788601002

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N	31.503339267	26.670543917	25.217005814
C	30.687073211	25.636509845	24.823216786

O	29.802231144	25.733343852	24.030888729
N	30.992992230	24.405751754	25.374897826
C	32.080477311	24.071863733	26.155494881
O	32.383383332	22.928585648	26.345931897
C	32.844647364	25.237165816	26.747833927
C	34.318475468	25.129591807	26.387155901
C	32.178075318	26.593142913	26.489326904
H	30.466208190	23.646254700	24.996565801
H	34.887122508	25.908220867	26.878569934
H	34.710946500	24.167146738	26.686273923
H	34.443725478	25.229505816	25.313100819
H	32.966281374	27.328133969	26.519236907
N	29.025476091	28.389201045	27.866710004
C	28.862113079	27.027003946	27.993620017
O	27.810817001	26.515864910	28.251502034
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C	31.366437255	26.721668922	27.816775002
S	32.473972338	25.386130825	28.599771060
C	31.352894255	28.080687021	28.465237048
C	31.474530265	28.144245024	29.965273157
C	30.316059183	28.919965080	27.780085000
H	29.809516147	25.299252822	27.911229008
H	31.215151248	29.129312097	30.333184185
H	30.852846218	27.413636973	30.470982194
H	32.501755340	27.944343010	30.247839176
H	30.412771189	29.981841157	27.678624994
H	31.168151243	27.561820981	24.920664792
H	28.200983027	28.934957084	27.993019014