

Hydrogen sharing between two nitroxyl radicals in the gas phase and other solvation aspects of a bulky hydroxylamine

Taija L. Fischer, Martijn A. Tepaske, Martin A. Suhm*

Institute of Physical Chemistry, University of Göttingen, Tammannstr. 6, 37077 Göttingen (Germany). E-mail: msuhm@gwdg.de

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1 Experiment

1.1 Investigated compounds

Tab. S1 contains details on the investigated compounds and introduces codes for their referencing in this supplement.

Table S1: Table of investigated compounds, their codes in this supplement, their CAS number, the supplier and purity.

Name	Code	CAS Number	Supplier	Purity	Lot#
TEMPO	T	2564-83-2	Sigma-Aldrich	98%	Lot#BCCF8320
TEMPO-H	TH	7031-93-8	synthesized by M. A. Tepaske		
Helium	-	7440-59-7	Nippon	99.996%	

1.2 Synthesis of TEMPO-H

The literature preparation of 2,2,6,6-tetramethyl-1-hydroxypiperidine (TEMPO-H) was adapted to give improved yield and high purity.[1] TEMPO (2.0 g, 0.013 mol, 1.0 eq) was dissolved in H₂O (20 mL) and sparged with N₂ for 15 min. Under a N₂ flow, sodium ascorbate (4.2 g, 0.021 mol, 1.x eq) was added as a solid to the deoxygenated TEMPO solution and vigorously stirred until the deep orange color was no longer observed (ca. 15 min). Subsequently, the white suspension was extracted with pentane (4x20 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and sublimation of the white solid at -35°C resulted in isolation of anhydrous white crystalline material in high purity and yield (1.8 g, 0.012 mmol, 91%). ¹H NMR (400 MHz, CD₃CN) δ [ppm]: 1.06 (s, 12H), 1.45 (s, 6H), 5.30 (s, 1H). The ¹H NMR spectrum was in accordance with previous reported data.[1]

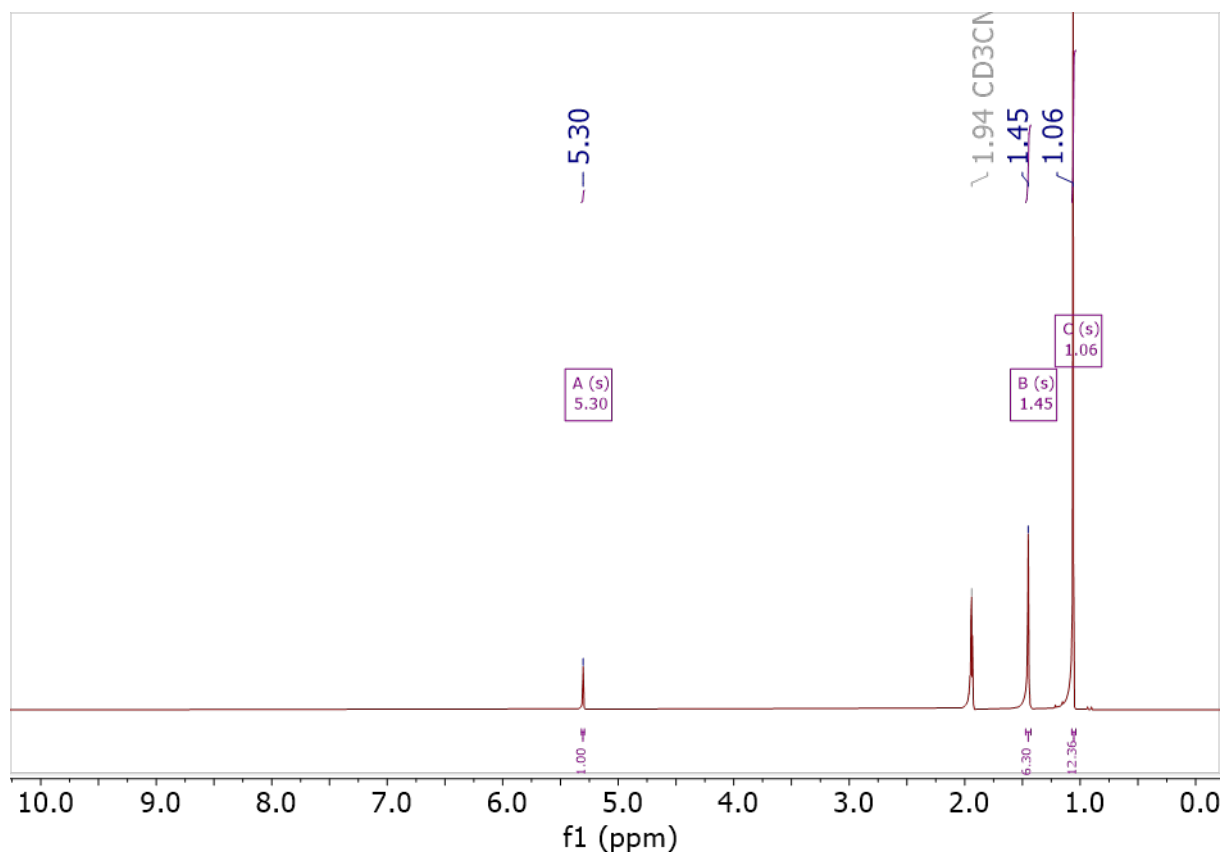


Figure S1: ¹H NMR (400 MHz) spectrum of TEMPO-H in CD₃CN.

1.3 Measurement details

A detailed description of the experimental setup used for the FTIR measurements can be found in [2], the experimental parameters are listed in tab. S2.

Table S2: The spectroscopic data for figure 2 and 3 in the main document were obtained by averaging # scans from 133 ms gas pulses with a stagnation pressure of 0.75 bar through a 700 mm×0.2 mm slit nozzle. The time between the gas pulses amounts to approximately half a minute. An InSb/HgCdTe sandwich detector, an optical filter ($<4000\text{ cm}^{-1}$) and a 150 W tungsten lamp with a Bruker VERTEX 70v FTIR spectrometer in double-sided mode at 140 kHz scanning speed was used to collect the spectral data. The date on which the spectrum was recorded is given as dd/mm/yyyy. The partial pressures for TEMPO-H (p_{TH}), TEMPO (p_{T}), and water (p_{w}) are also given in figures 2 and 3.

p_{TH}/hPa	p_{T}/hPa	p_{w}/hPa	#	dd/mm/yyyy
0.05	0.00	0.00	1000	01/11/2021
0.10	0.00	0.00	1000	20/10/2020
0.05	0.00	0.05	1000	19/08/2022
0.05	0.00	0.00	1000	01/11/2021
0.05	0.10	0.00	1000	13/05/2022
0.05	0.05	0.00	1000	04/11/2021
0.10	0.05	0.00	1000	22/08/2022

1.4 Extended spectra

The spectral range recorded typically exceeds that shown in the figures of the main text. CH fundamental absorptions can be useful to quantify the change in relative abundance of the components, because aggregation only has a small impact on their appearance.

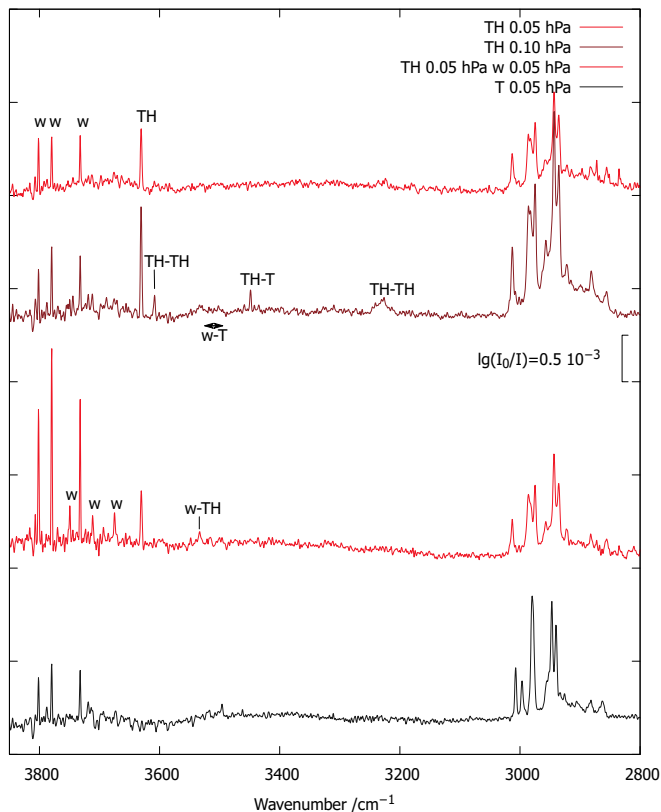


Figure S2: Extended wavenumber range for the spectra in Fig. 2 to allow for a quantification of the TEMPO impurity in the TEMPO-H expansions with and without additional water by also including a TEMPO spectrum (lowest trace).

2 Harmonic modeling

2.1 Details on harmonic calculations

The molecular structures were obtained by optimizing the monomeric structures using three-body-inclusive D3-dispersion-corrected [3, 4] B3LYP with the def2-TZVP basis set[5–7] (B3LYP/TZ) on ORCA 4.2.1 [8–10] with the keywords GRID5 NOFINALGRID VERYTIGHTSCF TIGHTOPT FREQ. The monomers were later put together using Chemcraft version 1.8 and the dimer structures were pre-optimized using CREST[11, 12]. The resulting dimer structures were later optimized on B3LYP/TZ level using ORCA 4.2.1 with the same keywords as for the monomers. For all radical species the multiplicity was set to 2. For the transition state search first a Nudged Elastic Band (NEB)

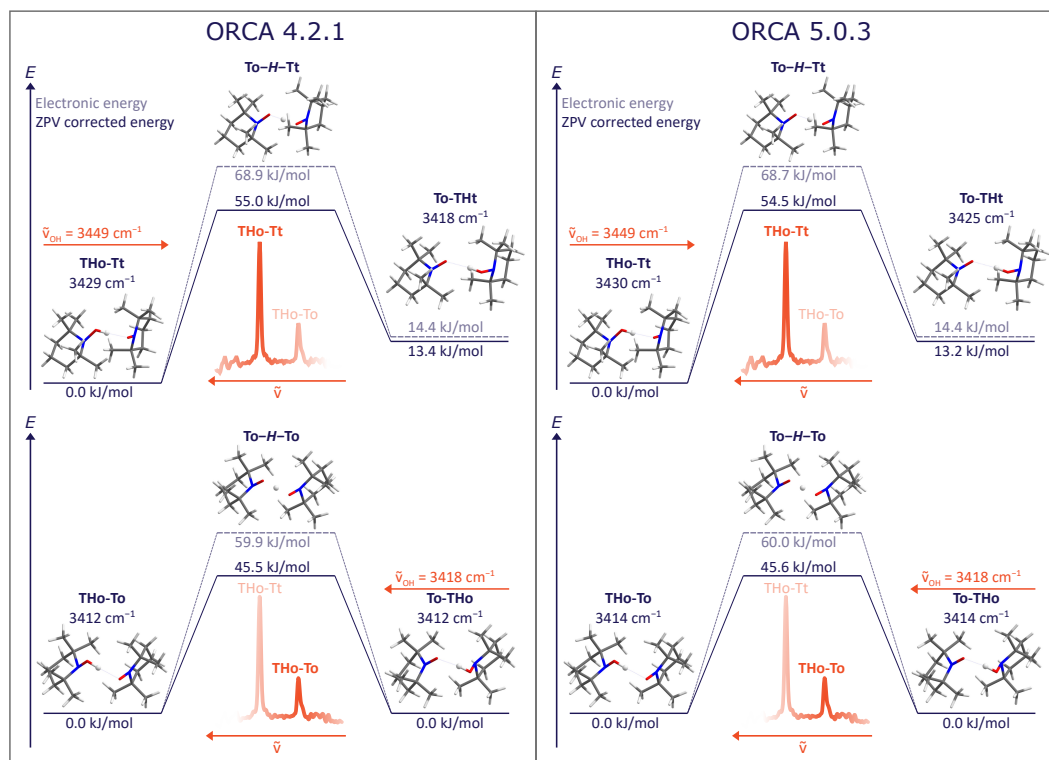


Figure S3: Comparison of energies obtained from the optimization of the start and end structure for the NEB scan and the resulting TS after TS search and OH stretching wavenumbers between ORCA 4.2.1 and ORCA 5.0.3.

scan in ORCA 4.2.1 was performed using the TH-T dimer structures lowest in energy (THo-To, THo-Tt) as starting points and generating the corresponding end structure (To-THo, To-Tt) in Chemcraft version 1.8. The keywords for the NEB scan are TightSCF Grid5 NoFinalGrid Mass2016 with SpringType DOF, PerpSpring cosTan, Tol_MaxF_CI 2.e-3, Tol_RMSF_CI 1.e-3. and Tol_Scale 10.0. The results obtained from the NEB scan were used as starting point for a transition state (TS) search. Here ORCA 5.0.3[8, 13] with the keywords TightSCF SlowConv OptTS Freq Mass2016 was used. The resulting TS, start and end structure of the NEB scan were again optimized using ORCA 4.2.1 with the keywords mentioned for earlier optimizations and ORCA 5.0.3 with the keywords SlowConv OptTS VeryTightSCF Freq defgrid3 Mass2016. The results are listed in table S3 and selected values are graphically shown in figure S3. The relative energy differences are small ($\Delta_{\text{ORCA}} \leq 0.5$ kJ/mol). Additionally the OH stretching wavenumber of the start and end structure of the TH-T complexes are given. The predicted wavenumbers deviate by ≤ 7 cm^{-1} between the different ORCA versions.

2.2 Harmonic scaling factor

In order to find a suitable common scaling factor for the observed OH stretching fundamentals of different complexes, experimental literature values of the smallest hydroxylamine[14] and the two water monomer stretching vibrations[15] (symmetric OH_{sym} and antisymmetric (OH_{asym}) as well as the straightforward TH monomer signal found in this work were compared to harmonic calculations on B3LYP/TZ level and a scaling factor f was derived. The results from theory predictions and the corresponding scaling factors can be found in table S4. An average rounded f value of 0.96 was used as the uniform scaling factor for all harmonic theory predictions in the present work.

Table S3: Theoretical predictions for different conformers of TH monomer and TH-T dimer on B3LYP/TZ level. Relative electronic energies (ΔE^e) and zero point corrected energies (ΔE^0) are given within the monomer and dimer group each. Additionally the energy differences for B3LYP/QZVP single point calculations are given for TH-T dimer structures. The predicted wavenumber (ω) of the TEMPO-H vibration (unscaled and scaled by multiplying with 0.96) and its infrared intensity is given.

Structure	ΔE_{TZVP}^e /kJ mol ⁻¹	ΔE_{TZVP}^0 /kJ mol ⁻¹	ω_{TZVP} /cm ⁻¹	$\omega_{\text{TZVP}}^{\text{scaled}}$ /cm ⁻¹	IR Int / km mol ⁻¹	$\Delta E_{\text{QZVP}}^{e, \text{sp}}$ /kJ mol ⁻¹
TH monomer						
THo	0.0	0.0	3794	3642	41	
THt	12.0	10.8	3631	3486	2	
TH-T dimer						
THo-To	0.0	0.0	3554	3412	560	0.0
THo-Tp	1.8	1.9	3588	3444	850	1.8
THo-Tt	0.9	0.5	3572	3429	610	0.7

Table S4: Experimental wavenumbers $\tilde{\nu}$ of hydroxylamine [14], water monomer[15] and TH (this work), their assignments and corresponding harmonic values ω on B3LYP/TZ level. f is the resulting scaling factor required to match the experimental value.

Assignment	$\tilde{\nu}/\text{cm}^{-1}$	ω/cm^{-1}	f
H ₂ NOH			
OH (stretch)	3649.89	3789.03	0.963
NH (stretch)	3358.76	3506.4	0.958
NH (stretch)	3294.25	3427.9	0.961
w			
OH _{asym}	3756	3887.57	0.966
OH _{sym}	3657	3782.40	0.967
TH			
OH (stretch)	3631	3794.21	0.957

3 Experimental wavenumbers and scaled harmonic predictions

Computational results are listed in table S3.

Comparisons between theory and experiment are made in figure S3 and table S5.

Table S5: Experimentally observed OH stretching wavenumbers $\tilde{\nu}$ compared to harmonic B3LYP/TZ predictions ω unscaled and scaled by 0.96 for all species including TH in figure 2 and 3 in the main document. The value in parentheses refers to an unlikely alternative assignment of the strong transition to the predicted third-most stable THo-Tp isomer, see Table S3.

Species	$\tilde{\nu}/\text{cm}^{-1}$	ω/cm^{-1}	$0.96 \omega/\text{cm}^{-1}$
THo	3631	3794	3642
THo-THo (accep.)	3609	3775	3624
w-TH	3534	3656	3510
THo-Tt (THo-Tp)	3449	3572 (3588)	3429 (3444)
THo-To	3418	3554	3412
THo-THo (don.)	≈ 3230	3372	3237

4 THo-Tx structures and their optimized coordinates

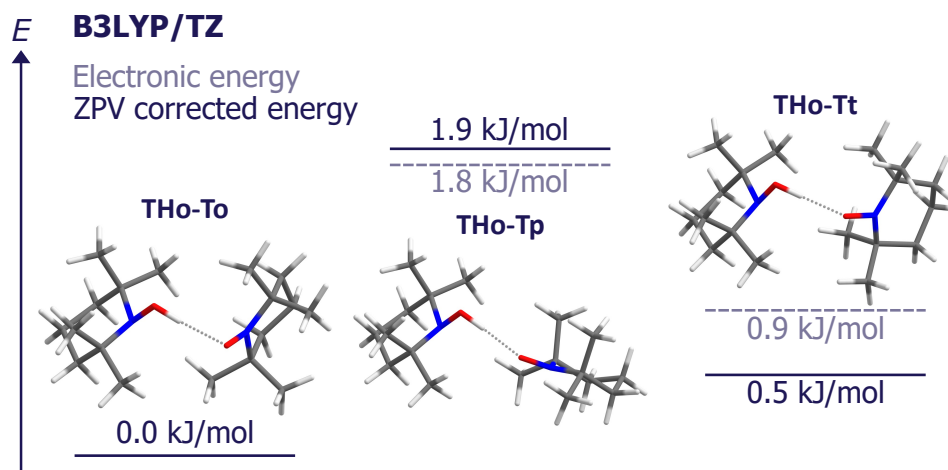


Figure S4: THo-Tx structures and their relative energies on B3LYP/TZ level.

Table S6: xyz coordinates of THo-To structure in Å optimized using B3LYP/TZ level on ORCA 4.2.1.

atom	x	y	z
C	2.95574535	-0.239728653	-1.982374088
C	4.141789675	0.555558261	-1.453205328
C	3.672633518	1.496603644	-0.351677463
H	3.27084683	-0.949410512	-2.751621857
H	4.916153187	-0.117819239	-1.07738613
H	2.980485885	2.227087094	-0.781885615
C	2.953952713	0.77048352	0.796400816
C	3.951185992	-0.011641785	1.670837909
H	4.65727786	-0.598964215	1.088517357
H	4.528139124	0.688231634	2.278653395
H	3.41294885	-0.681081075	2.340088651
C	2.268598651	1.819953847	1.679831372
H	1.506632706	2.35520264	1.114239427
H	1.793851001	1.357930039	2.544490951
H	3.007018827	2.539233911	2.04011928
C	2.208948166	-1.017409717	-0.886176585
C	3.017814558	-2.246823387	-0.430393499
H	2.583734616	-2.665070758	0.476539034
H	2.987373956	-3.012119976	-1.208913533
H	4.062828198	-2.016996131	-0.237857189
C	0.88274348	-1.517392361	-1.471506795
H	1.069924592	-2.099585413	-2.376196634
H	0.357961389	-2.152055816	-0.760074088
H	0.239345679	-0.675660102	-1.726704296
H	4.600751885	1.12642369	-2.26454192
H	2.249972105	0.451316648	-2.454016759
H	4.510550877	2.058703946	0.068183388
N	1.875503183	-0.054644078	0.191035955
O	1.213601749	-0.77740537	1.238907151
H	0.373358513	-0.298841172	1.366856556
H	-1.813940251	-1.836819784	2.410550968
C	-2.038951002	-2.103839995	1.380547654
H	-2.607971229	-3.03504865	1.375603296
H	-1.097160026	-2.267405829	0.859579374
C	-2.868767818	-1.018512776	0.693558713
H	-4.608673589	-1.633007009	1.816517139
C	-4.094637401	-0.703191717	1.566657908
H	-4.807500507	-0.049567827	1.067935031
H	-3.774797186	-0.226789001	2.49330131
H	-0.723045443	2.654442969	0.279985102
H	-1.088778425	2.759300043	-1.449176963
C	-0.969999784	2.075182475	-0.606793168
H	-0.136671849	1.401525911	-0.804171983
H	-3.06809693	2.552522529	1.171434409
H	-4.334195527	1.820248169	0.175489965
C	-3.339277219	2.260764275	0.156895314
H	-3.380984973	3.15967734	-0.460752968
C	-2.277151561	1.304908607	-0.411437875
O	-1.28619487	0.502168059	1.576432451
N	-2.018700935	0.206899891	0.570643421
C	-3.277306378	-1.49408058	-0.707517631
H	-4.025707959	-2.281274593	-0.590795659
H	-2.405579636	-1.952243009	-1.183456038
C	-3.795045298	-0.375897804	-1.602156644
H	-4.715856998	0.049367622	-1.195081812
H	-4.052248848	-0.777729268	-2.584798611
C	-2.725027992	0.697701925	-1.748380312
H	-1.851704772	0.260680828	-2.240556136
H	-3.072618707	1.512978082	-2.38703572

Table S7: xyz coordinates of THo-Tp structure in Å optimized using B3LYP/TZ level on ORCA 4.2.1.

atom	x	y	z
C	-3.818680277	-1.517526238	0.535321844
C	-4.604502196	-0.380876394	1.174780263
C	-3.64338963	0.716748577	1.611254385
H	-4.486462028	-2.307475838	0.18226657
H	-5.345519031	0.013689957	0.475312313
H	-2.985652793	0.319495428	2.390629131
C	-2.767190207	1.244685095	0.464280815
C	-3.583861205	2.127396635	-0.497429835
H	-3.01660866	2.30796425	-1.409154301
H	-4.541165079	1.687325914	-0.76685982
H	-3.786954671	3.090097004	-0.023880401
C	-1.649353481	2.104481691	1.067457468
H	-1.009931769	1.500904646	1.711702723
H	-1.028164796	2.549128239	0.291226607
H	-2.083789287	2.910862977	1.662045285
C	-2.944201155	-1.063517675	-0.644568377
C	-3.80456267	-0.757350493	-1.885684192
H	-4.666369291	-0.134827018	-1.658263811
H	-3.204689217	-0.253317212	-2.641835329
H	-4.176041825	-1.692134377	-2.310713218
C	-1.988215431	-2.207813232	-1.000712369
H	-2.558649075	-3.108411954	-1.237396578
H	-1.378921681	-1.950131888	-1.865509598
H	-1.328753153	-2.426409774	-0.16074118
H	-5.165396599	-0.752478261	2.036350287
H	-3.165988905	-1.963435131	1.29236538
H	-4.182720614	1.561186359	2.047784366
N	-2.11190846	0.069927001	-0.172063515
O	-1.332033943	0.528716107	-1.287407698
H	-0.424562744	0.577981716	-0.936734877
H	-0.000248835	-0.714926597	0.992118833
C	0.931448885	-0.989405281	1.482133892
H	0.812895562	-1.983104478	1.91863547
H	1.119859596	-0.281147307	2.290698888
C	2.116166709	-1.014947269	0.514130012
H	0.988372442	-1.493503659	-1.273987476
C	1.794213962	-1.923261237	-0.682196165
H	1.469431509	-2.900353258	-0.321632368
H	2.658850395	-2.071013297	-1.327722321
H	4.587433909	2.854942313	-0.516749994
H	3.420330687	2.676979902	0.803923147
C	3.616333424	2.439303666	-0.242538676
H	2.846479547	2.907042021	-0.851534841
H	2.910140295	0.959981984	-2.490216675
H	3.929330241	-0.44344425	-2.145894158
C	3.794808845	0.619877199	-1.953044915
H	4.665477725	1.147534454	-2.346096249
C	3.64234038	0.924297476	-0.454429411
O	1.297619695	0.995406069	-0.421550414
N	2.328570576	0.381229333	0.016021827
C	3.365996439	-1.500713672	1.261655618
H	3.25326794	-2.573455027	1.433128747
H	3.389261787	-1.025237625	2.246995116
C	4.670915577	-1.191895181	0.542956842
H	4.716793786	-1.706163705	-0.420124805
H	5.514546734	-1.562816524	1.129301115
C	4.789827962	0.314029573	0.360357669
H	4.80697688	0.785368969	1.347895733
H	5.727497219	0.580979299	-0.13214678

Table S8: xyz coordinates of THo-Tt structure in Å optimized using B3LYP/TZ level on ORCA 4.2.1.

atom	x	y	z
C	3.381397424	-0.66334379	-1.660544851
C	4.348349242	0.435205553	-1.239799093
C	3.578972961	1.54226499	-0.532662573
H	3.910418551	-1.48876246	-2.143614455
H	5.126976433	0.031971725	-0.58779106
H	2.884343059	1.998180716	-1.245084287
C	2.770754777	1.042344299	0.67530022
C	3.692737839	0.714558769	1.863633339
H	4.55831454	0.122322275	1.5764793
H	4.061255524	1.642625439	2.305234972
H	3.138298395	0.169986283	2.626215607
C	1.812625037	2.158857154	1.106004
H	1.232075155	1.869127874	1.980662106
H	2.378191598	3.059600133	1.353168845
H	1.121994069	2.394992906	0.296250051
C	2.565468582	-1.234890294	-0.490090371
C	3.440221971	-2.133269467	0.405651967
H	3.646579524	-3.071721071	-0.113205197
H	4.39662932	-1.680178974	0.654630654
H	2.916248638	-2.363852342	1.331851908
C	1.437895405	-2.098948162	-1.065972832
H	1.856359472	-2.871351843	-1.714614372
H	0.877271285	-2.586566758	-0.270910477
H	0.752223959	-1.486893057	-1.651299994
H	4.862504212	0.837197907	-2.116705544
H	2.683344254	-0.254831812	-2.39805551
H	4.251335529	2.333336403	-0.191207241
N	1.926872935	-0.091865416	0.209532424
O	1.211792846	-0.620983352	1.337038893
H	0.317695832	-0.241402434	1.258847736
H	-2.156292506	3.305291649	-1.047111171
C	-2.10832008	2.628248511	-0.192556506
H	-2.871152214	2.925904079	0.528404028
H	-1.133966988	2.722810813	0.279008861
C	-2.351939315	1.196628721	-0.673960555
H	-1.403289441	-0.204121321	-2.065584911
C	-1.21075967	0.765872254	-1.608149693
H	-0.2678344	0.707572997	-1.064400325
H	-1.104407698	1.498893424	-2.410188781
H	-4.001331766	-2.108519512	2.242268652
H	-3.977461327	-0.36153625	2.534180874
C	-3.406671541	-1.200017532	2.132682226
H	-2.493002349	-1.304085685	2.713020183
H	-1.242780721	-2.101113231	0.663498509
H	-2.006800174	-2.046485784	-0.926195887
C	-2.198645705	-2.118463708	0.143061228
H	-2.681998063	-3.077335423	0.337940365
C	-3.095966778	-0.980412168	0.650834778
O	-1.373384618	0.470646786	1.342741111
N	-2.348829663	0.311543979	0.53405522
C	-3.712035872	1.121543336	-1.380941495
H	-3.608227048	1.607398362	-2.353597997
H	-4.437770433	1.709593228	-0.81059803
C	-4.245154606	-0.296144887	-1.526732937
H	-3.576462635	-0.90213367	-2.142774628
H	-5.208448836	-0.280137322	-2.041375466
C	-4.407197002	-0.906398785	-0.142307393
H	-5.125835649	-0.304643232	0.42269675
H	-4.819341267	-1.916170818	-0.200410633

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