The shortest Th–Th distance from a new type of quadruple bond

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Supporting Information

Contents

I. Additional computational details

For calculations in the ADF 2014.01 program, the criteria of the grid size, SCF and geometry convergence are 6.0 (Accint), 1e-6 (SCFcnv) and 1e-4 (TolE and TolG) and the others (TolR & TolA) were set as defaults. As $Cy_3PThThPCy_3$ and $Ph_3PThThPPh_3$ are rather large systems, Slater type orbital basis sets of double-zeta plus one polarization function (DZP) were used for the atoms of these two molecules except Th, for which TZP was used.

For calculations in the Molpro 2015.1 program, the global threshold for the smallest allowed eigenvalue of the overlap matrix (THROVL) was set as 1.d-9, all other parameters were employed at their default value. D_{3d} symmetry was used for all *ab initio* studies on $H_3PThThPH_3$, including CASPT2, CCSD(T) and SOC calculations. Although the D_{3d} structure is not quite the most stable at the PBE level (0.54 kJ/mol less stable than the C_1 structure, with a small imaginary frequency of 21.2*i* cm^{-1}), high symmetry is so helpful for state specification in *ab initio* calculations that we felt the constraint to D_{3d} symmetry appropriate. The *xyz* coordinates of both of the D_{3d} and C_1 structures are given in Section III. Note that the Th–Th bond lengths are very similar between these two structures, 2.604 Å (D_{3d}) *vs* 2.607 Å (C_1).

II. Table

Table S1. An–An bond distances reported in the literature. See main text for the source reference numbers.

Compounds	An–An (Å)
Ac_2	3.64
Th_2	2.76
HThThH	2.71
Pa_2	2.37
U_2	2.43
PhUUPh	2.29
H_2UUH_2	2.28
$U(\mu\text{-}H_2)U$	2.18
U_2^{2+}	2.30
$[U_2X_8]^{2-}$ (X = Cl, Br)	2.35
$[Np_2X_8]^{2-}$ (X = Cl, Br)	2.20
$[Pu_2X_8]^{2-}$ (X = Cl, Br)	2.08
U_2X_6 (X = Cl, F, OH, NH_2, CH_3)	2.35, 2.38, 2.37, 2.35, 2.36
$U_2(OCHO)_4$	2.33
$U_2(OCHO)_6$	2.40
$U_2(OCHO)_4Cl_2$	2.80
$U_2@C_{60}$	2.72
$An_2(C_8H_8)_2$ (An = Th, Pa, U, Np)	2.81, 2.54, 2.24, 2.19
$An_2Cp^*_2$ (Cp*= $C_5(CH_3)_5$, An = Th, Pa, U, Np, Pu)	2.79, 2.37, 2.58, 2.78, 2.87

Table S2. The $\angle_{\text{L-Th-Th}}$ angles (°) and total bonding energies E (kJ/mol) of the optimised LThThL molecules. Also provided are the $\angle_{\text{L-Th-Th}}$ angles and energies for modified geometries, derived from the optimised geometries as follows. Starred structures are optimised with symmetry constraints that enforce linearity (*e.g.* D_{3d} for $H_3AsThThAsH_3$). For other compounds this approach did not lead to either SCF or geometry convergence, and hence the other angle data in the same column indicate structures based on the optimised geometries but fixing $\angle_{\text{L-Th-Th}}$ to be either linear (180°) or trans-bent (170°), depending on the angle in the fully optimised structure. The energy difference ΔE between the two forms is also given.

Compounds	Optimised Geometry		Modified Geometry		ΔE
	$\angle_{\text{L-Th-Th}}$	E	$\angle_{\text{L-Th-Th}}$	E	
$H_3AsThThAsH_3$	169.2	-3387.49	180.0*	-3387.70	0.21
$H_3PThThPH_3$	175.4	-3626.69	180.0*	-3626.15	-0.54
$Me_3PThThPMe_3$	179.5	-13339.22	170.0	-13336.1	-3.12
$Cy_3PThThPCy_3$	176.2	-56433.08	180.0	-56432.40	-0.68
$Ph_3PThThPPh_3$	173.8	-43077.79	180.0	-43074.78	-3.01
$H_3NThThNH_3$	180.0	-4451.27	170.0	-4446.04	-5.23
NHCThThNHC	177.9	-11722.65	180.0*	-11722.56	-0.09
$H_2FPThThPFH_2$	169.4	-3904.76	180.0	-3901.16	-3.60
$HF_2PThThPF_2H$	168.2	-4194.84	180.0	-4184.96	-9.88
OCThThCO	180.0	-3665.02	170.0	-3663.43	-1.59
ONThThNO	180.0	-3487.95	170.0	-3482.85	-5.10

III. xyz coordinates (Å) and total SCF energies from DFT (PBE) optimisations of the studied compounds.

$H_3AsThThAsH_3$ (E= -1.29022463 Hartree)

1.Th	0.016490	0.177982	1.282830
2.Th	-0.016490	-0.177982	-1.282830
3.As	0.052847	0.026569	4.319097
4.H	0.053225	1.176340	5.340517
5.H	-1.064935	-0.732545	5.038813
6.H	1.196053	-0.714165	5.018409
7.As	-0.052847	-0.026569	-4.319097
8.H	-0.053225	-1.176340	-5.340517
9.H	-1.196053	0.714165	-5.018409
10.H	1.064935	0.732545	-5.038813

$H_3PThThPH_3$ (E= -1.38112322 Hartree)_D_{3d}

1.Th	0.000000	0.000000	1.302182
2.Th	0.000000	0.000000	-1.302182
3.P	0.000000	0.000000	4.305639
4.H	-1.059078	-0.611459	5.056756
5.H	1.059078	-0.611459	5.056756
6.H	0.000000	1.222918	5.056756
7.P	0.000000	0.000000	-4.305639
8.H	1.059078	0.611459	-5.056756
9.H	0.000000	-1.222918	-5.056756
10.H	-1.059078	0.611459	-5.056756

$H_3PThThPH_3$ (E= -1.38132807 Hartree)_C_1

1.Th	0.010609	0.084382	1.300468
2.Th	-0.000624	-0.083983	-1.300617
3.P	0.003151	0.038622	4.293265
4.H	-1.068558	-0.612943	4.987321
5.H	1.064321	-0.611755	5.006019
6.H	-0.002390	1.203300	5.139195
7.P	-0.003213	-0.038750	-4.293164
8.H	1.065566	0.612370	-4.992467
9.H	-0.001573	-1.203385	-5.139159
10.H	-1.067290	0.612142	-5.000860

$Cy_3PThThPCy_3$ (E= -21.49422664 Hartree)

1.P	-4.287251	0.007663	0.039870
2.Th	-1.301360	0.037947	-0.041767
3.Th	1.303505	0.054305	0.054417
4.P	4.288553	0.017812	-0.031466
5.C	5.019541	-1.677516	-0.497383
6.C	4.044833	-2.777054	-0.032502
7.C	5.313996	-1.847114	-1.996168

8.H	5.974070	-1.782628	0.057532
9.C	4.565252	-4.183704	-0.345717
10.H	3.079079	-2.627873	-0.558718
11.H	3.826293	-2.683272	1.043459
12.C	5.831741	-3.257228	-2.312843
13.H	4.384946	-1.664533	-2.570458
14.H	6.057115	-1.107780	-2.335624
15.C	4.862367	-4.340420	-1.837756
16.H	3.825493	-4.933607	-0.016711
17.H	5.489810	-4.370371	0.234231
18.H	6.011138	-3.348150	-3.398392
19.H	6.809973	-3.401949	-1.814904
20.H	5.273437	-5.342817	-2.048293
21.H	3.916067	-4.256149	-2.405099
22.C	-5.077926	1.642088	0.614044
23.C	-5.373555	1.704614	2.120976
24.C	-4.147475	2.805725	0.219605
25.H	-6.037878	1.746505	0.068397
26.C	-5.944400	3.070618	2.527427
27.H	-4.436391	1.521377	2.681911
28.H	-6.087072	0.917609	2.413516
29.C	-4.723715	4.167952	0.619917
30.H	-3.175880	2.661785	0.735977
31.H	-3.927173	2.788425	-0.859795
32.C	-5.021322	4.219524	2.119263
33.H	-6.121599	3.085533	3.617234
34.H	-6.930336	3.207466	2.042486
35.H	-4.016807	4.966933	0.337161
36.H	-5.657460	4.352010	0.053752
37.H	-5.471874	5.189372	2.392321
38.H	-4.070159	4.138857	2.678895
39.C	5.011874	1.210601	-1.308867
40.C	4.180399	2.499919	-1.432191
41.C	6.508185	1.525710	-1.173289
42.H	4.863703	0.660770	-2.258243
43.C	4.674789	3.357031	-2.603231
44.H	4.241286	3.088173	-0.499961
45.H	3.113090	2.245586	-1.575838
46.C	6.994782	2.385836	-2.347857
47.H	6.687170	2.078116	-0.232768
48.H	7.101395	0.596373	-1.114026
49.C	6.169070	3.668654	-2.479334
50.H	4.088940	4.290708	-2.657208
51.H	4.493522	2.811780	-3.549113
52.H	8.064406	2.627505	-2.218791
53.H	6.909760	1.801513	-3.283991
54.H	6.511825	4.255728	-3.348892
55.H	6.335638	4.299193	-1.584703

56.C	-4.977921	-1.289068	1.231690
57.C	-6.462433	-1.642108	1.062733
58.C	-4.107260	-2.557157	1.279855
59.H	-4.853994	-0.797454	2.215776
60.C	-6.930187	-2.588778	2.176831
61.H	-6.615681	-2.140593	0.087925
62.H	-7.085061	-0.730202	1.055268
63.C	-4.581253	-3.499687	2.392511
64.H	-4.146002	-3.087935	0.312461
65.H	-3.048570	-2.280687	1.445788
66.C	-6.064135	-3.850155	2.237423
67.H	-7.990339	-2.856190	2.022034
68.H	-6.872291	-2.061086	3.148083
69.H	-3.966344	-4.416102	2.394439
70.H	-4.423289	-3.007722	3.371298
71.H	-6.393610	-4.499581	3.066867
72.H	-6.204140	-4.430274	1.304936
73.C	5.242125	0.407586	1.560896
74.C	4.840211	1.787057	2.108052
75.C	5.013679	-0.674045	2.630227
76.H	6.320288	0.418999	1.304218
77.C	5.559790	2.117303	3.421422
78.H	3.745352	1.795923	2.278971
79.H	5.045862	2.575302	1.366749
80.C	5.737459	-0.338082	3.940383
81.H	3.927159	-0.762028	2.827915
82.H	5.354878	-1.657774	2.268989
83.C	5.324744	1.034032	4.474788
84.H	5.219277	3.099413	3.793526
85.H	6.646395	2.208181	3.229023
86.H	5.530138	-1.122999	4.688604
87.H	6.830298	-0.346302	3.763456
88.H	5.877630	1.269565	5.400538
89.H	4.250293	1.012148	4.739429
90.C	-5.220093	-0.306618	-1.581272
91.C	-5.040592	0.858408	-2.569232
92.C	-4.753705	-1.623318	-2.223632
93.H	-6.296904	-0.385888	-1.331489
94.C	-5.744833	0.583980	-3.904040
95.H	-3.959088	1.011622	-2.753943
96.H	-5.429679	1.796027	-2.140326
97.C	-5.453997	-1.891157	-3.561353
98.H	-3.659303	-1.568772	-2.389480
99.H	-4.922960	-2.471456	-1.541409
100.C	-5.266904	-0.725277	-4.533079
101.H	-5.573214	1.429647	-4.592702
102.H	-6.837211	0.528083	-3.732990
103.H	-5.067265	-2.827055	-4.001099

104.H	-6.535643	-2.045438	-3.382144
105.H	-5.805889	-0.919181	-5.476477
106.H	-4.194042	-0.634511	-4.789199

$Me_3PThThPMe_3$ (E= -5.08064138 Hartree)

1.Th	-0.004095	-0.029420	1.300199
2.Th	-0.044397	0.012257	-1.300215
3.P	0.068051	-0.080293	4.295667
4.P	-0.081207	0.076665	-4.295966
5.C	-1.494647	0.962997	-5.100949
6.H	-2.438645	0.495854	-4.792351
7.H	-1.504326	2.008443	-4.766983
8.H	-1.413056	0.930952	-6.197325
9.C	-0.139551	-1.552167	-5.176248
10.H	0.736042	-2.149554	-4.891396
11.H	-1.041130	-2.097759	-4.869573
12.H	-0.148857	-1.416150	-6.267579
13.C	1.361742	0.879108	-5.135768
14.H	1.441027	1.921880	-4.802751
15.H	2.283959	0.357164	-4.849898
16.H	1.251776	0.852877	-6.229818
17.C	-1.318113	-0.951113	5.162834
18.H	-2.270434	-0.478434	4.890230
19.H	-1.349386	-1.998359	4.835896
20.H	-1.191602	-0.913371	6.254794
21.C	0.056791	1.553519	5.168673
22.H	0.923986	2.143382	4.845135
23.H	-0.852947	2.103795	4.896244
24.H	0.091045	1.422922	6.260230
25.C	1.537596	-0.889175	5.081390
26.H	1.597357	-1.933669	4.749635
27.H	2.451215	-0.374101	4.757971
28.H	1.470231	-0.858362	6.178799

$Ph_3PThThPPh_3$ (E= -16.40745734 Hartree)

1.P	-4.194856	-0.241288	-0.315895
2.Th	-1.297944	-0.125675	-0.182520
3.Th	1.297944	0.125675	0.182520
4.P	4.194856	0.241288	0.315895
5.C	5.111855	1.814374	-0.003757
6.C	4.519362	2.759049	-0.854119
7.C	6.348977	2.101997	0.586667
8.C	5.162765	3.963791	-1.127524
9.H	3.548755	2.539259	-1.310373
10.C	6.986755	3.313516	0.316862
11.H	6.812813	1.379183	1.260450
12.C	6.398645	4.243278	-0.541034
13.H	4.694872	4.690030	-1.795816

14.H	7.951494	3.531694	0.780415
15.H	6.901620	5.190110	-0.748902
16.C	-5.111855	-1.814374	0.003757
17.C	-4.519362	-2.759049	0.854119
18.C	-6.348977	-2.101997	-0.586667
19.C	-5.162765	-3.963791	1.127524
20.H	-3.548755	-2.539259	1.310373
21.C	-6.986755	-3.313516	-0.316862
22.H	-6.812813	-1.379183	-1.260450
23.C	-6.398645	-4.243278	0.541034
24.H	-4.694872	-4.690030	1.795816
25.H	-7.951494	-3.531694	-0.780415
26.H	-6.901620	-5.190110	0.748902
27.C	-5.130155	0.500471	-1.718993
28.C	-6.119551	1.476996	-1.528808
29.C	-4.782548	0.119215	-3.025215
30.C	-6.745903	2.059705	-2.630855
31.H	-6.397529	1.780058	-0.517124
32.C	-5.421995	0.692471	-4.119975
33.H	-4.007096	-0.636122	-3.181593
34.C	-6.402360	1.670344	-3.925615
35.H	-7.512571	2.822307	-2.475482
36.H	-5.151018	0.381642	-5.131347
37.H	-6.895581	2.129101	-4.784943
38.C	5.130155	-0.500471	1.718993
39.C	6.119551	-1.476996	1.528808
40.C	4.782548	-0.119215	3.025215
41.C	6.745903	-2.059705	2.630855
42.H	6.397529	-1.780058	0.517124
43.C	5.421995	-0.692471	4.119975
44.H	4.007096	0.636122	3.181593
45.C	6.402360	-1.670344	3.925615
46.H	7.512571	-2.822307	2.475482
47.H	5.151018	-0.381642	5.131347
48.H	6.895581	-2.129101	4.784943
49.C	4.595454	-0.812509	-1.129261
50.C	4.021995	-2.101269	-1.177603
51.C	5.364618	-0.366158	-2.215945
52.C	4.193523	-2.904091	-2.304308
53.H	3.462839	-2.483191	-0.317987
54.C	5.534593	-1.178383	-3.334549
55.H	5.827586	0.621894	-2.185362
56.C	4.944119	-2.445305	-3.386621
57.H	3.741934	-3.898018	-2.332069
58.H	6.133829	-0.819340	-4.174218
59.H	5.078200	-3.076741	-4.267149
60.C	-4.595454	0.812509	1.129261
61.C	-4.021995	2.101269	1.177603

62.C	-5.364618	0.366158	2.215945
63.C	-4.193523	2.904091	2.304308
64.H	-3.462839	2.483191	0.317987
65.C	-5.534593	1.178383	3.334549
66.H	-5.827586	-0.621894	2.185362
67.C	-4.944119	2.445305	3.386621
68.H	-3.741934	3.898018	2.332069
69.H	-6.133829	0.819340	4.174218
70.H	-5.078200	3.076741	4.267149

$H_3NThThNH_3$ (E= -1.69539852 Hartree)

1.Th	0.308149	0.082608	1.201432
2.Th	0.245147	0.321222	-1.434558
3.N	0.166344	0.546222	-4.081569
4.N	0.370136	-0.156877	3.847799
5.H	1.015925	0.998326	-4.442422
6.H	-0.636599	1.108376	-4.389845
7.H	0.091466	-0.373564	-4.533619
8.H	0.321552	0.760801	4.307941
9.H	-0.422613	-0.714516	4.189622
10.H	1.231494	-0.617226	4.166752

NHCThThNHC (E= -4.46492813 Hartree)

1.Th	-1.619608	0.978290	-0.093462
2.Th	0.955734	0.250374	-0.097769
3.C	-4.080184	1.757690	-0.027180
4.C	-6.329448	1.997169	-0.444444
5.C	-6.002034	2.892283	0.528356
6.H	-7.277958	1.788973	-0.923666
7.H	-6.610468	3.614519	1.058457
8.C	3.457327	-0.385722	-0.045454
9.C	5.716608	-0.438424	-0.472444
10.C	5.473532	-1.335100	0.523157
11.H	6.641131	-0.159592	-0.962619
12.H	6.145661	-1.987340	1.066790
13.N	-5.158898	1.329213	-0.759684
14.H	-5.071521	0.593725	-1.455364
15.N	-4.648188	2.727935	0.760483
16.H	-4.098902	3.254376	1.434526
17.N	4.491145	0.116714	-0.795561
18.H	4.336395	0.826266	-1.506579
19.N	4.111080	-1.284853	0.759672
20.H	3.614374	-1.837721	1.452770

ONThThNO (E= -1.32849595 Hartree)

1.O	0.000000	0.000000	4.748362
2.N	0.000000	0.000000	3.519295
3.Th	0.000000	0.000000	1.444051

4.Th	0.000000	0.000000	-1.444051
5.N	0.000000	0.000000	-3.519295
6.O	0.000000	0.000000	-4.748362

OCThThCO (E= -1.39592341 Hartree)

1.O	0.000000	0.000000	4.912205
2.C	0.000000	0.000000	3.730288
3.Th	0.000000	0.000000	1.382857
4.Th	0.000000	0.000000	-1.382857
5.C	0.000000	0.000000	-3.730288
6.O	0.000000	0.000000	-4.912205