Supporting Information for

Absolute Configuration Determination through the Unique Intramolecular Excitonic Coupling in the Circular Dichroisms of *o,p'*-DDT and *o,p'*-DDD. A Combined Experimental and Theoretical Study.

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General Experimental Details

Optical resolution of *o,p'*-**DDT** and *o,p'*-**DDD** were performed by chiral HPLC using Daicel Chiralcel OJ-H column (4.6 mm ϕ × 40 cm) under the following conditions: eluent: 9 : 1 mixture of hexane/2-propanol, flow rate: 0.5 mL min^{-1}, temperature: 38 °C, UV detector at 291 nm. Experimental circular dichroism (CD) spectra were measured in a conventional quartz cell (light path 1 cm) fitted with a temperature controller for hexane (spectroscopic grade) solutions of *o,p'*-**DDT** and *o,p'*-**DDD** on a JASCO J-720WI Spectropolarimeter under the following conditions: bandwidth, 1 nm; scan rate, 50 nm min^{-1}, response, 4 sec; accumulation, 4 times. Optical rotations were measured in a thermostated conventional quartz cell (Φ = 1.8 mm, l = 1 dm) at the sodium-D line (589.3 nm) by using a JASCO DIP-1000 Digital Polarimeter fitted with a temperature controller.

All calculations were performed on Linux-PCs by using Gaussian 09[S1] or Turbomole 7.0[S2] program suite. Geometries were fully optimized at the dispersion-corrected density functional theory (3rd generation, DFT-D3 with BJ dumping), with AO basis-set of valence triple-ξ quality (in standard notation: H, [3s1p]; C, [5s3p2d1f]; Cl, [5s5p2d1f]) at the TPSS-D3/def2-TZVP level. The resolution of identity (RI) approximation was employed and the corresponding auxiliary basis-sets were taken from the Turbomole basis-set library. The numerical quadrature grid m5 was employed and the convergence criterion for the optimization regarding the change of total energy between two subsequent optimization cycles was set to 10^{-7} E_h. Subsequent single-point energy calculations were performed with the spin-component-scaled (SCS)-MP2 method with a def2-TZVPP basis-set (in standard notation: H, [3s2p1d]; C, [5s3p2d1f]; Cl [5s5p3d1f]). The method has been shown to provide the most accurate relative energies (comparable to the computationally highly demanding CCSD(T) calculations). All excited-state calculations were performed with the above DFT-D3 optimized ground-state geometries, thus corresponding to the vertical transition approximation. The CD spectrum was simulated at the RI-CC2/def2-TZVP or SAC-CI/B95(d) level. Gaussian functions for each transition where the width of the band at 1/e height is fixed at 0.4 eV. The overall excitation energies obtained by the RI-CC2 method were shifted by 0.3 eV.

(S1) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(S2) Turbomole V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, Turbomole GmbH, since 2007; available from http://www.turbomole.com.

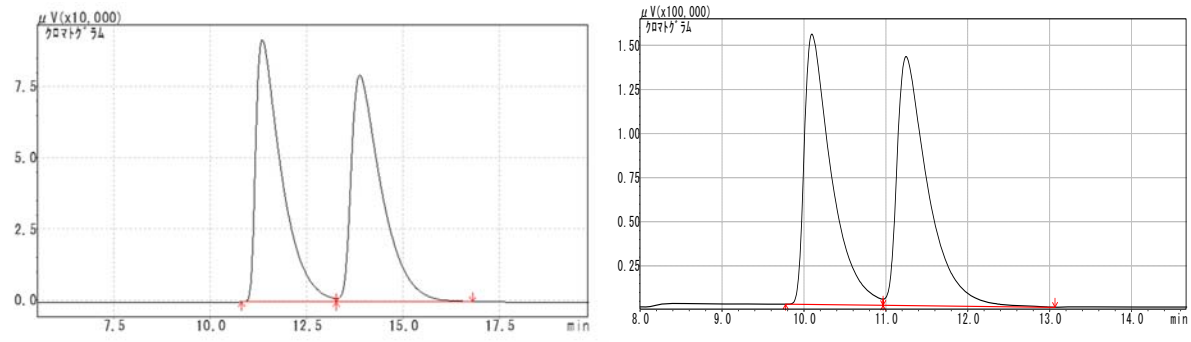

Figure S1. Typical chiral HPLC charts for optical resolution of *o,p'*-**DDT** (left) and *o,p'*-**DDD** (right).

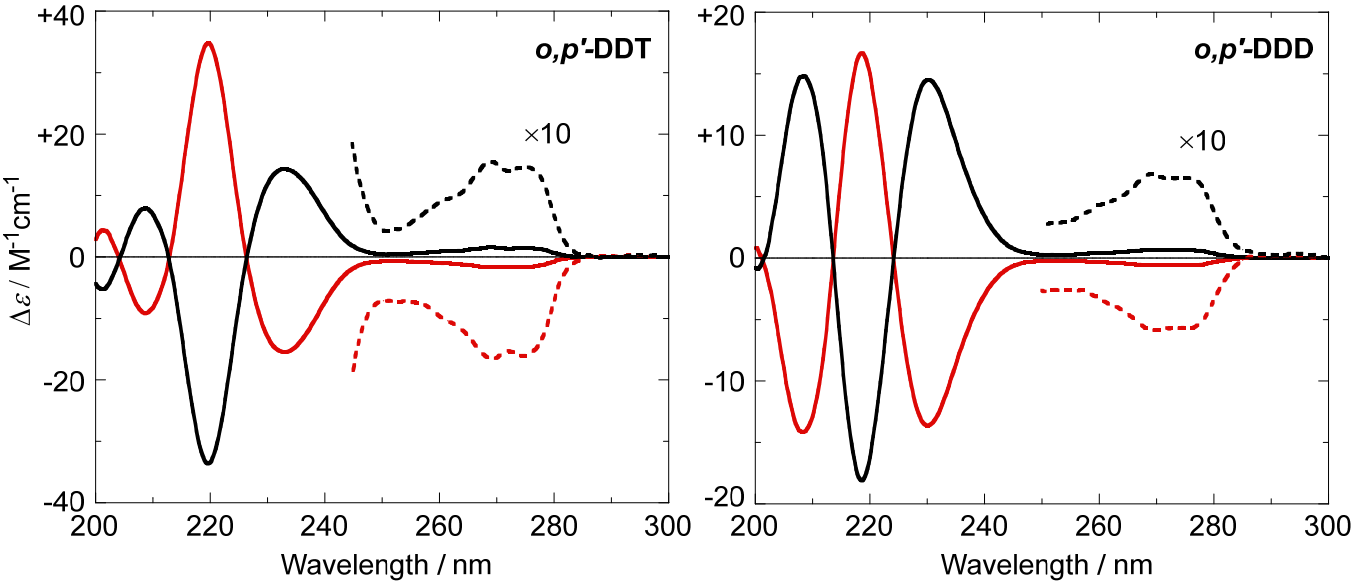

Figure S2. Experimental CD spectra of *o,p'*-**DDT** (left) and *o,p'*-**DDD** (right) in hexane at 25 °C. The 1st and 2nd elutes in chiral HPLC are shown in red and black lines, respectively.

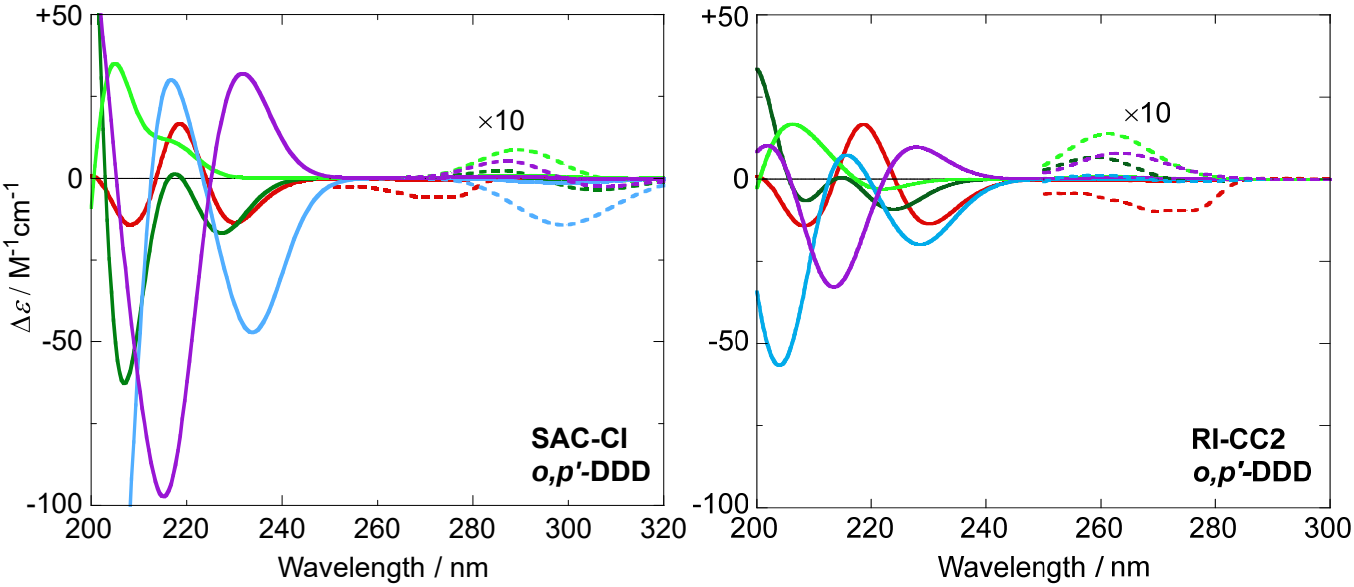

Figure S3. Comparison of experimental (red) and SAC-CI (left) and RI-CC2 (0.3 eV red-shifted, right) predicted CD spectra of various conformers of (*S*)-*o,p'*-**DDT**. Light blue: ***t/r***, green: ***g-/r***, light green: ***g+/r*** and purple: ***t/s***.

TABLE S1. Optimized Geometries of *o,p'*-**DDT** and *o,p'*-**DDD** at the DFT-D3(BJ)-TPSS/def2-TZVP level.

(*s*)-*o,p'*-DDT

E(DFT) = -2840.420380952 au
E(SCSMP2) = -2836.193186746 au

C	0.8832322	0.7449711	-0.0148504
C	2.4353570	0.6873713	-0.0328450
H	0.7092570	1.8258692	0.0561228
Cl	3.0486953	1.5978011	-1.4622946
C	0.1572377	0.3017316	-1.2842446
C	-1.1919921	0.6669899	-1.3680593
C	-1.9719870	0.3207073	-2.4667893
C	-1.3875917	-0.3999762	-3.5058882
C	-0.0467506	-0.7699014	-3.4513069
C	0.7178664	-0.4185251	-2.3407674
H	-1.6477867	1.2222843	-0.5519074
H	-3.0167708	0.6061611	-2.5198721
H	0.3950124	-1.3320177	-4.2666931
H	1.7538110	-0.7311857	-2.3084953
C	0.2728047	0.1645486	1.2602864
C	0.0112630	1.0671376	2.3043695
C	-0.5626992	0.6731710	3.5070490
C	-0.9049687	-0.6648089	3.6959147
C	-0.6810045	-1.5820298	2.6753351
C	-0.1048967	-1.1723168	1.4701341
H	-0.7439662	1.4063065	4.2867506
H	-1.3548124	-0.9964123	4.6268995
H	-0.9547550	-2.6247126	2.7934360
Cl	-2.3500032	-0.8432496	-4.8944323
H	0.2768430	2.1096031	2.1548201
Cl	0.0711603	-2.4089062	0.2522713
Cl	3.1061334	-0.9674283	-0.0488561
Cl	3.0813112	1.5168170	1.4339128

(*r*)-*o,p'*-DDT

E(DFT) = -2840.414166842 au
E(SCSMP2) = -2836.187287172 au

C	0.7686447	0.8892242	0.0517556
C	2.3183053	0.9788919	-0.0011886
H	0.4876445	1.9387960	0.1776057
Cl	2.7971293	1.8979756	-1.4670281
C	0.0890279	0.4219096	-1.2278992
C	-1.0234074	1.1579996	-1.6537964
C	-1.7532294	0.7870299	-2.7795544
C	-1.3577360	-0.3389124	-3.4979467
C	-0.2510503	-1.0860847	-3.1021202
C	0.4630459	-0.7050259	-1.9679778
H	-1.3277283	2.0376644	-1.0924813
H	-2.6130671	1.3646658	-3.1004732
H	0.0500628	-1.9552391	-3.6766336
H	1.3302063	-1.2879693	-1.6816986
C	0.2560479	0.1507989	1.2787240
C	-0.3185027	0.8332970	2.3617950
C	-0.8035093	0.1591147	3.4822591
C	-0.7286578	-1.2293896	3.5343049
C	-0.1881264	-1.9359327	2.4602104
C	0.2869526	-1.2480121	1.3488944
H	-1.2385605	0.7271180	4.2970615
H	-1.1056714	-1.7541378	4.4069922
H	-0.1430462	-3.0202739	2.4832437
H	0.6847305	-1.8031111	0.5073327
Cl	-0.4885733	2.5773515	2.3464875
Cl	-2.2572699	-0.8164002	-4.9161212
Cl	3.1697272	-0.6079066	-0.0214952
Cl	2.8966112	1.8665581	1.4497477

(*t*/*s*)-*o*,*p*′-DDD

E(DFT) = -2380.795524934 au
E(SCSMP2) = -2377.102332848 au

C	-0.5301084	-1.0289534	0.4201308
C	-1.0394522	-2.1712897	-0.4681240
H	-0.7674995	-1.3079116	1.4491108
Cl	-0.1926175	-3.7081909	-0.0789980
C	0.9731979	-0.8138897	0.3255181
C	1.6474486	-0.3489026	1.4596634
C	3.0117394	-0.0733216	1.4268325
C	3.7129433	-0.2699976	0.2387229
C	3.0688712	-0.7388605	-0.9038157
C	1.7023644	-1.0060704	-0.8520038
H	1.0956511	-0.1957652	2.3834846
H	3.5284579	0.2850805	2.3103600
H	3.6310257	-0.8979650	-1.8174230
H	1.2192060	-1.3878043	-1.7467234
C	-1.2746790	0.2594669	0.0935608
C	-2.1087639	0.9008338	1.0176220
C	-2.7840587	2.0799227	0.7014205
C	-2.6333049	2.6405248	-0.5635042
C	-1.8026009	2.0269646	-1.5015911
C	-1.1317280	0.8561274	-1.1653350
H	-3.4197777	2.5451296	1.4467292
H	-3.1604703	3.5572909	-0.8095686
H	-1.6725873	2.4620855	-2.4875985
H	-0.4664145	0.3944855	-1.8900085
Cl	-2.3365276	0.2461009	2.6260739
Cl	5.4253551	0.0675282	0.1830765
H	-0.8826214	-1.9950670	-1.5302229
Cl	-2.8130489	-2.3775518	-0.2673891

(*t*/*r*)-*o*,*p*′-DDD

E(DFT) = -2380.797028499 au
E(SCSMP2) = -2377.103910661 au

C	-0.4959056	-1.1028663	0.1465845
C	-1.1338223	-2.0575614	-0.8711058
H	-0.5814044	-1.6147566	1.1115736
Cl	-0.3522440	-3.6764329	-0.7743770
C	0.9914352	-0.8385162	-0.0883441
C	1.7200429	-0.2763966	0.9665338
C	3.0732745	0.0199943	0.8371886
C	3.7101887	-0.2532454	-0.3720611
C	3.0115774	-0.8145939	-1.4369996
C	1.6557175	-1.1016266	-1.2881306
H	1.2193276	-0.0577023	1.9064496
H	3.6298025	0.4545088	1.6602704
H	3.5210129	-1.0241698	-2.3710384
H	1.1290469	-1.5418525	-2.1272341
C	-1.2648570	0.2046567	0.3019473
C	-1.8138157	0.5026090	1.5563617
C	-2.4917299	1.6930179	1.8025193
C	-2.6405073	2.6257396	0.7777150
C	-2.1129064	2.3574013	-0.4827209
C	-1.4351695	1.1606831	-0.7080707
H	-2.9042322	1.8874544	2.7876693
H	-3.1673608	3.5591350	0.9508939
H	-2.2217637	3.0657227	-1.2967695
Cl	-0.8111501	0.8935371	-2.3228865
H	-1.7062375	-0.2312435	2.3508569
Cl	5.4089125	0.1114805	-0.5514149
H	-1.0403729	-1.7271621	-1.9008897
Cl	-2.8968593	-2.2178142	-0.5645211

(*g*-/*s*)-*o*,*p*′-DDD

E(DFT) = -2380.790723313 au
E(SCSMP2) = -2377.096857288 au

C	-0.4014888	-0.7348734	0.8294018
C	-1.0820325	-2.1055544	0.6782856
H	-0.4695749	-0.5476294	1.9088531
Cl	-0.1826226	-3.3807704	1.5688128
C	1.0676837	-0.6305116	0.4592243
C	1.7932074	0.4212606	1.0339985
C	3.1367186	0.6253863	0.7371395
C	3.7694663	-0.2434844	-0.1507514
C	3.0760616	-1.3008827	-0.7316359
C	1.7277098	-1.4876221	-0.4252535
H	1.2961789	1.0976610	1.7253509
H	3.6899779	1.4414971	1.1886911
H	3.5835949	-1.9728963	-1.4149764
H	1.1996518	-2.3148882	-0.8836760
C	-1.2538675	0.3245696	0.1427039
C	-2.4036603	0.8484939	0.7477314
C	-3.1979550	1.8078502	0.1224478
C	-2.8465261	2.2593309	-1.1471963
C	-1.7084963	1.7536778	-1.7758986
C	-0.9253965	0.8006064	-1.1320572
H	-4.0762020	2.1900519	0.6310165
H	-3.4620116	3.0070604	-1.6382793
H	-1.4291381	2.1026468	-2.7651760
H	-0.0337058	0.4116036	-1.6134866
Cl	-2.8857542	0.3035861	2.3464012
Cl	5.4568907	-0.0028636	-0.5336590
Cl	-1.3670990	-2.6004449	-1.0340918
H	-2.0716103	-2.0728612	1.1260794

(*g*-/*r*)-*o*,*p*′-DDD

E(DFT) = -2380.797943022 au
E(SCSMP2) = -2377.103909469 au

C	-0.3208928	0.9055725	-0.5413522
C	-1.1603738	2.1322801	-0.1490247
H	-0.2045041	1.0483710	-1.6252543
Cl	-0.3768120	3.6649175	-0.6959122
C	1.0908595	0.7803731	0.0077015
C	1.8755632	-0.2631989	-0.4984684
C	3.1836004	-0.4611084	-0.0692842
C	3.7191288	0.4086642	0.8787206
C	2.9659324	1.4626094	1.3878216
C	1.6555826	1.6437078	0.9483623
H	1.4509091	-0.9463281	-1.2302822
H	3.7819830	-1.2761514	-0.4612343
H	3.3977270	2.1330315	2.1227921
H	1.0776839	2.4598773	1.3635915
C	-1.1879709	-0.3466986	-0.4083205
C	-2.0131006	-0.6567630	-1.5017780
C	-2.8698730	-1.7518307	-1.5047410
C	-2.9148095	-2.5858983	-0.3884384
C	-2.1064528	-2.3116141	0.7095462
C	-1.2563027	-1.2024930	0.7029362
H	-3.4884408	-1.9559459	-2.3731327
H	-3.5713693	-3.4504982	-0.3692261
H	-2.1243517	-2.9491318	1.5867823
Cl	-0.2938501	-0.9595354	2.1358999
H	-1.9645442	-0.0128110	-2.3776341
Cl	5.3599947	0.1733100	1.4321246
Cl	-1.5930177	2.2206174	1.5911285
H	-2.1122988	2.0966749	-0.6733238

(*g*+/*s*)-*o*,*p*′-DDD

E(DFT) = -2380.790803693 au
E(SCSMP2) = -2377.097293883 au

C	-0.4754010	-0.6956042	0.8319571
C	-1.0424452	-2.1215602	0.7256039
H	-0.6148800	-0.4538280	1.8943242
H	-0.4895016	-2.8090999	1.3617822
C	1.0234528	-0.6093015	0.5504718
C	1.6081580	0.6631418	0.4819490
C	2.9761718	0.8244035	0.2895313
C	3.7801908	-0.3069935	0.1586550
C	3.2295833	-1.5827355	0.2236461
C	1.8558043	-1.7254044	0.4222290
H	0.9806881	1.5447939	0.5754130
H	3.4167591	1.8140592	0.2385205
H	3.8642729	-2.4554815	0.1162288
H	1.4500530	-2.7306219	0.4539319
C	-1.2712156	0.3246421	0.0393442
C	-2.1572804	1.2238110	0.6478096
C	-2.8901184	2.1505850	-0.0942489
C	-2.7381222	2.1955995	-1.4767955
C	-1.8442279	1.3295706	-2.1070809
C	-1.1182228	0.4151762	-1.3513108
H	-3.5648739	2.8280151	0.4172839
H	-3.3093657	2.9157989	-2.0549801
H	-1.7080443	1.3697522	-3.1833524
H	-0.4058211	-0.2437825	-1.8354621
Cl	-2.3578800	1.2514369	2.3887031
Cl	5.4978599	-0.1191212	-0.0941110
Cl	-0.9597546	-2.8257871	-0.9320890
Cl	-2.7358393	-2.1714644	1.3120462

(*g*+/*r*)-*o*,*p*′-DDD

E(DFT) = -2380.795340549 au
E(SCSMP2) = -2377.101392473 au

C	-0.3935251	-0.9379925	0.4495012
C	-1.1123615	-2.1781041	-0.1151230
H	-0.3407338	-1.1659290	1.5228894
H	-0.4619867	-3.0492667	-0.0718895
C	1.0572813	-0.8135385	-0.0054837
C	1.8399115	0.1740453	0.6059720
C	3.1812278	0.3394746	0.2793679
C	3.7540256	-0.5033350	-0.6722766
C	3.0021758	-1.4982875	-1.2892745
C	1.6575682	-1.6481145	-0.9505555
H	1.3871565	0.8365814	1.3393590
H	3.7786301	1.1105892	0.7532663
H	3.4593985	-2.1433870	-2.0314724
H	1.0795611	-2.4051178	-1.4700410
C	-1.2072725	0.3471106	0.3590280
C	-2.0411560	0.6536599	1.4462910
C	-2.8411001	1.7907503	1.4752840
C	-2.8156959	2.6737171	0.3974082
C	-1.9867906	2.4108580	-0.6881080
C	-1.1921809	1.2623498	-0.7066185
H	-3.4739729	1.9862478	2.3353221
H	-3.4294615	3.5695307	0.3997196
H	-1.9420761	3.0900782	-1.5324169
Cl	-0.1716501	1.0592118	-2.1092609
H	-2.0552576	-0.0333334	2.2872305
Cl	5.4371806	-0.3054810	-1.0951821
Cl	-1.6317525	-2.0169110	-1.8193743
Cl	-2.5371432	-2.6054067	0.9064377