

DFT Insights into JP-10 Tetrahydrodicyclopentadiene Fuel Properties

Dilip Rijal ¹, Vladislav Vasilyev ², Yunxia Yang ³, and Feng Wang ^{1,*}

¹ Department of Chemistry and Biotechnology, Swinburne University of Technology, Melbourne, Victoria 3122, Australia; drijal@swin.edu.au

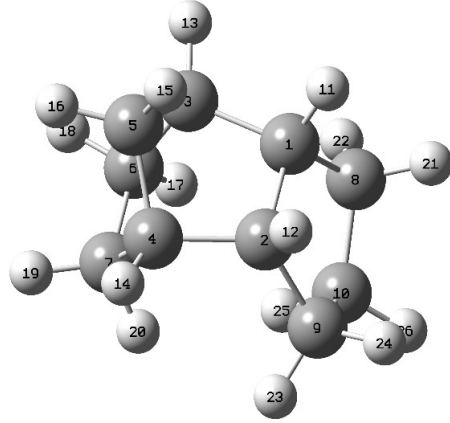
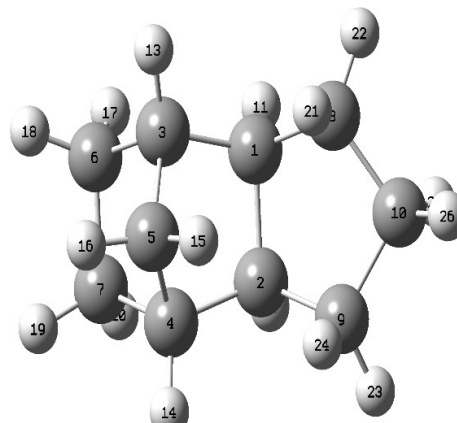
² National Computational Infrastructure, Australian National University, Canberra, ACT 0200, Australia; vvv900@nci.org.au

³ CSIRO Energy, 71 Normanby Road, Clayton North, Victoria 3169, Australia; Yunxia.Yang@csiro.au

* Correspondence: fwang@swin.edu.au

Supplementary Material

Table S1. Cartesian coordinates of exo-THDCPD and endo-THDCPD using B3LYP/aug-cc-pVTZ model.

Structure						
	Atom	X	Y	Z	X	Y
	Exo-THDCPD			Endo-THDCPD		
C	-0.36426	-0.78786	-0.51079	0.34737	-0.78632	-0.8723
C	-0.36426	0.78786	-0.51079	0.34737	0.78633	-0.8723
C	0.8857	-1.13226	0.32621	-1.03976	-1.13043	-0.27192
C	0.8857	1.13226	0.32621	-1.03976	1.13043	-0.27191
C	0.89875	0	1.37254	-1.8988	0.00001	-0.8758
C	2.13591	-0.78088	-0.5085	-1.10828	-0.78005	1.22867
C	2.13591	0.78088	-0.5085	-1.10828	0.78004	1.22867
C	-1.72707	-1.20584	0.07803	1.62242	-1.22071	-0.12183
C	-1.72707	1.20584	0.07803	1.62243	1.22071	-0.12182
C	-2.6453	0	-0.16663	2.08169	0	0.69789
H	-0.266	-1.1852	-1.52234	0.37124	-1.1736	-1.89185
H	-0.266	1.18521	-1.52234	0.37125	1.17361	-1.89184
H	0.88806	-2.14928	0.71728	-1.36268	-2.14703	-0.49429
H	0.88806	2.14928	0.71728	-1.36267	2.14703	-0.49428
H	0.03171	0	2.03203	-1.90821	0.00001	-1.96673
H	1.79852	0	1.9898	-2.92883	0.00001	-0.51436

H	2.08719	-1.20129	-1.51351	-0.2871	-1.20638	1.80227
H	3.03835	-1.17168	-0.03689	-2.03025	-1.1709	1.66121
H	3.03835	1.17168	-0.0369	-2.03024	1.17089	1.66122
H	2.08718	1.20129	-1.51351	-0.2871	1.20636	1.80228
H	-1.6377	-1.38597	1.15254	2.39405	-1.47882	-0.85038
H	-2.1059	-2.12626	-0.36754	1.47013	-2.10698	0.49643
H	-2.1059	2.12626	-0.36753	1.47014	2.10698	0.49643
H	-1.6377	1.38596	1.15255	2.39405	1.47882	-0.85038
H	-2.99012	0	-1.20438	1.60902	0	1.68006
H	-3.53223	0	0.46844	3.15874	0	0.87007

Table S2. Comparison of bond length, angles, and dihedrals of two isomers of THDCPD using B3PW91 and B3LYP functionals and aug-cc-pVTZ basis set.

Parameters	Endo-THDCPD		Exo-THDCPD		
	B3PW91	B3LYP	B3PW91	B3LYP	Experimental#
<u>Bond length (Å)</u>					
C7-C6	1.55	1.56	1.55	1.56	1.57
C3-C6	1.54	1.54	1.54	1.54	
C4-C5	1.54	1.54	1.54	1.54	1.55
C3-C5	1.54	1.54	1.54	1.54	
C1-C3	1.54	1.55	1.54	1.54	
C2-C4	1.54	1.55	1.54	1.54	1.55
C9-C2	1.54	1.54	1.54	1.54	1.55
C1-C8	1.54	1.54	1.54	1.54	
C9-C10	1.53	1.54	1.53	1.54	1.54
C8-C10	1.53	1.54	1.53	1.54	
C1-C2	1.57	1.57	1.57	1.58	1.58
C4-C7	1.54	1.54	1.54	1.54	1.55
<u>Bond angles (°)</u>					
< (2,1,3)	102.8503	102.8253	102.9273	102.8951	
< (2,1,8)	106.3465	106.362	105.6572	105.7245	
< (3,1,8)	119.0835	119.2685	116.4698	116.6255	
< (1,2,4)	102.8503	102.8252	102.9273	102.895	102.9
< (1,2,9)	106.3465	106.362	105.6572	105.7245	105.8
< (4,2,9)	119.0835	119.2684	116.4698	116.6254	
< (1,3,5)	100.6064	100.6021	102.1076	102.1838	
< (1,3,6)	111.2956	111.4762	108.0822	108.1733	
< (5,3,6)	100.9798	100.9302	101.1659	101.1242	
< (2,4,5)	100.6064	100.6021	102.1076	102.1839	102.2
< (2,4,7)	111.2956	111.4762	108.0822	108.1733	108.1
< (5,4,7)	100.9798	100.9302	101.1659	101.1243	101.1
< (3,5,4)	94.2479	94.2215	94.5525	94.5129	94.5
< (3,6,7)	103.1479	103.1296	103.1917	103.1563	
< (4,7,6)	103.148	103.1297	103.1917	103.1563	103.1
< (1,8,10)	106.2771	106.3967	104.66	104.7611	
< (2,9,10)	106.2771	106.3967	104.66	104.7611	104.7
< (8,10,9)	104.7296	104.8271	103.2438	103.5196	103.5

Dihedral angles (°)					
< (3,1,2,4)	0.0	0.0001	0.0	0.0	
< (3,1,2,9)	125.9077	126.1156	-122.6342	-122.8255	
< (8,1,2,4)	-125.9076	-126.1154	122.6342	122.8256	
< (8,1,2,9)	0.0	0.0	0.0	0.0001	
< (2,1,3,6)	-70.1642	-70.1283	-71.2613	-71.282	
< (8,1,3,5)	153.361	153.4969	-80.1604	-80.3038	
< (8,1,3,6)	47.043	47.1805	173.6756	173.5182	
< (2,1,8,10)	19.0252	18.6867	23.8143	23.3657	
< (3,1,8,10)	-96.338	-96.7651	137.3364	136.9746	
< (1,2,4,5)	-36.1539	-36.1884	-34.9027	-34.896	
< (1,2,4,7)	70.1641	70.1281	71.2613	71.2821	
< (9,2,4,5)	-153.361	-153.4971	80.1604	80.3036	
< (9,2,4,7)	-47.0431	-47.1806	-173.6756	-173.5182	
< (1,2,9,10)	-19.0252	-18.6867	-23.8143	-23.3659	
< (4,2,9,10)	96.3379	96.7649	-137.3364	-136.9746	-137.0
< (1,3,5,4)	-57.708	-57.7691	-55.2833	-55.2492	
< (6,3,5,4)	56.6674	56.7819	56.1803	56.3213	
< (1,3,6,7)	70.3555	70.3232	71.443	71.4612	
< (5,3,6,7)	-35.7173	-35.7786	-35.3761	-35.4525	
< (2,4,5,3)	57.7081	57.7692	55.2833	55.2492	
< (7,4,5,3)	-56.6673	-56.7818	-56.1803	-56.3212	
< (2,4,7,6)	-70.3556	-70.3234	-71.443	-71.4615	
< (5,4,7,6)	35.7172	35.7784	35.3761	35.4523	
< (3,6,7,4)	0.0	0.0001	0.0	0.0001	
< (1,8,10,9)	-30.8149	-30.2648	-38.7721	-38.0809	
< (2,9,10,8)	30.815	30.2648	38.7721	38.0809	38.00

Reference [1].

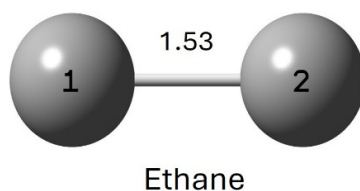


Figure S1. Optimized structure of Ethane using B3LYP/ aug-cc-pVTZ model.

Table S3. Comparison of bond length of Ethane with literature.

Bond	This work		Tamukong et al. ^a	Experimental ^b
	B3PW91	B3LYP	PW91/cc-pVTZ	
C-C	1.52	1.53	1.53	1.54
C-H	1.09	1.09	1.09	1.09

^a Reference [2], ^b Reference [3].

Table S4. Comparisons of ¹H-NMR of endo-and exo-THDCPD using B3LYP and B3PW91 functional and aug-cc-pVTZ basis set.

No.	Endo-THDCPD			Exo-THDCPD				Group
	This work		Exp	This work		Exp		
	B3LYP	B3PW91	#	B3LYP	B3PW91	#	@	
1-C	2.63	2.74	2.34	2.01	2.09	1.75	1.75	CH
2-C	2.63	2.74	2.34	2.01	2.09	1.75	1.75	CH
3-C	2.24	2.33	2.08	2.06	2.16	1.93	1.93	CH
4-C	2.24	2.33	2.08	2.06	2.16	1.93	1.93	CH
5-C	1.69,	1.80,	1.50,	1.55,	1.69,	1.31,	1.31,	CH2
	1.55	1.65	1.37	1.08	1.19	0.88	0.90	
6-C	1.64,	1.75,	1.42,	1.24,	1.79,	1.45,	1.45,	CH2
	1.48	1.57	1.27	1.68	1.33	1.05	1.05	
7-C	1.64,	1.75,	1.42,	1.24,	1.79,	1.45,1	1.45,	CH2
	1.48	1.57	1.27	1.68	1.33	.05	1.05	
8-C	1.82,	1.92,	1.49,	1.13,	2.12,	1.82,	1.82,	CH2
	1.71	1.80	1.43	2.03	1.23	1.90	0.90	
9-C	1.82,	1.92,	1.49,	1.13,	2.12,	1.82,1	1.82,	CH2
	1.71	1.80	1.43	2.03	1.23	.90	0.90	
10-C	1.72,	1.85,	1.60	1.43,	1.89,	1.59,	1.59,	CH2
	1.82	1.90		1.82	1.50	1.13	1.13	
RMSD ¹	0.24	0.34		0.32	0.38			
RMSD ²				0.31	0.31			

[#]Reference [4], and @= Reference [5]. RMSD¹ and RMSD² are RMSD in different functional with respect to experimental values from reference [4] and reference [5], respectively.

Root Mean Square Deviation (RMSD)

RMSD is a statistical measure used to quantify the difference between predicted values and experimental values in various fields [6], such as molecular dynamics, and machine learning. It provides a single value that represents the average magnitude of deviations, considering both direction and magnitude [6].

$$\text{RMSD} = \sqrt{\frac{1}{N} \sum (y_e - y_c)^2}$$

Where, N, represents the total number of data points, y_e denotes experimental values, and y_c refers to the calculated values obtained from DFT.

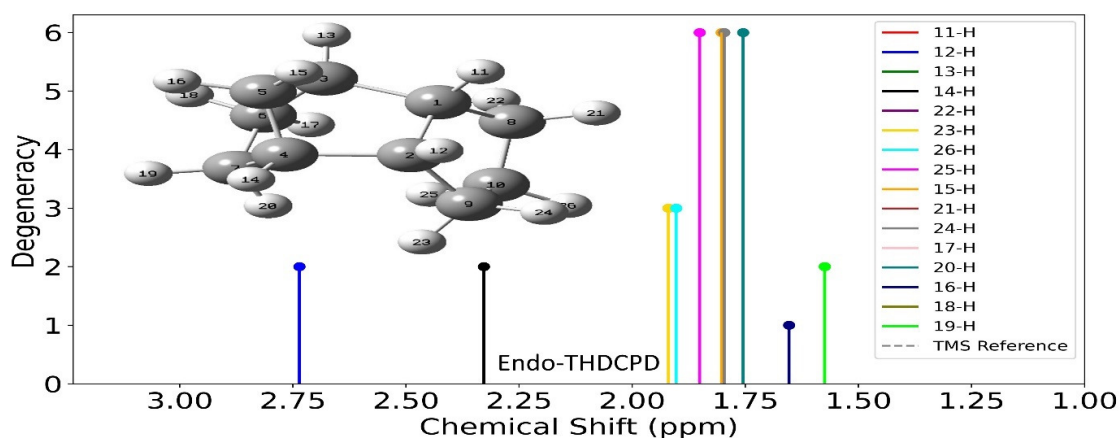


Figure S2. ^1H NMR spectra of endo-THDCPD using B3LYP/aug-cc-pVTZ model.

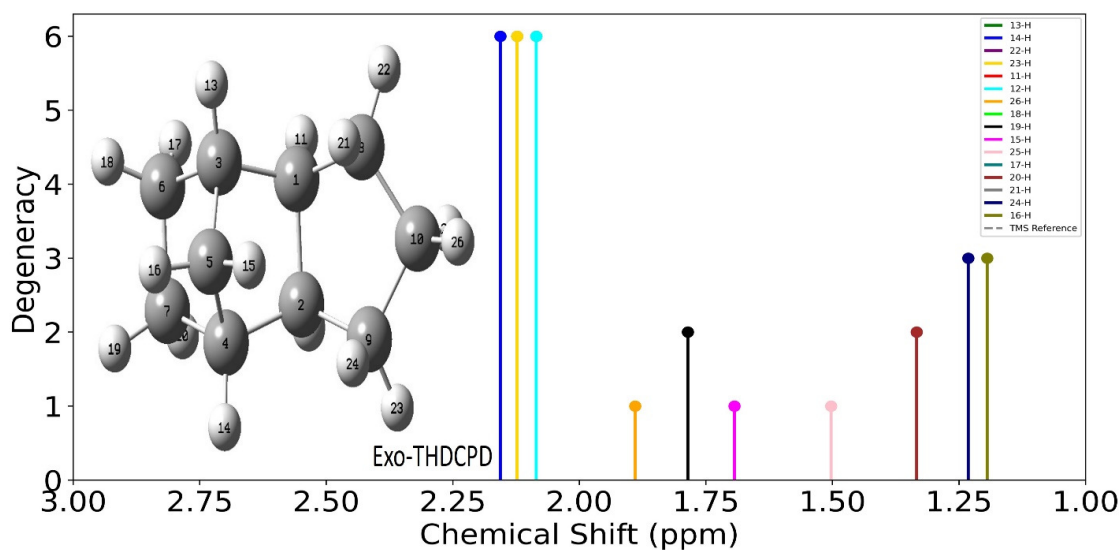


Figure S3. ^1H NMR spectra of exo-THDCPD using B3LYP/aug-cc-pVTZ model.

Table S5. Comparison of the calculated IR with the experimental values and those computed by Brotton et al. [7]

Mode	This work				Brotton et al.#		Exp#	Group
	Endo-THDCPD		Exo-THDCPD					
	Wave no.	IR intensity	Wave no.	IR intensity	Calculated Wave no.	Calculate IR intensity	IR wave no.	
1	147.74	0.0031	129.59	0.0112	140	0.009		Ring twist
2	211.56	0.033	173.78	0.0025	177	0.003		CCC bend
3	269.4	0.0533	263.18	0.0611	270	0.068		CCC bend
4	276.58	0.0003	312.93	0.0389	317	0.028		CH2 rock
5	379.01	0.1413	316.04	0.0597	319	0.046		Ring twist

6	446.92	0.1395	395	0.0300	398	0.043		CCC bend
7	453.82	0.4049	487.96	0.2171	495	0.237	513	CCC bend
8	504.31	0.0412	532.32	0.1819	534	0.180	528	Ring twist
9	621.98	0.999	553.57	0.6122	554	0.661	554	CCC bend
10	671.12	0.2373	670.66	0.6049	671	0.678	659	Ring Rock
11	700.59	0.3505	737.3	0.2657	739	0.369	733	Ring Rock
12	748.89	0.6538	751.9	0.3051	753	0.356	745	CC stretch
13	796.38	0.2246	789.85	1.3646	792	1.292	783	CC stretch
14	819.3	2.0647	827.91	0.5674	828	0.643	816	CH2 rock
15	824.25	0.0432	863.07	0.9359	864	0.067		CCC bend
16	846.1	1.8312	863.64	0.0148	865	1.181	855	CCC bend
17	868.48	0.6365	886.63	0.6299	889	0.626	883	CCC rock
18	884.37	1.3931	889.63	0.0935	894	0.116		CC stretch
19	896.63	0.8791	911.55	0.8145	913	0.882	907	Ring stretch
20	927.81	0.6213	916.27	0.0792	918	0.041		CH2 bend/ rock
21	937.72	0.2102	922.34	0.9963	926	1.102	918	CCC rock
22	962.39	1.6558	954.21	1.8651	955	2.044	945	Ring breathing
23	967.76	0.6346	959.32	0.0250	963	0.045		CC stretch
24	979.81	0.778	989.74	1.6094	992	1.882	980	CC stretch
25	984.64	0.0089	997.4	0.4842	999	0.806	988	CH2 bend
26	1034.8	0.4593	1041.1	0.2843	1041	0.206	1032	CH2 twist
27	1039.76	0.0089	1047.78	0.5064	1050	0.488		CH2 bend
28	1065.6	0.171	1051.44	0.0632	1052	0.083	1057	CH2 Rock
29	1082.19	0.0499	1052.53	0.0226	1054	0.001		CH2 bend
30	1119.39	0.5561	1072.41	0.5600	1073	0.780	1113	CH2 twist/rock
31	1133.91	0.0651	1135.58	0.1090	1138	0.097	1129	CH2 wag
32	1143.97	0.0355	1149.93	0.0121	1153	0.026		CH2 twist
33	1156.57	0.1079	1168.54	1.0196	1169	1.210	1144	CH2 twist
34	1180.63	0.2514	1193.45	0.2218	1193	0.188	1179	CH2 wag
35	1197.66	0.3915	1202.66	0.0797	1204	0.068		CH2 rock
36	1197.68	2.7961	1206.53	1.3851	1209	1.777	1186	CH2 bend
37	1237.29	1.0424	1224.88	1.2810	1227	1.564	1201	CH2 bend
38	1255.4	0.0011	1252.67	0.0080	1251	0.018		CH2 twist
39	1274.23	0.2512	1261.92	0.7642	1261	0.807	1233	CH2 twist
40	1283.65	0.9793	1289.88	1.2939	1289	1.3410	1254	CH2 wag
41	1307.35	0.0392	1304.13	0.0099	1301	0.0411		CH Wag
42	1307.62	0.1296	1306.59	0.2726	1306	0.1915	1270	CH2 wag
43	1321.31	1.207	1313.48	0.4400	1312	0.372		CH2 wag
44	1328.02	0.0181	1319.79	0.0039	1317	0.002		CH2 wag
45	1331.21	0.5822	1325.25	0.0868	1327	0.051	1277	CH2 wag
46	1340.23	0.8785	1331.83	1.0542	1331	1.908	1297	CH2 wag
47	1342.49	0.1173	1343.01	0.8331	1343	0.680	1310	CH wag
48	1366.12	1.3066	1350.63	1.0280	1349	0.982	1318	CH2 wag
49	1366.85	0.5198	1365.83	0.8085	1367	1.003	1330	CH2 wag

50	1375.02	0.1994	1370.31	0.4723	1372	0.514		CH2 twist
51	1490.24	1.8974	1492.34	0.1321	1492	0.776		CH wag
52	1497.1	0.3332	1494.31	3.9162	1494	2.166		CH2 rock
53	1500.11	5.3637	1495.11	0.0381	1496	1.794		CH2 rock
54	1503.65	5.1139	1501.31	6.6095	1503	6.403	1456	CH2 scissor
55	1511.86	12.2165	1512.33	9.5737	1514	11.009	1468	CH2 scissor
56	1529.58	6.8735	1522.83	3.6302	1526	4.457	1475	CH2 rock
57	3019.35	6.762	3014.65	17.9456	3016	20.073	2865	CH stretch
58	3022.52	14.5703	3019.34	29.4780	3021	30.463		CH stretch
59	3032.91	37.3653	3022.82	23.2461	3024	22.102		CH stretch
60	3034.3	50.2988	3027.67	1.3577	3030	1.097		CH2 stretch
61	3037.09	7.4811	3033.03	24.2137	3034	25.961		CH2 stretch
62	3041.29	36.1885	3041.19	19.2674	3042	58.93	2913	CH2 stretch
63	3048.62	16.9264	3042.97	80.4039	3044	12.198		CH2 stretch
64	3050.07	74.7016	3045.05	36.1319	3046	66.233		CH2 stretch
65	3058.09	35.3736	3061.59	6.9724	3065	6.172		CH2 stretch
66	3060.96	10.6934	3065.98	46.1525	3068	46.085		CH stretch
67	3069	116.2959	3068.82	24.3223	3071	38.453		CH stretch
68	3076.26	35.5502	3070.07	116.0290	3073	104.144	2942	CH stretch
69	3077.58	7.5972	3074.72	43.1047	3077	49.579		CH stretch
70	3077.61	26.5231	3077.56	14.5695	3080	9.511		CH stretch
71	3082.16	110.0539	3084.74	96.9839	3087	85.784		CH2 stretch
72	3095.14	41.5043	3089.36	39.4086	3088	61.510		CH2 stretch

*B3LYP/def2-TZVP Reference [7].

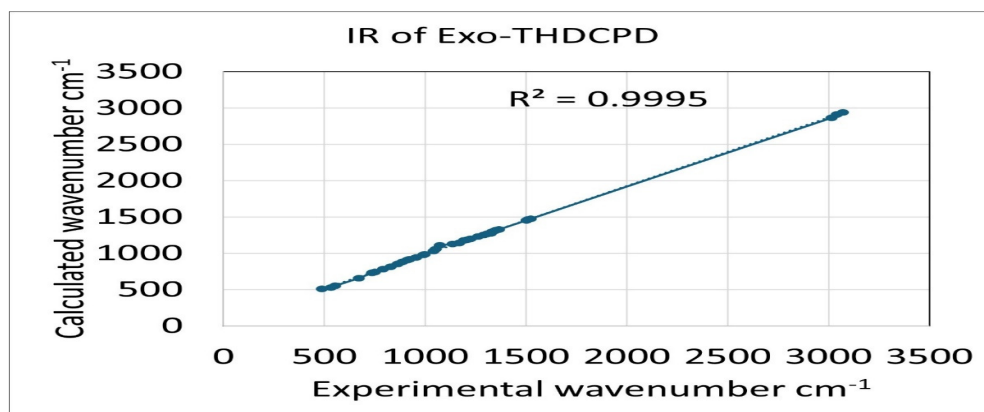


Figure S4. Comparison of the calculated IR wavenumbers of exo-THDCPD using B3LYP/aug-cc-pVTZ model with the experiment.

Formula to calculate reactivity parameters (descriptors) [8]

$$\text{Electronegativity } (\chi) = -\mu = \frac{(I+A)}{2}$$

$$\text{Chemical potential } (\mu) = -\chi$$

$$\text{Hardness } (\eta) = \frac{(I-A)}{2}$$

$$\text{Softness } (\sigma) = \frac{1}{\eta}$$

$$\text{Electrophilicity index } (\psi) = \frac{\mu^2}{2\eta}$$

Where Ionization potential (I) = -E_{HOMO} and Electron affinity (A) = -E_{LUMO}

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