Electronic Supplementary Material (ESI) for Faraday Discussions

Supporting Information for: Between Ethylene and Polyenes - The Non-adiabatic Dynamics of *cis*-dienes

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1 Vibrational Frequencies

Ground state harmonic vibrational frequencies for cyclopentadiene (CPD) and 1,2,3,4-tetramethylcyclopentadiene (Me_4-CPD) were calculated at the MP2/6-31G** level of theory in MOLPRO 2006.1[?] and are tabulated in Table 1.

Symmetry	CPD	Me_4-CPD
a_1	815, 961, 1052, 1154, 1444, 1470 1580, 3116, 3296, 3320	261, 288, 564, 706, 929, 1001 1156, 1288, 1401, 1458, 1470, 1477 1548, 1555, 1681, 3094, 3109, 3118 3220, 3229
a_2	502, 701, 902, 1142	88, 104, 133, 299, 560, 1037 1076, 1168, 1529, 1537, 3180, 3190
b_1	329, 682, 927, 941, 3164	101, 152, 161, 253, 420, 878 1073, 1091, 1535, 1544, 3141, 3180 3193
b_2	817, 1006, 1137, 1301, 1353, 1654 3287, 3314	298, 474, 558, 807, 1003, 1128 1174, 1211, 1383, 1457, 1462, 1542 1551, 1729, 3109, 3115, 3220, 3228

Table 1: Harmonic vibrational frequencies of CPD and Me_4-CPD for the four irreducible representations of the C_{2v} point group. Underlined frequencies indicate in-plane modes of the carbon skeleton.

2 Geometries

The ground state geometry of CPD was optimized at the MP2/6-31G** level of theory in MOLPRO 2006.1. The minimum energy conical intersections (MECI) were located either using the CIOpt code[?] or a locally modified version of MOLPRO at the MS-MR-CAS(4,4)PT2/6-31G** level of theory. The geometries can be found in Tables 2-6.

Atom	x	y	z
C	0.00000000	0.00000000	1.23323055
C	0.00000000	1.17806461	0.30358605
C	0.00000000	-1.17806461	0.30358605
C	0.00000000	-0.73254058	-0.97593469
C	0.00000000	0.73254058	-0.97593469
H	-0.87748432	0.00000000	1.88865115
H	0.87748432	0.00000000	1.88865115
H	0.00000000	2.20811211	0.62931865
H	0.00000000	-2.20811211	0.62931865
H	0.00000000	-1.34854889	-1.86459620
H	0.00000000	1.34854889	-1.86459620

Table 2: Ground state geometry of CPD in Angstrom.

Atom	x	y	z
C	-0.23730546	-0.04577135	1.33327123
C	0.13883119	1.07657060	0.35601549
C	0.16316254	-1.08357495	0.35137564
C	-0.48914022	-0.74985848	-0.97449042
C	-0.09569026	0.60173652	-0.97610231
H	-1.31303360	-0.06579692	1.53698164
H	0.33933679	-0.03681779	2.25528393
H	0.75663581	1.91786812	0.63421262
H	1.20129210	-1.43062834	0.37528276
H	-0.50868202	-1.39862739	-1.83601714
H	0.04459313	1.21489997	-1.86053296

Table 3: Geometry of the *eth*1-MECI in Angstrom.

Atom	x	y	z
C	-0.23620551	-0.03207978	1.29125179
C	0.21582432	1.01131434	0.36228091
C	0.11640985	-1.32558190	0.40632655
C	-0.23408547	-0.75547666	-0.97284483
C	-0.04860828	0.63283254	-1.00698991
H	-1.32302094	-0.02096105	1.40429375
H	0.24082002	-0.01010282	2.27000071
H	0.81822513	1.87379746	0.64401037
H	1.21946438	-1.33616823	0.42728585
H	-0.62227376	-1.35541845	-1.79093671
H	-0.14654973	1.31784456	-1.83939801

Table 4: Geometry of the *eth*2-MECI in Angstrom.

Atom	x	y	z
C	0.25713622	-0.01442850	1.31801782
C	-0.03924662	1.20976308	0.38599465
C	-0.19788299	-1.03157333	0.36288968
C	0.33641277	-0.70647949	-0.99902448
C	0.14729280	0.65582405	-0.99552032
H	-0.28284651	0.00837780	2.26122051
H	1.33511273	-0.08608677	1.49161179
H	-1.01754194	1.65218608	0.57776688
H	-1.12155174	-1.59606883	0.49969376
H	0.42510071	-1.38397407	-1.83247823
H	0.15801458	1.29245998	-1.87489159

Table 5: Geometry of the *dis*-MECI in Angstrom.

Atom	x	y	z
C	-0.22231217	0.00005503	1.29520997
C	0.17370508	1.09437066	0.34548772
C	0.17364066	-1.09486610	0.34554249
C	-0.17901085	-0.69878322	-1.00725516
C	-0.17839447	0.69854745	-1.00740104
H	-1.30292966	-0.00116207	1.50480849
H	0.33144770	0.00104405	2.23169011
H	0.90856361	1.85301554	0.59477020
H	0.91003643	-1.85208017	0.59409511
H	-0.30909945	-1.36200547	-1.85063405
H	-0.30564688	1.36186432	-1.85103338

Table 6: Geometry of the S_2S_1-MECI in Angstrom.

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