

Supporting Information for the Manuscript :

Cationic MethylenePyrene Isomers and Isomerization Pathways: Finite Temperature Theoretical Studies

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Table S1 : Harmonic B3LYP/6-31G(d,p) and DFTB spectra for both isomers $PyrCH_2^+$ and $PyrC_7^+$ (positions in cm^{-1} and intensities in km/mol). All normal modes (even inactive) are reported. The most intense modes differentiating the two isomers are reported in bold characters.

B3LYP				DFTB			
$PyrCH_2^+$		$PyrC_7^+$		$PyrCH_2^+$		$PyrC_7^+$	
pos.	I	pos.	I	pos.	I	pos.	I
63.	1.3	72.	0.6	64.	1.2	61.	0.5
102.	0.4	84.	0.0	94.	0.3	64.	0.0
178.	0.0	192.	0.0	165.	0.2	168.	0.0
200.	8.9	209.	0.8	187.	7.6	183.	0.1
257.	0.4	218.	8.3	237.	0.1	204.	7.7
293.	0.5	327.	1.0	267.	0.5	321.	0.0
294.	0.8	358.	0.0	297.	0.1	332.	0.3
393.	4.6	369.	1.0	375.	0.4	333.	0.9
407.	0.5	372.	0.1	400.	2.1	375.	0.0
417.	3.0	408.	0.1	421.	1.7	412.	0.2
455.	1.1	470.	0.7	440.	0.5	456.	0.0
471.	0.4	477.	2.7	457.	0.4	465.	0.3
491.	0.6	494.	0.0	460.	1.0	477.	0.2
501.	1.4	500.	0.2	496.	0.6	487.	1.6
520.	1.7	531.	0.8	500.	0.1	499.	0.7
540.	0.8	538.	0.5	531.	0.4	542.	0.1
540.	0.2	570.	1.4	548.	0.3	551.	0.0
598.	2.0	590.	0.0	573.	3.2	632.	1.9
606.	5.5	622.	1.1	594.	3.5	650.	0.4
630.	3.1	702.	0.1	668.	0.9	668.	21.8
693.	0.1	703.	29.3	685.	0.7	672.	0.0

Table S1 (continued)

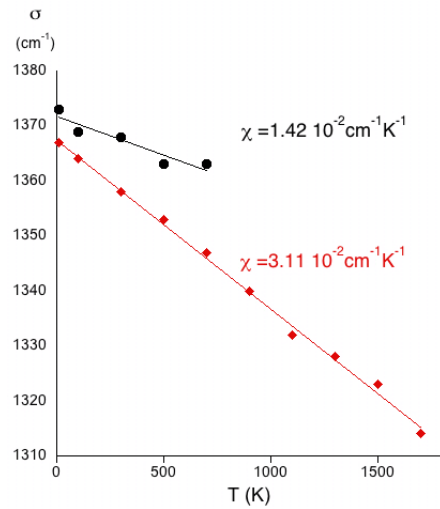
B3LYP		DFTB		B3LYP		DFTB	
$PyrCH_2^+$		$PyrC_7^+$		$PyrCH_2^+$		$PyrC_7^+$	
pos.	I	pos.	I	pos	I	pos	I
715.	0.2	727.	0.1	699.	7.5	720.	4.7
718.	2.5	747.	0.1	713.	0.6	745.	0.2
732.	10.0	763.	5.4	736.	2.1	754.	0.3
783.	0.7	788.	2.8	743.	0.2	761.	0.2
785.	3.6	821.	0.0	778.	0.6	795.	0.0
814.	2.2	836.	0.4	796.	0.9	797.	0.6
829.	4.4	837.	0.0	799.	0.2	826.	67.5
831.	1.0	874.	1.1	816.	14.9	853.	0.3
866.	22.0	882.	101.9	829.	42.3	873.	0.0
887.	65.1	928.	0.0	859.	1.1	879.	0.3
906.	0.5	940.	0.7	876.	26.1	886.	0.0
962.	0.5	955.	0.0	889.	0.2	910.	0.2
981.	3.3	999.	0.3	905.	0.1	915.	0.0
992.	4.1	1000.	8.0	912.	0.0	918.	0.2
1001.	3.0	1007.	0.0	914.	0.0	943.	0.0
1003.	5.2	1021.	1.3	918.	0.1	948.	0.8
1008.	8.4	1032.	1.3	972.	0.6	1006.	0.1
1019.	14.4	1047.	0.0	1009.	1.9	1082.	7.0
1022.	3.3	1057.	0.0	1075.	5.5	1132.	1.7
1104.	0.8	1125.	0.1	1134.	0.1	1145.	0.0
1146.	4.6	1151.	0.7	1150.	4.1	1153.	0.0

Table S1 (continued)

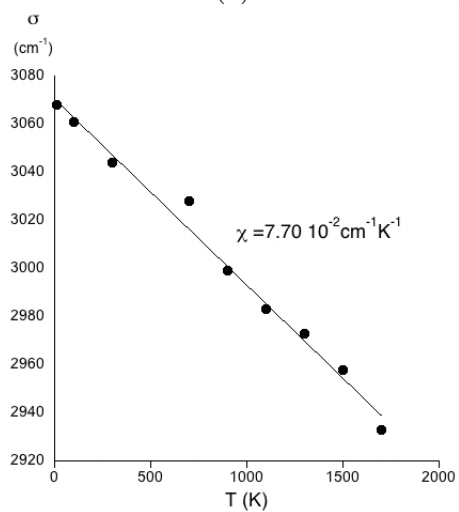
B3LYP				DFTB			
$PyrCH_2^+$		$PyrC_7^+$		$PyrCH_2^+$		$PyrC_7^+$	
pos.	I	pos.	I	pos	I	pos	I
1158.	6.7	1188.	5.2	1152.	8.4	1170.	7.2
1182.	25.1	1191.	6.8	1159.	8.4	1187.	4.3
1198.	2.3	1210.	2.5	1182.	2.6	1208.	1.0
1220.	0.2	1238.	13.6	1208.	1.2	1249.	0.6
1233.	43.0	1243.	137.7	1234.	3.4	1253.	7.7
1256.	22.8	1268.	1.4	1271.	1.4	1276.	8.3
1268.	104.3	1283.	1.6	1284.	4.1	1277.	0.5
1281.	55.9	1292.	79.0	1329.	4.8	1329.	1.7
1344.	52.3	1317.	14.7	1368.	48.9	1362.	71.9
1381.	8.7	1371.	18.4	1440.	4.0	1465.	2.7
1401.	72.3	1404.	0.1	1470.	17.3	1466.	0.1
1411.	116.5	1415.	39.1	1504.	11.6	1513.	30.6
1438.	15.0	1444.	18.0	1537.	18.0	1516.	4.1
1448.	36.5	1470.	1.2	1582.	42.2	1575.	7.5
1467.	14.1	1470.	0.0	1594.	198.6	1580.	202.4
1477.	19.7	1482.	2.8	1613.	135.2	1622.	22.7
1494.	15.6	1520.	39.0	1646.	49.8	1657.	167.4
1523.	45.2	1534.	265.9	1661.	21.6	1666.	7.2
1544.	6.5	1536.	1.7	1692.	8.8	1677.	10.0
1575.	94.0	1576.	12.6	1726.	96.9	1701.	108.5
1614.	113.4	1593.	12.2	1748.	87.5	1762.	10.6
1626.	77.2	1630.	20.6	1775.	10.6	1786.	2.3
1635.	24.6	1641.	56.2	1788.	74.2	1797.	45.3

Table S1 (continued)

B3LYP		DFTB		B3LYP		DFTB	
$PyrCH_2^+$		$PyrC_7^+$		$PyrCH_2^+$		$PyrC_7^+$	
pos.	I	pos.	I	pos	I	pos	I
1655.	395.4	1671.	12.0	1821.	272.4	1819.	0.1
1674.	63.0	1675.	22.7	1826.	191.4	1831.	23.2
3183.	1.5	3181.	0.2	3029.	1.6	3016.	7.4
3200.	0.0	3184.	0.2	3051.	3.8	3017.	1.4
3201.	0.1	3197.	1.6	3052.	3.4	3047.	3.5
3203.	0.0	3202.	0.0	3053.	2.0	3052.	6.0
3204.	0.3	3204.	0.1	3054.	0.9	3053.	0.3
3205.	0.9	3205.	0.0	3055.	2.0	3053.	0.0
3215.	0.8	3208.	0.8	3064.	7.2	3056.	0.3
3219.	1.6	3208.	0.7	3067.	5.1	3058.	8.4
3227.	1.4	3220.	3.1	3067.	4.0	3066.	6.0
3231.	1.3	3220.	0.1	3077.	4.4	3067.	4.2
3278.	0.1	3227.	1.4	3162.	0.9	3080.	4.8



(a)



(b)

Figure S1: Positions of the δ_{CH} (a) and ν_{CH} (b) modes as a function of T for PyrCH_2^+ (black) and PyrC_7^+ (red). The values determined for the χ factors are also reported.