M-XYLYLENE

The photochemistry of *m*-xylylene **2** has been studied by Sander[1] and, as might be anticipated, it's fascinating! Flash vapor pyrolysis of **1** produces **2**. Photolysis of **2** at wavelengths above 400nm gives **3** and **4**, while photolysis at 254 nm gives **5**. These are products are novel strained hydrocarbons. Confirmation of their structures was obtained by comparing their experimental IR spectra with that computed at B3LYP/6-311G(d,p). Table 1 compares the experimental and computed IR absorptions for **2-5**. Note in particular the fine agreement between the two, especially the predicted changes due to i>d_4 substitution for all the phenyl positions.

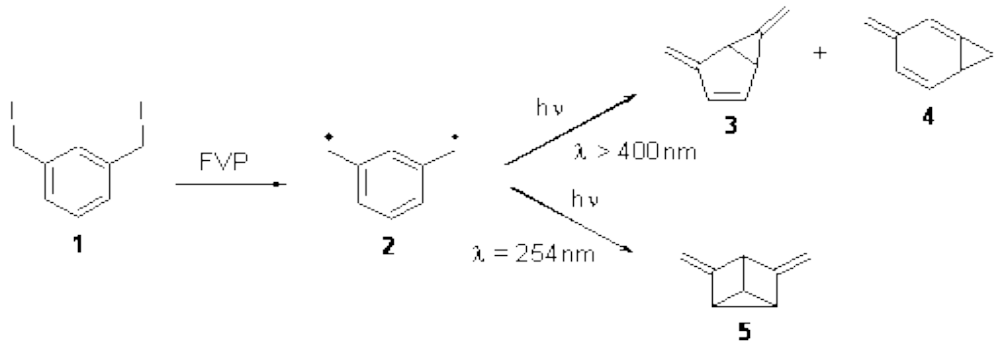
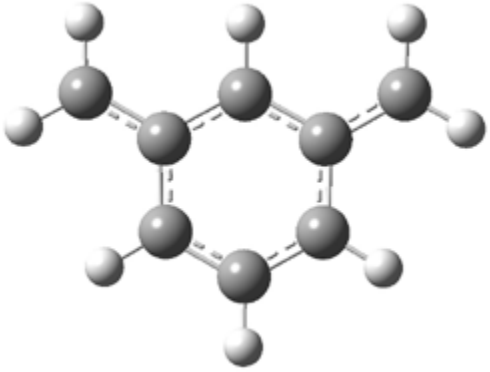


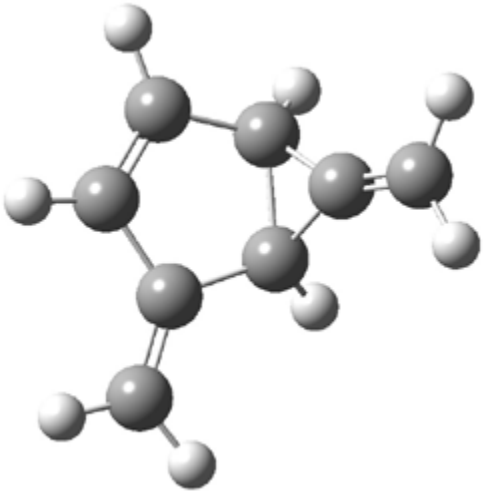
Table 1. Experimental and Calculated vibrational frequencies (cm^{-1}) of **2-5**.[1]

Mode	ν (expt)	ν (calc)	ν (expt)	ν (calc)
	2		**2-d_4**	
11	640.5	655.0	645.6	661.3
12	723.9	721.0	581.0	576.5
15	766.4	777.0	759.1	772.6
16	834.9	849.0	831.4	847.3
	3		**3-d_4**	
11	733.6	757.8	681.1	698.8
16	869.9	899.9	808.1	822.2
17	883.2	915.3	703.4	726.5
33	1640.6	1696.4	1614.4	1658.8
	4		**4-d_4**	
10	706.6	715.8	627.1	633.9
11	757.4	770.8	689.7	702.3
15	874.2	896.6	763.5	784.2
23	1065.2	1082.7	1001.4	1017.5
	5		**5-d_4**	
10	742.9	764.2	660.5	676.4
16	851.7	876.4	787.2	797.5
17	852.9	880.1	789.8	799.9
33	1678.6	1747.1	166.2	1709.7
34	1683.8	1758.7	1669.2	1719.9

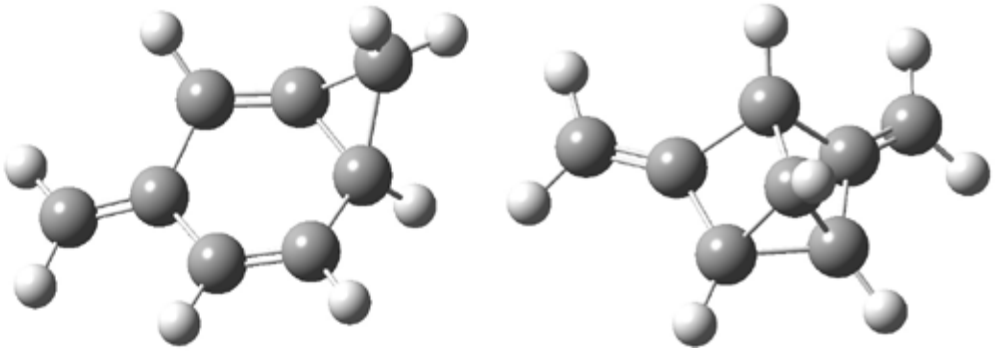
The computed structures of **2-5** and their relative energies are shown in Figure 1. Triplet **1** is the lowest energy isomer, with the singlet-triplet gap of 6.22 kcal mol^{-1}. This compares with recent high-level computations which give a value of 13.8 kcal mol^{-1}. [2] The other structures are much higher in energy. These other isomers have unusual bonding environments – **3** contains the strained methylenecyclopropane group, **4** is an anti-Bredt compound, and **5** is a very strained tricycle. These compounds can only be prepared by the application of light to provide the energy needed for their creation.



2
Triplet 0.0
Singlet 6.22



3
19.20



4
25.74

5
48.64

Figure 1. B3LYP/6-311G(d,p) optimized structures of **2-5** and their relative energies (kcal mol^{-1}).[1]

Source: http://comporgchem.com/blog/?p=65