

Supplementary Material

Evidence for widespread torsion–vibration interaction in substituted toluenes

Jason R. Gascooke^A and *Warren D. Lawrance*^{A,*}

^ACollege of Science and Engineering, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia

*Correspondence to: Email: warren.lawrance@flinders.edu.au

Extracting F_{Methyl} from experimental F values

When comparing the results of quantum chemistry structure optimisations with experimental constants, our focus is on the methyl group structure and the extent to which this varies among the set of substituted toluenes considered. In this context, F_{Methyl} values are extracted from the reported F constants, using Eqn 5a for the G_6 case or Eqn 5b for G_{12} , where the equation numbering matches the paper:

$$F_{Methyl} = \frac{1}{2} \left(F \pm \sqrt{F^2 - 4F(A \cos^2 \theta + B \sin^2 \theta)} \right) \quad (5a)$$

$$F_{Methyl} = F - G_{Frame} \quad (5b)$$

Here A and B are the usual rotational constants for the molecule, θ is the angle between the frame-methyl bond and the principal a axis and, in the G_{12} case where $\theta = 0^\circ$ or 90° , G_{Frame} corresponds to the rotational constant for rotation of the frame about the a or b axis respectively. These equations show that, in addition to F , the conversion to F_{Methyl} requires rotational constants and the angle of the methyl-frame bond to the a -axis. The constants required for the conversions are provided in the following tables.

In the case of S_0 , most of the molecules considered here have experimentally determined rotational constants, although θ values are not widely reported. For S_1 , there are considerably fewer experimental rotational constants whereas for D^+ there are no rotational constants reported. Where experimental rotational constants are not available, calculated values associated with the optimised quantum chemistry structures must necessarily be used. Given that θ values are not widely reported, the values used to convert from F to F_{Methyl} must generally be determined from optimised quantum chemistry structures. In fact, so few θ values are available, and where they are, the values from the optimised structures provide a good match with experiment, we have used the calculated values throughout. For example, for *trans-m*-methylanisole and *cis-m*-methylanisole, the experimental values are 33.1 and 51.7° respectively (see Fit III in Ferres *et al.* 2018^[1]), whereas the calculated values are 32.8 and 52.0° respectively.

Computed rotational constants and θ values are provided in Tables S1–S4 and, where experimental values have been reported, they are included in the tables for comparison. Tables S1 and S2 give the S_0 values calculated using the MP2 cc-pVTZ and DFT B3LYP cc-pVTZ quantum chemistry approaches, respectively, Table S3 shows the values for the molecules considered in S_1 (TD DFT B3LYP cc-pVTZ) and Table S4 gives those for D^+ (DFT B3LYP cc-pVTZ). The two quite different computational approaches were used for S_0 in order to test

the robustness of the computed F_{Methyl} values and their variation with substituent and its position on the ring. The Methods section of the paper gives details of the calculations. Note that, although there is considerable overlap in the molecules considered in the three electronic states, in many cases data are only available for a particular molecule for one or two of the electronic states. As there are comparatively few measurements of the S_1 rotational constants for the molecules considered, we have included in Table S3 a number of cresols deuterated at the O–H position, i.e. O–D, to give further insights into the likely differences between the observed and calculated rotational constants, although F values are not available for these deuterated isotopologues.

The tables show that the differences between the observed and calculated rotational constants are small: for S_0 , the A, B and C root mean square (RMS) percentage differences are 0.70, 0.47 and 0.42% respectively, for the MP2 cc-pVTZ calculations and 0.77, 0.33 and 0.35% respectively, for DFT B3LYP cc-pVTZ, whereas for S_1 they are 1.10, 0.91 and 0.92% respectively. These S_0 RMS values exclude *m*-toluidine, which shows significantly larger differences (see Tables S1 and S2).

To ascertain the errors introduced to the experimental F_{Methyl} values by using computed constants in Eqn 5a (or Eqn 5b for G_{12}) when experimental values are not available, F_{Methyl} values have been determined from experimental F values using both the experimental and computed rotational constants. The values are compared in Tables S5 and S6. The comparison reveals that the computed optimised structures are sufficiently accurate that the uncertainty introduced into the F_{Methyl} values is negligible when using computed versus experimental rotational constants. For S_0 , the average difference between the two is $0.0005 \pm 0.0008 \text{ cm}^{-1}$ for MP2 cc-pVTZ and $0.0008 \pm 0.0010 \text{ cm}^{-1}$ for DFT B3LYP cc-pVTZ, whereas for S_1 the difference is $0.0005 \pm 0.0016 \text{ cm}^{-1}$. The uncertainties correspond to \pm one standard deviation. There are no data available to compare the cation structures, but the uncertainties are likely to be similar to those for the S_0 and S_1 cases. The experimental F values are typically specified to two decimal places, so the uncertainties associated with using calculated constants are much smaller than typical experimental uncertainties.

Table S1. Rotational constants and θ values for substituted toluenes in the ground electronic state, S_0 , calculated using the MP2 cc-pVTZ combination of theory and basis set.

Molecule	Ref.	A^A (MHz)			B^A (MHz)			C (MHz)			θ ($^\circ$)
		Exp.	Comp.	% Diff.	Exp.	Comp.	% Diff.	Exp.	Comp.	% Diff.	
Toluene	[2]	5730	5756.2	-0.46	2518	2529	-0.44	1749	1757	-0.45	0
<i>o</i> -Fluorotoluene	[3]	3243	3265.8	-0.7	2181	2186	-0.23	1314	1320	-0.42	28.9
<i>m</i> -Fluorotoluene	[4]	3715	3662.9	1.41	1767	1768	-0.1	1198	1201	-0.32	30
<i>p</i> -Fluorotoluene	[5,6]	5702	5737.2	-0.61	1430	1433	-0.22	1144	1147	-0.29	0
<i>m</i> -Chlorotoluene (^{35}Cl)	[7]	3373	3340.9	0.96	1195	1194	0.07	882.5	884.7	-0.25	42.5
<i>p</i> -Chlorotoluene (^{35}Cl)	[8]	5711	5740.6	-0.52	968.2	970	-0.18	827.9	829.8	-0.23	0
<i>o</i> -Tolunitrile	[9]	2893	2920.9	-0.97	1500	1498	0.14	993.5	996.3	-0.28	52.1
<i>m</i> -Tolunitrile	[10]	3332	3315	0.5	1203	1198	0.4	883.9	884.9	-0.11	42.4
<i>p</i> -Tolunitrile			5726.6			980.5			837.2		0
<i>m</i> -Ethynyltoluene (3-Methylphenylacetylene)	[11]	3330	3299.1	0.94	1197	1196	0.08	880.4	882.4	-0.23	43.4
<i>trans-o</i> -Cresol	[12]	3274	3301	-0.83	2196	2202	-0.27	1325	1332	-0.48	27.8
<i>cis-o</i> -Cresol	[12]	3250	3272.3	-0.7	2202	2209	-0.33	1324	1330	-0.46	28.5
<i>trans-m</i> -Cresol	[13]	3661	3667.8	-0.18	1797	1806	-0.46	1215	1219	-0.36	29.5
<i>cis-m</i> -Cresol	[13]	3666	3678.1	-0.33	1793	1800	-0.37	1213	1218	-0.35	29.3
<i>p</i> -Cresol	[14]	5495	5525.7	-0.57	1457	1462	-0.32	1160	1164	-0.35	0.9
<i>o</i> -Toluidine ^B	[15]	3230	3261.3	-0.96	2189	2194	-0.25	1317	1324	-0.57	29
<i>m</i> -Toluidine ^B	[15]	3503	3651.6	-4.24	1924	1797	6.6	1210	1215	-0.38	29.6
<i>p</i> -Toluidine ^B	[16]	5656	5685.8	-0.52	1452	1457	-0.34	1157	1161	-0.4	0.8
<i>trans-o</i> -Methylanisole	[17]	2489	2501.5	-0.49	1558	1573	-0.95	970.5	977.3	-0.7	69.6
<i>trans-m</i> -Methylanisole	[1]	3522	3557.2	-1	1122	1128	-0.6	862.1	865.8	-0.43	32.8
<i>cis-m</i> -Methylanisole	[1]	2755	2758.4	-0.11	1291	1307	-1.21	890.9	896.7	-0.65	52
<i>p</i> -Methylanisole	[18]	4785	4795.1	-0.22	983.6	991.3	-0.78	824.7	830	-0.63	7.1
<i>trans-m</i> -Methylthioanisole			3057			869.1			682.5		36.9
<i>trans-m</i> -Methylstyrene			3527.6			1132			861.5		34.9
<i>cis-m</i> -Methylstyrene			2842.4			1278			886.4		50.8
<i>p</i> -Methylstyrene	[19]	4970	4962.3	0.15	980.3	984.8	-0.46	822.7	825.9	-0.39	6.5
<i>p</i> -Methylbenzaldehyde	[20]	4986	5018.7	-0.65	987.8	987.8	0.01	826.9	829.6	-0.32	6.7

For G_{12} molecules, the methyl axis lies parallel to the a or b axis and a respective value for θ of 0° or 90° is shown. The experimental rotational constants are shown (to one decimal place) where they are available. The percentage differences between the experimental and computed values

are shown for each constant:

$$\text{Percentage difference} = 100 \times \frac{(\text{Expt} - \text{Calc})}{\text{Expt}}$$

^A For G₁₂ molecules, the methyl axis lies parallel to either the *a* or *b* axis. In this case, the corresponding constant, *A* or *B*, respectively corresponds to that of the frame alone and is usually denoted *A_F* or *B_F*. The computed rotational constants are for the optimised lowest energy methyl configuration.

^BIn the S₀ state, toluidines are not strictly planar as the amino group hydrogen atoms tilt out of plane. However, due to the low H mass, these molecules are well approximated as planar for the purposes of these comparisons. Tan and Pratt assumed *p*-toluidine to be of effectively G₁₂ symmetry in their analysis of the rotational structure.^[16]

Table S2. As for Table S1, for constants calculated using the DFT B3LYP cc-pVTZ combination of theory and basis set.

Molecule	A^A (MHz)		B^A (MHz)		C (MHz)		θ (°)
	Comp.	% Diff.	Comp.	% Diff.	Comp.	% Diff.	
Toluene	5781.3	-0.9	2527.6	-0.4	1758.6	-0.55	0
<i>o</i> -Fluorotoluene	3258	-0.46	2187.4	-0.32	1319.3	-0.38	29
<i>m</i> -Fluorotoluene	3669.6	1.23	1767.3	-0.04	1201.6	-0.34	29.9
<i>p</i> -Fluorotoluene	5758	-0.98	1431.6	-0.09	1146.5	-0.26	0.8
<i>m</i> -Chlorotoluene (^{35}Cl)	3343.8	0.88	1188.1	0.61	881.4	0.13	42.5
<i>p</i> -Chlorotoluene (^{35}Cl)	5767.7	-1	964.1	0.42	826	0.23	0
<i>o</i> -Tolunitrile	2890.3	0.09	1510.3	-0.66	998	-0.45	53.5
<i>m</i> -Tolunitrile	3321.3	0.31	1203.5	-0.04	888.2	-0.49	42.3
<i>p</i> -Tolunitrile	5748		983.9		840.1		0
<i>m</i> -Ethylnyltoluene (3-Methylphenylacetylene)	3307	0.7	1199.4	-0.22	885	-0.52	43.1
<i>trans-o</i> -Cresol	3286.3	-0.38	2206.8	-0.48	1331	-0.42	28.1
<i>cis-o</i> -Cresol	3265.8	-0.5	2211.4	-0.42	1329.4	-0.44	28.6
<i>trans-m</i> -Cresol	3678.9	-0.48	1804.4	-0.41	1219.7	-0.42	29.3
<i>cis-m</i> -Cresol	3683.1	-0.47	1800.9	-0.42	1218.6	-0.43	29.2
<i>p</i> -Cresol	5546.4	-0.94	1460.1	-0.22	1164.2	-0.34	0.7
<i>o</i> -Toluidine ^B	3243.8	-0.42	2199.3	-0.48	1322.9	-0.45	29.5
<i>m</i> -Toluidine ^B	3659.6	-4.47	1797.2	6.57	1215.6	-0.44	29.4
<i>p</i> -Toluidine ^B	5708.2	-0.92	1455.3	-0.23	1160.9	-0.36	0.6
<i>trans-o</i> -Methylanisole	2502	-0.51	1557.7	0	971.6	-0.11	70.2
<i>trans-m</i> -Methylanisole	3557.1	-1	1121.2	0.02	861.7	0.04	33.1
<i>cis-m</i> -Methylanisole	2770.4	-0.55	1292.7	-0.12	891.2	-0.04	51.9
<i>p</i> -Methylanisole	4839.7	-1.15	982.1	0.16	824.8	-0.01	7
<i>trans-m</i> -Methylthioanisole	3064.3		858.8		676.5		37.1
<i>trans-m</i> -Methylstyrene	3528.6		1130.2		860.5		35
<i>cis-m</i> -Methylstyrene	2855		1271.6		884.5		50.6
<i>p</i> -Methylstyrene	4998.8	-0.59	980.7	-0.04	824	-0.16	6.3
<i>p</i> -Methylbenzaldehyde	5043.5	-1.15	986.6	0.13	829.4	-0.3	6.6

The experimental values are given in Table S1. The percentage differences between the experimental and computed values are shown for each constant:

$$\text{Percentage difference} = 100 \times \frac{(\text{Expt} - \text{Calc})}{\text{Expt}}$$

^AFor G_{12} molecules, the methyl axis lies parallel to either the a or b axis. In this case, the corresponding constant, A or B , respectively corresponds to that of the frame alone and is usually denoted A_F or B_F .

^BIn the S_0 state, toluidines are not strictly planar as the amino group hydrogen atoms tilt out of plane. However, due to the low H mass, these molecules are well approximated as planar for the purposes of these comparisons. Tan and Pratt assumed p -toluidine to be of effectively G_{12} symmetry in their analysis of the rotational structure.^[16]

Table S3. Rotational constants and θ values for substituted toluenes in the first excited singlet electronic state, S_1 , calculated using the TD DFT B3LYP cc-pVTZ combination of theory and basis set.

Molecule	Ref.	A^A (MHz)			B^A (MHz)			C (MHz)			θ ($^\circ$)
		Exp.	Comp.	% Diff.	Exp.	Comp.	% Diff.	Exp.	Comp.	% Diff.	
Toluene	[21]	5443	5510	-1.23	2472	2498	-1.04	1701	1719	-1.05	0
<i>o</i> -Fluorotoluene			3117			2178			1292		28
<i>m</i> -Fluorotoluene			3552			1751			1181		28.6
<i>p</i> -Fluorotoluene			5423			1443			1140		0
2,6-Difluorotoluene			2209			1737			972.6		90
<i>o</i> -Chlorotoluene (^{35}Cl)			2726			1538			989.4		58.4
<i>m</i> -Chlorotoluene (^{35}Cl)			3254			1188			874.9		41.4
<i>p</i> -Chlorotoluene (^{35}Cl)			5453			977			828.6		0
2-Chloro,6-fluorotoluene			2181			1143			753.5		80.4
<i>o</i> -Tolunitrile	[10]	2853	2902	-1.69	1460	1464	-0.26	971.7	978.7	-0.72	54.1
<i>m</i> -Tolunitrile	[10]	3256	3278	-0.67	1178	1181	-0.31	866.1	873	-0.8	44.2
<i>p</i> -Tolunitrile			5583			968.6			825.4		0
<i>m</i> -Ethynyltoluene (3-Methylphenylacetylene)			3261			1184			873		43.4
<i>p</i> -Ethynyltoluene (4-Methylphenylacetylene)			5523			978.7			831.3		0
<i>trans-o</i> -Cresol			3138			2212			1308		26
<i>cis-o</i> -Cresol			3129			2210			1305		28.2
<i>trans-o</i> -Cresol (OD)	[22]	3022	3033	-0.35	2168	2194	-1.21	1274	1283	-0.76	28.8
<i>cis-o</i> -Cresol (OD)	[22]	3128	3108	0.66	2120	2159	-1.81	1275	1284	-0.71	30.2
<i>trans-m</i> -Cresol			3587			1790			1203		26.8
<i>cis-m</i> -Cresol			3570			1796			1203		27
<i>trans-m</i> -Cresol (OD)	[22]	3539	3581	-1.18	1720	1733	-0.75	1166	1176	-0.83	27.5
<i>cis-m</i> -Cresol (OD)	[22]	3447	3479	-0.92	1752	1766	-0.8	1171	1180	-0.79	28.7
<i>p</i> -Cresol	[23]	5155	5222	-1.3	1471	1484	-0.93	1154	1164	-0.93	2.6
<i>o</i> -Toluidine ^B	[24]	3122	3098	0.77	2182	2218	-1.65	1296	1305	-0.7	29.5
<i>m</i> -Toluidine ^B	[25]	3537	3575	-1.08	1789	1799	-0.57	1198	1206	-0.7	26.9
<i>p</i> -Toluidine ^B	[16]	5313	5397	-1.57	1480	1487	-0.54	1158	1166	-0.71	0
<i>trans-o</i> -Methylanisole	[26]	2408	2420	-0.48	1550	1546	0.25	951.2	954.5	-0.35	73.3
<i>trans-m</i> -Methylanisole	[26]	3407	3442	-1.04	1111	1115	-0.29	847.2	850.8	-0.43	32.3
<i>cis-m</i> -Methylanisole	[26]	2676	2701	-0.92	1279	1282	-0.24	875.7	879	-0.38	50.5
<i>p</i> -Methylanisole ^B	[27]	4682	4627	1.17	984.5	987.8	-0.34	818.5	822.4	-0.47	7.9

Molecule	Ref.	A^A (MHz)			B^A (MHz)			C (MHz)			θ (°)
		Exp.	Comp.	% Diff.	Exp.	Comp.	% Diff.	Exp.	Comp.	% Diff.	
<i>trans-m</i> -Methylthioanisole			3011		865.5		677.9		37		
<i>trans-m</i> -Methylstyrene			3539		1135		863.7		30.2		
<i>cis-m</i> -Methylstyrene			2791		1277		880.7		52.5		
<i>p</i> -Methylstyrene	[19]	4764	4690	1.56	997.7	1011	-1.3	816.1	835.8	-2.42	6.4

For G_{12} molecules, the methyl axis lies parallel to the a or b axis and a respective value for θ of 0° or 90° is shown. The experimental rotational constants are shown to one decimal place where they are available. The computed values apply to the optimised lowest energy methyl configuration. The percentage differences between the experimental and computed values are shown for each constant:

$$\text{Percentage difference} = 100 \times \frac{(\text{Expt} - \text{Calc})}{\text{Expt}}$$

^AFor G_{12} molecules, the methyl axis lies parallel to either the a or b axis. In this case, the corresponding constant, A or B , respectively corresponds to that of the frame alone and is usually denoted A_F or B_F .

^BUnusually, the S_1 A values for $m = 0$ (A state) and $m = 1$ (E state) are reasonably different at 4682.0 and 4666.5 MHz respectively. The $m = 0$ A value is shown.

Table S4: The calculated rotational constants and θ value (DFT calculations using the B3LYP functional and cc-pVTZ basis set) for various substituted toluenes in the D^+ cation state.

Molecule	Calculated Constants			θ
	<i>A</i>	<i>B</i>	<i>C</i>	
Toluene	5482	2587	1757	
<i>o</i> -Fluorotoluene	3196	2228	1323	25
<i>m</i> -Fluorotoluene	3620	1791	1207	26
<i>p</i> -Fluorotoluene	5455	1478	1163	
2,6-Difluorotoluene	2215	1807	994.9	
<i>o</i> -Chlorotoluene	2783	1580	1014	55
2-Chloro,6-fluorotoluene	2186	1188	773.4	79
<i>m</i> -Tolunitrile	3310	1203	887.2	40
<i>p</i> -Tolunitrile	5473	1002	847.1	
<i>trans-o</i> -Cresol	3235	2238	1334	23
<i>cis-o</i> -Cresol	3222	2234	1330	23
<i>trans-m</i> -Cresol	3644	1821	1223	25
<i>cis-m</i> -Cresol	3659	1816	1223	24

Table S5: F_{Methyl} values for a range of substituted toluenes in their S_0 state calculated using Eqn 5a (or Eqn 5b for G_{12} molecules) (see paper) calculated using experimental and quantum chemistry rotational constants.

Molecule	F	Ref.	$F_{\text{Methyl}}^{\text{Expt}}$ (E)	$F_{\text{Methyl}}^{\text{Expt}}$ (C)	
				MP2 / cc-pVTZ	DFT B3LYP / cc-pVTZ
Toluene	5.471	[2]	5.28	5.279	5.278
<i>o</i> -Fluorotoluene	5.306	[28]	5.204	5.203	5.204
<i>m</i> -Fluorotoluene	5.28	[29]	5.17	5.171	5.171
<i>p</i> -Fluorotoluene	5.46	[30]c	5.27	5.269	5.268
<i>m</i> -Chlorotoluene	5.32	[31]	5.239	5.24	5.24
<i>p</i> -Chlorotoluene	5.4	[31]	5.21	5.209	5.208
<i>o</i> -Tolunitrile	5.49	[10]	5.422	5.421	5.423
<i>m</i> -Tolunitrile	5.26	[32]	5.18	5.18	5.18
<i>p</i> -Tolunitrile	5.4	[32]		5.209	5.208
<i>m</i> -Ethylnyltoluene	5.332	[33]	5.253	5.254	5.253
<i>trans-o</i> -Cresol	5.295	[34]	5.192	5.191	5.191
<i>cis-o</i> -Cresol	5.2	[34]	5.098	5.097	5.097
<i>trans-m</i> -Cresol	5.3	[35]	5.191	5.19	5.19
<i>cis-m</i> -Cresol	5.31	[35]	5.2	5.2	5.2
<i>p</i> -Cresol	5.224	[23]	5.034	5.033	5.032
<i>o</i> -Toluidine	5.28	[36]	5.178	5.178	5.178
<i>m</i> -Toluidine	5.37	[36]	5.264	5.261	5.261
<i>p</i> -Toluidine			5.284	5.283	5.283
<i>trans-o</i> -Methylanisole	5.32	^B	5.264	5.263	5.264
<i>trans-m</i> -Methylanisole	5.47	^C	5.144	5.143	5.144
<i>cis-m</i> -Methylanisole	5.46	[37]	5.538	5.537	5.537
<i>p</i> -Methylanisole	5.3	^C	5.137	5.137	5.135
<i>trans-m</i> -Methylthioanisole	5.34	[38]		5.163	5.163
<i>trans-m</i> -Methylstyrene	5.4	[39]		5.307	5.307
<i>cis-m</i> -Methylstyrene	5.2	[39]		5.136	5.135
<i>p</i> -Methylstyrene	5.253	[19]	5.083	5.084	5.082
<i>p</i> -Methylbenzaldehyde	5.431	[20]	5.261	5.26	5.259

Where available, the experimental F value comes from fits to the observed torsional energies; in a few cases, the value comes from fits to microwave spectra encompassing several torsional states. The rotational constants and θ values are given in Tables S1 and S2. $F_{\text{Methyl}}^{\text{Expt}}$ values were determined using the experimental

F , A and B constants and the calculated methyl angle θ by Eqn 5a (see Table S1 for the experimental rotational constants and Tables S1 and S2 for the MP2 cc-

pVTZ and DFT B3LYP cc-pVTZ θ values respectively). For G₁₂ molecules, $F_{Methyl}^{Expt}(E)$ values are determined using Eqn 5b. $F_{Methyl}^{Expt}(C)$ values were determined using the experimental F value and computed A , B and θ values by Eqn 5a (see Tables S1 and S2 for the MP2 cc-pVTZ and DFT B3LYP cc-pVTZ values respectively). For G₁₂ molecules, $F_{Methyl}^{Expt}(E)$ values are determined using Eqn 5b.

^AThe values are from fits to the energies of the $m \leq 4$ states reported in Gascooke *et al.* (2018).^[30]

^BThere are significant differences in the torsional parameters reported in Ichimura and Suzuki (2000)^[37] and Alvarez-Valtierra *et al.* (2006).^[26] We have re-fitted the torsional band positions reported in Ichimura and Suzuki (2000)^[37] and the table shows the constants determined.

^CValues are also reported in Alvarez-Valtierra *et al.* (2006).^[26] We have used the constants reported in Ichimura and Suzuki (2000)^[37] as they are based on fits to the observed torsional band energies.

Table S6: As for Table S5, for the S_1 state.

Molecule	F	Ref.	$F_{Methyl}^{Expt} (E)$	$F_{Methyl}^{Expt} (C)$
Toluene	5.3	[21]	5.116	5.114
<i>o</i> -Fluorotoluene	5.12	[28]		5.022
<i>m</i> -Fluorotoluene	5.2	[29]		5.093
<i>p</i> -Fluorotoluene	5.06	[30] ^A		4.879
2,6-Difluorotoluene	5.08	[40]		5.022
<i>o</i> -Chlorotoluene	5.2	[41]		5.137
<i>m</i> -Chlorotoluene	4.15	[31]		4.07
<i>p</i> -Chlorotoluene	4.91	[31]		4.728
2-Chloro,6-fluorotoluene	5	[42]		4.961
<i>o</i> -Tolunitrile	5.16	[10]	5.094	5.094
<i>m</i> -Tolunitrile	5.01	[32]	4.934	4.934
<i>p</i> -Tolunitrile	5.6	[32]		5.414
<i>m</i> -Ethynyltoluene	5.12	[33]		5.044
<i>p</i> -Ethynyltoluene	5.55	[43]		5.366
<i>trans-o</i> -Cresol	5.15	[34]		5.049
<i>cis-o</i> -Cresol	5.1	[34]		5.001
<i>trans-m</i> -Cresol	5.31	[35]		5.2
<i>cis-m</i> -Cresol	5.21	[35]		5.101
<i>p</i> -Cresol	5.11	[23]	4.93	4.928
<i>o</i> -Toluidine	5.4	[36]	5.302	5.302
<i>m</i> -Toluidine	5.24	[36]	5.132	5.131
<i>p</i> -Toluidine	5.41	[16]	5.231	5.228
<i>trans-o</i> -Methylanisole	5.43	^B	4.845	4.845
<i>trans-m</i> -Methylanisole	5.51	^B	5.347	5.346
<i>cis-m</i> -Methylanisole	5.51	[26]	5.448	5.447
<i>p</i> -Methylanisole	4.2	^B	4.04	4.042
<i>trans-m</i> -Methylthioanisole	5.33	[38]		5.254
<i>trans-m</i> -Methylstyrene	5.4	[39]		5.3
<i>cis-m</i> -Methylstyrene	6.1	[39]		6.038
<i>p</i> -Methylstyrene	5.19	[19]	5.025	5.027

Where available, the experimental F value comes from a fit to the observed torsional energies; in a few cases, the value comes from a fit to high resolution rotationally resolved spectra for two or more m / ν_t states. The rotational constants and θ values are given in Table S3.

^AThe values are from fits to the energies of the $m \leq 4$ states reported in Gascooke *et al.* (2018).^[30]

^BValues are reported in Ichimura and Suzuki (2000)^[37] and Alvarez-Valtierra *et al.* (2006).^[26] We have used the constants reported in Ichimura and Suzuki (2000)^[37] as they are based on fits to the observed torsional band energies.

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