

Figure S1: Comparison of two broadband microwave spectra for 3-PN recorded in the rapid adiabatic passage regime with 100%, 10% and 1% power on the TWTA. The spectrum recorded while sweeping 8 \rightarrow 18 GHz sweep (black trace) and the corresponding spectrum with an 18 \rightarrow 8 GHz sweep (blue trace). Note that with 100% power of TWTA the distortions in the two spectra with intensities of transitions at the end of each scan enhanced unlike in case of 10% and 1% power of the TWTA.

Table S1: Linelist of *syn* 3-pentenenitrile A-states from SPFIT.¹

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	Observed (MHz)	Calculated (MHz)
4	1	3	3	4	0	4	3	8272.76563	8272.72159
4	1	3	5	4	0	4	5	8272.9375	8272.94668
4	1	3	4	4	0	4	4	8273.8125	8273.81765
4	0	4	3	3	1	3	2	8583.92188	8583.93456
4	0	4	5	3	1	3	4	8584.14063	8584.14642
4	0	4	4	3	1	3	3	8584.71875	8584.72988
5	1	4	4	5	0	5	4	9332.48438	9332.47528
5	1	4	6	5	0	5	6	9332.65625	9332.66721
5	1	4	5	5	0	5	5	9333.625	9333.62475
1	1	1	1	0	0	0	1	9760.53125	9760.54345
1	1	1	2	0	0	0	1	9761.23438	9761.23561
1	1	1	0	0	0	0	1	9762.26563	9762.26571
3	1	3	3	2	1	2	3	10089.32812	10089.32285
3	1	3	4	2	1	2	3	10089.98438	10089.99676
3	1	3	2	2	1	2	2	10090.89062	10090.89169
3	0	3	4	2	0	2	3	10556.92188	10556.88851
6	1	5	5	6	0	6	5	10696.98438	10696.98168
6	1	5	7	6	0	6	7	10697.14062	10697.1569
6	1	5	6	6	0	6	6	10698.1875	10698.19737
3	1	2	2	2	1	1	2	11115.14062	11115.15336
3	1	2	4	2	1	1	3	11116.1875	11116.16284
3	1	2	3	2	1	1	3	11116.9375	11116.93749
7	1	6	6	7	0	7	6	12397.42188	12397.3995
7	1	6	8	7	0	7	8	12397.5625	12397.56058
7	1	6	7	7	0	7	7	12398.67188	12398.67941
5	0	5	4	4	1	4	3	12563.76562	12563.80637
5	0	5	6	4	1	4	5	12563.9375	12563.94755
5	0	5	5	4	1	4	4	12564.4375	12564.45977
2	1	2	2	1	0	1	1	12955.57812	12955.59097
2	1	2	3	1	0	1	2	12956.32812	12956.32469
2	1	2	1	1	0	1	0	12956.8125	12956.80477
4	1	4	4	3	1	3	4	13437.32812	13437.34127
4	1	4	5	3	1	3	4	13438.04688	13438.03963
4	0	4	5	3	0	3	4	14012.85938	14012.8557
4	2	3	5	3	2	2	4	14138.32812	14138.28485
4	2	2	5	3	2	1	4	14274.14062	14274.18248
8	1	7	8	8	0	8	8	14452.51562	14452.53513

4	1	3	3	3	1	2	3	14803.65625	14803.66981
4	1	3	5	3	1	2	4	14804.625	14804.64533
4	1	3	4	3	1	2	4	14805.42188	14805.42585
3	1	3	3	2	0	2	2	15984.89062	15984.87807
3	1	3	4	2	0	2	3	15985.60938	15985.59778
3	1	3	2	2	0	2	1	15985.875	15985.84377
6	0	6	5	5	1	5	4	16555.125	16555.07582
6	0	6	7	5	1	5	6	16555.17188	16555.17361
6	0	6	6	5	1	5	5	16555.60938	16555.60591
5	1	5	5	4	1	4	5	16773.25	16773.26171
5	1	5	6	4	1	4	5	16773.96875	16773.98868
5	1	5	4	4	1	4	4	16774.82812	16774.83507
5	0	5	6	4	0	4	5	17417.82812	17417.84075
5	2	4	6	4	2	3	5	17655.60938	17655.60292
6	2	4	6	6	1	5	6	16639.89062	16639.87288
6	2	4	7	6	1	5	7	16640.1875	16640.21723
5	2	3	5	5	1	4	5	17150.6875	17150.63439
5	2	3	6	5	1	4	6	17151.125	17151.10498
7	2	5	7	7	1	6	7	16242.90625	16242.92825
7	2	5	8	7	1	6	8	16243.125	16243.13829
4	2	2	4	4	1	3	4	17704.53125	17704.54747
4	2	2	5	4	1	3	5	17705.125	17705.12794
4	2	2	3	4	1	3	3	17705.26562	17705.27867
3	3	1	3	4	2	2	4	17638.78125	17638.7748
3	3	1	4	4	2	2	5	17639.07812	17639.06678
3	2	2	4	2	2	1	3	10611.8125	10611.76489
3	2	1	4	2	2	0	3	10666.51562	10666.50276
3	2	1	3	2	2	0	2	10666.64062	10666.64256
8	2	6	9	8	1	7	9	16028.25	16028.22027
9	2	7	10	9	1	8	10	16056.625	16056.6611
9	2	7	9	9	1	8	9	16056.78125	16056.72799
9	1	8	10	9	0	9	10	16856	16856.00781
9	1	8	9	9	0	9	9	16857.26562	16857.21759
5	3	3	6	4	3	2	5	17730.01562	17730.04856
5	3	2	6	4	3	1	5	17737.21875	17737.2546
5	3	2	5	4	3	1	4	17737.375	17737.31347
3	3	0	4	4	2	3	5	17843.70312	17843.76525
4	3	2	5	3	3	1	4	14175.65625	14175.64385
4	3	1	5	3	3	0	4	14177.71875	14177.70579
4	3	1	5	5	2	4	6	14365.89062	14365.86812
8	1	7	9	7	2	6	8	14737.25	14737.25512

8	1	7	8	7	2	6	7	14737.89062	14737.91451
3	3	1	3	4	2	2	4	17638.78125	17638.7748
3	3	1	4	4	2	2	5	17639.07812	17639.06678
5	4	1	6	4	4	0	5	17717.375	17717.37928

Table S2: Linelist of *eclipsed* 3-pentenitrile A-states from SPFIT.¹

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	Observed (MHz)	Calculated (MHz)
3	1	3	4	2	1	2	3	8513.25	8513.32845
3	1	3	3	2	1	2	2	8513.4375	8513.4095
3	0	3	4	2	0	2	3	8631.6875	8631.67795
3	1	2	4	2	1	1	3	8753.125	8753.15824
4	1	4	5	3	1	3	4	11350.5625	11350.57581
4	1	4	4	3	1	3	3	11350.6875	11350.61586
4	0	4	5	3	0	3	4	11506.875	11506.88577
4	0	4	3	3	0	3	2	11506.9375	11506.90593
2	1	1	3	2	0	2	3	11553.125	11553.12047
4	1	3	5	3	1	2	4	11670.3125	11670.32123
4	1	3	4	3	1	2	3	11670.375	11670.34193
5	1	5	6	4	1	4	5	14187.375	14187.34475
1	1	1	1	0	0	0	1	14270.6875	14270.64562
5	0	5	6	4	0	4	5	14380.375	14380.3591
5	1	4	6	4	1	3	5	14586.9375	14586.99718
5	1	4	5	4	1	3	4	14587	14587.00824
6	1	6	7	5	1	5	6	17023.5	17023.52687
2	1	2	3	1	0	1	2	17068.25	17068.30248
2	1	2	2	1	0	1	1	17068.625	17068.61222
6	0	6	7	5	0	5	6	17251.6875	17251.66943
6	1	5	7	5	1	4	6	17503.0625	17503.06122
1	1	0	1	1	0	1	1	11471.9375	11471.95046
1	1	0	2	1	0	1	2	11472.625	11472.66113
1	1	0	0	1	0	1	1	11473.1875	11473.18202
4	1	3	4	4	0	4	4	11837.625	11837.55188
4	1	3	5	4	0	4	5	11838	11838.03622

Table S3: Spectral fits of the hypothetical central frequencies using the XIAM program suite² are shown along with the values resulting from DFT calculations (Representation I^r Watson S reduction).

3-Pentenenitrile	<i>Syn</i>	<i>Eclipsed</i>
A (MHz) (pred^a/expt^b)	8312.7855 / 8163.609(18)	12901.0547 / 12.878(17)
B (MHz) (pred/expt)	1926.6016 / 1939.7349(30)	1484.7483 / 1478.8851(63)
C (MHz) (pred/expt)	1594.5939 / 1597.5068(32)	1406.0122 / 1398.9110(83)
F₀ (fixed)	158.0	158.0
D_J (kHz) (expt)	0.757(38)	0.502(37)
D_{JK} (kHz) (expt)	5.25(18)	-27.39(51)
D_K (kHz) (expt)	30.1(18)	-
d₁ (kHz) (expt)	0.219(10)	-0.105(58)
Dpi2J (expt)	0.00141(57)	-
Dpi2K (expt)	-0.0185(29)	-
Dpi2- (expt)	0.00144(33)	-
δ (fixed)	2.099929695	0.544274057
ε (fixed)	2.612459285	1.090581459
rms (kHz)	64	22
N^c	60	18
V₃ (cm⁻¹) (pred/expt)	609.3 / 553.8±2.4	588.6 / 619.9±0.9

^a pred: predicted values at B3LYP-GD3BJ/Def2TZVP

^b expt: experimental fit values

^c N is the number of hypothetical central transitions (not counting individual hyperfine transitions) fit.

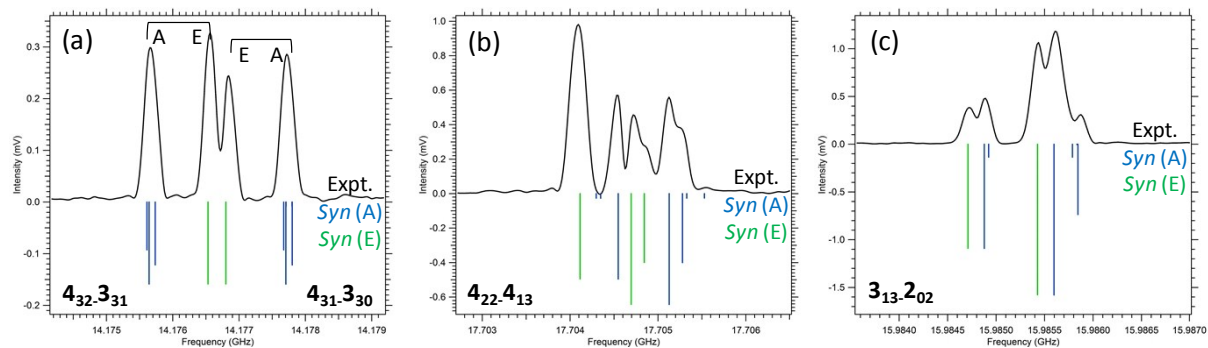


Figure S2: A closer look at additional *syn* 3-pentenenitrile transitions. The black trace in each case is the experimental spectrum while the final fits of the A states (blue trace) and E states (green trace) are shown as sticks below. (a) The $4_{32}-3_{31}$ and $4_{31}-3_{30}$ transitions exhibit only methyl rotor splittings whereas (b) $4_{22}-4_{13}$ and (c) $3_{13}-2_{02}$ show both hyperfine and methyl rotor splittings.

Table S4: Linelist of *syn* 3-pentenenitrile from XIAM.²

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	A state (MHz)		E state (MHz)	
								Calculated	Observed	Calculated	Observed
4	1	3	3	4	0	4	3	8272.7194	8272.7656	8272.5723	8272.5625
4	1	3	5	4	0	4	5	8272.9432	8272.9375	8272.7961	8272.7344
4	1	3	4	4	0	4	4	8273.8137	8273.8125	8273.6666	8273.6094
4	0	4	3	3	1	3	2	8583.9385	8583.9219	8584.0936	8584.1094
4	0	4	5	3	1	3	4	8584.1509	8584.1407	8584.306	8584.3282
4	0	4	4	3	1	3	3	8584.7347	8584.7188	8584.8898	8584.9063
5	1	4	4	5	0	5	4	9332.4687	9332.4844	9332.3321	9332.2969
5	1	4	6	5	0	5	6	9332.6633	9332.6563	9332.5267	9332.4688
5	1	4	5	5	0	5	5	9333.6184	9333.625	9333.4818	9333.4375
1	1	1	1	0	0	0	1	9760.546	9760.5312	9760.3721	9760.3594
1	1	1	2	0	0	0	1	9761.2372	9761.2343	9761.0633	9761.0625
1	1	1	0	0	0	0	1	9762.2741	9762.2656	9762.1001	9762.0938
7	1	6	7	6	2	5	6	10045.139	10045.215 8		
3	1	3	3	2	1	2	3	10089.329 7	10089.328 1		
3	1	3	4	2	1	2	3	10090	10089.984 4		
3	1	3	2	2	1	2	2	10090.890 8	10090.890 6		
3	0	3	4	2	0	2	3	10556.892 3	10556.921 9		
3	2	2	4	2	2	1	3	10611.765 3	10611.812 5	10612.400 4	10612.437 5
3	2	1	4	2	2	0	3	10666.503 5	10666.515 6	10665.861 3	10665.882 8
3	2	1	3	2	2	0	2	10666.647 1	10666.640 6	10666.006 7	10666.007 8
6	1	5	5	6	0	6	5	10696.978	10696.984 4	10696.856 3	10696.812 5
6	1	5	7	6	0	6	7	10697.153 5	10697.140 6	10697.031 8	10696.968 7
6	1	5	6	6	0	6	6	10698.192 9	10698.187 5	10698.071 2	10698.015 6
3	1	2	2	2	1	1	2	11115.152 6	11115.140 6		
3	1	2	4	2	1	1	3	11116.165 3	11116.187 5		
3	1	2	3	2	1	1	3	11116.942 7	11116.937 5		
7	1	6	6	7	0	7	6	12397.398	12397.421	12397.295	12397.312

								3	9	4	5
7	1	6	8	7	0	7	8	12397.559 5	12397.562 5	12397.456 6	12397.453 1
7	1	6	7	7	0	7	7	12398.677 4	12398.671 9	12398.574 5	12398.562 5
5	0	5	4	4	1	4	3	12563.81	12563.765 6	12563.957 5	12563.937 5
5	0	5	6	4	1	4	5	12563.951 5	12563.937 5	12564.099	12564.109 4
2	1	2	2	1	0	1	1	12955.592 3	12955.578 1	12955.421 1	12955.390 6
2	1	2	3	1	0	1	2	12956.327 3	12956.328 1	12956.156 1	12956.140 6
2	1	2	1	1	0	1	0	12956.81	12956.812 5	12956.638 8	12956.625
4	1	4	4	3	1	3	4	13437.348 4	13437.328 1		
4	1	4	5	3	1	3	4	13438.042 7	13438.046 9		
4	0	4	5	3	0	3	4	14012.859 5	14012.859 4		
4	2	3	5	3	2	2	4	14138.284 8	14138.328 1		
4	3	2	5	3	3	1	4	14175.639 6	14175.656 2	14176.531 6	14176.562 5
4	3	1	5	3	3	0	4	14177.703 1	14177.718 8	14176.801 8	14176.843 7
4	2	2	5	3	2	1	4	14274.185 1	14274.140 6		
4	2	2	4	3	2	1	3	14274.291 1	14274.171 9		
4	3	1	5	5	2	4	6	14365.866 7	14365.890 6		
8	1	7	8	8	0	8	8	14452.538 2	14452.515 6	14452.456 6	14452.484 4
8	1	7	9	7	2	6	8	14737.270 3	14737.25		
8	1	7	8	7	2	6	7	14737.929 4	14737.890 6		
4	1	3	3	3	1	2	3	14803.669 1	14803.656 2		
4	1	3	5	3	1	2	4	14804.648 1	14804.625		
4	1	3	4	3	1	2	4	14805.432	14805.421 8		
3	1	3	3	2	0	2	2	15984.883 6	15984.890 6	15984.710 2	15984.718 8
3	1	3	4	2	0	2	3	15985.600 9	15985.609 4	15985.427 5	15985.437 6

3	1	3	2	2	0	2	1	15985.861 7	15985.875		
9	2	7	10	9	1	8	10	16056.666 1	16056.625	16056.287	16056.265 6
9	2	7	9	9	1	8	9	16056.732 3	16056.781 2	16056.353 2	16056.421 8
7	2	5	7	7	1	6	7	16242.921 3	16242.906 3	16242.481 2	16242.492 2
7	2	5	8	7	1	6	8	16243.131 5	16243.125	16242.691 4	16242.711
10	2	8	10	10	1	9	10	16380.512 9	16380.515 6		
6	0	6	5	5	1	5	4	16555.077 5	16555.125	16555.213 5	16555.187 5
6	0	6	7	5	1	5	6	16555.175 7	16555.171 9	16555.311 7	16555.234 4
6	0	6	6	5	1	5	5	16555.607 8	16555.609 4	16555.743 8	16555.671 9
6	2	4	6	6	1	5	6	16639.864 9	16639.890 6		
6	2	4	7	6	1	5	7	16640.209 8	16640.187 5		
5	1	5	5	4	1	4	5	16773.267 4	16773.25		
5	1	5	6	4	1	4	5	16773.99	16773.968 8		
5	1	5	4	4	1	4	4	16774.831 5	16774.828 1		
9	1	8	10	9	0	9	10	16856.017 9	16856		
9	1	8	9	9	0	9	9	16857.247	16857.265 6		
11	2	9	11	11	1	10	11	17042.683 5	17042.687 5	17042.398 9	17042.406 2
5	2	3	5	5	1	4	5	17150.629 4	17150.687 5		
5	2	3	6	5	1	4	6	17151.099 3	17151.125		
5	0	5	6	4	0	4	5	17417.843 3	17417.828 1		
3	3	1	3	4	2	2	4	17638.763	17638.781 3		
3	3	1	3	4	2	2	4	17638.763	17638.781 3		
3	3	1	4	4	2	2	5	17639.063 3	17639.078 2		
3	3	1	4	4	2	2	5	17639.063 3	17639.078 2		
5	2	4	6	4	2	3	5	17655.599 9	17655.609 4		

4	2	2	4	4	1	3	4	17704.543 9	17704.531 2	17704.113 7	17704.117 2
4	2	2	5	4	1	3	5	17705.125 2	17705.125	17704.695	17704.710 9
4	2	2	3	4	1	3	3	17705.274 7	17705.265 6	17704.844 6	17704.851 6
5	4	1	6	4	4	0	5	17717.366 6	17717.375		
5	3	3	6	4	3	2	5	17730.042 3	17730.015 6	17731.873 4	17731.843 7
5	3	2	6	4	3	1	5	17737.248 6	17737.218 8	17735.406 4	17735.390 6
5	3	2	5	4	3	1	4	17737.309 4	17737.375	17735.467 1	17735.546 8
3	3	0	4	4	2	3	5	17843.763 5	17843.703 1		
5	2	3	6	4	2	2	5	17923.537 3	17923.5		
5	2	3	5	4	2	2	4	17923.637 9	17923.546 9		

Table S5: Linelist of *eclipsed* 3-pentenitrile from XIAM.²

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	State	Calculated (MHz)	Observed (MHz)
3	1	3	4	2	1	2	3	A	8513.2989	8513.25
3	0	3	4	2	0	2	3	A	8631.6466	8631.6875
3	1	2	4	2	1	1	3	A	8753.1405	8753.125
4	1	4	5	3	1	3	4	A	11350.547	11350.5625
4	1	4	4	3	1	3	3	A	11350.5849	11350.6875
4	0	4	5	3	0	3	4	A	11506.8547	11506.875
4	0	4	3	3	0	3	2	A	11506.8727	11506.9375
2	1	1	3	2	0	2	3	A	11553.1391	11553.125
4	1	3	5	3	1	2	4	A	11670.3069	11670.3125
4	1	3	4	3	1	2	3	A	11670.3243	11670.375
5	1	5	6	4	1	4	5	A	14187.3267	14187.375
1	1	1	1	0	0	0	1	A	14270.6641	14270.6875
5	0	5	6	4	0	4	5	A	14380.3381	14380.375
5	1	4	6	4	1	3	5	A	14586.9966	14586.9375
5	1	4	5	4	1	3	4	A	14587.0058	14587
6	1	6	7	5	1	5	6	A	17023.532	17023.5
2	1	2	3	1	0	1	2	A	17068.2765	17068.25
2	1	2	2	1	0	1	1	A	17068.6202	17068.625
6	0	6	7	5	0	5	6	A	17251.6706	17251.6875
6	1	5	7	5	1	4	6	A	17503.0869	17503.0625
1	1	0	1	1	0	1	1	A	11471.9668	11471.9375
1	1	0	2	1	0	1	2	A	11472.6677	11472.625
1	1	0	0	1	0	1	1	A	11473.2275	11473.1875
4	1	3	4	4	0	4	4	A	11837.5784	11837.625
6	2	5	7	5	2	4	6	A	17265.7751	17265.7812
6	2	5	7	5	2	4	6	E	17266.7624	17266.7813
6	2	4	7	5	2	3	6	A	17280.435	17280.4375
6	2	4	7	5	2	3	6	E	17279.4283	17279.4375

5	2	4	6	4	2	3	5	A	14388.8923	14388.9062
5	2	4	6	4	2	3	5	E	14390.4082	14390.3906
5	2	3	6	4	2	2	5	A	14397.2743	14397.25
5	2	3	6	4	2	2	5	E	14395.7421	14395.7344

Table S6: Linelist of *eg*+ 4-pentenenitrile from SPFIT.¹

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	Observed (MHz)	Calculated (MHz)
2	1	1	1	1	1	0	1	7585.375	7585.36953
2	1	1	2	1	1	0	1	7585.984	7585.98653
2	1	1	3	1	1	0	2	7586.156	7586.16076
2	1	1	2	1	1	0	2	7586.547	7586.55744
2	1	1	1	1	1	0	0	7586.781	7586.7968
4	1	3	3	4	0	4	3	7768.891	7768.89758
4	1	3	5	4	0	4	5	7769.078	7769.06568
4	1	3	4	4	0	4	4	7769.719	7769.71316
5	1	4	6	5	0	5	6	8535.344	8535.34971
5	1	4	5	5	0	5	5	8536.031	8536.03363
2	2	0	1	3	1	3	2	8932.109	8932.10427
2	2	0	3	3	1	3	4	8932.469	8932.47713
2	2	0	2	3	1	3	3	8933.406	8933.41064
4	0	4	4	3	1	3	4	8938.75	8938.76864
4	0	4	3	3	1	3	2	8938.938	8938.93404
4	0	4	5	3	1	3	4	8939.098	8939.09284
4	0	4	4	3	1	3	3	8939.469	8939.46517
4	0	4	3	3	1	3	3	8939.875	8939.87437
6	1	5	7	6	0	6	7	9512.188	9512.21414
6	1	5	6	6	0	6	6	9512.953	9512.94163
1	1	1	1	0	0	0	1	9912.406	9912.4098
1	1	1	2	0	0	0	1	9912.781	9912.78006
1	1	1	0	0	0	0	1	9913.328	9913.33541
1	1	0	0	0	0	0	1	10170.609	10170.58848
1	1	0	2	0	0	0	1	10171.453	10171.44483
1	1	0	1	0	0	0	1	10172.016	10172.01575
3	1	3	3	2	1	2	3	10597.203	10597.21336
3	1	3	3	2	1	2	2	10597.813	10597.82506

3	1	3	4	2	1	2	3	10597.906	10597.90988
3	1	3	2	2	1	2	2	10598.766	10598.76538
7	1	6	8	7	0	7	8	10723.484	10723.49438
7	1	6	7	7	0	7	7	10724.281	10724.26828
3	0	3	3	2	0	2	3	10959.094	10959.08609
3	0	3	4	2	0	2	3	10959.344	10959.3616
3	0	3	2	2	0	2	2	10959.688	10959.69336
3	2	2	3	2	2	1	2	10991.125	10991.13626
3	2	2	4	2	2	1	3	10991.359	10991.35128
3	2	1	3	2	2	0	2	11022.594	11022.59403
3	2	1	4	2	2	0	3	11022.781	11022.77848
3	1	2	2	2	1	1	2	11373.609	11373.59715
3	1	2	4	2	1	1	3	11374.125	11374.11591
3	1	2	3	2	1	1	3	11374.469	11374.4648
5	0	5	6	4	1	4	5	12979.797	12979.7954
5	0	5	5	4	1	4	4	12980.172	12980.15856
2	1	2	2	1	0	1	2	13317.094	13317.09048
2	1	2	2	1	0	1	1	13317.297	13317.29117
2	1	2	3	1	0	1	2	13317.703	13317.70218
2	1	2	1	1	0	1	1	13318.25	13318.24271
2	1	1	3	1	0	1	2	14093.922	14093.92498
2	1	1	2	1	0	1	1	14094.516	14094.52236
4	1	4	4	3	1	3	4	14120.813	14120.79864
4	1	4	5	3	1	3	4	14121.516	14121.54355
4	1	4	3	3	1	3	3	14122.438	14122.43164
4	0	4	4	3	0	3	4	14575.625	14575.61805
4	0	4	5	3	0	3	4	14575.938	14575.94224
4	0	4	3	3	0	3	3	14576.297	14576.30276
4	1	3	3	3	1	2	3	15155.313	15155.2977
4	1	3	5	3	1	2	4	15155.719	15155.7297
4	1	3	4	3	1	2	4	15156.063	15156.05298
3	1	3	3	2	0	2	3	16595.5	16595.51448
3	1	3	3	2	0	2	2	16595.75	16595.74981
3	1	3	4	2	0	2	3	16596.219	16596.211
3	1	3	2	2	0	2	2	16596.688	16596.69014
5	1	5	6	4	1	4	5	17637.906	17637.93217
7	2	5	8	7	1	6	8	16591	16591.02159
4	2	3	4	3	2	2	3	14648.672	14648.70397
4	2	3	5	3	2	2	4	14648.813	14648.80021
4	2	2	5	3	2	1	4	14727.094	14727.04361
6	2	4	6	6	1	5	6	17025.328	17025.37952

6	2	4	7	6	1	5	7	17025.719	17025.63788
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Table S7: Linelist of *et* 4-pentenenitrile from SPFIT.¹

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	Observed (MHz)	Calculated (MHz)
2	1	2	3	3	0	3	4	7656.359	7656.38675
2	1	2	2	3	0	3	3	7656.828	7656.81065
3	1	3	3	2	1	2	3	8443.625	8443.6188
3	1	3	3	2	1	2	2	8444.281	8444.28069
3	1	3	4	2	1	2	3	8444.578	8444.5766
3	1	3	2	2	1	2	2	8445.563	8445.57391
3	0	3	3	2	0	2	3	8483.703	8483.71437
3	0	3	2	2	0	2	1	8484.594	8484.59862
3	0	3	4	2	0	2	3	8484.797	8484.80016
3	0	3	2	2	0	2	2	8486.219	8486.22701
3	1	2	3	2	1	1	3	8524.813	8524.82988
3	1	2	3	2	1	1	2	8525.203	8525.21433
3	1	2	4	2	1	1	3	8525.5	8525.49998
3	1	2	2	2	1	1	2	8526.125	8526.11921
1	1	1	0	2	0	2	1	10510.172	10510.17842
1	1	1	1	2	0	2	1	10511.063	10511.07539
1	1	1	2	2	0	2	3	10511.297	10511.29841
1	1	1	1	2	0	2	2	10512.703	10512.70378
4	1	4	4	3	1	3	4	11258.234	11258.20191
4	1	4	4	3	1	3	3	11259.203	11259.15971
4	1	4	5	3	1	3	4	11259.297	11259.29259
4	1	4	3	3	1	3	3	11260.531	11260.53098
4	0	4	4	3	0	3	4	11311.734	11311.7431
4	0	4	5	3	0	3	4	11312.844	11312.85407
4	0	4	3	3	0	3	3	11314.234	11314.22567
4	1	3	4	3	1	2	4	11366.406	11366.40791
4	1	3	5	3	1	2	4	11367.172	11367.20437

4	1	3	3	3	1	2	3	11368.094	11368.07945
5	1	5	5	4	1	4	5	14072.797	14072.80579
5	1	5	6	4	1	4	5	14073.922	14073.96975
5	1	5	4	4	1	4	4	14075.328	14075.29764
5	0	5	5	4	0	4	5	14139.625	14139.6265
5	0	5	6	4	0	4	5	14140.766	14140.75519
5	1	4	5	4	1	3	5	14208	14208.00863
5	1	4	6	4	1	3	5	14208.875	14208.87385
5	1	4	4	4	1	3	4	14209.844	14209.84669
6	1	6	7	5	1	5	6	16888.578	16888.57964
6	0	6	7	5	0	5	6	16968.438	16968.46017
6	1	5	6	5	1	4	6	17049.625	17049.57452
6	1	5	7	5	1	4	6	17050.469	17050.48211
1	1	0	1	1	0	1	0	16194.016	16194.02742
1	1	0	2	1	0	1	2	16194.875	16194.8749
1	1	0	1	1	0	1	2	16195.484	16195.49261
1	1	0	2	1	0	1	1	16195.843	16195.85153
1	1	0	1	1	0	1	1	16196.453	16196.46924
2	1	1	2	2	0	2	1	16221.078	16221.08833
2	1	1	1	2	0	2	1	16221.688	16221.68681
2	1	1	3	2	0	2	3	16222.063	16222.05452
2	1	1	2	2	0	2	2	16222.719	16222.71672
2	1	1	3	2	0	2	2	16223.094	16223.10117
2	1	1	1	2	0	2	2	16223.328	16223.3152
3	1	2	3	3	0	3	2	16261.75	16261.70404
3	1	2	3	3	0	3	4	16262.094	16262.08424
3	1	2	4	3	0	3	4	16262.75	16262.75434
3	1	2	3	3	0	3	3	16263.188	16263.17003
3	1	2	4	3	0	3	3	16263.859	16263.84013
4	1	3	5	4	0	4	5	16317.141	16317.10465
4	1	3	4	4	0	4	4	16317.422	16317.41916
5	1	4	6	5	0	5	6	16385.203	16385.22332
5	1	4	5	5	0	5	5	16385.437	16385.48678
6	1	5	7	6	0	6	7	16467.219	16467.24526
6	1	5	6	6	0	6	6	16467.516	16467.47965
7	1	6	8	7	0	7	8	16563.313	16563.32845
7	1	6	7	7	0	7	7	16563.563	16563.54496
8	1	7	9	8	0	8	9	16673.656	16673.65561
8	1	7	8	8	0	8	8	16673.859	16673.86053
5	2	3	5	4	2	2	4	14142.344	14142.35614
5	2	3	6	4	2	2	5	14142.593	14142.58783

6	2	5	7	5	2	4	6	16970.109	16970.1286
6	2	4	7	5	2	3	6	16971.313	16971.3093

Table S8: Linelist of *eg*- 4-pentenenitrile from SPFIT.¹

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	Observed (MHz)	Calculated (MHz)
4	0	4	5	3	1	4	4	14717.58	14717.59
4	0	4	4	3	1	4	3	14717.94	14717.92
3	1	3	3	2	0	4	2	14996.05	14996.05
3	1	3	4	2	0	3	3	14996.77	14996.78
3	1	3	2	2	0	3	1	14997.08	14997.04
4	1	4	4	3	1	3	4	16203.2	16203.2
4	1	4	5	3	1	5	4	16203.89	16203.92
4	1	4	3	3	1	5	3	16204.8	16204.78
4	0	4	4	3	0	5	3	16852.39	16852.39
4	0	4	5	3	0	0	4	16852.61	16852.6
1	1	1	1	0	0	0	1	7696	7695.994
1	1	1	2	0	0	0	1	7696.766	7696.774
1	1	1	0	0	0	2	1	7697.938	7697.945
2	1	2	1	1	1	2	0	8167.703	8167.679
2	1	2	3	1	1	2	2	8168.5	8168.484
2	1	2	1	1	1	2	1	8169.641	8169.63
2	0	2	3	1	0	6	2	8693.391	8693.42
2	0	2	1	1	0	6	0	8693.641	8693.639
2	1	1	1	1	1	6	1	9365.688	9365.682
2	1	1	3	1	1	1	2	9366.766	9366.76
2	1	1	2	1	1	1	1	9366.984	9366.982
2	1	1	1	1	1	1	0	9367.219	9367.217
2	1	1	2	1	1	7	2	9367.594	9367.596
5	1	4	4	5	0	7	4	9776	9775.99
5	1	4	6	5	0	7	6	9776.25	9776.252
5	1	4	5	5	0	4	5	9777.531	9777.535

3	0	3	2	2	1	4	1	10073.42	10073.42
3	0	3	4	2	1	4	3	10073.73	10073.74
3	0	3	3	2	1	1	2	10074.27	10074.27
2	1	2	2	1	0	1	1	11480.63	11480.62
2	1	2	3	1	0	1	2	11481.44	11481.44
2	1	2	1	1	0	3	1	11481.64	11481.64
2	1	2	1	1	0	3	0	11482.05	11482.06
3	1	3	3	2	1	3	3	12208.08	12208.08
3	1	3	4	2	1	2	3	12208.73	12208.75
3	1	3	2	2	1	1	2	12209.63	12209.65
3	0	3	3	2	0	8	2	12861.56	12861.58
3	0	3	4	2	0	2	3	12861.75	12861.76
3	1	2	4	2	1	2	3	14000.27	14000.26
3	2	2	2	3	1	2	2	12678.34	12678.33
3	2	2	4	3	1	2	4	12678.56	12678.56
3	2	2	3	3	1	2	3	12679.23	12679.23
5	2	4	6	5	1	2	6	15554.75	15554.81
5	2	4	5	5	1	5	5	15555.67	15555.62
3	2	2	4	2	2	5	3	13151.59	13151.57
3	2	2	3	2	2	5	2	13151.75	13151.74
3	2	1	4	2	2	4	3	13440.83	13440.84
3	2	1	3	2	2	4	2	13441.2	13441.2
4	2	3	3	4	1	4	3	13951.48	13951.5
4	2	3	5	4	1	4	5	13951.7	13951.69
4	2	3	4	4	1	3	4	13952.45	13952.46
2	2	1	2	2	1	5	1	11735.2	11735.2
2	2	1	1	2	1	5	1	11735.48	11735.48
2	2	1	3	2	1	4	3	11735.75	11735.75
2	2	1	2	2	1	4	2	11736.22	11736.23
2	2	0	2	2	1	6	2	10011.7	10011.71
2	2	0	3	2	1	6	3	10012.61	10012.6
2	2	0	1	2	1	3	1	10013.11	10013.1
5	2	3	6	5	1	3	6	8998.359	8998.356
4	2	2	4	4	1	3	4	9045.578	9045.574
4	2	2	5	4	1	2	5	9045.813	9045.834
3	2	1	3	3	1	2	3	9452.625	9452.627
3	2	1	4	3	1	1	4	9453.188	9453.185
3	2	1	2	3	1	0	2	9453.391	9453.381
4	1	3	3	3	2	0	2	9475.594	9475.592
4	1	3	5	3	2	7	4	9475.813	9475.805
4	1	3	4	3	2	8	3	9476.625	9476.636

6	1	5	5	6	0	8	5	12683.72	12683.7
6	1	5	7	6	0	9	7	12683.97	12683.92
6	1	5	6	6	0	9	6	12685.23	12685.23

Table S9: Linelist of *st* 4-pentenenitrile from SPFIT.¹

J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	Observed (MHz)	Calculated (MHz)
3	1	3	3	2	1	2	3	9016.891	9016.88703
3	1	3	3	2	1	2	2	9017.563	9017.55223
3	1	3	4	2	1	2	3	9017.906	9017.90366
3	1	3	2	2	1	2	2	9018.922	9018.92497
3	0	3	3	2	0	2	3	9207.109	9207.09256
3	0	3	2	2	0	2	1	9208.172	9208.1573
3	0	3	4	2	0	2	3	9208.422	9208.39996
3	1	2	3	2	1	1	3	9404.438	9404.42711
3	1	2	3	2	1	1	2	9405.016	9405.02175
3	1	2	4	2	1	1	3	9405.375	9405.37057
3	1	2	2	2	1	1	2	9406.297	9406.2957
4	1	4	4	3	1	3	3	12022.578	12022.54259
4	1	4	5	3	1	3	4	12022.688	12022.69951
4	0	4	4	3	0	3	4	12272.125	12272.10289
4	0	4	5	3	0	3	4	12273.438	12273.44066
4	0	4	3	3	0	3	3	12275.125	12275.09224
4	2	3	5	3	2	2	4	12282.25	12282.23768
4	2	2	4	3	2	1	3	12291.094	12291.1205
4	2	2	5	3	2	1	4	12291.641	12291.65449
5	1	5	6	4	1	4	5	15026.609	15026.60044
5	0	5	6	4	0	4	5	15334.719	15334.73063
5	2	3	5	4	2	2	4	15370.047	15370.07063
5	2	3	6	4	2	2	5	15370.359	15370.34956
5	1	4	6	4	1	3	5	15672.297	15672.29881
6	1	6	6	5	1	5	5	18029.297	18029.32318

6	0	6	7	5	0	5	6	18391.313	18391.3423
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Table S10: Linelist of *sg*- 4-pentenenitrile from SPFIT.¹

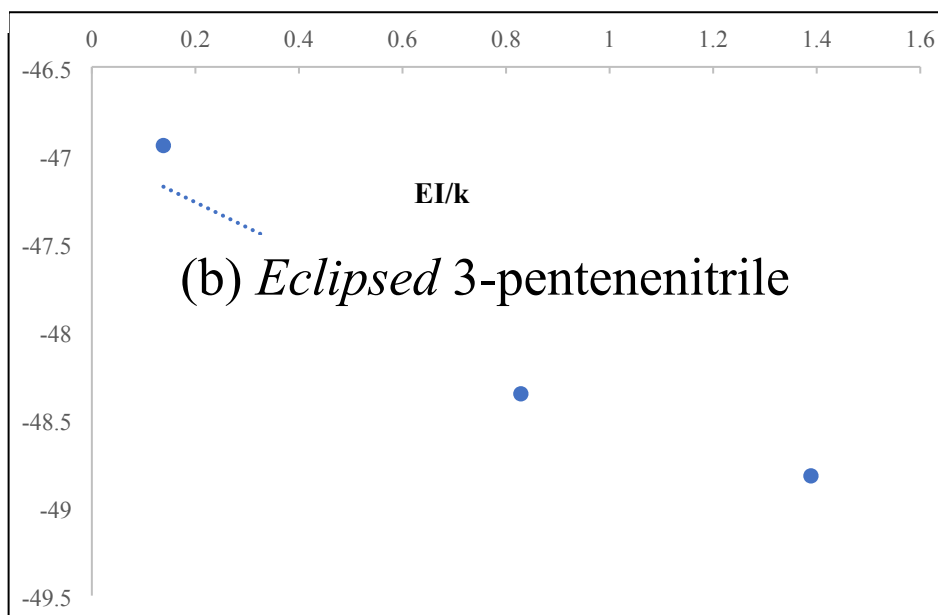
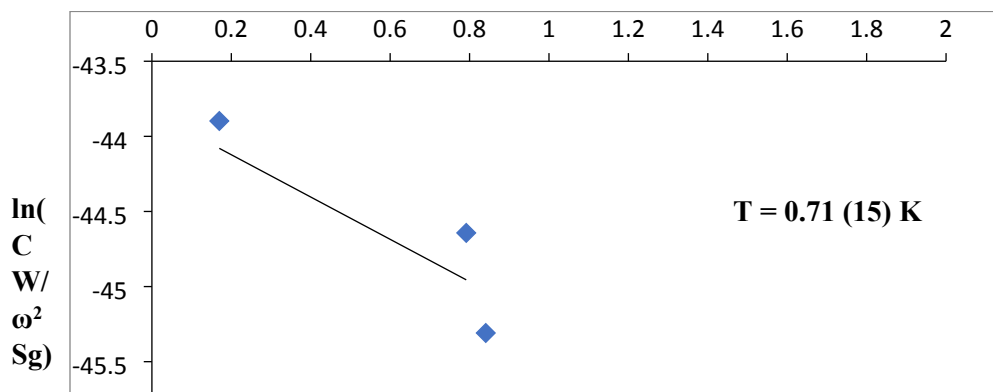
J up	Ka up	Kc up	F up	J low	Ka low	Kc low	F low	Observed (MHz)	Calculated (MHz)
1	1	1	1	0	0	0	1	7963.547	7963.536
1	1	1	2	0	0	0	1	7963.781	7963.766
2	1	2	2	1	1	1	2	8693.984	8693.995
2	1	2	2	1	1	1	1	8694.203	8694.225
2	1	2	3	1	1	1	2	8694.453	8694.458
4	2	2	5	4	1	3	5	9118.094	9118.109
2	0	2	3	1	0	1	2	9183.125	9183.102
2	0	2	1	1	0	1	1	9183.438	9183.452
3	2	1	4	3	1	2	4	9545.781	9545.8
2	1	1	1	1	1	0	1	9796.875	9796.878
2	1	1	2	1	1	0	1	9797.266	9797.262
2	1	1	3	1	1	0	2	9797.453	9797.447
2	1	1	2	1	1	0	2	9797.688	9797.694
2	1	1	1	1	1	0	0	9797.969	9797.958
3	0	3	4	2	1	2	3	10770.58	10770.63
2	1	2	2	1	0	1	1	12034.97	12034.97
2	1	2	3	1	0	1	2	12035.23	12035.23
2	1	2	1	1	0	1	1	12035.67	12035.69
3	0	3	4	2	0	2	3	13622.73	13622.75
3	2	2	3	2	2	1	2	13868.73	13868.72
3	2	2	4	2	2	1	3	13868.97	13868.94
3	1	3	3	2	0	2	3	15855.84	15855.85
3	1	3	3	2	0	2	2	15856.13	15856.11
3	1	3	4	2	0	2	3	15856.42	15856.4

Figure S3: The Boltzmann plot for (a) *syn* and (b) *eclipsed* 3-pentenenitrile. The rotational temperature

$$W = \frac{4\pi^2 \omega_0^2 S \mu_i^2 g_l g_l \epsilon N_{tot}}{c \sqrt{\alpha} k T_{rot}} e^{\frac{-E_l}{kT_{rot}}}$$

calculated using the equation: $T = \frac{E_l}{k \ln\left(\frac{4\pi^2 \omega_0^2 S \mu_i^2 g_l g_l \epsilon N_{tot}}{c \sqrt{\alpha} k T_{rot} W}\right)}$, are shown in the respective plots.³ The errors on the rotational temperatures were derived from the best-fit plot based on the scatter in the intensities within the set of transitions rather than based on errors from multiple measurements of each rotational transition.

(a) *Syn* 3-pentenenitrile



ln(
C
W/
 ω^2
Sg)

T = 0.70 (11) K

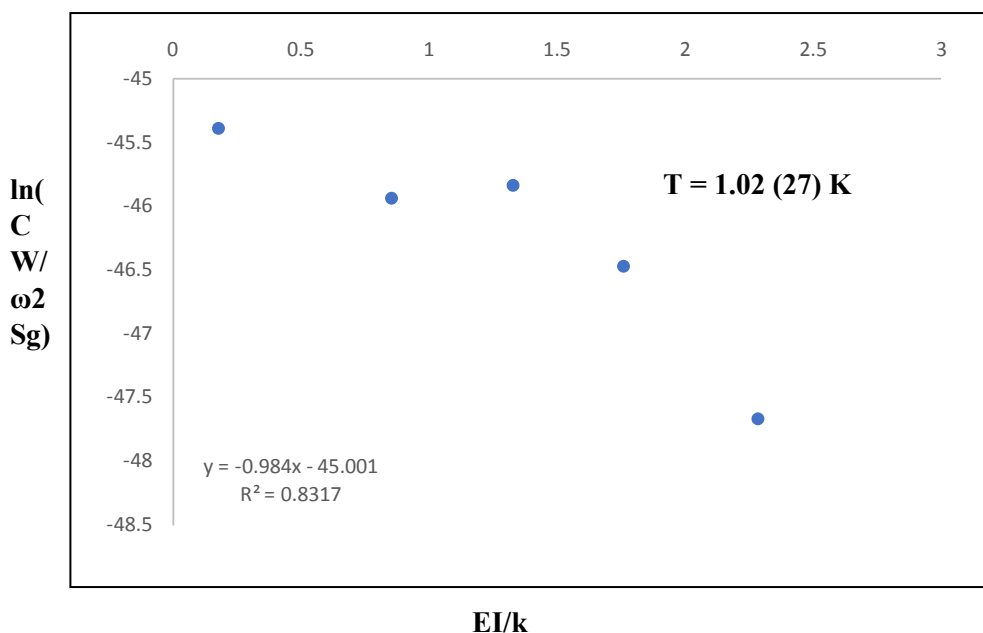
EI/k

Figure S4: The Boltzmann plot for (a) *eg+*, (b) *et*, (c) *eg-*, (d) *st* and (e) *sg-* 4-pentenenitrile. The

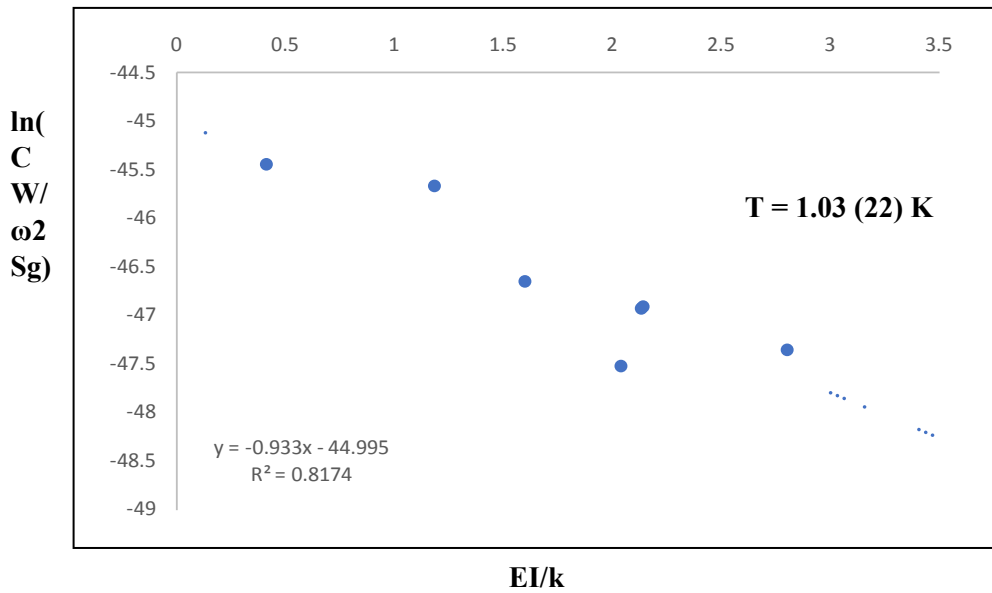
$$W = \frac{4\pi^2 \omega_0^2 S \mu_i^2 g_l g_l \epsilon N_{tot}}{c \sqrt{a} k T_{rot}} e^{\frac{-E_l}{kT_{rot}}}$$

rotational temperature calculated using the equation: , are shown in the respective plots.³ The errors on the rotational temperatures were derived from the best-fit plot based on the scatter in the intensities within the set of transitions rather than based on errors from multiple measurements of each rotational transition.

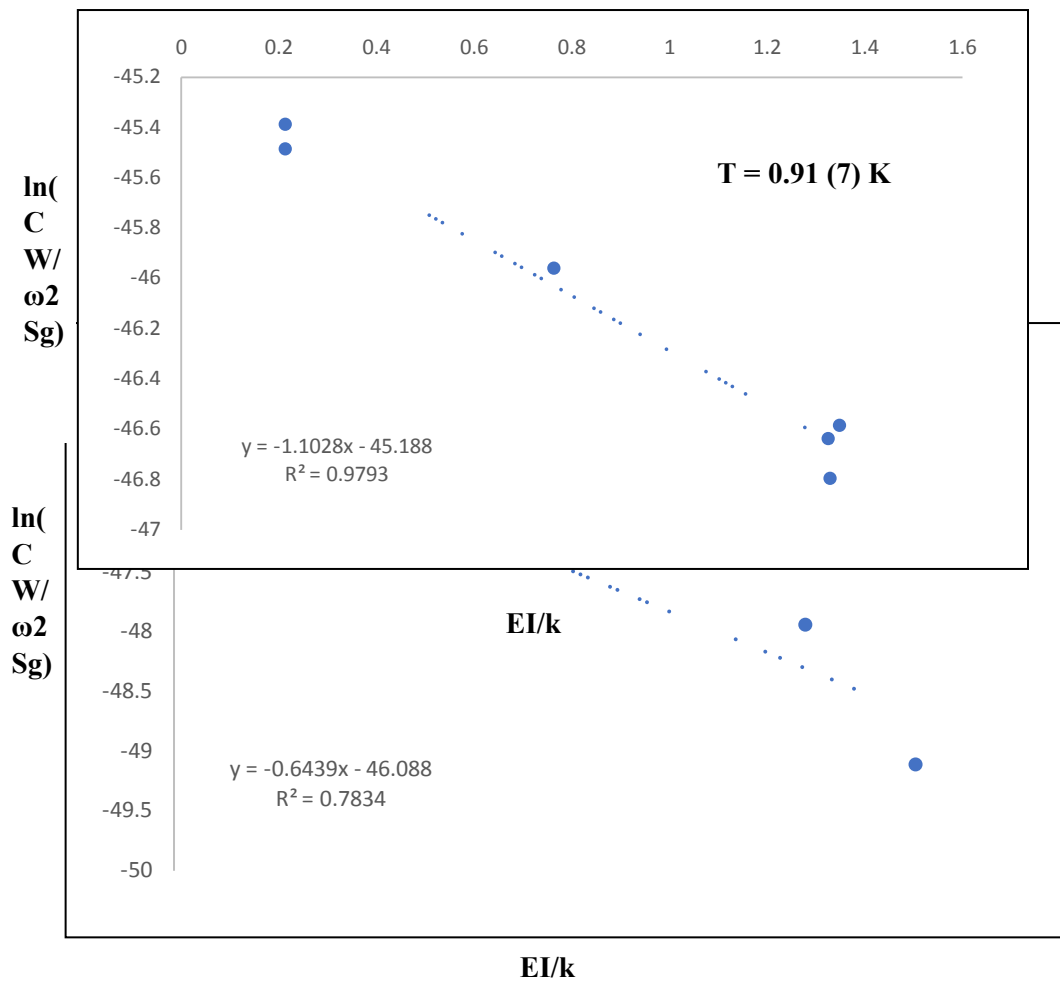
(a) *eg+* 4-Pentenenitrile



(b) *et* 4-pentenenitrile



(c) *eg*- 4-Pentenenitrile



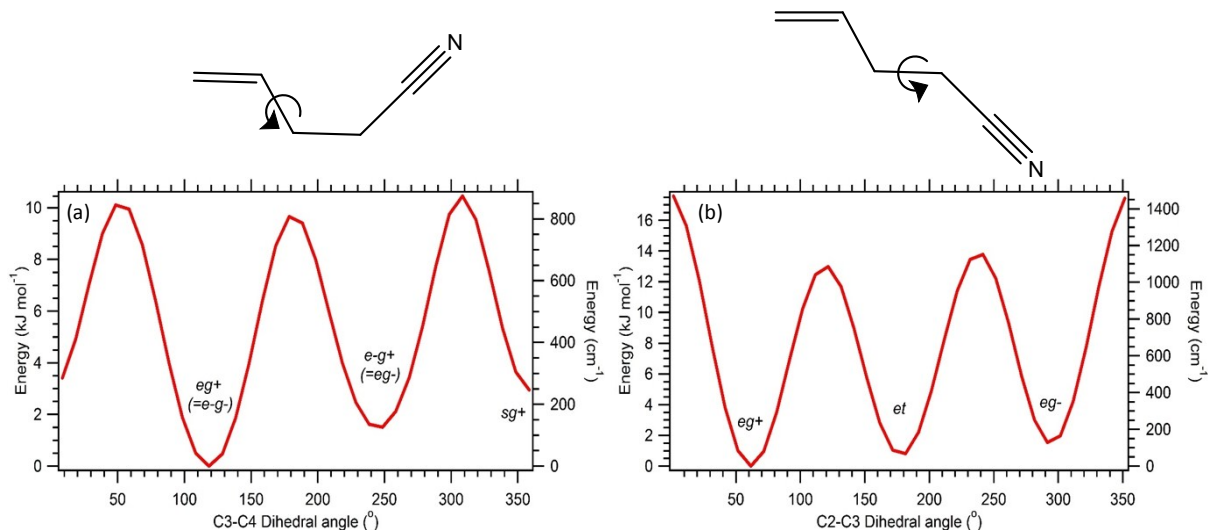


Figure S5: Relaxed potential energy scans for 4-PN of the dihedral angle indicated above it, calculated at the dispersion corrected DFT B3LYP-GD3BJ/Def2TZVP level of theory. (a) The C3-C4 dihedral with C2-C3 in gauche(+) ($xg+$), and (b) the C2-C3 dihedral with C3-C4 in its eclipsed configuration (ex). The flexible dihedral angle was rotated in 10° steps.

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