

Predicting Vibrational Satellite transitions of precursor *syn* 3-pentenenitrile

Anharmonic frequency calculation was performed on *syn* 3-pentenenitrile (3-PN), using Gaussian 09 suite of program¹ at the dispersion-corrected B3LYP-GD3BJ/Def2TZV level of theory.^{2,3} The predicted rotational constants obtained, correspond to its equilibrium geometry, labelled A_e , B_e , and C_e , and vibrational zero-point energy state, labelled A_0 , B_0 , and C_0 in the table labelled ‘Rotational Constants (in MHz)’ in the output file. We also have the experimental A_0 , B_0 , and C_0 , from our ground vibrational state fits.⁴ The ‘Vibro-Rot alpha Matrix (in MHz)’ (**Table S1**) from the calculated output file lists the coupling between the rotational constants and the corresponding vibrational mode. Vibrational mode assignments to the α_i 's were also confirmed by inspecting the vibrational displacements and its effect over the inertial axes. For example, The vibrational mode frequency 1437.016 cm^{-1} has the highest $\alpha_{A,i}$, implying this vibration is primarily along the A inertial axis. Applying the following equation, we predicted the rotational constants corresponding to a specified vibrational state:⁵

$$B_v = B_e - \sum \alpha_i \left(v_i + \frac{1}{2} \right)$$

Here, B refers to rotational constant, v corresponds to the vibrational quantum number of a particular mode of vibration (i), and e refers to equilibrium. Hence, when $v_i=0$ for all i 's, $B_v=B_0$. As a check, if all v_i 's are set to -0.5, then $B_v=B_e$. After obtaining the rotational constants of the vibrational satellites, we add the difference between the predicted and experimental A_0 , B_0 , and C_0 to get rotational constants that are more accurate. These ‘updated’ rotational constant predictions are typically accurate to within 1% of the experimental rotational constants. The distortion coefficients were taken from the fit of *syn* 3-PN for the initial assessment in our previous work.⁴ No rotational transitions were found around the predicted lines, implying there was no evidence for vibrational satellite transitions in our expansion, probably because, as seen in **Table S1**, the vibrational mode frequencies are $>100\text{cm}^{-1}$.

Table S1: α along with the corresponding i^{th} vibrational mode.

$\alpha_{A,i}$ (MHz)	$\alpha_{B,i}$ (MHz)	$\alpha_{C,i}$ (MHz)	Vibrational mode frequency (cm^{-1})
-3.40995	2.80596	1.77293	149.075
-3.68552	3.20436	2.01165	128.079
0.00876	0.40339	0.19944	220.931
5.56682	-0.46312	-0.1947	241.737
-9.4367	1.7931	0.83823	292.338
4.40075	0.08059	0.02848	373.261
-4.2125	1.42019	0.58195	432.555
30.30481	2.14441	2.5775	673.866
23.74138	0.92025	1.57666	743.547
-67.6891	-0.38762	-1.41882	837.031
74.26156	-2.55024	-0.11017	936.187
-2.2529	0.53326	-1.06944	952.233
1.08064	3.35404	1.92887	989.07
5.50546	-0.98951	0.97837	1032.583
-0.43155	-0.42071	0.36827	1053.493
9.6067	-1.70946	0.69677	1101.625
25.21405	-3.31536	-2.33988	1210.856
-11.932	2.25505	2.45238	1283.697
7.01331	2.08339	0.49632	1336.784
34.164	-1.45868	0.39507	1342.872
10.5327	-1.04906	-0.97954	1382.876
-67.9412	3.25592	1.65463	1422.443
75.90597	2.18154	1.84222	1437.016
-12.0761	6.22368	4.56789	1450.668
10.34386	0.20569	-0.10648	1705.391
2.86076	0.34069	1.11335	2330.356
-35.221	2.32783	2.51712	2908.028
-9.13638	1.28033	-1.05012	2930.497
-70.967	-1.25018	-0.56342	2891.42
52.08521	1.27884	-0.37004	2922.716
15.68952	0.51028	-0.40245	2948.751
-71.0843	-0.44373	2.2935	2979.761
2.00319	6.4789	0.58668	3022.156

Predicting and fitting ^{13}C isotopologues of precursor *syn* 3-pentenenitrile

All five ^{13}C isotopologue calculations were performed on *syn* 3-pentenenitrile (3-PN), using Gaussian 09 suite of program¹ at the dispersion-corrected B3LYP-GD3BJ/Def2TZV level of theory.^{2,3} The following formula was used to obtain a more accurate rotational constant prediction:

$$\text{Accurate pred.}(^{13}\text{C}) = \frac{\text{expt.}(^{12}\text{C})}{\text{pred.}(^{12}\text{C})} \times \text{pred.}(^{13}\text{C})$$

Pred. refers to predicted and *expt.* refers to experimental rotational constants, from our previous work.⁴ The ‘*Accurate pred.* (^{13}C)’ rotational constants, we looked for the ^{13}C isotopologue peaks, all five of which were found within our spectrum. Following the C atom numbering from the nitrile group, the ^{13}C isotopologues for *syn* 3-PN are labelled $^{13}\text{C}(1)$, $^{13}\text{C}(2)$, $^{13}\text{C}(3)$, $^{13}\text{C}(4)$, and $^{13}\text{C}(5)$ with the C atom numbers written in brackets. Nuclear quadrupolar coupling and methyl internal rotation were not considered in our fitting process as the number of lines were very few and we could not resolve the hyperfine and A/E methyl rotor state splittings. The experimental line list of all the ^{13}C isotopologues are listed in **Table S2**. These were partially fit using SPFIT as part of the CALPGM suite,⁶ and the rotational constants are listed in **Table 1**. The SPFIT/SPCAT input files are available in the **Supplementary Information**. The ^{15}N isotopologue was not found within our rotational spectrum. We did not attempt to look for isotopologues of *eclipsed* 3-PN as the population trapped was too low to observe.

Table S2: Line list of the ^{13}C isotopologues of *syn* 3-PN.

Isotopologue label	J up	K _a up	K _c up	J low	K _a low	K _c low	Observed (MHz)
$^{13}\text{C}(1)$	4	1	3	3	1	2	14655.6875
	5	1	5	4	1	4	16621.0000
	5	0	5	4	0	4	17256.8750
	5	2	4	4	2	3	17485.4375
	5	2	3	4	2	2	17742.8750
	4	0	4	3	0	3	13881.1250
$^{13}\text{C}(2)$	4	1	3	3	1	2	14749.9375
	5	1	5	4	1	4	16681.5625
	5	0	5	4	0	4	17326.1250
	5	2	4	4	2	3	17576.0000
	5	2	3	4	2	2	17857.5625
	4	0	4	3	0	3	13943.3750
$^{13}\text{C}(3)$	4	1	3	3	1	2	14775.4375
	5	1	5	4	1	4	16722.4375
	5	0	5	4	0	4	17366.9375
	5	2	3	4	2	2	17888.3125
	4	0	4	3	0	3	13974.5000
$^{13}\text{C}(4)$	4	1	3	3	1	2	14727.7500
	5	1	5	4	1	4	16692.1250
	5	0	5	4	0	4	17332.1875
	5	2	4	4	2	3	17566.3750
	5	2	3	4	2	2	17830.2500
	4	0	4	3	0	3	13943.3750
$^{13}\text{C}(5)$	5	1	5	4	1	4	16376.2500
	5	2	4	4	2	3	17218.3125
	5	2	3	4	2	2	17463.5625
	4	0	4	3	0	3	13672.5625

Table S3. Zero-point corrected energies (kJ mol⁻¹) of 2,4-pentadienenitrile isomers and conformers relative to *Z-trans*-2,4-pentadienenitrile, calculated at the DFT B3LYP-GD3BJ/Def2TZVP^{2,3} level of theory.

2,4-Pentadienenitrile	Z-isomer	E-isomer
<i>Trans</i> -conformer	0	0.3
<i>Cis</i> -conformer	15.1	14.5

References

- (1) D. J. Frisch, M. J. Trucks, G. W. Schlegel, H. B. Scuseria, G. E. Robb, M. A. Cheeseman, J. R. Scalmani, G. Barone, V. Mennucci, B. Petersson, G. A. Nakatsuji, H. Caricato, M. Li, X. Hratchian, H. P. Izmaylov, A. F. Bloino, J. Zheng and G. Sonnenb, GAUSSIAN 09, Revision A. 1, Gaussian, Inc., Wallingford CT, **2009**.
- (2) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
- (3) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
- (4) P. Mishra, S. M. Fritz, B. M. Hays, D. N. Mehta-Hurt, K. M. Jawad and T. S. Zwier, *Phys. Chem. Chem. Phys.*, 2019, **21**, 23651.
- (5) P. F. Bernath, *Spectra of Atoms and Molecules*, 2nd Edition.; Oxford University Press, 2005.
- (6) H. M. Pickett, *J. Mol. Spectrosc.*, 1991, **148**, 371.