

# *Supporting Information*

## Pure rotational and vibrational investigation of cyanophenylacetylene ( $\text{C}_6\text{H}_5\text{C}_3\text{N}$ )

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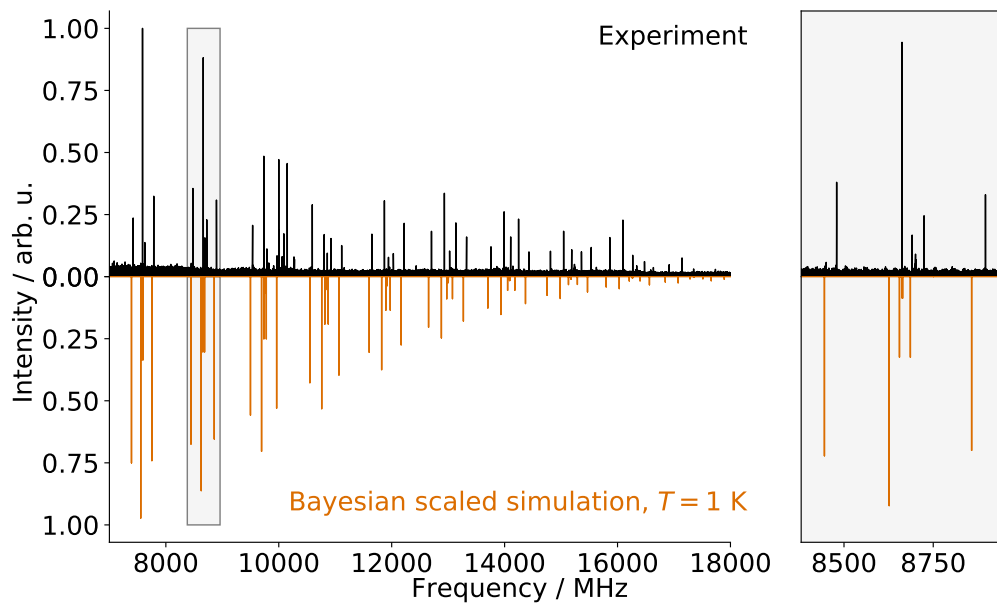


Figure S1: Experimental CP-FTMW spectrum (in black) of PhC<sub>3</sub>N and comparison with a simulation at  $T_{\text{rot}} = 1$  K using the Bayesian scaled set of rotational constants (in orange). Simulation performed using the PGOPHER software [1].

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PhC<sub>3</sub>N - wB97XD/cc-pVQZ

C	0.00000	0.00000	-0.37697
C	-0.00000	1.20783	-1.07655
C	-0.00000	1.20212	-2.45919
C	0.00000	0.00000	-3.15123
C	-0.00000	-1.20783	-1.07655
C	-0.00000	-1.20212	-2.45919
H	0.00000	0.00000	-4.23221
H	0.00000	-2.13859	-2.99859
H	0.00000	2.13859	-2.99859
H	-0.00000	2.13971	-0.52977
C	-0.00000	-0.00000	1.04708
H	-0.00000	-2.13971	-0.52977
C	-0.00000	-0.00000	2.24846
C	-0.00000	-0.00000	3.61995
N	-0.00000	-0.00000	4.77057

Table S1: Optimized equilibrium structure for PhC<sub>3</sub>N

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PhCCNC - wB97XD/cc-pVQZ

C	0.00000	-0.00000	0.34801
C	0.00000	1.20610	1.05012
C	0.00000	1.20113	2.43316
C	0.00000	-0.00000	3.12656
C	0.00000	-1.20610	1.05012
C	0.00000	-1.20113	2.43316
C	-0.00000	0.00000	-1.07877
H	0.00000	-2.13857	0.50420
H	-0.00000	2.13857	0.50420
H	0.00000	2.13823	2.97177
H	0.00000	-0.00000	4.20756
H	0.00000	-2.13823	2.97177
C	-0.00000	0.00000	-2.27706
N	-0.00000	0.00000	-3.58777
C	-0.00000	0.00000	-4.75947

Table S2: Optimized equilibrium structure for PhCCNC

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2-CEB - wB97XD/cc-pVQZ

N	2.03046	2.29735	-0.00000
C	1.13723	1.57719	-0.00000
C	0.00000	0.70670	-0.00000
C	-1.27703	1.25948	-0.00000
C	-2.38810	0.43728	-0.00000
C	-2.22851	-0.94055	0.00000
C	-0.96308	-1.49784	0.00000
C	0.16962	-0.68639	0.00000
C	1.47265	-1.26646	0.00000
C	2.56688	-1.74980	0.00000
H	-1.38577	2.33413	-0.00000
H	-3.37744	0.87135	-0.00000
H	-3.09573	-1.58553	0.00000
H	-0.83535	-2.57029	0.00000
H	3.54307	-2.16882	0.00000

Table S3: Optimized equilibrium structure for 2-cyanoethynylbenzene (CEB).

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3-CEB - wB97XD/cc-pVQZ

N	-3.41959	-1.41606	-0.00000
C	-2.43943	-0.81962	-0.00000
C	-1.21675	-0.07068	-0.00000
C	-0.00000	-0.74224	0.00000
C	1.18921	-0.01921	0.00000
C	2.44509	-0.70232	0.00000
C	3.49696	-1.27279	0.00000
C	1.14276	1.37538	0.00000
C	-0.07306	2.03599	-0.00000
C	-1.25750	1.32147	-0.00000
H	0.02394	-1.82174	0.00000
H	4.42990	-1.78083	0.00000
H	2.06790	1.93333	0.00000
H	-0.09777	3.11610	-0.00000
H	-2.21048	1.82977	-0.00000

Table S4: Optimized equilibrium structure for 3-cyanoethynylbenzene (CEB).

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4-CEB - wB97XD/cc-pVQZ

N	0.00000	-0.00000	3.98815
C	0.00000	-0.00000	2.84052
C	0.00000	-0.00000	1.40784
C	0.00000	-1.20724	0.71302
C	-0.00000	-1.20528	-0.66698
C	-0.00000	0.00000	-1.37042
C	-0.00000	0.00000	-2.79927
C	-0.00000	0.00000	-3.99611
C	0.00000	1.20528	-0.66698
C	0.00000	1.20724	0.71302
H	0.00000	-2.13957	1.25833
H	-0.00000	-2.13790	-1.21161
H	-0.00000	0.00000	-5.05843
H	0.00000	2.13790	-1.21161
H	0.00000	2.13957	1.25833

Table S5: Optimized equilibrium structure for 4-cyanoethynylbenzene (CEB).

Table S6: Theoretical rotational constants for the  $\text{PhC}_3\text{N}$  isomers of interest. Values are given in MHz.  $A(BC)_e$  and  $A(BC)'$  values correspond to theoretical equilibrium values, calculated at the  $\omega\text{B97X-D/cc-pVQZ}$  level of theory, without and with (respectively) the mean Bayesian scaling correction ( $0.9866 \times A(BC)_e$ ) from Table 3 of Ref. [2].  $A(BC)_0$  values correspond to ground state predictions from the anharmonic (VPT2) calculation at the same level of theory.  $A(BC)_{se}$  values correspond to values scaled using semi-empirical scaling factors derived as the ratio of the  $\text{PhC}_3\text{N}$  equilibrium values and the experimentally determined parameters reported in this work. Dipole moments are given in Debye, with a nominal Bayesian uncertainty of  $\pm 0.25$  D.

Parameter	$\text{PhC}_3\text{N}$	$\text{PhCCNC}$	<i>o</i> -CEB	<i>m</i> -CEB	<i>p</i> -CEB
$A_e$	5733.690	5744.789	2029.195	2734.488	5724.561
$B_e$	574.729	594.030	1347.768	915.351	715.683
$C_e$	522.368	538.362	809.865	685.788	636.151
$A_0$	5695.809				
$B_0$	573.722				
$C_0$	521.119				
$A'$	5656.859	5667.809	2002.004	2697.846	5647.852
$B'$	567.027	586.070	1329.708	903.086	706.093
$C'$	515.368	531.148	799.013	676.599	627.627
$A_{se}$	—	5670.050	2002.796	2698.913	5650.085
$B_{se}$	—	588.710	1335.696	907.153	709.273
$C_{se}$	—	533.247	802.170	679.272	630.107
$\mu_a$	5.89	4.42	3.94	3.63	4.28
$\mu_b$	0	0	2.32	2.51	0
$\mu_c$	0	0	0	0	0



- [1] C. M. Western, PGOPHER: A Program for Simulating Rotational, Vibrational and Electronic Spectra, *J. Quant. Spectrosc. Radiat. Transfer* 186 (2017) 221–242.
- [2] K. L. K. Lee, M. McCarthy, Bayesian Analysis of Theoretical Rotational Constants from Low-Cost Electronic Structure Methods, *The Journal of Physical Chemistry A* 5 (2020) 898–910.