Supplementary Information.

Microwave spectrum of 2-phenylindole (PI).

Figure S-1 shows a typical segment of the pure rotational spectrum of PI. The *a*-type transitions were the most intense ones owing to the higher dipole moment along this axis; the *b*-type transitions required a larger number of accumulations. 13 ^{a}R- and 5 ^{b}R-type transitions were assigned using jb95 (see Table S-1). Only the ^{b}R-type transitions showed a ^{14}N quadrupole splitting pattern. Unfortunately, the quadrupole splitting of the *a*-type signals was too small to be resolved. Thus, the quadrupole constants were set equal to their theoretical values in the final fit of all the data (Table S-2).

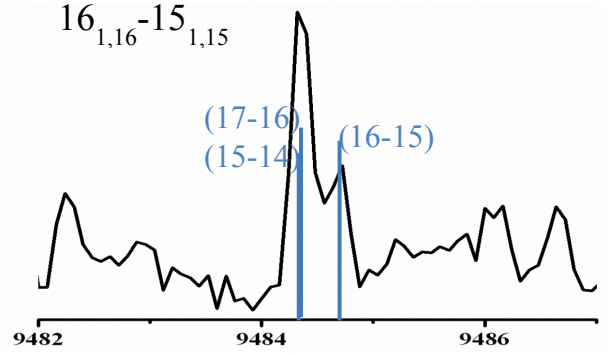

Figure S-1. $16_{1,16}$-$15_{1,15}$ rotational transition of 2-phenylindole. The black trace shows the experimental lines, while the blue bars show the predicted ^{14}N quadrupole splitting. The hyperfine components are labeled by the quantum number *F*.

Table S-1. Assigned transitions of 2-phenylindole.

Transition	Observed (MHz)	Calculated (MHz)	Obs-calc (MHz)
12_{111}- 11_{110} (13-12)	6919.60	6919.51	0.08
13_{013}- 12_{012} (14-13)	7207.05	7207.05	0.00
13_{211}- 12_{210} (14-13)	7422.80	7422.84	-0.04
13_{112}- 12_{111} (14-13)	7490.30	7490.29	0.01
14_{114}- 13_{113} (15-14)	7638.50	7638.46	0.04
14_{014}- 13_{013} (15-14)	7744.70	7744.71	-0.01
12_{112}- 11_{011} (13-12)	7748.94	7748.95	-0.01
12_{112}- 11_{011} (12-11)	7749.49	7749.45	0.04
14_{212}- 13_{211} (15-14)	8006.80	8006.79	0.01
15_{115}- 14_{114} (16-15)	8179.40	8179.38	0.01
15_{015}- 14_{014} (16-15)	8280.16	8280.16	0.00
15_{213}- 14_{212} (16-15)	8592.00	8592.09	-0.09
14_{114}- 13_{013} (15-14)	8610.20	8610.26	-0.06
16_{116}- 15_{115} (17-16)	8719.60	8719.60	0.00
15_{115}- 14_{014} (16-15)	9044.99	9044.94	0.05
15_{115}- 14_{014} (15-14)	9045.32	9045.31	0.01
16_{214}- 15_{213} (17-15)	9178.40	9178.33	0.07
16_{116} -15_{015} (17-16)	9484.39	9484.38	0.01
16_{116} -15_{015} (16-15)	9484.70	9484.71	-0.01
17_{215}- 16_{214} (18-17)	9765.00	9765.04	-0.04
17_{117} -16_{016} (18-17)	9929.74	9929.74	0.00
17_{117} -16_{016} (17-16)	9929.99	9930.03	-0.04

Table S-2. Rotational parameters of 2-phenylindole in its ground electronic state.

Parameters	**Experiment**	**Theory**[a]
A (MHz)	2305.270(56)	2318
B (MHz)	297.15977(80)	298
C (MHz)	266.31594(71)	268
μ_a (D)	-	1.6
μ_b (D)	-	1.2
χ_{aa} (MHz)	[1.64] [b]	1.64
χ_{bb} (MHz)	[1.35]	1.35
χ_{cc} (MHz)	[-2.99]	-2.99

[a] Calculated using Gaussian03 (M052x/6-311++g(d,p)). [b] Parameters fixed in the fit.