Spectroscopic and Theoretical Study of the Intramolecular π-Type Hydrogen Bonding and Conformations of 3-Cyclopentene-1-amine

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SUPPORTING INFORMATION

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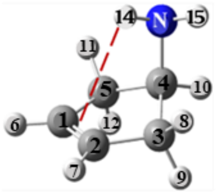
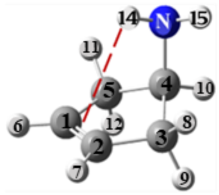
Table S1. Structural Parameters for all of the Six Conformers of 3CPAM from CCSD/cc-pVTZ computations



3CPAM Conformer

	A1	A2	B1	B2	C	D
Bond lengths (Å)						
$C_1{=}C_2$	1.334	1.334	1.335	1.335	1.334	1.332
$C_1{-}C_5$	1.511	1.510	1.509	1.510	1.510	1.508
$C_2{-}C_3$	1.510	1.511	1.510	1.509	1.510	1.508
$C_3{-}C_4$	1.550	1.543	1.548	1.540	1.540	1.544
$C_4{-}C_5$	1.543	1.550	1.540	1.548	1.540	1.544
$C_1{-}H_6$	1.081	1.081	1.081	1.081	1.081	1.081
$C_2{-}H_7$	1.081	1.081	1.081	1.081	1.081	1.081
$C_3{-}H_8$	1.092	1.090	1.096	1.096	1.094	1.092
$C_3{-}H_9$	1.095	1.093	1.091	1.090	1.091	1.094
$C_4{-}H_{10}$	1.089	1.089	1.092	1.092	1.097	1.094
$C_5{-}H_{11}$	1.090	1.092	1.096	1.096	1.094	1.092
$C_5{-}H_{12}$	1.093	1.095	1.090	1.091	1.091	1.094
$C_4{-}N_{13}$	1.466	1.466	1.458	1.458	1.463	1.468
$N_{13}{-}H_{14}$	1.014	1.013	1.013	1.012	1.013	1.013
$N_{13}{-}H_{15}$	1.013	1.014	1.012	1.013	1.013	1.013
Angles (degrees)						
$C_1{=}C_2{-}C_3$	111.3	111.5	111.3	111.6	111.5	111.8
$C_5{-}C_1{=}C_2$	111.5	111.3	111.6	111.3	111.5	111.8
$C_2{-}C_3{-}C_4$	103.0	103.1	102.7	102.8	102.8	103.6
$C_4{-}C_5{-}C_1$	103.1	103.0	102.8	102.7	102.8	103.6
$C_3{-}C_4{-}C_5$	104.1	104.1	104.3	104.3	104.8	105.1
$C_3{-}C_4{-}N_{13}$	114.0	108.5	118.0	112.1	112.1	108.6
$C_5{-}C_4{-}N_{13}$	108.5	114.0	112.1	118.0	112.1	108.6
$C_1{=}C_2{-}H_7$	125.1	125.1	125.0	125.0	125.1	125.1
$C_1{-}C_5{-}H_{11}$	113.8	113.5	110.7	110.6	110.9	112.8
$C_1{-}C_5{-}H_{12}$	110.4	110.3	114.0	113.6	113.3	110.8
$C_2{=}C_1{-}H_6$	125.1	125.1	125.0	125.0	125.1	125.1
$C_2{-}C_3{-}H_8$	113.5	113.8	110.6	110.7	110.9	112.8
$C_2{-}C_3{-}H_9$	110.3	110.4	113.6	114.0	113.3	110.8
$C_3{-}C_2{-}H_7$	123.5	123.3	123.6	123.4	123.3	123.1
$C_3{-}C_4{-}H_{10}$	111.5	111.6	107.4	107.4	107.3	110.9
$C_4{-}C_3{-}H_8$	111.4	110.5	110.4	110.4	109.8	110.9
$C_4{-}C_3{-}H_9$	111.5	111.6	112.4	112.1	112.5	111.6
$C_4{-}C_5{-}H_{11}$	110.5	111.4	110.4	110.4	109.8	110.9

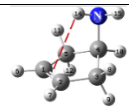
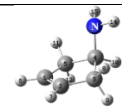
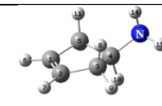
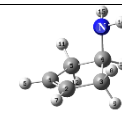
Table S1. *Continued*



3CPAM Conformer

	A1	A2	B1	B2	C	D
Angles (degrees)						
C_4-C_5-H_{12}	111.6	111.5	112.1	112.4	112.5	111.6
C_4-N_{13}-H_{14}	108.7	109.4	109.4	109.9	109.6	109.5
C_4-N_{13}-H_{15}	109.4	108.7	109.9	109.4	109.6	109.5
C_5-C_4-H_{10}	111.6	111.5	107.4	107.4	107.3	110.9
C_5-C_1-H_6	123.3	123.5	123.4	123.6	123.3	123.1
H_8-C_3-H_9	107.1	107.5	107.1	106.9	107.6	107.3
H_{10}-C_4-N_{13}	107.3	107.3	107.1	107.1	112.8	112.6
H_{11}-C_5-H_{12}	107.5	107.1	106.9	107.1	107.6	107.3
Angles between bonds						
C_1=C_2 / N_{13}-H_{14}	83.5	-2.9	93.2	-25.2	-158.9	-10.8
C_1=C_2 / N_{13}-H_{15}	-177.8	85.4	-159.5	87.2	-26.1	-172.1
C_1=C_2 / C_3-C_4	16.4	16.1	-16.6	-16.4	-15.9	12.7
C_2=C_1 / C_5-C_4	-16.1	-16.4	16.4	16.6	15.9	-12.7
C_3-C_2 / C_1-C_5	-0.3	0.3	0.1	-0.1	0.0	0.0
C_2-C_3 / C_4-C_5	-25.1	-25.0	25.6	25.5	24.6	-19.6
C_5-C_1 / C_3-C_4	16.5	16.7	-16.9	-17.0	-16.3	12.9
C_3-C_4 / N_{13}-H_{14}	-56.4	-174.0	-55.4	178.1	63.6	-179.0
C_3-C_4 / N_{13}-H_{15}	58.6	-59.0	60.7	-65.8	179.0	65.3
C_5-C_4 / N_{13}-H_{14}	59.0	-58.6	65.8	-60.7	-179.0	-65.3
C_5-C_4 / N_{13}-H_{15}	174.0	56.4	-178.1	55.4	-63.6	179.0
Selected distances (Å)						
C_1-H_{14}	2.906	3.690	3.830	4.165	4.351	3.714
C_1-H_{15}	3.953	2.948	4.383	3.846	4.097	3.993
C_2-H_{14}	2.948	3.953	3.846	4.383	4.097	3.993
C_2-H_{15}	3.690	2.906	4.164	3.830	4.351	3.714
Mid(C_1=C_2)-H_{14}	2.850	3.765	3.780	4.223	4.173	3.798
Mid(C_1=C_2)-H_{15}	3.765	2.850	4.223	3.780	4.173	3.798

Table S2. Observed and Calculated Vibrational Frequencies for the Conformers of 3CPAM

		A				B			C			D		
		Observed (OB)		Calculated		OB	Calculated		OB	Calculated		OB	Calculated	
		Freq.[a]	(IR, R)[b]	Freq.[a,c]	(IR, R)[b,c]	Δ	Δ[c]	(IR, R)[b,c]	Δ	Δ[c]	(IR, R)[b,c]	Δ	Δ[c]	(IR, R)[b,c]
Ring - Pseudo C_{2v}														
A1														
ν_1	=C-H stretch	3072	(s, 141)	3075	(25,100)	0	-1	(18, 85)	8	1	(16, 86)	8	1	(15, 57)
ν_2	CH_2 symmetric stretch	2849	(s, 67)	2894	(43, 88)	-14	-15	(26, 100)	6	8	(12, 100)	13	8	(42, 100)
ν_3	C=C stretch	1613	(m, 88)	1605[d]	(28, 46)[d]	4	5[d]	(13, 26)[b]	4	5[d]	(10, 28)[b]	16	18	(3, 65)[d]
ν_4	CH_2 deformation	1452	(m, 17)	1447	(3, 77)	3	6	(2, 82)	3	9	(2, 81)	-4	-5	(2, 99)
ν_5	CH_2 wag	1296	(w, 10)	1283	(1, 15)	6	14	(3, 11)	-12	-15	(0.4, 21)	6	9	(2, 17)
ν_6	=C-H in plane wag	1109	(w, 58)	1090	(0.1, 94)	0	2	(0.4, 100)	0	0	(2, 100)	0	4	(0.2, 100)
ν_7	Ring stretch	967	(w, 100)	962	(1, 79)	0	3	(0.8, 76)	0	4	(0.3, 75)	0	4	(2, 91)
ν_8	Ring stretch	804	(s, 43)	817	(62, 100)	28	8	(23, 51)	36	17	(12, 53)	31	12	(5, 87)
ν_9	Ring angle bend	735	(w, 9)	728	(3, 3)	-181	-180	(3, 27)	-161	-180	(0.8, 20)	-15	-8	(30, 4)
A2														
ν_{10}	CH_2 antisymmetric stretch	2929	(s, 59)	2951	(31, 48)	10	6	(27, 43)	10	8	(18, 43)	0	1	(6, 33)
ν_{11}	CH_2 twist	1235	(w, 6)	1245	(10, 32)	-132	-135	(4, 4)	-122	-126	(2, 3)	15	21	(4, 1)
ν_{12}	=C-H out-of-plane wag	934	(m, 4)	934	(27, 4)	7	5	(22, 2)	0	0	(0.01, 3)	0	-2	(0.5, 4)
ν_{13}	CH_2 rock	849	(m, 5)	870	(23, 9)	10	17	(11, 3)	24	21	(0.02, 2)	5	13	(2, 8)
ν_{14}	Ring C=C twist	358	(w, 22)	353	(9, 30)	41	38	(0.3, 15)	32	35	(0.7, 14)	-9	-10	(2, 23)
B1														
ν_{15}	=C-H stretch	3064	(s, 75)	3051	(5, 44)	0	-1	(4, 36)	0	0	(4, 37)	0	1	(4, 25)
ν_{16}	CH_2 symmetric stretch	2912	(s, 48)	2908	(38, 65)	-24	-24	(24, 22)	-7	-10	(29, 11)	-5	-10	(43, 10)
ν_{17}	CH_2 deformation	1437	(m, 4)	1436	(10, 83)	6	6	(2, 67)	11	10	(2, 61)	-4	-3	(5, 66)
ν_{18}	=C-H in-plane wag	1353	(m, 6)	1343	(5, 10)	-5	-4	(2, 13)	19	-34	(0.1, 8)	13	19	(1, 7)
ν_{19}	CH_2 wag	1284	(w, 4)	1268	(4, 4)	6	10	(6, 8)	29	-19	(4, 2)	---	23	(0.1, 0.2)
ν_{20}	Ring stretch	1026	(w, 3)	1023	(15, 30)	31	36	(12, 20)	---	-14	(1, 22)	---	-19	(2, 28)
ν_{21}	Ring stretch	926	(m, 2)	941	(48, 6)	0	-2	(0.2, 3)	---	-11	(10, 1)	---	-19	(5, 0.5)
ν_{22}	Ring angle bend	797	(w, 5)	757	(7, 8)	-12	-14	(0.5, 14)	-5	-7	(0.4, 11)	0	2	(1, 9)
B2														
ν_{23}	CH_2 antisymmetric stretch	2947	(s, 80)	2972	(20, 43)	0	1	(19, 47)	-8	-12	(21, 36)	-27	-20	(6, 33)
ν_{24}	CH_2 twist	1122	(w, 2)	1143	(2, 30)	117	102	(3, 18)	---	43	(3, 18)	---	56	(5, 49)
ν_{25}	CH_2 rock	934	(m, 4)	934	(24, 4)	50	51	(4, 16)	---	97	(2, 27)	59	56	(8, 6)
ν_{26}	=C-H out-of-plane wag	671	(s, 11)	668	(66, 29)	9	16	(41, 27)	15	22	(27, 30)	-10	-4	(15, 27)
ν_{27}	Ring puckering	---	(---, ---)	143	(1, 11)	---	-12	(0.3, 5)	---	-23	(0.7, 3)	---	-22	(0.6, 13)
C-H vibrations														
ν_{CH}	C-H stretch	2939	(s, 67)	2959	(56, 75)	-37	-37	(18, 25)	-97	-106	(36, 54)	-82	-79	(29, 19)
ω_{CH}	C-H wag (up and down)	1379	(m, 7)	1371	(9, 38)	9	5	(11, 34)	-19	-18	(24, 46)	-24	-26	(18, 45)
ω'_{CH}	C-H wag (sideways)	1244	(w, 5)	1214	(17, 19)	-48	31	(3,8)	95	9	(1, 2)	-39	-39	(0.9, 43)
NH_2 vibrations														
ν_{a-NH_2}	NH_2 antisymmetric stretch	3391	(vw, 7)	3406	(2, 28)	12	13	(1, 25)	3	8	(2, 30)	5	11	(0.9, 19)
ν_{s-NH_2}	NH_2 symmetric stretch	3329	(w, 32)	3313	(0.4, 53)	6	13	(0.3, 50)	6	13	(0.05, 65)	6	12	(0.1, 40)
δ_{NH_2}	NH_2 deformation	1623	(m, 27)	1612[d]	(16, 58)[d]	0	0[d]	(13, 73)[d]	6	6[d]	(13, 65)[d]	-6	-2	(23, 29)
t_{NH_2}	NH_2 twist	1109	(w, 58)	1119	(7, 12)	122	122	(0.7, 18)	115	104	(0.1, 24)	8	8	(0.9, 0.2)
ω_{NH_2}	NH_2 wag	849	(m, 4)	891	(100, 13)	-36	-36	(100, 6)	-18	-19	(100, 9)	-40	-41	(100, 24)
τ_{NH_2}	NH_2 torsion	264	(m, 1)	279	(54, 11)	-7	-14	(32, 8)	13	22[e]	(21, 6)	-10	-14[e]	(27, 9)
C-N vibrations														
ν_{CN}	C-N stretch	1086	(vw, 2)	1068	(2, 34)	44	54	(10, 30)	36	34	(7, 22)	0	0	(1, 44)
ω_{CN}	C-N wag	448	(vw, 6)	429	(14, 2)	11	4	(1, 9)	44	19	(10, 5)	-19	-19	(2, 0.9)
ω'_{CN}	C-N wag	366	(w, 8)	379	(5, 6)	-38	-34	(13, 12)	-12	-18	(8, 3)	8	6	(6, 4)

[a]Observed frequencies in cm^{-1}.
[b]Relative infrared (IR) and Raman (R) intensities.
[c]From MP2/cc-pVTZ computations unless indicated.
[d]C=C stretch and NH_2 deformation vibrations are coupled.
[e]Approximate shifts calculated from torsional PEFs from eq. 3.

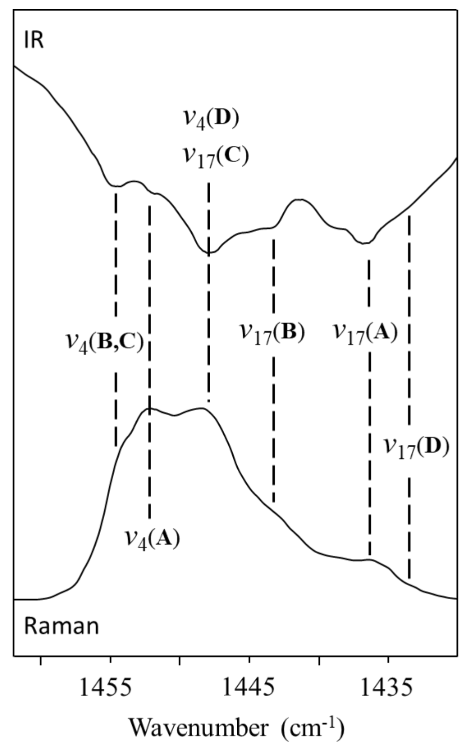


Figure S1. Vibrational spectra of the CH_2 deformation vibrations (ν_4 and ν_{17}).

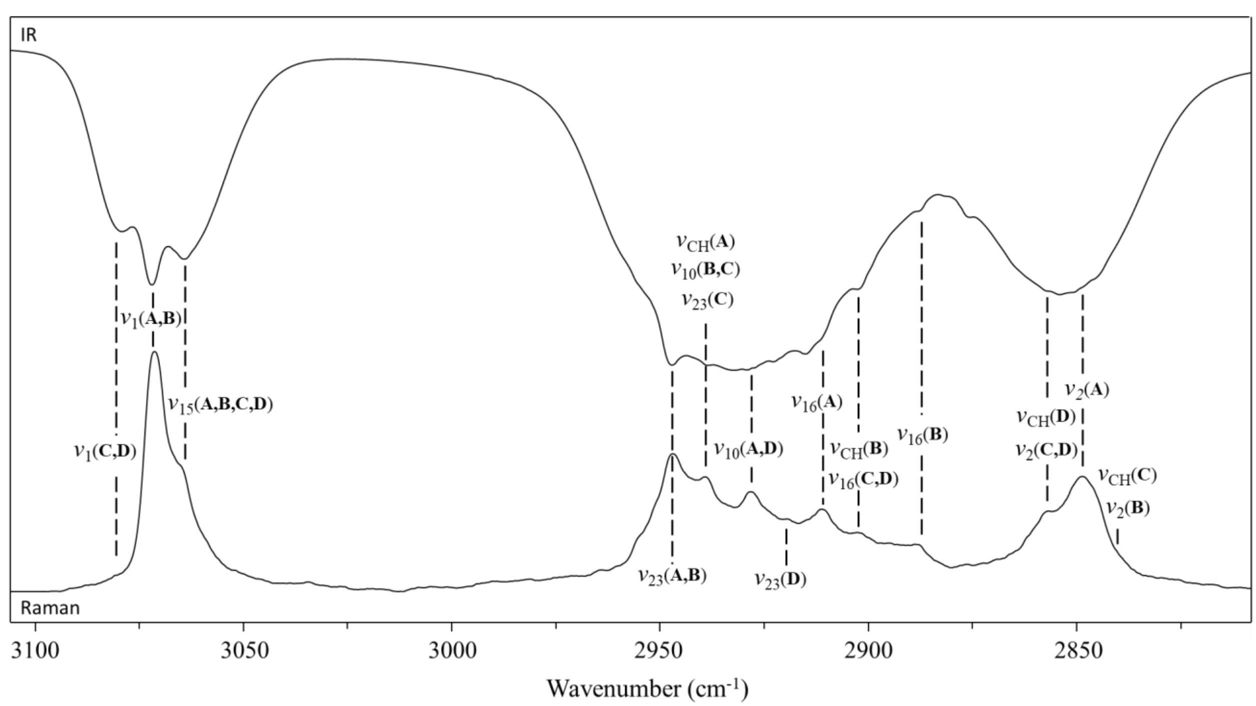


Figure S2. 3CPAM vibrational spectra in the 2800 - 3100 cm^{-1} region.

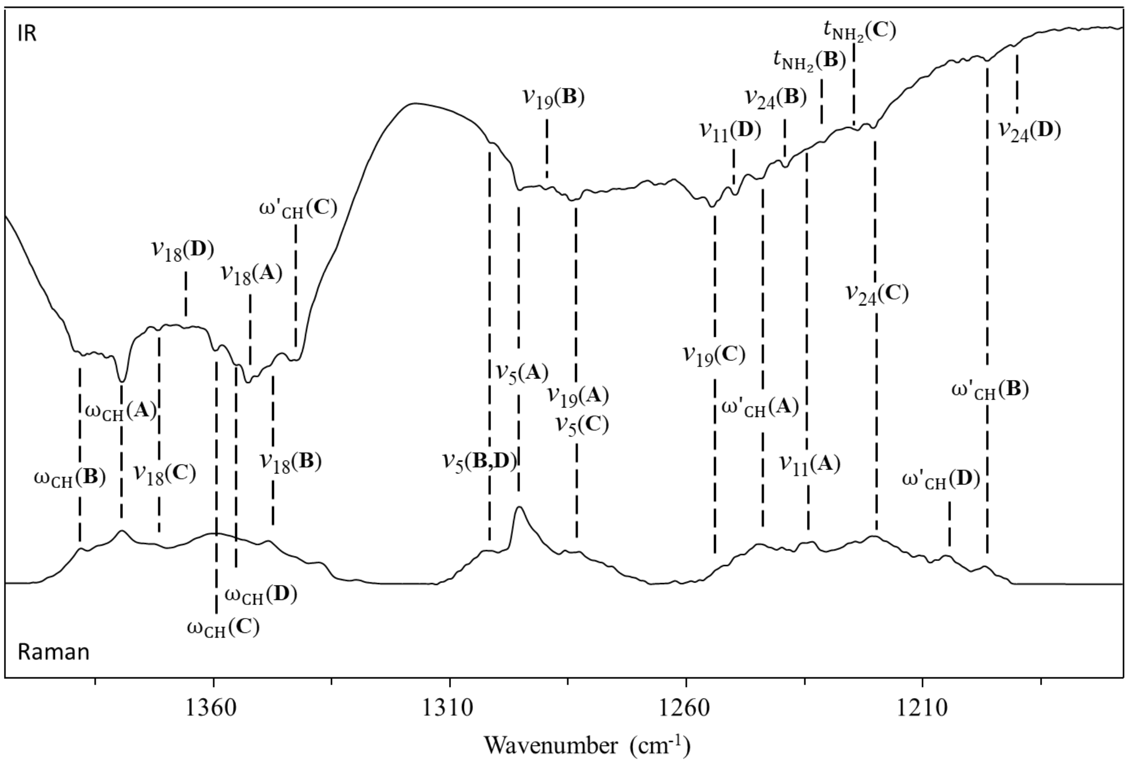


Figure S3. 3CPAM vibrational spectra in the 1180 - 1450 cm^{-1} region.

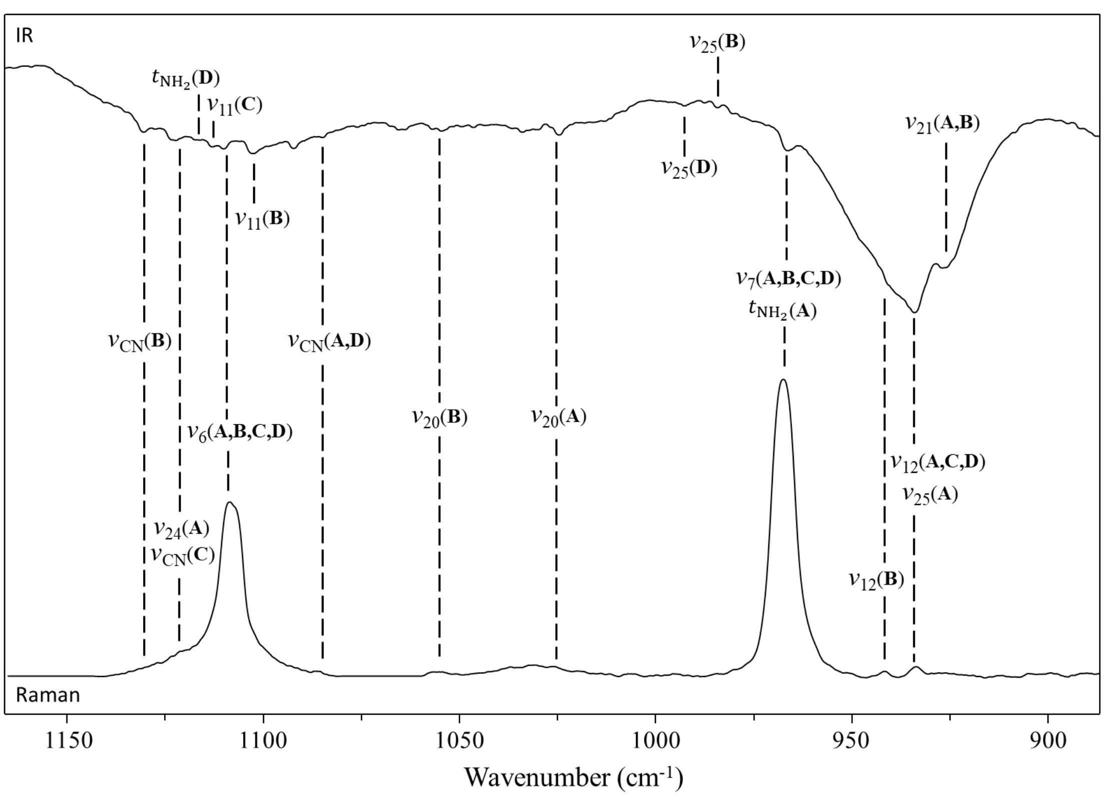


Figure S4. 3CPAM vibrational spectra in the 900 - 1150 cm^{-1} region.

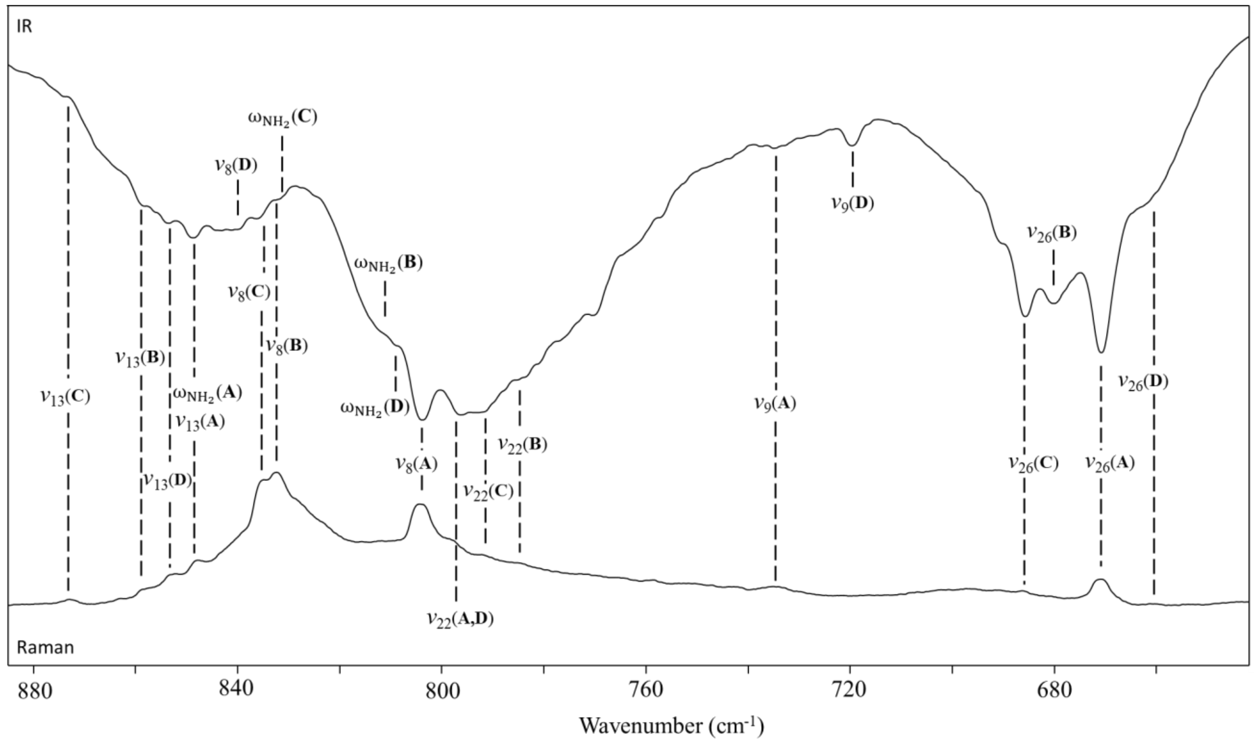


Figure S5. 3CPAM vibrational spectra in the 630 - 880 cm^{-1} region.

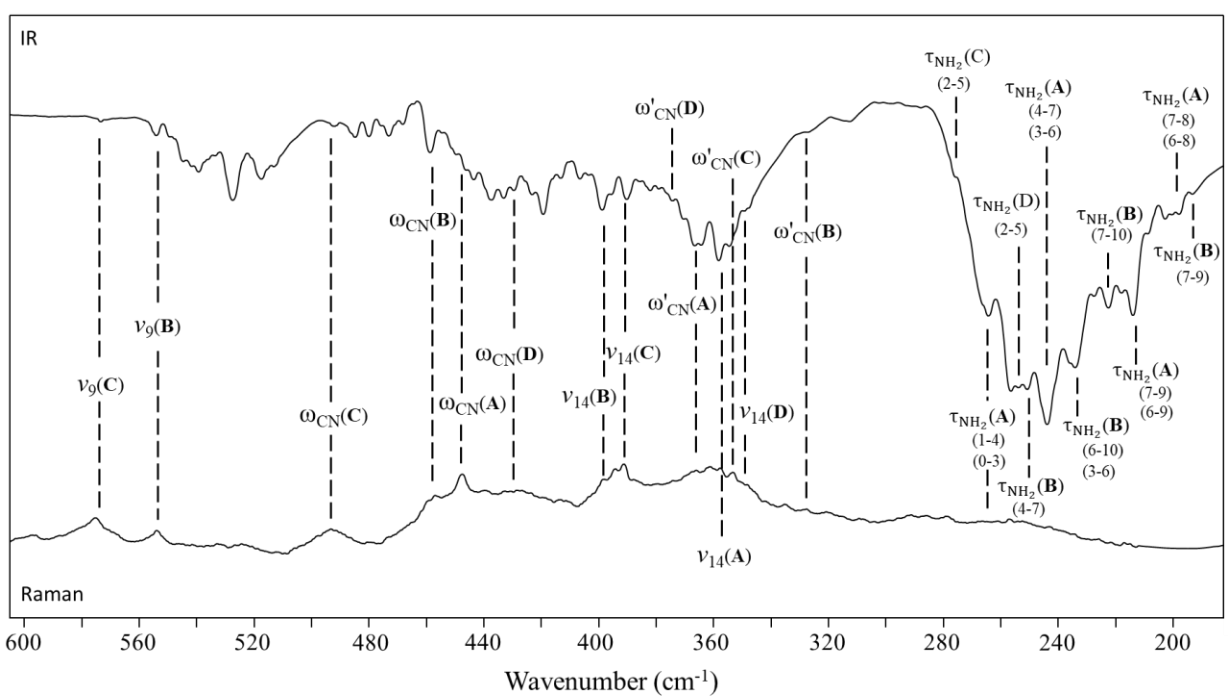


Figure S6. 3CPAM vibrational spectra in the 185 - 600 cm^{-1} region.