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Theoretical investigation of protonated thiophene and two of its nitrile substituted derivatives (2-Cyanothiophene and 3-Cyanothiophene†

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here].

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Table S1: Proton Affinity (PA in kJ/mol) of thiophene at different sites, for different levels of theory and at $T = 298.15\,K$ and $T = 10.00\,K$.

	Sites of protonation[a]					
	$T = 298.15\,K$			$T = 10.00\,K$		
Level of theory	S	$\alpha-$position	$\beta-$position	S	$\alpha-$position	$\beta-$position
M06-2X/6-31G(d,p)	622.83	818.70	782.21	617.42	813.60	777.32
M06-2X/aug-cc-pVTZ	627.86	803.24	769.96	622.41	798.20	765.08
G2MP2	739.84	816.66	785.64	734.51	811.61	780.66
G3MP2	739.47	812.98	782.59	734.11	807.90	777.61
G4MP2	637.59	811.94	783.09	632.14	806.80	778.08
G3B3	634.09	813.96	783.90	628.79	808.77	778.84
CBS-QB3	690.93	808.24	777.56	624.82	802.96	772.49
NIST			815[b]			

[a]The site with higher PA is the position with higher susceptibility of proton attack.
[b] NIST value (Hunter and Lias (1998)).

Table S2: G2(MP2) and G3B3 Proton Affinity (PA in kJ/mol) at different sites of 2CNT and 3CNT for $T = 298.15\,K$ and $T = 150.00\,K$.

	Protonation sites											
	1		**2**		**3**		**4**		**5**		**6**	
T (K)	298.15	150.00	298.15	150.00	298.15	150.00	298.15	150.00	298.15	150.00	298.15	150.00
						G2MP2						
2CNT	676.65	677.62	732.32	732.87	723.51	724.44	726.48	727.31	752.89	753.70	812.23	812.24
3CNT	673.84	671.74	758.97	756.58	697.68	695.16	728.30	726.06	752.89	751.06	813.01	810.83
						G3B3						
2CNT	674.93	676.09	727.75	728.30	721.24	722.40	724.53	725.36	750.15	750.84	809.03	810.23
3CNT	672.67	670.70	756.24	753.75	694.00	675.23	726.20	723.91	750.30	747.88	812.84	811.27

1= Sulfur atom; **2**= α-position; **3**= β-position; **4**= position equivalent to β-position; **5**= position equivalent to α-position; **6**= Protonation at N atom.

Table S3: G2(MP2) and G3B3 Proton Affinity (PA in kJ/mol) at different sites of 2CNT and 3CNT for $T = 10.00\,K$ and $T = 5.00\,K$.

	Protonation sites											
	1		**2**		**3**		**4**		**5**		**6**	
$T\,(K)$	10.00	5.00	10.00	5.00	10.00	5.00	10.00	5.00	10.00	5.00	10.00	5.00
						G2MP2						
2CNT	671.89	671.79	727.27	727.17	718.79	718.69	721.66	721.56	748.07	747.97	807.49	807.39
3CNT	669.08	668.97	754.03	753.94	692.65	692.54	723.49	723.38	748.48	743.55	808.06	807.95
						G3B3						
2CNT	670.36	670.28	722.72	722.63	716.71	716.61	719.69	719.60	745.18	745.08	804.54	804.44
3CNT	668.06	667.96	751.18	751.08	689.02	688.92	721.32	721.22	745.28	745.17	809.10	793.05

1= Sulfur atom; **2**= α-position; **3**= β-position; **4**= position equivalent to β-position; **5**= position equivalent to α-position; **6**= Protonation at N atom.

Table S4: Milliken charges for $2CNTH^+$, $3CNTH^+$ and $HCNH^+$

Atom	$2CNT\text{-}H^+$	$3CNT\text{-}H^+$	$HCNH^+$
S1	0.332	0.352	
C2	-0.137	-0.182	
C3	-0.056	0.025	
C4	-0.142	-0.184	
C5	-0.152	-0.180	
C6	0.577	0.582	
N	-0.358	-0.347	-0.429
C			0.071

Table S5: G2(MP2) Proton Affinity (PA in kJ/mol) at different sites of some dicyanothiophenes at $T = 10.00$ and $298.15\,K$.

	2		**3**		**4**		**5**		**6**		**7**		**8**	
	10.00	298.15	10.00	298.15	10.00	298.15	10.00	298.15	10.00	298.15	10.00	298.15	10.00	298.15
23CNT	681.51	686.45	643.23	648.04	675.01	679.68	696.81	701.49	777.06	782.39	777.91	781.87	1224.52	1229.04
24CNT	666.39	675.13	667.85	674.15	637.95	644.44	694.70	703.22	767.65	773.85	770.60	776.58	1261.86	1269.79

2= α-position; **3**= β-position; **4**= position equivalent to β-position; **5**= position equivalent to α-position; **6**= Protonation only at N atom of the cyano-group in α-position; **7**= Protonation only at N atom of the cyano-group in β-position; **8**= Protationation at both the two Nitrogen atoms of the cyano-groups.

Table S6: Gase phase G2(MP2) and G3B3 calculated enthalpy, entropy and Gibbs free energy ($\Delta_r H$, $\Delta_r S$ and $\Delta_r G$ in $kJ\,mol^{-1}$) of the reactions yielding hydrogen cyanide, cyano-thiophenes and their protonated forms ($T = 298.15\,K$ and $T = 10.00\,K$ for $P = 1\,atm$).

Reaction		$\Delta_r H^{298.15}$	$\Delta_r G^{298.15}$	$\Delta_r S^{298.15}$	$\Delta_r H^{10.00}$	$\Delta_r G^{10.00}$	$\Delta_r S^{10.00}$	Lev. of theory
$H_3^+ + CN^- \longrightarrow HCN + H_2$	**(1)**	-1047.03	-1038.98	-0.027	-1046.24	-1046.10	0.015	**a**
		-1048.61	-1045.03	-0.012	-1047.93	-1047.93	-0.000	**b**
$C_4H_4S^+ + CN^- \longrightarrow 2CNT + H$	**(2)**	-611.21	-597.15	-0.047	-577.91	-570.55	-0.736	**a**
		-607.98	-595.00	-0.044	-609.84	-609.43	-0.041	**b**
$C_4H_4S^+ + CN^- \longrightarrow 3CNT + H$	**(3)**	-615.65	-601.54	-0.047	-582.33	-574.97	-0.736	**a**
		-612.64	-599.65	-0.044	-614.51	-614.09	-0.041	**b**
$CN\text{-}H + H_3^+ \longrightarrow HCN\text{-}H^+ + H_2$	**(4)**	352.21	-342.91	-0.031	-350.67	-350.69	0.002	**a**
		-353.63	348.77	-0.016	-352.18	-352.18	0.000	**b**
$C_4H_4SCN + H_3^+ \longrightarrow 2CNT\text{-}H^+ + H_2$	**(5)**	-392.19	-385.01	-0.024	-392.22	-392.22	0.000	**a**
		-387.27	-385.072	-0.008	-391.56	-391.54	-0.002	**b**
$C_4H_4SCN + H_3^+ \longrightarrow 3CNT\text{-}H^+ + H_2$	**(6)**	-392.98	-385.42	-0.025	-392.79	-392.79	0.000	**a**
		-391.04	-390.81	-0.001	-392.10	-392.08	-0.002	**b**

a=G2(MP2); **b**=G3B3.

Table S7: Gase phase G3B3 calculated enthalpy, entropy and Gibbs free energy ($\Delta_r H$, $\Delta_r S$ and $\Delta_r G$ in $kJ\,mol^{-1}$) of the reactions producing hydrogen cyanide, cyano-thiophenes and their protonated forms ($T = 1000.00\,K$ and $T = 5.00\,K$ for $P = 10^{-5}\,atm$).

Reaction		$\Delta_r H^{1000.00}$	$\Delta_r G^{1000.00}$	$\Delta_r S^{1000.00}$	$\Delta_r H^{5.00}$	$\Delta_r G^{5.00}$	$\Delta_r S^{5.00}$
$H_3^+ + CN^- \longrightarrow HCN + H_2$	**(1)**	-1044.11	-1030.32	-0.046	-1018.84	-1170.50	0.509
$C_4H_4S^+ + CN^- \longrightarrow 2CNT + H$	**(2)**	-562.64	-433.66	-0.433	-574.21	-574.00	-0.001
$C_4H_4S^+ + CN^- \longrightarrow 3CNT + H$	**(3)**	-567.05	-438.47	-0.431	-578.93	-578.72	-0.001
$CN\text{-}H + H_3^+ \longrightarrow HCN\text{-}H^+ + H_2$	**(4)**	381.56	-327.04	-0.094	-352.18	-290.50	-0.207
$C_4H_4SCN + H_3^+ \longrightarrow 2CNT\text{-}H^+ + H_2$	**(5)**	-381.56	-374.56	-0.023	-391.58	-391.50	-0.0002
$C_4H_4SCN + H_3^+ \longrightarrow 3CNT\text{-}H^+ + H_2$	**(6)**	-384.86	-385.77	0.003	-392.05	-391.97	-0.0002

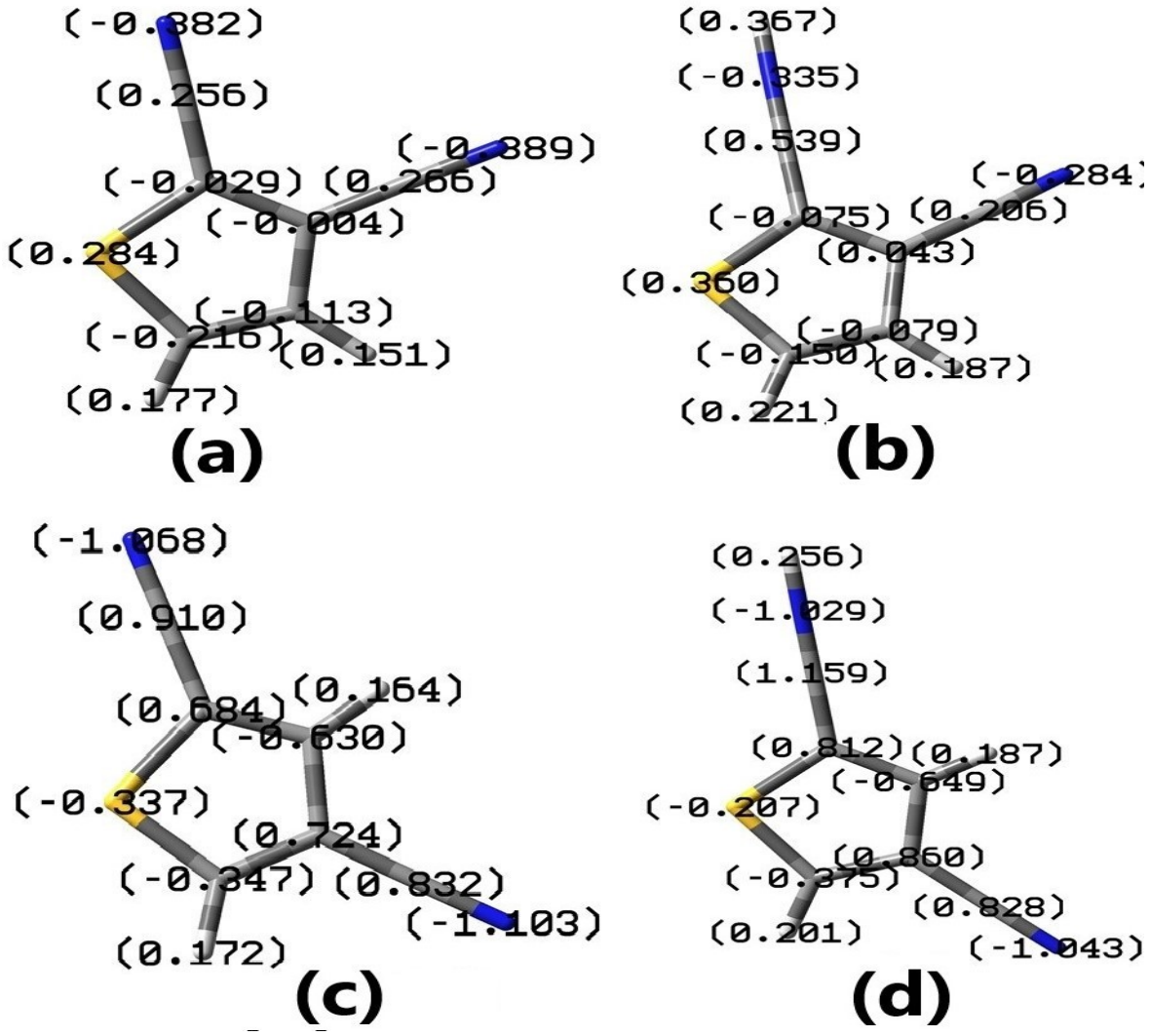

Figure S1: Partial atomic charges for (a) Neutral 2,3-dicyanothiophene and (b) Monoprotonated 2,3-dicyanonophene (c) Neutral 2,5-dicyanothiophene and (d) Monoprotonated 2,5-dicyanothiophene.

Table S8: Potential energy distribution for $2CNTH^{+}$

Frequency	PED	Mode	Atoms[1]				PED	Mode	Atoms[1]			
(cm^{-1})	(%)		h	k	l	m	(%)		h	k	l	m
In - plane modes												
3539.33	97%	ν_{NH}	7	11	0	0						
3101.63	66%	ν_{CH}	4	9	0	0	27%	ν_{CH}	5	10	0	0
	5%	ν_{CH}	3	8	0	0						
3089.33	65%	ν_{CH}	5	10	0	0	19%	ν_{CH}	3	8	0	0
	16%	ν_{CH}	4	9	0	0						
3081.49	75%	ν_{CH}	3	8	0	0	18%	ν_{CH}	4	9	0	0
	7%	ν_{CH}	5	10	0	0						
2237.41	83%	$\nu_{C\equiv N}$	6	7	0	0	14%	ν_{CC}	2	6	0	0
1497.37	29%	$\nu_{C=C}$	2	3	0	0	23%	$\nu_{C=C}$	4	5	0	0
	11%	δ_{CCH}	4	3	8	0	7%	δ_{CCH}		3	8	0
	7%	ν_{CC}	2	6	0	0	8%	δ_{CCH}	3	4	9	0
1408.49	40%	ν_{CC}	3	4	0	0	15%	δ_{CCH}	5	4	9	0
	11%	δ_{CCH}	3	4	9	0	11%	$\nu_{C=C}$	4	5	0	0
	6%	δ_{CCH}	2	3	8	0						
1335.64	24%	$\nu_{C=C}$	4	5	0	0	23%	$\nu_{C=C}$	2	3	0	0
	14%	δ_{SCH}	1	5	10	0	14%	ν_{CC}	2	6	0	0
	14%	δ_{CCH}	4	5	10	0						
1236.89	20%	δ_{CCH}	2	3	8	0	18%	δ_{CCH}	4	3	8	0
	10%	ν_{CC}	2	6	0	0	10%	δ_{CCH}	5	4	9	0
	9%	δ_{CCH}	3	4	9	0	8%	δ_{CCH}	4	5	10	0
1173.73	29%	ν_{CC}	2	6	0	0	22%	ν_{SC}	1	2	0	0
	12%	$\nu_{C=C}$	2	3	0	0	7%	ν_{CC}	3	4	0	0
	6%	δ_{CCH}	2	3	8	0						
1086.10	27%	δ_{CCH}	4	5	10	0	25%	δ_{SCH}	1	5	10	0
	19%	$\nu_{C=C}$	4	5	0	0	14%	δ_{CCH}	5	4	9	0
	11%	δ_{CCH}	3	4	9	0						
1057.05	26%	ν_{CC}	3	4	0	0	21%	δ_{CCH}	4	3	8	0
	10%	δ_{CCH}	2	3	8	0	10%	δ_{CCH}	3	4	9	0
	9%	δ_{CCH}	5	4	9	0	6%	ν_{CC}	2	6	0	0
855.06	49%	ν_{SC}	1	5	0	0	16%	δ_{SCC}	1	5	4	0
	12%	δ_{CCC}	3	4	5	0	7%	δ_{SCH}	1	5	10	0
	6%	δ_{SCH}	3	4	9	0						
738.13	35%	ν_{SC}	1	5	0	0	22%	ν_{SC}	1	2	0	0
	13%	δ_{CCC}	3	4	5	0	13%	δ_{CCC}	2	3	4	0
	5%	δ_{CCH}	2	3	8	0	5%	δ_{CCH}	5	4	9	0
681.15	26%	ν_{SC}	1	2	0	0	12%	δ_{CCN}	2	6	7	0
	10%	δ_{CSC}	2	1	5	0	9%	ν_{CC}	2	6	0	0
	8%	ν_{SC}	1	5	0	0	8%	δ_{SCC}	1	5	4	0
634.21	93%	δ_{CNH}	6	7	11	0	6%	δ_{CCN}	2	6	7	0
520.93	51%	δ_{CCN}	2	6	7	0	18%	ν_{SC}	1	2	2	0
	9%	δ_{CCC}	3	2	6	0	7%	δ_{CSC}	2	1	5	0
	6%	δ_{SCC}	1	2	6	0						
477.06	30%	ν_{CC}	2	6	0	0	20%	δ_{SCC}	1	2	3	0
	13%	δ_{CSC}	2	1	5	0	10%	ν_{SC}	1	2	0	0
	6%	δ_{CCC}	2	3	4	00						
143.33	44%	δ_{CCN}	2	6	7	0	28%	δ_{SCC}	1	2	6	0
	26%	δ_{CCC}	3	2	6	0						

(Continued)

Table S8 – *(Continued)*

Frequency	PED	Mode	Atoms[1]				PED	Mode	Atoms[1]			
(cm^{-1})	(%)		h	k	l	m	(%)		h	k	l	m
Out - of - plane modes												
943.69	31%	γ_{HCCH}	8	3	4	9	27%	γ_{HCCH}	9	4	5	10
	10%	γ_{HCCS}	9	4	5	1	8%	γ_{CCCH}	2	3	4	9
	6%	γ_{CCCH}	6	2	3	8	6%	γ_{SCCH}	1	2	3	8
866.48	25%	γ_{HCCH}	9	4	5	10	15%	γ_{CCCH}	3	4	5	10
	14%	γ_{HCCC}	6	2	3	8	13%	γ_{HCCC}	8	3	4	5
	12%	γ_{SCCH}	1	2	3	8	9%	γ_{CSCH}	2	1	5	10
751.15	22%	γ_{CCCH}	3	4	5	10	22%	γ_{HCCS}	9	4	5	1
	20%	γ_{CCCH}	2	3	4	9	16%	γ_{CSCH}	2	1	5	10
	7%	γ_{CCCH}	6	2	3	8	6%	γ_{SCCH}	1	2	3	8
551.49	60%	γ_{CCN}	0	2	6	7	8%	γ_{SCCC}	1	2	3	4
	7%	γ_{CCCC}	2	3	4	5						
525.46	61%	γ_{CCN}	0	2	6	7	9%	γ_{CCCS}	3	4	5	1
	6%	γ_{CCCC}	2	3	4	5						
420.34	36%	γ_{CCN}	0	2	6	7	16%	γ_{CSCC}	5	1	2	3
	14%	γ_{CSCC}	2	1	5	4	11%	γ_{SCCC}	1	2	3	4
	9%	γ_{CCCS}	3	4	5	1						
287.26	69%	γ_{CNH}	0	6	7	11	17%	γ_{CCN}	0	2	6	7
134.42	32%	γ_{CCN}	0	2	6	7	24%	γ_{CSCCC}	6	2	3	4
	19%	γ_{CSCC}	5	1	2	6	17%	γ_{CCCH}	6	2	3	8
	5%	γ_{CNH}	0	6	7	11						

[1] See Figure 1 for atom numbering.
ν: stretching, δ: in-plane bending and γ: out-of-plane bending modes.

Table S9: Potential energy distribution for $3CNTH^+$

Frequency	PED	Mode	Atoms[1]				PED	Mode	Atoms[1]			
(cm^{-1})	(%)		h	k	l	m	(%)		h	k	l	m
In - plane modes												
3545.56	97%	ν_{NH}	7	11	0	0						
3122.71	82%	ν_{CH}	5	10	0	0	16%	ν_{CH}	4	9	0	0
3111.54	99%	ν_{CH}	2	8	0	0						
3103.59	83%	ν_{CH}	4	9	0	0	17%	ν_{CH}	5	910	0	0
2243.78	85%	$\nu_{C\equiv N}$	6	7	0	0	12%	ν_{CC}	3	6	0	0
1495.04	49%	$\nu_{C=C}$	4	5	0	0	11%	δ_{CCH}	3	4	9	0
	10%	$\nu_{C=C}$	2	3	0	0	6 %	δ_{CCH}	5	4	9	0
1402.09	25%	$\nu_{C=C}$	2	3	0	0	16%	$\nu_{C=C}$	4	5	0	0
	15%	δ_{CCH}	3	2	8	0	14%	δ_{SCH}	1	2	8	0
	10%	ν_{CC}	3	6	0	0	5%	δ_{SCH}	1	5	10	0
1351.97	36%	ν_{CC}	3	4	0	0	25%	$\nu_{C=C}$	2	3	0	0
	9%	δ_{CCH}	5	4	9	0	8%	δ_{CCH}	4	5	10	0
1227.94	24%	δ_{CCH}	3	2	8	0	13%	δ_{SCH}	1	2	8	0
	12%	δ_{CCH}	4	5	10	0	11%	δ_{SCH}	5	4	9	0
	10%	δ_{SCH}	1	5	10	0	9%	δ_{SCH}	3	4	9	0
1167.85	34%	δ_{CCH}	1	2	8	0	27%	δ_{SCH}	3	2	8	0
	20%	ν_{CC}	3	6	0	0						

(Continued)

Table S9 – *(Continued)*

Frequency	PED	Mode	Atoms[1]				PED	Mode	Atoms[1]			
(cm^{-1})	(%)		h	k	l	m	(%)		h	k	l	m
1091.36	20%	δ_{CCH}	5	4	9	0	19%	δ_{CCH}	4	5	10	0
	18%	δ_{CCH}	3	4	9	0	17%	δ_{SCH}	1	5	10	0
	10%	$\nu_{C=C}$	4	5	0	0						
920.50	15%	δ_{CCC}	3	4	5	0	15%	ν_{CC}	3	6	0	0
	14%	ν_{CC}	3	4	0	0	13%	$\nu_{C=C}$	2	3	0	0
	11%	δ_{SCH}	1	5	10	0	8%	δ_{SCC}	1	5	4	0
880.44	72%	ν_{SC}	1	2	0	0	15%	δ_{CCH}	1	2	8	0
	6%	δ_{CCC}	2	3	4	0						
800.41	63%	ν_{SC}	4	5		0	11%	δ_{SCC}	1	5	4	0
	6%	ν_{CC}	3	4	0	0						
637.28	64%	δ_{CNH}	6	7	11	0	8%	δ_{CSC}	2	1	5	0
	8%	ν_{SC}	1	5	0	0	7%	δ_{CCN}	3	6	7	0
627.50	53%	δ_{CNH}	6	7	11	0	13%	δ_{CSC}	2	1	5	0
	13%	ν_{SC}	1	5	0	0						
558.52	61%	δ_{CCN}	3	6	7	0	13%	δ_{CCC}	4	3	6	0
	11%	δ_{CCC}	2	3	6	0						
472.43	37%	ν_{CC}	3	6	0	0	14%	δ_{CCC}	2	3	4	0
	13%	ν_{SC}	1	2	0	0	9%	δ_{SCC}	2	1	5	0
147.54	47%	δ_{CCN}	3	6	7	0	25%	δ_{CCC}	2	3	6	0
	25%	δ_{CCC}	4	3	6	0						
Out - of - plane modes												
894.08	49%	γ_{HCCH}	9	4	5	10	11%	γ_{HCCS}	9	4	5	1
	10%	γ_{CCCH}	2	3	4	9	9%	γ_{CCCH}	3	4	5	10
	9%	γ_{CCCH}	6	3	4	9	7%	γ_{CSCH}	2	1	5	10
799.58	33%	γ_{HCCC}	8	2	3	6	26%	γ_{HCCC}	8	2	3	4
	21%	γ_{CSCH}	5	1	2	8						
713.74	27%	γ_{CCCH}	3	4	5	10	17%	γ_{CSCH}	2	1	5	10
	14%	γ_{HCCS}	9	4	5	1	11%	γ_{HCCC}	2	3	4	9
	10%	γ_{CCCH}	8	2	3	4	9%	γ_{CCCH}	6	3	4	9
604.43	53%	γ_{CCN}	3	6	7	0	10%	γ_{CCCC}	2	3	4	5
	8%	γ_{SCCC}	1	2	3	4	5%	γ_{CCCH}	8	2	3	4
497.78	74%	γ_{CCN}	0	3	6	7	6%	γ_{CCCS}	3	4	5	1
	5%	γ_{CCCC}	2	3	4	5						
441.05	21%	γ_{CCN}	0	3	6	7	20%	γ_{CSCC}	2	1	5	4
	19%	γ_{CSCC}	5	1	2	3	14%	γ_{SCCC}	1	2	3	4
	5%	γ_{CCCS}	3	4	5	1						
366.92	82%	γ_{CNH}	0	6	7	11	14%	γ_{CCN}	0	3	6	7
132.27	34%	γ_{CCN}	0	3	6	7	21%	γ_{SCCCC}	1	2	3	6
	18%	γ_{CCCC}	6	3	4	5	12%	γ_{CCCH}	6	3	4	9
	12%	γ_{HCCC}	8	2	3	6						

[1] See Figure 1 for atom numbering.
ν: stretching, δ: in-plane bending and γ: out-of-plane bending modes.

Table S10: M06-2X/6-31G(d,p) calculated frequencies (cm^{-1}), infrared intensities ($km.mol^{-1}$) and Raman activities (Å$^4/amu$) and Raman intensities ($\times 10^{-24} F^2.m^{-1}.kg^{-1}$) for $2CNTH^+$ and $3CNTH^+$.

$2CNTH^+$						$3CNTH^+$					
Sym	NSc.Freq.	Sc.Freq.	IR int.	Ram. Activ	Ram. Int.	Sym	NSc.Freq.	Sc.Freq.	IR int.	Ram. Activ	Rama. Int
A'	3753	3539	1380.68	16.58	1.10	A'	3747	3546	1337.37	12.96	1.79
A'	3289	3102	23.22	209.08	21.15	A'	3301	3123	20.99	150.13	73.06
A'	3276	3089	29.15	73.37	7.51	A'	3289	3112	34.28	55.95	8.29
A'	3268	3081	1.65	74.84	7.72	A'	3280	3104	13.57	63.80	1.27
A'	2388	2237	667.39	322.88	75.72	A'	2395	2244	573.87	343.51	35.43
A'	1560	1497	23.65	1.35	0.70	A'	1573	1495	59.30	36.55	10.82
A'	1467	1408	144.82	66.51	38.44	A'	1479	1402	95.13	24.85	4.86
A'	1395	1336	162.92	58.68	37.11	A'	1419	1352	14.53	4.04	0.13
A'	1278	1237	38.13	4.45	3.19	A'	1262	1228	21.69	7.30	10.42
A'	1231	1174	12.48	3.43	2.67	A'	1214	1168	61.18	9.65	4.18
A'	1121	1086	7.14	12.90	11.37	A'	1121	1091	12.52	1.75	5.26
A'	1094	1057	28.14	1.08	1.00	A'	958	920	7.03	5.79	0.20
A"	977	944	0.13	0.77	0.84	A"	934	894	0.36	0.15	31.68
A"	907	866	0.38	0.94	1.17	A'	928	880	30.25	5.00	6.05
A'	889	855	24.93	6.58	8.31	A'	846	800	0.58	22.77	0.18
A"	783	751	79.80	1.80	2.74	A"	833	800	65.76	0.14	6.56
A'	767	738	5.38	9.86	15.44	A"	745	714	23.43	3.20	1.53
A'	711	681	1.65	21.09	37.05	A'	662	637	69.17	2.16	7.60
A'	658	634	132.93	0.36	0.69	A'	652	627	65.12	5.27	5.30
A"	571	551	6.66	0.33	0.78	A"	625	604	14.52	0.06	2.50
A"	544	525	0.53	0.46	1.17	A'	581	559	4.42	2.08	14.47
A'	543	521	1.62	2.08	5.39	A"	515	498	0.50	3.91	19.05
A'	495	477	7.22	10.67	31.42	A'	494	472	12.55	11.86	80.05
A"	431	420	4.56	2.98	10.58	A"	453	441	0.35	0.39	6.44
A"	298	287	179.53	2.26	14.42	A"	381	367	173.99	1.90	5.60
A'	149	143	4.85	4.75	97.22	A'	153	148	3.06	3.76	14.88
A"	137	134	5.37	0.19	4.40	A"	136	132	4.71	0.08	0.86

Table S11: Potential energy distribution for stretching and bending modes of $HCNH^+$ and IR intensities.

Frequency	IR Int.	PED	Mode	Atoms[1]				PED	Mode	Atoms[1]			
(cm^{-1})	(km/mol)	(%)		h	k	l	m	(%)		h	k	l	m
3482.94	611.57	98%	ν_{NH}	2	4	0	0						
3187.90	249.68	96%	ν_{CH}	1	3	0	0						
2155.69	35.05	98%	$\nu_{C\equiv N}$	1	2	0	0						
791.15	183.41	51%	γ_{NCH}	0	2	1	3	49%	γ_{CNH}	0	1	2	4
791.15	183.41	51%	δ_{NCH}	2	1	3	0	49%	δ_{CNH}	1	2	4	0
756.00	21.77	51%	δ_{CNH}	1	2	4	0	49%	δ_{NCH}	2	1	3	0
756.00	21.77	51%	γ_{CNH}	0	1	2	4	49%	γ_{NCH}	0	2	1	3

[1] See Figure 1 for atom numbering.
ν: stretching, δ: in-plane bending and γ: out-of-plane bending modes.

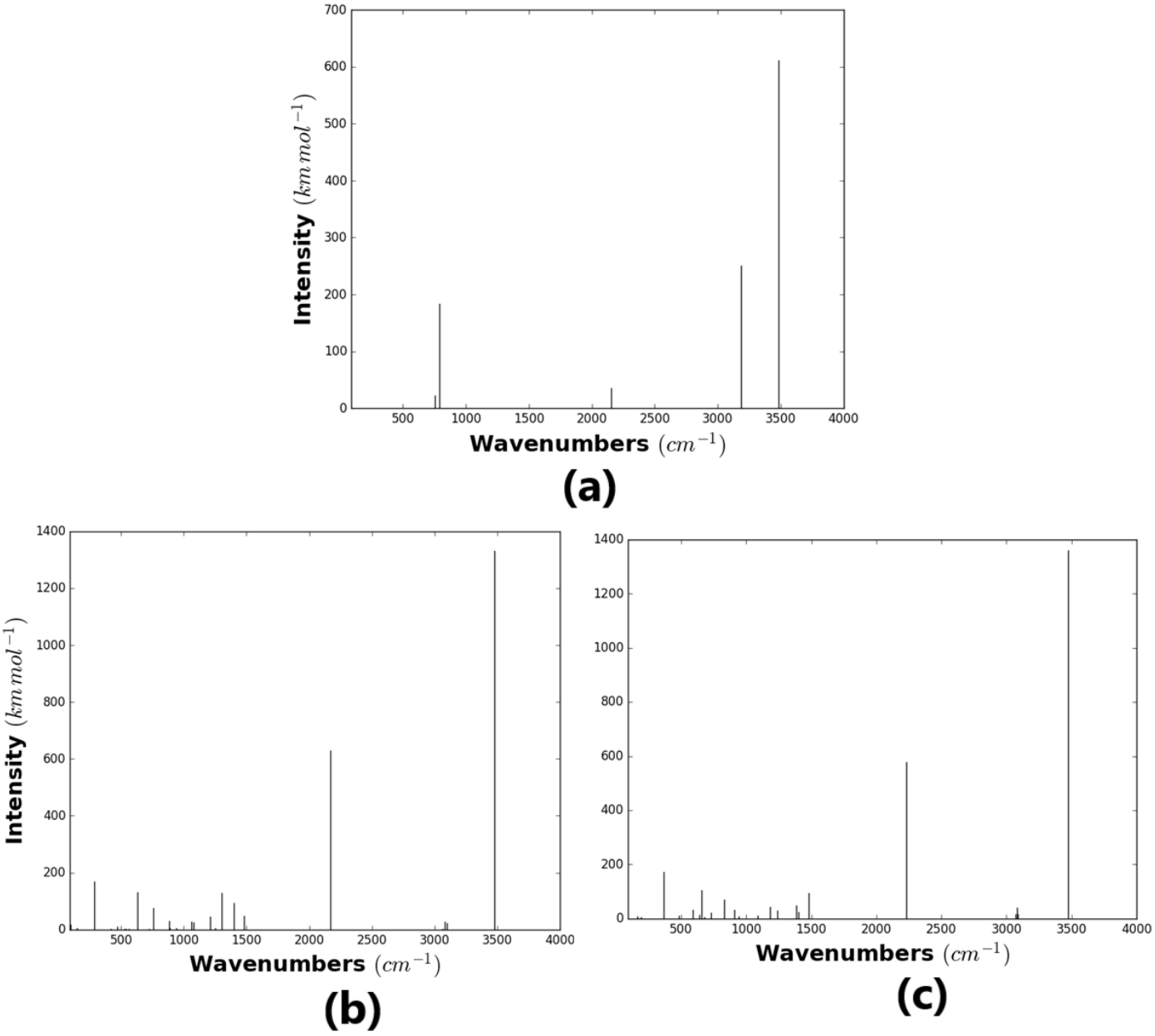

Figure S2: M06-2X/6-31G(d,p) gas phase simulated IR spectra of (a) $HCNH^+$, (b) $2CNTH^+$ and (c) $3CNTH^+$.

Table S12: M06-2X/6-31G(d,p) calculated frequencies and intensities for hyperfine structures of $HCNH^+$ and for strongest rotational lines at 10.00 K of $3CNTH^+$.

CNH^+						$2CNTH^+$				
J'	←	J''	ν_{exp}	ν_{calc}	$Int\ (nm^2MHz)$	$J'_{K_{-1}K_{+1}}F'$	←	$J''_{K_{-1}K_{+1}}F''$	ν_{calc}	$Int\ (nm^2MHz)$
3,4	←	2,3	222329.2990	222329.2990	3.565E-02	$8_{8,1}9$	←	$7_{7,0}8$	80552.491	3.051E-02
2,3	←	1,2		148221.4671	2.726E-02	$8_{8,0}9$	←	$7_{7,1}8$	80552.491	3.051E-02
3,3	←	2,2		222329.2939	2.465E-02	$9_{9,1}10$	←	$8_{8,0}9$	91083.833	2.903E-02
4,5	←	3,4	296433.6520	296433.6613	2.398E-02	$9_{9,0}10$	←	$8_{8,1}9$	91083.833	2.903E-02
4,4	←	3,3		296433.6580	1.840E-02	$7_{7,1}8$	←	$6_{6,0}7$	70020.211	2.901E-02
3,2	←	2,1		222329.2725	1.664E-02	$7_{7,0}8$	←	$6_{6,1}7$	70020.211	2.901E-02
2,2	←	1,1		148221.4580	1.460E-02	$9_{8,2}10$	←	$8_{7,1}9$	83644.940	2.865E-02
4,3	←	3,2		296433.6489	1.402E-02	$9_{8,1}10$	←	$8_{7,2}9$	83644.940	2.865E-02
5,6	←	4,5		370533.3955	9.567E-03	$8_{7,2}9$	←	$7_{6,1}8$	73112.444	2.790E-02
5,5	←	4,4		370533.3932	7.771E-03	$8_{7,1}9$	←	$7_{6,2}8$	73112.446	2.790E-02
1,2	←	0,1	74111.3300	74111.3290	6.809E-03	$8_{8,1}8$	←	$7_{7,0}7$	80552.471	2.687E-02
2,1	←	1,0	148221.4500	148221.3512	6.491E-03	$8_{8,0}8$	←	$7_{7,1}7$	80552.471	2.687E-02
5,4	←	4,3	370533.3750	370533.3882	6.296E-03	$10_{9,1}11$	←	$9_{8,2}10$	94176.399	2.667E-02
2,2	←	1,2		148221.3298	4.868E-03	$10_{9,2}11$	←	$9_{8,1}10$	94176.399	2.667E-02
2,2	←	1,2		148221.3298	4.868E-03	$10_{8,3}11$	←	$9_{7,2}10$	86735.919	2.660E-02
1,1	←	0,1	74111.1400	74111.2008	4.085E-03	$10_{8,2}11$	←	$9_{7,3}10$	86735.920	2.660E-02
3,3	←	2,3		222329.1565	3.081E-03	$9_{7,3}10$	←	$8_{6,2}9$	76202.620	2.654E-02
3,3	←	2,3		222329.1565	3.081E-03	$9_{7,2}10$	←	$8_{6,3}9$	76202.635	2.654E-02
6,7	←	5,6	444627.3610	444627.3439	2.411E-03	$9_{9,1}9$	←	$8_{8,0}8$	91083.817	2.594E-02
6,6	←	5,5		444627.3422	2.031E-03	$9_{9,0}9$	←	$8_{8,1}8$	91083.817	2.594E-02
6,5	←	5,4		444627.3390	1.709E-03	$9_{8,2}9$	←	$8_{7,1}8$	83644.903	2.560E-02
1,0	←	0,1	74111.5400	74111.5213	1.362E-03	$9_{8,1}9$	←	$8_{7,2}8$	83644.903	2.560E-02
4,4	←	3,4		296433.5156	1.226E-03	$10_{10,1}11$	←	$9_{9,0}10$	101614.120	2.526E-02
4,4	←	3,4		296433.5156	1.226E-03	$10_{10,0}11$	←	$9_{9,1}10$	101614.120	2.526E-02
7,8	←	6,7	518714.3310	518714.3490	3.970E-04	$7_{7,1}7$	←	$6_{6,0}6$	70020.186	2.507E-02
7,7	←	6,6		518714.3478	3.431E-04	$7_{7,0}7$	←	$6_{6,1}6$	70020.186	2.507E-02
2,1	←	1,2		148221.5435	3.246E-04	$10_{7,4}11$	←	$9_{6,3}10$	79289.079	2.492E-02
5,5	←	4,5		370533.2476	3.238E-04	$10_{7,3}11$	←	$9_{6,4}10$	79289.156	2.492E-02
5,5	←	4,5		370533.2476	3.238E-04	$8_{7,2}8$	←	$7_{6,1}7$	73112.399	2.457E-02
7,6	←	6,5		518714.3455	2.964E-04	$8_{7,1}8$	←	$7_{6,2}7$	73112.401	2.457E-02
3,2	←	2,3		222329.3488	8.802E-05	$6_{6,1}7$	←	$5_{5,0}6$	59487.103	2.456E-02
6,6	←	5,6		444627.1943	5.804E-05	$6_{6,0}7$	←	$5_{5,1}6$	59487.108	2.456E-02

[a]Experimental values for $HCNH^+$ in Quénard *et al.* (2017)

Table S13: M06-2X/6-31G(d,p) calculated frequencies and intensities for hyperfine strongest lines of $2CNTH^+$ and $3CNTH^+$ at 10.00 K.

$2CNTH^+$					$3CNTH^+$				
$J'_{K_{-1}K_{+1}}F'$	←	$J''_{K_{-1}K_{+1}}F''$	ν_{calc}	$Int\ (nm^2MHz)$	$J'_{K_{-1}K_{+1}}F'$	←	$J''_{K_{-1}K_{+1}}F''$	ν_{calc}	$Int\ (nm^2MHz)$
$8_{8,1}9$	←	$7_{7,0}8$	80552.491	3.051E-02	$7_{7,1}8$	←	$6_{6,0}7$	91719.252	1.220E-01
$8_{8,0}9$	←	$7_{7,1}8$	80552.491	3.051E-02	$7_{7,0}8$	←	$6_{6,1}7$	91719.252	1.220E-01
$9_{9,1}10$	←	$8_{8,0}9$	91083.833	2.903E-02	$8_{7,1}9$	←	$7_{6,2}8$	94375.606	1.165E-01
$9_{9,0}10$	←	$8_{8,1}9$	91083.833	2.903E-02	$8_{7,2}9$	←	$7_{6,1}8$	94375.606	1.165E-01
$7_{7,1}8$	←	$6_{6,0}7$	70020.211	2.901E-02	$8_{8,1}9$	←	$7_{7,0}8$	105623.208	1.150E-01
$7_{7,0}8$	←	$6_{6,1}7$	70020.211	2.901E-02	$8_{8,0}9$	←	$7_{7,1}8$	105623.208	1.150E-01
$9_{8,2}10$	←	$8_{7,1}9$	83644.940	2.865E-02	$6_{6,1}7$	←	$5_{5,0}6$	77814.426	1.133E-01
$9_{8,1}10$	←	$8_{7,2}9$	83644.940	2.865E-02	$6_{6,0}7$	←	$5_{5,1}6$	77814.426	1.133E-01
$8_{7,2}9$	←	$7_{6,1}8$	73112.444	2.790E-02	$9_{7,3}10$	←	$8_{6,2}9$	97031.498	1.106E-01
$8_{7,1}9$	←	$7_{6,2}8$	73112.446	2.790E-02	$9_{7,2}10$	←	$8_{6,3}9$	97031.498	1.106E-01
$8_{8,1}8$	←	$7_{7,0}7$	80552.471	2.687E-02	$7_{6,2}8$	←	$6_{5,1}7$	80470.751	1.105E-01
$8_{8,0}8$	←	$7_{7,1}7$	80552.471	2.687E-02	$7_{6,1}8$	←	$6_{5,2}7$	80470.752	1.105E-01
$10_{9,1}11$	←	$9_{8,2}10$	94176.399	2.667E-02	$9_{8,2}10$	←	$8_{7,1}9$	108279.540	1.077E-01
$10_{9,2}11$	←	$9_{8,1}10$	94176.399	2.667E-02	$9_{8,1}10$	←	$8_{7,2}9$	108279.540	1.077E-01
$10_{8,3}11$	←	$9_{7,2}10$	86735.919	2.660E-02	$8_{6,3}9$	←	$7_{5,2}8$	83126.400	1.074E-01
$10_{8,2}11$	←	$9_{7,3}10$	86735.920	2.660E-02	$8_{6,2}9$	←	$7_{5,3}8$	83126.403	1.074E-01
$9_{7,3}10$	←	$8_{6,2}9$	76202.620	2.654E-02	$7_{7,1}7$	←	$6_{6,0}6$	91719.227	1.054E-01
$9_{7,2}10$	←	$8_{6,3}9$	76202.635	2.654E-02	$7_{7,0}7$	←	$6_{6,1}6$	91719.227	1.054E-01
$9_{9,1}9$	←	$8_{8,0}8$	91083.817	2.594E-02	$10_{7,4}11$	←	$9_{6,3}10$	99686.583	1.041E-01
$9_{9,0}9$	←	$8_{8,1}8$	91083.817	2.594E-02	$10_{7,3}11$	←	$9_{6,4}10$	99686.584	1.041E-01
$9_{8,2}9$	←	$8_{7,1}8$	83644.903	2.560E-02	$9_{6,4}10$	←	$8_{5,3}9$	85780.837	1.036E-01
$9_{8,1}9$	←	$8_{7,2}8$	83644.903	2.560E-02	$9_{6,3}10$	←	$8_{5,4}9$	85780.851	1.036E-01
$10_{10,1}11$	←	$9_{9,0}10$	101614.120	2.526E-02	$8_{7,1}8$	←	$7_{6,2}7$	94375.562	1.026E-01
$10_{10,0}11$	←	$9_{9,1}10$	101614.120	2.526E-02	$8_{7,2}8$	←	$7_{6,1}7$	94375.562	1.026E-01
$7_{7,1}7$	←	$6_{6,0}6$	70020.186	2.507E-02	$8_{8,1}8$	←	$7_{7,0}7$	105623.189	1.013E-01
$7_{7,0}7$	←	$6_{6,1}6$	70020.186	2.507E-02	$8_{8,0}8$	←	$7_{7,1}7$	105623.189	1.013E-01
$10_{7,4}11$	←	$9_{6,3}10$	79289.079	2.492E-02	$10_{8,3}11$	←	$9_{7,2}10$	110935.530	1.002E-01
$10_{7,3}11$	←	$9_{6,4}10$	79289.156	2.492E-02	$10_{8,2}11$	←	$9_{7,3}10$	110935.530	1.002E-01
$8_{7,2}8$	←	$7_{6,1}7$	73112.399	2.457E-02	$10_{6,5}11$	←	$9_{5,4}10$	88433.410	9.885E-02
$8_{7,1}8$	←	$7_{6,2}7$	73112.401	2.457E-02	$10_{6,4}11$	←	$9_{5,5}10$	88433.459	9.885E-02
$6_{6,1}7$	←	$5_{5,0}6$	59487.103	2.456E-02	$9_{7,3}9$	←	$8_{6,2}8$	97031.448	9.882E-02
$6_{6,0}7$	←	$5_{5,1}6$	59487.108	2.456E-02	$9_{7,2}9$	←	$8_{6,3}8$	97031.448	9.882E-02

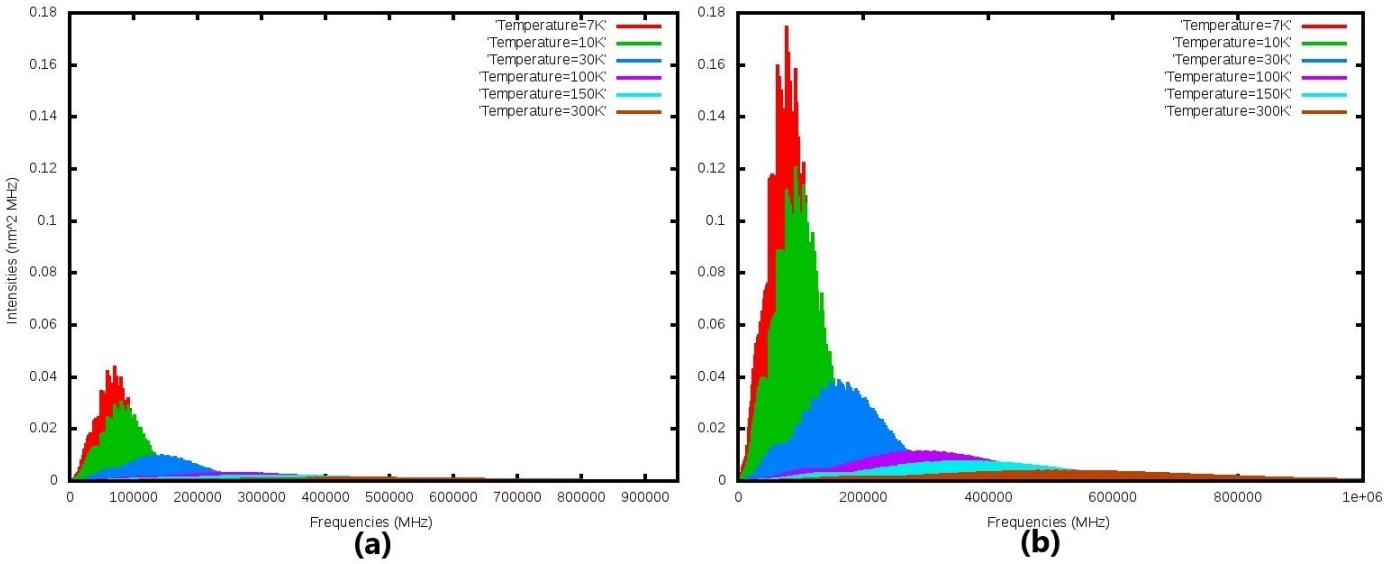

Figure S3: Comparison of ^{14}N quadrupole hyperfine spectra of (a) $2CNTH^+$ and (b) $3CNTH^+$ for different temperatures ($T = 7, 10, 30, 100$ and $300\,K$).