Electronic Supplementary Information (ESI)

HC_nN ANIONS IN THE ISM: EXPLORING THEIR EXISTENCE AND NEW PATHS TO ANIONS CARBONITRILES FOR n=3,5

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Table S1. Equilibrium geometries and rotational constants of **3.*n*.1**, **3.*a*.1**, **5.*n*.1**, and **5.*a*.1,** and linear anions **3.*a*.lin** and **5.*a*.lin**, calculated at the RHF-CCSD(T)-F12/cc-pVTZ-F12 level of theory. Rotational constants are calculated from equilibrium geometries with average atomic masses.

Table S2. Configurational isomers of HC_3N^- calculated by USOGGA11X/d-aug-cc-pVTZ method. The energies and dipole moments of the neutral HC_3N at the geometry of the corresponding anion are shown in parenthesis below the values for the anion. IR intensities are presented in parenthesis.

Table S3. Configurational isomers of HC_5N^- calculated by USOGGA11X/d-aug-cc-pVTZ method.The energies and dipole moments of the neutral HC_5N at the geometry of the corresponding anion are shown in parenthesis below the values for the anion. IR intensities are presented in parenthesis.

Table S4. Electronic energies, harmonic frequencies, zero-point vibrational energies (ZPVE), and dipole moments of different states of HC_3N/HC_3N^- system, calculated by using the theoretical models discussed in this work and listed at the end of the Table, with experimental values given in italics. In the case of the **3.*a*.1** system we also present (in brackets) the energy and dipole moment of the neutral at **3.*a*.1** geometry.

Table S5. Electronic energies, harmonic frequencies, zero-point vibrational energies (ZPVE), and dipole moments of different states of HC_5N/HC_5N^- system, calculated by using various theoretical models presented in this work. Their references are at the end of Table. In the case of the **5.*a*.1** system we present in brackets the energy and dipole moment of the neutral at the **5.*a*.1** geometry.

Table S1. Equilibrium geometries and rotational constants of **3.*n*.1**, **3.*a*.1**, **5.*n*.1**, and **5.*a*.1,** and linear anions **3.*a*.lin** and **5.*a*.lin**, calculated at the RHF-CCSD(T)-F12/cc-pVTZ-F12 level of theory. Rotational constants are calculated from equilibrium geometries with average atomic masses.

Species	Geometry	Rotational constants / GHz
3.*n*.1	rC_1H=1.0640 Å, rC_1C_2=1.2080 Å, rC_2C_3=1.3804 Å, rC_3N=1.1624 Å; all angles = 180º. Previous experimental results: rC_1H=*1.058*[1], *1.062*[2]; rC_1C_2=*1.205*[1], *1.206*[2]; rC_2C_3= *1.378*[1], *1.376*[2]; and rC_3N=*1.159*[1], *1.161*[2].	4.5270852 4.5270852 0.0000000
3.*a*.lin	rC_1H = 1.0693 Å, rC_1C_2 = 1.2106 Å, rC_2C_3 = 1.3766 Å, rC_3N = 1.1629Å; all angles = 180º.	4.5296524 4.5296524 0.0000000
3.*a*.1	rC_1H =1.0950 Å, rC_1C_2 =1.3039 Å, rC_2C_3 =1.3887 Å, rC_3N =1.1780 Å, <(HCC) = 123.6º; <(CCC) = 137.4º; <(CCN)= 173.0º; dihedral angles = 180º	4.6514770 4.7682720 189.9010614
5.*n*.1	rC_1H = 1.0639 Å, rC_1C_2 = 1.2114 Å, rC_2C_3 = 1.3694 Å, rC_3C_4= 1.2151 Å, rC_4C_5= 1.3748 Å, rC_5N = 1.1639 Å; all angles = 180º.	1.3231222 1.3231222 0.0000000
5.*a*.lin	rC_1H = 1.0679 Å, rC_1C_2 = 1.2139 Å, rC_2C_3 = 1.3648 Å, rC_3C_4= 1.2180 Å, rC_4C_5= 1.3715 Å, rC_5N = 1.1644 Å; all angles = 180º.	1.3243379 1.3243379 0.0000000
5.*a*.1	rC_1H =1.0806 Å, rC_1C_2 =1.2706 Å, rC_2C_3 =1.3272 Å, rC_3C_4 =1.2736 Å, rC_4C_5 =1.3754 Å, rC_5N =1.1768 Å, <(HCC) = 134.3º; <($C_1C_2C_3$) = 168.2º; <($C_2C_3C_4$) = 168.2º , <($C_3C_4C_5$) = 144.1º; <(CCN)= 174.0º; dihedral angles = 180º	1.3669609 1.3865222 96.8912467

[1] Dorofeeva, 1991
[2] Kuchitsu, 1998.

Table S2. Configurational isomers of HC_3N^- calculated by USOGGA11X/d-aug-cc-pVTZ method. The energies and dipole moments of the neutral HC_3N at the geometry of the corresponding anion are shown in parenthesis below the values for the anion. IR intensities are presented in parenthesis.

Isomer	Electronic energy/ *a.u.*	Frequencies / cm^{-1} (IR intensities, $kmmol^{-1}$)	ZPVE/a.u.	Dipole moment/D
3.*a*.1 $^2A'$	−169.5744563 (−169.5249239)	169(7), 348(6), 524(27), 680(42), 871(59), 928(85), 1814(14), 2195(551), 3024(151)	0.024040	1.111 (3.405)
3.*a*.2	−169.562199 (−169.486253)	256(34), 439(0), 598(10), 705(27), 948(3), 1213(7), 1502(50), 2294(265), 2968(124)	0.024886	3.509 (2.995)
3.*a*.3	−169.5340407 (−169.4566053)	207(12), 241(24), 420(4), 698(54), 908(2), 1122(108), 1752(178), 1939(547), 3221(276).	0.023938	4.350 (3.246)
3.*a*.4	−169.5336730 (−169.3519058)	214(10), 260(0), 529(22), 898(0), 963(61), 1237(5), 1644(183), 2085(318), 2922(90)	0.024495	5.142 (4.833)
3.*a*.5	−169.529191 (−169.472739)	241(9), 327(1), 516(63), 700(52), 855(40), 932(99), 1713(12), 2117(22), 3104(64)	0.023934	0.878 (2.670)
3.*a*.6	−169.5218720 (−169.4437857)	237(22), 352(0), 553(19), 709(24), 880(20), 1262(12), 1523(3), 2218(11), 3035(105)	0.024535	3.753 (2.506)
3.*a*.7	−169.5210818 (−169.4287570)	419(45), 445(66), 565(14), 648(104), 906(22), 1108(188), 1528(107), 1777(733), 3484(23).	0.024783	2.205 (1.111)
3.*a*.8	−169.5005510 (−169.4124170)	211(29), 271(2), 420(30), 586(12), 931(113), 1052(239), 1782(107), 1968(455), 2848(268)	0.022938	5.267 (5.340)
3.*a*.9	−169.4707660 (−169.3911138)	353(24), 619(25), 704(25), 861(11), 1030(35), 1107(13), 1330(22), 1366(13), 3032(143).	0.023697	2.894 (2.236)
3.*a*.10	−169.460785 (−169.337711)	213(14), 293(3), 553(25), 724(18), 939(22), 1375(2), 1518(4), 2099(111), 3375(2)	0.025263	5.395 (6.630)

Table S3. Configurational isomers of HC_5N^- calculated by USOGGA11X/d-aug-cc-pVTZ method.The energies and dipole moments of the neutral HC_5N at the geometry of the corresponding anion are shown in parenthesis below the values for the anion. IR intensities are presented in parenthesis.

Isomer	Electronic Energy / *a.u.*	Frequencies/cm^{-1} (IR intensities, $kmmol^{-1}$)	ZPVE/a.u.	Dipole moment/D
5.*a*.1 ^{2}A'	−245.7505665 (−245.6904719)	44(1), 117(5), 232(3), 285(7), 383(9), 476(7), 555(0), 586(9), 635(95), 691(456), 1246(45), 1914(182), 2149(293), 2259(1096), 3191(92).	0.033628	1.5007 (3.779)
5.*a*.2	−245.7453192 (−245.6293754)	92(12), 174(3), 275(2), 381(1), 408(6), 553(1), 561(4), 728(37), 908(4), 1074(5), 1310(7), 1679(49), 1915(895), 2326(281), 3104(39),	0.035281	4.986 (2.137)
5.*a*.3	−245.7169582 (−245.6328207)	115(20), 127(0), 254(35), 424(2), 525(28), 544(10), 575(10), 706(21), 729(3), 1202(5), 1225(14), 1472(228), 2220(243), 2355(1454), 2977(111).	0.035195	4.489 (3.928)
5.*a*.4	−245.7125671 (−245.6183144)	144(2), 234(8), 269(33), 440(9), 501(25), 537(69), 625(4), 638(0), 655(43), 746(1), 1141(8), 1454(58), 2188(200), 2315(184), 3519(68).	0.035094	4.658 (3.391)
5.*a*.5	−245.7084253 (−245.6226443)	105(6), 111(7), 213(7), 250(8), 316(1), 400(0), 546(6), 588(0), 653(1), 1131(245), 1236(96), 1801(489), 1899(1471), 2083(560), 3419(27),	0.033606	7.075 (5.655)
5.*a*.6	−245.7047472 (−245.5905465)	97(12), 174(2), 250(1), 344(1), 407(5), 498(0), 512(4), 721(29), 917(15), 1072(6), 1334(35), 1694(2), 1935(577), 2230(39), 3142(35)	0.034912	5.574 (2.089)
5.*a*.7	−245.7006173 (−245.6320745)	104(2), 202(2), 272(40), 329(0), 404(211), 466(125), 530(7), 565(244), 593(45), 742(5), 1172(18),	0.033654	1.442 (3.523)

		1858(236), 2096(56), 2136(19), 3303(16).		
5.*a*.8	−245.6723402 (−245.5829066)	284(64), 411(13), 580(162), 587(3), 618(1), 718(266), 809(24), 897(41), 961(87), 1066(61), 1098(1), 1280(16), 1440(32), 1765(200), 3242(34)	0.035896	1.356 (2.036)
5.*a*.9	−245.6694167 (−245.5489128)	111(0), 132(4), 420(74), 440(18), 518(79), 519(17), 544(12), 595(7), 668(186), 813(41), 1191(26), 1505(217), 1784(1430), 2200(758), 3532(104),	0.034111	3.101 (0.393)
5.*a*.10	−245.6632304 (−245.5707224)	135(12), 157(4), 249(5), 397(1), 458(106), 535(9), 608(58), 773(166), 812(74), 959(0), 991(25), 1511(223), 1817(30), 2251(592), 3101(87)	0.033617	3.496 (3.741)

Table S4. Electronic energies, harmonic frequencies, zero-point vibrational energies (ZPVE), and dipole moments of different states of HC_3N/HC_3N^- system, calculated by using the theoretical models discussed in this work and listed at the end of the Table, with experimental values given in italics. In the case of the **3.*a*.1** system we also present (in brackets) the energy and dipole moment of the neutral at **3.*a*.1** geometry.

Isomer	Electronic energy/ *a.u.*	Frequencies/cm-1	ZPVE/a.u.	Dipole moment/D
3.*n*.1 **($^1\Sigma^+$)**	−169.5672400 [a] −169.5784335 [b] −169.3502637 [c] −169.3528759 [d] −169.2903628 [e] −169.3244578 [f] −169.3314740 [g] −169.2804743 [h] −169.2902261 [i] −169.2892771 [j] −169.2895561 [k] −169.2892480 [l] −169.5667065 [m]	242(0), 242(0), 555(7), 555(7), 735(38), 735(38), 909(0), 2219(1), 2437(30), 3504(83). [a] 221, 221, 496, 496, 677, 677, 879, 2113, 2318, 3453. [c] 224, 224, 506, 506, 673, 673, 885, 2043, 2229, 3477. [f] *222, 499*, *663*, *864*, *2079, 2274, 3327* [n]	0.027641 [a] 0.026313 [c] 0.026061 [f] *0.025771* [n]	−3.912 [a] −3.909 [b] −3.994 [g] −3.840 [h] −4.182 [i] −4.183 [j] −4.182 [k] −4.183 [l] −3.929 [m] *−3.72* [o]
3.*a*.lin **$^2\Sigma^+$**	−169.5686812 [a] −169.5815316 [b] −169.3273999 [c] −169.3319822 [d] −169.2881478 [e] −169.3008507 [f] −169.3013204 [g] −169.2776269 [h] −169.2879667 [i] no conv. [j] no conv. [k] no conv. [l] no conv. [m]	330, 330, 760, 760, 883, 902, 902, 2097, 2307, 3332 [c] 230, 230, 493, 493, 831, 831, 889, 2032, 2223, 3351. [f]	0.028709 [c] 0.026436 [f]	+19.622 [a] +12.182 [b] +15.289 [g] +19.754 [h] +19.868 [i]
3.*a*.1 **^{2}A'**	−169.5744563 [a] (−169.5249239) [a] −169.5837159 [b] −169.3502936 [c] −169.3530713 [d] (-169.3129127) [d] −169.2902153 [e] −169.3247399 [f] −169.2905820 [i] −169.2893629 [j] −169.5737715 [m]	169(7), 348(6), 524(27), 680(42), 871(59), 928(85), 1814(14), 2195(551), 3024(151) [a] 227, 371, 546, 680, 866, 941, 1714, 2132, 3003. [c] 218, 345, 511, 687, 880, 1527, 1727, 2094, 3026 [f]	0.024040 [a] 0.023874 [c] 0.025092 [f]	1.111 [a] (3.405) [a] 0.919 [i] 0.922 [j] 0.991 [m]

a) USOGGA11X/d-aug-cc-pVTZ
b) USOGGA11X/d-aug-cc-pVQZ//RCCSD(T)-F12/cc-pVTZ-F12
c) RCCSD(T)-F12a/cc-pVTZ-F12

d) RCCSD(T)-F12a/cc-pVQZ-F12// RCCSD(T)-F12/cc-pVTZ-F12
e) RCCSD(T)/d-aug-cc-pVTZ// RCCSD(T)-F12/cc-pVTZ-F12
f) RMP2-F12/cc-pVTZ-F12
g) CAS-MRCISD(Q)-F12/cc-pVTZ-F12// RCCSD(T)-F12/cc-pVTZ-F12
h) CAS-MRCISD(Q)/d-aug-cc-pVTZ// RCCSD(T)-F12/cc-pVTZ-F12
i) UHF-CCSD(T)/d-aug-cc-pVTZ// RCCSD(T)-F12/cc-pVTZ-F12
j) UHF-CCSD(T)/aug-cc-pVTZ+4(sp)// RCCSD(T)-F12/cc-pVTZ-F12
k) UHF-CCSD(T)/aug-cc-pVTZ+4(sp)1d// RCCSD(T)-F12/cc-pVTZ-F12
l) UHF-CCSD(T)/aug-cc-pVTZ+4(sp)H+1(s,p)C,N// RCCSD(T)-F12/cc-pVTZ-F12
m) USOGGA11X/ aug-cc-pVTZ+4(sp)1d// RCCSD(T)-F12/cc-pVTZ-F12
n) [3]
o) [4]; [5]

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Isomer	Electronic energy/a.u.	Frequencies / cm-1	ZPVE/a.u.	Dipole moment/D
Neutral $^1\Sigma^+$	-245.7183235 [a] -245.7334428 [b] -245.3906561 [c] -245.3944063 [d] -245.3561761 [e] -245.3324649 [f] -245.3049575 [g] -245.3030309 [h] -245.3035067 [i] -245.3029722 [j] -245.7174895 [k]	106, 106, 247, 247, 447, 447, 474, 474, 609, 657, 657, 1164, 2098, 2233, 2320, 3452. [c] 97, 97, 248, 248, 458, 458, 483, 483, 614, 643, 643, 1178, 2026, 2149, 2223, 3473. [e]	0.038031 [a] 0.035856 [c] 0.035361 [e]	-4.648 [a] -4.668 [b] −5.033 [f] -4.888 [g] -4.888 [h] -4.888 [i] -4.888 [j] -4.674 [k]
5.*a*.lin $^2\Sigma^+$	-245.7273446 [b] -245.3710823 [c] -245.3764349 [d] -245.3358805 [e] -245.3055020 [f] -245.3035343 [g] -245.3036148 [h] -245.3040947 [i] -245.3035563 [j] no conv. [k]	74, 74, 174, 174, 275, 276, 533, 533, 617, 741, 741, 1186, 2013, 2146, 2214, 3368. [e]	0.034487 [e]	+16.099 [b] +19.399 [f] +23.859 [g] +65.109 [h] +65.111 [i] +55.817 [j]
5.*a*.1 $^2A'$	-245.7505667 [a] (-245.6904719) [a] -245.7627827 [b] -245.4126438 [c] -245.4165681 [d] (-245.3617062) [d] -245.3810656 [e] -245.3266112 [g] -245.3247451 [h] -245.7489382 [k]	195, 317, 318, 408, 424, 477, 558, 662, 666, 939, 1230, 1849, 2032, 2189, 3248. [e]	0.033628 [a] 0.035337 [e]	1.501 [a] (3.779) [a] 1.652 [b] 2.109 [g] 2.111 [j] 1.904 [k]

a) USOGGA11X/d-aug-cc-pVTZ
b) SOGGA11X/aug-cc-pVQZ//RCCSD(T)-F12/cc-pVTZ-F12
c) RCCSD(T)-F12a/cc-pVTZ-F12
d) RCCSD(T)-F12a/cc-pVQZ-F12// RCCSD(T)-F12/cc-pVTZ-F12
e) RMP2-F12/cc-pVTZ-F12
f) CAS-MRCISD(Q)-F12/cc-pVTZ-F12// RCCSD(T)-F12/cc-pVTZ-F12
g) UHF-CCSD(T)/d-aug-cc-pVTZ// RCCSD(T)-F12/cc-pVTZ-F12
h) UHF-CCSD(T)/aug-cc-pVTZ+4(sp)// RCCSD(T)-F12/cc-pVTZ-F12
i) UHF-CCSD(T)/aug-cc-pVTZ+4(sp)1d// RCCSD(T)-F12/cc-pVTZ-F12
j) UHF-CCSD(T)/aug-cc-pVTZ+4(sp)H+1(s,p)C,N// RCCSD(T)-F12/cc-pVTZ-F12
k) USOGGA11X/ aug-cc-pVTZ+4(sp)1d// RCCSD(T)-F12/cc-pVTZ-F12

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