Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

**Supplementary material**

# STRUCTURAL PROPERTIES OF POSSIBLE INTERSTELLAR VALENCE ANIONS OF THE SERIES $HC_nN^-$ ($n$=3,5,7,9)

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**Table S1.** Additional computational data for rotational spectroscopy: Rotational constants, dipole moments, quartic centrifugal distortion constants for the Hund's case (*b*) in the asymmetrically reduced Hamiltonian and symmetrically reduced Hamiltonian forms, and the spin rotation interaction constants. Equilibrium geometry is obtained with the SOGGA11-X DFT functional in the aug-cc-pVTZ basis set. **3.a.1**, **5.a.1** and **7.a.1** isomers are open-shell systems and have $^2A'$ ground electronic states; all molecules are planar asymmetric tops. Representation: $III^l$, Iy < Ix < Iz.

**Table S2.** Data for configurational isomers of $HC_3N^-$ computed by USOGGA11-X/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 Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

**Table S3.** Equilibrium distances, harmonic frequencies, dipole moment (μ), and equilibrium rotational constant ($B_e$) of the $HC_3N$ neutral molecule calculated by different DFT functionals, and compared to RCCSD(T)-F12 results. Note: the lowest RMS deviations (root-mean-square deviations) is marked yellow.

**Table S4.** Data for configurational isomers of $HC_5N^-$ computed by USOGGA-11X/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 Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

**Table S5.** Equilibrium geometry of the neutral $HC_7N$ computed with different DFT functionals and compared to MP2-F12 and CCSD(T)-F12 values, with the root-mean-square deviations (from experimental data) indicated in the last row.

**Table S6**. For the neutral linear molecules: experimental rotational constants in the ground electronic state ($B_{exp}$), equilibrium rotational constants computed by SOGGA11-X/aug-cc-pVTZ ($B_e$), experimental electric dipole moment in the ground state ($\mu_{exp}$), computed equilibrium dipole moment $\mu_e$ and scaling factors obtained by dividing experimental to computed values.

**Table S7.** Data for configurational isomers of $HC_7N^-$ computed by USOGGA-11X/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 Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

**Table S8.** Equilibrium geometry of the neutral $HC_9N$ computed with different DFT functionals and compared to MP2-F12 values, with the root-mean-square errors (from experimental data) indicated in the last row.

**Table S9.** Data for configurational isomers of $HC_9N^-$ computed by USOGGA-11X/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 Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

**Figure S1**. Graphical representation of the computed IR spectra (SOGGA11-X/aug-cc-pVTZ) of the lowest-energy isomers **3.a.1**, **5.a.1**, **7.a.1**, and **9.a.1**, from the top to the bottom, obtained with the Gaussview program.

**Table S1.** Additional computational data for rotational spectroscopy: Rotational constants, dipole moments, quartic centrifugal distortion constants for the Hund's case (*b*) in the asymmetrically reduced Hamiltonian and symmetrically reduced Hamiltonian forms, and the spin rotation interaction constants. Equilibrium geometry is obtained with the SOGGA11-X DFT functional in the aug-cc-pVTZ basis set. **3.a.1**, **5.a.1** and **7.a.1** isomers are open-shell systems and have $^2A'$ ground electronic states; all molecules are planar asymmetric tops. Representation: III[1], Iy < Ix < Iz.

**3.a.1**

```
Principal inertia moments (amu-bohr**2):
 Iaa = 0.673097D+01 Ibb= 0.383040D+03 Icc= 0.389771D+03
Rotational constants (MHZ):    268125.05     4711.62     4630.26
Dipole moment (Debye):
   -0.6111638      0.9135246      0.0000000  Tot=      1.0991125
Quartic Centrifugal Distortion Constants (MHz)
   (Asymmetrically reduced)            (Symmetrically reduced)
   DELTA N  =    0.001129976          D N  =    0.000985276
   DELTA K  =  211.955436638          D K  =  211.954713139
   DELTA NK =    3.853870885          D NK =    3.854739084
   delta N  =    0.000014775          d 1  =   -0.000014775
   delta K  =   -1.696736261          d 2  =   -0.000072350

electronic spin - molecular rotation tensor [epsilon] (MHZ):
  aa=  2975.0414   ba=  -623.8614   ca=     0.0000
  ab=     1.8923   bb=     0.9828   cb=     0.0000
  ac=     0.0000   bc=     0.0000   cc=    -8.3242
 nuclear spin - molecular rotation tensor [C] (MHz):
 $^{1}$H          aa=    0.0498   ba=   -0.0301   ca=    0.0000
                  ab=   -0.0003   bb=   -0.0002   cb=    0.0000
                  ac=    0.0000   bc=    0.0000   cc=   -0.0004
 $^{14}$N        aa=    0.0594   ba=   -0.0053   ca=    0.0000
                 ab=    0.0002   bb=    0.0009   cb=    0.0000
                 ac=    0.0000   bc=    0.0000   cc=    0.0007
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**5.a.1**

```
Principal inertia moments (amu-bohr**2):
 Iaa = 0.194057D+01 Ibb= 0.135371D+04 Icc= 0.135565D+04
Rotational constants (MHZ):    930007.6997519   1333.1791105   1331.2707152
Dipole moment (Debye):
    1.0805643      1.0644003      0.0000000  Tot=      1.5167621
Quartic Centrifugal Distortion Constants (MHz)
   (Asymmetrically reduced)            (Symmetrically reduced)
   DELTA N  =    0.000026741          D N  =    0.000026727
   DELTA K  =22336.060617279          D K  =22336.060617207
   DELTA NK =   -0.320335755          D NK =   -0.320335669
   delta N  =   -0.000000230          d 1  =    0.000000230
   delta K  =   -0.025939319          d 2  =   -0.000000007

electronic spin - molecular rotation tensor [epsilon] (MHZ):
  aa= 26329.4277   ba=  2293.6997   ca=     0.0000
  ab=     2.5358   bb=     0.4804   cb=     0.0000
  ac=     0.0000   bc=     0.0000   cc=    -3.0876
 nuclear spin - molecular rotation tensor [C] (MHz):
 $^{14}$N
  aa=     0.4681   ba=    -0.0064   ca=     0.0000
  ab=     0.0000   bb=     0.0003   cb=     0.0000
  ac=     0.0000   bc=     0.0000   cc=     0.0002
 $^{1}$H
  aa=     0.2777   ba=     0.2099   ca=     0.0000
  ab=     0.0002   bb=     0.0000   cb=     0.0000
  ac=     0.0000   bc=     0.0000   cc=    -0.0001
```

**7.a.1**

```
Principal inertia moments (amu-bohr**2):
 Iaa = 0.245260D+01 Ibb= 0.319013D+04 Icc= 0.319259D+04
 Rotational constants (MHZ):
 735847.6770507    565.7258132    565.2912126
Dipole moment (Debye):
     2.7204488       0.8369903       0.0000000  Tot=      2.8462949
 Quartic Centrifugal Distortion Constants (MHz)
    (Asymmetrically reduced)          (Symmetrically reduced)
    DELTA N  =    0.000005841         D N  =    0.000005842
    DELTA K  =***************    D K  =***************
    DELTA NK =   -2.338333500       D NK =   -2.338333504
    delta N  =   -0.000000386            d 1  =    0.000000386
    delta K  =    0.001859515            d 2  =    0.000000000

electronic spin - molecular rotation tensor [epsilon] (MHZ):
   aa= 50163.5063   ba=  3623.0997   ca=     0.0000
   ab=     1.1371   bb=     0.2133   cb=     0.0000
   ac=     0.0000   bc=     0.0000   cc=    -1.2740
 nuclear spin - molecular rotation tensor [C] (MHz):
  $^{1}$H
   aa=     0.5499   ba=     0.1990   ca=     0.0000
   ab=     0.0001   bb=     0.0000   cb=     0.0000
   ac=     0.0000   bc=     0.0000   cc=    -0.0001
  $^{14}$N
   aa=     0.7036   ba=     0.0455   ca=     0.0000
   ab=     0.0000   bb=     0.0001   cb=     0.0000
   ac=     0.0000   bc=     0.0000   cc=     0.0001
```

**Table S2.** Data for configurational isomers of $HC_3N^-$ computed by USOGGA11-X/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 Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

| Isomer | Electronic energy/ *a.u.* | Frequencies/cm-1 (IR intensities, kmmol$^{-1}$) | ZPVE Hartree /particle | Dipole moment/D | Rotational constants/ GHz | VDE/eV |
|---|---|---|---|---|---|---|
| **3.*a*.1** | -169.5739765<br>(-169.5238630) | 168(6), 349(5), 526(25), 682(42), 874(65), 933(114), 1812(12), 2196(513), 3024(139) | 0.024070 | 1.0991<br>(3.4160) | 268.1250546<br>4.7116247<br>4.6302595 | 1.36 |
| **3.*a*.2** | -169.5618088<br>(-169.4857583) | 256(34), 441(0), 598(10), 707(27), 948(3), 1213(6), 1503(50), 2294(266), 2971(123). | 0.024902 | 3.5064<br>(2.9972) | 63.3253834<br>5.4540937<br>5.0215935 | 2.07 |
| **3.*a*.3** | -169.5365044<br>(-169.4607512) | 238(1), 241(2), 467(7), 691(5), 920(7), 1179(154), 1737(257), 1933(593), 3432(3) | 0.024695 | 5.4460<br>(4.5629) | 271.1028366<br>4.7056787<br>4.6253932 | 2.06 |
| **3.*a*.4** | -169.5333130<br>(-169.3514709) | 214(10), 261(0), 530(22), 900(0), 963(60), 1237(5), 1644(184), 2085(317), 2921(90) | 0.024500 | 5.1367<br>(4.8395) | 82.7889510<br>5.2032434<br>4.8955599 | 4.95 |
| **3.*a*.5** | -169.5287788<br>(-169.4722559) | 242(8), 326(1), 517(60), 701(53), 856(42), 937(110), 1714(12), 2117(22), 3105(62). | 0.023956 | 0.8641<br>(2.6731) | 158.7886398<br>5.3114571<br>5.1395402 | 1.54 |
| **3.*a*.6** | -169.5214716<br>(-169.4432504) | 235(22), 352(0), 552(19), 707(24), 878(20), 1262(11), 1522(3), 2218(11), 3036(104). | 0.024516 | 3.7528<br>(2.5099) | 66.3618304<br>5.8150039<br>5.3465119 | 2.13 |
| **3.*a*.7** | -169.5206422<br>(-169.4282000) | 417(47), 449(66), 564(14), 645(107), 904(22), 1107(189), 1527(107), 1776(737), 3481(23). | 0.024765 | 2.2094<br>(1.1127) | 43.5501245<br>8.1190889<br>6.8432885 | 2.52 |
| **3.*a*.8** | -169.5001549<br>(-169.4118849) | 211(29), 271(2), 421(30), 588(12), 931(114), 1053(246), 1782(110), 1968(448), 2851(264). | 0.022955 | 5.2929<br>(5.3463) | 337.6497526<br>5.0583064<br>4.9836468 | 2.40 |
| **3.*a*.9** | -169.4604128<br>(-169.3372559) | 214(14), 293(3), 554(26), 725(18), 939(22), 1376(2), 1518(4), 2097(110), 3372(2). | 0.025258 | 5.3993<br>(6.6346) | 85.0556633<br>5.5224464<br>5.1857490 | 3.35 |
| **3.*a*.10** | -169.4572170<br>(-169.3797967) | 185(18), 417(2), 653(52), 734(97), 816(15), 1007(48), 1358(100), 1830(56), 2844(236). | 0.022423 | 3.4153<br>(4.0113) | 36.0261018<br>8.5049961<br>7.0075843 | 2.11 |

**Table S3.** Equilibrium distances, harmonic frequencies, dipole moment ($\mu$), and equilibrium rotational constant ($B_e$) of the linear $HC_3N$ neutral molecule calculated by different DFT functionals, and compared to RCCSD(T)-F12 results. Note: the lowest RMS deviations (root-mean-square deviations) is marked.

| $HC_3N$ | Exp.[1] | SOGGA11-X | SOGGA11-X | M06-2X | M06-2X | B3LYP | B3LYP | RCCSD(T)-F12 |
|---|---|---|---|---|---|---|---|---|
| | | aug-cc-pVTZ | aug-cc-pVQZ | aug-cc-pVTZ | aug-cc-pVQZ | aug-cc-pVTZ | aug-cc-pVQZ | cc-pVTZ-F12 |
| H-C1 | 1.058 | 1.0631 | 1.0636 | 1.064 | 1.0632 | 1.0625 | 1.0622 | 1.0640 |
| C1-C2 | 1.205 | 1.1993 | 1.199 | 1.196 | 1.1953 | 1.2007 | 1.2 | 1.2080 |
| C2-C3 | 1.378 | 1.3769 | 1.3776 | 1.38 | 1.38 | 1.3684 | 1.3683 | 1.3803 |
| C3-N | 1.159 | 1.1525 | 1.152 | 1.1486 | 1.1477 | 1.1551 | 1.1543 | 1.1624 |
| RMSD | | **0.0050** | 0.0054 | 0.0076 | 0.0080 | 0.0060 | 0.0063 | **0.0039** |
| $\nu_7$ ($\pi$) | 222[2] | 246(0) | 242(0) | 240(0) | 241(0) | 241(0) | 241(0) | 221 |
| $\nu_6$ ($\pi$) | 499[2] | 558(7) | 553(7) | 555(9) | 555(9) | 546(7) | 545(7) | 496 |
| $\nu_5$ ($\pi$) | 663[2] | 739(39) | 736(39) | 748(37) | 754(36) | 706(39) | 706(38) | 676 |
| $\nu_4$ ($\sigma$) | 878[2] | 910(0) | 909(0) | 900(0) | 900(0) | 903(0) | 902(0) | 879 |
| $\nu_3$ ($\sigma$) | 2079 | 2219(0) | 2219(1) | 2226(1) | 2225(1) | 2173(0) | 2171(0) | 2113 |
| $\nu_2$ ($\sigma$) | 2274 | 2437(31) | 2435(28) | 2449(27) | 2447(26) | 2367(25) | 2365(24) | 2318 |
| $\nu_1$ ($\sigma$) (CH stretch.) | 3327 | 3505(84) | 3502(85) | 3475(83) | 3478(80) | 3460(86) | 3459(85) | 3452 |
| RMSD | | 113 | 111 | 110 | 111 | 76 | **75** | **52** |
| $\mu$ / D | −3.72[3,4] | −3.9154 | −3.9049 | −3.8973 | −3.8717 | −3.8872 | −3.8855 | - |
| $B_e$ / GHz | $B_0$=4.549[2] | 4.579 | 4.578 | 4.585 | 4.589 | 4.595 | 4.598 | 4.527 |
| $B_e – B_0$/ GHz | | 0.030 | 0.029 | 0.036 | 0.040 | 0.046 | 0.049 | −0.022 |

**Table S4.** Data for configurational isomers of $HC_5N^-$ computed by USOGGA-11X/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 Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

| Isomer | Electronic energy/ *a.u.* | Frequencies/cm$^{-1}$ (IR intensities, kmmol$^{-1}$) | ZPVE/a.u. | Dipole moment/D | Rotational constants/ GHz | VDE/eV |
|---|---|---|---|---|---|---|
| **5.*a*.1** | -245.7499338<br>(-245.6898016) | 46(1), 118(6), 237(3), 288(7), 390(8), 478(7), 558(0), 591(9), 635(96), 691(472), 1246(45), 1914(185), 2149(317), 2261(1050), 3192(89). | 0.033700 | 1.5168<br>(3.7787) | 930.0076997<br>1.3331791<br>1.3312707 | 1.64 |
| **5.*a*.2** | -245.7446593<br>(-245.6286166) | 91(12), 173(2), 274(2), 379(1), 409(6), 553(1), 560(4), 724(37), 907(4), 1073(5), 1309(7), 1679(50), 1915(898), 2325(285), 3105(39), | 0.035262 | 4.9842<br>(2.1427) | 39.4977114<br>1.5358206<br>1.4783372 | 3.16 |
| **5.*a*.3** | -245.7188249<br>(-245.6226788) | 48(2), 55(0), 387(7), 451(2), 468(8), 550(14), 599(5), 754(22), 865(1), 990(14), 1232(14), 1520(7), 1836(95), 2078(575), 3216(51), | 0.034281 | 3.7467<br>(3.9641) | 37.0817157<br>1.7600515<br>1.6802977 | 2.62 |
| **5.*a*.4** | -245.7169701<br>(-245.5380592) | 80(21), 118(1), 233(0), 280(0), 466(2), 500(7), 544(8), 847(27), 851(1), 1097(91), 1303(23), 1734(402), 2036(1217), 2107(42), 3025(35) | 0.034673 | 5.8680<br>(5.2695) | 56.5379918<br>1.4749658<br>1.4374651 | 4.87 |
| **5.*a*.5** | -245.7163541<br>(-245.6321935) | 113(21), 128(0), 256(36), 427(2), 525(28), 548(10), 578(11), 704(21), 729(3), 1201(5), 1225(13), 1471(227), 2221(237), 2355(1472), 2972(111). | 0.035203 | 4.4864 | 45.2580981<br>1.4881196<br>1.4407468 | 2.29 |
| **5.*a*.6** | -245.7119245<br>(-245.6176649) | 145(2), 232(8), 269(33), 438(9), 500(24), 532(69), 625(2), 636(0), 656(45), 746(1), 1140(8), 1455(58), 2188(201), 2316(187), 3517(69). | 0.035074 | 4.6601 | 7.5457667<br>2.8496157<br>2.0684699 | 2.56 |
| **5.*a*.7** | -245.7078368<br>(-245.6221837) | 107(6), 111(6), 215(7), 254(7), 320(2), 403(0), 550(6), 591(1), 653(1), 1129(246), 1237(97), 1801(506), 1902(1140), 2087(597), 3415(28). | 0.033657 | 7.0646<br>5.6373 | 614.8240410<br>1.3398314<br>1.3369180 | 2.33 |
| **5.*a*.8** | -245.7041281<br>(-245.5899320) | 95(12), 175(2), 250(1), 344(1), 407(5), 498(0), 511(4), 719(29), 915(15), 1072(6), 1333(35), 1693(2), 1936(578), 2230(39), 3140(36) | 0.034899 | 5.5766<br>(2.0917) | 44.1609036<br>1.5931420<br>1.5376693 | 3.11 |
| **5.*a*.9** | -245.7000178<br>(-245.6319390) | 102(0), 192(12), 262(80), 334(31), 411(27), 457(196), 543(3), 564(275), 574(35), | 0.033633 | 1.3045<br>(3.2803) | 86.2145960<br>1.4880304<br>1.4627833 | 1.85 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | 739(22), 1174(21), 1864(240), 2109(47), 2135(25), 3304(11). | | | | |
| **5.*a*.10** | -245.6973878 (-245.4857434) | 101(9), 127(0), 241(4), 269(8), 465(7), 544(8), 555(6), 735(105), 887(2), 1210(0), 1245(8), 1659(398), 2062(78), 2272(1745), 2967(79). | 0.034943 | 7.6437 | 67.3264053<br>1.4342482<br>1.4043318 | 5.76 |

**Table S5.** Equilibrium geometry of the linear neutral $HC_7N$ computed with different DFT functionals and compared to MP2-F12 and CCSD(T)-F12 values, with the root-mean-square deviations (from experimental data) indicated in the last row.

| $HC_7N$ | | SOGGA11X G09 | SOGGA11X G09 | B3LYP G09 | M062X G09 | MP2 G09 | RMP2-f12 Molpro | RMP2-f12 Molpro | RCCSD(T)-f12 |
|---|---|---|---|---|---|---|---|---|---|
| | exp[5] | aug-cc-pvtz | aug-cc-pvqz | aug-cc-pvtz | aug-cc-pvtz | aug-cc-pvtz | cc-pvdz-F12 | cc-pvtz-F12 | cc-pvtz-F12 |
| HC1 | 1.0570 | 1.0628 | 1.0632 | 1.0621 | 1.0637 | 1.0633 | 1.0625 | 1.0623 | 1.0639 |
| C1C2 | 1.2101 | 1.2046 | 1.2043 | 1.2069 | 1.2008 | 1.2238 | 1.2195 | 1.2193 | 1.2124 |
| C2C3 | 1.3610 | 1.3616 | 1.3623 | 1.3513 | 1.3657 | 1.3560 | 1.3538 | 1.3532 | 1.3673 |
| C3C4 | 1.2141 | 1.2123 | 1.2121 | 1.2171 | 1.2079 | 1.2344 | 1.2303 | 1.2302 | 1.2192 |
| C4C5 | 1.3616 | 1.3551 | 1.3559 | 1.3440 | 1.3599 | 1.3482 | 1.3460 | 1.3454 | 1.3619 |
| C5C6 | 1.2149 | 1.2101 | 1.2099 | 1.2149 | 1.2057 | 1.2328 | 1.2284 | 1.2283 | 1.2172 |
| C6C7 | 1.3657 | 1.3683 | 1.3692 | 1.3582 | 1.3724 | 1.3612 | 1.3597 | 1.3591 | 1.3736 |
| C7N | 1.1611 | 1.1549 | 1.1543 | 1.1584 | 1.1506 | 1.1814 | 1.1772 | 1.1769 | 1.1643 |
| RMSD | | **0.0047** | **0.0049** | 0.0080 | 0.0074 | 0.0141 | 0.0120 | 0.0121 | **0.0049** |

**Table S6**. For the neutral linear molecules: experimental rotational constants in the ground electronic state ($B_{exp}$), equilibrium rotational constants computed by SOGGA11-X/aug-cc-pVTZ ($B_e$), experimental electric dipole moment in the ground state ($\mu_{exp}$), computed equilibrium dipole moment $\mu_e$ and scaling factors obtained by dividing experimental to computed values.

| | $B_{exp}$ / GHz | $B_e$ / GHz | Scaling f | $M_{exp}$ / D [3,4] | $\mu_e$ / D | Scaling f |
|---|---|---|---|---|---|---|
| $HC_3N$ | 4.54906[1,4] | 4.5789959 | 0.99346 | −3.72 | −3.9154 | 0.9501 |
| $HC_5N$ | 1.331331[1,4] | 1.3378679 | 0.99511 | −4.33 | −4.6499 | 0.9312 |
| $HC_7N$ | 0.56400112[5] | 0.5665431 | 0.99551 | −5.0 | −5.2761 | 0.9477 |
| $HC_9N$ | 0.29051832[5] | 0.2917129 | 0.99590 | −5.6 | −5.8074 | 0.9643 |
| Average Scaling factor | | | **0.99500** | | | **0.9483** |

**Table S7.** Data for configurational isomers of HC$_7$N$^-$ computed by USOGGA-11X/aug-cc-pVTZ method: The energies and dipole moments of the neutral HC$_3$N at the geometry of the corresponding anion are shown in parenthesis below the Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

| Isomer | Electronic energy / *a.u.* | Frequencies/cm$^{-1}$ (IR intensities, kmmol$^{-1}$) | ZPVE/a.u. | Dipole moment/D | Rotational constants/ GHz | VDE (eV) |
|---|---|---|---|---|---|---|
| **7.*a*.1**<br>$^2$A' | -321.9204174<br>(-321.8523787) | 51(1), 68(1), 120(1), 177(6), 280(6), 309(0), 383(1060), 427(1), 440(3), 490(10), 501(55), 526(6), 573(0), 622(4), 961(32), 1407(12), 1967(492), 2109(784), 2206(300), 2257(1850), 3375(2) | 0.043851 | 2.8463<br>(4.9228) | 735.8476771<br>0.5657258<br>0.5652912 | 1.85 |
| **Linear (TS)** | -321.9198414<br>(-321.8627376) | **-238(99),** 47(0), 69(1), 110(2), 178(4), 262(3), 318(0), 439(2), 456(1), 481(10), 493(0), 528(2), 580(4), 642(35), 652(12), 958(11), 1408(1), 2012(182), 2117(1533), 2183(985), 2269(860), 3519(201) | 0.044924 | 4.2752<br>(5.5868) | 0.0000000<br>0.5635584<br>0.5635584 | 1.55 |
| **7.*a*.2** | -321.9118583<br>(-321.7871560) | 50(6), 102(1), 139(4), 246(8), 284(9), 372(0), 415(1), 442(1), 502(2), 504(3), 560(2), 700(33), 740(5), 988(1), 1200(63), 1370(11), 1750(618), 1933(2066), 2047(43), 2334(262), 3149(26) | 0.045174 | 6.7546<br>(3.3132) | 18.5073504<br>0.6502214<br>0.6281525 | 3.39 |
| **7.*a*.3** | -321.8968516<br>(-321.7764074) | 56(11), 128(0), 149(0), 174(1), 271(8), 375(6), 405(5), 481(7), 520(3), 545(8), 578(7), 743(33), 767(1), 954(6), 1241(54), 1333(8), 1658(203), 1900(1809), 2246(201), 2372(1480), 3094(35) | 0.045537 | 6.5602<br>(2.6882) | 18.1169667<br>0.6496943<br>0.6272021 | 3.28 |
| **7.*a*.4** | -321.8855100<br>(-321.7210866) | 55(15), 88(0), 122(3), 202(4), 256(1), 272(0), 402(2), 470(2), 491(8), 503(2), 533(11), 697(13), 852(2), 1006(80), 1185(62), 1379(100), 1812(676), 1930(2473), 2085(344), 2197(217), 3063(25) | 0.044653 | 6.6615<br>(5.9299) | 21.9643139<br>0.6327862<br>0.6150663 | 4.47 |
| **7.*a*.5** | -321.8820541<br>(-321.6979561) | 152(6), 184(3), 346(67), 430(0), 440(0), 585(10), 599(5), 646(16), 666(0), 711(1), 856(14), 889(5), 1069(1), 1149(8), 1207(3), 1330(3), 1361(17), 1429(57), 1658(250), 2350(191), 3177(41) | 0.048377 | 2.3026<br>(3.8358) | 7.4543806<br>1.6113618<br>1.3249554 | 5.01 |
| **7.*a*.6** | -321.8782000<br>(-321.6742457) | 51(12), 109(0), 140(0), 153(0), 244(7), 284(9), | 0.045014 | 8.5330<br>(8.1112) | 29.7238548<br>0.6215625 | 5.55 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  | 403(1), 483(5), 532(6), 536(11), 560(3), 750(131), 832(3), 924(36), 1239(3), 1350(37), 1734(956), 2058(21), 2067(1311), 2262(2422), 3046(30) |  |  | 0.6088311 |  |
| **7.*a*.7** | -321.8738500<br>(-321.7676268) | 64(11), 66(5), 156(5), 172(6), 267(2), 297(7), 344(8), 387(0), 463(0), 502(4), 509(0), 570(2), 584(6), 969(112), 1099(407), 1403(103), 1792(2538), 1875(2817), 2042(321), 2185(384), 3459(6) | 0.043749 | 8.8345<br>(7.3789) | 642.5587377<br>0.5684205<br>0.5679183 | 2.89 |
| **7.*a*.8** | -321.8734180<br>(-321.7832234) | 68(13), 77(0), 156(39), 186(4), 260(57), 430(1), 475(38), 526(3), 533(1), 567(9), 579(19), 605(23), 709(20), 988(11), 1197(9), 1366(19), 1459(379), 2177(621), 2285(2988), 2354(1108), 2993(104) | 0.045537 | 5.5889<br>(4.7078) | 38.2040069<br>0.6086625<br>0.5991174 | 2.45 |
| **7.*a*.9** | -321.8709563<br>(-321.8011956) | 60(0), 101(0), 133(2), 210(84), 249(4), 282(17), 343(4), 396(9), 446(30), 451(5), 502(1), 558(2), 587(120), 606(51), 943(46), 1346(13), 1936(13), 2108(702), 2130(77), 2164(586), 3518(193) | 0.043439 | 3.8188<br>(4.7890) | 67.4975227<br>0.6074858<br>0.6020672 | 1.90 |
| **7.*a*.10** | -321.87173830<br>(-321.7488965) | 44(5), 101(1), 141(5), 246(6), 246(9), 343(0), 367(1), 453(1), 460(2), 469(1), 545(2), 707(24), 738(14), 985(46), 1221(30), 1378(17), 1770(291), 1966(1610), 2041(7), 2229(107), 3171(23) | 0.044699 | 7.5768<br>(3.6680) | 22.8030193<br>0.6560032<br>0.6376589 | 3.34 |

**Table S8.** Equilibrium geometry of the neutral linear $HC_9N$ computed with different DFT functionals and compared to MP2-F12 values, with the root-mean-square errors (from experimental data) indicated in the last row.

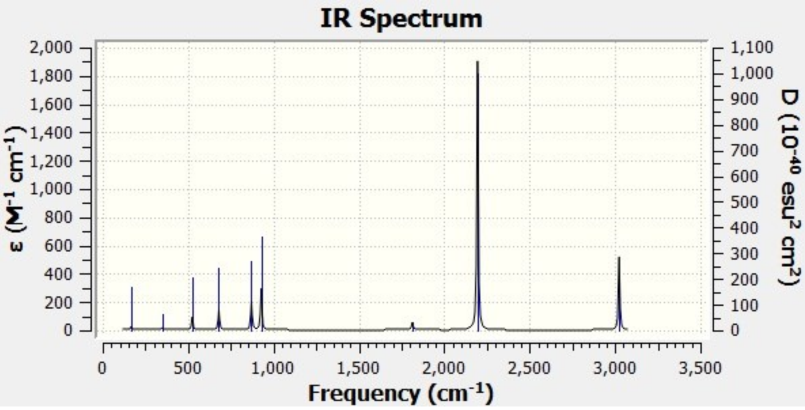
| $HC_9N$ | | SOGGA11-X G09 | B3LYP G09 | M062X G09 | RMP2-f12 Molpro | RMP2-f12 Molpro |
|---|---|---|---|---|---|---|
| | exp[5] | aug-cc-pvtz | aug-cc-pvtz | aug-cc-pvtz | cc-pvdz-F12 | cc-pvtz-F12 |
| HC1 | 1.057 | 1.0627 | 1.0620 | 1.0636 | 1.0624 | 1.0623 |
| C1C2 | 1.211 | 1.2050 | 1.2076 | 1.2011 | 1.2203 | 1.2202 |
| C2C3 | 1.360 | 1.3608 | 1.3499 | 1.3653 | 1.3522 | 1.3515 |
| C3C4 | 1.217 | 1.2139 | 1.2192 | 1.2093 | 1.2329 | 1.2328 |
| C4C5 | 1.350 | 1.3518 | 1.3393 | 1.3570 | 1.3406 | 1.3400 |
| C5C6 | 1.229 | 1.2154 | 1.2214 | 1.2106 | 1.2355 | 1.2354 |
| C6C7 | 1.349 | 1.3528 | 1.3404 | 1.3580 | 1.3418 | 1.3411 |
| C7C8 | 1.217 | 1.2111 | 1.2164 | 1.2064 | 1.2303 | 1.2303 |
| C8C9 | 1.366 | 1.3680 | 1.3573 | 1.3723 | 1.3586 | 1.3580 |
| C9N | 1.161 | 1.1550 | 1.1587 | 1.1507 | 1.1778 | 1.1774 |
| RMSD | | **0.0060** | 0.0069 | 0.0098 | 0.0106 | 0.0107 |

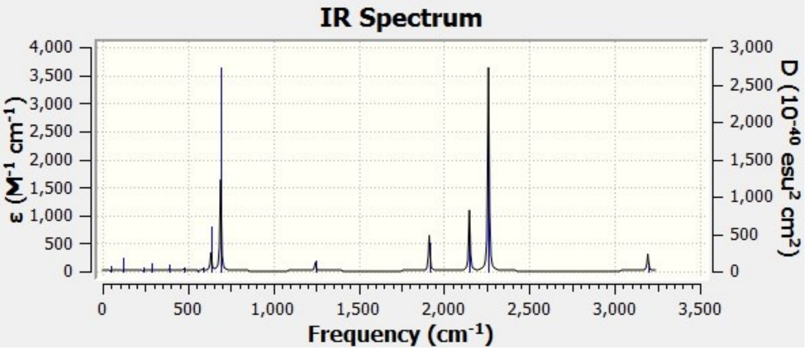
**Table S9.** Data for configurational isomers of HC$_9$N$^-$ computed by USOGGA-11X/aug-cc-pVTZ method: The energies and dipole moments of the neutral HC$_3$N at the geometry of the corresponding anion are shown in parenthesis below the Electronic energy and Dipole moment values for anions; IR intensities are presented in parenthesis; Equilibrium rotational constants for a molecule in standard orientation are in GHz; Vertical detachment energy (VDE) is without ZPVE correction.

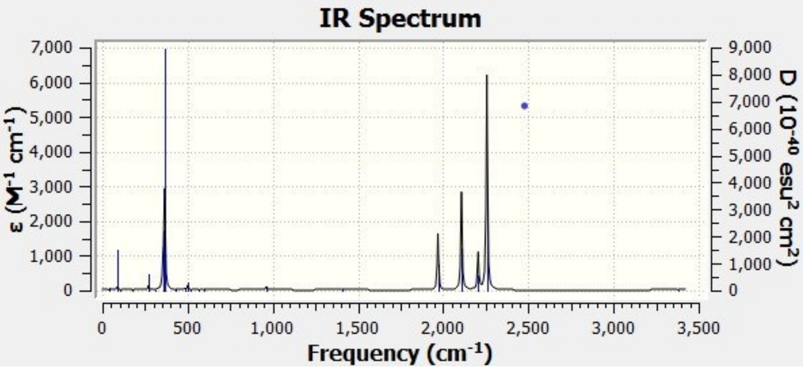
| Isomer | Electronic energy / *a.u.* | Frequencies/cm$^{-1}$ (IR intensities, kmmol$^{-1}$) | ZPVE/a.u. | Dipole moment/D | Rotational constants/ GHz | VDE (eV) |
|---|---|---|---|---|---|---|
| **9.*a*.1**<br>$^2\Pi$ | -398.0887116<br>(-398.0158839) | 37(0), 42(0), 86(2), 116(3), 154(0), 213(0), 289(78), 313(2), 329(3), 399(0), 455(7), 477(0), 496(11), 508(0), 562(3), 615(7), 638(43), 661(0), 780(7), 784(0), 1141(1), 1490(11), 2029(237), 2131(3172), 2148(1176), 2208(316), 2259(1641), 3513(307) | 0.056666 | 5.2204<br>(6.2309) | 0.0000000<br>0.2908698<br>0.2908698 | 1.98 |
| **9.*a*.2** | -398.0733457<br>(-397.9361982) | 39(6), 61(1), 93(2), 157(9), 191(6), 267(0), 299(2), 369(2), 420(1), 437(6), 462(1), 481(1), 493(0), 539(2), 598(3), 651(12), 703(32), 923(30), 1054(58), 1279(18), 1432(120), 1796(1007), 1825(4615), 2041(84), 2151(118), 2340(310), 3164(14) | 0.055283 | 8.1795<br>(4.2012) | 14.5413787<br>0.3251047<br>0.3179952 | 3.73 |
| **9.*a*.3** | -398.0628964<br>(-397.9354130) | 28(5), 96(1), 109(1), 131(0), 158(7), 244(8), 279(6), 370(1), 402(5), 430(0), 447(5), 483(0), 536(10), 556(2), 571(7), 707(29), 723(4), 763(3), 1152(26), 1246(85), 1394(130), 1727(1259), 1915(3293), 2045(173), 2254(166), 2380(1467), 3133(24) | 0.055312 | 8.3776<br>(3.7359) | 6.1346263<br>0.3566336<br>0.3370400 | 3.47 |
| **9.*a*.4** | -398.0519849<br>(-397.9281035) | 36(10), 76(0), 94(1), 165(0), 186(7), 190(7), 277(7), 376(3), 401(7), 433(10), 498(1), 534(2), 536(3), 575(8), 601(5), 645(1), 746(33), 911(2), 1048(87), 1291(5), 1403(39), 1645(439), 1888(3324), 2202(402), 2300(2973), 2367(937), 3101(32) | 0.055872 | 8.2715<br>(3.1992) | 12.4659879<br>0.3265952<br>0.3182572 | 3.37 |
| **9.*a*.5** | -398.0481590<br>(-397.8844644) | 41(11), 59(0), 95(4), 144(5), 176(4), 237(0), 274(0), 277(0), 392(2), 433(0), 492(3), 510(5), 534(4), 567(2), 611(8), 620(20), 854(3), 901(6), 1086(161), 1261(23), 1431(308), 1804(5546), 1836(88), 2071(683), 2131(35), 2264(471), 3089(20) | 0.055107 | 7.4413<br>(6.1690) | 17.8006311<br>0.3173541<br>0.3117953 | 4.45 |
| **9.*a*.6** | -398.0455931 | 40(5), 84(4), 89(3), 154(14), | 0.055229 | 8.0203 | 1.6383052 | 3.51 |

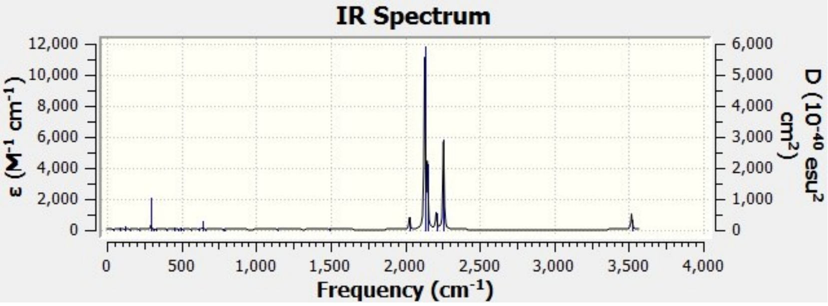
| | | | | | | |
|---|---|---|---|---|---|---|
| | (-397.9164872) | 185(1), 264(1), 283(3), 386(6), 407(0), 494(13), 510(0), 517(1), 524(0), 553(3), 586(57), 611(2), 641(4), 653(46), 932(7), 1117(4), 1298(9), 1633(60), 1904(1396), 2178(17), 2323(634), 2353(218), 3522(151) | | (3.5184) | 0.7690245<br>0.5233587 | |
| **9.*a*.7** | -398.0446038<br>(-397.8622866) | 31(9), 92(0), 96(1), 137(0), 159(3), 215(6), 255(2), 285(7), 376(4), 432(0), 490(7), 502(0), 529(5), 533(11), 558(5), 691(10), 772(169), 830(6), 1136(24), 1248(19), 1427(250), 1808(1843), 1920(2829), 2049(169), 2203(230), 2251(3136), 3087(20) | 0.054931 | 9.5948<br>(9.5265) | 7.7703712<br>0.3418522<br>0.3274464 | 4.96 |
| **9*a*.8** | -398.0466082<br>(-397.8989631) | 116(2), 118(3), 180(4), 206(3), 367(12), 376(8), 478(11), 495(5), 526(2), 538(10), 591(0), 615(25), 624(49), 638(0), 675(40), 725(1), 727(12), 1050(49), 1181(20), 1237(7), 1281(37), 1364(20), 1485(94), 1751(358), 2220(59), 2358(138), 3522(71) | 0.057968 | 2.7137<br>(1.6599) | 2.1657542<br>1.4616477<br>0.8726824 | 4.02 |
| **9.*a*.9** | -398.0401376<br>(-397.9127957) | 44(9), 77(6), 80(1), 157(1), 186(4), 255(6), 277(2), 389(3), 401(1), 450(21), 503(1), 543(9), 548(11), 571(62), 592(12), 601(2), 643(0), 696(35), 924(1), 1119(9), 1310(38), 1629(80), 1899(1655), 2209(168), 2259(119), 2383(1302), 3523(89) | 0.055287 | 6.4803<br>(3.4229) | 2.2086075<br>0.6427907<br>0.4978864 | 3.47 |
| **9.a.10.** | -398.0382616<br>(-397.9608718) | 39(0), 61(0), 96(8), 160(2), 166(16), 281(0), 298(31), 342(7), 370(69), 387(24), 414(0), 449(8), 476(202), 478(5), 482(0), 537(0), 598(3), 625(47), 799(87), 1128(4), 1465(3), 1982(422), 2111(133), 2130(27), 2149(2202), 2188(447), 3522(299) | 0.054065 | 4.5855<br>(4.8895) | 73.5971853<br>0.3042632<br>0.3030105 | 2.11 |

**Figure S1**. Graphical representation of the computed IR spectra (SOGGA11-X/aug-cc-pVTZ) of the lowest-energy isomers **3.a.1**, **5.a.1**, **7.a.1**, and **9.a.1**, from the top to the bottom, obtained with the Gaussview program.









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