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# Thermodynamic properties of linear carbon chain molecules with conjugated triple bonds
## Part 2. Free radicals $C_nH$ ($n = 2$–12) and $C_nN$ ($n = 2$–11)

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### Abstract

Reported values of rotational constants, vibrational fundamentals, excited electronic state energies, enthalpies of formation for $C_nH$ ($n = 2$–12) and $C_nN$ ($n = 2$–11) radicals are reviewed and the recommended values selected. Molecular constants and enthalpies of formation for most of the radicals, which are known as the components of the interstellar gas or that are candidates for discovery in interstellar space, are estimated because the experimental data are not available. The similarity transference procedure is developed for the calculation of bond distances and force constants. Based on the selected values of molecular constants, the ideal gas thermodynamic functions for 21 radicals are calculated by the standard statistical mechanical method using rigid-rotor and harmonic-oscillator approximations. The calculated values of heat capacities $C_p^\circ$, Gibbs energies $-(G^\circ - H_0^\circ)/T$, and enthalpies $H^\circ - H_0^\circ$, are fitted to the polynomial functions. The constants of these polynomials allow the values of $C_p^\circ$, $-(G^\circ - H_0^\circ)/T$ and $H^\circ - H_0^\circ$ for considered radicals between 298.15 and 2000 K to be calculated. These constants together with the values of enthalpy of formation $\Delta_f H^\circ$ (298.15 K), predicted using the estimates of bond dissociation energies are presented in this paper.

## INTRODUCTION

In the past 20 years spectral lines of many molecular species have been identified in radio observations of interstellar gas clouds. There is particular interest in the well-studied linear chain cyanopolyacetylenes, $H(C{\equiv}C)_nC{\equiv}N$, and their fragments, $C_nH$ and $C_nN$ radicals. (Part 1 of this series [1] was concerned with cyanopolyacetylenes, polyacetylenes and dicyanopolyacetylenes.) Free radicals $C_2N$, $C_3N$ and $C_nH$ with $n$ up to 6 have been identified in the envelope of the carbon stars and have been detected in the laboratory [2–11]. The existence of these radicals in space suggests a possibility that the longer chain radicals, such as $C_7H$, $C_8H$ and so on, could also be detected in certain astrophysical sources [10,12–15].

As is well known, for many of the molecular species the astronomical identifications were based on theoretical predictions of spectroscopic constants [5,7,12,16–18]. The experimental and theoretical studies of rotational, vibrational and electronic spectra of carbon chain molecules are therefore of considerable interest to both chemists and astrophysicists. Due to the lack of experimental data several attempts have been made to predict spectroscopic and thermochemical constants for carbon chain radicals [13,17,19–25].

This report involves the estimation of structural parameters, vibrational frequencies, excited electronic states and enthalpies of formation for 21 $C_nH$ and $C_nN$ radicals with maximum number of heavy atoms being equal to 12. (Spectroscopic and thermodynamic properties of CH and CN radicals are well known (see, for example, ref. 26) and these radicals are not considered in the present work.) For $C_2N$ only, all molecular constants have been taken from reported experimental data. For the rest of the radicals molecular constants have been estimated partially or completely. The similarity transference procedure has been developed for the calculation of bond distances and force constants. The details of the selection or estimation of molecular constants and enthalpies of formation as well as the calculation of thermodynamic functions are presented below.

## MOMENTS OF INERTIA AND GEOMETRIES

The radicals $C_nH$ and $C_nN$ have a linear unsymmetrical structure (symmetry group $C_{\infty v}$). The rotational constants, $B_0$, of radicals $C_nH$ with $n$ up to 6, $C_2N$ and $C_3N$ ($C_2H$ [2, 27–29], $C_3H$ [4], $C_4H$ [5,6,30,31], $C_5H$ [5,8], $C_6H$ [9,10,14,18,32], $C_2N$ [11,33], $C_3N$ [5,6,34,35]) have been determined by microwave spectroscopy and in the case of $C_2N$ from the rotational analysis of the electronic spectra. The moments of inertia for these radicals (Table 1) were calculated using the more precise rotational constants [2,4,6,8,10,11].

To calculate the moments of inertia for other radicals, whose rotational constants were not determined, a knowledge of structural parameters is

TABLE 1

Assumed bond lengths (Å) and computed moments of inertia for $C_nH$ and $C_nN$ radicals [a]

| Molecule | H–C | C≡C | C–C | C≡N | $I \times 10^{39}$ (g cm$^2$) |
|---|---|---|---|---|---|
| $C_2H$ | 1.06 | 1.216 | | | *1.9215* |
| $C_3H$, $C_5H$, $C_7H$, $C_9H$, $C_{11}H$ | 1.06 | 1.21 | 1.36 | | *7.502*, *35.038*, 96, 204, 372 |
| $C_4H$, $C_6H$, $C_8H$, $C_{10}H$, $C_{12}H$ | 1.06 | 1.215 | 1.36 | | *17.636*, *60.324*, 143, 280, 483 |
| $C_2N$ | | | 1.399 | 1.16 | *7.0297* |
| $C_3N$, $C_5N$, $C_7N$, $C_9N$, $C_{11}N$ | | 1.215 | 1.37 | 1.16 | *16.962*, 60, 145, 283, 490 |
| $C_4N$, $C_6N$, $C_8N$, $C_{10}N$ | | 1.21 | 1.37 | 1.16 | 35, 97, 207, 377 |

[a] Values of moments of inertia calculated using the experimental rotational constants are given in italics.

necessary. Molecular geometries of $C_nH$ and $C_nN$ radicals have not been determined experimentally and only the theoretical calculations have been carried out [7,13,17,18,21,23–25,36–43]. The bond lengths predicted from theoretical calculations reproduce reasonably well the experimental rotational constants where they are known. However, we obtained a somewhat better fit with bond lengths given in Table 1. The length of the C≡C bond in $C_2H$ (Table 1) was estimated using the experimental value for rotational constant of $C_2H$ and assuming the length of the C–H bond to be equal to that in the $C_2H_2$ molecule [44]. In the same way the C–C bond length in $C_2N$ was estimated from the rotational constant of $C_2N$ and the C≡N bond length in $HC_3N$ [45]. The sets of structural parameters for $C_nH$ and $C_nN$ radicals with an even and odd number of non-hydrogen atoms (Table 1) have been transferred from parent molecules [1] and these parameters have been used in this work to calculate the moments of inertia of $C_nH$ ($n = 7–12$) and $C_nN$ ($n = 4–11$) radicals. The rotational constants for $C_3H$, $C_4H$, $C_5H$, $C_6H$ and $C_3N$ calculated from assumed structural parameters are within 0.1–0.4% of the experimental $B_0$ values. We believe that the assumed bond lengths predict $B_0$ values for unknown radicals with an error of less than 3%.

## VIBRATIONAL FREQUENCIES

### *$C_2H$*

The vibrational spectrum of the $C_2H$ radical has been studied experimentally [46–56] and theoretically [23,43,57,58] but there is still controversy about its assignment, especially about the C–H stretch and the C≡C–H bending frequencies. From the first spectroscopic study an absorption at 1848 $cm^{-1}$ was assigned to the C≡C stretching fundamental of $C_2H$ isolated in an argon matrix [46]. The values of $\nu_3$(C≡C) obtained from theoretical calculations (1970–2100 $cm^{-1}$) [43,57,58] differ markedly from the spectroscopic value and they are close to $\nu$(C≡C) in $C_2H_2$. However, recent spectroscopic studies [53–55] and ab initio calculation [23] have given evidence that the first spectroscopic assignment of $\nu_3$ is correct. The $\nu_3$ value of $C_2H$ given in Table 2 was obtained from the gas-phase infrared spectrum [55].

In a matrix isolation study Jacox [47] has assigned an absorption at 3612 $cm^{-1}$ to the C–H stretching vibration. This value is significantly higher than the $\nu$(C–H) in $C_2H_2$ (3374, 3282 $cm^{-1}$) [59] and the $\nu_1$(C–H) values of $C_2H$ predicted by ab initio calculations (3375–3500 $cm^{-1}$) [23,43,57]. The determination of $\nu_1$ is very uncertain because of the presence of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ band system in that region [48,49,60–62]. Yan et al. [52] have studied gas-phase electronic transitions of $C_2H$ and have concluded that the symmetry of the 3600 $cm^{-1}$ band ($^2\Pi \leftarrow {}^2\Sigma^+$) clearly indicates that this

TABLE 2

Vibrational frequencies ($cm^{-1}$) for the reference radicals [a]

| Molecule | Frequencies |
|---|---|
| $C_2H$ | 3500, *371.6(2), 1841* |
| $C_3H$ | 3400, *1834,* 1050, 625(2), 300(2) |
| $C_4H$ | 3333, 2218, *2060,* 885, 627(2), 505(2), 233(2) |
| $C_5H$ | 3323, 2230, 2078, 1273, 729, 625(2), 540(2), 350(2), 148(2) |
| $C_6H$ | 3321, 2214, 2120, 2044, 1131, 619, 624(2), 515(2), 408(2), 274(2), 109(2) |
| $C_7H$ | 3321, 2223, 2154, 2055, 1317, 1004, 535, 625(2), 527(2), 457(2), 336(2), 201(2), 80(2) |
| $C_8H$ | 3321, 2228, 2176, 2095, 2046, 1227, 898, 471, 624(2), 531(2), 478(2), 384(2), 290(2), 160(2), 62(2) |
| $C_9H$ | 3321, 2232, 2191, 2125, 2052, 1336, 1133, 810, 420, 625(2), 537(2), 497(2), 430(2), 333(2), 229(2), 128(2), 49(2) |
| $C_{10}H$ | 3321, 2235, 2202, 2147, 2082, 2048, 1275, 1046, 736, 380, 624(2), 538(2), 506(2), 451(2), 371(2), 300(2), 194(2), 106(2), 40(2) |
| $C_{11}H$ | 3321, 2237, 2210, 2165, 2106, 2050, 1346, 1204, 968, 675, 346, 625(2), 541(2), 516(2), 473(2), 412(2), 331(2), 246(2), 162(2), 88(2), 33(2) |
| $C_{12}H$ | 3321, 2238, 2216, 2178, 2127, 2075, 2048, 1301, 1134, 900, 622, 318, 624(2), 541(2), 520(2), 484(2), 432(2), 361(2), 306(2), 216(2), 140(2), 75(2), 28(2) |
| $C_2N$ | *1916, 324(2), 1061* |
| $C_3N$ | 2332, 2252, 929, 496(2), 242(2) |
| $C_4N$ | 2324, 2256, 1312, 772, 490(2), 333(2), 151(2) |
| $C_5N$ | 2330, 2316, 2255, 1176, 658, 488(2), 354(2), 267(2), 109(2) |
| $C_6N$ | 2330, 2310, 2255, 1356, 1052, 572, 488(2), 366(2), 315(2), 195(2), 80(2) |
| $C_7N$ | 2329, 2325, 2307, 2255, 1272, 948, 505, 488(2), 361(2), 338(2), 278(2), 157(2), 62(2) |
| $C_8N$ | 2330, 2322, 2304, 2255, 1374, 1183, 859, 452, 488(2), 366(2), 352(2), 310(2), 218(2), 126(2), 49(2) |
| $C_9N$ | 2329, 2327, 2318, 2302, 2255, 1318, 1099, 785, 409, 488(2), 363(2), 352(2), 329(2), 284(2), 187(2), 105(2), 40(2) |
| $C_{10}N$ | 2329, 2326, 2315, 2300, 2255, 1383, 1253, 1022, 722, 374, 488(2), 368(2), 353(2), 348(2), 306(2), 231(2), 158(2), 87(2), 33(2) |
| $C_{11}N$ | 2329, 2326, 2324, 2312, 2299, 2255, 1344, 1186, 954, 667, 343, 488(2), 364(2), 354(2), 350(2), 322(2), 287(2), 206(2), 137(2), 75(2), 28(2) |

[a] Experimental vibrational frequencies are given in italics; numbers in parentheses represent the degeneracies of frequencies.

transition is not a C–H stretch. Subsequently Jacox and Olson [54] reexamined the assignment of the 3600 $cm^{-1}$ absorption. However, they found problems with alternative assignments to $\nu_1 + \nu_2$ or $\nu_1 + 2\nu_2$, and concluded that the assignment to $\nu_1$ is still the best possibility. A recent matrix IR study [53] has also revealed no satisfactory alternative for $\nu_1$. Since the assignments of $\nu_1$ seem to be questionable, the value of $\nu_1 = 3500$ $cm^{-1}$ obtained from ab initio calculation [23], the accuracy of which is substantially improved compared to the previous studies, has been adopted in the present work (Table 2). Its uncertainty is estimated to be 100 $cm^{-1}$.

The bending fundamental $\nu_2$ of $C_2H$ has not yet been directly observed. Experimental values ranging from 248 to 550 $cm^{-1}$ have been proposed from analysis of the observed spectroscopic data [48–51, 53–56]. Ab initio [23,43,57] and semiempirical [58] calculations predict values of bending vibration from 298 to 542 $cm^{-1}$. The value of $\nu_2$ presented in Table 2 was determined by simultaneous analysis of all the bands observed in the IR diode laser spectroscopic study [56].

### $C_3H$

Jacox and Milligan [63,64] studied the photolysis of allene and methylacetylene in an argon matrix and assigned an absorption at 1834 $cm^{-1}$ to C≡C stretching of $C_3H$. This value is adopted here for $\nu_2$ (Table 2).* Other fundamentals were estimated by comparison with frequencies of $C_2H$, $C_2H_2$, $C_4H_2$. Spangenberg et al. [65] have estimated the vibrational frequencies of $C_3H$ using the frequencies of HCN and $C_3$ molecules. Their values differ substantially from those given in Table 2.

### $C_4H$

Dismuke et al. [66] have reported an IR spectroscopic study of the $C_4H$ radical isolated in argon matrix. The bands at 2060 and 735 $cm^{-1}$ have been assigned to the stretching $\nu_3$(C≡C) and the bending $\nu_5$(HCC) modes, respectively.* From the rotational analysis of microwave spectrum [67], the value of bending frequency $\nu_7$(C≡C–C) was roughly estimated to be 131 $cm^{-1}$. In the present work the vibrational frequencies of $C_4H$ (Table 2) were calculated using a simplified valence force field for $C_4H_2$ (Table 3, see also ref. 1). Spangenberg et al. [65] have estimated the vibrational frequencies of $C_4H$ based on the frequencies of $C_4H_2$, $C_3$ and HCN molecules. Several frequencies of Spangenberg et al. [65] differ markedly

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* As our calculations were being completed, three papers concerning the vibrational frequencies of $C_3H$ and $C_4H$ radicals appeared [88–90]. The high resolution Fourier transform IR isotopic studies of matrix isolated $C_3H$ [88] and $C_4H$ [89] have enabled confirmation of the earlier identification of the C≡C stretching mode ($\nu_2$(C≡C) = 1824.8 $cm^{-1}$ for $C_3H$ and $\nu_3$(C≡C) = 2060.6 $cm^{-1}$ for $C_4H$) and identification of two new vibrational modes, $\nu_1$(C–H) = 3238.0 $cm^{-1}$, $\nu_3$(C–C) = 1159.7 $cm^{-1}$ for $C_3H$ and $\nu_1$(C–H) = 3307.4 $cm^{-1}$, $\nu_2$(C≡C) = 2083.9 $cm^{-1}$ for $C_4H$. Although these values are different from those estimated in this work (Table 2), the use of experimental values for stretching modes will not result in a marked difference in the calculated thermodynamic functions. The accurate experimental values of low-frequency bending modes are more important because of their larger contributions to the thermodynamic functions.

The vibrational frequencies of $C_4H$ radical have recently been calculated in the semiempirical and ab initio approximation [90]. The values of bending modes calculated by the ab initio method are close to those in Table 2.

TABLE 3

Valence force fields for $C_4H_2$, $C_6H_2$ and $C_4N_2$ molecules which were used for calculation of vibrational frequencies of $C_nH$ and $C_nN$ radicals

| | Force constants [a] | | |
|---|---|---|---|
| | $C_4H_2$ | $C_6H_2$ | $C_4N_2$ |
| $C-H$ | 5.946 | 6.137 | |
| $C\equiv N$ | | | 18.446 |
| $C\equiv C$ | 15.403 | 15.026 | 19.142 |
| $C-C$ | 6.640 | 6.596 | 6.937 |
| $C\equiv C-H$ | 0.203 | 0.205 | |
| $C-C\equiv N$ | | | 0.370 |
| $C\equiv C-C$ | 0.326 | 0.303 | 0.241 |
| $C-H$, $C\equiv C$ | 0.032 | 1.203 | |
| $C\equiv N$, $C-C$ | | | 1.107 |
| $C\equiv C$, $C-C$ | 0.734 | 0.946 | 1.865 |
| $C\equiv C-H$, $C\equiv C-C$ | 0.061 | 0.064 | |
| $C-C\equiv N$, $C\equiv C-C$ | | | 0.019 |
| $C\equiv C-C$, $C\equiv C-C$ | 0 | 0.042 | 0.077 |

[a] Units are mdyn $Å^{-1}$ for stretching constants and stretching–stretching interaction constants; mdyn Å for bending constants and bending–bending interaction constants.

from those presented in Table 2. The unreasonably large value of $\nu_5 = 2089$ $cm^{-1}$ seems to be erroneous.

### $C_nH$ (n = 5–12)

No experimental or theoretical data on vibrational frequencies of $C_nH$ radicals with $n \geqslant 5$ are available. The vibrational frequencies of these radicals (Table 2) were calculated using the force constants of $C_6H_2$ (Table 3).

### $C_2N$

The vibrational frequencies of $C_2N$ radical were determined from an analysis of observed electronic spectra [33,68–71]. The fundamental frequencies used in this work (Table 2) were taken from the high-resolution Fourier transform spectroscopic study [71]. The Renenr–Teller splitting of the vibrational level $\nu_2 = 1$ has been ignored.

### $C_nN$ (n = 3–11)

No experimental or theoretical data on vibrational frequencies of $C_nN$ radicals with $n \geqslant 3$ are known. From the rotational analysis of microwave spectrum of $C_3N$ [72], the value of the lowest bending frequency $\nu_5$ was roughly estimated to be 179 $cm^{-1}$. The vibrational frequencies of these radicals (Table 2) were calculated using the force constants transferred from $C_4N_2$ molecule (Table 3, see also ref. 1).

## ELECTRONIC STATES

### $C_2H$, $C_4H$, $C_6H$, $C_8H$, $C_{10}H$, $C_{12}H$

ESR data [73] showed that $C_2H$ possesses a $^2\Sigma^+$ ground electronic state. Ab initio calculations [28,43,60,61] predict that the lowest excited electronic state $\tilde{A}^2\Pi$, lies 2000–4000 $cm^{-1}$ above the $\tilde{X}^2\Sigma^+$ ground state, with the next lowest states lying at about 58 000 $cm^{-1}$. Curl and co-workers [48,49,52,62] have reported the observation and rotational analysis of the $\tilde{A}^2\Pi \leftarrow \tilde{X}^2\Sigma^+$ electronic transition using color center laser spectroscopy. A band at 3772 $cm^{-1}$ has been assigned [49] to a purely electronic transition. This value is adopted for the energy of the first excited electronic state of $C_2H$ (Table 4).

TABLE 4

Electronic states for the reference radicals

| Molecule | State | Energy ($cm^{-1}$) | Molecule | State | Energy ($cm^{-1}$) |
|---|---|---|---|---|---|
| $C_2H$ | $\tilde{X}^2\Sigma^+$ | 0 | $C_2N$ | $\tilde{X}^2\Pi$ | 0 |
| | $\tilde{A}^2\Pi$ | 3772 | | $\tilde{a}^4\Sigma^-$ | 10600 |
| $C_3H$ | $\tilde{X}^2\Pi$ | 0 | | $\tilde{A}^2\Delta$ | 21259 |
| $C_4H$ | $\tilde{X}^2\Sigma^+$ | 0 | | $\tilde{B}^2\Sigma^-$ | 22413 |
| | $\tilde{A}^2\Pi$ | 1000 | | $\tilde{C}^2\Sigma^+$ | 26662 |
| $C_5H$ | $\tilde{X}^2\Pi$ | 0 | $C_3N$ | $\tilde{X}^2\Sigma^+$ | 0 |
| $C_6H$ | $\tilde{X}^2\Pi$ | 0 | | $\tilde{A}^2\Pi$ | 5000 |
| | $\tilde{A}^2\Sigma^+$ | 1000 | $C_4N$ | $\tilde{X}^2\Pi$ | 0 |
| $C_7H$ | $\tilde{X}^2\Pi$ | 0 | $C_5N$ | $\tilde{X}^2\Sigma^+$ | 0 |
| $C_8H$ | $\tilde{X}^2\Pi$ | 0 | | $\tilde{A}^2\Pi$ | 2000 |
| | $\tilde{A}^2\Sigma^+$ | 3000 | $C_6N$ | $\tilde{X}^2\Pi$ | 0 |
| $C_9H$ | $\tilde{X}^2\Pi$ | 0 | $C_7N$ | $\tilde{X}^2\Pi$ | 0 |
| $C_{10}H$ | $\tilde{X}^2\Pi$ | 0 | | $\tilde{A}^2\Sigma^+$ | 1000 |
| | $\tilde{A}^2\Sigma^+$ | 5000 | $C_8N$ | $\tilde{X}^2\Pi$ | 0 |
| $C_{11}H$ | $\tilde{X}^2\Pi$ | 0 | $C_9N$ | $\tilde{X}^2\Pi$ | 0 |
| $C_{12}H$ | $\tilde{X}^2\Pi$ | 0 | | $\tilde{A}^2\Sigma^+$ | 4000 |
| | $\tilde{A}^2\Sigma^+$ | 7000 | $C_{10}N$ | $\tilde{X}^2\Pi$ | 0 |
| | | | $C_{11}N$ | $\tilde{X}^2\Pi$ | 0 |
| | | | | $\tilde{A}^2\Sigma^+$ | 7000 |

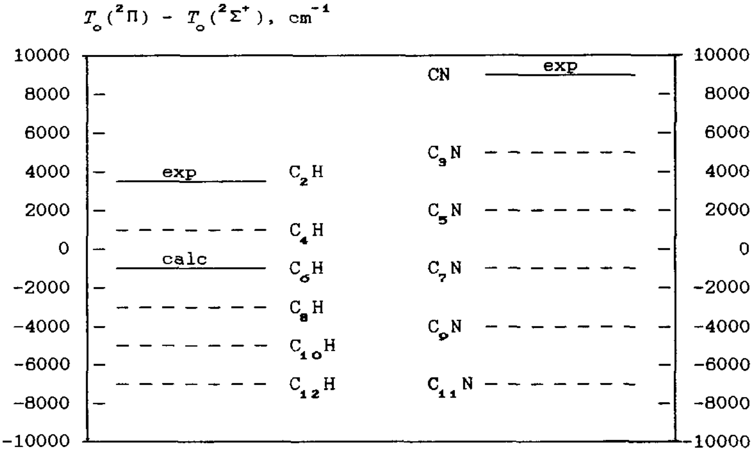

Fig. 1. Estimation of the energy differences between $^2\Sigma^+$ and $^2\Pi$ states for the isoelectronic radicals $C_{2n}H$ and $C_{2n-1}N$ ($n = 2$–6). The dotted lines correspond to the $T_0(^2\Pi) - T_0(^2\Sigma^+)$ values estimated in this work.

It was established from microwave studies [5,6,30,67] that, like $C_2H$, the $C_4H$ radical also has a $^2\Sigma^+$ ground state. The surprisingly large spin–orbit interaction for the $\nu_7$ and $2\nu_7(\Delta)$ states suggests that $C_4H$ radical has a low-lying electronically excited state $\tilde{A}^2\Pi$ [67]. In contrast to the preceding radicals with an even number of carbon atoms which have $^2\Sigma^+$ electronic ground states, $C_6H$ has a $^2\Pi$ ground state [9,10,14,18,32]. According to ab initio calculations, the $^2\Pi$ state of $C_6H$ lies approximately 550 cm$^{-1}$ [13] or 2000 cm$^{-1}$ [25] below the $^2\Sigma^+$ state. When the carbon chain grows, the possible number of chemical bond structures related to the $^2\Pi$ state increases, and the $^2\Pi$ state may be stabilized more than the $^2\Sigma^+$ [13]. Based on this, the ground state of the carbon-chain radicals longer than $C_6H$ was presumed to be $\tilde{X}^2\Pi$ [13,18,25,32].

We have adopted a $^2\Sigma^+$ electronic ground state for $C_2H$ and $C_4H$ radicals and a $^2\Pi$ ground state for other $C_{2n}H$ radicals. The energy of the excited electronic state $T_0(\tilde{A}^2\Sigma^+)$, of $C_6H$ is assumed to be 1000 cm$^{-1}$ (Table 4). This value was estimated by averaging the values of energy obtained in ab initio calculations [13,25]. The rough estimation of energies of excited electronic states for the rest of $C_{2n}H$ radicals was carried out according to Fig. 1. It was assumed that the energy difference between the $^2\Sigma^+$ and $^2\Pi$ states decreases strongly from $C_2H$ to $C_4H$ and changes sign for higher members of the $C_{2n}H$ family.

### *$C_3H$, $C_5H$, $C_7H$, $C_9H$, $C_{11}H$*

According to the microwave data [3,4,7,8,74], the ground state of the $C_3H$ and $C_5H$ radicals is $^2\Pi$ and it is expected that $C_nH$ radicals with

$n \geqslant 5$ will also have the $^2\Pi$ ground state [32]. The $\tilde{X}\,^2\Pi$ ground state was adopted for all $C_{2n+1}H$ radicals (Table 4).

The $C_2N$ radical which is isoelectronic with the $C_3H$ radical has no low-lying electronically excited states (see below). By analogy with $C_2N$, the excited electronic states of the $C_{2n+1}H$ radicals are expected to lie much higher than the $\tilde{X}\,^2\Pi$ state and, for that reason, they have not been taken into account in this work.

### *C₂N, C₄N, C₆N, C₈N, C₁₀N*

Three excited states $\tilde{A}\,^2\Delta$, $\tilde{B}\,^2\Sigma^-$ and $\tilde{C}\,^2\Sigma^+$ were observed in the absorption spectrum of the $C_2N$ radical [33]. The semiempirical calculation [75] conformed to what is known about the three observed excited states and pointed to the unobserved excited state being $\tilde{a}\,^4\Sigma^-$. According to these data, four excited electronic states of $C_2N$ are given in Table 4.

By analogy with the $C_2N$ radical, the $^2\Pi$ electronic ground state was assumed for all the $C_{2n}N$ radicals and it was suggested that there are no low-lying electronic excited states for these radicals.

### *C₃N, C₅N, C₇N, C₉N, C₁₁N*

Data obtained from the microwave studies [5,6,30,34,35] showed that the $C_3N$ radical has the $^2\Sigma^+$ ground state. There are no experimental or theoretical data on the electronic states for the rest of the $C_{2n+1}N$ radicals. In this work the rough estimation of the ground and excited electronic states for the $C_{2n+1}N$ radicals was made by comparison with the isoelectronic $C_{2n}H$ radicals (see Fig. 1 and Table 4).

## THERMODYNAMIC FUNCTIONS

Based on the recommended values of molecular constants, ideal gas thermodynamic functions for 21 linear carbon chain radicals between 298.15 and 2000 K were calculated by a standard statistical thermodynamic method using the rigid-rotor and harmonic-oscillator approximation. The calculated values of Gibbs energy $-(G^\circ - H^\circ_0)/T$, heat capacity $C^\circ_p$, and enthalpy $H^\circ - H^\circ_0$, were fitted to polynomial functions. The constants of these polynomials, given in Tables 5–7, were obtained by the least squares method. The fitting errors are less than 0.01% for $-(G^\circ - H^\circ_0)/T$, $H^\circ - H^\circ_0$ and 0.1% for $C^\circ_p$. The uncertainties in the calculated thermodynamic functions are presented in Table 8. The principal sources of error in the calculated thermodynamic functions at low temperatures arise from the uncertainties in the vibrational frequencies and excited electronic state energies estimated in this work. The uncertainties at high temperatures are

TABLE 5

Constants of polynomial function for calculating the values of standard Gibbs energy $-[G^\circ(T)-H^\circ(0)]/T = g_0 + g_1 \ln x + g_2 x^{-2} + g_3 x^{-1} + g_4 x + g_5 x^2 + g_6 x^3$ (J $K^{-1}$ $mol^{-1}$) for 298.15 K $\leqslant T \leqslant$ 2000 K and $x = T \times 10^{-4}$

| Molecule | $g_0$ | $g_1$ | $g_2$ | $g_3$ | $g_4$ | $g_5$ | $g_6$ |
|---|---|---|---|---|---|---|---|
| $C_2H$ | 310.505 | 39.9485 | −0.000409371 | 0.213774 | 37.0134 | 172.936 | −335.795 |
| $C_3H$ | 347.943 | 48.3316 | −0.00298334 | 0.641513 | 213.779 | −326.929 | 282.887 |
| $C_4H$ | 431.230 | 76.9658 | −0.00813049 | 1.62089 | 173.225 | −244.936 | 203.896 |
| $C_5H$ | 444.827 | 73.1344 | −0.00521667 | 1.21567 | 359.677 | −546.547 | 461.953 |
| $C_6H$ | 503.515 | 88.7454 | −0.00636617 | 1.53595 | 423.350 | −655.941 | 561.959 |
| $C_7H$ | 550.556 | 99.6246 | −0.00673236 | 1.68452 | 509.626 | −795.849 | 685.550 |
| $C_8H$ | 598.146 | 110.833 | −0.00687983 | 1.82587 | 581.220 | −856.756 | 688.667 |
| $C_9H$ | 653.864 | 125.535 | −0.00841548 | 2.15468 | 662.659 | −1049.93 | 913.492 |
| $C_{10}H$ | 707.665 | 138.940 | −0.00900915 | 2.37110 | 711.554 | −1084.30 | 916.813 |
| $C_{11}H$ | 757.245 | 151.455 | −0.0100946 | 2.62008 | 815.626 | −1303.92 | 1141.37 |
| $C_{12}H$ | 808.537 | 164.087 | −0.0105662 | 2.81239 | 877.053 | −1380.93 | 1199.30 |
| $C_2N$ | 317.029 | 36.1882 | −0.000662955 | 0.190999 | 185.889 | −338.549 | 330.688 |
| $C_3N$ | 374.547 | 53.2842 | −0.00233909 | 0.613306 | 151.591 | −115.637 | 28.5192 |
| $C_4N$ | 423.309 | 62.9426 | −0.00260996 | 0.744571 | 302.801 | −486.689 | 425.079 |
| $C_5N$ | 419.830 | 59.1023 | −0.000296021 | 0.420104 | 597.229 | −1085.67 | 1017.86 |
| $C_6N$ | 537.546 | 90.8146 | −0.00366073 | 1.15834 | 430.641 | −680.675 | 585.308 |
| $C_7N$ | 601.837 | 107.581 | −0.00473278 | 1.46725 | 472.617 | −734.682 | 621.741 |
| $C_8N$ | 651.565 | 118.572 | −0.00466405 | 1.55530 | 559.489 | −876.809 | 747.868 |
| $C_9N$ | 712.634 | 133.488 | −0.00496019 | 1.74757 | 583.020 | −834.672 | 651.045 |
| $C_{10}N$ | 765.444 | 146.296 | −0.00566444 | 1.94716 | 688.722 | −1073.80 | 911.339 |
| $C_{11}N$ | 824.147 | 160.581 | −0.00591027 | 2.12568 | 726.117 | −1092.22 | 903.041 |

due to uncertainties in the molecular constants and the effect of vibrational anharmonicity.

The calculations of thermodynamic functions are known in the literature for $C_2H$ [20,26 and references cited therein,76], $C_nH$ ($n = 3$–$10$) [20], $C_2N$ [26 and references cited therein]. The calculated values of $-(G^\circ - H_0^\circ)/T$ and $C_p^\circ$ for $C_2H$ and $C_2N$ agree with those reported previously within some 0.1 J $K^{-1}$ $mol^{-1}$. The discrepancies are due to more precise values of vibrational frequencies used in this work. Duff and Bauer [20] have computed thermodynamic functions of $C_nH$ ($n = 2$–$10$) radicals from the molecular constants. Unfortunately, these authors have not reported the moments of inertia and vibrational frequencies which were adopted for the calculation of thermodynamic functions and have presented the polynomial forms for $(H^\circ - H_0^\circ)/T$ and $(G^\circ - H_0^\circ)/T$ only. The discrepancies with the $-(G^\circ - H_0^\circ)/T$ values at 298.15 K calculated by Duff and Bauer [20] range from 1.5 to 50 J $K^{-1}$ $mol^{-1}$ for different radicals.

TABLE 6

Constants of polynomial function for calculating the values of standard heat capacity $C_p^\circ(T) = c_0 + c_1x^{-2} + c_2x + c_3x^2 + c_4x^3$ (J K$^{-1}$ mol$^{-1}$) for 298.15 K $\leqslant T \leqslant$ 2000 K and $x = T \times 10^{-4}$

| Molecule | $c_0$ | $c_1$ | $c_2$ | $c_3$ | $c_4$ |
|---|---|---|---|---|---|
| $C_2H$ | 39.9485 | −0.000818742 | 74.0268 | 1037.62 | −4029.53 |
| $C_3H$ | 48.3316 | −0.00596667 | 427.559 | −1961.58 | 3394.64 |
| $C_4H$ | 76.9658 | −0.0162610 | 346.450 | −1469.62 | 2446.75 |
| $C_5H$ | 73.1344 | −0.0104333 | 719.355 | −3279.28 | 5543.44 |
| $C_6H$ | 88.7454 | −0.0127323 | 846.700 | −3935.65 | 6743.51 |
| $C_7H$ | 99.6246 | −0.0134647 | 1019.25 | −4775.09 | 8226.60 |
| $C_8H$ | 110.833 | −0.0137597 | 1162.44 | −5140.53 | 8264.00 |
| $C_9H$ | 125.535 | −0.016831 | 1325.32 | −6299.60 | 10961.9 |
| $C_{10}H$ | 138.940 | −0.0180183 | 1423.11 | −6505.78 | 11001.8 |
| $C_{11}H$ | 151.455 | −0.0201892 | 1631.25 | −7823.54 | 13696.5 |
| $C_{12}H$ | 164.087 | −0.0211325 | 1754.11 | −8285.57 | 14391.5 |
| $C_2N$ | 36.1882 | −0.00132591 | 371.779 | −2031.29 | 3968.26 |
| $C_3N$ | 53.2842 | −0.00467817 | 303.182 | −693.820 | 342.230 |
| $C_4N$ | 62.9426 | −0.00521992 | 605.602 | −2920.14 | 5100.95 |
| $C_5N$ | 59.1023 | −0.000592043 | 1194.46 | −6514.01 | 12214.3 |
| $C_6N$ | 90.8146 | −0.00732146 | 861.282 | −4084.05 | 7023.69 |
| $C_7N$ | 107.581 | −0.00946557 | 945.234 | −4408.09 | 7460.89 |
| $C_8N$ | 118.572 | −0.0093281 | 1118.98 | −5260.86 | 8974.42 |
| $C_9N$ | 133.488 | −0.00992038 | 1166.04 | −5008.03 | 7812.54 |
| $C_{10}N$ | 146.296 | −0.0113289 | 1377.44 | −6442.80 | 10936.1 |
| $C_{11}N$ | 160.581 | −0.0118205 | 1452.23 | −6553.30 | 10836.5 |

## ENTHALPIES OF FORMATION

### $C_nH$

Several different values have been reported for the enthalpy of formation of the $C_2H$ radical, showing considerable scatter [22, 26 and references cited therein, 77–80]. In the present work, the value of $\Delta_fH^\circ(C_2H)$ (Table 7) has been calculated using the C–H bond dissociation energies of acetylene determined recently from experimental measurements [50,81,82]. Among radicals reviewed in this paper, $C_2H$ is the only radical whose enthalpy of formation is determined sufficiently reliably.

The enthalpy of formation of $C_3H$, $\Delta_fH^\circ$ ($C_3H$, g, 298.15 K) $= 603 \pm 50$ kJ mol$^{-1}$, has been obtained from mass-spectrometric studies of reactions of $C_3H^+$ ions in the gas phase [83]. The enthalpies of formation of $C_nH$ ($n = 2$–$10$) radicals were estimated by means of an empirical theory [19] and semiempirical calculations [22,78]. Taking into account the low accuracy of the experimental value of $\Delta_fH^\circ(C_3H)$ [83], we have estimated the enthalpy of formation of $C_3H$ (Table 7) by averaging the available estimates [19,78,83]. Although this estimate is somewhat higher than the

TABLE 7

Constants of polynomial function for calculating the values of standard enthalpy $H°(T) - H°(0) = h_0 + h_1x^{-1} + h_2x + h_3x^2 + h_4x^3 + h_5x^4$ (kJ mol$^{-1}$) for $298.15\ \text{K} \leqslant T \leqslant 2000$ K and $x = T \times 10^{-4}$ and also accepted values of $\Delta_f H°(298.15\ \text{K})$ (kJ mol$^{-1}$)

| Molecule | $h_0$ | $h_1$ | $h_2$ | $h_3$ | $h_4$ | $h_5$ | $\Delta_f H^0$ |
|---|---|---|---|---|---|---|---|
| $C_2H$ | −2.13774 | 0.00818742 | 399.485 | 370.134 | 3458.72 | −10073.8 | 569 |
| $C_3H$ | −6.41513 | 0.059666 | 483.316 | 2137.79 | −6538.59 | 8486.60 | 630 |
| $C_4H$ | −16.2089 | 0.162610 | 769.658 | 1732.25 | −4898.72 | 6116.88 | 780 |
| $C_5H$ | −12.1567 | 0.104333 | 731.344 | 3596.77 | −10930.9 | 13858.6 | 860 |
| $C_6H$ | −15.3595 | 0.127323 | 887.454 | 4233.50 | −13118.8 | 16858.8 | 1000 |
| $C_7H$ | −16.8452 | 0.134647 | 996.246 | 5096.26 | −15917.0 | 20566.5 | 1090 |
| $C_8H$ | −18.2587 | 0.137597 | 1108.33 | 5812.20 | −17135.1 | 20660.0 | 1230 |
| $C_9H$ | −21.5468 | 0.16831 | 1255.35 | 6626.59 | −20998.7 | 27404.8 | 1310 |
| $C_{10}H$ | −23.7110 | 0.180183 | 1389.40 | 7115.54 | −21685.9 | 27504.4 | 1450 |
| $C_{11}H$ | −26.2008 | 0.201892 | 1514.55 | 8156.26 | −26078.5 | 34241.2 | 1530 |
| $C_{12}H$ | −28.1239 | 0.211325 | 1640.87 | 8770.53 | −27618.6 | 35978.9 | 1670 |
| $C_2N$ | −1.90999 | 0.0132591 | 361.882 | 1858.89 | −6770.98 | 9920.65 | 560 |
| $C_3N$ | −6.13306 | 0.0467817 | 532.842 | 1515.91 | −2312.73 | 855.575 | 609 |
| $C_4N$ | −7.44571 | 0.0521992 | 629.426 | 3028.01 | −9733.78 | 12752.4 | 790 |
| $C_5N$ | −4.20104 | 0.00592043 | 591.023 | 5972.29 | −21713.4 | 30535.8 | 830 |
| $C_6N$ | −11.5834 | 0.0732146 | 908.146 | 4306.41 | −13613.5 | 17559.2 | 1010 |
| $C_7N$ | −14.6725 | 0.0946557 | 1075.81 | 4726.17 | −14693.6 | 18652.2 | 1060 |
| $C_8N$ | −15.5530 | 0.0932810 | 1185.72 | 5594.89 | −17536.2 | 22436.0 | 1240 |
| $C_9N$ | −17.4757 | 0.0992038 | 1334.88 | 5830.20 | −16693.4 | 19531.4 | 1280 |
| $C_{10}N$ | −19.4716 | 0.113289 | 1462.96 | 6887.22 | −21476.0 | 27340.2 | 1460 |
| $C_{11}N$ | −21.2568 | 0.118205 | 1605.81 | 7261.17 | −21844.3 | 27091.2 | 1500 |

experimental value, it is within the experimental uncertainty. In addition, the –C≡CH bond dissociation energy for this value of $\Delta_f H°(C_3H)$ is practically the same ($\approx 780$ kJ mol$^{-1}$) for two processes, $C_4H_2 \rightarrow C_3H + CH$ and $C_4H_2 \rightarrow 2CH + C_2$.

The enthalpies of formation of the free radicals are related to the corresponding bond strengths by the equation

$$D_0(\text{R–X}) = \Delta_f H°(\dot{\text{R}}) + \Delta_f H°(\dot{\text{X}}) - \Delta_f H°(\text{RX}) \qquad (1)$$

Using the assumed values of $\Delta_f H°(C_2H)$ and $\Delta_f H°(C_3H)$ and eqn. (1) the enthalpies of formation of all other $C_nH$ radicals were approximately estimated in the present work. For instance, from $\Delta_f H°(C_2H)$, $\Delta_f H°(CN)$ and $\Delta_f H°(HC_3N)$ ($\Delta_f H°(CN)$ and $\Delta_f H°(HC_3N)$ values were taken from refs. 26 and 1, respectively), $D_0(HC_2\text{–}CN) \approx 620$ kJ mol$^{-1}$ can be obtained. Then, assuming $D_0(HC_2\text{–}CN) = D_0(HC_{2n} - CN)$ the enthalpies of formation of $C_{2n}H$ radicals were calculated (Table 7). Similarly, other reactions with $C_2H$ radical may be used for calculation of $\Delta_f H°(C_{2n}H)$. In the case of $C_{2n+1}H$ radicals, their enthalpies of formation were calculated assuming $D_0(HC{\equiv}C_3H) = D_0(HC{\equiv}C_{2n+1}H) \approx 780$ kJ mol$^{-1}$. The values of $\Delta_f H°$ for

TABLE 8

The uncertainties of the calculated thermodynamic functions (J $K^{-1}$ $mol^{-1}$) and adopted enthalpies of formation (kJ $mol^{-1}$)

| Molecule | Uncertainties in $-(G^\circ - H_0^\circ)/T$ | | Uncertainties in $C_p^\circ$ | | Uncertainties in $\Delta_f H^\circ(298.15\ K)$ |
|---|---|---|---|---|---|
| | 298.15 K | 2000 K | 298.15 K | 2000 K | |
| $C_2H$ | 0.2 | 1.5 | 0.5 | 1.5 | 3 |
| $C_3H$ | 2.5 | 6.0 | 2.5 | 3.0 | 50 |
| $C_4H$ | 5.0 | 8.0 | 3.5 | 6.0 | 50 |
| $C_5H$ | 4.0 | 10.0 | 4.0 | 5.0 | 75 |
| $C_6H$ | 10.0 | 15.0 | 5.5 | 7.0 | 75 |
| $C_7H$ | 7.0 | 16.0 | 6.0 | 7.0 | 100 |
| $C_8H$ | 9.0 | 19.0 | 7.0 | 10.0 | 100 |
| $C_9H$ | 10.0 | 14.0 | 8.0 | 10.0 | 125 |
| $C_{10}H$ | 11.0 | 24.0 | 9.0 | 13.0 | 125 |
| $C_{11}H$ | 12.0 | 26.0 | 10.0 | 12.0 | 150 |
| $C_{12}H$ | 13.0 | 29.0 | 10.0 | 15.0 | 150 |
| $C_2N$ | 1.5 | 4.0 | 1.5 | 2.5 | 50 |
| $C_3N$ | 2.5 | 7.0 | 2.5 | 8.0 | 12 |
| $C_4N$ | 4.0 | 9.0 | 3.5 | 4.0 | 75 |
| $C_5N$ | 12.0 | 15.0 | 4.5 | 10.0 | 75 |
| $C_6N$ | 7.0 | 16.0 | 5.5 | 6.0 | 100 |
| $C_7N$ | 15.0 | 20.0 | 7.0 | 9.0 | 100 |
| $C_8N$ | 10.0 | 22.0 | 7.0 | 9.0 | 125 |
| $C_9N$ | 11.0 | 24.0 | 8.0 | 12.0 | 125 |
| $C_{10}N$ | 12.0 | 26.0 | 9.0 | 11.0 | 150 |
| $C_{11}N$ | 15.0 | 30.0 | 10.0 | 14.0 | 150 |

$HC_{2n+1}N$ and $C_{2n}H_2$ molecules needed in these calculations were taken from ref. 1. The calculated enthalpies of formation of $C_nH$ radicals and the uncertainties in their values are given in Tables 7 and 8, respectively.

### *$C_nN$*

Dibeler et al. [84] have used electron impact mass spectroscopy to measure the enthalpies of formation of $C_nN$ radicals ($n = 2$–$6$). Their values of $\Delta_f H^\circ$ for $C_2N$ and $C_3N$ are 515 and 548 kJ $mol^{-1}$, respectively. From cross-section data for formation of parent and fragment ions by electron impact from $C_2N_2$, the value of 644 kJ $mol^{-1}$ is obtained for $\Delta_f H^\circ(C_2N)$ [85]. The enthalpy of formation of $C_3N$ ($629 \pm 17$ kJ $mol^{-1}$) was measured by the photodissociative excitation of $C_4N_2$ [86].

The value of $\Delta_f H^\circ(C_3N)$ given in Table 7 is based on the experimental data of Halpern et al. [86] and it was obtained using the more accurate values of enthalpies of formation of $C_4N_2$ [87] and CN [26]. Combining this value with the experimental $\Delta_f H^\circ$ values of $C_4N_2$ [87] and CN [26] gives

$D_0(\text{NC–C}_3\text{N}) \approx 520$ kJ mol$^{-1}$ via eqn. (1). Assuming $D_0(\text{NC–C}_3\text{N}) = D_0(\text{NC–C}_{2n+1}\text{N})$ the enthalpies of formation of $C_{2n+1}N$ radicals were calculated in this work (Table 7). The same results for $\Delta_f H°(C_{2n+1}N)$ can be obtained for other reactions with $C_3N$ radical. Thus, for example, when $\Delta_f H°(C_3N)$ is combined with the values of $\Delta_f H°$ for $C_2H$ (Table 7) and $HC_3N$ [1], $D_0(\text{HC}_2\text{–C}_3\text{N})$ is calculated to be about 570 kJ mol$^{-1}$. The enthalpies of formation of $C_{2n+1}N$ radicals calculated assuming $D_0(\text{HC}_2\text{–C}_3\text{N}) = D_0(\text{HC}_2\text{–C}_{2n+1}\text{N})$ are almost the same as given in Table 7.

The experimental value of $\Delta_f H°(C_2N) = 644$ kJ mol$^{-1}$ [85] appears to be much too high. The value of $\Delta_f H°(C_2N) = 560$ kJ mol$^{-1}$ was adopted in the present work. For this value, $D_0(\text{–C≡N})$ is almost the same (about 730 kJ mol$^{-1}$) for two reactions $C_2N_2 \rightarrow C_2N + N$ and $C_2N_2 \rightarrow 2N + C_2$, and $D_0(\text{–C≡CH})$ value of about 780 kJ mol$^{-1}$ for the dissociation $\text{HC≡C}_2\text{N} \rightarrow \text{HC} + C_2N$ is close to $D_0(\text{–C≡CH})$ for the dissociation $\text{HC≡C}_3\text{H} \rightarrow \text{HC} + C_3H$. We believe that it is reasonable to assume a similarity for these $D_0$ values. The enthalpies of formation of $C_{2n}N$ radicals were calculated (Table 7) using the value of $D_0(\text{HC≡C}_{2n}\text{N}) \approx 780$ kJ mol$^{-1}$ and eqn. (1). Although the uncertainties of the estimated $\Delta_f H°$ values are rather large (Table 8), the proposed set of $\Delta_f H°$ values for $C_nN$ and $C_nH$ radicals (Table 7) * and $C_{2n}H_2$, $C_{2n}N_2$ and $HC_{2n+1}N$ molecules [1] is self-consistent.

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* As this work was being completed, the results of MNDO calculations of heats of formation of the $C_nH$ and $C_nN$ radicals ($n = 1$–9) were published [91]. For $C_2H$, $C_3H$, $C_2N$, $C_3N$ and $C_5N$ radicals, the differences between calculated [91] and our estimated values of $\Delta_f H°$ (Table 7) exceed the uncertainties of the $\Delta_f H°$ values given in Table 8. As our values of $\Delta_f H°$ for $C_2H$, $C_3H$, $C_2N$ and $C_3N$ are based on experimental data, one can give preference to our estimates.

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