Thermochimica Acta, 178 (1991) 273–286
Elsevier Science Publishers B.V., Amsterdam

THERMODYNAMIC PROPERTIES OF LINEAR CARBON CHAIN MOLECULES WITH CONJUGATED TRIPLE BONDS

Part I. Polyacetylenes, $H(C{\equiv}C)_nH$ (n = 2–6), cyanopolyacetylenes, $H(C{\equiv}C)_nC{\equiv}N$ (n = 1–5), and dicyanopolyacetylenes, $N{\equiv}C(C{\equiv}C)_nC{\equiv}N$ (n = 1–4)

OLGA V. DOROFEEVA and LEV V. GURVICH

Institute for High Temperatures, Academy of Sciences of the U.S.S.R., Izhorskaya ul. 13/19, Moscow 127412 (U.S.S.R.)

(Received 29 June 1990)

ABSTRACT

The available structural parameters, fundamental frequencies and enthalpies of formation, if any, for polyacetylenes, $C_{2n}H_2$ ($n = 2$–6), cyanopolyacetylenes, $HC_{2n+1}N$ ($n = 1$–5), and dicyanopolyacetylenes, $C_{2n}N_2$ ($n = 2$–5), which are known to be interstellar molecules, were critically evaluated and the recommended values selected. Molecular constants and enthalpies of formation for most of the molecules were estimated as the experimental values for these compounds are not available. The similarity transference procedure has been developed for the calculation of bond distances and force constants. Using a rigid-rotor and harmonic-oscillator approximation, this information was utilized to calculate the ideal gas thermodynamic functions for 14 molecules. The calculated values of heat capacities, C_p°, Gibbs energies, $-(G^\circ - H_0^\circ)/T$, and enthalpies, $H^\circ - H_0^\circ$, were fitted to the suitable polynomial functions. The constants of these polynomials allow the values of C_p°, $-(G^\circ - H_0^\circ)/T$ and $H^\circ - H_0^\circ$ for considered compounds 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), estimated using the group additivity method are presented in the paper.

INTRODUCTION

Linear carbon chain molecules have been observed in interstellar space in the form of cyanopolyynes, $HC_{2n+1}N$ with n up to 5, and radicals C_nH and C_nN with n up to 6 and 3, respectively. Most of these molecules, first identified in molecular clouds and the envelope of the evolved carbon stars [1–11], have been detected in the laboratory, using both chemical and discharge techniques, conclusively confirming the astronomical identification and allowing a more accurate set of molecular constants to be derived [7,12–18]. Other linear carbon chain molecules, polyacetylenes ($C_{2n}H_2$) and dicyanopolyacetylenes ($C_{2n}N_2$), might also be expected to exist in certain astrophysical sources [19–22].

0040-6031/91/$03.50 © 1991 – Elsevier Science Publishers B.V.

The identification of carbon chain molecules in the interstellar medium has aroused interest in the study of vibrational and rotational spectra and thermodynamic properties of these molecules [21,23–41]. This report involves the calculation of the ideal gas thermodynamic properties of 14 polyacetylene, cyanopolyacetylene and dicyanopolyacetylene molecules with the maximum number of heavy atoms being equal to 12 *. Experimental data on rotational constants and vibrational frequencies needed for calculating the thermodynamic functions, as well as experimental enthalpy of formation values are not known for all compounds. For this reason some or all constants for most of the compounds considered have been estimated in this work. The similarity transference procedure has been developed for the calculation of bond distances and force constants. In constructing the force field special attention was paid to the transferability of the force constants since they are intended to be used in large molecules. The details of the methods proposed for estimation are presented below.

MOMENTS OF INERTIA AND GEOMETRIES

Cyanopolyacetylenes, $HC_{2n+1}N$ are linear unsymmetrical molecules (symmetry group $C_{\infty v}$). The rotational constants, B_0, of molecules $HC_{2n+1}N$ with $n \leqslant 5$ (HC_3N [12,43–47], HC_5N [13,48,49], HC_7N [14], HC_9N [4], $HC_{11}N$ [5,6]) have been determined by microwave spectroscopy and in some cases by high-resolution IR spectroscopy. The moments of inertia for these molecules (Table 1) were calculated using the more precise rotational constants [4,6,12–14].

From microwave studies [45,48] the structural parameters of HC_3N and HC_5N have been obtained (Table 1). To estimate the equilibrium geometries of cyanopolyynes semiempirical and ab initio calculations were carried out [27,29,30,34,41]. Using the numerical extrapolation method, Oka [25] achieved the best agreement between calculated and experimental rotational constants. It should be noted that averaged bond lengths transferred from HC_5N yield the B_0 values for HC_7N, HC_9N and $HC_{11}N$ which are consistent with experimental ones within 0.1–0.4%, whereas theoretical B_0 values differ rather more from those observed experimentally. These averaged bond distances, given in Table 1, were considered in this work as a rough estimation for structural parameters of HC_7N, HC_9N and $HC_{11}N$.

---

* Spectroscopic and thermodynamic properties of C_2H_2, HCN and C_2N_2 molecules are well known (see, for example, ref. 42) and these molecules were not considered in the present work. Thermodynamic properties of 21 radicals which may be formed from polyacetylene, cyanopolyacetylene and dicyanopolyacetylene molecules will be presented in Part II of this series, "Free radicals C_nH ($n = 2$–12) and C_nN ($n = 2$–11)".

TABLE 1

Assumed bond lengths (Å) and computed moments of inertia for polyacetylenes, cyanopolyacetylenes and dicyanopolyacetylenes [a]

Molecule	H–C	C≡C	C–C	C≡N	$I \times 10^{-39}$ (g cm^2)
C_4H_2	1.06	1.205	1.378		*19.12*
C_6H_2	1.06	1.216	1.363		64
C_8H_2, $C_{10}H_2$, $C_{12}H_2$	1.06	1.21	1.36		148, 286, 492
C_4N_2 [b]		1.216	1.363	1.16	63
C_6N_2, C_8N_2, $C_{10}N_2$		1.21	1.36	1.16	149, 290, 499
HC_3N	*1.058*	*1.205*	*1.378*	*1.159*	*18.448*
HC_5N	*1.0569*	*1.2087* *1.2223*	*1.3623* *1.3636*	*1.1606*	*63.036*
HC_7N, HC_9N, $HC_{11}N$	1.06	1.21	1.36	1.16	*148.80, 288.90, 495.77*

[a] Experimental bond lengths and values of moments of inertia calculated using the experimental rotational constants are given in italics.

[b] The experimental bond lengths of C_4N_2 molecule, r(C≡N) = 1.161 Å, r(C–C) = 1.367 Å and r(C≡C) = 1.198 Å, were determined recently from an electron diffraction investigation [50] (see footnote on page 276).

They may be useful for estimating moments of inertia of long linear polyynes whose rotational constants have not been obtained experimentally.

Polyacetylenes, $C_{2n}H_2$, and dicyanopolyacetylenes, $C_{2n}N_2$, are linear symmetrical molecules (symmetry group $D_{\infty h}$). Owing to the symmetry present, no microwave spectrum is expected for these molecules. The rotational constant was determined from high-resolution IR and Raman spectra for C_4H_2 only [20,51–57]. The moment of inertia of C_4H_2 (Table 1) was calculated using the more precise rotational constants [20,56,57]. The bond distances of C_4H_2 were determined from electron diffraction data [58]. However, these values as ones derived from theoretical calculations [23,24,37,59,60] give B_0 values which do not agree well enough with experiment. For this reason we recommend the bond lengths of C_4H_2 (Table 1) selected to fit the experimental B_0 value. These bond lengths are close to those in the HC_3N molecule.

There are no experimental data on the molecular structure of $C_{2n}H_2$ ($n \geq 3$) and $C_{2n}N_2$ ($n \geq 2$). Structural parameters of C_6H_2 [23,30,36,59], C_8H_2 and $C_{10}H_2$ [23] were obtained from theoretical calculations. Also the crystal structure of C_4N_2 is known [61]. In the present work the bond lengths for molecules with six heavy atoms, C_6H_2 and C_4N_2, were assumed to be the same as in the HC_5N molecule. The bond distances for C_8H_2 and C_6N_2, $C_{10}H_2$ and C_8N_2, $C_{12}H_2$ and $C_{10}N_2$ were adopted the same as in HC_7N, HC_9N and $HC_{11}N$ molecules, respectively. The moments of inertia of C_6H_2, C_8H_2, $C_{10}H_2$, $C_{12}H_2$, C_4N_2 *, C_6N_2, C_8N_2 and $C_{10}N_2$ (Table 1) were calculated based on these estimated structural parameters.

VIBRATIONAL FREQUENCIES

Vibrational spectra of C_4H_2 [19,20,32,35,52,54–57,62–72], C_6H_2 [38,73], C_4N_2 [21,74–77], C_6N_2 [78–80] and HC_3N [47,81–92] have been reported by a number of authors and the fundamental assignments are reasonably well known. The vibrational frequencies from the more reliable and complete studies were adopted in the present work for C_4H_2 [20], C_6H_2 [73], C_4N_2 [21] and HC_3N [47,86,89,92] (Table 2). For other polyynes vibrational studies are either not complete or not available at all, and for this reason, the vibrational frequencies needed for statistical calculations of thermodynamic functions should be estimated for most of the polyynes.

Stretching frequencies for polyacetylenes $C_{2n}H_2$ ($n = 2$–5) have been calculated by Dewar et al., [23] using the semiempirical MNDO method. Comparison of known vibrational spectra of C_4H_2 and C_6H_2 with the calculated values indicate the latter to be systematically overestimated. Nevertheless, Dessau and Spangenberg [39] have used these values together with bending frequencies estimated by them for calculation of the thermodynamic functions of C_4H_2, C_6H_2, C_8H_2 and $C_{10}H_2$. In the present work the vibrational frequencies of long chain polyyne molecules were calculated using simplified valence force fields for molecules containing the C≡C and C≡N groups and assuming the transferability of force constants between large polyyne molecules. Vibrational frequencies of C_8H_2, $C_{10}H_2$ and $C_{12}H_2$ molecules (Table 2) were calculated using 9 force constants of C_6H_2 (Table 3). The force field for C_6H_2 was obtained by us from normal coordinate calculations. The program NCA, written by Novikov and Malyshev [93], based on the general method of Gwinn [94] was used for the calculations. This force field reproduces the experimental frequencies of C_6H_2 reasonably well ($|\Delta\nu|_{av} = 12$ cm^{-1}). The frequencies of bending vibrations for $C_{2n}H_2$

---

* As our calculations were being completed, the paper concerning the structure of C_4N_2 molecule appeared. Brown et al. [50] presented an electron diffraction and high-resolution pure rotational Raman spectroscopy investigation. The bond lengths, $r(\mathrm{C{\equiv}C}) = 1.198$ Å, $r(\mathrm{C{-}C}) = 1.367$ Å and $r(\mathrm{C{\equiv}N}) = 1.161$ Å, were obtained from the refinement of the electron diffraction data. The B_0 rotational constant derived from these bond lengths is nearly identical with the B_{av} value deduced from the Raman data. Although the value of C≡C bond length estimated in the present work (Table 1) is longer than that obtained from electron diffraction data by ≈ 0.02 Å, the moment of inertia calculated using the experimental rotational constants (62.4×10^{-39} g cm^2) is close to value given in Table 1. Thus, the use of electron diffraction data will not result in a marked difference in the calculated thermodynamic functions.

TABLE 2

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

Molecule	Frequencies
C_4H_2	*3332, 2189, 872, 3334, 2022, 626(2), 483(2), 628(2), 220(2)*
C_6H_2	*3313, 2201, 2019, 625, 3328, 2125, 1115, 625(2), 491(2), 258(2), 622(2), 443(2), 105(2)*
C_8H_2	3321, 2227, 2077, 1223, 466, 3321, 2170, 2039, 891, 625(2), 531(2), 374(2), 156(2), 625(2), 473(2), 283(2), 60(2)
$C_{10}H_2$	3321, 2234, 2140, 2042, 1041, 377, 3321, 2199, 2065, 1273, 732, 625(2), 538(2), 446(2), 294(2), 104(2), 625(2), 504(2), 362(2), 190(2), 39(2)
$C_{12}H_2$	3321, 2238, 2174, 2059, 1300, 896, 316, 3321, 2214, 2120, 2044, 1131, 619, 625(2), 542(2), 482(2), 354(2), 213(2), 73(2), 625(2), 520(2), 428(2), 301(2), 137(2), 27(2)
C_4N_2	*2333, 2267, 640, 2241, 1154, 504(2), 263(2), 471(2), 107(2)*
C_6N_2	2313, *2235, 1288*, 495, 2332, *2266*, 929, *501(2)*, 340(2), *156(2), 491(2), 276(2), 62(2)*
C_8N_2	2331, 2305, 2254, 1084, 402, 2324, 2256, 1312, 772, 490(2), 354(2), 285(2), 104(2), 490(2), 334(2), 186(2), 40(2)
$C_{10}N_2$	2328, 2301, 2255, 1340, 941, 339, 2330, 2316, 2255, 1176, 658, 490(2), 354(2), 325(2), 206(2), 74(2), 490(2), 356(2), 288(2), 136(2), 28(2)
HC_3N	*3327, 2274, 2079, 864, 663(2), 499(2), 222(2)*
HC_5N	3330, *2256*, 2181, 2114, 1162, 636, 626(2), 488(2), 381(2), 260(2), 105(2)
HC_7N	3330, 2256, 2207, 2162, 2116, 1263, 926, 487, 624(2), 490(2), 426(2), 359(2), 276(2), 154(2), 60(2)
HC_9N	3330, 2256, 2215, 2190, 2152, 2116, 1313, 1081, 763, 394, 624(2), 490(2), 437(2), 407(2), 346(2), 285(2), 186(2), 103(2), 39(2)
$HC_{11}N$	3330, 2256, 2218, 2204, 2177, 2146, 2116, 1340, 1172, 933, 647, 331, 624(2), 490(2), 440(2), 425(2), 392(2), 337(2), 290(2), 207(2), 135(2), 73(2), 27(2)

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

molecules, given in Table 2, are close to those estimated by Dessau and Spangenberg [39].

Before proceeding to the consideration of C_6N_2 molecule and the next members of the dicyanopolyacetylene family, the vibrational studies of C_4N_2 are to be discussed in more detail. Miller et al. [74,75] have studied the IR spectrum of the vapour phase and the Raman spectrum of the liquid phase and have assigned all fundamentals for C_4N_2. More recently, Khanna et al. [21] have reported the Raman and IR spectra for solid C_4N_2 as well as the liquid-phase Raman and vapour-phase IR spectra and have made new assignments for ν_1, ν_2 and ν_3. These assignments have been supported by a normal coordinate analysis. The vibrational frequencies given in Table 2 are those obtained by Khanna et al. [21]. It should be noted that our attempt to reproduce the vibrational assignment of Miller et al. [75] was also unsuccessful. In addition to poor agreement between calculated and experimental

TABLE 3

Valence force fields for C_6H_2, C_4N_2 and HC_5N molecules which were used for calculation of vibrational frequencies of long chain polyynes

Force constant [a]	C_6H_2	C_4H_2	HC_5N
C–H	6.137		6.164
C≡N		18.446	16.115
C≡C	15.026	19.142	17.942
C–C	6.596	6.937	6.964
C≡C–H	0.205		0.206
C–C≡N		0.370	0.326
C≡C–C	0.303	0.241	0.263
C–H, C≡C	1.203		1.203
C≡N, C–C		1.107	1.107
C≡C, C–C	0.946	1.865	1.406
C≡C–H, C≡C–C	0.064		0.064
C–C≡N, C≡C–C		0.019	0.019
C≡C–C, C≡C–C	0.042	0.077	0.060

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

values of vibrational frequencies, the C≡C, C–C interaction constant had a very large positive value whereas the C≡N, C–C term had a negative value. At the same time, the experimental frequencies of Khanna et al. [21] were reproduced quite closely using nine force constants from Table 3.

The IR and Raman spectra of C_6N_2 in the vapour and liquid phases have been reported by Miller and Lemmon [78]. To reproduce this vibrational assignment we performed valence force field calculations using 11 and 9 force constants. For the two sets of calculations, no stable convergence with reasonable values of force constants were found. One can reasonably suggest that the vibrational assignment for C_6N_2 suggested by Miller and Lemmon [78] as well as the vibrational assignment for C_4N_2 given by Miller et al. [75] (see above) is not quite correct. For this reason the fundamental frequencies for C_6N_2 used in the present work (Table 2) were taken from the experimental study [78] if they are consistent with values calculated using force constants from C_4N_2 (Table 3). These values are given in Table 2 in italics. Other vibrational frequencies of C_6N_2 as well as all vibrational frequencies of C_8N_2 and $C_{10}N_2$ were calculated using the force constants transferred from C_4N_2 (Table 3).

The C≡N stretching band, $\nu_2 = 2256$ cm^{-1}, of HC_5N has been detected from the high resolution IR spectrum [95,96]. Hutchinson et al. [49] have analyzed in the microwave region the bending vibrations ν_{10} and ν_{11} which are considerably lower in energy than all other fundamental vibrations ($\nu_{10} \approx 190$ cm^{-1} and $\nu_{11} \approx 75$ cm^{-1}). The frequencies for the bending fundamentals of HC_5N have been predicted based on an ab initio calculation ($\nu_7 = 691$, $\nu_8 = 565$, $\nu_9 = 457$, $\nu_{10} = 249$, $\nu_{11} = 101$ cm^{-1}) [31,33]. Herrera et al. [97] have reported ab initio (STO-3G) and similarity transference estimates of the vibrational frequencies of HC_5N. The similarity transferred frequencies were based on the experimental and theoretical force constants of the parent molecules. In the present work the fundamental vibrations of HC_5N were estimated by normal coordinate calculations. The final force field for HC_5N molecule (Table 3) was generated using the force constants transferred from C_6H_2 and C_4N_2 molecules, the experimental value of ν_2 for HC_5N and the correlation with experimental frequencies of C_6H_2 and C_4N_2. The calculated vibrational frequencies of HC_5N are shown in Table 1. It should be noted that vibrational frequencies calculated in this work are close to those obtained by the ab initio method [31,33] and the similarity transference technique [97]. Vibrational frequencies of HC_7N, HC_9N and $HC_{11}N$ molecules (Table 2) were calculated using the force constants transferred from HC_5N (Table 3).

ELECTRONIC STATES

Linear polyyne molecules have singlet electronic ground states $^1\Sigma_g^+$ (polyacetylenes and dicyanopolyacetylenes) or $^1\Sigma^+$ (cyanopolyacetylenes). From UV spectra and theoretical investigations the energies of the lowest excited electronic states of C_4H_2 [55,98–100], C_6H_2 [98], C_4N_2 [101,102], C_6N_2 [102,103], HC_3N [83,102,104,105] were found to be ≈ 30000 cm^{-1} and up. The excited states for other molecules considered here might be believed to have the same high energies, and therefore the excited states were ignored in this work.

THERMODYNAMIC FUNCTIONS

Based on the selected values of molecular constants, ideal gas thermodynamic functions for 14 molecules of polyacetylenes, cyanopolyacetylenes and dicyanopolyacetylenes 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, $-(G^\circ - H_0^\circ)/T$, heat capacities, C_p°, and enthalpy, $H^\circ - H_0^\circ$, were fitted to suitable polynomial functions. The constants of these polynomials, given in Tables 4–6, were obtained by the least squares method. On average, the polynomial fits reproduce tabulated values of $-(G^\circ - H_0^\circ)/T$ to 0.001%, C_p° to 0.05% and $H^\circ - H_0^\circ$ to 0.01% or better. The uncertainties in the calculated thermodynamic functions are presented in Table 7. The principal sources of error in the calculated thermodynamic functions at low temperatures arise from the uncertainties in the vibrational frequencies estimated

TABLE 4

Constants of polynomial function for calculation of the values of standard Gibbs energy $-[G^\circ(T)-H^\circ(0)]/T=g_0+g_1\ln x+g_2x^{-2}+g_3x^{-1}+g_4x+g_5x^2+g_6x^3$ in J K^{-1} mol^{-1} for 298.15 K $\leq T \leq$ 2000 K, $x=T\times10^{-4}$

Molecule	g_0	g_1	g_2	g_3	g_4	g_5	g_6
C_4H_2	405.416	71.3282	−0.00612665	1.34799	301.939	−369.485	250.788
C_6H_2	509.991	97.6540	−0.00783492	1.84792	453.313	−621.172	476.319
C_8H_2	614.755	123.730	−0.00934481	2.29996	604.608	−871.262	699.765
$C_{10}H_2$	717.911	149.633	−0.0110220	2.76733	757.747	−1125.60	927.990
$C_{12}H_2$	821.447	175.505	−0.0127075	3.23061	911.083	−1380.29	1156.57
C_4N_2	456.894	75.7283	−0.00353515	1.00498	357.538	−543.816	450.458
C_6N_2	568.509	102.874	−0.00451924	1.39656	491.296	−749.423	622.438
C_8N_2	684.045	131.189	−0.00558325	1.80623	615.852	−937.465	777.059
$C_{10}N_2$	797.747	158.918	−0.00659036	2.19834	745.005	−1134.30	940.394
HC_3N	381.387	59.4362	−0.00397788	0.912240	267.875	−364.357	275.575
HC_5N	492.945	86.9388	−0.00513257	1.35533	403.953	−579.524	459.913
HC_7N	601.036	113.587	−0.00643907	1.78753	548.616	−814.013	665.737
HC_9N	708.622	140.157	−0.0077311	2.21217	694.016	−1050.06	873.210
$HC_{11}N$	816.737	166.753	−0.00901043	2.63099	839.221	−1285.77	1080.37

from force constant calculations, especially in the assignment of the low-frequency normal modes. The uncertainties at high temperatures are due to uncertainties in the molecular constants, estimates of the effect of vibrational anharmonicity and inaccuracies of polynomial approximation.

TABLE 5

Constants of polynomial function for calculation of the values of standard heat capacity $C_p^\circ(T)=c_0+c_1x^{-2}+c_2x+c_3x^2+c_4x^3$ in J K^{-1} mol^{-1} for 298.15 K $\leq T \leq$ 2000 K, $x=T\times10^{-4}$

Molecule	c_0	c_1	c_2	c_3	c_4
C_4H_2	71.3282	−0.0122533	603.877	−2216.91	3009.45
C_6H_2	97.6540	−0.0156698	906.626	−3727.03	5715.83
C_8H_2	123.730	−0.0186896	1209.22	−5227.57	8397.17
$C_{10}H_2$	149.633	−0.0220440	1515.49	−6753.61	11135.9
$C_{12}H_2$	175.505	−0.025415	1822.17	−8281.77	13878.8
C_4N_2	75.7283	−0.00707031	715.076	−3262.90	5405.50
C_6N_2	102.874	−0.00903847	982.593	−4496.54	7469.25
C_8N_2	131.189	−0.0111665	1231.70	−5624.79	9324.71
$C_{10}N_2$	158.918	−0.0131807	1490.01	−6805.79	11284.7
HC_3N	59.436	−0.00795575	535.751	−2186.14	3306.90
HC_5N	86.9388	−0.0102651	807.906	−3477.14	5518.96
HC_7N	113.587	−0.0128781	1097.23	−4884.08	7988.85
HC_9N	140.157	−0.0154623	1388.03	−6300.38	10478.5
$HC_{11}N$	166.753	−0.0180209	1678.44	−7714.62	12964.5

TABLE 6

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

Molecule	h_0	h_1	h_2	h_3	h_4	h_5	$\Delta_f H°$
C_4H_2	−13.4799	0.122533	713.282	3019.39	−7389.69	7523.63	450
C_6H_2	−18.4792	0.156698	976.540	4533.13	−12423.4	14289.6	670
C_8H_2	−22.9996	0.186896	1237.30	6046.08	−17425.2	20993.0	900
$C_{10}H_2$	−27.6733	0.220440	1496.33	7577.47	−22512.0	27839.7	1120
$C_{12}H_2$	−32.3061	0.254150	1755.05	9110.83	−27605.9	34697.1	1340
C_4N_2	−10.0498	0.0707031	757.283	3575.38	−10876.3	13513.8	529.2
C_6N_2	−13.9656	0.0903847	1028.74	4912.96	−14988.5	18673.1	750
C_8N_2	−18.0623	0.111665	1311.89	6158.52	−18749.3	23311.8	980
$C_{10}N_2$	−21.9834	0.131807	1589.18	7450.05	−22686.0	28211.8	1200
HC_3N	−9.12240	0.0795575	594.362	2678.75	−7287.14	8267.24	380
HC_5N	−13.5533	0.102651	869.388	4039.53	−11590.5	13797.4	600
HC_7N	−17.8753	0.128781	1135.87	5486.16	−16280.3	19972.1	820
HC_9N	−22.1217	0.154623	1401.57	6940.16	−21001.3	26196.3	1050
$HC_{11}N$	−26.3099	0.180209	1667.53	8392.21	−25715.4	32411.2	1270

A number of calculations of thermodynamic functions are known in the literature for C_4H_2 [39,63,106–108], C_6H_2, C_8H_2, $C_{10}H_2$ [39,106], C_4N_2 [76,109], C_6N_2 [79,80,109] and HC_3N [108]. The calculated values of $-(G° - H_0°)/T$ and $C_p°$ for C_4H_2 agree with those reported by other authors

TABLE 7

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

Molecule	Uncertainties in $-(G° - H_0°)/T$		Uncertainties in $C_p°$		Uncertainties in $\Delta_f H°$ (298.15 K)
	298.15 K	2000 K	298.15 K	2000 K	
C_4H_2	0.5	4.5	2.0	4.5	20
C_6H_2	2.0	9.0	4.0	7.0	40
C_8H_2	6.0	17.0	7.0	9.5	60
$C_{10}H_2$	10.0	23.0	8.0	12.0	80
$C_{12}H_2$	10.5	27.0	10.0	14.0	100
C_4N_2	2.0	7.0	3.0	5.0	1.4
C_6N_2	4.0	12.0	5.5	7.0	60
C_8N_2	10.0	22.0	7.0	10.0	80
$C_{10}N_2$	11.0	25.0	9.0	12.0	100
HC_3N	0.5	4.0	2.0	4.0	20
HC_5N	6.0	14.0	5.0	6.0	40
HC_7N	9.0	20.0	7.0	8.5	60
HC_9N	13.0	27.0	9.0	11.0	80
$HC_{11}N$	15.0	30.0	11.0	13.0	100

[63,107,108] within 0.1 J K^{-1} mol^{-1}. Duff and Bauer [106] have computed thermodynamic functions of $C_{2n}H_2$ ($n = 2$–5) molecules 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 only the polynomial forms for $(H^\circ - H_0^\circ)/T$ and $(G^\circ - H_0^\circ)/T$. The largest discrepancies with the thermodynamic functions calculated in the present work exist for Gibbs energies at 298.15 K and amount to 10, 15, 46 and 49 J K^{-1} mol^{-1} for C_4H_2, C_6H_2, C_8H_2 and $C_{10}H_2$, respectively. The bending vibrational frequencies which have been estimated (except for C_4H_2, for which experimental vibrational frequencies have been used) and the stretching frequencies taken from the semiempirical calculation [23] were used by Dessau and Spangenberg [39] to compute the thermodynamic functions of $C_{2n}H_2$ ($n = 2$–5) molecules. The discrepancies between our values of Gibbs energies at 298.15 K and those calculated by Dessau and Spangenberg [39] amount to 0.2, 3, 7 and 12 J K^{-1} mol^{-1} for C_4H_2, C_6H_2, C_8H_2 and $C_{10}H_2$, respectively. The discrepancies at 2000 K are equal to 2, 9, 18 and 26 J K^{-1} mol^{-1}. The complete vibrational assignments are well known for C_4H_2 and C_6H_2 (see above) and the use of estimated values for vibrational frequencies of these molecules is not justified. In the case of C_4H_2 and C_6H_2 the values of stretching frequencies from the semiempirical calculation [23] are systematically overestimated. Since more recent and more reliable data have been used in the present work, one can believe that our calculated values of thermodynamic functions for $C_{2n}H_2$ molecules should be more reliable than those reported previously [39,106]. Our values of Gibbs energy at 298.15 K for C_4N_2 and C_6N_2 are in good agreement with those calculated by Moffat and Knowles [109]. The discrepancies are equal to 0.3 and 1.7 J K^{-1} mol^{-1} for C_4N_2 and C_6N_2, respectively, and they are due to the difference in molecular constants used in the calculations. However, the values of Gibbs energy for C_4N_2 and C_6N_2 reported in several works [76,79,80] are 25–40 J K^{-1} mol^{-1} less than our values. As in these works almost the same molecular constants were used as in the present work one can suggest that the calculations [76,79,80] are erroneous.

Values of Gibbs energies for HC_3N calculated by Spangenberg et al. [108] are 18 J K^{-1} mol^{-1} less than values obtained in the present work. This discrepancy is due to the incorrect moment of inertia adopted by the above authors.

ENTHALPIES OF FORMATION

The reliable value of $\Delta_f H^\circ$ has been obtained from experimental data for C_4H_2 only [110]. The experimental and theoretical data for other polyacetylenes, cyanopolyacetylenes and dicyanopolyacetylenes are either unreliable or unavailable. Most of the reported studies are concerned with C_4H_2 and HC_3N molecules and there is significant scatter in their published $\Delta_f H°$ values, i.e., 381 [28], 427 [23], 439 [37], 440 [111], 456 [112], 462 [113], 466 [106,114] and 473 kJ mol^{-1} [115] for C_4H_2 and 354 [116] *, ≥ 355 [117] *, 364 [37] and 382 kJ mol^{-1} [121] for HC_3N. Rough estimates of $\Delta_f H°$ have also been made for C_6H_2, C_8H_2, $C_{10}H_2$ [23,114] and C_6N_2 [121].

In this work, the group additivity method was employed for the estimation of $\Delta_f H°$ values. The values for groups involving triply bonded carbon, C_t, were based on enthalpies of formation of the gaseous C_2H_2, C_2N_2 and C_4N_2 molecules reported by Pedley et al. [110]. The enthalpies of formation of [≡C–(H)] and [–C≡(N)] groups, $\Delta_f H°[C_t–(H)] = 114.1$ kJ mol^{-1} and $\Delta_f H°[C_t–(N)] = 153.4$ kJ mol^{-1}, were obtained from $\Delta_f H°(C_2H_2$, g, 298.15 K) = 228.2 kJ mol^{-1} and $\Delta_f H°(C_2N_2$, g, 298.15 K) = 306.7 kJ mol^{-1}. From the values of $\Delta_f H°[C_t–(N)]$ and $\Delta_f H°(C_4N_2$, g, 298.15 K) = 529.2 kJ mol^{-1}, the enthalpy of formation of [≡C–(C)] group, $\Delta_f H°[C_t–(C_t)] = 111.3$ kJ mol^{-1}, was calculated. Using these three values of the group contribution the enthalpies of formation of all compounds were calculated. Their rounded values are given in Table 6. Uncertainties in the estimated values of $\Delta H_f°$ are presented in Table 7.

The value of $\Delta_f H°(HC_3N) = 380$ kJ mol^{-1} calculated in this work is in satisfactory accord with the reported estimates of 364 [37] and 382 kJ mol^{-1} [121]. The estimate for $\Delta_f H°$ of C_4H_2 is 450 kl mol^{-1}, which is close to the published values of 439 [37], 440 [111] and 456 kJ mol^{-1} [112]. The values of enthalpies of formation for C_6H_2, C_8H_2 and $C_{10}H_2$ (Table 6) lie between available estimates [23,114,122] and the enthalpy of formation of C_6N_2 (Table 6) is in good agreement with the reported estimate [121]. Although the group values used in this work are somewhat different from the published values [111,121–123] (especially in the case of the $[C_t–(C_t)]$ group), the comparison with published data points to the conclusion that proposed group values yield reasonable estimation of $\Delta_f H°$ values for linear long chain polyyne molecules.

ACKNOWLEDGMENT

We thank Natalia Moiseeva for assistance in performing the computer calculation.

---

* In making the thermochemical calculations, incorrect values of $\Delta_f H°(C_2H)$ were employed by Harland [116] and Okabe and Dibeler [117]. Using the value of $\Delta_f H°(C_2H) = 565$ kJ mol^{-1} based on the C–H bond dissociation energies of acetylene determined recently [118–120], the recalculation of the above data gives $\Delta_f H°(HC_3N) = 439$ [116] and 404 kJ mol^{-1} [117], respectively.

REFERENCES

1 B.E. Turner, Astrophys. J., 163 (1971) 138.
2 L.W. Avery, N.W. Broten, J.M. MacLeod, T. Oka and H.W. Kroto, Astrophys. J., 205 (1976) L173.
3 H.W. Kroto; C. Kirby, D.R.M. Walton, L.W. Avery, N.W. Broten, J.M. MacLeod and T. Oka, Astrophys. J., 219 (1978) L133.
4 N.W. Broten, T. Oka, L.W. Avery, J.M. MacLeod and H.W. Kroto, Astrophys. J., 223 (1978) L105.
5 M.B. Bell, P.A. Feldman, S. Kwok and H.E. Mattews, Nature (London), 295 (1982) 389.
6 M.B. Bell and H.E. Matthews,, Astrophys. J., 291 (1985) L63.
7 C.A. Gottlieb, E.W. Gottlieb and P. Thaddeus, Astrophys. J., 264 (1983) 740.
8 P. Thaddeus, C.A. Gottlieb, A. Hjalmarson, L.E.B. Johansson, W.M. Irvine, P. Friberg and R.A. Linke, Astrophys. J., 294 (1985) L49.
9 M. Guélin, P. Friberg and A. Mezaoni, Astron. Astrophys., 109 (1982) 23.
10 J. Cernicharo, C. Kahane, J. Gomez-Gonzalez and M. Guélin, Astron. Astrophys., 164 (1986) L1.
11 J. Cernicharo, M. Guélin, K.M. Menten and C.M. Walmsley, Astron. Astrophys., 181 (1987) L1.
12 R.A. Creswell, G. Winnewisser and M.C.L. Gerry, J. Mol. Spectrosc., 65 (1977) 420.
13 G. Winnewisser, M. Winnewisser and J.J. Christiansen, Astron. Astrophys., 109 (1982) 141.
14 C. Kirby, H.W. Kroto and D.R.M. Walton, J. Mol. Spectrosc., 83 (1980) 261.
15 C.A. Gottlieb, J.M. Vrtilek, E.W. Gottlieb and P. Thaddeus, Astrophys. J., 294 (1985) L55.
16 C.A. Gottlieb, E.W. Gottlieb, P. Thaddeus and H. Kawamura, Astrophys. J., 275 (1983) 916.
17 J.C. Pearson, C.A. Gottlieb, D.R. Woodward and P. Thaddeus, Astron. Astrophys., 189 (1988) L13.
18 M. Kakimoto and T. Kasuya, J. Mol. Spectrosc., 94 (1982) 380.
19 H.L. Buijs and D.A. Ramsay, Astrophys. J., 235 (1980) L115.
20 G. Guelachvili, A.M. Craig and D.A. Ramsay, J. Mol. Spectrosc., 105 (1984) 156.
21 R.K. Khanna, M.A. Perera-Jarmer and M.J. Ospina, Spectrochim. Acta, Part A, 43 (1987) 421.
22 E. Herbst and C.M. Leung, Astrophys. J., Suppl. Ser., 69 (1989) 271.
23 M.J.S. Dewar, G.P. Ford and H.S. Rzepa, Chem. Phys. Lett., 50 (1977) 262.
24 S. Wilson and S. Green, Astrophys. J., 212 (1977) L87.
25 T. Oka, J. Mol. Spectrosc., 72 (1978) 172.
26 S. Green, Astrophys. J., 240 (1980) 962.
27 R.J. Boyd, W.E. Jones and K.W. Ling, Chem. Phys., 58 (1981) 203.
28 W. Kühnel, E. Gey and H.-J. Spangenberg, Z. Phys. Chem., 263 (1982) 641.
29 T.-K. Ha and M.T. Nguyen, Z. Naturforsch., Teil A, 37 (1982) 1272.
30 N.N. Haese, Chem. Phys. Lett., 88 (1982) 166.
31 S. Deguchi and M. Uyemura, Astrophys. J., 285 (1984) 153.
32 T. Koops, T. Visser and W.M.A. Smit, J. Mol. Struct., 125 (1984) 179.
33 M. Uyemura, Bull. Chem. Soc. Jpn., 59 (1986) 1303.
34 J. Yu, S. Zheng and T. Tang, J. Mol. Struct., 149 (1987) 51.
35 N.L. Owen, C.H. Swith and G.A. Williams, J. Mol. Struct., 161 (1987) 33.
36 A. Murakami, K. Kawaguchi and S. Saito, Publ. Astron. Soc. Jpn., 39 (1987) 189.
37 C.A. Deakyne, M. Meot-Ner (Mautner), T.J. Buckley and R. Metz, J. Chem. Phys., 86 (1987) 2334.

38 K. Matsumura, H. Kanamori, K. Kawaguchi, E. Hirota and T. Tanaka, J. Mol. Spectrosc., 131 (1988) 278.

39 L. Dessau and H.J. Spangenberg, Z. Phys. Chem., 269 (1988) 187.

40 D.L. Cooper and S.C. Murphy, Astrophys. J., 333 (1988) 482.

41 D.J. Defrees and A.D. McLean, Chem. Phys. Lett., 158 (1989) 540.

42 L.V. Gurvich, I.V. Veyts and C.B. Alcock, (Eds.) Thermodynamic Properties of Individual Substances, 4th edn., Vol. 2, Hemisphere, New York, 1990.

43 A.A. Westenberg and E.B. Wilson, Jr., J. Am. Chem. Soc., 72 (1950) 199.

44 C.C. Costain, J. Chem. Phys., 29 (1958) 864.

45 J.K. Tyler and J. Sheridan, Trans. Faraday Soc., 59 (1963) 2661.

46 R.L. De Zafra, Astrophys. J., 170 (1971) 165.

47 K. Yamada, R. Schieder, G. Winnewisser and A.W. Mantz, Z. Naturforsch., Teil A, 35 (1980) 690.

48 A.J. Alexander, H.W. Kroto and D.R.M. Walton, J. Mol. Spectrosc., 62 (1976) 175.

49 M. Hutchinson, H.W. Kroto and D.R.M. Walton, J. Mol. Spectrosc., 82 (1980) 394.

50 K.W. Brown, J.W. Nibler, K. Hedberg and L. Hedberg, J. Phys. Chem., 93 (1989) 5679.

51 A.V. Jones, J. Chem. Phys., 20 (1952) 860.

52 G.D. Craine and H.W. Thompson, Trans. Faraday Soc., 49 (1953) 1273.

53 J.H. Callomon and B.P. Stoicheff, Can. J. Phys., 35 (1957) 373.

54 F. Winter, Z. Naturforsch., Teil A, 28 (1973) 1179.

55 J.L. Hardwick and D.A. Ramsay, Chem. Phys. Lett., 48 (1977) 399.

56 J.L. Hardwick, D.A. Ramsay, J.-M. Garneau, J. Lavigne and A. Cabana., J. Mol. Spectrosc., 76 (1979) 492.

57 L. Pasternack and J.R. McDonald, J. Mol. Spectrosc., 108 (1984) 143.

58 M. Tanimoto, K. Kuchitsu and Y. Morino, Bull. Chem. Soc. Jpn., 44 (1971) 386.

59 J.B. Moffat, J. Mol. Struct., 42 (1977) 251.

60 N.N. Haese and R.C. Woods, J. Chem. Phys., 73 (1980) 4521.

61 R.B. Hannan and R.L. Collin, Acta Crystallogr., 6 (1953) 350.

62 S.M. Ferigle, F.F. Cleveland and A.G. Meister, Phys. Rev., 81 (1951) 302.

63 S.M. Ferigle and A. Weber, J. Chem. Phys., 20 (1952) 1657.

64 A.V. Jones, Proc. R. Soc., Ser. A, 211 (1952) 285.

65 F.A. Miller, D.H. Lemmon and R.E. Witkowski, Spectrochim. Acta, 21 (1965) 1709.

66 Yu.N. Panchenko and G.S. Koptev, Vestn. Mosk. Univ., Khim., 1 (1968) 44.

67 P.A. Sipos and M.K. Phibbs, Can. J. Spectrosc., 19 (1974) 159.

68 S. Mohan, Proc. Indian Acad. Sci., Sect. A, 88 (1979) 351.

69 O.V. Novoselova and L.A. Gribov, Izv. Timiryazevsk. Skh. Akad., 6 (1981) 162.

70 Yu.N. Panchenko and L.N. Bazhenova, Vestn. Mosk. Univ., Khim., 23 (1982) 345.

71 O.V. Novoselova and L.A. Gribov, Zh. Prikl. Spektrosk., 40 (1984) 988.

72 B. Mannfors, L.O. Pietila and K. Palmo, J. Mol. Struct., 144 (1986) 287.

73 E. Bjarnov, D.H. Christensen, O.F. Nielsen, E. Augdahl, E. Kloster-Jensen and A. Rogstad, Spectrochim. Acta, Part A, 30 (1974) 1255.

74 F.A. Miller and R.B. Hannan, Jr., J. Chem. Phys., 21 (1953) 110.

75 F.A. Miller, R.B. Hannan and L.R. Cousins, J. Chem. Phys., 23 (1955) 2127.

76 K. Venkateswarlu, M.P. Mathew and V.M. Devi, J. Mol. Struct., 3 (1969) 119.

77 K. Ramaswamy and K. Srinivasan, Aust. J. Chem., 22 (1969) 1123.

78 F.A. Miller and D.H. Lemmon, Spectrochim. Acta, Part A, 23 (1967) 1415.

79 G. Nagarajan and J.R. Durig, Bull. Soc. R. Sci. Liege, 36 (1967) 552.

80 D.V. Malathy, S.Y. Anantarama and K. Venkateswarlu, Bull. Soc. R. Sci. Liege, 37 (1968) 508.

81 G.C. Turrell, W.D. Jones and A. Maki, J. Chem. Phys., 26 (1957) 1544.

82 V.A. Job and G.W. King, Can. J. Chem., 41 (1963) 3132.

83 V.A. Job and G.W. King, J. Mol. Spectrosc., 19 (1966) 155.

84 K. Ramaswamy and K. Srinivasan, Aust. J. Chem., 21 (1968) 575.
85 M. Uyemura and S. Maeda, Bull. Chem. Soc. Jpn., 47 (1974) 2930.
86 P.D. Mallinson and A. Fayt, Mol. Phys., 32 (1976) 473.
87 P. Botschwina, Chem. Phys., 68 (1982) 41.
88 M. Uyemura, S. Deguchi, Y. Nakada and T. Onaka, Bull. Chem. Soc. Jpn., 55 (1982) 384.
89 K. Yamada, R. Best and G. Winnewisser, Z. Naturforsch., Teil A, 38 (1984) 1296.
90 J.S. Hutchinson, J. Chem. Phys., 82 (1985) 22.
91 T.A. Holme and J.S. Hutchinson, Chem. Phys., 93 (1985) 419.
92 K.M.T. Yamada and H. Bürger, Z. Naturforsch., Teil A, 41 (1986) 1021.
93 V.P. Novikov and A.I. Malyshev, Zh. Prikl. Spektrosk., 33 (1980) 545.
94 W.D. Gwinn, J. Chem. Phys., 55 (1971) 477.
95 K. Yamada and G. Winnewisser, Z. Naturforsch., Teil A, 36 (1981) 1052.
96 K.M.T. Yamada and G. Winnewisser, Z. Naturforsch., Teil A, 40 (1985) 476.
97 O.M. Herrera, R.E. Bruns and B.B. Neto, J. Chem. Phys., 90 (1989) 6933.
98 H.-J. Haink and M. Jungen, Chem. Phys. Lett., 61 (1979) 319.
99 K.W. Chang and W.R.M. Graham, J. Mol. Spectrosc., 94 (1982) 69.
100 A. Karpfen and H. Lischka, Chem. Phys., 102 (1986) 91.
101 F.A. Miller and R.B. Hannan, Jr., Spectrochim. Acta, 12 (1958) 321.
102 R.E. Connors, J.L. Roebber and K. Weiss, J. Chem. Phys., 60 (1974) 5011.
103 H.D. McSwiney, Jr. and J.A. Merritt, J. Chem. Phys., 52 (1970) 5184.
104 V.A. Job and G.W. King, J. Mol. Spectrosc., 19 (1966) 178.
105 C. Baker and D.W. Turner, Proc. R. Soc. London, Ser. A, 308 (1968) 19.
106 R.E. Duff and S.H. Bauer, J. Chem. Phys., 36 (1962) 1754.
107 J. Nagarajan, Acta Phys. Polon., 30 (1966) 743.
108 H.-J. Spangenberg, I. Börger and W. Schirmer, Z. Phys. Chem., 255 (1974) 1.
109 J.B. Moffat and A.J. Knowles, J. Chem. Eng. Data, 14 (1969) 215.
110 J.B. Pedley, R.D. Naylor and S.P. Kirby, Thermochemical Data of Organic Compounds, 2nd edn., Chapman and Hall, London, 1986.
111 S.E. Stein and A. Fahr, J. Phys. Chem., 89 (1985) 3714.
112 J.D. Bittner, Ph.D. Thesis, Massachusetts Institute of Technology, Boston, MA, 1981.
113 W. Kühnel, T. Steger, E. Gey and H.J. Spangenberg, Z. Phys. Chem., 259 (1978) 363.
114 M. Cowperthwaite and S.H. Bauer, J. Chem. Phys., 36 (1962) 1743.
115 D.R. Stull, E.F. Westrum and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
116 P.W. Harland, Int. J. Mass Spectrom. Ion Processes, 70 (1986) 231.
117 H. Okabe and V.H. Dibeler, J. Chem. Phys., 59 (1973) 2430.
118 A.M. Wodtke and Y.T. Lee, J. Phys. Chem., 89 (1985) 4744.
119 H.Shiromaru, Y. Achiba, K. Kimura and Y.T. Lee, J. Phys. Chem., 91 (1987) 17.
120 Y. Chen, D.M. Jonas, C.E. Hamilton, P.G. Green, J.L. Kinsey and R.W. Field, Ber. Bunsenges. Phys. Chem., 92 (1988) 329.
121 V.H. Dibeler, R.M. Reese and J.L. Franklin, J. Am. Chem. Soc., 83 (1961) 1813.
122 E.S. Domalski and E.D. Hearing, J. Phys. Chem. Ref. Data, 17 (1988) 1637.
123 J.Y. Chu, T.T. Nguyen and K.D. King, J. Phys. Chem., 86 (1982) 443.