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186. The Electronic Spectra of Unsubstituted Mono- to Penta-acetylene in the Gas Phase and in Solution in the Range 1100 to 4000 Å

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(14. VI. 73)

Summary. The electronic spectra of the title compounds I(n), $n = 1$ to 5, were recorded under standard conditions for quantitative comparison. Spectra of I(1) to I(4) in the gas phase and of I(2) to I(5) in nonpolar solutions are presented in a computer plotted form, and wave length maxima and intensities are listed. Tentative assignments of the medium-intensity, first transition (**A** band) and the ultrahigh-intensity, second transition (**B** band) are given. Finally, spectra of I(2) to I(5) recorded at -150° are presented and discussed (**A** band). The syntheses of I(3) to I(5) are given in detail.

Introduction. – The unsubstituted polyacetylenes (polyynes) $H-(C\equiv C)_n-H$ (I(n)) are among the simplest compounds in organic chemistry. In spite of their interest to experimental as well as to theoretical chemists, only the first two members of the series ($n = 1, 2$) have, until recently, been studied more thoroughly. The extreme instability of the higher homologues ($n > 2$) has strongly hampered their investigation.

We recently reported [1] the preparation and spectral characteristics of pure triacetylene (hexatriyne, I(3)) [2–4], tetraacetylene (octatetrayne, I(4)) [5] [6] and pentaacetylene (decapentayne, I(5)) [5]. They were all isolated as colourless, crystalline solids (in the cold), from which solutions were prepared for various spectroscopic investigations. I(3) and I(4) were also measured in the gas phase. Lately, the photoelectron spectrum of I(3) has been investigated [7]. Furthermore, the infrared, far infrared and *Raman* spectra of I(3) have been recorded and a vibrational analysis of this compound has been published [8]. Finally, the proton magnetic resonance spectra of I(1) to I(4) have been reported [9].

In this paper we want to present the experimental results of an investigation of the electronic spectra of the series I(1) to I(5) as observed in the gas phase and/or in solution in the range of 1100–4000 Å. A low-temperature investigation of the longest wavelength, medium-intensity band of the series, not previously recorded for I(4) and I(5), is further presented. A reinvestigation of acetylene I(1) [10] and diacetylene I(2) [11] has been undertaken in order to compare directly spectral details in the whole series under identical experimental conditions. A preliminary interpretation of some of the electronic transitions is given; a more comprehensive theoretical treatment will appear in a separate paper [12].

After completion of the present work *Eastmond, Johnson & Walton* [13] published the preparation of polyacetylenes I(n) with $4 \leq n \leq 12$. Oxidative coupling of triethylsilyl polyacetylenes to bis(triethylsilyl) polyacetylenes yielded I(n). They report

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λ_{\max} values of the most intense electronic absorption band of the polyacetylenes in methanol or hexane solution. The two λ_{\max} values given for this band in I(4) and the three λ_{\max} values given for I(5), both in hexane solution, agree with our spectra recorded in nonpolar solvents. The additional five maxima at longer wavelength in the spectrum of I(4) measured in methanol solution show a hypsochromic shift of -80 to -20 Å relative to our recordings in a nonpolar solvent (pentane).

The electronic spectra of the more stable, substituted polyynes $R-(C\equiv C)_n-R$ ($R = \text{Me}$; $n = 1$ to 6 [4] [5] [14]), ($R = t\text{-Bu}$; $n = 1$ to 8, 10 [15] [16]), ($R = \text{Ph}$; $n = 1$ to 6, 8 [17] [18]), ($R = \text{aryl}$ [19]) are known.

The influence of the size of alkyl substituents in disubstituted polyynes with 4 or 5 conjugated triple bonds, on the spectroscopic solvent effect has been investigated recently [20].

Results and Discussion. – The electronic spectra in the gas phase of I(1) to I(4) are shown in Fig. 1 and 2 and the spectra of I(4) and I(5) in nonpolar solution are given in Fig. 3. Tab. 1 and 2 contain the λ_{\max} values of I(2) and of I(3) in the gas phase, and Tab. 3 gives the λ_{\max} values of the high-intensity transitions of I(4) in the gas phase and of I(4) to I(5) in solution at room temperature.

As far as the interpretation of the spectra is concerned, we limit ourselves to proposing an assignment. A more thorough discussion of the underlying theory will be the subject of a forthcoming paper [12]. The longest wavelength, medium-intensity

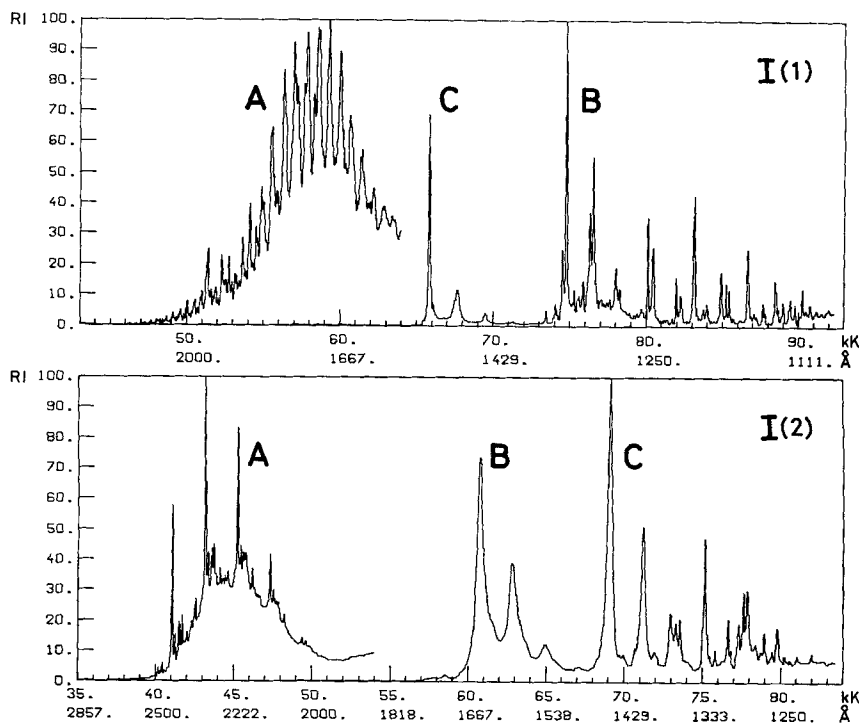


Fig. 1. The electronic spectrum of Acetylene (I(1)) and Diacetylene (I(2)) in the gas phase

bands marked **A** are assigned to the vibrational progressions of two forbidden electronic transitions, ${}^1\Sigma_u^- \leftarrow {}^1\Sigma_g^+$ and ${}^1\Delta_u \leftarrow {}^1\Sigma_g^+$, which overlap each other. This is in agreement with MO calculations [21–24]. A plot of the vibrational maxima of the higher-intensity progression of the two bands as a function of the number *n* of triple bonds in the molecule is shown in Fig. 4. The change in spectral features of the **A** band system as a consequence of lowering the recording temperature from 25 to -150° for solutions of I(2) to I(5) is shown in Fig. 5³⁾. Tab. 4 contains the corresponding λ_{\max} values and the relative intensities (RI.) observed. The low-temperature

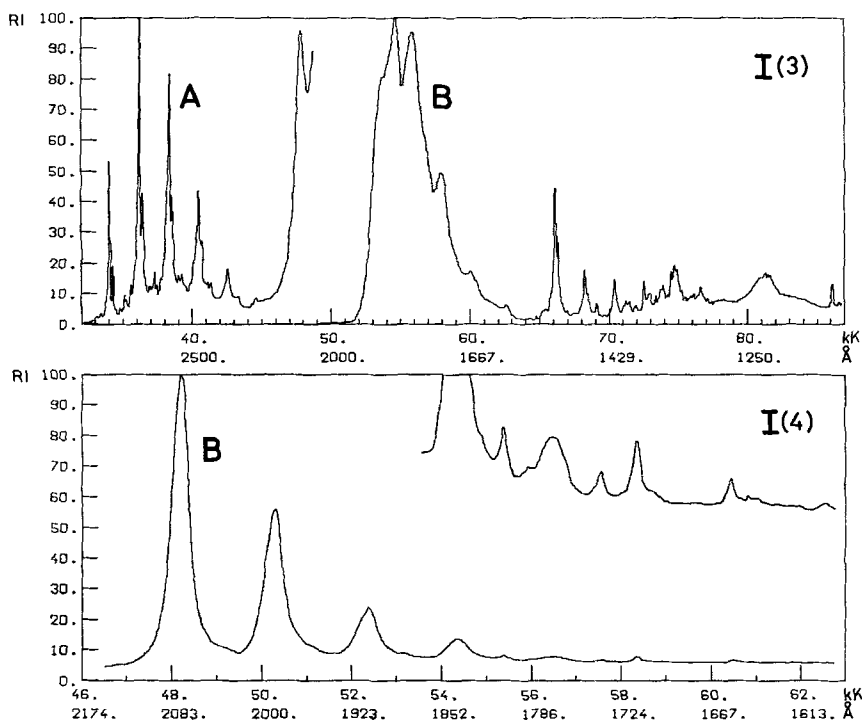


Fig. 2. The electronic spectrum of Triacetylene (I(3)) and Tetraacetylene (I(4)) in the gas phase

spectra are characterized by an overall bathochromic shift, an increased band intensity and a better resolution of the second vibrational progression of lower intensity. The observed changes in band position and intensity can easily be explained by the volume contraction of the solvent, leading to higher concentrations and hence enhanced solvent-solute interaction. Recent investigations [25] revealed that the energy shifts induced by nonpolar solvents on solute molecules are proportional to the density of the solvent. As a matter of fact, the 2,2-dimethylbutane/*n*-pentane solvent mixture used in this investigation contracts on cooling to -150° by an amount corresponding to an increase in density of about one fourth. A similar in-

³⁾ The spectra recorded at -50 , -100 and -120° are omitted in the plot (except for I(5)). Further data are available on request.

Table 1. λ_{\max} values and relative intensities (RI.) of the electronic transitions of I(2) in the gas phase

	λ	RI	kK		λ	RI	kK
1	2757.	0.1	36.27	66	2162.	37.1	46.25
2	2754.	0.1	36.31	67	2157.	30.7	46.36
3	2749.	0.1	36.38	68	2147.	28.3	46.58
4	2726.	0.1	36.68	69	2140.	27.7	46.73
5	2703.	0.4	37.00	70	2120.	26.0	47.17
6	2697.	0.3	37.08	71	2111.	42.4	47.37
7	2692.	0.2	37.15	72	2102.	30.3	47.57
8	2681.	0.2	37.30	73	2098.	27.0	47.66
9	2673.	0.4	37.41	74	2092.	26.1	47.80
10	2670.	0.3	37.45	75	2087.	25.7	47.92
11	2655.	0.5	37.66	76	2074.	22.2	48.22
12	2651.	0.7	37.72	77	2061.	17.1	48.52
13	2645.	0.4	37.81	78	2051.	14.2	48.76
14	2641.	0.5	37.86	79	2032.	12.6	49.21
15	2634.	0.4	37.97	80	2025.	14.4	49.38
16	2619.	0.6	38.18	81	2014.	13.4	49.65
17	2610.	0.6	38.31	82	2007.	11.5	49.83
18	2602.	0.6	38.43	83	2002.	11.1	49.95
19	2595.	0.6	38.54	84	1988.	9.6	50.30
20	2590.	0.5	38.61	85	1977.	8.3	50.58
21	2561.	0.9	39.05	86	1966.	7.5	50.86
22	2558.	0.9	39.09	87	1952.	7.0	51.23
23	2535.	0.8	39.45	88	1973.	7.1	51.63
24	2527.	1.0	39.57	89	1911.	7.3	52.33
25	2515.	1.5	39.76	90	1898.	8.3	52.69
26	2509.	1.6	39.86	91	1897.	8.3	52.71
27	2501.	1.7	39.98	92	1884.	8.5	53.08
28	2487.	4.7	40.21	93	1868.	9.0	53.53
29	2478.	3.3	40.36	94	1853.	9.5	53.97
30	2471.	6.2	40.47	95	1738.	1.2	57.54
31	2461.	3.3	40.63	96	1728.	1.5	57.87
32	2452.	3.9	40.78	97	1709.	2.3	58.51
33	2448.	4.5	40.85	98	1645.	73.9	60.79
34	2441.	10.8	40.97	99	1623.	19.2	61.61
35	2434.	58.0	41.08	100	1592.	39.3	62.81
36	2423.	15.9	41.27	101	1570.	13.9	63.69
37	2409.	19.8	41.51	102	1540.	12.3	64.94
38	2405.	18.8	41.58	103	1522.	6.6	65.70
39	2396.	21.8	41.74	104	1491.	5.2	67.07
40	2391.	12.9	41.82	105	1446.	100.0	69.16
41	2378.	16.1	42.05	106	1429.	9.1	69.98
42	2365.	17.7	42.28	107	1414.	11.4	70.72
43	2361.	20.0	42.35	108	1404.	51.4	71.23
44	2353.	21.1	42.50	109	1390.	10.0	71.94
45	2348.	27.2	42.59	110	1370.	23.1	72.99
46	2328.	26.7	42.96	111	1363.	19.8	73.37
47	2314.	100.0	43.22	112	1358.	20.9	73.64
48	2305.	42.5	43.38	113	1350.	6.8	74.07
49	2294.	41.4	43.59	114	1330.	47.5	75.19
50	2290.	44.0	43.67	115	1319.	10.7	75.82
51	2285.	45.4	43.76	116	1311.	7.3	76.28
52	2278.	35.0	43.90	117	1305.	21.0	76.63
53	2264.	37.4	44.17	118	1302.	10.6	76.80
54	2258.	33.0	44.29	119	1293.	19.6	77.34
55	2255.	33.7	44.35	120	1289.	14.7	77.58
56	2248.	34.6	44.48	121	1287.	29.7	77.70
57	2241.	35.0	44.62	122	1283.	30.7	77.94
58	2238.	36.3	44.68	123	1275.	12.6	78.43
59	2216.	36.6	45.13	124	1269.	10.2	78.80
60	2207.	83.4	45.31	125	1266.	16.7	78.99
61	2198.	44.8	45.50	126	1257.	10.4	79.55
62	2191.	42.2	45.64	127	1252.	18.2	79.87
63	2187.	41.6	45.72	128	1245.	8.8	80.32
64	2184.	42.1	45.79	129	1233.	8.7	81.10
65	2177.	37.0	45.93	130	1219.	9.5	82.03

Table 2. λ_{\max} values and relative intensities (RI.) of the electronic transitions of I(3) in the gas phase

	\AA	RI	kK		\AA	RI	kK
1	3017.	2.8	33.15	57	1464.	18.2	68.31
2	2988.	3.8	33.47	58	1459.	10.4	68.54
3	2933.	53.4	34.09	59	1453.	4.0	68.82
4	2914.	19.3	34.32	60	1446.	7.0	69.16
5	2899.	5.0	34.49	61	1444.	4.2	69.25
6	2874.	5.6	34.79	62	1441.	3.1	69.40
7	2857.	5.2	35.00	63	1436.	2.8	69.64
8	2843.	9.9	35.17	64	1433.	2.9	69.78
9	2833.	8.2	35.30	65	1425.	4.0	70.18
10	2808.	12.8	35.61	66	1419.	14.9	70.47
11	2758.	100.0	36.26	67	1417.	10.0	70.57
12	2742.	42.7	36.47	68	1413.	5.1	70.77
13	2732.	15.2	36.60	69	1406.	6.2	71.12
14	2708.	12.2	36.93	70	1402.	7.1	71.33
15	2682.	17.1	37.29	71	1398.	7.5	71.53
16	2670.	12.9	37.45	72	1392.	5.3	71.84
17	2659.	11.1	37.61	73	1390.	6.2	71.94
18	2649.	15.2	37.75	74	1378.	14.3	72.57
19	2606.	82.0	38.37	75	1370.	10.4	72.99
20	2592.	42.4	38.58	76	1362.	9.5	73.42
21	2580.	18.3	38.76	77	1358.	8.6	73.64
22	2562.	16.1	39.03	78	1356.	11.4	73.75
23	2543.	13.7	39.32	79	1354.	11.2	73.86
24	2508.	13.3	39.87	80	1352.	12.7	73.96
25	2480.	30.5	40.32	81	1346.	9.7	74.29
26	2469.	43.8	40.50	82	1342.	17.7	74.52
27	2457.	27.4	40.70	83	1337.	19.5	74.79
28	2445.	13.7	40.90	84	1334.	18.1	74.96
29	2432.	13.7	41.12	85	1328.	11.0	75.30
30	2417.	13.5	41.37	86	1324.	9.1	75.53
31	2349.	18.5	42.57	87	1321.	8.2	75.70
32	2305.	9.3	43.38	88	1319.	8.5	75.82
33	2237.	8.7	44.70	89	1317.	9.5	75.93
34	2092.	0.4	47.80	90	1313.	10.2	76.16
35	2030.	0.5	49.26	91	1308.	9.6	76.45
36	2013.	0.6	49.68	92	1305.	12.5	76.63
37	1996.	0.7	50.10	93	1300.	10.6	76.92
38	1863.	80.9	53.68	94	1296.	8.4	77.16
39	1850.	85.1	54.05	95	1291.	7.4	77.46
40	1831.	100.0	54.61	96	1288.	7.7	77.64
41	1793.	95.4	55.77	97	1285.	7.9	77.82
42	1761.	61.0	56.79	98	1277.	8.2	78.31
43	1727.	49.5	57.90	99	1261.	7.8	79.30
44	1665.	17.3	60.06	100	1238.	14.3	80.78
45	1596.	6.3	62.66	101	1236.	15.3	80.91
46	1543.	2.8	64.81	102	1234.	15.6	81.04
47	1533.	4.4	65.23	103	1229.	17.0	81.37
48	1528.	4.9	65.45	104	1226.	16.7	81.57
49	1512.	45.0	66.14	105	1224.	16.4	81.70
50	1507.	26.8	66.36	106	1221.	14.6	81.90
51	1500.	7.1	66.67	107	1215.	11.4	82.30
52	1493.	4.4	66.98	108	1211.	10.1	82.58
53	1490.	3.2	67.11	109	1195.	8.1	83.68
54	1484.	3.4	67.39	110	1160.	13.5	86.21
55	1480.	3.5	67.57	111	1154.	7.4	86.66
56	1470.	6.1	68.03				

crease in the peak heights of the fine structured **A** band is reflected in the spectra of I(2) to I(5), given in Fig. 5.

The next, *ca.* 10^3 times more intense band marked **B**, is attributed to the ${}^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transition. In the case of diacetylene, the third band **C** of similar oscillator strength as **B**, is associated with the first ${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition. In acetylene the **C**

Table 3. λ_{\max} values and relative intensities (RI.) of the high-intensity electronic transitions of I(4) in the gas phase, and of the medium-intensity transition (B band) of I(4) and I(5) in solutions of n-pentane at 25°

I(4) gas phase				I(4) solution			
	\AA	RI	kK		\AA	RI	kK
1	2073.	100.0	48.24	1	2256.	99.4	44.33
2	2040.	9.8	49.02	2	2154.	71.2	46.42
3	1987.	56.2	50.33	3	2060.	31.5	48.54
4	1955.	8.2	51.15	4	1974.	16.0	50.66
5	1908.	24.1	52.41				
6	1882.	8.8	53.13				
7	1872.	7.7	53.42				
8	1841.	13.9	54.32				
9	1806.	8.3	55.37				
10	1788.	7.1	55.93				
11	1771.	8.0	56.47				
12	1738.	6.9	57.54				
13	1714.	7.9	58.34				
14	1701.	6.2	58.79				
15	1677.	5.9	59.63				
16	1654.	6.7	60.46				
17	1643.	6.2	60.86				
18	1612.	5.8	62.03				
19	1597.	5.9	62.62				

I(5) solution			
	\AA	RI	kK
1	2513.	100.0	39.79
2	2442.	13.1	40.95
3	2387.	74.6	41.90
4	2277.	30.8	43.92
5	2173.	10.6	46.03
6	2110.	3.3	47.38

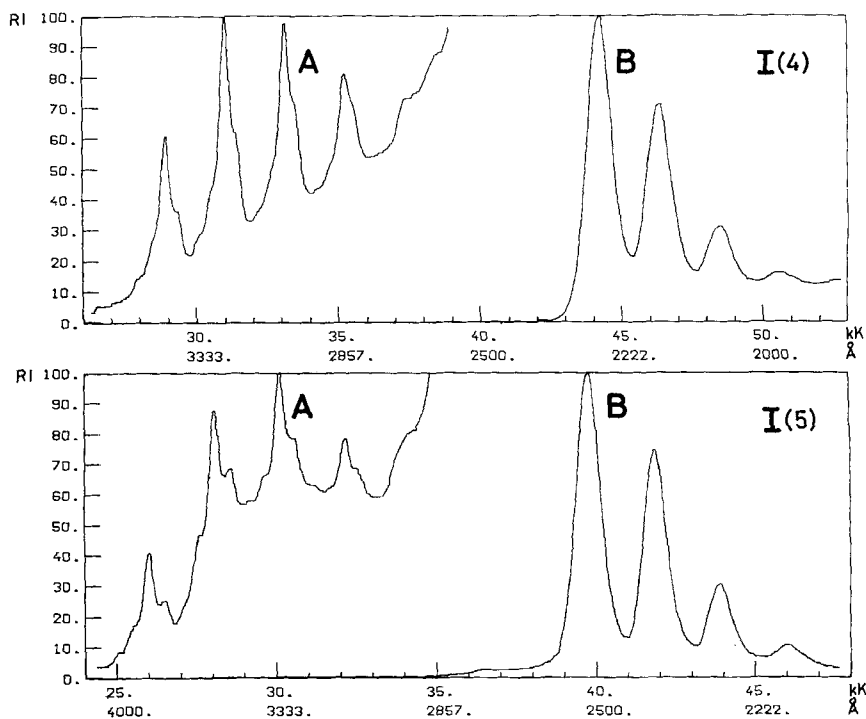


Fig. 3. The electronic spectrum of Tetraacetylene (I(4)) and Pentaacetylene (I(5)) in n-pentane solution at 25°

band is situated between the **A** and **B** bands [10]. In Fig. 6 the transition energies of the **A**, **B**, and **C** band maxima of I(1) to I(5), measured in the gas phase, are plotted against the number of triple bonds in the molecule. The first ionization potentials of I(1) to I(3) included in the plot have been taken from the photoelectron spectra [7]. The approximately parallel trend of these relations strongly supports the above assignment.

Due to the lack of a gas spectrum of I(5) and of the longest wavelength band of I(4), the transition energies of the **A** bands in these two compounds are those taken

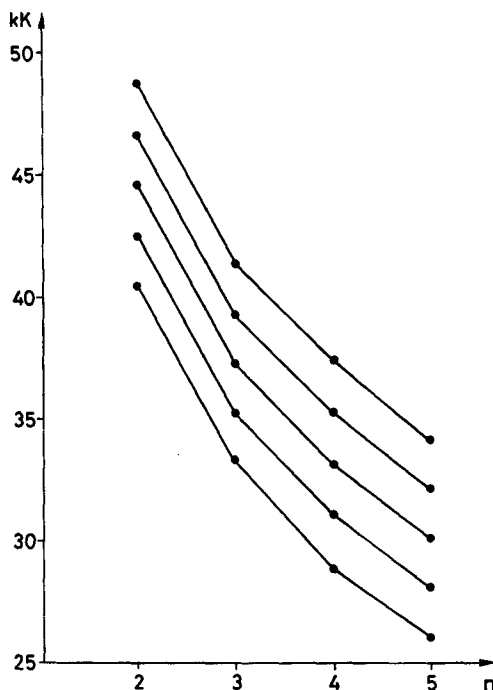


Fig. 4. Vibrational maxima of the higher-intensity progression of the **A** band in I(2) to I(5) as a function of n , the number of triple bonds. Solutions in n -pentane at 25°

from the spectra in solution, corrected by an increment of 700 cm^{-1} . This shift is in accordance with the solvent shifts of the **A** bands in I(2) and in I(3), which are 600 and 700 cm^{-1} , respectively.

The far greater shift of the **B** band in I(5) of *ca.* 4090 cm^{-1} is explained by means of a theoretical model presented recently [25]. According to this model the energy shift $\delta\nu$ induced by the solvent can be calculated for an electronic transition in the following way:

$$\delta\nu = \nu(\text{gas}) - \nu(\text{solvent}) = \text{const.} - \frac{\mu^2}{\nu_s - \nu(\text{gas})} \quad (1)$$

where μ is the transition moment, ν the frequency of the transition and ν_s the frequency of the first strong absorption of the solvent. The constant contains geometrical

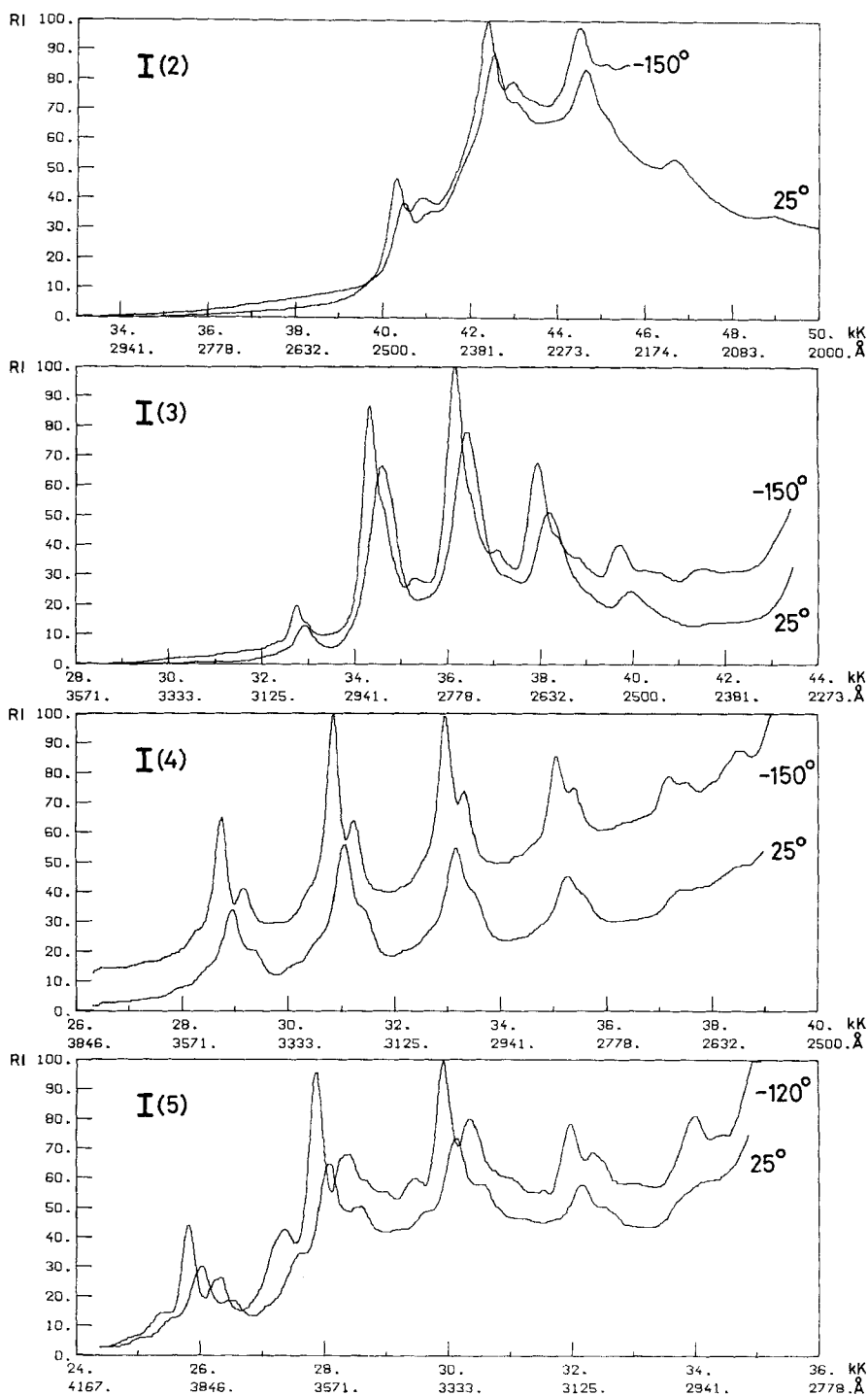


Fig. 5. Vibrational fine structure of the A band of I(2) to I(4) in solutions of 2,2-dimethylbutane/n-pentane 8:3 at 25 and -150° and of I(5) in solution of n-pentane at 25 and -120° (see footnote³))

Table 4. λ_{\max} values and relative intensities (RI) of the electronic transitions of the A band of I(2) to I(4) in solutions of 2,2-dimethylbutane n-pentane 8:3 at 25 and -150° and of I(5) in n-pentane solution at 25 and -120°

<u>25°</u>				<u>-150°</u>			
	λ	RI	kK		λ	RI	kK
I(2)	1 2471.	38.8	40.46	1 2481.	46.8	40.30	
	2 2350.	88.9	42.56	2 2444.	40.3	40.91	
	3 2323.	72.5	43.06	3 2357.	100.0	42.42	
	4 2241.	83.8	44.63	4 2352.	90.3	42.51	
	5 2141.	54.0	46.70	5 2327.	79.7	42.96	
	6 2040.	34.6	49.03	6 2305.	73.4	43.38	
	7 2015.	31.8	49.63	7 2246.	98.0	44.53	
				8 2216.	85.6	45.13	
I(3)	1 3034.	13.1	32.96	1 3203.	4.0	31.22	
	2 2890.	66.9	34.60	2 3052.	20.0	32.76	
	3 2744.	78.2	36.44	3 2913.	86.8	34.33	
	4 2616.	51.1	38.22	4 2831.	29.1	35.32	
	5 2502.	24.7	39.96	5 2765.	100.0	36.17	
				6 2696.	38.3	37.09	
				7 2635.	68.0	37.96	
				8 2575.	35.9	38.83	
				9 2516.	40.6	39.75	
				10 2484.	31.9	40.26	
				11 2463.	30.9	40.59	
				12 2406.	32.5	41.56	
I(4)	1 3451.	34.2	28.98	1 3773.	14.9	26.50	
	2 3402.	20.4	29.40	2 3538.	27.4	28.26	
	3 3369.	12.6	29.68	3 3478.	65.3	28.75	
	4 3217.	56.1	31.08	4 3430.	41.4	29.15	
	5 3014.	55.0	33.18	5 3240.	100.0	30.86	
	6 2835.	45.5	35.27	6 3202.	64.2	31.23	
				7 3035.	99.1	32.95	
				8 3001.	74.1	33.32	
				9 2919.	51.9	34.26	
				10 2850.	85.3	35.09	
				11 2825.	75.4	35.40	
				12 2753.	63.6	36.32	
				13 2690.	79.1	37.17	
				14 2664.	77.1	37.54	
				15 2597.	87.7	38.51	
I(5)	1 3840.	30.3	26.04	1 3928.	14.9	25.46	
	2 3766.	18.6	26.56	2 3871.	44.4	25.83	
	3 3560.	64.9	28.09	3 3796.	26.8	26.34	
	4 3524.	49.0	28.38	4 3653.	43.1	27.37	
	5 3497.	50.7	28.59	5 3631.	38.3	27.54	
	6 3315.	73.4	30.16	6 3585.	95.9	27.89	
	7 3267.	57.7	30.61	7 3518.	67.9	28.43	
	8 3223.	46.7	31.03	8 3485.	59.1	28.69	
	9 3208.	46.5	31.17	9 3447.	55.5	29.01	
	10 3200.	46.2	31.25	10 3390.	60.2	29.50	
	11 3179.	45.1	31.46	11 3342.	100.0	29.92	
	12 3108.	57.9	32.18	12 3297.	80.3	30.33	
	13 3074.	50.5	32.53	13 3252.	62.7	30.75	
	14 3041.	44.5	32.89	14 3222.	60.2	31.04	
	15 3029.	43.8	33.01	15 3167.	55.9	31.58	
				16 3124.	78.5	32.01	
				17 3091.	68.8	32.35	
				18 3035.	58.6	32.95	
				19 2938.	81.2	34.04	
				20 2904.	75.1	34.44	

factors characteristic for the absorbing molecules as well as specific parameters for the solvent. If the polarizability α of the solute molecules is expressed in terms of the transition moment μ and if α is considered to be proportional to the solute particle volume, *i.e.* $\mu^2 = c\alpha = c'n$ (where n is the number of triple bonds and c and c' are constants), then eq. (1) gives:

$$\nu(\text{gas}) - \nu(\text{solvent}) = C \frac{n}{\nu_s - \nu(\text{gas})}. \quad (2)$$

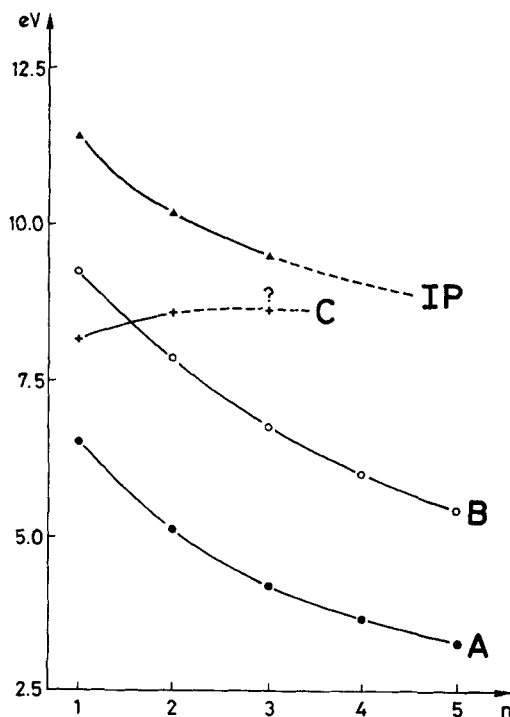


Fig. 6. The **A**, **B** and **C** band maxima of $I(n)$ in the gas phase and the ionization potentials (**IP**.) of $I(n)$ as a function of the number n of triple bonds. Concerning the corrections for solvent shifts in the case of $I(4)$ and $I(5)$ see text

The constant C can be determined from the electronic spectrum of tetraacetylene, since $I(4)$ has been measured both in the gas phase and in solution. Thus

$$C = \frac{1}{n} (\nu_4(\text{gas}) - \nu_4(\text{solvent})) (\nu_s - \nu_4(\text{gas})) \quad (3)$$

If one uses for ν_4 the first vibrational maximum of the **B**-band and sets ν_s equal to 73 kK (authors' measurement for pentane), then $C = 24.9 \text{ kK}^2$.

The shift of the **B**-band of $I(5)$ can hence be determined by solving the following quadratic equation:

$$\nu_5(\text{gas}) - \nu_5(\text{solvent}) = C \frac{5}{\nu_s - \nu_5(\text{gas})} \quad (4)$$

which gives $\nu_5(\text{gas}) = 43.9 \text{ kK}$.

As recently reported by *Jungen* [10] two new *Rydberg* series have been assigned in the electronic spectrum of acetylene. Thus the following four series are now known for I(1), T_n being the energy of the n 'th term in kK:

$$T_n = 91.95 - R/(n - 0.06)^2 \quad n = 3 \dots 10 \dots$$

$$T'_n = 91.95 - R/(n - 0.47)^2 \quad n = 3 \dots 10 \dots$$

$$T''_n = 91.95 - R/(n + 0.08)^2 \quad n = 3 \dots 6 \dots$$

$$T'''_n = 91.95 - R/(n - 0.51)^2 \quad n = 3, 4 \dots$$

The same author gave a revised assignment of the *Rydberg* series of diacetylene on the basis of the spectra of I(1) to I(3), *i.e.* for I(2):

$$T_n = 82.11 - R/(n - 1.0)^2 \quad n = 4, 5, 6 \dots$$

$$T'_n = 82.11 - R/(n - 0.5)^2 \quad n = 3, 4, 5 \dots$$

In the spectrum of triacetylene only one *Rydberg* series could be identified although other features in the spectrum seem to indicate the presence of two closely overlapping series. Thus for I(3):

$$T_n = 76.71 - R/(n - 0.81)^2 \quad n = 4, 5, 6 \dots$$

Experimental Part

General remarks. – All glass-ware was fitted with high vacuum stop cocks and greased with *Dow Corning* High Vacuum Silicon lubricant. Uvasol grade of solvents (*Merck*) was used and column chromatography was accomplished on alumina (*Woelm*, activity II). Samples of the polyacetylenes were manipulated in soft daylight and were measured immediately after preparation.

Preparation of $H-(C\equiv C)_n-H$ (I(n)) $n=2$ to 5). – *Acetylene* (I(1)) was taken from a *Matheson & Co.* (N. Y.) lecture bottle. *Diacetylene* (butadiyne), (I(2)) was prepared from 1,4-dichloro-2-butyne by the action of aqueous KOH as described [26]. Bulb-to-bulb distillation on a vacuum line yielded MS. pure diacetylene (I(2)).

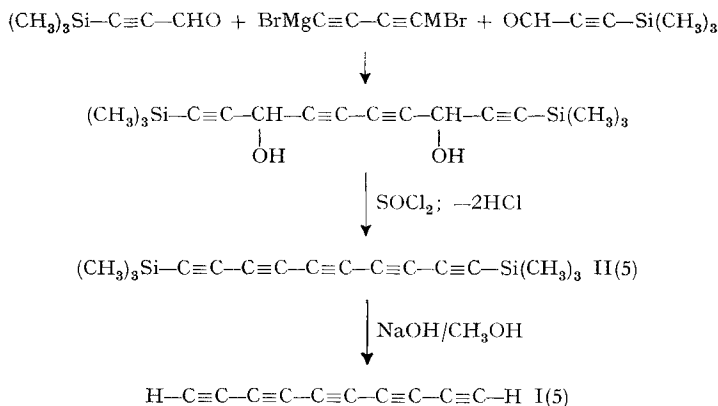
Triacetylene (hexatriyne, I(3), [2]–[4]) was synthesized on a 100 mg scale by treatment of 1,6-dichloro-2,4-hexadiyne [5] with solid KOH according to [3]. Bulb-to-Bulb distillation on a vacuum line at *ca.* $-50^\circ/0.01$ Torr yielded MS. pure triacetylene as a colourless solid in the cold. The use of *n*-pentane as a solvent, instead of ether as described [3], was essential to obtaining triacetylene free of solvent, and also of an accompanying compound which exhibited $m/e = 110$, 112, *i.e.* corresponding to $H_2C=C=C=C=CHCl$, produced by elimination of 1 equiv. HCl from the starting material (*cf.* $H_2C=C=C=CHCl$ formed by the action of KOH on $ClH_2C-C\equiv C-CH_2Cl$ [27]). **Warning:** At room temperature and even under exclusion of air triacetylene is turning black after a few minutes and is known to explode violently [4].

Tetraacetylene (octatetrayne, I(4) [5] [6] [13]). Oxidative coupling of trimethylsilylbutadiyne, prepared according to [28], with $Cu(Ac)_2/Cu_2Cl_2$ in CH_3OH/H_2O /pyridine as described [29] yielded the air and light sensitive 1,8-bis(trimethylsilyl)octatetrayne (II(4)), m. p. $94.0-94.2^\circ$ [30]. – λ_{max} : 371, 344.6, 321.6, 301.6 nm (*n*-pentane: 2,2-dimethylbutane 3:8); 254, 241.2, 229.8, 219.2 nm (cyclohexane). – IR. spectrum, see [1]. – Desilylation of II(4) and isolation of I(4) were performed as follows: To resublimed II(4) (12 mg) in pentane (2 ml) was added 5% NaOH in MeOH (0.5 ml). Shaking and acidification with 10% H_2SO_4 were carried out quickly (within 10 s), and the aqueous phase was removed. The organic layer was washed with distilled water until neutral (3 times) and chromatographed on alumina (neutral, 10×1 cm). Elution with *n*-pentane or *n*-hexane (fractions of 4 ml) was followed by UV. spectroscopy. The main fraction of tetraacetylene (I(4)) was concentrated at $-60^\circ/0.001$ Torr and rechromatographed. The purity of the eluates of I(4) was checked by their UV. absorption in the range 400–200 nm, including the 10^{-2} to 10^{-3} weaker,

longest wavelength band, which remained unchanged after a third chromatography of a small sample. Removal of solvent to completion in the cold yielded solid, colourless I(4).

For preparation of samples in solution and in the gas phase, see Instrumental.

Pentaacetylene (decapentayne, I(5) [5] [13]) was synthesized according to the following reaction scheme:



To diacetylene (0.50 g, 0.010 mol) in dry tetrahydrofuran (7 ml) ethylmagnesiumbromide (from 0.48 g Mg, 0.020 mol) in tetrahydrofuran (15 ml) was added dropwise under stirring at 0° in an atmosphere of nitrogen. After stirring at room temperature for another 20 min trimethylsilylpropionaldehyde [31] (2.62 g, 0.020 mol) in tetrahydrofuran (3 ml) was added dropwise, and stirring was continued for 3 h. Hydrolysis was accomplished by saturated aqueous ammonium chloride (3.5 ml), and the organic phase was filtered through alumina (acid, 9 g). Volatiles were removed *in vacuo*, and the dark residue was extracted with benzene/petrolether 1:4 (10 ml) and filtered again through alumina (9 g). The brown filtrate was extracted with MeOH/H₂O 7:3 (10 × 5 ml) and the combined extracts were shaken with benzene/petrolether 1:4 (10 ml). An equal volume of water was added, whereby a yellowish oil precipitated, which was extracted with ether (6 ×) and dried over sodium sulfate. After removal of the solvent *in vacuo*, the oily residue was extracted with pentane (6 ×⁴). By concentration of the first pentane extract *in vacuo* a slightly coloured crystalline solid of 1,10-bis(trimethylsilyl)-1,4,6,9-decatetrayne-3,8-diol precipitated on cooling, m.p. 118–119°. Second band: λ_{max} (in MeOH): 259.5, 246, 234, 222 (sh) nm. One third of the partly oily residue (total yield 1.0 g) was dissolved in ether (3 ml) after removal of pentane and thionyl chloride (0.6 ml) was added at 0°. Stirring under nitrogen was continued for 3 h at room temp. Volatiles were removed sharply *in vacuo*, and the residue dissolved in ether/pentane 1:1 (2 ml). Its chromatography on alumina (neutral 10 × 1 cm) with pentane was followed by UV. spectroscopy of the eluates. The main fractions was concentrated *in vacuo* and rechromatographed. Eluates in pentane yielded pure 1,10-bis(trimethylsilyl)-decapentayne II(5), as characterized by its UV. absorption in the range 400–200 nm. Second band: 274.3, 259.8, 247.1, 235.2, 224.9 nm (*n*-pentane).

Obviously, chlorination of the diol and complete dehydrochlorination to II(5) occurred in one reaction step. This was shown in a separate test, in which treatment of the isolated chlorination product with LiNH₂ in ether, neutralization with NH₄Cl and chromatography gave an unchanged UV. spectrum. A similar behaviour of 2,5,7,10-dodecatetrayne-4,9-diol towards SOCl₂ under formation of 2,4,6,8,10-dodecapentayne was reported previously [20].

Desilylation of II(5) by alkaline hydrolysis, and isolation of the product by chromatography, as described above for I(4), yielded pure pentaacetylene (I(5)). By removal of the solvent at –60°/0.001 Torr solid, colourless I(5) was isolated.

Preparation of samples in solution for recording of the electronic spectra is given below.

⁴) For the working-up procedure of a similar diol, see [16].

Instrumental. – For product characterization the electronic spectra of samples in solution were scanned on a *Unicam* SP 800 D spectrophotometer.

The spectra in the gas phase were recorded in the range 3000 to 1050 Å on a *McPherson* 225 Spectrometer fitted with a double beam attachment (model 665). Samples of I(1) to I(4) were vacuum transferred into 10 cm stainless steel cells fitted with lithium fluoride windows.

Solutions of I(2) to I(5) were recorded on a *Cary* 14 Recording Spectrometer from 4000 to 1900 Å. Below 2200 Å the cell compartment was flushed with nitrogen. At room temperature the spectra were run in solutions of *n*-pentane using matched 0.1 mm quartz cells of the type used in the *McPherson* spectrometer. Low temperature recordings of I(2) to I(5) were carried out in solutions of 2,2-dimethylbutane/*n*-pentane 8:3, using 10 mm quartz cells cooled by a stream of nitrogen in a homebuilt low temperature equipment. The solutions were prepared on a vacuum line (0.001 Torr). The eluates of the polyacetylene were concentrated to dryness at -60° , and the cooled solvent mixture was evaporated into the colourless solid polyacetylene, which was cooled at -180° . The solution of a sample was recorded at intervals of ca. 50° from room temp. down to -150° . Due to the low vapour pressure of solid I(4), recording of the low-intensity, longest-wave length band in the gas phase was not possible. When the temperature of a cooled sample of dry tetraacetylene was allowed to raise to about room temperature, the vapour pressure being ca. 0.1 Torr, about 80% of the compound decomposed within 10 min, leaving behind carbonized material. The vapour pressure of I(5) was too low to allow any recording in the gas phase, so that pentaacetylene was run in solution only. Multiple scans over the whole range during the gas phase recordings gave no indication of photoproducts from the irradiation.

Due to the instability of the polyacetylenes exact weighing of the samples could not be performed. Therefore, only rough estimates of the relative band intensities are given, and the intensity of each λ_{\max} in a band is given in percent of the most intense maximum within a given band.

The recorded spectra were digitalized and stored on a paper tape. Recalculation of the spectra in terms of wave numbers, including corrections due to the base line of the spectrometer were effected on a *PDP-9* computer. The final spectra were plotted by a *Calcomp* 565 plotter. The characteristic data for the absorption maxima were determined by the computer program from the raw data.

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187. Einsatz von Hochleistungs-Trennkapillaren in der GC.-EIMS./GC.-CIMS.-Analyse: Eine Möglichkeit zur massenspektrometrischen Doppelbindungscharakterisierung in komplexen Monoalkengemischen

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(17. IV. 74)

Summary. In an attempt to determine *position* and *substitution of double bonds* in complex mixtures of straight-chain and branched *monoalkenes* without actually isolating the constituents, GC.-MS. analysis is performed after in-batch preparation of derivatives of a judiciously chosen type. Cyclic *phenylboronates* (4,5-substituted 2-phenyl-1,3,2-dioxaborols) are prepared from 1,2-diols which are, in turn, obtained from the original alkenes by treatment with osmium tetroxide. *Chemical ionization mass spectrometry* (CIMS.) is used in addition to conventional *electron impact* techniques (EIMS.) in sequential GC./CIMS.- and GC./EIMS.runs, yielding complementary structural information for the single components of the mixture. In order to cope with the potential severity of the separation problem, high-efficiency glass capillary columns were employed throughout. The performance of the system used is demonstrated by a complete double bond analysis of a 35-component mixture of monoalkenes in the C_5 to C_9 range.

Die vollständige Strukturermittlung offenkettiger Alkene auf rein massenspektrometrischem Weg gehört keineswegs in den Bereich des Trivialen und der Routine. Besonders in verzweigten Verbindungen dieser Stoffklasse lassen sich selbst bei Anwesenheit von nur einer Doppelbindung die verschiedenen Bestimmungsgrößen wie *Molekulargewicht* (Anzahl von Doppelbindungen), *Lage der Doppelbindung* und *räumliche Anordnung ihrer Substituenten* (Stellungs- und *cis/trans*-Isomerie), sowie *Art, Ort und Anzahl von Verzweigungen der Kette* (Kettenisomerie) meist nicht gleichzeitig an der unveränderten Molekel oder auch nur einem einzigen speziell angefertigten Derivat mittels nur einer Technik bestimmen.

Bestimmung der Doppelbindungs-lage und Molekelgrösse in Reinstoffen. – Infolge der geringen bruchinduzierenden Wirkung einer ionisierten Doppelbindung lässt sich deren Lage in einer längeren aliphatischen Kette aus dem Massenspektrum der unveränderten Molekel nur schwer, wenn überhaupt, erkennen. Rasche mehrfache H-Verschiebung wird zur vorherrschenden Konkurrenzreaktion des gewünschten glatten Bruchs und bewirkt Wanderung der Doppelbindung über grössere mole-