

The vibrational spectra of 2,4-hexadiyne (dimethyldiacetylene), 2,4-hexadiyne- d_6 and 2,4-hexadiyne-1,1,1- d_3

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Abstract—Infrared and Raman spectra in the region 5000–20 cm^{-1} were recorded for solutions and crystalline solids at 90 K of 2,4-hexadiyne, 2,4-hexadiyne- d_6 and 2,4-hexadiyne-1,1,1- d_3 . Semiquantitative Raman polarization data were obtained. The fundamental frequencies were assigned according to D_{3d} (C_{3v}) symmetry in good agreement with the results from a normal coordinate analysis.

INTRODUCTION

We have been interested in the physical properties of acetylenes for a long time. In connection with a photoelectron investigation [1] it was decided to re-investigate the vibrational spectra of 2,4-hexadiyne (dimethyldiacetylene, later to be called DMDA). DMDA has been subjected to several investigations by physical methods. Vibrational spectra [2–5] and normal coordinate analyses [6–8] have been reported. The molecular structure has been determined by electron diffraction [9] and by X-ray crystallography [10] (monoclinic, space group $C2/m$). In the present paper the vibrational spectra of DMDA, of the new compounds DMDA- d_6 and DMDA-1,1,1- d_3 (later to be called DMDA- d_3) and the results from a normal coordinate analysis are presented.

EXPERIMENTAL

The sample of DMDA was a commercial product from K & K Rare and Fine Chemicals. Preparation of DMDA- d_6 and DMDA- d_3 has been described elsewhere [1]. The isotopic purities of DMDA- d_6 and DMDA- d_3 , checked by mass spectrometry, were ca. 93 and 97%, respectively.

Infrared spectra of DMDA in various solvents and as a crystalline solid at 90 K were recorded on a Perkin-Elmer model 225 spectrometer (5000–200 cm^{-1}) and with a Bruker IFS-114C Fourier transform spectrometer (4000–20 cm^{-1}). The Raman spectra of solutions (including semiquantitative polarization measurements) and of the solid at 90 K were recorded on a Cary 81 spectrometer, modified for perpendicular illumination. The 5145 and 4880 Å lines of a CRL 52G argon ion laser were used for excitation.

RESULTS

DMDA possesses free rotation around the molecular axis [5]. Hence, the wavefunctions are to be classified according to the double group G_{36}^+ [11]. Since the vapour phase spectra of DMDA will not be discussed in this paper, the subgroup D_{3d} of G_{36}^+ will be used for classifying the vibrational modes. The selection rules according to G_{36}^+ symmetry are less restrictive than for D_{3d} symmetry: e_u and e_g modes may be observed in both i.r. and Raman, but the e_g modes will generally be weak in the i.r. spectra and the e_u modes very weak in the Raman spectra. According to D_{3d} symmetry, the 30

fundamental modes of vibration divide into: $\Gamma = 5a_{1g} + 1a_{1u} + 4a_{2u} + 5e_u + 5e_g$. For DMDA- d_3 , the vibrational modes have been assigned according to C_{3v} symmetry: $\Gamma = 9a_1 + 1a_2 + 10e$.

With a monoclinic ($C2/m$) crystal structure and only one molecule in the primitive unit cell, the factor group and the site group (C_{2h}) are isomorphic. Hence, only the e modes will show correlation splitting in the crystal spectra. Further, the torsional mode, ν_6 (a_{2g}), which is inactive for the “free” molecule, becomes Raman active in the crystal. Finally, only three librations corresponding to rotations of the molecule (all Raman active and i.r. inactive) are expected in the crystal spectra.

Various i.r. and Raman spectra of DMDA have been reported earlier [2–5]. In view of the improved technique, the i.r. spectra of DMDA in solutions and as a crystalline solid at ca. 90 K are shown in Figs 1 and 2, respectively, while the Raman spectrum of DMDA as a crystalline solid at ca. 90 K is given in Fig. 3. For DMDA- d_6 and DMDA- d_3 , the analogous spectra are presented in Figs 4–6 and Figs 7–9. The spectral data are collected in Tables 1–3 for DMDA, DMDA- d_6 and DMDA- d_3 , respectively, whereas the assigned fundamentals are given in Table 4.

Spectral assignments in DMDA

Our Raman spectra of DMDA are practically identical to that of FERIGLE *et al.* [4], but our i.r. spectra are much more detailed than those published before [2–4]. The present assignments for DMDA (Table 1) are, with a few exceptions, identical to those proposed earlier [4, 5] and will only be briefly discussed.

The ν_{11} (e_u) mode (CH stretching), previously assigned as coinciding with the ν_7 (a_{2u}) mode at 2920 cm^{-1} , has now been assigned to the medium intensity i.r. band at 2961 cm^{-1} in better agreement with the assignment of the corresponding e_g mode (ν_{16}) to 2954 cm^{-1} . The ν_8 (a_{2u}) mode (asymmetrical $\text{C}\equiv\text{C}$ stretching) is expected around 2200 cm^{-1} . In the i.r. solution spectra two equally intense bands at 2212 and 2149 cm^{-1} are observed. In the solid state spectrum, the former band is definitely the more intense and has been accordingly attributed to ν_8 while the latter band

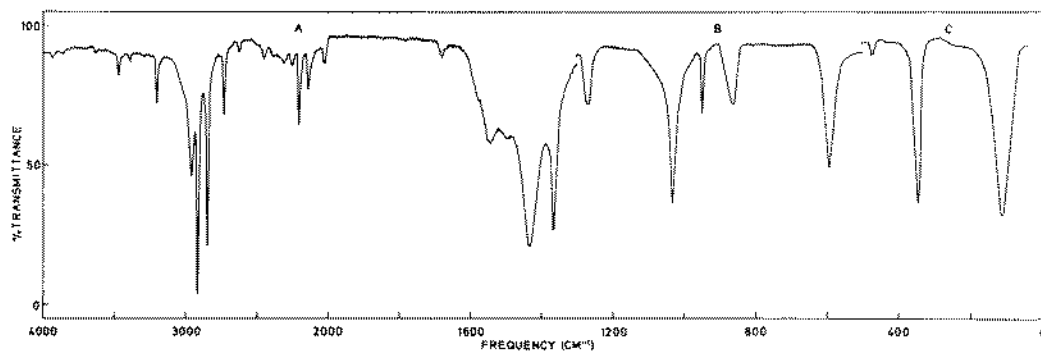


Fig. 1. Infrared spectrum of 2,4-hexadiyne in solution. (A) CCl₄ solution, (B) CS₂ solution, (C) C₆H₁₂ solution.

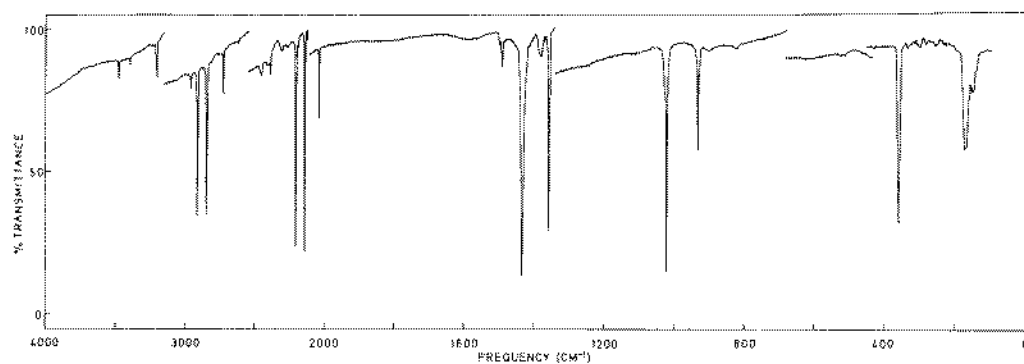


Fig. 2. Infrared spectrum of 2,4-hexadiyne as a crystalline solid at ca. 90 K.

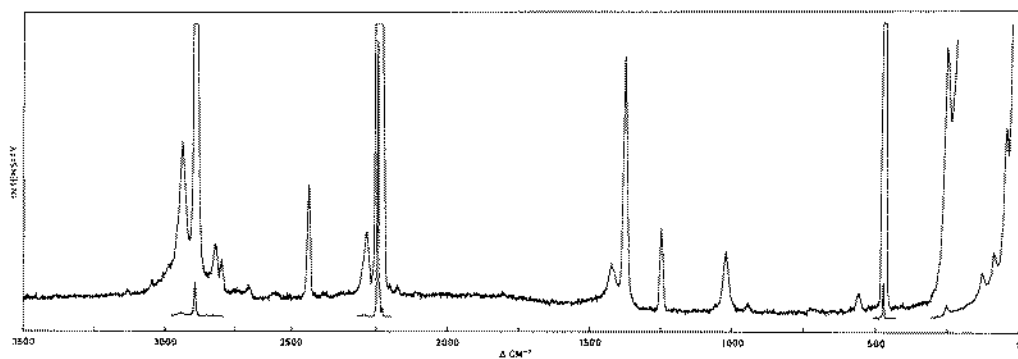


Fig. 3. Raman spectrum of 2,4-hexadiyne as a crystalline solid at ca. 90 K.

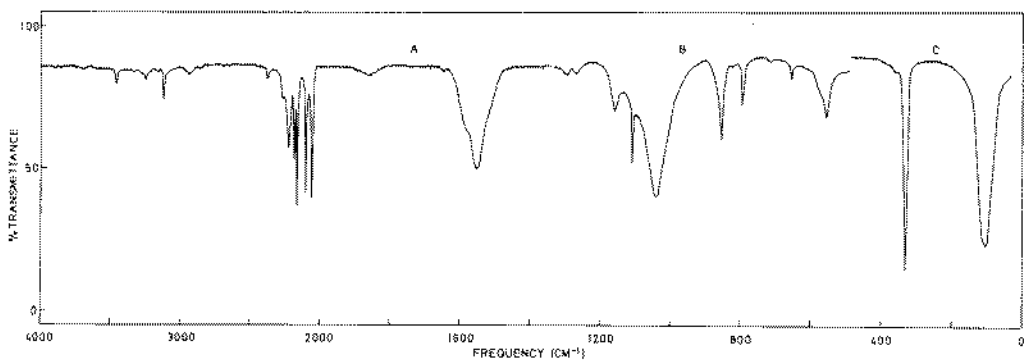


Fig. 4. Infrared spectrum of 2,4-hexadiyne-d₆ in solution. (A) CCl₄ solution, (B) CS₂ solution, (C) C₆H₁₂ solution.

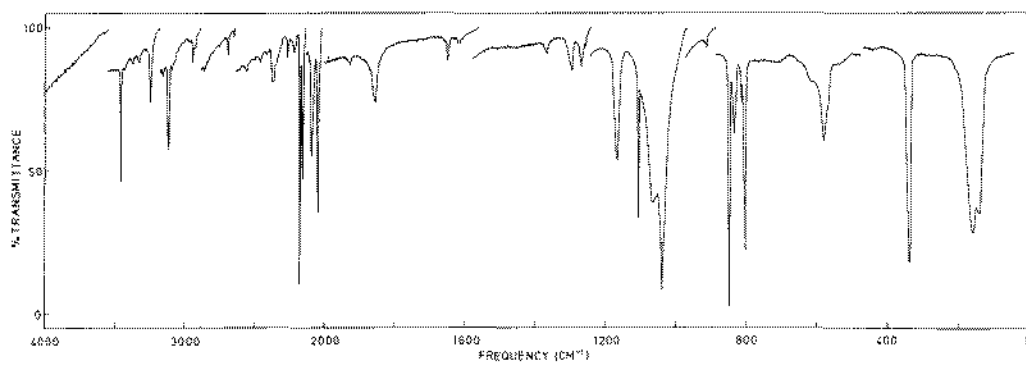


Fig. 5. Infrared spectrum of 2,4-hexadiyne- d_6 as a crystalline solid at *ca.* 90 K.

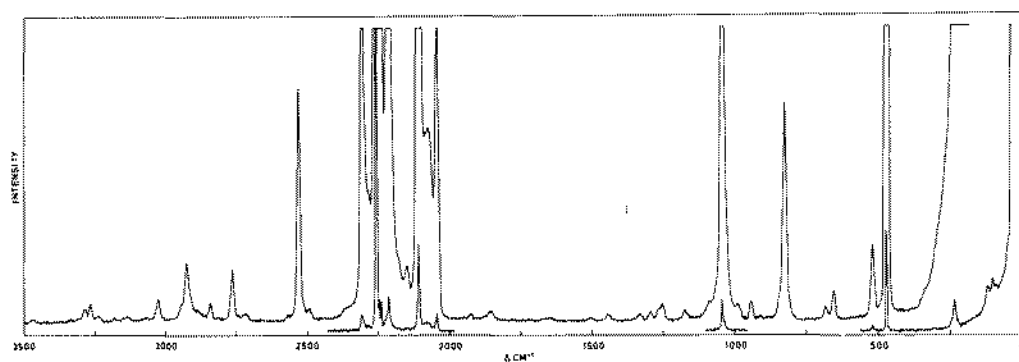


Fig. 6. Raman spectrum of 2,4-hexadiyne- d_6 as a crystalline solid at *ca.* 90 K.

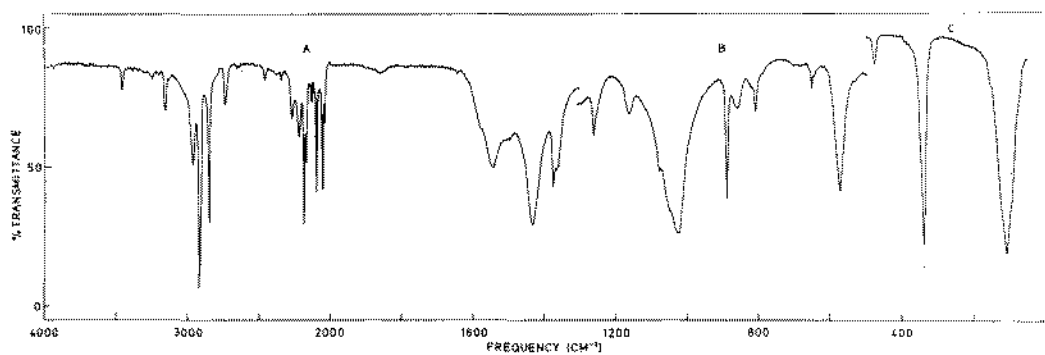


Fig. 7. Infrared spectrum of 2,4-hexadiyne-1,1,1- d_3 in solution. (A) CCl_4 solution, (B) CS_2 solution, (C) C_6H_{12} solution.

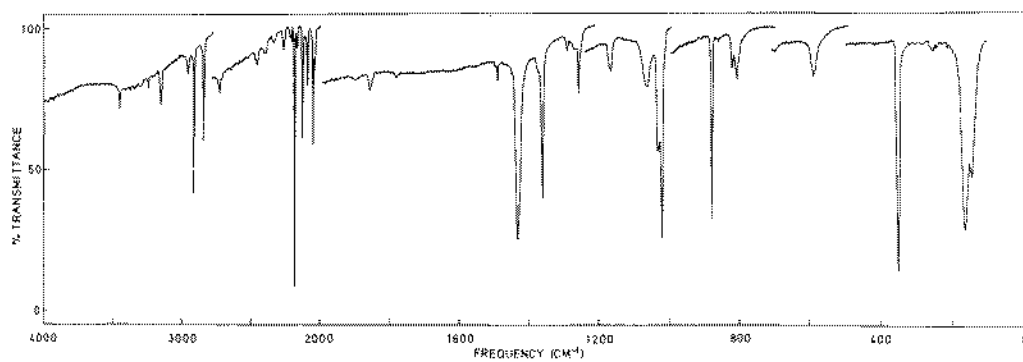


Fig. 8. Infrared spectrum of 2,4-hexadiyne-1,1,1- d_3 as a crystalline solid at *ca.* 90 K.

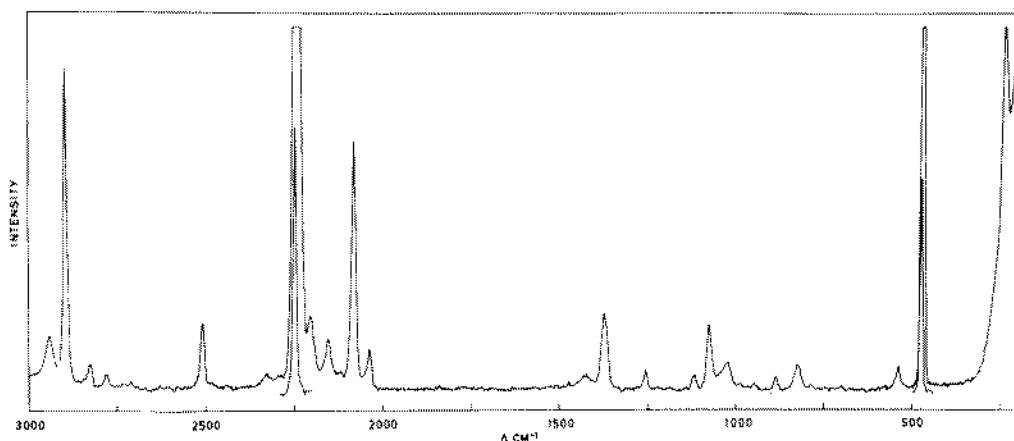


Fig. 9. Raman spectrum of 2,4-hexadiyne-1,1,1- d_3 as a crystalline solid at ca. 90 K.

has been assigned as a combination band in Fermi resonance.

A very weak Raman band at 1228 cm^{-1} , observed by MEISTER and CLEVELAND[2] and attributed to the ν_4 (a_{1g}) mode (C–C stretching), was not observed in any of our spectra and is probably due to an impurity in their sample. Instead the ν_4 mode was assigned to the weak, polarized Raman band at 1255 cm^{-1} . Finally, the lowest e_u mode (ν_{15}) was assigned to the strong, broad i.r. band at 121 cm^{-1} . This band has been claimed to be observed at 94 cm^{-1} in the vapour phase [5], but the spectra have never been published.

Spectral assignments in DMDA- d_6

The a_{1g} modes ν_1 , ν_2 and ν_4 were all easily assigned to strong, polarized Raman bands at 2268, 2217 and 1042 cm^{-1} . The ν_3 mode was assigned to the weak, polarized band at 515 cm^{-1} , while the ν_3 mode (C–C stretching) was assigned to the very weak, but definitely polarized band at 1273 cm^{-1} . Likewise, the e_g modes ν_{16} , ν_{19} and ν_{20} were assigned to strong, depolarized Raman bands at 2219, 473 and 219 cm^{-1} , respectively. The ν_{18} mode (C–C–D bending) was assigned to the very weak band at 823 cm^{-1} and ν_{17} mode to the bands at 1042 cm^{-1} , overlapped by the ν_4 (a_{1g}) mode.

Most of the a_{2u} and e_u modes could be assigned to strong or medium intensity i.r. bands. However, the ν_{13} (e_u) mode (C–C–D bending) was assigned to the very weak band at 824 cm^{-1} close to the corresponding e_g mode (ν_{18}) at 823 cm^{-1} . The ν_7 (a_{2u}) mode (asymmetric C=C stretching) was assigned to the medium intensity i.r. band at 2182 cm^{-1} although a stronger band is situated at 2163 cm^{-1} . In the solid state spectra, the relative intensities of these two bands are reversed. As in the parent compound, these two bands are obviously in Fermi resonance, however for DMDA- d_6 no suitable binary combination of the proper symmetry can be suggested.

Since the isotopic purity of DMDA- d_6 was ca. 93%

some weak bands due to DMDA- d_5 were detected in the spectra. These bands have been labeled " d_5 " in Table 2.

Spectral assignments in DMDA- d_3

The vibrational spectra of DMDA- d_3 offer an excellent opportunity to check the assignments for DMDA and DMDA- d_6 . Most of the bands considered as fundamentals were strong or medium intensity in either the i.r. or the Raman spectra. The a_1 fundamentals ν_1 , ν_2 , ν_4 , ν_5 , ν_7 and ν_9 were readily assigned to the bands (all polarized in the Raman spectra) at 2916, 2268, 2100, 1377, 1081 and 534 cm^{-1} , respectively. The ν_3 mode (asymmetric C=C stretching) was assigned to the strong i.r. band at 2187 cm^{-1} for which only a very weak Raman counterpart was observed. In DMDA- d_3 , this mode is apparently not so strongly perturbed by Fermi resonance as in DMDA and DMDA- d_6 . The remaining two a_1 modes ν_6 and ν_8 (mainly C–C stretching) were assigned to the bands at 1263 and 890 cm^{-1} , respectively, both of medium intensity in the i.r. spectra and weak in the Raman spectra.

Six of the ten e modes (ν_{11} – ν_{16}) are typical CH_3 or CD_3 group frequencies and were readily assigned. The remaining four e modes all fall below 500 cm^{-1} . The ν_{17} and ν_{19} fundamentals were assigned to the strong or medium intensity depolarized Raman bands at 472 and 236 cm^{-1} , respectively, while the ν_{18} and ν_{20} modes were assigned to the strong i.r. bands at 341 and 116 cm^{-1} .

Force constant calculations

In Table 5, internal valence symmetry coordinates for DMDA are given, which can be interpreted by reference to Fig. 10. For DMDA- d_3 (C_{3v} symmetry), the corresponding symmetry coordinates involving the methyl groups are labeled: S_{1H} , S_{1D} , S_{2H} , S_{2D} , etc. The molecular geometry was taken as follows:

Table 1. Infrared and Raman spectral data for 2,4-hexadiyne*

Solution	Infrared Solid	Raman Solution	Raman Solid	Interpretation
3933 vw				$\nu_{16} + \nu_{18} = 3976, \nu_{13} + \nu_{18} = 3977 A_{2u} + E_u$
3862 vw				$\nu_{10} + \nu_{16} = 3895 E_u$
3631 vw				$\nu_8 + \nu_{17} = 3640 E_u$
3590 vw				$\nu_2 + \nu_9 = 3635 A_{2u}$
3464 w	3473 w		3570 w	$\nu_8 + \nu_9 = 3581 A_{1g}$
3390 w	3389 vw			$\nu_5 + \nu_7 = 3478 A_{2u}$
3290 vw				$\nu_{11} + \nu_{19} = 3435 A_{2u} + E_u$
3240 vw				$\nu_{14} + \nu_{16} = 3304 A_{2u} + E_u$
		3234 vw		$\nu_1 + \nu_{14} = 3261 E_u$
3203 m	3199 m			$\nu_7 + \nu_{14} = 3270 E_g$
3196 w,sh				$\nu_8 + \nu_{18} = 3234 E_u$
3018 w,sh				$\nu_2 + \nu_{10} = 3207 A_{2u}, \nu_{11} + \nu_{20} = 3206 A_{2u} + E_u$
2961 m,bd	2958 w			$\nu_1 + \nu_{15} = 3032 E_u$
2918 s	2913 s	2954 w,bd	2963 m	$\nu_{11} e_u$
				$\nu_{16} e_g$
		2911 s,P	2915 vs	$\nu_7 a_{2u}$
2849 s	2848 s			$\nu_1 a_g$
		2844 w,P	2845 w	$\nu_{12} + \nu_{17} = 2858 A_{2u} + E_u$
		2820 vw,P	2823 w	$2\nu_{12} = 2860, 2\nu_{17} = 2856 A_{1g} + E_g$
2800 vw,sh				$\nu_2 + \nu_5 = 2826 A_{1g}$
2761 vw				$\nu_3 + \nu_{12} = 2808 E_u$
2732 m	2729 m			$\nu_5 + \nu_8 = 2772 A_{2u}$
				$\nu_3 + \nu_9 = 2747 A_{2u}$
2684 vw			2724 vw	$2\nu_9 = 2738 A_{1g}, \nu_2 + \nu_{19} = 2740 E_g$
2622 vw	2620 vw			$\nu_8 + \nu_{19} = 2686, \nu_4 + \nu_{12} = 2685 E_u$
		2509 w,P	2510 m	$\nu_4 + \nu_9 = 2624 A_{2u}$
2455 w	2457 w			$2\nu_4 = 2510 A_{1g}$
2392 w	2389 w			$\nu_8 + \nu_{20} = 2457 E_u$
2318 w				$\nu_3 + \nu_{13} = 2401 E_u$
		2308 w,P	2303 w	$\nu_3 + \nu_{10} = 2319 A_{2u}$
2266 w		2266 vs,P	2261 vs	$\nu_9 + \nu_{10} = 2310 A_{1g}$
2260 w,sh				$\nu_2 a_{1g}$
			2256 s	$\nu_4 + \nu_{13} = 2278 E_u$
			2252 s	$^{13}C?$
		2254 s,sh	2244 m	$\nu_4 + \nu_{18} = 2277 E_g$
				$^{13}C?$
2212 m	2211 vs			$\nu_8 a_{2u}$
2193 vw,sh				
2149 m	2148 vs			$\nu_4 + \nu_{10} = 2196 A_{2u} FR$
2128 vw,sh				
2039 m	2044 m			$\nu_{13} + \nu_{18} = 2045 A_{2u} + E_u$
1496 w,bd,sh	1494 w			$\nu_5 + \nu_{10} = 1501 A_{2u}$
1430 s,bd	1435 vs			$\nu_{12} e_u$
		1428 vw,bd,D	1428 w	$\nu_{17} e_g$
1381 w,sh	1385 w,bd			$\nu_{10} + \nu_{19} = 1415 E_u$
		1378 m,P	1379 s	$\nu_3 a_{1g}$
1369 s	1359 vs			$\nu_9 a_{2u}$
1255 w,bd				$\nu_{13} + \nu_{20} = 1268 A_{2u} + E_u$
		1255 w,P	1255 m	$\nu_4 a_{1g}$
1023 m,bd	1030 vs			$\nu_{13} e_u$
		1022 w,bd,D	1027 w	$\nu_{18} e_g$
		951 vw,P	950 vw	$2\nu_{19} = 948 A_{1g} + E_g$
941 m	934 m			$\nu_{10} a_{2u}$
	825 vw			$\nu_{14} + \nu_{19} = 824 A_{2u} + E_u$
593 m,bd				$\nu_{14} + \nu_{20}, \nu_{15} + \nu_{19} = 595 A_{2u} + E_u$
474 w		560 w,P	562 vw	$\nu_5 a_g$
350 s	359 m	474 s,D	475 vs	$\nu_{19} e_g$
247 vw		350 vw		$\nu_{14} e_u$
		245 s,D	255 s	$\nu_{20} e_g$
121 s,bd	171 m,bd } 150 m,bd }			$\nu_{15} e_u$
			130 ms } 90 ms } 50 ms }	lattice modes

*Abbreviations: w (weak), m (medium), s (strong), v (very), bd (broad), sh (shoulder), P (polarized), D (depolarized), FR (Fermi resonance), ^{13}C (bands due to ^{13}C isotopic species).

Table 2. Infrared and Raman spectral data for 2,4-hexadiyne- d_8^*

Infrared		Raman		Interpretation
Solution	Solid	Solution	Solid	
3456 w	3454 m			$\nu_3 + \nu_{11} = 3493 E_u$
	3420 vw			$\nu_3 + \nu_7 = 3454 A_{2u}$
~3370 vw	3376 vw } 3366 vw }			$\nu_1 + \nu_9 = 3375, \nu_3 + \nu_8 = 3372 A_{2u}$
~3330 vw	3324 vw			$\nu_9 + \nu_{16} = 3326 E_u$
			3302 vw	$\nu_9 + \nu_{11} = 3328 E_g$
			3282 vw	$\nu_i + \nu_{17} = 3310 E_g, \nu_i + \nu_4 = 3310 A_{1g}$
3245 vw	3242 m			$\nu_{11} + \nu_{17} = 3263, \nu_{12} + \nu_{16} = 3259 A_{2u} + E_u$
				$\nu_4 + \nu_{16} = 3263 E_u$
			3242 vw	$\nu_{11} + \nu_{12}, \nu_{16} + \nu_{17} = 3261 A_{1g} + E_g, \nu_4 + \nu_{16} = 3261 E_g$
			3196 vw	$\nu_7 + \nu_{12} = 3222 E_g, \nu_8 + \nu_9 = 3207 A_{1g}$
3158 vw	3153 vw			$\nu_2 + \nu_{12} = 3157 E_u$
			3147 vw	$\nu_2 + \nu_{17} = 3159 E_g$
3116 w	3113 m, bd			$\nu_8 + \nu_{17} = 3142 E_u, \nu_4 + \nu_8 = 3142 A_{2u}$
	3087 vw			$\nu_1 + \nu_{10} = 3120 A_{2u}$
	3069 vw			$\nu_1 + \nu_{13} = 3092 E_u$
	3052 vw			$\nu_{10} + \nu_{16} = 3071 E_u$
	3042 vw			$\nu_{11} + \nu_{18} = 3044, \nu_{13} + \nu_{16} = 3043 A_{2u} + E_u$
		3040 w, P	3037 vw	$\nu_{11} + \nu_{13} = 3045, \nu_{16} + \nu_{18} = 3042 A_{1g} + E_g$
	3001 vw, bd			$\nu_7 + \nu_{18} = 3005 E_u$
2960 vw	2960 vw, bd			$\nu_2 + \nu_{10} = 2969 A_{2u}$
			2955 vw	
2939 vw	2938 w	2940 w, P	2939 w	$d_5 ?$
2920 vw	2920 vw, bd			$\nu_2 + \nu_{13} = 2941 E_u$
			2927 vw, sh	$\nu_2 + \nu_{18} = 2940 E_g$
			2897 vw	$\nu_8 + \nu_{13} = 2923 E_g$
		2865 vw	2854 vw	
2850 vw	2853 vw			
		2778 w, P	2776 w	$\nu_1 + \nu_5 = 2783 A_{1g}$
			2718 vw, bd	$\nu_1 + \nu_{19} = 2739, \nu_5 + \nu_{16} = 2734 E_g$
2695 vw	2686 vw			$\nu_5 + \nu_7 = 2697 A_{2u}, \nu_5 + \nu_{11} = 2736 E_u$
2650 vw	2642 vw			$\nu_7 + \nu_{19} = 2653 E_u, \nu_{11} + \nu_{19} = 2692 A_{2u} + E_u$
			2576 vw	$\nu_2 + \nu_{19} = 2588 E_g$
~2550 vw	2556 vw			$\nu_8 + \nu_{19} = 2571 E_u$
		2541 m, P	2541 m	$2\nu_3 = 2544 A_{1g}, \nu_{11} + \nu_{14} = 2552 A_{1g} + E_g$
			2523 vw, sh	
			2503 vw	$\nu_7 + \nu_{14} = 2513 E_g$
	2455 vw			
	2414 vw			
			~2380 vw, sh	

2377 w	2370 w 2356 vw			$v_3 + v_9 = 2379 A_{2u}$
		2316 s, P	~2355 vw, sh 2315 s ~2305 m, sh 2291 w 2273 vvs	$v_2 + v_4 = 2314 A_{1g}$ FR
		2268 vvs, P		$v_1 a_{1g}$
2264 w	2269 vw 2264 w		2252 s 2245 s	$^{13}\text{C} ?$ $^{13}\text{C} ?$
2221 m, bd	2219 w, bd 2206 vw	2219 s, D	2219 s	$v_{11} e_u$ $v_{16} e_g$
2182 m 2163 s	2180 vs 2159 m 2154 w	2186 w, sh 2154 w, P 2117 vs, P	2184 vw 2153 w 2114 vs	$2v_9 = 2214 A_{1g}$ $v_7 a_{2u}$ $d_5 ?$ $v_2 a_{1g}$
2115 vw 2100 s	2109 w 2095 m, bd			$v_3 + v_{10} = 2124 A_{2u}$ $v_8 a_{2u}$
2056 s	2049 s	2077 m, P 2053 s, P	2077 m, bd 2049 s 1931 vw	$2v_4 = 2084 A_{1g}$ $v_{12} + v_{17} = 2082 A_{2u} + E_u$ $2v_{12} = 2080, 2v_{17} = 2084 A_{1g} + E_g$ $v_9 + v_{10} = 1959 A_{1g}, v_9 + v_{13} = 1931 E_g$ $v_9 + v_{18} = 1930 E_u$
	1929 w		1860 vw, bd	$v_{12} + v_{13} = 1864, v_{17} + v_{18} = 1865 A_1 + E_g$ $v_4 + v_{18} = 1865 E_g$
1855 w, bd	1861 m 1856 m 1650 w			$v_{12} + v_{18} = 1863, v_{13} + v_{17} = 1866 A_{2u} + E_u$ $v_4 + v_{13} = 1866 E_u$ $v_{10} + v_{18} = 1675 E_u$
			1650 vvw 1505 vw 1444 vw	$v_{10} + v_{13} = 1676 E_g$ $v_{17} + v_{19} = 1513 A_{1g} + E_g$ $v_9 + v_{14} = 1438 E_g$
	1365 w			$v_4 + v_{14} = 1373 E_u, v_5 + v_{10} = 1367 A_{2u}$ $v_{14} + v_{17} = 1373 A_{2u} + E_u$
			1335 vw, bd 1292 vw	$v_5 + v_{16} = 1338 E_g$ $v_{18} + v_{19} = 1294 A_{1g} + E_g$
1291 w	1294 w } 1291 w }	1292 vw	1292 vw	$v_{13} + v_{19} = 1295 A_{2u} + E_u$
1262 w	1266 w 1253 vw	1272 vw, P 1253 vw, P	1270 vw 1254 vw 1175 vw	$v_3 a_{1g}$ $d_5 ?$ $d_5 ?$
1156 m 1107 m	1162 m, bd 1102 m 1094 vw			$v_{10} + v_{14} = 1183 E_g$ $v_{14} + v_{18} = 1154 A_{2u} + E_u$ FR $v_9 a_{2u}$

Table 2. (Contd)

Solution	Infrared		Raman		Interpretation
	Solid	Solution	Solid	Solid	
	1090 vw, sh. 1060 m, bd	1086 vw	1090 vw	$d_5 ?$ $\nu_{10} + \nu_{20} = 1071 E_u$	
		1042 s, P	1043 s 1035 m, sh	$\nu_4 a_{1g}, \nu_{17} e_g$ $\nu_{12} e_u$	
1040 s, bd	1036 vs } 1028 s, sh }	~990 vw 946 vw	990 vw 944 vw	$\nu_5 + \nu_{19} = 986 E_g$ $2\nu_{19} = 946 A_{1g} + E_g$	
852 m 824 vw	910 vw 844 vs 830 m		~910 vvw	$d_5 ?$ $\nu_{10} a_{2u}$ $\nu_{13} e_u$	
794 w	810 w 799 s	823 w, D	827 m	$\nu_{18} e_g$ $d_5 ?$ $\nu_{14} + \nu_{19} = 802 A_{2u} + E_u$ $\nu_{19} + \nu_{20} = 692 A_{1g} + E_g$	
552 m, bd	572 m, bd		683 vw 655 vw	$2\nu_{14} = 662 A_{1g} + E_g$ $\nu_{14} + \nu_{20} = 550 A_{2u} + E_u$	
470 vw 331 s	339 s 336 s	515 w, P 471 vs, D	519 w 471 vs	$\nu_5 a_{1g}$ $\nu_{19} e_g$ $\nu_{14} e_u$	
111 s, bd	157 s, bd 138 s, bd	219 vs, D	233 s	$\nu_{20} e_g$ $\nu_{15} e_u$	
			115 ms } 88 ms } 48 ms }	lattice modes	

* Abbreviations: w(weak), m(medium), s(strong), v(very), bd(broad), sh(shoulder), P(polarized), D(depolarized), FR(Fermi resonance), ^{13}C (bands due to ^{13}C isotopic species), d_5 (bands due to DMDA- d_5).

Table 3. Infrared and Raman spectral data for 2,4-hexadiyne- d_3^*

Solution	Infrared		Raman		Interpretation
	Solid	Solid	Solution	Solid	
3455 w	3455 w				$\nu_4 + \nu_8 = 3477 A_1, \nu_6 + \nu_{12} = 3481 E$
3381 vw	3381 vw				$\nu_1 + \nu_{17} = 3390 E$
3349 vw	3349 vw				$\nu_4 + \nu_6 = 3363 A_1$
~ 3300 vw, bd	3304 vw				$\nu_2 + \nu_7 = 3348 A_1$
3246 vw	3242 w				$\nu_1 + \nu_{18} = 3257 E, \nu_3 + \nu_7 = 3268 A_1$
3201 vw	3215 w, bd				$\nu_{12} + \nu_{14} = 3247, \nu_{12} + \nu_{15} = 3244 A_1 + E$
3159 w	3154 w				$\nu_{11} + \nu_{19} = 3196 A_1 + E$
3151 w					$\nu_4 + \nu_7 = 3181 A_1$
3126 vw	3128 vw, sh				$\nu_2 + \nu_6 = 3157 A_1, \nu_1 + \nu_{19} = 3152 E$
2960 m	2959 w	2958 w, bd, D	2959 w, bd		$\nu_{11} e$
2916 vs	2914 s	2916 vs, P	2914 vs		$\nu_1 a_1$
2847 s	2848 m } 2843 m }	2847 m, P	2844 vw		$2\nu_{13} = 2872 A_1 + E$
2806 vw		2803 w			$\nu_5 + \nu_{13} = 2813 E$
~ 2790 vw		2792 w			$\nu_2 + \nu_9 = 2802 A_1$
	~ 2740 vw				$\nu_9 + \nu_{12} = 2753 E$
2733 w	2728 w	2731 w, bd			$2\nu_5 = 2754 A_1$
	2715 vw				$\nu_2 + \nu_{17} = 2741 E$
2654 vw					$\nu_{12} + \nu_{17} = 2692 A_1 + E$
2640 vw					$\nu_3 + \nu_{17} = 2661 E$
2524 vw		2524 m, P	2524 m		$2\nu_6 = 2526 A_1, \nu_{12} + \nu_{18} = 2559 A_1 + E$
2459 w	2459 w				$\nu_{13} + \nu_{14} = 2465, \nu_{13} + \nu_{15} = 2462 A_1 + E$
2392 vw	2392 vw				$\nu_5 + \nu_{14} = 2406, \nu_5 + \nu_{15} = 2403 E$
2375 vw					$\nu_2 + \nu_{20} = 2383 E$
2344 w	2346 w	2343 vw	2341 vw		$\nu_6 + \nu_7 = 2344 A_1$
		2315 vw			$\nu_3 + \nu_{19} = 2336, \nu_8 + \nu_{13} = 2326 E, \nu_{12} + \nu_{20} = 2334 A_1 + E$
2270 w	2268 w	2270 vvs, P	2263 vvs		$\nu_2 a_1$
2264 w	2257 w	2264 vs, sh, P	2255 m, sh		$\nu_5 + \nu_8 = 2267 A_1 \text{ FR}$
2218 m	2217 vw	2217 m, sh	2218 m		$\nu_{12} e$
	2205 vw		~ 2205 w, sh		
2187 s	2187 vs		2186 vw		$\nu_3 a_1$
2171 m	2168 w	2171 m, P	2171 w		
	2149 vw		2152 vw		$2\nu_7 = 2162 A_1$
2131 w	2131 ms	2132 vw	2130 vw		$\nu_6 + \nu_8 = 2153 A_1$
2100 s	2096 m	2101 vs, P	2096 vs		$\nu_4 a_1$
2055 s	2051 ms	2056 m, P	2049 m		$2\nu_{14} = 2058 A_1 + E \text{ FR}$
2039 w	2044 w, sh				$\nu_{14} + \nu_{15} = 2055, 2\nu_{15} = 2052 A_1 + E$
	1902 vw				$\nu_8 + \nu_{14} = 1919, \nu_8 + \nu_{15} = 1919 E, \nu_5 + \nu_9 = 1019 A_1$
1893 vw, bd	1895 vw				$\nu_{13} + \nu_{17} = 1910 A_1 + E, \nu_7 + \nu_{16} = 1903 E$
~ 1855 vw, bd	1859 w				
1785 vw, bd	1781 vw, bd				$\nu_6 + \nu_9 = 1798 A_1$

Table 3. (Contd)

Infrared		Raman		Interpretation
Solution	Solid	Solution	Solid	
1495 m, bd	1494 vw			$\nu_{14} + \nu_{17} = 1503, \nu_{15} + \nu_{17} = 1500 A_1 + E$
1436 s, bd	1438 m, sh } 1436 s } 1430 m, sh }	~1433 w, bd	1432 w	$\nu_{13} e$
1377 m	~1370 w, sh	1377 m, P	1382 m } 1372 m, sh }	$\nu_5 a_1$
1365 m, bd	1365 s			$\nu_{14} + \nu_{18} = 1370, \nu_{15} + \nu_{18} = 1367 A_1 + E$
1263 m	1295 vw			$\nu_{16} + \nu_{17} = 1296 A_1 + E$
~1165 w, bd	1263 m	1263 w	1264 w	$\nu_6 a_1$
1081 w, sh	1173 w, bd			$\nu_{16} + \nu_{18} = 1163 A_1 + E$
1058 m, bd, sh	1084 vw, sh	1081 m, P	1083 m	$\nu_7 a_1$
~1035 m, bd, sh	1068 w, bd		~1079 w, sh	$2\nu_9 = 1070 A_1$
1026 s, bd	1037 m, sh } 1034 m, sh }	1029 w, bd	1033 w, bd	$\nu_{14} e$
	1025 s			$\nu_{15} e$
890 m	883 s	948 vw	950 vw	$2\nu_{17} = 948 A_1 + E$
822 vw, sh	826 w	892 w	890 w	$\nu_8 a_1$
810 w	812 w } 807 vw, sh }	~820 w	827 w	$\nu_{16} e$
790 vw, bd				$\nu_{17} + \nu_{18} = 815 A_1 + E$
706 vw				$\nu_{15} - \nu_{19} = 790 A_1 + E$
655 vw				$\nu_{17} + \nu_{19} = 710, \nu_{16} - \nu_{20} = 706 A_1 + E$
575 m, bd	596 w, bd } 582 vw, sh }			$\nu_8 - \nu_{19} = 654 A_1 + E$
535 vw	~535 vw	534 w, P	540 w	$\nu_{18} + \nu_{19} = 577 A_1 + E$
472 w	474 vw	474 s, D	475 vs	$\nu_9 a_1$
341 s	350 s, bd	~340 w	351 yw	$\nu_{17} e$
~235 vw, sh		236 m, D	244 m	$\nu_{18} e$
116 s, bd	163 s, bd } 143 m, bd }			$\nu_{19} e$
				$\nu_{20} e$

*Abbreviations: w(weak), m(medium), s(strong), v(very), bd(broad), sh(shoulder), P(polarized), D(depolarized), FR(Fermi resonance).

Table 4. Observed and calculated vibrational frequencies, uncertainties and errors for 2,4-hexadiyne (DMDA), 2,4-hexadiyne- d_6 (DMDA- d_6) and 2,4-hexadiyne-1,1,1- d_3 (DMDA- d_3)

No.		Obs.	Calc.		PED*	
DMDA						
a_{1g}	ν_1	2911	29	2925	-14	99S ₁ †
	ν_2	2266	23	2267	-1	85S ₃ + 22S ₅
	ν_3	1378	14	1372	6	99S ₂ + 15S ₃
	ν_4	1255	13	1256	-1	42S ₃ + 44S ₅
	ν_5	560	6	562	-2	38S ₃ + 16S ₄ + 33S ₅
a_{2u}	ν_7	2920	29	2925	-5	99S ₇
	ν_8	2212	44	2190	22	90S ₁₀
	ν_9	1369	14	1369	0	103S ₈
	ν_{10}	941	9	946	-5	84S ₉
e_u	ν_{11}	2961	30	2974	-13	100S ₁₁
	ν_{12}	1430	14	1439	-9	89S ₁₂
	ν_{13}	1023	10	1038	-15	88S ₁₃
	ν_{14}	350	4	346	4	99S ₁₄ + 79S ₁₅
	ν_{15}	121	1	122	-1	24S ₁₄ + 45S ₁₅
e_g	ν_{16}	2953	30	2974	-21	100S ₁₆
	ν_{17}	1428	14	1439	-11	89S ₁₇
	ν_{18}	1022	10	1037	-15	89S ₁₈
	ν_{19}	474	5	473	-1	24S ₁₉ + 139S ₂₀
	ν_{20}	245	2	243	2	115S ₁₉
DMDA-d_6						
a_{1g}	ν_1	2268	23	2269	-1	83S ₄ + 21S ₅
	ν_2	2117	21	2102	15	97S ₁
	ν_3	1272	13	1271	1	57S ₃ + 39S ₅
	ν_4	1042	10	1032	10	89S ₂
	ν_5	515	5	513	2	36S ₃ + 15S ₄ + 29S ₅
a_{2u}	ν_7	2182	43	2196	-14	83S ₁₀
	ν_8	2100	21	2096	4	92S ₇
	ν_9	1107	11	1110	-3	75S ₈ + 44S ₉
	ν_{10}	852	9	843	9	28S ₈ + 47S ₉
e_u	ν_{11}	2221	22	2208	13	100S ₁₁
	ν_{12}	1040	10	1033	7	93S ₁₂
	ν_{13}	824	8	818	6	90S ₁₃
	ν_{14}	331	3	334	-3	92S ₁₄ + 83S ₁₅
	ν_{15}	111	1	110	1	27S ₁₄ + 40S ₁₅
e_g	ν_{16}	2219	22	2208	11	100S ₁₆
	ν_{17}	1042	10	1033	9	93S ₁₇
	ν_{18}	823	8	816	7	91S ₁₈
	ν_{19}	471	5	472	-1	23S ₁₉ + 138S ₂₀
	ν_{20}	219	2	224	-5	113S ₁₉
DMDA-d_3						
a_1	ν_1	2916	29	2925	-9	99S _{1H}}
	ν_2	2270	23	2268	2	84S ₄ + 22S ₅
	ν_3	2187	43	2193	-6	86S ₁₀
	ν_4	2100	21	2099	1	94S _{1D}}
	ν_5	1377	14	1371	6	101S _{2H}}
	ν_6	1263	13	1264	-1	50S ₃ + 41S ₅
	ν_7	1081	11	1079	2	73S _{2D} + 32S ₉
	ν_8	890	9	888	2	22S _{2D} + 55S ₉
	ν_9	534	5	536	-2	37S ₃ + 16S ₄ + 30S ₅
	ν_{10}	2960	30	2974	-14	100S _{11H}}
e	ν_{11}	2218	22	2208	10	100S _{11D}}
	ν_{12}	1436	14	1439	-3	89S _{12H}}
	ν_{13}	1038	10	1037	1	88S _{12D}}
	ν_{14}	1026	10	1033	-7	93S _{13H}}
	ν_{15}	820	8	817	3	90S _{13D}}
	ν_{16}	472	5	472	0	24S ₁₉ + 138S ₂₀
	ν_{17}	341	3	340	1	95S ₁₄ + 80S ₁₅
	ν_{18}	236	2	233	3	113S ₁₉
	ν_{19}	116	1	116	0	26S ₁₄ + 42S ₁₅

*The potential energy distribution is defined as:

$$X_{ik} = 100 \cdot F_{ik} \cdot L_{ik}^2 / \lambda_k.$$

†For meaning of symbols see Table 5 and Fig. 10.

Table 5. Internal valence symmetry coordinates for 2,4-hexadiyne (DMDA) with reference to Fig. 10

a_{1g}	$S_1 = 6^{-1/2}(\Delta r_4 + \Delta r_5 + \Delta r_6 + \Delta r'_4 + \Delta r'_5 + \Delta r'_6)$
	$S_2 = 12^{-1/2}(\Delta \alpha_4 + \Delta \alpha_5 + \Delta \alpha_6 + \Delta \alpha'_4 + \Delta \alpha'_5 + \Delta \alpha'_6 - \Delta \beta_4 - \Delta \beta_5 - \Delta \beta_6 - \Delta \beta'_4 - \Delta \beta'_5 - \Delta \beta'_6)$
	$S_3 = 2^{-1/2}(\Delta R + \Delta R')$
	$S_4 = 2^{-1/2}(\Delta T + \Delta T')$
	$S_5 = \Delta S$
a_{2u}	$S_7 = 6^{-1/2}(\Delta r_4 + \Delta r_5 + \Delta r_6 - \Delta r'_4 - \Delta r'_5 - \Delta r'_6)$
	$S_8 = 12^{-1/2}(\Delta \alpha_4 + \Delta \alpha_5 + \Delta \alpha_6 - \Delta \alpha'_4 - \Delta \alpha'_5 - \Delta \alpha'_6 - \Delta \beta_4 - \Delta \beta_5 - \Delta \beta_6 + \Delta \beta'_4 + \Delta \beta'_5 + \Delta \beta'_6)$
	$S_9 = 2^{-1/2}(\Delta R - \Delta R')$
	$S_{10} = 2^{-1/2}(\Delta T - \Delta T')$
e_u	$S_{11} = 12^{-1/2}(2\Delta r_4 - \Delta r_5 - \Delta r_6 - 2\Delta r'_4 + \Delta r'_5 + \Delta r'_6)$
	$S_{12} = 12^{-1/2}(2\Delta \alpha_4 - \Delta \alpha_5 - \Delta \alpha_6 - 2\Delta \alpha'_4 + \Delta \alpha'_5 + \Delta \alpha'_6)$
	$S_{13} = 12^{-1/2}(2\Delta \beta_4 - \Delta \beta_5 - \Delta \beta_6 - 2\Delta \beta'_4 + \Delta \beta'_5 + \Delta \beta'_6)$
	$S_{14} = 2^{-1/2}(\Delta \theta_x + \Delta \theta'_x)$
	$S_{15} = 2^{-1/2}(\Delta \phi_x - \Delta \phi'_x)$
e_g	$S_{16} = 12^{-1/2}(2\Delta r_4 - \Delta r_5 - \Delta r_6 + 2\Delta r'_4 - \Delta r'_5 - \Delta r'_6)$
	$S_{17} = 12^{-1/2}(2\Delta \alpha_4 - \Delta \alpha_5 - \Delta \alpha_6 + 2\Delta \alpha'_4 - \Delta \alpha'_5 - \Delta \alpha'_6)$
	$S_{18} = 12^{-1/2}(2\Delta \beta_4 - \Delta \beta_5 - \Delta \beta_6 + 2\Delta \beta'_4 - \Delta \beta'_5 - \Delta \beta'_6)$
	$S_{19} = 2^{-1/2}(\Delta \theta_x + \Delta \theta'_x)$
	$S_{20} = 2^{-1/2}(\Delta \phi_x + \Delta \phi'_x)$

*The angle redundancy has been removed: $\Delta \alpha = K \Delta \beta$, $K = 3 \sin \beta \cos \beta / \sin \alpha$ ($K = -1$ for tetrahedral angles).

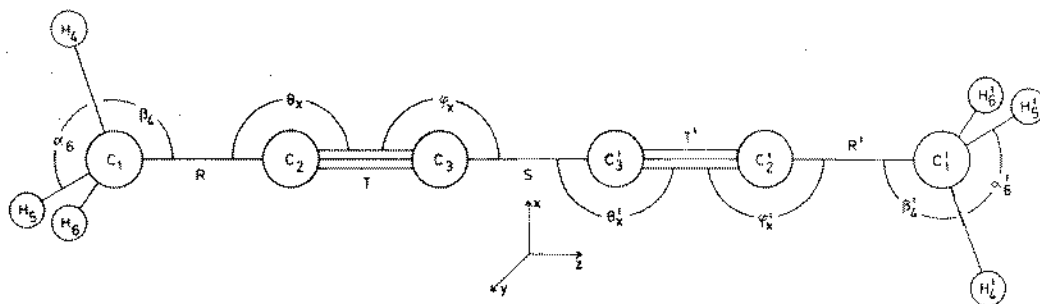


Fig. 10. Valence coordinates for 2,4-hexadiyne.

Table 6. Valence force constants and standard errors for 2,4-hexadiyne (DMDA)

Description	Values*
K_r CH str.	4.815 \pm 0.022
K_R -C-C≡str.	5.299 \pm 0.094
K_T C≡C str.	15.70 \pm 0.26
K_S ≡C-C≡ str.	7.05 \pm 0.17
H_α HCH bend	0.5121 \pm 0.0034
H_β CCH bend	0.6603 \pm 0.0045
H_θ (H)C-C≡C bend	0.3000 \pm 0.0022
H_ϕ C≡C-C(C) bend	0.4662 \pm 0.0041
$F_{r\phi}$ CH str./CH str.	0.061 \pm 0.015
F_{RT} (H)C-C str./C≡C str.	0.34 \pm 0.19
F_{ST} C≡C str./≡C-C≡ str.	1.14 \pm 0.13
$F_{r\beta}$ CH str./CCH bend	0.1 †
$F_{R\beta}$ C-C str./CCH bend, C-C common	0.300 \pm 0.012
$F_{\beta\beta}$ CCH bend/CCH bend, C-C common	-0.02
$F_{\alpha\beta}$ HCH bend/CCH bend, C-H common	-0.01
$F_{\theta\phi}$ (H)C-C≡C bend/C≡C-C(C) bend, C≡C common	-0.0866 \pm 0.0033
$F_{\phi\phi}$ C≡C-C(C) bend/C≡C-C(C) bend, C-C common	0.1840 \pm 0.0024

*1 mdyn $\text{\AA}^{-1} = 10^2 \text{ N/m}$, 1 mdyn $\text{\AA}/\text{rad}^{-2} = 10^{-18} \text{ Nm rad}^{-2}$, 1 mdyn $\text{rad}^{-1} = 10^{-8} \text{ N rad}^{-1}$.

†Constrained, see ref. [12].

Stretching force constants in mdyn \AA^{-1} , bending force constants in mdyn $\text{\AA}^{-1} \text{ rad}^{-2}$ and stretch-bend interactions in mdyn rad^{-1} .

$r = 109.5$ pm, $R = 145.5$ pm, $T = 120.8$ pm,
 $S = 137.5$ pm, $\alpha = \beta = 109.47^\circ$ and $\theta = \phi = 180^\circ$.

All observed fundamental frequencies for the three isotopic molecules have been used for determining the force field. This was decided, in spite of the isotopic rules, in order to reduce the effects of errors in the measurements. The weights assigned to the data were calculated as: $1/\sigma^2$, where σ was taken as 1% of the observed frequencies, except for the asymmetric C \equiv C stretching modes. As mentioned before, these modes are perturbed by Fermi resonance and hence, σ was taken as 2% of the frequency for these fundamentals.

The results of the least squares refinement of the force constants are given in Table 6. Of the total of 17 force constants, three small interaction constants ($F_{r\beta}$, $F_{\beta\beta}$ and $F_{\alpha\beta}$) were constrained to their values in dimethylacetylene [12]. The force constants are all well determined and comparable in magnitude to those of methylacetylene [12], dimethylacetylene [12], methyldiacetylene [13], diacetylene [14] (see below) and triacetylene [15].

In a recent paper on diacetylene [14] it was reported that a (negative) C \equiv C/C \equiv C interaction constant was necessary in order to reproduce the experimental data on HCCCCH and DCCCCD. However, a closer analysis reveals that this interaction constant is indeterminate from the existing experimental data [14, 16]. Further, *ab initio* calculations on methyldiacetylene [13, 17] indicate a zero value for the C \equiv C/C \equiv C stretching interaction constant in this molecule.

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