Acta Chemica Scandinavica A 37 (1983) 267–275

Structure and Force Field of 1,3-Pentadiyne (Methyldiacetylene)

CLAUS J. NIELSEN and SVEIN SÆBØ

Department of Chemistry, University of Oslo, Oslo 3, Norway

Microwave spectra of 1,3-pentadiyne-5,5,5-d_3 ([5,5,5-$^2H_3$]-1,3-pentadiyne), including four of the ^{13}C isotopic species, and 1,3-pentadiyne-5,5-d_2 have been measured of the vibrational ground state. On the basis of the existing and the new spectroscopic data, the molecular structure (r_o, r_m, r_s) was derived and compared with results from *ab initio* calculations.

The infrared vapour spectrum of 1,3-pentadiyne-5,5,5-d_3 was reinvestigated and the Coriolis coupling constant ζ_{79}^a was determined. Far infrared spectra of the parent molecule were measured and the heretofore unobserved vapour phase frequencies for the $\nu_{13}(e)$ and $\nu_{14}(e)$ modes obtained. A symmetry force field was derived from the vibrational and rotational spectroscopic data.

1,3-Pentadiyne (methyldiacetylene, later to be called MDA) has been subjected to only a few spectroscopic investigations. The microwave spectra of the vibrational ground state and of the first vibrational excited state of $\nu_{14}(e)$ have been studied for MDA and the three deuterated molecules: MDA-1-*d*, MDA-5,5,5-d_3 and MDA-d_4.[1] This investigation was later extended to include a number of ^{13}C isotopes of the parent molecule and of the 1-*d* species.[2] From these data an r_o-structure assuming equal acetylenic bond lengths was proposed.[2] More recently, the microwave spectra of the vibrational excited states, ν_{13}, ν_{14}, $2\nu_{14}$ and $3\nu_{14}$, have been studied in greater detail [3] leading to very accurate rovibronic parameters.

The vibrational spectra of MDA, MDA-1-*d*, MDA-5,5,5-d_3 and MDA-d_4 have been reported.[4] The vibrational spectrum af MDA,[5] including the Coriolis coupling constants for the degenerate methyl vibrations, and a normal coordinate analysis [6] were reported from this laboratory.

EXPERIMENTAL

Small samples of MDA and MDA-5,5,5-d_3 were collected as "intermediates" in the synthesis of 2,4-hexadiyne (dimethyldiacetylene), 2,4-hexadiyne-1,1,1-d_3 and 2,4-hexadiyne-d_6.[7] The isotopic purity of MDA-5,5,5-d_3, checked by mass spectrometry, was *ca.* 97 %.

Microwave spectra were recorded on a Hewlett-Packard 8460A MRR spectrometer. Sample temperatures varied from −40 to −60 °C at pressures less than 0.01 Torr. Frequencies were measured to an accuracy of 0.05 MHz.

Infrared gas phase spectra were measured using a 10 cm cell (CsI windows) and a 20 cm cell (polyethylene windows) on a Bruker IFS 114C Fourier transform spectrometer.

MICROWAVE SPECTRA

The rotational spectra of MDA are those of a strictly symmetric top molecule with a positive value of D_{JK}. A number of strong lines due to vibrational excited states were observed but not studied in any detail. The spectrum of MDA-5,5-d_2, measured as an "isotopic impurity", is that of an extremely near prolate rotor with only the K=1 lines split.

Derived rotational parameters for MDA-5,5,5-d_3, four of the ^{13}C isotopic species and MDA-5,5-d_2 are presented in Table 1. In all cases the rotational constant and D_J are strongly correlated (0.9) and D_J poorly determined. A complete list of frequencies is available from the authors upon

0302-4377/83 $02.50

Table 1. Rotational parameters for 1,3-pentadiyne-5,5,5-d_3, ^{13}C isotopic species and 1,3-pentadiyne-5,5-d_2.

Molecule	B_o [MHz]	D_J [Hz]	D_{JK} [kHz]	N_{obs}	rms [MHz]
$D_3CCCCCH$	1834.8522(4) [a]	70.3(25)	14.553(5)	45	0.012
$D_3{}^{13}CCCCCH$	1795.8834(9)	62(5)	13.981(19)	29	0.023
$D_3C^{13}CCCCH$	1828.2555(23)	113(14)	14.52(6)	19	0.042
$D_3CCC^{13}CCH$	1818.587(3)	81(17)	14.26(5)	16	0.042
$D_3CCCC^{13}CH$	1785.0385(8)	70(4)	13.941(12)	21	0.015
$D_2HCCCCCH$	1899.3777(21) [C_o=1891.3084(21)]	64.(10)	14.189(21)	33	0.034

[a] Errors represent one standard deviation.

Table 2. Structure parameters for 1,3-pentadiyne (MDA) and butadiyne (DA).

	r_o [a]	r_m	r_s	*Ab initio*	
				MDA	DA
$r_{C_8-H_9}$	105.6(1) [b]	105.71(1)	105.5(1)	105.1	105.1
$r_{C_7\equiv C_8}$	120.8(1)	120.86(1)	120.9(1)	119.3	119.3
$r_{C_6-C_7}$	137.6(2)	137.22(1)	137.5(4)	137.9	137.8
$r_{C_5\equiv C_6}$	120.9(2)	120.82(2)	120.8(4)	119.4	119.3
$r_{C_4-C_5}$	145.4(1)	145.43(1)	145.6(3)	146.5	
$r_{C_4-H_1}$	110.7(1)	110.70(2)	110.5(1)	108.1	
$\alpha_{C_5C_4H_1}$	110.32(3)	110.46(1)	110.35(5)	110.6	

[a] Distances in pm. [b] Numbers in parantheses represent the standard deviation.

request or from NBS,* where it has been deposited.

STRUCTURE

The structures of more than 40 molecules containing the acetylenic group have been determined by spectroscopy and electron diffraction.[8] Disregarding the exceptionally short C≡C distance in fluoroacetylene [9] (r_s=119.8±0.3 pm), the C≡C bond distance appears to be almost unaffected by the substituents (r_s=120.4±0.3 and 120.9±0.2 pm in chloroacetylene [9] and *tert*-butylacetylene,[10] respectively). In spite of the experimental uncertainties, the expected trend of sigma electron donating substituents to lengthen and of sigma electron accepting substituents to shorten the C≡C bond is observed. For MDA, with two conjugated C≡C bonds, one would expect much smaller effects upon substitution, but the C≡C bond adjacent to the methyl group to be the longest.

Ab initio *calculations.* The fully optimized structures for 1,3-butadiyne (diacetylene, DA) and MDA were calculated by *ab initio* gradient calculations.

The calculations were carried out using the computer program MOLFORC,[11] in which the energy gradient with respect to the nuclear coordinates is calculated for a single-determinant SCF wavefunction and the molecular geometry determined by the force relaxation method.[12] This program is based on the program MOLECULE,[13] which solves the Roothaan-Hall equations for a basis set of contracted gaussian functions.

The basis set applied was the (7,3)→⟨4,2⟩ basis of Roos and Siegbahn [14] for the carbon atoms, and Huzinagas' (4)→⟨2⟩ [15] basis set scaled by the factor 1.2 for the hydrogen atoms.[16] This basis set is widely used and is expected to

* Microwave Data Center, Molecular Spectroscopy Section, National Bureau of Standards, Washington D. C. 20234, U.S.A.

give consistent descriptions of molecular geometries, with the CC triple bonds about 0.02 Å too short.

For DA the calculations were carried out starting with C_{2v} and C_{2h} symmetries. In both cases the calculations converged to the linear form. The geometry of MDA was optimized without symmetry restrictions. However, the geometry converged to the linear C_{3v} form with almost equal acetylenic bond lengths. In Table 2 the results from the *ab initio* calculations are compared with the experimental structure.

r_o-*structure.* The main problem in determining the structure of MDA is caused by the absence of experimental data for ^{13}C isotopic substitution of the central carbon atom (C_3). Hence, the (small) coordinate for C_3 has to be determined by the first moment equations which are not suited at all for small coordinates. The r_o-structure, given in Table 2, was derived by a least squares procedure using all the experimental moments of inertia for MDA and the isotopically substituted molecules (Table 3). The standard deviation of the fit, being five times larger than the experimental errors, indicates large zero-point vibrational effects. However, attempts to include bond shortening upon deuteration in the refinement leads to large correlation between the structural parameters and unreasonable values for $r_{CH}-r_{CD}$.

r_m-*structure.* It is possible to overcome the apparent inconsistency between the experimental moments of inertia and the structure parameters. This can be accomplished by assuming a functional mass dependence of the vibrational contribution to the effective moments of inertia.[17] As suggested by Watson,[17] a functional relationship of the form:

$$I^\circ = I'(r_m)+\varepsilon_1+\varepsilon_2$$

$$\varepsilon_1 = I'(r_m)^{1/2}$$

$$\varepsilon_2 = \left[\frac{m_1^3\, m_2^3\, m_3^3 \ldots m_N^3}{M^3 I'_a\, I'_b\, I'_c}\right]^{1/2(3N-6)}$$

should give (1) internal consistency between experimental data and structure parameters and (2) a better approximation to the equilibrium structure. As seen, both ε_1 and ε_2 are (as required) [18] homogeneous functions of degree ½ in the mass. Though this definition of the r_m-structure differs from that originally given by Watson,[18] the same labeling of the structure has been used in order to indicate the mass dependence.

In Table 2 are given the results of a least squares refinement where all experimental data (also I_c for MDA-5,5-d_2) have been fitted to the above expression. In view of the uncertainties in the r_o-structure, the differences in the r_m- and r_o-structures are insignificant. However, the parameters in the r_m-structure are far less correlated than in the r_o-structure and all the moments of inertia are reproduced within their experimental uncertainties.

r_s-*structure.* Five of the total of eight substitution coordinates in MDA can readily be determined from the Kraitchman equations [19] using either MDA, MDA-1-*d* or MDA-5,5,5-d_3 as the parent molecule. The two methyl group coordinates, the off-axis distances (x) and the along the axis coordinate (z), for the hydrogen atoms can be determined with either MDA or MDA-5,5,5-d_3 as the parent molecule. This can be accomplished by combining the Kraitchman equations for multiple substitution:

Table 3. Experimental values for the moments of inertia with standard errors for 1,3-pentadiyne.

Molecule	I_b° [u Å^2] [a]
$H_3CCCCCH$ [b]	248.25260(13)
$H_3{}^{13}CCCCCH$ [c]	254.897(6)
$H_3C^{13}CCCCH$ [c]	249.532(6)
$H_3CCC^{13}CCH$ [c]	250.317(6)
$H_3CCCC^{13}CH$ [c]	255.214(6)
$H_3CCCCCD$ [d]	261.8853(27)
$H_3{}^{13}CCCCCD$ [c]	268.829(7)
$H_3C^{13}CCCCD$ [c]	263.298(7)
$H_3CCC^{13}CCD$ [c]	263.790(7)
$H_3CCCC^{13}CD$ [c]	268.550(7)
D_3CCCCH	275.43314(6)
$D_3{}^{13}CCCCH$	281.40975(14)
$D_3C^{13}CCCH$	276.4270(4)
$D_3CCC^{13}CCH$	277.8966(5)
$D_3CCCC^{13}CH$	283.11945(13)
$D_3CCCCCD$ [d]	290.078(3)
$D_2HCCCCCH$	266.07615(29)
	[I_c°=267.2114(3)]

[a] Conversion factor: I B=505379.1 MHz u Å^2. 1 u Å^2=1.660531 10^{-47} kg m^2. [b] From Ref. 3. [c] From Ref. 2. [d] From Ref. 1.

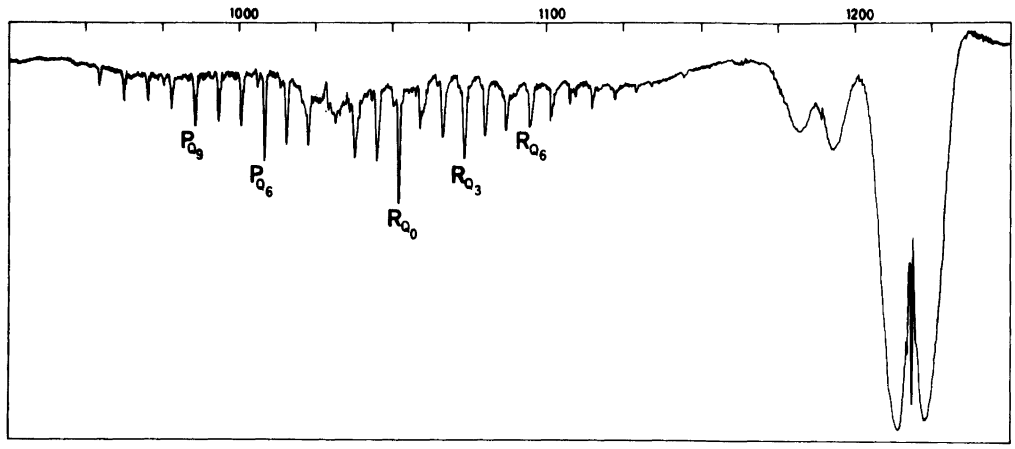

Fig. 1. Infrared spectrum in the region 1250–925 cm^{-1} of 1,3-pentadiyne-5,5,5-d_3 (resolution 0.25 cm^{-1}) showing the ν_6 (a_1) band at 1025 cm^{-1}, the ν_9(e) band at 1046 cm^{-1}, the ν_5(a_1) band at 1187 cm^{-1} and the $2\nu_{11}$(a_1+e) band at 1218 cm^{-1}.

$CH_3 \rightarrow CD_3$:

$$\Delta I_3 = \frac{3}{2}\Delta m x^2 + \mu_3 z^2,\ \mu_3 = \frac{3\,\Delta m M}{M+3\Delta m}$$

$CH_3 \rightarrow CD_2H$:

$$\Delta I_2 = \frac{1}{4}\mu_2 x^2 + \mu_2 z^2,\ \mu_2 = \frac{2\,\Delta m M}{m+2\Delta m}$$

$CD_3 \rightarrow CH_3$:

$$\Delta I_3 = \frac{3}{2}\Delta m x^2 + \mu_3 z^2,\ \mu_3 = \frac{3\,\Delta m M}{M+3\Delta m}$$

$CD_3 \rightarrow CD_2H$:

$$\Delta I_1 = \mu_1 x^2 + \mu_1 z^2,\ \mu_1 = \frac{\Delta m M}{M+\Delta m}$$

In both cases (the determinant being *ca.* 1.5) the equations are easily solved. If the x-coordinate for the methyl hydrogen is transferred from MDA or MDA-5,5,5-d_3 to MDA-1-*d*, then the corresponding z-coordinate in MDA-1-*d* can be found from the equation for the $CH_3 \rightarrow CD_3$ substitution.

The remaining coordinate for the central carbon atom has to be determined from the first moment equations. This coordinate was found to be +0.070±0.004, +0.204±0.001 and +0.013±0.005 Å in MDA, MDA-5,5,5-d_3 and MDA-1-*d*, respectively. The derived r_s-structure is compared with the r_o- and the r_m-structure in Table 2.

VIBRATIONAL SPECTRA

Coriolis coupling constants in MDA-5,5,5-d_3. The Coriolis coupling constants for the degenerate methyl vibrations have been determined for MDA.[5] For MDA-5,5,5-d_3 the corresponding vibrational bands (ν_8, ν_9 and ν_{10}) should all show resolvable rotational fine structure. However, due to the limited amount of sample, the ν_{10} band at *ca.* 850 cm^{-1} was too weak to be observed with any confidence. The ν_8 band at *ca.* 2250 cm^{-1} was partly obscured by the stronger ν_2(a_1) band at 2258 cm^{-1} and it was not possible to determine the band centre. Hence, only the ν_9 band at *ca.* 1050 cm^{-1} was studied in detail.

The Q-branches of the sub-bands that arise from the $\Delta K=\pm 1$, $\Delta J=0$ transitions are given by the expression:[20]

$$\nu_9^K = \nu_9 + [A'(1-\zeta_9)^2 - B'] \pm 2[A'(1-\zeta_9) - B']K + [(A'-A'') - (B'-B'')]K^2$$

Using the experimental value for B'', a value for A'' calculated from the r_o-structure (A''=2.590 cm^{-1}) and further assuming that $B'=B''$, ζ_9 and ν_9 can be calculated from the above equation.

As shown in Fig. 1, the ν_9 band is overlapped by the weak ν_6(a_1) band at *ca.* 1025 cm^{-1}. The intensity distribution among the sub-bands permits a choice of either *ca.* 1051 or *ca.* 1031 cm^{-1} as the $K=0\rightarrow 1$ transition. That the former is prob-

Table 4. ν_9 of 1,3-pentadiyne-5,5,5-d_3.

K-Value in sub-bands	P_{Q_K}		R_{Q_K}	
	Obs. [cm^{-1}]	Obs.−calc.	Obs. [cm^{-1}]	Obs.−calc.
0			1051.33	−0.24
1	1044.58	0.26	1058.56	−0.23
2	1037.34	0.31	1066.28	0.31
3			1073.03	−0.09
4	1021.91	−0.43	1080.26	0.03
5	1014.68	−0.26	1087.01	−0.30
6	1007.44	−0.07	1094.73	0.39
7	1000.21	0.17	1101.48	0.13
8	992.49	−0.04		
9	985.26	0.27	1114.99	−0.25
10	977.54	0.13	1122.22	0.08
11	969.83	0.03	1128.97	−0.26
12	962.11	−0.04		
13	954.39	−0.07		
14	946.68	−0.06		
	ν_9^0=1046.4±0.3 cm^{-1} [a]			
	ζ_9=−0.41±0.02			

[a] Estimated from an uncertainty in A′ of 5 %.

ably the correct assignment is supported by a solution/vapour shift of 20 cm^{-1} for this type of vibration.[5]

The observed Q-branches are listed in Table 4 together with the derived parameters. A standard error of 0.3 cm^{-1} for the fit is rather larger in view of the resolution used in obtaining the spectrum (*ca.* 0.25 cm^{-1}), but a secord order Coriolis coupling with ν_5 and/or ν_6 is a plausible explanation for this.

Vibrational fundamentals. From the two previous investigations of the vibrational spectra of MDA [4,5] and the deuterated molecules [5] a reliable assignment of most of the fundamental modes of vibration is known. Three obvious cases of Fermi resonance are observed. The ν_3 mode

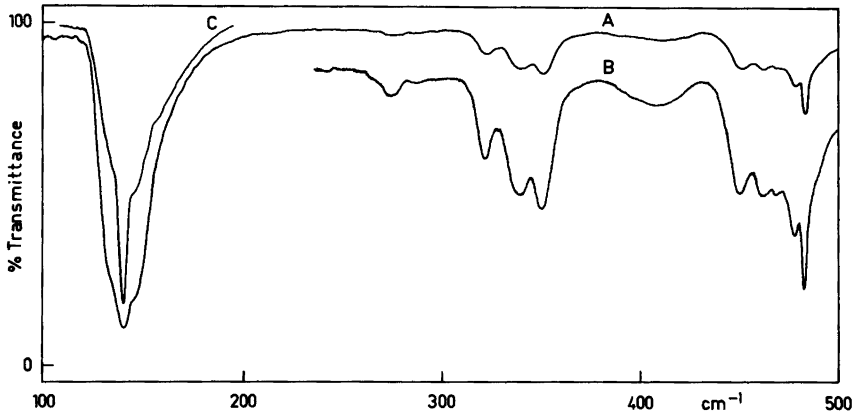

Fig. 2. Far infrared spectrum of 1,3-pentadiyne as a vapour. (A) 50 Torr, 20 cm, (B) scale expansion of A and (C) 10 Torr, 20 cm.

Table 5. Far infrared vapour phase spectral data for 1,3-pentadiyne.

Wavenumber	Interpretation [a]
482 w,⊥	ν_{12} *e*
476 w,⊥	$\nu_{11}-\nu_{14}=475$ A_1+E, $2\nu_{12}-\nu_{12}$ *E*
470 vw, sh,⊥	$3\nu_{12}-2\nu_{12}$ *E* ?
461, 449 w,∥	$\nu_{13}+\nu_{14}=459$ A_1+E
~420 vw,bd	$\nu_{10}-\nu_{11}=415$ A_1+E
349, 338 w,∥	$\nu_{12}-\nu_{14}=343$ A_1+E
320 w,⊥	ν_{13} *e*
~290 vvw ?	$\nu_{11}-\nu_{13}=294$ A_1+E
~274 vw,⊥ ?	$2\nu_{14}=278$ A_1+E
139 s,⊥	ν_{14} *e*

[a] Abbreviations: s: strong; v: very; w: weak; ||: parallel; ⊥: perpendicular; bd: broad; sh: shoulder.

(C≡C asym. stretch) in MDA and MDA-1-*d* is in resonance with the $2\nu_6$ mode.[4] Assuming an anharmonicity $X_6=0.001$, estimated from the 1-halogenated 1,5-pentadiynes,[5] corrections were made for the ν_3 fundamentals. Fermi resonance is also observed between ν_2 (≡C–D stretch) and $\nu_4+\nu_7$ in MDA-d_4. Since no frequency shift is expected for this mode in going from MDA-1-*d* to MDA-d_4, ν_2 is assumed to have the same frequency in these two molecules. In a few cases the fundamentals above 400 cm^{-1} have not been observed in the vapour phase. When possible, these fundamental frequencies were corrected by transferring the corresponding liquid/vapour shifts observed for the other isotopic species.

The two lowest degenerate fundamentals, ν_{13} and ν_{14}, have not been observed in the vapour phase previously. In Fig. 2 the far IR vapour phase spectrum of MDA is shown, while the wave numbers of the observed bands are given in

Table 6. Internal valence symmetry coordinates for 1,3-pentadiyne with reference to Fig. 3.

A_1

$$S_1=3^{-1/2}(\Delta r_1+\Delta r_2+\Delta r_3)$$
$$S_2=-(3(1+K^2))^{-1/2}(K(\Delta\alpha_1+\Delta\alpha_2+\Delta\beta_3)+(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3))\ ^a$$
$$S_3=\Delta r_4$$
$$S_4=\Delta r_5$$
$$S_5=\Delta r_6$$
$$S_6=\Delta r_7$$
$$S_7=\Delta r_8$$

E

$$S_{8a}=6^{-1/2}(2\Delta r_1-\Delta r_2-\Delta r_3) \qquad S_{8b}=2^{-1/2}(\Delta r_2-\Delta r_3)$$
$$S_{9a}=6^{-1/2}(2\Delta\alpha_1-\Delta\alpha_2-\Delta\alpha_3) \qquad S_{9b}=2^{-1/2}(\Delta\alpha_2-\Delta\alpha_3)$$
$$S_{10a}=6^{-1/2}(2\Delta\beta_1-\Delta\beta_2-\Delta\beta_3) \qquad S_{10b}=2^{-1/2}(\Delta\beta_2-\Delta\beta_3)$$
$$S_{11a}=\Delta\gamma_x \qquad S_{11b}=\Delta\gamma_y$$
$$S_{12a}=\Delta\delta_x \qquad S_{12b}=\Delta\delta_y$$
$$S_{13a}=\Delta\varepsilon_x \qquad S_{13b}=\Delta\varepsilon_y$$
$$S_{14a}=\Delta\zeta_x \qquad S_{14b}=\Delta\zeta_y$$

[a] The angle redundancy has been removed: $\Delta\alpha=K\Delta\beta$, $K=3\sin\beta\cos\beta/\sin\alpha$.

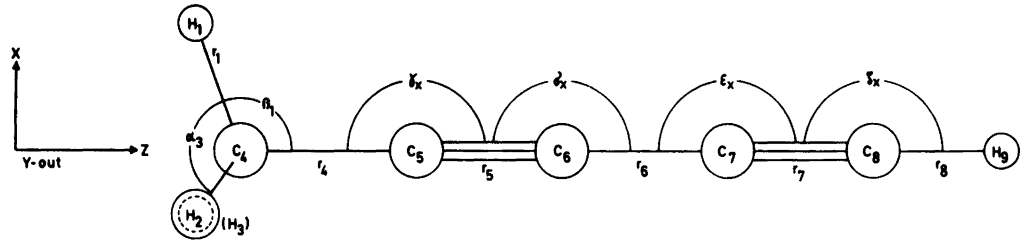

Fig. 3. Valence coordinates for 1,3-pentadiyne.

Table 7. Force constants and standard errors, in symmetry coordinate representation, for 1,3-pentadiyne. Stretching force constants in mdyn/Å, bending force constants in mdynÅ/rad^2 and stretch-bend interactions in mdyn/rad.

	F [a]	σ(F)	R,B,C [b]		F	σ(F)	R,B,C
$F_{1,1}$	4.953	0.034	4.96	$F_{8,8}$	4.777	0.032	4.71
$F_{1,2}$	0		0	$F_{8,9}$	0		0
$F_{2,2}$	0.5866	0.0070	0.51	$F_{8,10}$	0		0
$F_{2,3}$	–0.426	0.037	–0.34	$F_{9,9}$	0.559	0.014	0.53
$F_{3,3}$	5.54	0.23	5.57	$F_{9,10}$	–0.01	0.03	0
$F_{3,4}$	0.34	–	0	$F_{10,10}$	0.639	0.025	0.68
$F_{4,4}$	15.67	0.21	15.17	$F_{10,11}$	–0.062	0.019	0
$F_{4,5}$	1.14	–	0	$F_{11,11}$	0.316	0.029	0.42
$F_{4,6}$	0		0	$F_{11,12}$	0.071	0.017	0
$F_{5,5}$	7.23	0.35	7.52	$F_{12,12}$	0.314	0.021	0.38
$F_{5,6}$	0.72	0.30	0	$F_{12,13}$	0.015	0.015	0
$F_{6,6}$	15.14	0.31	14.39	$F_{13,13}$	0.348	0.036	0.37
$F_{6,7}$	0		0	$F_{13,14}$	0.127	0.009	0
$F_{7,7}$	5.979	0.047	5.95	$F_{14,14}$	0.212	0.002	0.17

[a] 1 mdyn/Å=10^2 N/m, 1 mdynÅ/rad^2=10^{-18} Nm/rad^2, 1 mdyn/rad=10^{-8} N/rad. [b] Rogstad, Benestad and Cyvin (Ref. 6) assumed tetrahedral angles and the following geometry: r_1=110.0, r_4=145.8, r_5=r_7=120.7, r_6=137.5 and r_8=105.7 pm.

Table 5 with the proposed assignment. Apart from the possible hot-band progression of the ν_{12} mode at 482 cm^{-1}, the rest of the observed bands are unambiguously assigned.

FORCE CONSTANT CALCULATION

In Table 6, internal valence symmetry coordinates are given which can be interpreted by reference to Fig. 3. The molecular geometry is taken as the r_s-structure given in Table 2 and the atomic masses are based upon the ^{12}C-scale.

All the available data on vibrational frequencies, centrifugal distortion constants and Coriolis coupling constants for the various isotopic species have been used for calculating the force field. Since anharmonicity constants for MDA are unknown, and the corrections to harmonic frequencies would have to be guessed, the anharmonic vapour phase frequencies have been used whenever possible.

The weights, w_i, assigned to the data were calculated from the equation: $w_i=1/\sigma_i^2$, where σ_i is the estimated probable error in the ith datum. σ_i has been taken equal to 0.01(frequency), but not less than 5 cm^{-1} for the vibrational frequencies. For the ζ constants, an uncertainty of 0.05 has been allowed to account for unknown anhar-

Table 8. 1,3-Pentadiyne; observed data and uncertainties (σ), calculated data and errors (ε). Fundamental modes of vibration in wavenumbers, D_J in Hz, D_{JK} in kHz, ζ-constants dimensionless and l-type doubling constants, q_i, in MHz.

	Obs.	σ	Calc.	ε
$H_3CCCCCH$ [a]				
ν_1	3333	33	3343	–10
ν_2	2935	29	2938	–3
ν_3	2257 [b]	23	2261	–4
ν_4	2079	21	2082	–3
ν_5	1385	14	1394	1
ν_6	1150	12	1170	–20
ν_7	696	7	687	–9
ν_8	2977	30	2996	–19
ν_9	1446	14	1449	–3
ν_{10}	1029	10	1031	–2
ν_{11}	614	6	616	–2
ν_{12}	484	5	486	–2
ν_{13}	320	5	320	0
ν_{14}	139	5	138	1
ζ_8	0.08	0.05	0.15	–0.07
ζ_9	–0.34	0.05	–0.37	0.03
ζ_{10}	0.40	0.05	0.36	0.04
ζ_{13}	0.94	0.05	0.93	0.01
ζ_{14}	0.96	0.05	0.96	0.

q_{13}	0.985	–	1.027	
q_{14}	2.108	–	2.161	
D_J	68.	15.	77.	–9.
D_{JK}	19.83	0.99	20.07	–0.24
$H_3CCCCCD$ [c]				
ν_1	2935	29	2938	–3
ν_2	2600	26	2588	12
ν_3	2244 [b]	22	2247	–3
ν_4	1968	20	1969	–1
ν_5	1385	14	1384	1
ν_6	1148	11	1161	–13
ν_7	681	7	678	3
ν_8	2976 [d]	30	2996	–20
ν_9	1446 [d]	14	1449	–3
ν_{10}	1029	10	1031	–2
ν_{11}	491	5	492	–1
ν_{12}	469	5	466	3
ν_{13}	314 [c]	5	315	–1
ν_{14}	131 [f]	5	134	–3
q_{14}	1.956	–	2.002	
D_J	62.	6.	67.	–5.
D_{JK}	18.31	0.92	18.47	–0.16
$D_3CCCCCH$ [c]				
ν_1	3334	33	3343	–9
ν_2	2258	23	2264	–6
ν_3	2123	21	2122	1
ν_4	2079	21	2076	3
ν_5	1187	12	1188	–1
ν_6	1025	10	1030	–5
ν_7	652	7	645	7
ν_8	2250	22	2234	16
ν_9	1046	10	1043	3
ν_{10}	827 [f]	8	825	2
ν_{11}	614	6	616	–2
ν_{12}	478	5	479	–1
ν_{13}	308 [e]	5	305	3
ν_{14}	134 [f]	5	131	3
ζ_9	–0.41	0.05	–0.44	0.03
q_{14}	1.804	–	1.913	
D_J	70.	5.	63.	7.
D_{JK}	14.55	0.73	14.51	0.04
$D_3CCCCCD$ [c]				
ν_1	2600 [b]	26	2588	12
ν_2	2250	23	2251	–1
ν_3	2121	21	2118	3
ν_4	1964	20	1968	–4
ν_5	1185	12	1181	4
ν_6	1028	10	1026	2
ν_7	646	6	638	6
ν_8	2250	23	2234	16
ν_9	1045 [d]	10	1043	2
ν_{10}	826	8	825	1
ν_{11}	490	5	485	5
ν_{12}	466	5	466	0
ν_{13}	298 [e]	5	301	–3
ν_{14}	125 [f]	5	127	–2
q_{14}	1.684	–	1.772	
D_J	103.	–	55.	
D_{JK}	13.48	0.67	13.41	0.07
$D_3{}^{13}CCCCCH$				
D_J	62.	10.	61.	1.
D_{JK}	13.98	0.70	13.89	0.09
$D_3C^{13}CCCCH$				
D_J	113.	–	62.	
D_{JK}	14.52	0.73	14.47	0.05
$D_3CCC^{13}CCH$				
D_J	81.	34.	62.	19.
D_{JK}	14.26	0.71	14.23	0.03
$D_3CCCC^{13}CH$				
D_J	70.	8.	59.	11.
D_{JK}	13.94	0.70	13.86	0.08
$D_2HCCCCCH$				
D_J	64.	20.	69.	–5.
D_{JK}	14.19	0.71	14.35	–0.16

[a] Vibrational frequencies from Ref. 5, Coriolis coupling constants from Ref. 5 and Ref. 3, *l*-type doubling constants from Ref. 2 and distortion constants from Ref. 1. [b] Corrected for Fermi resonance. [c] Vibrational frequencies from Ref. 4, distortion constants and *l*-type doubling constants from Ref. 1. [d] Corrected from (R_{Q_0}) to center frequency. [e] Solution data from Raman spectrum. [f] Corrected for liquid/vapour frequency shift.

monicity effects. The $\sigma(D_J)$ have been taken as two times the standard error on these constants (poorly determined) and the $\sigma(D_{JK})$ have been taken as 5 % of their values to allow for anharmonicity.

The results of a convergence to a 23 parameter force field are given in Table 7. In the A_1 species it was found necessary to constrain the

stretch–stretch interaction constants $F_{3,4}$ and $F_{4,5}$ to their values in 2,4-hexadiyne (dimethyldiacetylene).[21] The E species force constants are more reliably fixed, primarily due to the availability of D_{jk} for a number of ^{13}C isotopic substituted molecules. The reproduction of the observed data for all isotopes of MDA, calculated using the force field of Table 7, is given in Table 8.

Acknowledgements. The authors are grateful to the Department of Chemical Physics, University of Copenhagen, for the use of their microwave spectrometer. Financial support from the Norwegian Research Council for Science and the Humanities is acknowledged.

REFERENCES

1. Heath, G. A., Thomas, L. F., Sherrad, E. I. and Sheridan, J. *Discuss. Faraday Soc. 19* (1955) 38.
2. Thomas, L. F., Heeks, J. S. and Sheridan, J. *Arch. Sci. 10* (1957) 180.
3. Maier, M. *Thesis,* University of Sussex, Sussex 1977.
4. Lamotte, J., Lavalley, J. C. and Romanet, R. *J. Chim. Phys. Phys. Chim. Biol. 70* (1973) 1077.
5. Benestad, L., Augdahl, E. and Kloster-Jensen, E. *Spectrochim. Acta A 31* (1975) 1329.
6. Rogstad, A., Benestad, L. and Cyvin, S. J. *J. Mol. Struct. 23* (1974) 265.
7. Maier, J. P., Marthaler, O. and Kloster-Jensen, E. *J. Chem. Phys. 72* (1980) 701.
8. Callomon, J. H., Hirota, E., Kuchitsu, K., Lafferty, W. J., Maki, A. G. and Pote, C. S. *Structure Data of Free Polyatomic Molecules,* Springer, Berlin 1976.
9. Tyler, J. K. and Sheridan, J. *Trans. Faraday Soc. 59* (1963) 2661.
10. Nugent, L. J., Mann, D. E. and Lide, D. R. *J. Chem. Phys. 36* (1962) 965.
11. Sæbø, S. *The Program System MOLFORC,* Program Manual, Department of Chemistry, University of Oslo, Oslo 1979.
12. Pulay, P. *Mol. Phys. 17* (1969) 197.
13. Almlöf, J. *The Program System MOLECULE,* USIP Report 74–29, University of Stockholm, Stockholm 1974.
14. Roos, B. and Siegbahn, P. *Theor. Chim. Acta 17* (1970) 209.
15. Huzinaga, S. *J. Chem. Phys. 42* (1965) 1293.
16. Dunning, T. H., Jr., *J. Chem. Phys. 53* (1970) 2823.
17. Watson, J. K. G. *5th International Seminar on High Resolution Infrared Spectroscopy,* Prague 1978.
18. Watson, J. K. G. *J. Mol. Spectrosc. 48* (1973) 479.
19. Kraitchman, J. *Am. J. Phys. 21* (1953) 17.
20. Thomas, R. K. and Thompson, H. W. *Spectrochim. Acta A 24* (1968) 1337.
21. Nielsen, C. J. *To be published.*

Received August 30, 1982.