

THE MICROWAVE SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF 1,4-PENTADIYNE

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ABSTRACT

The microwave spectra of 1,4-pentadiyne and 1,4-pentadiyne-1,5- d_2 are assigned and rotational and centrifugal distortion constants obtained. A unique structure could not be determined. However, analysis of the moments of inertia indicates that the bond distances in C_5H_4 are close to typical values found in other related compounds. An interaction involving the acetylene moieties is evidenced by the derived bond angles. The data are consistent with either the central CCC angle being close to the tetrahedral value with the acetylene groups pushed away from linearity by approximately 3–4° or opening of the central CCC angle to about 113° along with linear acetylene groups. A range of structures between these two is also possible. The dipole moment is determined to be 0.516(5) D.

INTRODUCTION

1,4-Pentadiyne with two acetylene moieties bonded to the same carbon atom is an interesting species for investigation by microwave (MW) spectroscopy. The photoelectron spectrum of this compound has revealed electronic interactions between the nominally degenerate π orbitals sufficient to result in three distinct π orbital ionization energies [1]. This raises the question of whether some structural perturbations may also occur similar to the angular deformations observed for other acetylene groups such as in propynal [2], 1,8-bis-(prop-1-ynyl)naphthalene [3] (cf. Fig. 1) or in isoelectronic malononitrile [4] (cf. Fig. 2).

The MW spectrum of pentadiyne should also be of interest as a possible interstellar species. The discovery of molecules such as HC_nN ($n=1,3 \dots 9$) in interstellar clouds has led to proposals that acetylene-based ion chemistry gives rise to these long chains [5]. Such a reaction chemistry could also lead to linear acetylenic species (HC_nH) and the non-linear 1,4-pentadiyne. Pure rotational transitions of the linear species cannot normally be detected although it has been suggested that diffuse interstellar bands at $\lambda > 4000 \text{ \AA}$ could be due to long carbon-chain molecules [6].

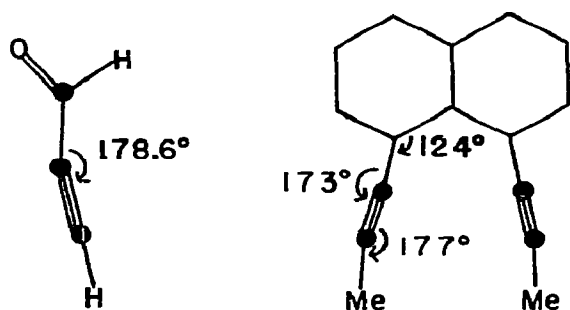


Fig. 1. Angular deformations in propynal [2] and 1,8-bis(prop-1-ynyl)naphthalene [3].

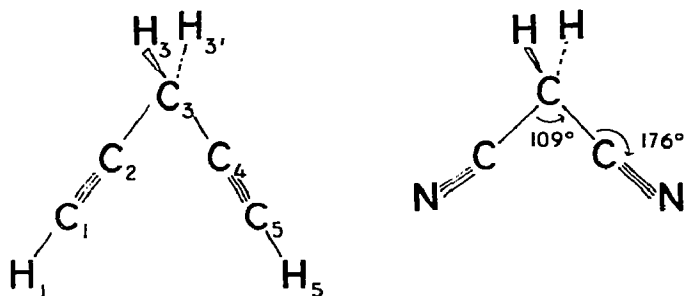


Fig. 2. Numbering scheme for 1,4-pentadiyne; angular deformation in malononitrile.

EXPERIMENTAL*

Materials

1,4-Pentadiyne

This was prepared by the cuprous chloride catalyzed coupling reaction of ethynyl magnesium bromide with propargyl bromide in tetrahydrofuran [7]. This reaction is inefficient and produces several products. The yields of product were low and variable (1–20%) precluding the economical preparation of isotopic species. In the later stages of this study, 1,4-pentadiyne was supplied as a 10% solution in tetrahydrofuran-heptane from Farchan Division, Story Chemical Company, Willoughby, Ohio. Separation was achieved by gas-liquid phase chromatography (GLPC) on a Varian 90P chromatograph using a 2 m × 1 cm column containing 20% Apiezon L on Chromosorb W. On elution at 70°C, 1.7 × 10⁵ Pa helium pressure, 1,4-pentadiyne has a 2 min retention time.

1,4-Pentadiyne-1,5-d₂

A solution containing 10 ml of 10% 1,4-pentadiyne in tetrahydrofuran-heptane was added to 100 ml of dibutyl ether. After cooling to -78°C,

*Certain commercial instruments and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the items identified are necessarily the best available for the purpose.

15 ml of 1.24 N t-butyllithium in pentane was added dropwise. A large yellowish-white precipitate formed. After warming to 25°C, 75% of the solvent was removed in vacuo and 10 ml of D₂O was added. The organic layer was separated, dried over MgSO₄ and distilled. 1,4-Pentadiyne-1,5-*d*₂ was separated by GLPC (see above). Enrichment was in excess of 90%.

Spectrometers

The spectra were obtained using 33 and 80 KHz Stark spectrometers with klystron and backward wave oscillator sources at the University of Michigan and the National Bureau of Standards (NBS). The measurements above 100 GHz were obtained on the NBS spectrometer using a phase locked OKI 120V10 klystron under computer control [8]. The accuracy of the measurements was ±0.2 MHz. However, many of the high frequency transitions were only partially modulated and their true line centers may be shifted by as much as 0.3 MHz from the reported values. Spectra were normally recorded at temperatures of approximately -25°C where the sample had sufficient vapor pressure.

Spectra

The spectrum was characteristic of a slightly asymmetric prolate top ($\kappa = 0.96$) with C_{2v} symmetry and μ_b transitions. This resulted in two prominent, low K , R branch series with transitions separated by roughly $(B + C)$ and several Q branch series with origins at rough multiples of $[A - 1/2(B + C)](2K + 1)$. The initial assignment of several low J transitions between 18–36 GHz was obtained from their resolved Stark effects. The centrifugal distortion parameters derived from these frequencies enabled a straightforward assignment of the millimeter-wave transitions. The $K' = 4 \leftarrow K'' = 3$ Q branch series originating at 114.56 GHz had transitions of opposite symmetry close enough to readily observe the 1:6 alternation of intensity expected for C_{2v} symmetry. For example, the two $J = 6$ transitions are illustrated in Fig. 3. The assigned transitions are listed in Table 1. The rotational constants and centrifugal distortion constants obtained from the Watson formulation [9] as programmed by Kirchhoff [10] are listed in Table 3.

The doubly deuterated species, CH₂(C≡CD)₂, was synthesized (see above) and a number of low J transitions were assigned. These transition frequencies are listed in Table 2. The derived rotational constants and centrifugal distortion constants are listed in Table 3. The small number of transitions for this species (and the excited vibrational state described below) does not allow very well determined centrifugal distortion constants.

Considerable effort was expended to assign the ¹³C species in natural abundance using the sensitive spectrometer at NBS. The high J , R branch transitions in the region of 100–122 GHz were intense enough for detection. However, it was difficult to obtain assignments which could be confidently

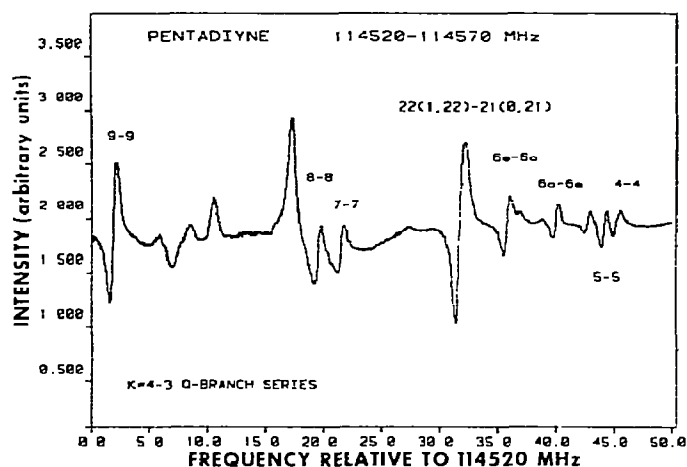


Fig. 3. Spectrum between 114.52–114.57 GHz. Stark field = 2500 V cm⁻¹.

TABLE 1

Transitions assigned for the ground state of C₅H₄

$J'(K'_-,K'_+)-J''(K''_-,K''_+)$	ν (MHz)	$\Delta\nu$ (MHz) ^a	$J'(K'_-,K'_+)-J''(K''_-,K''_+)$	ν (MHz)	$\Delta\nu$ (MHz)
2(1,1)–2(0,2)	16899.14	0.00	14(2,13)–13(1,12)	109584.52	0.04
6(0,6)–5(1,5)	18100.37	0.04	21(1,21)–20(0,20)	109808.00	0.13
4(1,3)–4(0,4)	18143.73	0.03	18(4,14)–18(3,15)	111968.50	–0.02
5(1,4)–5(0,5)	19071.16	0.06	22(0,22)–21(1,21)	111991.90	–0.14
6(1,5)–6(0,6)	20225.36	0.05	14(4,10)–14(3,11)	113790.93	–0.03
1(1,1)–0(0,0)	21596.93	–0.18	12(4,8)–12(3,9)	114197.88	0.05
7(1,6)–7(0,7)	21627.28	0.06	6(3,3)–5(2,4)	114255.51	–0.26
8(1,7)–8(0,8)	23299.28	0.03	11(4,7)–11(3,8)	114324.65	0.10
7(0,7)–6(1,6)	24244.96	0.02	16(4,13)–16(3,14)	114353.96	–0.06
9(1,8)–9(0,9)	25264.01	0.06	15(4,12)–15(3,13)	114362.56	–0.06
2(1,2)–1(0,1)	26638.85	–0.05	17(4,14)–17(3,15)	114364.44	–0.04
10(1,9)–10(0,10)	27542.53	0.14	14(4,11)–14(3,12)	114383.65	–0.04
11(1,10)–11(0,11)	30152.26	0.14	18(4,15)–18(3,16)	114401.67	–0.02
8(0,8)–7(1,7)	30442.87	0.04	13(4,10)–13(3,11)	114411.77	0.01
3(1,3)–2(0,2)	31513.62	–0.09	10(4,6)–10(3,7)	114414.55	0.10
4(1,4)–3(0,3)	36227.87	–0.15	12(4,9)–12(3,10)	114442.45	–0.01
19(1,19)–18(0,18)	100496.36	0.01	9(4,6)–9(3,7)	114522.22	0.01
26(4,22)–26(3,23)	101169.15	0.01	8(4,5)–8(3,6)	114539.83	0.00
20(0,20)–19(1,19)	101278.05	–0.04	7(4,3)–7(3,4)	114541.85	0.02
22(1,21)–21(2,20)	101333.49	–0.07	22(1,22)–21(0,21)	114552.25	0.36
12(2,11)–11(1,10)	102758.06	0.02	6(4,2)–6(3,3)	114556.12	0.03
27(2,25)–26(3,24)	103791.43	0.04	6(4,3)–6(3,4)	114560.32	–0.01
24(4,20)–24(3,21)	104876.70	–0.01	5(4,1)–5(3,2)	114563.05	0.01
25(2,24)–25(1,25)	105081.94	–0.10	5(4,2)–5(3,3)	114564.45	–0.01
20(1,20)–19(0,19)	105120.35	0.09	29(1,28)–29(0,29)	116980.68	0.10
13(2,12)–12(1,11)	106230.55	0.07	23(0,23)–22(1,22)	117268.50	–0.03
27(1,26)–27(0,27)	106273.67	–0.02	29(2,28)–29(1,29)	122174.89	–0.02
23(4,19)–23(3,20)	106496.20	0.05	24(0,24)–23(1,23)	122502.40	–0.00
21(0,21)–20(1,20)	106664.48	–0.03			

^a $\nu_{\text{obs.}} - \nu_{\text{calc.}}$

TABLE 2

Transitions assigned for the excited vibrational state of C_5H_4 and ground state of $C_5H_2D_2$

$J'(K'_-, K'_+) - J''(K''_-, K''_+)$	C_5H_4 (vib. state)		$CH_2(CCD)_2$	
	ν (MHz)	$\Delta\nu$ (MHz) ^a	ν (MHz)	$\Delta\nu$ (MHz) ^a
6(0,6)–5(1,5)	18018.53	0.03		
4(1,3)–4(0,4)	18396.02	0.02		
5(1,4)–5(0,5)	19343.51	–0.02		
6(1,5)–6(0,6)	20523.09	–0.01	18428.85	0.02
1(1,1)–0(0,0)	21823.07	0.04	19674.14	–0.01
7(1,6)–7(0,7)	21956.17	0.04	19686.03	0.02
8(1,7)–8(0,8)	23665.60	–0.05	21184.71	–0.02
7(0,7)–6(1,6)	24192.14	–0.00		
9(1,8)–9(0,9)	25674.78	0.01	22945.11	–0.05
2(1,2)–1(0,1)	26872.62	–0.07	24214.72	0.01
10(1,9)–10(0,10)	28005.01	0.02	24986.27	
8(0,8)–7(1,7)	30419.34	–0.02	27194.30	0.00
11(1,10)–11(0,11)	30674.16	–0.01	27323.91	0.00
3(1,3)–2(0,2)	31751.77	0.07	28604.97	–0.01
9(0,9)–8(1,8)			32804.24	0.00
4(1,4)–3(0,3)	36466.88	–0.03	32850.84	0.01
13(1,12)–13(0,13)			32928.62	–0.01
14(1,13)–14(0,14)			36199.12	0.00
22(0,22)–21(1,21)	112209.61	0.00		
22(1,22)–21(0,21)	114756.95	0.00		

^a $\nu_{\text{obs.}} - \nu_{\text{calc.}}$

TABLE 3

Rotational and centrifugal distortion constants for 1,4-pentadiyne

Parameter	C_5H_4 ($\nu = 0$)	C_5H_4 ($\nu = 1$)	$C_5H_3D_2$ ($\nu = 0$)
A (MHz)	19076.77 ± 0.02^a	19300.82 ± 1.12	17408.28 ± 11.2
B (MHz)	2859.224 ± 0.003	2870.209 ± 0.002	2574.372 ± 0.013
C (MHz)	2520.801 ± 0.003	2524.656 ± 0.005	2270.134 ± 0.013
τ_1 (kHz)	239.2 ± 0.1	237.9 ± 9.0	201.2 ± 6.3
τ_2 (kHz)	21.82 ± 0.01	24.91 ± 3.8	20.7 ± 8.9
τ_3 (kHz) ^b	606.8 ± 1.1	1579 ± 900	1252 ± 2195
τ_{aaaa} (kHz)	-2963 ± 3	-10231 ± 4466	-17460 ± 45000
τ_{bbbb} (kHz)	-11.38 ± 0.01	-12.96 ± 1.46	-10.59 ± 1.71
τ_{cccc} (kHz)	-3.165 ± 0.011	-3.94 ± 0.83	-3.16 ± 0.57

^aThe uncertainties represent one standard deviation as estimated by the least squares fit.^b τ_3 is not strictly speaking an independently determinable parameter but it is fixed by setting $R_3 = 0$. See ref. 10.

attributed to these species. The expected transition regions often had several weak candidates and several plausible fits could be obtained. It was finally decided not to include this data in the structural analysis.

Satellite transitions from one excited vibrational state were also readily apparent. The transitions that were assigned are listed in Table 2 and derived constants are found in Table 3. Rough relative intensities suggested that this was a symmetric vibrational state, with a frequency of $140 \pm 20 \text{ cm}^{-1}$. By comparison, malononitrile also has an A_1 vibration at 167 cm^{-1} assigned to a CCN bending mode. The next three fundamentals in malononitrile are near 367 cm^{-1} [11].

Dipole moment

The Stark splittings for 3 transitions were measured at various electric field values. The observed ratios of $\Delta\nu/\epsilon^2$ are listed in Table 4. The resulting dipole moment is $0.516(5) \text{ D}$. OCS was used to calibrate the waveguide cell spacing where $\mu_{\text{OCS}} = 0.7159(3)$ [12].

STRUCTURE DETERMINATION

The alternation of intensity and near identity of $I_a + I_b - I_c$ for the two isotopic species is consistent with the expected C_{2v} symmetry. For this point group, there are 8 independent structural parameters if the C—C≡C—H linkages are not assumed to have fixed bond angles of 180° . The two isotopic species result in 5 independent moments of inertia and so a completely unambiguous structural determination is not possible. Nevertheless, because the central HCH angle and the C—H interatomic distances can be expected to fall close to "standard" values, some insight into the other structural parameters can be obtained.

One complication is apparent with the moments of inertia that was also observed in malononitrile as well as other molecules that contain two hydrogen atoms projecting above and below a planar, heavy atom framework [13]. In such cases $I_a + I_b - I_c = 4m_{\text{H}}d^2 \sin^2\theta$, where d is the C—H distance and θ is $1/2$

TABLE 4

Stark coefficients and dipole moment for C_2H_4

Transition	$\Delta\nu/\epsilon^2$ (meas.) (MHz cm ² V ⁻²)	$\Delta\nu/\epsilon^2$ (obs.) (MHz cm ² V ⁻²)
$M = 0$ $1_{11} - 0_{00}$	2.69×10^{-6}	2.71×10^{-6}
$M = 5$ $5_{13} - 5_{05}$	2.48×10^{-6}	2.46×10^{-6}
$M = 8$ $8_{17} - 8_{08}$	1.73×10^{-6}	1.72×10^{-6}

$\mu_{\text{B}} = \mu_{\text{total}} = 0.516 \pm 0.005 \text{ D}$

(\angle HCH). If d is set at 1.105 Å (1 Å = 0.1 nm) in C_5H_4 , then the resultant \angle HCH is 97.1°. This value is much too low to be realistic. The discrepancy results from vibration—rotation interactions involving the heavy in-plane atoms contributing to an inertial defect analogous to the quantity $I_c^o - I_b^o - I_a^o = \Delta$ found in planar molecules. In order to obtain more plausible values in the range of 1.09–1.105 Å for $d(\text{CH})$ and 106–109° for \angle HCH, the size of the inertial defect must be 0.3–0.45 u Å². A defect of 0.33 u Å² was previously determined for malononitrile from measurements on the normal, d_1 and d_2 isotopic species [4]. The necessary moments for a similar determination in C_5H_4 are not available and a value of 0.35 u Å² was assumed for many of the structure calculations.

It was also possible to show that there is an anomalous structural parameter associated with the acetylene groups by a similar calculation. The central C—C—C angle ($\angle C_2C_3C_4 = 2\theta$, see Fig. 2 for atom numbering) can be calculated from $I_b + I_c - I_a$ if values are assumed for the C—C, C≡C, and C—H bond distances along with linearity for the C—C≡C—H chains. In that case, $I_b + I_c - I_a = 4\sin^2\theta [m_C d_{C-C}^2 + m_C (d_{C-C} + d_{C\equiv C})^2 + m_H (d_{C-C} + d_{C\equiv C} + d_{CH})^2]$. If the bond distances are set at the values found in propyne ($d_{C-C} = 1.4589$ Å, $d_{C\equiv C} = 1.2062$ Å and $d_{C-H} = 1.0562$ Å) [14] then $\angle C_2C_3C_4$ is calculated to be 113.96°. This large value is not likely to result from an inertial defect contribution or some large amplitude vibrational motion for two reasons. First, $I_b + I_c - I_a$ is a large quantity (389.89 u Å²) and a small inertial defect like contribution of 0.4 u Å² makes only a minor change to any calculated angle. Secondly, the value for $\angle C_2C_3C_4$ is virtually identical when calculated using the moments of $H_2C(C\equiv CD)_2$. Hence, it appears safe to conclude that either $\angle C_2C_3C_4$ is 3–4.5° greater than tetrahedral or that the bond lengths and/or linearity assumptions in this calculation are incorrect.

The results of more comprehensive structure computations are listed in Table 5. The calculations were carried out using the STRFIT program discussed by Schwendeman [15]. In this procedure the five independent planar moments of inertia (i.e., $1/2(I_b + I_c - I_a) = \sum m_i a_i^2 = P_{aa}$, etc.), the planarity condition ($\sum m_i b_i = 0$) and three assumed structural parameters were employed to determine the remaining bond distances and angles. SI and SII show the differences that occur if P_{cc} is corrected by an inertial defect of 0.35 u Å². Apart from the large change in the HCH angle, most other parameters are only slightly affected although $\angle C_2C_3C_4$ is also noted to move closer to the tetrahedral value. SIII and SIV show the result of releasing the linearity restraint on the CCH chains. For SIII it is seen that a value for $\angle C_2C_3C_4$ much closer to tetrahedral can be obtained but that the acetylene groups must then bend several degrees off the linear axes as if repelling each other. Conversely, SIV shows another fit to the data with a relatively shorter C_2-C_3 distance, a very large value for $\angle C_2C_3C_4$ and non-linear acetylene groups now bent towards each other as judged by $\angle C_2C_3C_4$ being greater than $\angle C_1C_3C_5$.

TABLE 5

Selected structures which fit the moments of inertia

Method ^a	SI	SII	SIII	SIV	Pref. ^c
Δ^b (u Å ²)	0.0	0.35	0.35	0.35	
C ₁ H ₁ (Å)	1.055a	1.055a	1.055a	1.055a	1.055(10)
C ₃ H ₃	1.090a	1.090a	1.089a	1.09a	1.090(10)
C ₁ C ₂	1.203	1.205	1.207a	1.206	1.206(10)
C ₂ C ₃	1.463	1.468	1.475	1.459a	1.471(10)
H ₃ C ₃ H ₃ ' (deg.)	98.3	107.0	107.0	107.0	107.0(20)
H ₁ C ₁ C ₂	180.0a	180.0a	177.5	176.7	178.8(20)
C ₁ C ₂ C ₃	179.9	179.4	176.3	176.3	177.8(20)
C ₂ C ₃ C ₄	113.8	112.9	110.2	116.6	111.5(20)
C ₁ C ₃ C ₅	113.9	113.4	113.5	113.3	113.4(10)
H ₁ C ₃ H ₅	113.9	113.6	113.2	114.1	113.4(10)

^aSI–SIV calculated by fixing 3 parameters and fitting the others using the STRFIT program [15]. The letter "a" after a parameter indicates it was held fixed during the fitting. The unit Å = 0.1 nm. ^b $I_a + I_b - I_c + \Delta = 2P_{aa}$. The listed value of Δ was used during the fitting process. ^cPreferred structure; see text.

DISCUSSION

Bond distances for the 4 bond types found in C₅H₄ generally do not deviate widely in the absence of perturbations from conjugation, electro-negative groups or steric interactions. Typical values for these bond distances are listed in Table 6 for several species. It is reasonable to expect that values similar to these examples should also occur in C₅H₄. The sets of 4 bond distances for the various calculations in Table 5 compare favorably with this expectation.

It is more difficult to choose an unambiguous set of bond angles for C₅H₄. Rejection of SI and SIV as plausible structures can be made due to their unusual values for \angle HCH and \angle C₂C₃C₄, respectively. However, choosing

TABLE 6

Selected values of comparable bond distances

Species	CH _{acet}	CH _{meth}	C≡C	C–C	Ref.
C ₂ H ₂	1.058		1.207		16
CH ₂ (C≡N) ₂		1.088		1.468	4
CH ₃ CCH	1.056	1.105	1.206	1.459	14
HCCCHO	1.054		1.205	1.449	2
SiH ₃ CCH	1.058		1.208		17
(CH ₃) ₃ CCCH	1.056		1.209	1.496	18
C ₆ H ₅ CCH	1.055		1.208	1.448	19
C ₅ H ₄	1.055(10)	1.090(10)	1.206(10)	1.471(10)	

between SII and SIII is not as clear cut. Deviations from tetrahedral values about a central carbon of 2–3° and deviations from linearity for π systems such as cyanides and acetylenes are not without precedent. Nevertheless, it is clear that both of these structures point to an interaction involving the acetylene linkages which increases the distance between them. The data strongly argues that either $\angle C_2C_3C_4$ is close to the tetrahedral value with the acetylene groups deviating by about 3–4° from linearity or linearity is retained but $\angle C_2C_3H_4$ opens to about 113°. Of course a range of structures between these two possibilities is also consistent with the data. Since there is more precedence for deviations of acetylene groups from linearity than for four coordinate carbon with a bond angle as large as 113°, it seems more likely to us that the actual situation corresponds more closely to structure SIII than SII. However, this is speculation; further work will be needed to more precisely delineate the angular parameters associated with the acetylene groups. In the interim, it is safe to conclude that the structure of C_5H_4 has parameters within about 0.01 Å and 2° of the average of SII and SIII. This structure is listed in the last column of Table 5 as the best estimate available with the present data.

Although the precise nature of the anomaly in the acetylenic bond angles cannot be uniquely resolved with the MW data, the effect is undoubtedly associated with the four π orbitals which are nominally degenerate. Brogli et al. [1] have outlined the type of through space and through bond interactions including a breakdown of the σ/π separation which leads to loss of the degeneracy. It was estimated that the four π molecular orbitals are slightly destabilized from the zeroth order position and spread over 0.75 eV. Presumably this also leads to the angular perturbation delineated by the microwave analysis.

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