

## CONFORMATION AND VIBRATIONAL SPECTRA OF 1,5-HEXADIYNE (BIPROPARGYL) AND 1,5-HEXADIYNE-1,6- $d_2$

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### ABSTRACT

The infrared spectra of 1,5-hexadiyne (bipropargyl) and 1,5-hexadiyne-1,6- $d_2$ , as vapours, liquids, as solutes in various solvents and as crystalline solids at low temperatures and at high pressures have been recorded. Raman spectra were obtained for the liquids, including semiquantitative polarization measurements, and for the low temperature crystals.

The data were interpreted in terms of two conformers, *anti* and *gauche*, in the vapour and liquid state and one, the *anti*, in the crystalline forms. A phase transition for 1,5-hexadiyne was observed at ca. 240 K. Both the high and low temperature crystals had molecules in the *anti* conformer.

Interpretation of the spectra in terms of conformational equilibria was facilitated by a thorough vapour phase band contour analysis. With a few exceptions, all the vibrational fundamentals for both conformers were assigned and found to be in good agreement with results from normal coordinate calculations.

### INTRODUCTION

The infrared and Raman spectra of 1,5-hexadiyne (bipropargyl, abbreviated to BP in this paper) were studied in our laboratories a few years ago [1], while the C—H stretching region was independently investigated [2] to evaluate the hydrogen bonding in the liquid state and in solution. Our results revealed that BP exists as an equilibrium of two conformers in the vapour phase, in the liquid and in solution. The more abundant conformer in these phases was present alone in the crystalline solid at 90 K [1].

With some doubt we concluded from the spectra that the more stable conformer was *anti*, later verified by the results from gaseous electron diffraction [3]. However, the spectra of BP were difficult to interpret, since a number of accidental degeneracies and fundamentals coinciding with combination modes of the opposite conformer, among others, occurred. The *gauche* spectrum was particularly difficult to analyze since the bands were often weak and superposed on the frequently more intense *anti* bands.

Thus, we decided to repeat the spectral work on BP, and a deuterated compound i.e. 1,5-hexadiyne-1,6- $d_2$  (hereinafter called BP- $d_2$ ) was also synthesized and studied. In addition, various other spectral features are emphasized in the present study: (1) an improved band contour analysis of *anti* and *gauche* bands was carried out, (2) the  $\text{CH}_2$  stretching band intensities were estimated, (3) improved far IR spectra were obtained including spectra of the low temperature crystals below  $200\text{ cm}^{-1}$ , (4) a more extensive force field was derived for BP and BP- $d_2$ , (5) the solid state spectra were carefully studied in the temperature range 200–270 K and (6) infrared high pressure spectra were recorded at ambient temperature.

Further information for the spectral interpretations was provided by the recent results for related compounds such as hexa-1,2-diene-5-yne [4], 1,6-dibromo-1,5-hexadiyne [5], 1-bromo-1,5-hexadiyne [6] and 1-cyano-3-butyne [7].

#### EXPERIMENTAL

The sample of BP used in the present study was partly leftover from the earlier study [1] and partly a commercial sample from K & K. Both samples were dried with molecular sieves and subsequently distilled, and gas chromatographic analyses revealed high purities. In a 1 m gas cell, however, some very small discrepancies between their IR spectra were detected by expanding the ordinate scale (using the FT-IR spectrometer) and these peaks were ascribed to impurities.

For the preparation of 1,6-dideuterio-1,5-hexadiyne, 7.8 g (0.1 mol) BP in 50 ml of dry tetrahydrofuran was added under nitrogen to 200 ml of a well-stirred 0.3 m solution of ethylmagnesium bromide in tetrahydrofuran (prepared from 7.3 g (0.3 mol) magnesium turnings and 34.9 g (0.32 mol) of freshly distilled ethyl bromide), and the mixture stirred overnight. To complete the exchange, the solution was subsequently refluxed for 2 h and then decomposed with an excess of  $\text{D}_2\text{O}$ . Extraction with ether provided the BP- $d_2$  which was purified by preparative gas chromatography (6m-Carbowax, 65 C). The NMR and IR spectra of the sample showed it to be essentially free of acetylenic hydrogen.

Infrared spectra were recorded on a Perkin-Elmer model 225 spectrometer ( $5000\text{--}200\text{ cm}^{-1}$ ) and on a Bruker IFS-114C Fourier transform spectrometer ( $4000\text{--}20\text{ cm}^{-1}$ ). Spectra were recorded of the neat liquid, of  $\text{C}_6\text{H}_6$  solutions and of the solid at ca. 90 K before and after annealing. Further spectra of the solid were recorded in the temperature region 200–270 K. Vapour spectra at various pressures were recorded at ambient temperature in 10 cm, 20 cm and 1 m cells equipped with windows of CsI, polyethylene and KRS 5, respectively. For the high pressure experiments a cell with type II diamonds was used with a 4X beam condenser and the spectra recorded on the interferometer [8].

Raman spectra were recorded with a modified [9] Cary 81 spectrometer

excited by a CRL model 52G argon ion laser. Spectra of the liquid, including semiquantitative polarization measurements, were obtained from ampoules sealed under vacuum; spectra of the crystalline solid at ca. 90 K were obtained from samples deposited on a copper block at 80 K and annealed to ca. 210 K.

## RESULTS

Various IR and Raman spectra of BP in different phases have been reported [1] and the spectra are not repeated here. Corresponding spectra for BP- $d_2$  are given, showing the IR vapour (Fig. 1), liquid (Fig. 2) and crystalline solid (Fig. 3) spectra. Raman spectra of BP- $d_2$  as a liquid and as a crystalline solid are shown in Figs. 4 and 5, respectively. Additional far IR curves of the

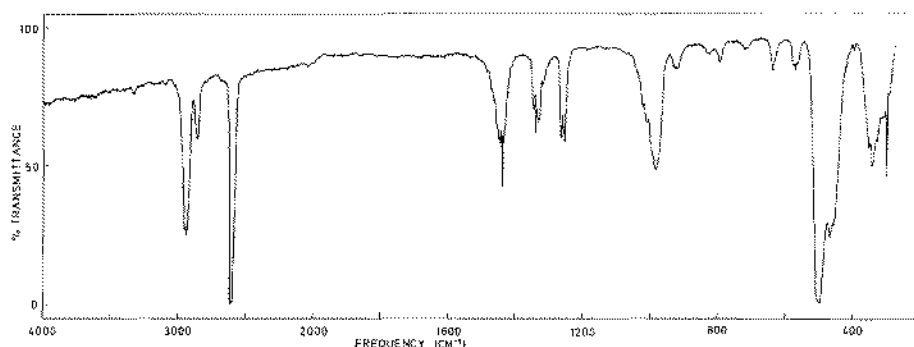


Fig. 1. The infrared spectrum of 1,5-hexadiyne-1,6- $d_2$  (BP- $d_2$ ) in the vapour phase, 10 cm cell, 45 torr pressure.

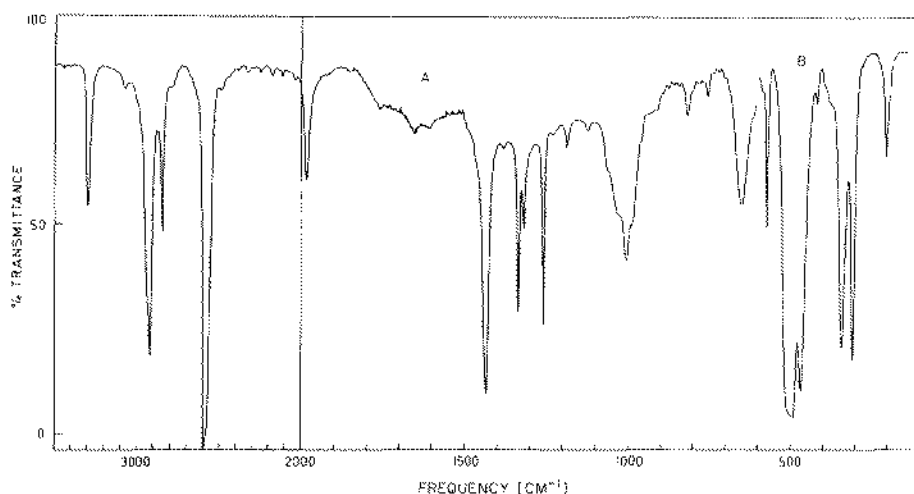


Fig. 2. The infrared spectrum of BP- $d_2$ ; A, neat liquid in 0.025 mm cell; B, 0.7% solution in benzene, 1 mm cell.

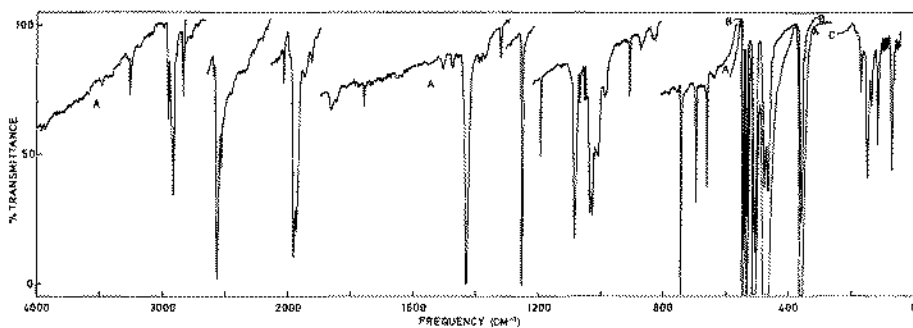


Fig. 3. The infrared spectrum of  $BP-d_2$  at 90 K after annealing to ca. 190 K.

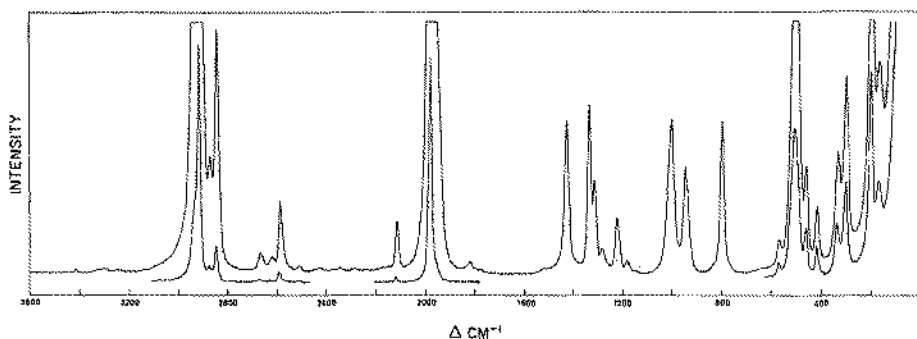


Fig. 4. The Raman spectrum of  $BP-d_2$  in the liquid phase.

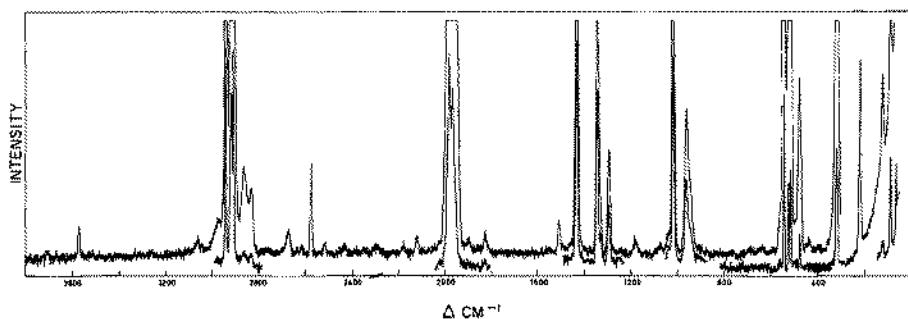


Fig. 5. The Raman spectrum of  $BP-d_2$  at 90 K after annealing to ca. 190 K.

unannealed and the annealed crystalline solids at 90 K deposited on the window of silicon are shown in Figs. 6 (BP) and 7 ( $BP-d_2$ ).

The wave numbers of the observed IR and Raman bands are listed in Tables 1 (BP) and 2 ( $BP-d_2$ ) whereas the assigned fundamentals are listed in Tables 3 (BP) and 4 ( $BP-d_2$ ).

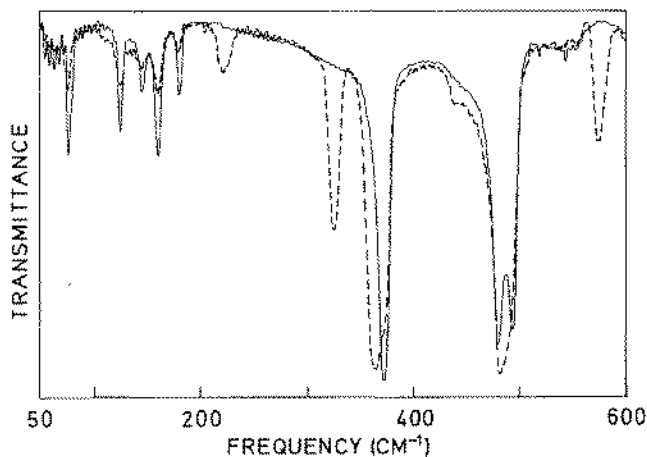


Fig. 6. The far infrared spectrum of 1,5-hexadiyne (BP) at 190 K; dotted line, amorphous solid; solid line, annealed crystalline phase.

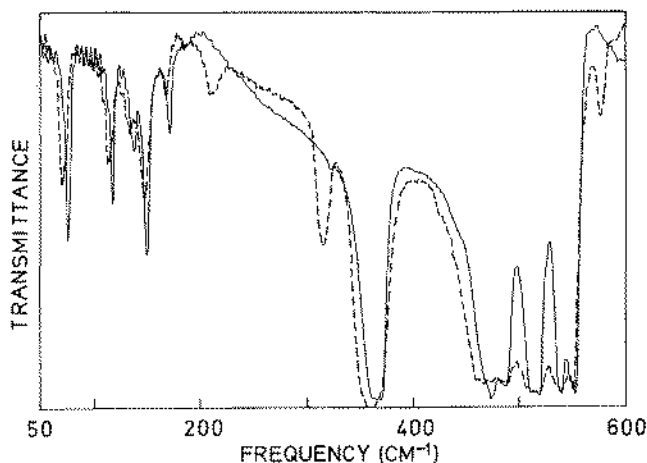


Fig. 7. The far infrared spectrum of BP- $d_2$  at 90 K; dotted line, amorphous solid; solid line, annealed crystalline solid.

#### *Infrared vapour band contours*

The structures of the *anti* and *gauche* conformers of BP have been determined by electron diffraction [3]. From the method outlined by Ueda and Shimanouchi [10] the band contours were calculated. The three theoretical vapour curves (*A*, *B* and *C* type contours) of the *anti* and *gauche* conformers, both being asymmetric tops are given in Figs. 8 and 9, respectively. As is apparent from Fig. 8, the *A*-type bands of the *anti* conformer have a *PR* separation of ca.  $9\text{ cm}^{-1}$  and a weak central *Q*-branch. The *B*-type bands have two intense *Q*-branches separated by ca.  $10\text{ cm}^{-1}$  with the *P* and *R* branches

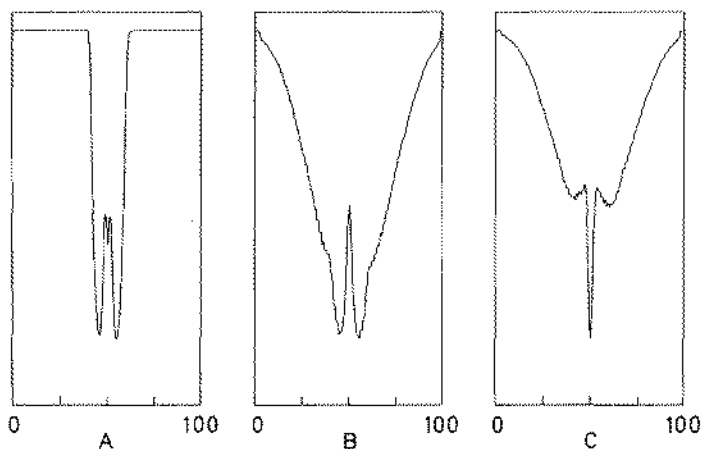


Fig. 8. Predicted vapour contours for A, B and C type bands of the *anti* conformer of BP.

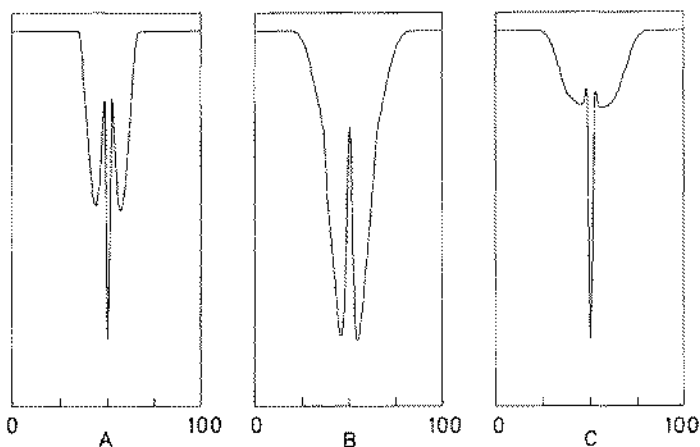


Fig. 9. Predicted vapour contours for the A, B and C type bands of the *gauche* conformer of BP.

appearing as medium intense shoulders. For the C-type bands a strong central Q-branch and medium intense P and R branches separated by ca.  $23\text{ cm}^{-1}$  are expected.

For the *gauche* conformer (Fig. 9) we expect "normal" A-type bands with PR separations of ca.  $14\text{ cm}^{-1}$ ; the B-type bands consist of two intense Q-branches separated by ca.  $9\text{ cm}^{-1}$  with very weak P and R shoulders, the C-type bands appear with a very intense central Q-branch and weak P and R branches separated by ca.  $17\text{ cm}^{-1}$ . These accurately determined vapour contours deviate considerably from those predicted previously for BP [1] based upon standard procedures [11].

The  $a_u$  modes of the *anti* conformer will have C-type contours and the  $b_u$  modes A/B hybrid contours. For the *gauche* conformer the a modes should have B-type contours and the b modes A/C hybrid contours.

In conclusion it can be predicted that: (1) IR vapour bands with a central *Q*-branch and a *PR* separation of  $23\text{ cm}^{-1}$  should belong to the  $a_u$  species (*anti*), whereas (2) a sharp central *Q*-branch and *PR* separation of  $14\text{ cm}^{-1}$  indicate species *b* (*gauche*). (3) Bands with two branches separated by approximately  $10\text{ cm}^{-1}$  can be either  $b_u$  (*anti*) or *a* (*gauche*). However, these bands may be identified by the Raman polarization measurements. The present results are in excellent agreement with our experimental IR vapour curves and were of great help in the assignments.

### Infrared $\text{CH}_2$ stretching band intensities

With two methylene groups in the molecule, BP (and BP- $d_2$ ) should have two IR active stretching modes  $\nu_{11}$  ( $a_u$ ) and  $\nu_{22}$  ( $b_u$ ) of *anti* and four of the *gauche* conformer ( $\nu_1, \nu_2$  of species *a* and  $\nu_{17}, \nu_{18}$  of species *b*) (numbered for BP- $d_2$ ). The spectra reveal that these bands overlap considerably in the region  $3000\text{--}2900\text{ cm}^{-1}$ .

We expect three *Q*-branches,  $\nu_{11}$  *anti* (*C*-type) and  $\nu_{17}$  and  $\nu_{18}$ , *gauche* (*A/C* hybrid). Three *Q*-branches were observed at  $2932, 2956$  and  $2964\text{ cm}^{-1}$ ; the  $2956\text{ cm}^{-1}$  band is the most intense and was assigned as  $\nu_{11}$ , *anti*, and the other two as  $\nu_{17}$  and  $\nu_{18}$  (*gauche*). Figure 10 (showing the methylene stretching region of BP- $d_2$ ) shows at least one additional band, apparently of *B*-type, between  $2932$  and  $2956\text{ cm}^{-1}$ .

To facilitate the spectral interpretation the relative band intensities were estimated. For localized normal vibrations such as  $\text{CH}_2$  stretch, the relative band intensities can be predicted from the *L*-matrix if the bond moment ( $\partial\mu/\partial r$ ) is constant [12]. The calculated relative intensities of the six IR active  $\text{CH}_2$  stretching bands are listed in Table 5. Three bands without sharp *Q*-branches  $\nu_{22}$  ( $b_u$ ),  $\nu_1$  (*a*) and  $\nu_2$  (*a*) were assumed to be situated at  $2943, 2969$  and  $2934\text{ cm}^{-1}$ , respectively, to make the best fit in the band contour analysis. The band intensities were added and the *anti/gauche* concentration ratio in the vapour phase estimated to be 5:1 (within the limits determined [3]). The constructed IR intensity curve is shown in Fig. 11 and gives fair agreement with the experimental curve (Fig. 10). Additional weak components of combination bands may contribute to the latter curve.

### Spectral assignments in BP

We were previously [1] reluctant to make a very firm conclusion regarding which conformer was present in the crystalline phase, although it was assumed to be *anti*. The four relatively weak IR bands in BP at  $1340, 571, 312$  and  $204\text{ cm}^{-1}$  present in the amorphous spectrum at  $90\text{ K}$  disappeared after annealing (Fig. 6). In the vapour phase these bands all had *A/C* hybrid contours with a *PR* separation of  $14\text{ cm}^{-1}$ . Therefore, they were *gauche* bands of species *b* and assigned as  $\nu_{22}, \nu_{28}, \nu_{29}$  and  $\nu_{30}$ . The latter two modes

TABLE 1

IR and Raman spectral data<sup>a</sup> for 1,5-hexadiyne (bipropargyl)

IR				Raman		Interpretation			
Vapour	Liquid	Amorphous <sup>b</sup> 90 K	Crystalline <sup>c</sup> 90 K	Liquid	Crystalline <sup>c</sup> 90 K	<i>Anti</i>	<i>Gauche</i>		
3374 m,sh <sup>d</sup>						$\nu_9 + \nu_{23}$			
3337 vs	A/B	3301 vs	3264 vs	3299 m,P	3270 s	$\nu_{22}, \nu_{11}$	$\nu_{11}, \nu_{17}$		
3332 vs			3262 vs					3248 m	3258 s
3326 vs									
3314 ms	B				3050 w	$\nu_3 + \nu_{26}$			
3306 ms						$\nu_3 + \nu_7$			
2971 m,sh	A/C	2946 m,sh					$\nu_{18}$		
2964 s,Q									
2959 s									
2956 s,Q	C	2935 m,sh	2955 s	2938 s,sh,D	2942 vs	$\nu_{11}, \nu_{17}$			
2945 s							2933 ms		
2951 s	B	2921 s	2918 s	2917 s	2921 vs,P	$\nu_{23}, \nu_2$			
2939 s									
2932 s,Q	A/C						$\nu_{19}$		
2926 m,sh						2912 vs			
2872 m	B								
2866 m					2875 w,P	2864 m	$\nu_{13} + \nu_{24}$		
2863 m	A/C	2849 m	2843 m	2837 m	2849 m,P	$2\nu_4 + \nu_{25}$			
2861 m									2832 m
		2150 w,sh					$\nu_{22} + \nu_{25}$		
2140 m				2134 w,sh					
2138 m	A/B	2121 m	2118 m	2116 mw	2118 vs,P	$\nu_{24}, \nu_3$	$\nu_4, \nu_{20}$		
2130 m									
1447 m	A/C	1473 m,sh				$\nu_{10} + \nu_{26}$			
1441 s,Q		1441 s,sh	1431 s	1436 m,P	1431 s	$\nu_{25}, \nu_4$	$\nu_3, \nu_{21}$		
1435 m		1435 s	1439 s						
			1412 m			Comb. of			
			1392 m			crystal			
			1383 m			inter-			
			1344 m			actions			
			1315 m						
				1346 m,P		$\nu_5$			
					1345 s				
					1334 s	$\nu_{15} + \nu_{19}$			
1348 m	A/C	1338 ms	1345 m				$\nu_{22}$		
1343 m									
1340 m									
1334 m									
1322 w,m	B	1321 ms	1317 m		1322 w,m,P		$\nu_6$		
1317 w								*e	
1273 s,sh									
1267 s,Q		1290 ms,br	1297 ms,sh	1295 m	1286 w,D	1293 ms	comb., $\nu_{18}$		
1263 s	B			1256 s					
1255 s		1260 s	1259 s				$\nu_{26}$		
		1228 m,sh		1252 m					
			*		1225 mw,P	*	$\nu_7$		



TABLE 1 (continued)

IR				Raman		Interpretation	
Vapour	Liquid	Amorphous <sup>b</sup> 90 K	Crystalline <sup>c</sup> 90 K	Liquid	Crystalline <sup>c</sup> 90 K	Anti	Gauche
1191vw,Q C	1189 wm	1188m	1196m			$\nu_{12}$	
1187vw							
1184vw							
1181vw,Q A/C				1187vw,D			$\nu_{23}$
1071vw	1079 w	1075w	1072w			$\nu_{13} + \nu_{21}$	$\nu_n?$
	1024vw	1022vw		1030s,sh,D			
1010vw				1022s,P	1022s	$\nu_6$	
1000vw	1002wm	1002w	*	1003m,P	1007 w	$\nu_{19}$	$\nu_9$
974vw,Q	970 w	975 w	976w			$\nu_{14} + \nu_{21}$	
				975m,P	975w	$\nu_8 + \nu_{21}$	$\nu_{24}$
		949 w	*	952m,P	950w	$\nu_7$	$\nu_{27} + \nu_{29}$
935m							
927m	930wm	927wm	928w			$\nu_{27}$	
872vw	866vw					$\nu_{10} + \nu_{28}$	
862vw							
834w							
828w	825wm	824w	*				$\nu_{25}$
821w							
805w	813w	810w,sh	*	815m,P	*		$\nu_{10}$
780vw							
769vw				790s,sh			$\nu_{28} + \nu_{10}$
	755w,sh	750m	749m			$\nu_{13}$	
743vw							
737vw,Q							
728vw,Q	735wm,sh		732w			$\nu_8 + \nu_{16}?$	$\nu_{13} + \nu_{29}$
720vw							
711vw	720wm,sh						
			710vs				
			685vs		688s		interac-
			667s		671s		tions in
							the crystal
644vs,sh							
641vvs,Q				650s,br,D	651s	$\nu_8, \nu_{20}$	$\nu_{11}, \nu_{12}$
638vvs,Q	648vs,br	650vs,br	650s			$\nu_{14}, \nu_{28}$	$\nu_{26}, \nu_{27}$
634vs,sh							
578m							
571s	574m	573m	*	575w,D	*		$\nu_{28}$
564m							
483s			493s				
475s	484ms	488s	480s	487m,P	490s	$\nu_{29}, \nu_9$	
	436w <sup>f</sup>	437w	* 467m,sh	437m,P	*		$\nu_{13}$
363m							
353s	352s <sup>f</sup>	364s	372s	351m,D?	*	$\nu_{15}$	$\nu_{14}$
340m							
320m							
312s	318ms <sup>f</sup>	324m	*	323ms,D	326vs	$\nu_{21}$	$\nu_{29}$
306m							

TABLE 1 (continued)

IR				Raman		Interpretation	
Vapour	Liquid	Amorphous <sup>b</sup> 90 K	Crystalline <sup>c</sup> 90 K	Liquid	Crystalline <sup>c</sup> 90 K	<i>Anti</i>	<i>Gauche</i>
212 w 204 mw 198 w	A/C	215 mw <sup>f</sup>	220 wm	*	221 s,P	$\nu_{10}$	$\nu_{30}$
					183 vw <sup>f</sup>		
			178 m				
			160 m				
			143 m				
			122 m		123 s	Lattice modes	
	107 w,bd <sup>f</sup>				118 s	$\nu_{16}, \nu_{30} ?$	
				74 m		90 vs 80 mw	Lattice modes
					66 vs 51 s		

<sup>a</sup>Weak bands outside the fundamental regions 4000–3400, 2800–2150 and 2100–1480  $\text{cm}^{-1}$  are omitted. <sup>b</sup>Condensed from vapour at liquid  $\text{N}_2$  temperatures. <sup>c</sup>Condensed from vapour at liquid  $\text{N}_2$  temperatures, annealed at 190 K and recooled to liquid  $\text{N}_2$  temperatures. <sup>d</sup>s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad; P, polarized; D, depolarized; Q, Q-branch; A, B, C, vapour contours; comb., combination band. <sup>e</sup>An asterisk signifies that the band vanishes in the crystalline solid spectra. <sup>f</sup>Benzene solution.

( $\nu_{29}$  and  $\nu_{30}$ ) overlapped the Raman active *anti* fundamentals  $\nu_{21}$  ( $b_g$ ) and  $\nu_{10}$  ( $a_g$ ). In BP- $d_2$  exactly the same features were observed (cf. Fig. 7 and Table 2).

Our present assignments for BP are listed in Tables 1 and 3, and will be briefly discussed if they deviate from our earlier results [1]. All the  $a_g$  modes of the *anti* conformer were left unchanged. The  $b_g$  modes  $\nu_{18}$  and  $\nu_{19}$  were assigned to the Raman bands at 1286 and 1003  $\text{cm}^{-1}$ , respectively, the latter coinciding with the *gauche* fundamental  $\nu_9$  ( $a$ ). Previously, the  $a_u$  mode  $\nu_{13}$  was unassigned but it is now ascribed to a distinct band at 756  $\text{cm}^{-1}$  in the BP- $d_2$  spectrum, appearing as a weak shoulder in the parent IR spectrum. The  $b_u$  fundamental  $\nu_{26}$  is now attributed to the intense bands at 1260  $\text{cm}^{-1}$ , partly covered by the overtones of the  $\text{C}\equiv\text{C}-\text{H}$  bending modes (see below). A band at 1337  $\text{cm}^{-1}$  previously assigned to the  $\nu_{26}$  *anti* fundamental [1], is now assigned to the *gauche* mode  $\nu_{22}$ .

Comparatively few *gauche* fundamentals were assigned previously. Presently, a number of observed IR and Raman bands are assigned to the *gauche* conformer when fulfilling the requirements: (a) bands vanishing in the crystal spectra, (b) bands having the expected IR vapour contours and (c) bands corresponding to the calculated wavenumbers for the appropriate *gauche* fundamental.

Two Raman bands observed at 1225 and 1030  $\text{cm}^{-1}$  were assigned as the  $a$  fundamentals  $\nu_7$  and  $\nu_8$ . Six new  $b$  fundamentals of the *gauche* conformer were assigned to observed IR and/or Raman bands:  $\nu_{18}$ ,  $\nu_{19}$ ,  $\nu_{21}$ ,  $\nu_{22}$ ,  $\nu_{23}$  and  $\nu_{24}$ . Our present force constant calculations indicated a number of instances in which the *anti* and *gauche* fundamentals should overlap. Additional

*gauche* fundamentals were assigned to bands overlapping *anti* fundamentals whenever acceptable from the various criteria.

Nearly all the *gauche* fundamentals were assigned, as is apparent from Table 3. Exceptions are two of the  $\text{CH}_2$  stretching modes  $\nu_2$  and  $\nu_3$  as well as the torsional mode  $\nu_{16}$ . Weak broad absorption bands were observed at ca.  $105\text{ cm}^{-1}$  in the IR spectrum of BP and at  $95\text{ cm}^{-1}$  for BP- $d_2$  (Fig. 12), both in concentrated benzene solutions. The bands may be attributed to the torsional mode  $\nu_{16}$  eventually overlapping the lowest in-phase bending mode  $\nu_{30}$  of the *anti* conformer.

### *Spectral assignments in BP- $d_2$*

A comparison between Tables 1 and 2 as well as 3 and 4 reveals the striking similarities between the spectra of BP and BP- $d_2$ . Approximately 20 of the 30 *anti* fundamentals in BP lie within  $5\text{ cm}^{-1}$  of the corresponding fundamentals in BP- $d_2$ . The deuterated spectrum greatly facilitated the interpretation of the parent spectrum (and vice versa).

The main spectral differences are that the acetylenic C—H stretches (coinciding for the  $a_g$ ,  $b_u$ ,  $a$  and  $b$  modes) are shifted from  $3332\text{ cm}^{-1}$  in BP to  $2612\text{ cm}^{-1}$  in BP- $d_2$ . Correspondingly, the  $\text{C}\equiv\text{C}$ —H bending modes are shifted from ca.  $650$  to ca.  $500\text{ cm}^{-1}$ . Also, the bands around  $2120\text{ cm}^{-1}$  in BP ( $\nu_3$  and  $\nu_{24}$  of *anti* and  $\nu_4$  and  $\nu_{20}$  of *gauche*) are shifted to ca.  $1985\text{ cm}^{-1}$  in BP- $d_2$ . Thus, the  $\text{C}\equiv\text{C}$  stretch contains a significant contribution from C—H(D) stretch. The low frequency modes below  $500\text{ cm}^{-1}$  involving various skeletal bending motions also shift slightly more than the high frequency modes (stretching) upon deuteration.

It is well known that the acetylenic C—H bending modes give rise to very intense and broad overtones in the IR and Raman, appearing at ca.  $1270\text{ cm}^{-1}$  (vapour) for BP and around  $1010\text{ cm}^{-1}$  for BP- $d_2$ . In the low temperature crystal, the fundamentals as well as the overtones are found at higher wave numbers for BP as well as for BP- $d_2$ . The *anti* fundamentals  $\nu_{26}$  ( $1260\text{ cm}^{-1}$ ) and  $\nu_{18}$  ( $1286\text{ cm}^{-1}$ ) for both compounds were partly hidden in the BP spectra but could easily be observed in the BP- $d_2$  spectra. The range  $1020$ — $950\text{ cm}^{-1}$ , partly covered in the BP- $d_2$  spectra, was easily interpreted for BP. The force constant calculations indicate that the fundamentals in this region ( $\nu_6$  and  $\nu_{19}$ , *anti* and  $\nu_8$  and  $\nu_9$ , *gauche*) should occur at approximately the same wave numbers for BP and BP- $d_2$ . The complex spectra for BP- $d_2$  in this region have prevented a clear-cut identification of these bands and the modes have been left unassigned for BP- $d_2$ .

### *Force constant calculations*

A normal coordinate analysis was carried out with various purposes in mind. From the fairly reliable assignments of fundamentals to the *anti* and *gauche* conformers we wanted to derive a common set of force constants for

TABLE 2

IR and Raman spectral data<sup>a</sup> for 1,5-hexadiyne, 1,6-d<sub>2</sub> (dideutrobipropargyl)

IR				Raman		Interpretation	
Vapour	Liquid	Amorphous <sup>b</sup> 90 K	Crystalline <sup>c</sup> 90 K	Liquid	Crystalline <sup>c</sup> 90 K	Anti	Gauche
	2978 w,sh <sup>d</sup>		2988 vw			$\nu_{26} + \nu_{24}$	
2971 m,sh 2964 s,Q 2959 s	} A/C 2946 m,sh						$\nu_{17}$
2956 s,Q		} C 2935 m,sh	2930 m,sh	2955 s	2936 s,sh	2939 vs	$\nu_{11}, \nu_{17}$
2945 s 2951 s	} B 2921 s			2933 m		2918 vs	
2939 s 2932 s 2926 m,sh 2871 m		} A/C 2866 m	2918 s	2917 s	2921 vs,P	2908 vs	$\nu_{22}, \nu_1$
2861 m 2858 m	} A/C 2804 w,sh		2843 m	2837 m	2874 m,P	2860 w	comb.
2617 vs 2612 vs 2606 vs		} A/B 2599 vs	2583 vs	2585 w	2672 w,P 2626 vw,P	2670 w	$\nu_{10} + \nu_{23}$ $\nu_{25} + \nu_{26}$
			2559 s,sh 2548 s,sh 2535 m	2570 vs 2558 s + <sup>e</sup>	2592 m,P	2573 m	$\nu_{23}, \nu_2$
	2122 w		2121 w,P	2118 w		$\nu_{24}, \nu_3$ parent	
	2045 w	2036 w	2035 w 1982 s		1976 vs	$\nu_3 + \nu_{16} ?$	
	1986 s	1983 s	1973 s 1945 w 1922 w	1983 vs,P	1961 s	$\nu_{24}, \nu_3$	$\nu_{41}, \nu_{20}$
	1922 w	1920 w	1861 w	1894 w		$\nu_{20} + \nu_{25}$	$\nu_{22} + \nu_{26}$
	1857 w	1859 w	1843 w			$\nu_7 + \nu_{27}$	
	1764 w	1756 w		1825 vw,P 1780 vw,P	1822 w	$\nu_5 + \nu_{20}$ $\nu_{18} + \nu_{20}$ $\nu_8 + \nu_{26}$ $\nu_6 + \nu_8$ $\nu_6 + \nu_{20}$ $\nu_{14} + \nu_{19}$	
~1490 w,sh	1490 m,sh	1490 w	1506 w 1474 w		1504 w		
~1465 w,sh	1461 m,sh	1465 w	1472 w 1457 vw 1430 s			$\nu_6 + \nu_{29}$	
1447 m 1441 s,Q 1437 m	} A/C 1441 s,sh 1435 s	1435 s	1435 s	1435 m,D?	1426 s	$\nu_{25}$ $\nu_4$	$\nu_5, \nu_{21}$
1348 m 1341 m 1334 m		} A/C 1337 m	1345 mw,sh		1344 m,P	1339 s	$\nu_5$
1322 wm	} B 1320 m		1337 m	*			
			1318 wm	1320 w	1321 m,P	1324 w	$\nu_{16} + \nu_{26} ?$

TABLE 2 (continued)

IR		Raman				Interpretation	
Vapour	Liquid	Amorphous <sup>b</sup> 90 K	Crystalline <sup>c</sup> 90 K	Liquid	Crystalline <sup>c</sup> 90 K	<i>Anti</i>	<i>Gauche</i>
~1290 vw 1266s		1290 w	*	1287 w,D	1289 m	$\nu_{18}$	$\nu_{10} + \nu_{12}$
1260s } A/B	1260s	1258s	1256s			$\nu_{26}$	
1256s } A/B			1254s				
~1240 w,sh	1232w	~1233 w ~1220 w	*	1230m,P	*		$\nu_7$ $\nu_{13} + \nu_{25}$
1203 vw 1190 vw,Q 1182 vw	1188m	1187mw	1197 m	1186 w,D	*	$\nu_{12}$	$\nu_{23}$
1175 vw,Q 1170 vw 1130 vw							
	1125w		~1130vw 1085s 1071m			$\nu_{10} + \nu_{27}$	comb. of interaction in the crystal
	1064m,sh						
1044w } B	1032s,sh	1033ms,br	1055m 1038s				
1036w } B				1030s			
1025m } A/B?							comb.
1020m } A/B?							
1015m } A/B?							
1012m } A/B?							
1003m } B	1007s	1011s	1011s	1010m,P	1010s		
985s,br	990s,sh 963m,sh	990m,sh 961 w	990w *				$\nu_{24}?$
				949m,P	955m	$\nu_7$	
					935m,sh	$\nu_9 + \nu_{14}$	
933m } B	941m,sh					$\nu_{27}$	
925m } B	915m,sh	912w	912w				
		875w,bd	876w	875vw		$\nu_8 + \nu_{15}$	
830w } A/C	820m	817w	832w,bd	830vw,sh		$\nu_{15} + \nu_{20}$	$\nu_{25}$
822w } A/C							
816vw } A/C							
801w } A/C							
793w } B	805vw,sh			802m,P	*		$\nu_{10}$
768vw } B							$\nu_{26} + \nu_{30}$
756vw } B							
	756w	753m	747s			$\nu_{13}$	
736vw } A/C							$\nu_{15} + \nu_{26}$
730vw } A/C							
722w } A/C							
712vw } B						$\nu_{10} + \nu_{28}$	
		696w	698m				

TABLE 2 (continued)

IR				Raman		Interpretation		
Vapour	Liquid	Amorphous <sup>b</sup> 90 K	Crystalline <sup>c</sup> 90 K	Liquid	Crystalline <sup>c</sup> 90 K	<i>Anti</i>	<i>Gauche</i>	
644 w	C	648 m	663 m, bd	667 w	682 vw, bd	$\nu_8, \nu_{14},$ $\nu_{20}, \nu_{28}$ parent		
641 w								
638 w								
634 w								
577 m	A/C	574 m	575 m	*	575 w, D	*	$\nu_{26}$	
571 m								
565 m								
				549 vs	555 vs	interac- tions in the crystal		
				537 vs	536 vs			
				517 s, sh	517 vs			
507 vs	C, B	508 s, sh <sup>f</sup>	507 vs, bd	511 vs	514 s, bd, D	$\nu_{81}, \nu_{20}$ $\nu_{28}$	$\nu_{11}, \nu_{12},$ $\nu_{27}, \nu_{28}$	
503 vs								
497 vs, Q								
466 s								
459 s	B	466 s <sup>f</sup>	470 vs	482 vs	486 vw	$\nu_9$		
				469 vs	469 m			
		420 w <sup>f</sup>	425 w	*	463 m, P			
350 s	C	341 s <sup>f</sup>	352 s	363 s	419 m, P	*	$\nu_{13}$	
342 s								
~330 s								
307 m								
300 s	A/C	307 s <sup>f</sup>	313 m	*	338 m, D?	$\nu_{15}$	$\nu_{14}$	
293 m								
					306 m, D	312 s	$\nu_{24}$	$\nu_{29}$
					207 s, D?	219 m	$\nu_{10}$	
						211 s		
201 w	A/C	203 w <sup>f</sup>	210 w	*	172 m, D?	*	$\nu_{30}$	
194 w								
187 w								
			168 w	170 m				
			147 w	148 m				
			134 w	136 m				
			115 w	116 m		117 s	Lattice modes $\nu_{16}, \nu_{30}$	
		95 vw, bd <sup>f</sup>				82 s	Lattice modes	
			70 m	74 m		58 s		
						48 m		

<sup>a</sup>Bands above 3000  $\text{cm}^{-1}$  and weak bands in the region 2500–2200  $\text{cm}^{-1}$  are omitted.

<sup>b</sup>Condensed from vapour at liquid  $\text{N}_2$  temperatures. <sup>c</sup>Condensed from vapour at liquid  $\text{N}_2$  temperatures, annealed at 190 K and recooled to liquid  $\text{N}_2$  temperatures. <sup>d</sup>s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad; P, polarized; D, depolarized; Q, Q-branch; A, B, C, vapour contours; comb., combination band. <sup>e</sup>An asterisk signifies that the band vanishes in the crystalline solid spectra. <sup>f</sup>Benzene solution.

TABLE 3

Observed<sup>a</sup> and calculated fundamental frequencies (cm<sup>-1</sup>) for 1,5-hexadiyne

<i>Anti conformer</i>			<i>Gauche conformer</i>				
Obs.	Calc.	PED <sup>b</sup>	Obs.	Calc.	PED		
$a_g$			$a$				
$\nu_1$	3332 <sup>c</sup>	3346	96r <sup>d</sup>	$\nu_1$	3332 <sup>c</sup>	3346	96r
$\nu_2$	2921 <sup>e</sup>	2935	99s	$\nu_2$		2964	98s
$\nu_3$	2118	2120	83d	$\nu_3$		2934	98s
$\nu_4$	1436	1421	80 $\rho$	$\nu_4$	2121	2122	83d
$\nu_5$	1346	1355	57 $\delta'$ + 39 $\delta$ + 15p	$\nu_5$	1435 <sup>e</sup>	1427	80 $\rho$
$\nu_6$	1022	1023	91h	$\nu_6$	1321	1318	60 $\delta'$ + 32 $\delta'$
$\nu_7$	952	947	45p + 36 $\omega$	$\nu_7$	1225	1214	61 $\delta'$ + 42 $\delta$ + 15h
$\nu_8$	650	647	111 $\phi$	$\nu_8$	1030 <sup>e</sup>	1021	81h
$\nu_9$	487	483	35 $\omega$ + 23 $\theta$ + 20p	$\nu_9$	1002	992	44 $\delta'$ + 29 $\delta$
$\nu_{10}$	221	217	92 $\theta$ + 17 $\omega$	$\nu_{10}$	815	823	57p + 15 $\delta$
$a_u$				$\nu_{11}$	648	648	110 $\phi'$
$\nu_{11}$	2956 <sup>c</sup>	2958	99s	$\nu_{12}$	648	646	111 $\phi$
$\nu_{12}$	1191 <sup>c</sup>	1193	74 $\delta'$ + 25 $\delta$	$\nu_{13}$	436	433	45 $\omega$ + 42 $\theta$
$\nu_{13}$	756	754	72 $\delta$ + 19 $\delta'$	$\nu_{14}$	351	346	94 $\theta'$
$\nu_{14}$	648	648	110 $\phi'$	$\nu_{15}$	182	185	63 $\theta$ + 30 $\omega$
$\nu_{15}$	352	351	98 $\theta'$	$\nu_{16}$		73	71r
$\nu_{16}$		71	80r	$b$			
$b_g$				$\nu_{17}$	3332 <sup>c</sup>	3346	96r
$\nu_{17}$	2938 <sup>e</sup>	2966	99s	$\nu_{18}$	2964 <sup>e</sup>	2962	98s
$\nu_{18}$	1287	1290	71 $\delta$ + 28 $\delta'$	$\nu_{19}$	2932 <sup>c</sup>	2932	98s
$\nu_{19}$	1003	1003	69 $\delta'$ + 26 $\delta$	$\nu_{20}$	2121	2124	83d
$\nu_{20}$	650	648	110 $\phi'$	$\nu_{21}$	1435	1445	76 $\rho$ + 22 $\delta'$
$\nu_{21}$	323	319	112 $\theta'$	$\nu_{22}$	1338	1335	54 $\delta$ + 34 $\delta'$
$b_u$				$\nu_{23}$	1181 <sup>c</sup>	1180	62 $\delta'$ + 38 $\delta$
$\nu_{22}$	3332 <sup>c</sup>	3346	96r	$\nu_{24}$	975	989	32p + 28 $\delta'$ + 20 $\omega$
$\nu_{23}$	2921 <sup>e</sup>	2930	99s	$\nu_{25}$	825	822	47p + 29 $\delta$
$\nu_{24}$	2121	2125	83d	$\nu_{26}$	648	648	107 $\phi'$
$\nu_{25}$	1441	1446	77 $\rho$ + 20 $\delta'$	$\nu_{27}$	648	648	107 $\phi$
$\nu_{26}$	1260	1265	47 $\delta$ + 45 $\delta'$	$\nu_{28}$	574	580	52 $\omega$ + 23 $\delta$ + 20 $\theta$
$\nu_{27}$	930	927	82p	$\nu_{29}$	318	322	111 $\theta'$
$\nu_{28}$	648	648	110 $\phi$	$\nu_{30}$	215	214	96 $\theta$ + 15 $\omega$
$\nu_{29}$	484	474	52 $\omega$ + 49 $\theta$				
$\nu_{30}$		132	69 $\theta$ + 39 $\omega$				

<sup>a</sup>When possible frequencies are taken from liquid or solution spectra. <sup>b</sup>The potential energy distribution is defined as  $\chi_{ik} = 100 F_{ii} L_{ik}^2 / \lambda_k$ . <sup>c</sup>Frequencies from the vapour phase spectrum. <sup>d</sup>For meaning of symbols see Fig. 1. Terms below 15 are neglected. <sup>e</sup>Not included in the refinement of the force constants.

both conformers. It was clear from our earlier work in which a diagonal force field with 11 independent force constants was employed [1] that a considerable number of interaction constants had to be included in order to improve the agreement.

TABLE 4

Observed<sup>a</sup> and calculated fundamental frequencies (cm<sup>-1</sup>) for 1,5-hexadiyne-1,6-d<sub>2</sub>

<i>Anti conformer</i>			<i>Gauche conformer</i>				
Obs.	Calc.	PED <sup>b</sup>	Obs.	Calc.	PED		
<i>a<sub>g</sub></i>			<i>a</i>				
$\nu_1$	2921 <sup>c</sup>	2935	99s <sup>d</sup>	$\nu_1$	2964	98s	
$\nu_2$	2612 <sup>e</sup>	2595	70r + 27d	$\nu_2$	2934	98s	
$\nu_3$	1983	1986	58d + 28r	$\nu_3$	2612 <sup>e</sup>	2596	70r + 27d
$\nu_4$	1435	1421	80 $\rho$	$\nu_4$	1986	1987	58d + 28r
$\nu_5$	1344	1354	57 $\delta$ + 39 $\delta'$	$\nu_5$	1435 <sup>c</sup>	1427	80 $\rho$
$\nu_6$		1022	93h	$\nu_6$	1320	1318	60 $\delta$ + 32 $\delta'$
$\nu_7$	949	939	44p + 36 $\omega$	$\nu_7$	1225	1214	61 $\delta'$ + 42 $\delta$ + 15h
$\nu_8$	514	513	94 $\phi$ + 20 $\theta$	$\nu_8$		1019	84h
$\nu_9$	463	461	25 $\omega$ + 22 $\phi$	$\nu_9$		990	43 $\delta'$ + 30 $\delta$
$\nu_{10}$	207	208	89 $\theta$ + 16 $\omega$	$\nu_{10}$	805	814	58p + 15 $\delta$
<i>a<sub>u</sub></i>			$\nu_{11}$	497 <sup>c</sup>	507	97 $\phi$ + 15 $\phi'$	
$\nu_{11}$	2956 <sup>e</sup>	2958	99s	$\nu_{12}$	497 <sup>c</sup>	503	101 $\phi'$ + 15 $\phi$
$\nu_{12}$	1190 <sup>c</sup>	1193	74 $\delta'$ + 25 $\delta$	$\nu_{13}$	420	422	41 $\omega$ + 28 $\theta$
$\nu_{13}$	756	754	72 $\delta$ + 19 $\delta'$	$\nu_{14}$	338	336	84 $\theta'$
$\nu_{14}$	497	504	116 $\phi'$	$\nu_{15}$	172	178	63 $\theta$ + 29 $\omega$
$\nu_{15}$	341	341	90 $\theta'$	$\nu_{16}$		62	70r
$\nu_{16}$		68	79r	<i>b</i>			
<i>b<sub>g</sub></i>			$\nu_{17}$	2964 <sup>e</sup>	2962	98s	
$\nu_{17}$	2936 <sup>c</sup>	2966	99s	$\nu_{18}$	2932 <sup>e</sup>	2932	98s
$\nu_{18}$	1287	1290	71 $\delta$ + 28 $\delta'$	$\nu_{19}$	2612 <sup>e</sup>	2596	70r + 27d
$\nu_{19}$		1002	69 $\delta'$ + 26 $\delta$	$\nu_{20}$	1986	1989	58d + 28r
$\nu_{20}$	514 <sup>c</sup>	503	116 $\phi'$	$\nu_{21}$	1435	1445	76 $\rho$ + 22 $\delta'$
$\nu_{21}$	306	307	105 $\theta'$	$\nu_{22}$	1337	1334	53 $\delta$ + 35 $\delta'$
<i>b<sub>u</sub></i>			$\nu_{23}$	1175 <sup>c</sup>	1179	62 $\delta'$ + 38 $\delta$	
$\nu_{22}$	2921 <sup>c</sup>	2930	99s	$\nu_{24}$	963 <sup>c</sup>	983	29p + 29 $\delta'$ + 20 $\omega$
$\nu_{23}$	2612 <sup>e</sup>	2596	70r + 27d	$\nu_{25}$	820	814	48p + 28 $\delta$
$\nu_{24}$	1986	1990	58d + 28r	$\nu_{26}$	574	581	51 $\omega$ + 23 $\delta$ + 22 $\theta$
$\nu_{25}$	1441	1446	77 $\rho$ + 20 $\delta'$	$\nu_{27}$	497 <sup>c</sup>	503	110 $\phi'$
$\nu_{26}$	1260	1264	48 $\delta'$ + 45 $\delta$	$\nu_{28}$	497 <sup>c</sup>	498	103 $\phi$
$\nu_{27}$	915	915	80p	$\nu_{29}$	307	311	103 $\theta'$
$\nu_{28}$	508	508	108 $\phi$ + 23 $\theta$	$\nu_{30}$	203	204	93 $\theta$
$\nu_{29}$	466	463	44 $\omega$ + 28 $\theta$				
$\nu_{30}$		124	69 $\theta$ + 37 $\omega$				

<sup>a</sup>When possible frequencies are taken from liquid or solution spectra. <sup>b</sup>The potential energy distribution is defined as  $\chi_{ik} = 100 F_{ik} L_{ik}^2 / \lambda_k$ . <sup>c</sup>Not included in the refinement of the force constants. <sup>d</sup>For meaning of symbols see Fig. 1. Terms below 15 are neglected. <sup>e</sup>Frequencies from the vapour phase spectrum.

The notation of the applied valence coordinates is defined in Fig. 13. The structural parameters were taken as follows:  $r = 1.065$ ,  $d = 1.220$ ,  $p = 1.459$ ,  $h = 1.555$  and  $s = 1.095$  Å,  $\theta = \phi = 180$ ,  $\omega = 110.7$ ,  $\rho = 110.2$ ,  $\delta = 108.7$  and  $\tau = 180^\circ$  (77 *gauche*). The initial diagonal valence force field [1] was



TABLE 5

Calculated relative integrated infrared intensities for the methylene stretching vibrations in 1,5-hexadiyne-1,6- $d_2$

Fundamental	Frequency	Contour	Relative intensity
$\nu_{11}$ $a_u$ anti	2956	C-type	3.02
$\nu_{22}$ $b_u$ anti	2942	$I_A/I_B = 8.7$	1.36
$\nu_1$ $a$ gauche	2964 <sup>a</sup>	B-type	0.76
$\nu_2$ $a$ gauche	2934 <sup>a</sup>	B-type	0.70
$\nu_{17}$ $b$ gauche	2964	$I_C/I_A = 2.7$	2.26
$\nu_{18}$ $b$ gauche	2932	$I_C/I_A = 5.9$	0.66

<sup>a</sup>Estimated from normal coordinate analysis.

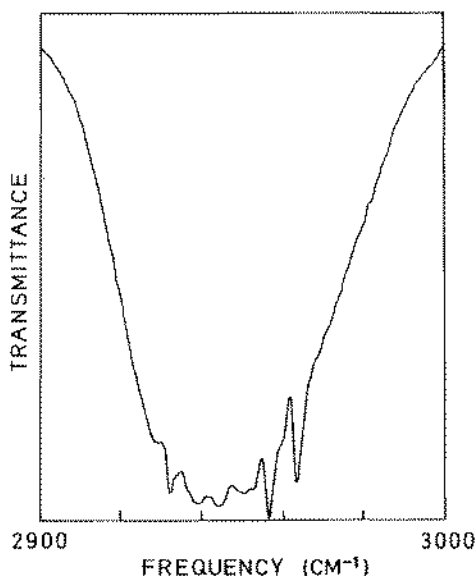


Fig. 10. The observed  $\text{CH}_2$  stretching bands of  $\text{BP-}d_2$  in the vapour phase; 20 cm path, 39 torr pressure.

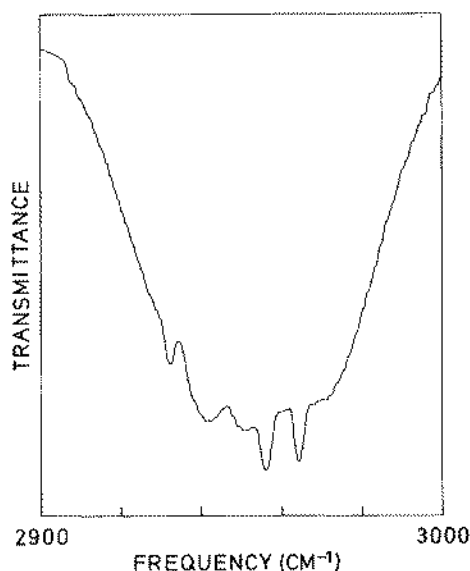


Fig. 11. The computed  $\text{CH}_2$  stretching bands of  $\text{BP-}d_2$  (see Table 5).

extended by transferring the interaction constants found for the n-alkanes [13]. Only minor adjustments were necessary in order to obtain an excellent agreement with the experimental observations as shown in Tables 3 and 4 for BP and  $\text{BP-}d_2$ , respectively. On the average, the deviation is better than 1%.

The final force field is given in Table 6 and consists of 35 parameters of which 13 were constrained to their values in the n-alkanes [13] during the least squares refinement. As seen, practically all the force constants are well

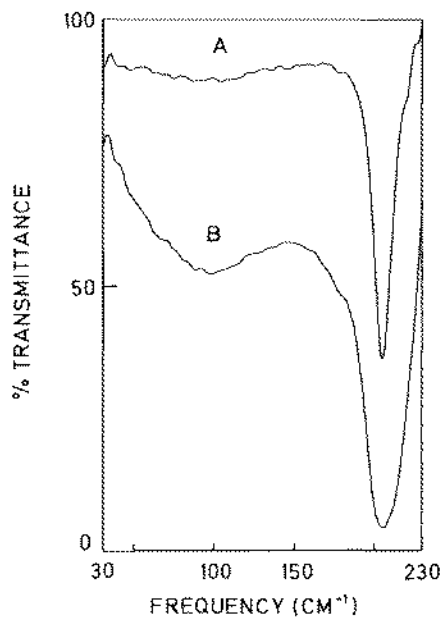


Fig. 12. The far infrared spectrum of BP- $d_2$  dissolved in benzene; A, 11% solution; B, 66% solution; 1 mm cell of polyethylene.

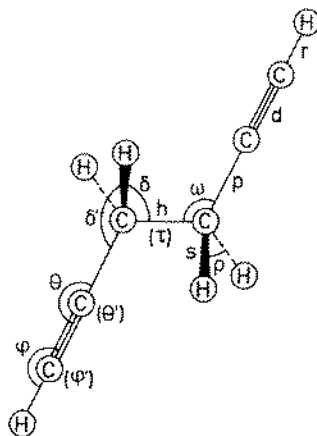


Fig. 13. The valence coordinates of BP (*anti* conformer).

determined and have the correct magnitudes. As noted in Tables 3 and 4 some of the assigned fundamental frequencies were not employed in the refinement procedure. However, all together 91 fundamental frequencies of the *anti* and *gauche* fundamentals of BP and BP- $d_2$  were used to determine the 22 force constants which were not constrained.

The potential energy distribution (PED) in Tables 3 and 4 reveals that many of the modes are fairly well localized to one internal coordinate. Moreover, the "corresponding" vibrational modes are frequently equally well localized in the BP and BP- $d_2$  spectra for both *anti* and *gauche*.

### Solid state spectra

As reported [1] the shock-frozen solid condensed from the vapour on a CsI plate or on a copper block at 90 K contained both conformers, while the annealed crystalline solid contained only the *anti* conformer (Figs. 6 and 7). At higher temperatures (200–260 K), but below the melting point at 267 K certain spectral changes of band width and intensities were observed, suggesting a phase transition in this region. By differential scanning calorimetry (DSC) a sharp peak indicating a first order phase transition was observed at ca. 240 K. Semiquantitative DSC measurements gave a  $\Delta H$  value for the phase transition equal to  $-0.6 \text{ kcal mol}^{-1}$  and a  $\Delta S$  equal to  $-2.6 \text{ cal mol}^{-1} \text{ K}$ .

TABLE 6

Valence force constants for 1,5-hexadiyne

Force constant	Group	Coordinate(s) involved	Atoms common to interacting coordinates	Calculated value $\phi_i$	Standard error $\sigma(\phi_i)$
Stretch <sup>a</sup>				mdyn Å <sup>-1</sup>	
$K_s$	—CH <sub>2</sub> —CH <sub>2</sub> —	C—H	—	4.737	0.035
$K_x$	—C≡C—H	C—H	—	5.983	0.044
$K_d$	—C≡C—H	C≡C	—	15.22	0.14
$K_p$	CH <sub>2</sub> —C≡C	—C—C≡	—	5.138	0.065
$K_h$	CH <sub>2</sub> —CH <sub>2</sub>	C—C	—	4.87	0.17
Bend				mdyn Å rad <sup>-2</sup>	
$H_\rho$	CH <sub>2</sub> —CH <sub>2</sub>	HCH	—	0.5385	0.0049
$H_\delta$	CH <sub>2</sub> —CH <sub>2</sub>	HCC	—	0.6464	0.0083
$H_\delta'$	C≡C—CH <sub>2</sub>	CCH	—	0.6734	0.0089
$H_\phi, H_\phi'$	C≡C—H	CCH	—	0.2348	0.0020
$H_\theta$	C≡C—CH <sub>2</sub>	CCC	—	0.2933	0.0042
$H_\theta'$	C≡C—CH <sub>2</sub>	CCC	—	0.3317	0.0031
$H_\omega$	C—CH <sub>2</sub> —CH <sub>2</sub>	CCC	—	1.143	0.019
Torsion <sup>b</sup>				mdyn Å rad <sup>-2</sup>	
$\tau$	CH <sub>2</sub> —CH <sub>2</sub>	HCCCH	—	0.0314	0.0023
Stretch-stretch				mdyn Å <sup>-1</sup>	
$F_s$	CH <sub>2</sub> —CH <sub>2</sub>	C—H, C—H	C	0.080	0.036
$F_{hp}$	CH <sub>2</sub> —CH <sub>2</sub> —C≡	C—C, C—C≡	C	0.577	0.088
Stretch-bend				mdyn rad <sup>-1</sup>	
$F_{p\omega}$	CH <sub>2</sub> —CH <sub>2</sub> —C	C—C≡, CCC	C—C	0.524	0.052
$F_{h\omega}$	CH <sub>2</sub> —CH <sub>2</sub> —C	C—C, CCC	C—C	0.686	0.094
$F_{h\delta}$	CH <sub>2</sub> —CH <sub>2</sub>	C—C, HCC	C—C	0.350	0.015
$F_{p\delta'}$	C≡C—CH <sub>2</sub>	C—C, CCH	C—C	0.079	— <sup>c</sup>
$F_{h\delta'}$	≡C—CH <sub>2</sub> —CH <sub>2</sub> —	—C—C—, ≡CCH	C	0.079	— <sup>c</sup>
$F_{p\delta}$	≡C—CH <sub>2</sub> —CH <sub>2</sub> —	≡C—C, HCC—	C	0.079	— <sup>c</sup>
Bend-bend				mdyn Å rad <sup>-2</sup>	
$F_{\phi\theta}$	CH <sub>2</sub> —C≡C—H	CCH, CCC	C≡C	0.1102	0.0043
$F_{\omega\delta}$	≡C—CH <sub>2</sub> —CH <sub>2</sub> —	CCC, HCC—	—C—C—	—0.031	—
$F_{\omega\delta'}$	≡C—CH <sub>2</sub> —CH <sub>2</sub> —	CCC, ≡CCH	≡C—C	—0.031	—
$F_\delta$	CH <sub>2</sub> —CH <sub>2</sub>	HCC, HCC	C—C	—0.021	—
$F_{\delta'}$	≡C—CH <sub>2</sub>	CCH, CCH	C—C	—0.021	—
$F_{\delta\delta'}$	≡C—CH <sub>2</sub> —CH <sub>2</sub> —	≡CCH, HCC—	C	0.012	—
$f_{\omega}^t$	C—CH <sub>2</sub> —CH <sub>2</sub> —C	CCC, CCC	(C)—C— <i>trans</i> —C—(C)	0.026	0.026
$f_{\omega}^g$	C—CH <sub>2</sub> —CH <sub>2</sub> —C	CCC, CCC	(C)—C— <i>gauche</i> —C—(C)	—0.200	0.019
$f_{\omega\delta}^t$	CH <sub>2</sub> —CH <sub>2</sub> —C	CCC, HCC	(H)—C— <i>trans</i> —C—(C)	0.049	—
$f_{\omega\delta}^g$	CH <sub>2</sub> —CH <sub>2</sub> —C	CCC, HCC	(H)—C— <i>gauche</i> —C—(C)	—0.052	—
$f_{\delta}^t$	CH <sub>2</sub> —CH <sub>2</sub>	H <sub>a</sub> CC, H <sub>b</sub> CC	(H <sub>a</sub> )—C— <i>trans</i> —C—(H <sub>b</sub> )	0.1151	0.0065
$f_{\delta}^g$	CH <sub>2</sub> —CH <sub>2</sub>	H <sub>a</sub> CC, H <sub>b</sub> CC	(H <sub>a</sub> )—C— <i>gauche</i> —C—(H <sub>b</sub> )	—0.005	—
$f_{\delta\delta'}^t$	CH <sub>2</sub> —CH <sub>2</sub> —C≡	H <sub>a</sub> CC—, H <sub>b</sub> CC≡	(H <sub>a</sub> )—C— <i>trans</i> —C—(H <sub>b</sub> )	0.002	—
$f_{\delta\delta'}^g$	CH <sub>2</sub> —CH <sub>2</sub> —C≡	H <sub>a</sub> CC—, H <sub>b</sub> CC≡	(H <sub>a</sub> )—C— <i>gauche</i> —C—(H <sub>b</sub> )	0.009	—
$f_{\delta}^t$	≡C—CH <sub>2</sub> —CH <sub>2</sub> —C≡	H <sub>a</sub> CC—, HCC <sub>b</sub> ≡	(H <sub>a</sub> )—C— <i>trans</i> —C—(C <sub>b</sub> ≡)	—0.014	—
$f_{\delta}^g$	≡C—CH <sub>2</sub> —CH <sub>2</sub> —C≡	H <sub>a</sub> CC—, HCC <sub>b</sub> ≡	(H <sub>a</sub> )—C— <i>gauche</i> —C—(C <sub>b</sub> ≡)	—0.025	—

<sup>a</sup>Internal coordinates and symbols are defined in Fig. 1. <sup>b</sup>The torsion is defined as a normalized sum of three *trans*-torsions. <sup>c</sup>Values from ref. 13.

The corresponding values for the melting were  $\Delta H = -2.6 \text{ kcal mol}^{-1}$  and  $\Delta S = -9.6 \text{ cal mol}^{-1} \text{ K}$ .

Complete mid-IR spectra were recorded for every five degrees in the range 280 to 200 K (passing the melting point at 267 K) of BP in a sandwich cell, by means of the Fourier transform spectrometer. The liquid state spectra above 270 K were essentially identical to those at ambient temperature, with slightly sharper bands. At ca. 265 K the *gauche* bands practically vanished and the spectrum remained the same until 240 K. Below this temperature, the spectrum still consists of *anti* bands. In addition, an intense band appeared around  $1377 \text{ cm}^{-1}$ , similar to the 90 K spectrum (Fig. 2 of ref. 1), except that sharp peaks at 1412, 1392, 1383, 1344 and  $1315 \text{ cm}^{-1}$  (Table 1) were resolved in the latter spectrum. These bands are attributed to overtones and combination bands of  $\nu_8$ ,  $\nu_{14}$ ,  $\nu_{20}$  and  $\nu_{28}$  of the *anti* conformer in the crystalline state. Upon heating, the  $1377 \text{ cm}^{-1}$  band disappeared around 240 K but the *gauche* bands did not return before melting at 270 K.

Thus, the high temperature solid phase of BP (phase I, above 240 K) consists of molecules in the *anti* conformer, as in the low temperature phase (phase II, below 240 K). Various reversible spectral changes occurred in the *anti* bands on going from phase I to phase II at ca. 240 K, but the appearance of the  $1377 \text{ cm}^{-1}$  band (and the bands around  $685 \text{ cm}^{-1}$ ) were most prominent.

BP was further crystallized at ambient temperature in a high pressure diamond anvil cell, frequently employed for conformational studies in our laboratory [14]. At ca. 1–2 kbar (estimated pressure) the liquid crystallized probably into phase I and the *gauche* bands disappeared. At ca. 5–10 kbar a phase transition (probably into phase II) could be visually observed in a polarization microscope. The *anti* bands were still present and the  $1380 \text{ cm}^{-1}$  band appeared. No further phase transitions at higher pressures were detected.

The low temperature (and high pressure) solid of BP was accordingly different from those of 1,2-dicyanoethane [15, 16] and 1-cyano-3-butyne [7]. In 1,2-dicyanoethane a reversible phase transition occurred at 223 K [15]; below this temperature the *gauche* conformer was stable, above an *anti-gauche* equilibrium existed, indicating that the high temperature phase was plastic (cubic). 1-Cyano-3-butyne, on the other hand, had a stable crystal, containing what was believed to be the *anti* conformer. However, an apparently metastable crystal could be formed by annealing the amorphous solid from 90 K to ca. 140 K, containing the *gauche* conformer [7]. When the *anti* conformer was formed, however, we were unable to reform the *gauche* conformer [7], indicating an irreversible transition. At high pressure only the *anti* conformer of 1-cyano-3-butyne was detected. Accordingly, these three isoelectronic molecules i.e. BP, 1-cyano-3-butyne and 1,2-dicyanoethane, of which 1-cyano-3-butyne can be considered a hybrid of the others, have quite different conformational features in the solid. Although the three compounds are isoelectronic, the crystals are probably greatly influenced by the vast difference in dipole moments between the  $\text{C}\equiv\text{C}-\text{H}$  and  $\text{C}\equiv\text{N}$  groups.

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