Vibrational Spectra of Biphenylene

In-plane Normal Modes of Biphenylene, [2,3,6,7-²H₄]Biphenylene and [²H₈]Biphenylene †

By Alberto Girlando and Cesare Pecile*

Institute of Physical Chemistry, The University, via Loredan, 2, 35100 Padua, Italy

The Raman spectra of powders and solutions of biphenylene, [2,3,6,7-²H₄]biphenylene, and [²H₈]biphenylene are presented. The frequencies assigned to the a_g modes, together with those attributed in a previous paper to the b_{1u} and b_{2u} modes, are used as a reliable experimental basis to develop a normal coordinate analysis of the in-plane vibrations.

A 28 parameter Valence Force Field, derived from the one which works successfully in the similar case of aromatic hydrocarbons, gives a satisfactory description of the vibrational modes, reproduces the observed frequencies with an average error of less than 10 cm^{-1}, and supports the proposed assignment of the b_{3g} modes.

Raman active out-of-plane modes and lattice vibrations are discussed, and the assignment of the librational modes is proposed through Cruickshank's equation, relating the frequencies of these motions to their mean square amplitude.

The knowledge of the optical spectra of biphenylene, the parent member of a unique series of polynuclear aromatic hydrocarbons,[1] is far from being complete. The electronic absorption spectrum has been only partially studied,[2] and the suggested interpretation of the electronic transitions is limited by the lack of vibrational assignment.[2, 3]

A complete assignment of the ground state vibrational modes, besides its own interest, is stimulated also by the fact that neither biphenylene fluorescence nor phosphorescence spectra display any significant efficiency.[4] Although the infra-red absorption spectra of biphenylene and [²H₈]biphenylene have been thoroughly studied,[5] Raman spectra have not yet been reported, and only a rough attempt to calculate some of the b_{2u} vibrational modes is found in the literature.[3]

In the present paper we report the Raman spectra of biphenylene (BPH), [2,3,6,7-²H₄]biphenylene ([²H₄]BPH) and [²H₈]biphenylene ([²H₈]BPH), carry out a normal coordinate calculation of the in-plane modes and discuss the overall vibrational assignment.

EXPERIMENTAL

The biphenylene used was prepared from benzenediazonium-2-carboxylate.[6] [²H₈]-biphenylene and [2,3,6,7-²H₄]biphenylene were prepared as described elsewhere.[5, 7] All the compounds were carefully purified by repeated crystallization from methanol (m.p. 112°C corrected).

The Raman spectra were recorded on a Jarrell-Ash 25-300 spectrophotometer, equipped with an He-Ne laser (Spectra Physics 125 A) and an ITT-FW 130 phototube. The performance of this experimental set-up falls off rapidly to the Stokes side of the exciting line, so that the sensitivity is quite reduced in the CH stretching region.[8]

The powders enclosed in standard silica capillary cells were examined by the well known transverse viewing method [9] at room temperature, and using a cell similar to that described by Bates [10] for measurements at liquid nitrogen temperature. The depolarization ratios were measured according to method B described by Allemand,[11] with a double pass cell for liquids and a polarization scrambler in front of the entrance slit of the spectrometer; the use of a double-pass cell does not substantially influence the determined values of the depolarization ratio.[11]

RESULTS AND DISCUSSION

VIBRATIONAL IN-PLANE MODES

INTRODUCTIVE ASSIGNMENT

The Raman spectra of BPH, [^{2}H$_4$]BPH, and [^{2}H$_8$]BPH powders are shown in fig. 1; the observed frequencies and the depolarization ratios from solutions are listed in table 1.
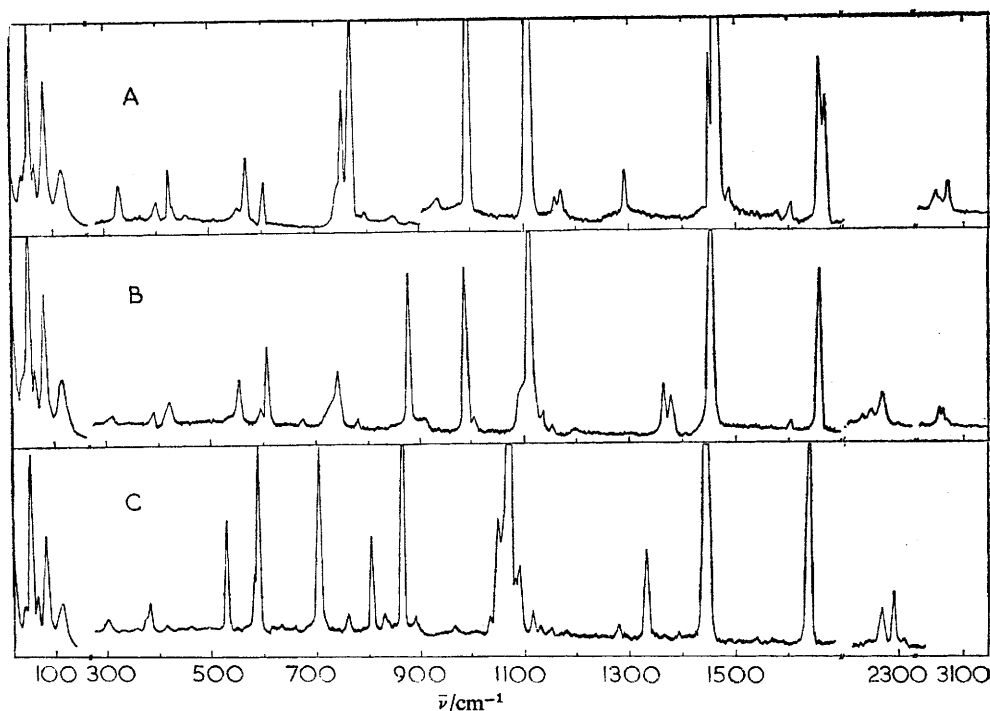

FIG. 1.—Raman spectra of powders of (A) biphenylene, (B) [2,3,6,7-^{2}H$_4$]biphenylene and (C) [^{2}H$_8$]-biphenylene. In the 0-150 cm^{-1} region the gain is 5×10^3 c.p.s., while in the 150-3000 cm^{-1} it is 10^3 c.p.s.

The BPH molecule, as well as its deuterated analogues here considered, belongs to the D_{2h} point group,[12] and its vibrational modes are distributed into symmetry species such that 27 g fundamentals ($10a_g + 4b_{1g} + 4b_{2g} + 9b_{3g}$) are Raman active, 22 u fundamentals ($9b_{1u} + 9b_{2u} + 4b_{3u}$) are infra-red active, and 5 a_u modes are inactive both in absorption and diffusion spectra.[5]

The totally symmetric a_g fundamentals should be distinguishable from the other g ones by the values of the solution depolarization ratios, and the disentangling

between fundamental and combination a_g polarized modes should be favoured by the high intensity of the former. The data in table 1 allow direct attribution of the following a_g fundamentals :

BPH :   1666,   1462,   1399,   1166,   1105,   989,   765 cm^{-1} ;
[^{2}H$_4$]BPH : 1654,   1448,   1372,   1105,   984,   872,   738 cm^{-1} ;
[^{2}H$_8$]BPH : 1640,   1443,   — ,   1070,   863,   808,   707 cm^{-1}.

In the very few cases in which the polarized lines are intrinsically weak, attributing them to fundamentals is assisted by comparison of the BPH spectra with those of the deuterated analogues.

TABLE 1.—RAMAN SPECTRA OF BIPHENYLENE, [2,3,6,7-^{2}H$_4$]BIPHENYLENE and [^{2}H$_8$]BIPHENYLENE
(RAMAN SHIFTS IN cm^{-1})

biphenylene powder [a] room temp.	biphenylene powder [a] low temp.	[^{2}H$_4$]biphenylene powder [a] room temp.	[^{2}H$_4$] powder low temp.	[^{2}H$_8$]biphenylene powder [a] room temp.	[^{2}H$_8$] powder [a] low temp.
37 s	44 m, br	36 s		36 s	44 m, br
41 sh	48 w	40 sh		40 sh	
45 sh				42 sh	
54 vs	60 s	52 vs		50 vs	58 s
64 s	73 m	64 s		63 s	71 m
84 vs	92 s	80 vs		79 vs	88 s
	102 w				100 w
116 s, br	125 m	112 s, br		110 s, br	116 m
	134 m				126 m

biphenylene powder [a] room temp.	solution $\bar{\nu}$/cm^{-1} [b]	ρ [c]	[^{2}H$_4$]biphenylene powder [a] room temp.	solution $\bar{\nu}$/cm^{-1} [b]	ρ [c]	[^{2}H$_8$]biphenylene powder [a] room temp.	solution $\bar{\nu}$/cm^{-1} [b]	ρ [c]
326 m	319	0.72	310 w	300	0.71	305 w	294	0.74
395 w	395	0.12	390 w	388	0.10	376 sh	376 sh	
420 m	417	0.77	421 m	418	0.76	383 m	381	0.20
426 sh			537 vw			415 vw		
452 vw	450 br	dp	555 m	552	0.78	529 s	527	0.78
550 sh			595 w, sh	594 vw		582 sh	582 sh	
568 m	567	0.75	607 s	607	0.70	590 s	590	0.76
603 m	600[d]	0.76	645 vw			633 vw		
740 sh	733	0.10*	674 vw	674 br	dp	707 s	707	0.03
750 s	750	0.74*	722 sh	712	(0.25)	762 w		
768 vs	765	0.04	733 sh			806 m	808	0.01
793 vw	788 br		742 m	738	0.05	834 w, br	835 w,br	
850 vw			777 vw	772 br	0.76	866 vs	863	0.04
	917 br		802 vw	solv.		893 w, br	883 br	p
935 vw, br	932 br	p?	854 vw	solv.		964 vw		
975 vw, br			874 vs	872	0.05	1034 w		
990 vs	989 [d]	0.04	897 w,sh	885 vw, br		1048 s, sh	1046	0.20
1106 vs	1105	0.21	906 w	903 vw, br		1070 vs	1070	0.17
1157 w	1149 [e] br		916 vw	926 br	p	1090 m,sh	1088	(0.24)
1166 m	1166 [e]	0.18	982 s	984 [d]	0.09	1114 w	1109	p?
1288 m	1288 [d]	0.75	999 sh	999 [d]	0.30	1150 vw	1150 vw	
1399 vw	1399	0.12	1038 vw	1034 [d]	p	1278 w		
1436 vw	1441 sh		1090 sh	1085	(0.18)		1330 sh	
1450 s,sh	1449 [e]	(0.75)	1104 vs	1105	0.22	1332 m	1334	0.71
	1457 sh		1128 sh	1127	(0.18)	1444 vs	1443	0.24
1459 vs	1462	0.27	1150 w	1150	(0.40)	1538 vw		
1484 w	1480	0.19*	1360 m	1360 [d]	0.76	1632 m, sh		

TABLE 1—*continued*

solution $\bar{v}$/cm^{-1} [b]	ρ [c]		solution $\bar{v}$/cm^{-1} [b]	ρ [c]		solution $\bar{v}$/cm^{-1} [b]	ρ
1601 w	1602 [e]	dp?	1374 m	1372 [d]	0.14	1638 vs	1640	0.13
1656 s	1564	0.18*	1448 vs	1448	0.25	2244 vw		
1666 s	1666	0.15*	1600 w	solv.		2267 m, sh		
3010 vw			1648 sh			2271 m	2271	0.65
3048 w, br	3057 [f]	0.75	1654 vs	1654	0.16	2291 m	2294	0.10
3070 m	3074 [f]	0.16	2195 vw			2312 vw		
			2249 w	2253 sh				
			2265 w	2268 sh				
			2282 vw					
			2287 vw	2288	0.18			
			2320 vw	2320	p			
			3055 w	solv.				
			3059 w	solv.				
			3069 vw	solv.				

[a] Relative intensities of the powder spectra are indicated by: vs, very strong, s, strong, m, medium, w, weak, vw, very weak, sh, shoulder, br, broad. Low temperature: sample effective temperature approximately 100 K. [b] Frequency values and depolarization ratios are measured in a solution 1 M in benzene, if not otherwise indicated. solv. indicates the presence of a solvent Raman line in that region. [c] Values of depolarization ratio (ρ) marked with * are measured in a solution 0.6 M in benzene. Values in parentheses refer to cases in which there is band overlapping. p and dp stand for polarized and depolarized, respectively, and are used when it is not possible to get meaningful numerical values from the spectra. [d] Solution in methylene chloride; [e] solution in carbon disulphide; [f] solution in acetone.

The comparison between the a_g frequencies above assigned and the a_g frequencies from v_3 to v_8 of naphthalene [13] and [$^2H_8$]naphthalene [14] shows a strictly parallel trend, except for the presence of one additional mode for BPH. Within the limits of a correlative discussion, it can be suggested that the unassigned [$^2H_8$]BPH mode, roughly associated with those at 1399 and 1372 cm^{-1} of BPH and [$^2H_4$]BPH respectively, is probably located at 1278 cm^{-1}. At this frequency a weak line is observed in the powder spectra. Moreover, the lowest a_g mode of the examined compounds is presumably located below 750 cm^{-1}, since the lowest a_g frequency of naphthalene is at 512 cm^{-1}. The data in table 1 indicate as possibilities the lines at 395 (BHP), 388 ([$^2H_4$]BPH), and 381 ([$^2H_8$]BPH) cm^{-1}.

Four CH/CD stretching modes are expected, two of a_g and two of b_{3g} species. The collected data in the corresponding spectral regions are, however, relatively poor owing partly to the low instrumental response (see Experimental). We shall, therefore, limit our proposal to the following assignments:

BPH: 3074 (a_g) and 3057 (b_{3g}) cm^{-1}; [$^2H_4$]BPH: 2288 (a_g) cm^{-1};
[$^2H_8$]BPH: 2294 (a_g) cm^{-1}.

In regard to the seven remaining b_{3g} modes, at this stage we limit ourselves to attributing the following depolarized lines: 1449 and 1288 cm^{-1} (BPH); 1360 cm^{-1} ([$^2H_4$]BPH); and 1334 cm^{-1} ([$^2H_8$]BPH). The assignment of the in-plane modes can be extended no further, because the nontotally symmetric modes are often intrinsically weak, and because the location of b_{3g} fundamentals interferes with that of the depolarized b_{1g} and b_{2g} out-of-plane modes in the spectral region below 1000 cm^{-1}.

From the present Raman, and the previous infra-red work,[5, 7] an almost complete assignment of the in-plane a_g, b_{1u}, and b_{2u} fundamentals of BPH and its deuterated

analogues has been achieved ; a normal coordinate analysis founded on this experimental basis offers a suitable way to rationalize and complete the assignment.

NORMAL COORDINATE CALCULATION

A schematic drawing of the BPH molecule and the nomenclature of the internal coordinates are shown in fig. 2. Bond lengths and bond angles used for the construction of the G matrix were taken from the crystal structure.[12]

The choice of an initial force field is simple when we consider the BPH molecular structure,[12] which is rather similar to that of alternant aromatic hydrocarbons. Thus, application of the Valence Force Field developed for aromatic hydrocarbons,[15] and extensively applied in many cases,[16-22] seems reasonable. The refined values of the 28 force constants used in the calculation, together with their standard errors estimated from standard errors in the frequency parameters, are collected in table 2.

TABLE 2.—VALENCE FORCE CONSTANTS FOR BIPHENYLENE

symbol	coordinates involved	force const.[a] Φ_i	$\sigma(\Phi_i)^b$
K_1	$r_1 r_1 = r_2 r_2$	5.06	0.01
K_2	$R_1 R_1$	6.75	0.06
K_3	$R_2 R_2$	5.76	0.06
K_4	$R_3 R_3$	6.56	0.10
K_5	$R_{13} R_{13}$	5.79	0.08
K_6	$R_6 R_6$	4.40	0.10
H_1	$\beta_1 \beta_1 = \beta_2 \beta_2$	0.462	0.005
H_2	$\beta_3 \beta_3 = \beta_4 \beta_4$	0.506	0.005
H_3	$\vartheta_1 \vartheta_1 = \vartheta_2 \vartheta_2$	1.011	0.020
H_4	$\vartheta_5 \vartheta_5$	0.610	0.038
H_5	$\varphi_1 \varphi_1'$	0.546	0.027
H_6	$\varphi_1 \varphi_1$	1.586	0.060
F_1	$r_1 r_2 = r_2 r_3$	0.068	0.010
F_2	$R_1 R_2 = R_2 R_3$	0.670	0.028
F_3	$R_1 R_{13}$	0.716	0.038
F_4	$R_6 R_{13}$	0.451	0.040
F_5	$R_1 R_{12}$	0.067	0.038
F_6	$R_1 R_3 = R_1 R_5 = R_2 R_4 = R_2 R_{13}$	-0.316	0.019
F_7	$R_{13} R_{14}$	0.398	0.085
F_8	$R_1 R_4 = R_2 R_5 = R_3 R_{13}$	0.480	0.032
F_9	$R_6 \varphi_2 = R_{13} \varphi_1$	0.650	0.036
F_{10}	$R_1 \vartheta_1 = R_1 \vartheta_{12} = R_{13} \vartheta_5$	0.467	0.033
F_{11}	$R_2 \vartheta_1 = R_2 \vartheta_2 = R_3 \vartheta_2$	0.275	0.033
F_{12}	$R_1 \varphi_2'$	0.274	0.040
F_{13}	$R_6 \varphi_1'$	0.055	0.061
F_{14}	$R_1 \beta_1 = R_2 \beta_2 = R_2 \beta_3 = R_3 \beta_4$	0.128	0.008
F_{15}	$\vartheta_1 \vartheta_2 = \vartheta_2 \vartheta_3 = \vartheta_4 \vartheta_5$	-0.030	0.011
F_{16}	$\varphi_1 \varphi_2 = \varphi_2 \varphi_3 = \varphi_1 \varphi_4' = $ $\varphi_1' \varphi_4' = \varphi_1 \vartheta_5 = \vartheta_5 \vartheta_{12}$	0.108	0.019

[a] Stretch constants are in units of mdyn/Å ; stretch-bend, mdyn/rad ; bend, mdyn Å/(rad)².
[b] $\sigma(\Phi_i)$ is the standard error in Φ_i estimated from the standard error in frequency parameters and the variance-covariance matrix.

The zero order CC stretching force constants were estimated by interpolation from a CC force constants against interatomic distances plot.[16]

A few force constants with no correspondence in aromatic hydrocarbons were

chosen as follows. The C—C bond length of the BPH central bridge is 1.514 Å,[12] and compares with the C—C bond length of cyclohexa-1,3-diene [23] and acenaphthene [21]; correspondingly an initial force constant of 4.44 mdyn/Å was chosen.
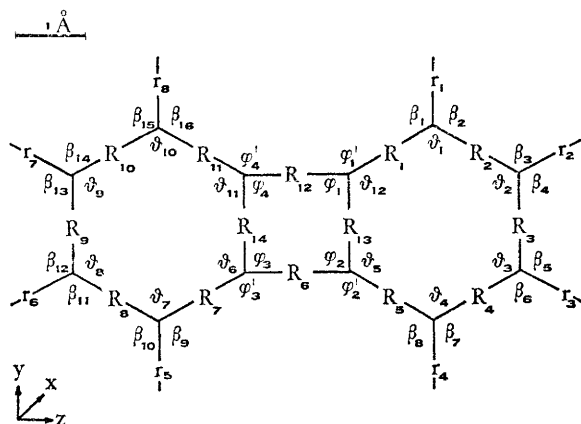

FIG. 2.—Internal coordinates of biphenylene.

For the external and internal bending of the central ring, H_5 and H_6, trial values of 0.7 and 1.0 mdyn/Å were assumed. Independently from close structural analogies, these values are similar to those used for many closed chain molecules.[15, 19-22, 24] Analogous criteria were adopted for the F_9, F_{12}, F_{13} and F_{16} interaction force constants.

The value of 0.2 rather than 0.6 mdyn/Å (as in conjugated aromatic structures) was given initially to the F_4 interaction constant between the two adjacent stretches of the central ring, according to the value used in the case of cyclohexa-1,3-diene [23] and toluene.[25] Stretch–stretch interactions between non-adjacent bonds of different rings were ignored.

The calculation was performed on a CDC 6600 computer, using a somewhat modified version of a program written by Schachtschneider.[26]

The zero order calculation, performed with the initial force field, led to acceptable agreement between calculated and directly assigned infra-red and Raman active fundamental frequencies. The average error was reduced to 9.1 cm^{-1} by a standard refinement process, and the results are collected in table 3. The refined force constants (table 2) are consistent with the initial choices based on the above mentioned criteria, and the variations observed at the end of the refinement are within reasonable limits.

The approximate description of the vibrational modes in terms of percent of potential energy distribution (PED), given in table 3, is also satisfactory in comparison with the reported results for analogous molecular structures treated with similar force fields.[15, 19]

FINAL ASSIGNMENT

Using the calculated frequencies (table 3) of the in-plane modes, it is possible to reanalyse the spectra of BPH and its deuterated analogues.

As far as the a_g and b_{1u} vibrations are concerned, the normal coordinate analysis supports all the assignments of the a_g modes already discussed, and those of the b_{1u}

TABLE 3.—OBSERVED [a] AND CALCULATED IN-PLANE FREQUENCIES AND APPROXIMATE PTEONTIAL ENERGY DISTRIBUTION

sym. species [b]	biphenylene $\bar{\nu}$/cm⁻¹ obs.	calc.	pot. energy distr. (%)[c]	[2,3,6,7-²H₄]biphenylene $\bar{\nu}$/cm⁻¹ obs.	calc.	pot. energy distr. (%)[c]	[²H₈]biphenylene $\bar{\nu}$/cm⁻¹ obs.	calc.	pot. energy distr. (%)[c]
ν_1	3074	3086	$K_1(97)$	3059*	3054	$K_1(99)$	2294	2300	$K_1(94)$
ν_2	(3057)	3040	$K_1(100)$	2288	2289	$K_1(95)$	(2271)	2269	$K_1(95)$
ν_3	1666	1671	$K_2(39), K_4(17)$	1654	1657	$K_2(44), K_5(16), K_6(17)$	1640	1642	$K_2(42), K_5(17), K_6(17)$
ν_4	1462	1455	$K_2(26), K_3(24), K_4(35), K_6(19), H_2(23)$	1448	1433	$K_2(20), K_3(37), K_4(30), H_1(17)$	1443	1423	$K_2(22), K_3(34), K_4(43), K_6(17)$
ν_5	1399	1391	$K_5(23), H_1(54)$	1372	1362	$K_4(24), K_5(18), H_1(49)$	1278*	1263	$K_4(19), K_5(45), H_1(24)$
ν_6	1166	1174	$H_1(18), H_2(52)$	1105	1109	$K_5(64), K_6(24), H_1(16)$	1070	1070	$K_3(50), K_5(37), K_6(24)$
ν_7	1105	1097	$K_3(31), K_5(58), K_6(20)$	984	973	$K_3(56), H_1(17)$	863	849	$H_2(77)$
ν_8	989	971	$K_3(44), K_4(23), H_1(18)$	872	849	$K_4(23), H_2(61)$	808	817	$K_3(17), K_4(16), H_1(35)$
ν_9	765	779	$K_2(31), K_6(16), H_3(29)$	738	768	$K_2(27), H_3(29)$	707	714	$K_2(22), H_1(26), H_3(24)$
ν_{10}	395	390	$K_2(16), K_6(29), H_3(27)$	388	382	$K_2(16), K_6(29), H_3(27)$	381	375	$K_2(17), K_6(29), H_3(26)$
$b_{1u}\ \nu_{20}$	(3072)	3086	$K_1(97)$	(3071)	3054	$K_1(99)$	2285	2299	$K_1(94)$
ν_{21}	3030	3040	$K_1(100)$	(2281)	2289	$K_1(94)$	2258	2268	$K_1(95)$
ν_{22}	1598	1590	$K_4(40), H_2(24)$	1571	1557	$K_3(16), K_4(39), K_5(17)$	1556	1541	$K_3(16), K_4(41), K_5(18)$
ν_{23}	1426	1415	$K_3(17), K_5(16), H_1(56)$	1405	1405	$H_1(63)$	1315	1306	$K_2(30), K_5(22), H_1(30)$
ν_{24}	1260	1274	$K_2(58), K_5(37), H_2(30)$	1239	1240	$K_2(61), K_3(21), K_4(34), K_5(45)$	1240	1238	$K_2(55), K_5(20), K_4(34), K_5(51)$
ν_{25}	1151	1152	$K_2(16), K_4(29), H_2(40)$	1024	1037	$K_2(26), K_5(23), H_1(32)$	948	960	$K_3(42), K_5(18)$
ν_{26}	1019	1021	$K_2(23), K_5(33), H_1(20)$	949	954	$K_3(63)$	842	848	$H_2(78)$
ν_{27}	962	967	$K_5(57), K_4(20)$	848	837	$K_4(16), H_2(76)$	782	776	$H_1(59)$
ν_{28}	612	610	$H_3(59)$	603	606	$H_3(59)$	591	592	$H_3(59)$
$b_{2u}\ \nu_{33}$	3072	3064	$K_1(98)$	3071	3053	$K_1(99)$	2292	2283	$K_1(95)$
ν_{34}	3022	3022	$K_1(101)$	2281	2263	$K_1(96)$	2271	2256	$K_1(97)$
ν_{35}	1638*	1651	$K_2(52), K_3(17), K_6(22)$	—	1646	$K_2(53), K_6(23)$	1621	1634	$K_2(55), K_6(25)$
ν_{36}	1444	1461	$K_3(26), H_2(64)$	1348	1356	$K_3(48), K_6(16), H_2(19)$	(1315)	1340	$K_3(53), H_2(23)$
ν_{37}	1267	1285	$K_6(18), H_1(56)$	1219	1235	$H_1(70), H_2(16)$	1091	1097	$K_6(19), H_1(16), H_2(25), H_3(20)$
ν_{38}	1128	1113	$H_1(31), H_2(16)$	1095	1077	$K_2(18), H_3(34)$	963*	959	$H_1(38), H_2(21), H_3(19)$
ν_{39}	1053	1040	$K_3(25), H_2(26)$	906	888	$K_3(20), H_2(59)$	—	813	$K_5(16), H_1(45), H_2(31)$
ν_{40}	751	727	$K_6(17), H_3(43)$	690	701	$H_3(44)$	683	701	$H_3(44)$
ν_{41}	212	214	$K_6(24), H_4(22), H_5(38)$	206	206	$K_6(24), H_4(22), H_5(38)$	197	199	$K_6(24), H_4(22), H_5(38)$
$b_{3g}\ \nu_{42}$	3057	3064	$K_1(98)$	3055*	3053	$K_1(99)$	(2271)	2283	$K_1(95)$
ν_{43}	3010*	3022	$K_1(101)$	2268	2263	$K_1(96)$	2267*	2257	$K_1(97)$
ν_{44}	1602	1601	$K_2(54), K_5(24)$	1600*	1592	$K_2(58), K_3(20)$	—	1577	$K_2(61), K_3(22)$
ν_{45}	1449	1457	$K_3(20), H_2(63)$	1360	1358	$K_2(17), K_3(40), H_2(17)$	1334	1333	$K_3(45), K_2(23)$
ν_{46}	1288	1287	$H_1(59)$	—	1238	$H_1(68), H_2(17)$	1034*	1044	$H_1(43), H_2(40)$
ν_{47}	(1105)	1080	$K_3(37), H_1(26), H_2(23)$	(984)	958	$H_3(56), H_4(17)$	—	942	$H_3(56), H_4(16)$
ν_{48}	975*	977	$H_3(59)$	903	903	$H_2(62)$	(808)	810	$K_3(17), H_1(42), H_2(34)$
ν_{49}	600	608	$H_4(22), H_5(44)$	594	598	$H_4(24), H_5(41)$	590	585	$H_3(20), H_4(30), H_5(37)$
ν_{50}	567	553	$K_2(16), H_3(20), H_4(16), H_6(38)$	552	539	$K_2(17), H_3(19), H_6(38)$	527	525	$K_2(21), H_6(43)$

[a] Frequency values marked with asterisk (*) refer to lines observed in the powder spectra only, the others to lines observed in the solution spectra. [b] According to Mulliken's convention.[28] [c] Only contributions greater than 15 % are included. Coordinates involved in potential energy distribution: K_1, CH stretch; K_2 to K_5, ring CC stretch; K_6, bridge CC stretch; H_1, α-CH bend; H_2, β-CH bend; H_3 and H_4, ring CCC bend; H_5 and H_6, ring bridge CCC bend.

modes previously reported.[5, 7] This fact proves particularly useful in the case of those polarized Raman lines whose attribution is somewhat uncertain due to their comparatively low intensity (namely: BPH, 1399, 1166 and 395 cm^{-1}; [^{2}H$_4$]BPH, 1372 and 388 cm^{-1}; [^{2}H$_8$]BPH, 381 cm^{-1} and the very weak line at 1278 cm^{-1}, detected in the powder spectrum only). It is equally useful in the case of the weak infra-red bands polarized along the b crystal axis and attributed to b_{1u} fundamentals (namely: BPH, 1019 cm^{-1}; [^{2}H$_4$]BPH, 1024 and 848 cm^{-1}). It must be pointed out, however, that among the highest ring stretch frequencies, only the $a_g\nu_3$ mode is safely recognized in the spectra, while the infra-red active modes, on the other hand, are of very low intensity. This behaviour can be compared with that of the corresponding modes of *ortho*-substituted benzenes for substituents having weak perturbing effect.[27] The experimental absorption pattern makes a definite assignment intrinsically difficult. In fact, for b_{2u} modes in particular, we limit ourselves to the proposal of the observed frequencies as given in table 3.

The b_{2u} mode left unassigned in the previous work [5, 7] is easily located by the normal coordinate analysis: the calculated values at 1040 (BPH), 888 ([^{2}H$_4$]BPH) and 959 ([^{2}H$_8$]BPH) cm^{-1}, can well be related to the perpendicularly polarized bands at 1053 and 963 cm^{-1} of BPH and [^{2}H$_8$]BPH, respectively. In the case of [^{2}H$_4$]BPH, the strong absorption at 890 cm^{-1}, due to the out-of-plane $b_{3u}\nu_{51}$ fundamental, makes it difficult to sort out the b_{2u} mode; a plausible candidate seems to be the band at 906 cm^{-1} observed in solution.

A more detailed discussion is required in reanalysing the assignment of some of the b_{2u} fundamentals. As far as BPH is concerned, only the location of the $b_{2u}\nu_{40}$ remains to some extent uncertain, due to the interference of a strong parallel band at 733 cm^{-1}, related to the $b_{3u}\nu_{53}$ mode, and to the presence at 717 and 751 cm^{-1} of two perpendicularly polarized bands, which are both possibilities. The calculated value of 727 cm^{-1} does not add information to guide the choice and so we prefer to leave the previous attribution of the 751 cm^{-1} band unmodified.

In the case of [^{2}H$_4$]BPH b_{2u} vibrations, the assignment of the $b_{2u}\nu_{37}$ to the weak and correctly polarized band at 1219 cm^{-1} is confirmed, while the absorption at 1348 cm^{-1}, which displays inverted polarization, remains the only available choice for the $b_{2u}\nu_{36}$ vibration.

The [^{2}H$_8$]BPH $b_{2u}\nu_{36}$ fundamental, as the calculation indicates, has a frequency value near that of the $b_{1u}\nu_{23}$, which is associated with the correctly polarized strong absorption at 1315 cm^{-1}. In the solution spectrum a doublet is observed at 1315 and 1319 cm^{-1}. The crystal spectrum, however, does not allow isolation of a perpendicular absorption. Therefore we assume the $b_{2u}\nu_{36}$ to be overlapped by the $b_{1u}\nu_{23}$, and attribute both at the same frequency. The [^{2}H$_8$]BPH $b_{2u}\nu_{39}$ mode is calculated 40 cm^{-1} apart from the previously assigned weak perpendicular band at 853 cm^{-1}. The calculated value, which is chiefly determined by CH bending force constants adjusted to numerous frequencies given by the three isotopic analogues, has a good degree of reliability. We therefore prefer to leave this mode unassigned, although many very weak perpendicular bands are present in the 800-850 cm^{-1} region.

Few remarks need be added to those given in the Introductive Assignment section on b_{3g} fundamentals. The depolarized lines at 600 and 567 cm^{-1} (BPH), 552 cm^{-1} ([^{2}H$_4$]BPH), 590 and 527 cm^{-1} ([^{2}H$_8$]BPH) are easily recognized as due to in-plane modes, according to the calculated values. The same criterion allows us to propose other b_{3g} fundamental frequencies in correspondence to Raman lines which are too weak for their depolarization ratio to be measured, or which are likely overlapped by strong a_g lines (table 3).

The application of the product and sum rules to the symmetry blocks of frequencies

(table 5) supports the overall assignment within the known limits of these tests for large molecules. Attempts to assign absorption combination tones, which in the case of large molecules have numerous alternatives, cannot significantly contribute to the interpretation of the spectra.

Raman frequency shifts of the order of 5 cm^{-1} or less have been observed and clear Davydov splittings of some fundamentals have been detected in the low temperature powder spectrum only. Small static and correlation crystal field effects were also noticed in the absorption infra-red work previously reported.[5]

VIBRATIONAL OUT-OF-PLANE MODES

The frequencies attributed to out-of-plane fundamentals are collected in table 4. The assignment of the u modes [5, 7] requires no further comment. The above discussed choice of the depolarized lines below 1000 cm^{-1} associated with b_{3g} modes, has to some extent simplified the discussion on the depolarized out-of-plane modes.

TABLE 4.—VIBRATIONAL ASSIGNMENT OF THE b_{2g} AND b_{3u} OUT-OF-PLANE FUNDAMENTALS [a] (cm^{-1}) OF BIPHENYLENE, [2,3,6,7-^{2}H$_4$]BIPHENYLENE AND [^{2}H$_8$]BIPHENYLENE

symmetry species	designation [b]	$C_{12}H_8$	$C_{12}H_4D_4$	$C_{12}D_8$
b_{2g}	ν_{29}	917	885	762*
	ν_{30}	750	607	582
	ν_{31}	417	418	376
	ν_{32}	319	300	294
b_{3u}	ν_{51}	915	890	750
	ν_{52}	733	591	558
	ν_{53}	366	356	321
	ν_{54}	120	114	113

[a] Wavenumber values marked with asterisk (*) refer to lines observed in the powder spectra only, the others to lines observed in the solution spectra.   [b] According to Mulliken's convention.[28]

The ν_{29}, ν_{30} and ν_{31} b_{2g} are identified mainly on the basis of the well settled comparative scheme offered by naphthalene [28] and *ortho*-substituted benzenes.[29] The b_{2g} ν_{32} mode, which presumably implies an out-of-plane deformation of the two aromatic rings with respect to the tetratomic central skeleton, has no correspondence in the

TABLE 5.—PRODUCT AND SUM RULES FOR BIPHENYLENE, [2,3,6,7-^{2}H$_4$]BIPHENYLENE AND [^{2}H$_8$]BIPHENYLENE

symmetry species	$\dfrac{\Pi\nu_i(\text{BPH})}{\Pi\nu_i([^2\text{H}_4]\text{BPH})}$		$\dfrac{\Pi\nu_i(\text{BPH})}{\Pi\nu_i([^2\text{H}_8]\text{BPH})}$		$\dfrac{\Sigma\nu_i^2(\text{BPH})+\Sigma\nu_i^2([^2\text{H}_8]\text{BPH})-2\Sigma\nu_i^2([^2\text{H}_4]\text{BPH})}{\Sigma\nu_i^2(\text{BPH})+\Sigma\nu_i^2([^2\text{H}_8]\text{BPH})}$
	calc.	expt.	calc.	expt.	
a_g	2.00	1.97	4.00	3.89	0.0015
b_{1u}	1.97	1.94	3.90	3.82	0.0054
b_{2u}	1.97		3.90		
b_{3g}	1.93		3.78		
b_{2g}	1.36	1.36	1.90	1.87	0.0023
b_{3u}	1.40	1.37	1.95	1.94	0.0198

naphthalene case, but may be correlated with the lowest frequency b_{2g} mode of anthracene. Although the assignment of the out-of-plane g modes of anthracene has not been completely defined, there is general agreement [30, 31] on the assignment

of the lowest b_{2g} mode at 290 cm^{-1}. For this reason, the only depolarized line observed below 400 cm^{-1}, attributable equally well to a b_{1g} or a b_{2g} mode, is assigned to the b_{2g} ν_{32}. The b_{2g} block assignment is thus completed with very good agreement in terms of product and sum rules (table 5).

A correlative scheme as good as the one for the b_{2g} vibrations is not available for those of b_{1g}.[32] Therefore, we do not try to localize these modes, but just list the depolarized Raman lines left unassigned : BPH, 450 cm^{-1} ; [^{2}H$_4$]BPH, 772 and 672 cm^{-1}.

LATTICE MODES

Biphenylene crystallizes in the monoclinic system,[12] space group C_{2h}^5 ($P2_1/a$). As there are six molecules in the unit cell, they occupy two crystallographically independent sets, one with two molecules on C_i sites and the other with four molecules on C_1 sites. So we expect 18 Raman active lattice modes, distributed as follows :

molecules on C_i : librations $3A_g + 3B_g$
molecules on C_1 : librations $3A_g + 3B_g$
            translations $3A_g + 3B_g$

and 15 infra-red active lattice modes, namely 9 translations ($5A_u + 4B_u$) and 6 librations ($3A_u + 3B_u$).

Mixing of the translational and librational motions is only permitted for molecules on C_1 sites and no interaction is possible between lattice modes of molecules located on two symmetry unrelated sets.
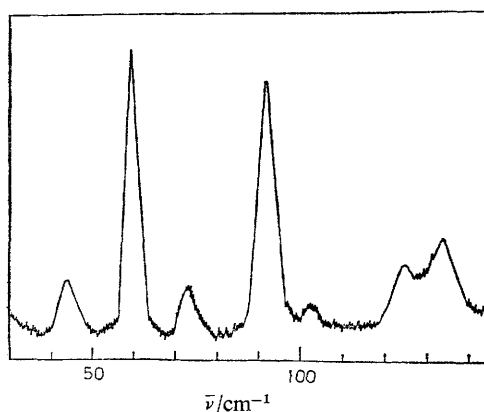

FIG. 3.—Raman spectra of biphenylene powder at liquid nitrogen temperature.

Assuming that there is no phase transition by lowering temperature, the assignment of the Raman active lattice vibrations can be based on powder spectra of BPH and [^{2}H$_8$]BPH, which have been measured at room temperature and at liquid nitrogen temperature (table 1 and fig. 3). The temperature frequency shifts of the assigned intramolecular modes are, as expected, much smaller than those observed for Raman lines below 200 cm^{-1}, which display the typical temperature pattern of lattice vibrations.[33] As a consequence, the Raman lines observed in this region for both BPH and [^{2}H$_8$]BPH can be confidently attributed to lattice modes. The low temperature powder spectrum (fig. 3) gives us the advantage of a clear pattern, in which seven lines are recognizable, whereas at room temperature the broadness of the lines makes the pattern less clear. The spectra display a number of lattice frequencies which is

much lower than the number predicted by the group theoretical analysis. In the far infra-red region BPH powder shows two previously unreported weak absorptions at 58 and 115 cm^{-1}.

With such a complex crystal structure and with the available data, a sufficiently rigorous attempt to rationalize the assignment of BPH lattice vibrations is not possible. The relative simplicity of the observed experimental pattern, however, prompts us to suggest a very rough interpretation based on the following drastically simplified model.

A first approximation is the assumption of a rigid molecule model, although its limitations are freely admitted.[34] Furthermore, we assume that the possible mixing between translational and librational motions for the molecules on C_1 sites can be neglected, and the intermolecular interactions are comparable for C_i and C_1 molecules. In this way the energy of the rotational motions of the same symmetry around the same axis should be practically identical for C_i and C_1 molecules.

With these assumptions we expect to observe only six distinct rotational lattice Raman lines, arranged in the form of three pairs, each of which consists of A_g and B_g lines. Furthermore, in the absence of mixing between translational and librational modes, we expect the Raman active translational modes and the infra-red active librational motions to display low intensity. It follows that the Raman spectrum may be chiefly interpreted in terms of librational modes and that the observed infra-red bands may be attributed to translational modes.

In the rigid molecule approximation we can use Cruickshank's relationship [35] to estimate the average librational frequencies. The X-ray values [12] of $(\overline{\Phi^2})_I$ at 300 K give, for rotational oscillations around the X, Y, Z molecular axes respectively, the mean frequencies of 68, 103 and 100 cm^{-1} for molecules on C_i and 56, 83 and 95 cm^{-1} for molecules on C_1. This interpretative scheme leads to the assignment of the frequency pairs at 60, 73 cm^{-1}; 92, 102 cm^{-1}; 125, 134 cm^{-1}, observed at low temperature, to the librations around the X, Y, Z axes respectively.

TABLE 6.—LIBRATIONAL LATTICE MODES (cm^{-1}) OF BIPHENYLENE, [2,3,6,7-^{2}H$_4$]BIPHENYLENE AND [^{2}H$_8$]BIPHENYLENE

molecular axis	BPH room temp.	BPH low temp.[a]	[^{2}H$_4$]BPH room temp.	[^{2}H$_8$]BPH room temp.	[^{2}H$_8$]BPH low temp.[a]	$\nu(^2H_8)/\nu(^1H_8)$ low temp.	$[I(^1H_8)/I(^2H_8)]^{\frac{1}{2}}$
X	54 64	60 73	52 64	50 63	58 71	0.970	0.945
Y	84	92 102	80	79	88 100	0.969	0.951
Z	116	125 134	112	110	116 126	0.934	0.923

[a] Liquid nitrogen coolant: sample effective temperature approximately 100 K.

The corresponding frequencies observed at room temperature (54, 64 cm^{-1}; 84 cm^{-1} and 116 cm^{-1}) give r.m.s. amplitudes of vibrations of 2.7°, 2.1° and 3.2°. These values must be compared with the X-ray values [12] of 2.3°, 1.7° and 3.6° for C_i molecules. A corresponding comparison with the X-ray r.m.s. amplitudes for C_1 molecules (2.8°, 2.1° and 3.8°) is less meaningful because the frequencies of the infra-red active librations are not known.

The assignment given above leaves unattributed the line at 44 cm^{-1} (low temperature), which may be connected with translational motions. An alternative choice is the

following: pairs at 44, 60 cm^{-1}; 73, 92 cm^{-1}; 125, 134 cm^{-1} in the low temperature spectrum. The problem with this choice is that it gives a worse fit between X-ray and spectroscopic $(\overline{\Phi^2})_l$ values. However, the line left unassigned at 102 cm^{-1} is more likely to be explained as a translational vibration than the line at 44 cm^{-1}.

Table 6 summarizes the proposed assignment of the librational lattice vibrations of the three compounds, with a comparison of the related [33] ratios $\nu_i(^2H_8)/\nu_i(^1H_8)$ and $[I_i(^1H_8)/I_i(^2H_8)]^{\frac{1}{2}}$ in the last two columns.

CONCLUSIONS

The 37 in-plane vibrational modes of biphenylene and its deuterated analogues have been satisfactorily assigned. The assignments are supported by the calculation of the normal frequencies, essentially based on a 28 parameter Califano's [15] Valence Force Field.

Our earlier assignments [5, 7] of the infra-red active modes have been confirmed and completed with minor changes. The collected data are not sufficient to warrant the assignment of the four b_{1g} out-of-plane frequencies. This problem, as well as that of confirming the nontotally symmetric g vibrational frequencies, is therefore left open. This is also partly a consequence of the experimental difficulties encountered in the attempt to obtain single-crystal Raman spectra. On the whole, however, the presented assignment of BPH intramolecular modes is almost as extended as that of naphthalene, whose complete assignment is still in some dispute.[32] Although with the introduction of drastic assumptions, the Raman active lattice frequencies, which are much less numerous than predictable, have been reasonably accounted for.

The knowledge of the ground state vibrational behaviour achieved in the present paper offers a valuable reference point in the interpretation of the high resolution absorption electronic spectrum of biphenylene which is in progress in this laboratory.[36]

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