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The vibrational spectra of d_{10} and $4,4' d_2$ biphenyl

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Abstract—The vibrational frequencies of $4,4' d_2$ biphenyl and d_{10} biphenyl have been calculated for various dihedral angles between the rings. The vibrational spectra have been recorded in solution and in the crystal state, and the results are interpreted, with the aid of the computed fundamental frequencies, in terms of a D_{2h} molecular structure in the crystal and a D_2 structure in solution. For the planar structure only minor differences exist between the current assignments and those of Zerbi and Sandroni.

IN AN EARLIER paper [1] it was demonstrated that the spectra of biphenyl and of 4,4' diffuorobiphenyl showed unequivocal evidence for a change in dihedral angle in going from crystal to solution phase. It was shown that the dihedral angle change away from 0° resulted in interaction of the b_{1g} and b_{1u} species and of the b_{2g} and b_{2u} species. Neglecting any force constant changes the mergence of these species caused frequency shifts and eigenvector changes primarily in those vibrations with frequencies below 1000 cm⁻¹. The observed frequency shifts and relaxation of the selection rules were in good accord with predictions and with computed changes using a vibrational force field transferred from benzene.

In principle it should be possible to determine the dihedral angle of biphenyl in solution by comparing the observed frequency shifts with the calculated. This presupposes that the eigenvector descriptions are sufficiently good to give a reasonable description of the vibrational wavefunction overlap and that the eigenvalue separations are close to the observed. These requirements follow from first order perturbation theory in which the perturbation to the energy levels is given by

$$\frac{(\beta - E_i S)^2}{E_i - E_i}$$

where $\beta = \int \Psi_i H' \Psi_j \, d\tau$, H' is the perturbation operator, S is the overlap integral and E_i and E_j are the unperturbed energy levels which are interacting. The observed and calculated frequencies were, for assignment purposes, very satisfactory, the average frequency error being about 16 cm⁻¹. For the purposes of determining the dihedral angle however this is somewhat large since the separation of the vibrational frequencies which mix on lowering the symmetry is less than 100 cm⁻¹ in several cases. The data on biphenyl itself suggested an angle in solution of $45 \pm 15^{\circ}$. It has been shown in another publication [2] that improvement of the eigenvectors based on a restricted force field correction procedure to the data of biphenyl, d_{10} biphenyl and d_2 biphenyl changes the value to $32 \pm 2^{\circ}$. Although the spectra of the deuterated biphenyls have been the subject of earlier papers there are several

^[1] R. M. BARRETT and D. STEELE, J. Mol. Structure 11, 105 (1972).

^[2] V. J. EATON and D. STEELE, J. Chem. Soc., Far Trans II 69, 1601 (1973).

unsatisfactory features of earlier work. In the present paper we shall endeavour to correlate this earlier work and add to the data where necessary to produce a satisfactory set of assignments.

EXPERIMENTAL

Biphenyl d_{10} was purchased from Merck, Sharp & Dohme Ltd. Biphenyl d_2 was synthesised as follows. 4,4' dibromobiphenyl was made following the method of BUCKLES and WHEELER [3]. *n*-butyl lithium reagent was prepared [4] at -10° C in dry ethyl ether by the action of *n*-butyl bromide on freshly cut lithium metal. The reaction was carried out in an atmosphere of dry nitrogen and the final product was filtered free of reaction precipitate. The freshly prepared *n*-butyl lithium reagent was then rapidly added to an ether solution of dibromobiphenyl and stirred overnight. The mixture was then treated with 99.8% deuterium oxide. The ether phase was washed out, dried and the solvent removed by rotary evaporation. The product was sublimed twice to yield white crystals with a melting point of 66°C.

The purity of these deutero-biphenyls was assessed by means of their mass spectra kindly run by Dr. W. Wheatley on an AEI MS12 double focussing spectrometer using a direct insertion sample probe. Spectra were run at 12, 11, 10 and 9 eV ionising voltages to ensure that no fragmentation of the molecular ion occurred. For biphenyl d_2 the composition was $C_{12}H_8D_2$ 96.5%, $C_{12}H_9D$ 2.3%, $C_{12}H_{10}$ 1.2% (97.6% deuteration). For biphenyl d_{10} the composition was $C_{12}D_{10}$ 93.3%, $C_{12}HD_9$ 5.6%, and $C_{12}H_9D_8$ 1.1% (99.2% deuteration).

Raman spectra were recorded on a Spex Ramalog using 5147 Å Ar⁺ radiation. The calibration was checked against a neon line. Infrared spectra were measured using a Perkin-Elmer 325 using spectral resolutions of 1 cm^{-1} or better.

The measured band frequencies are in good accord with those listed by ZERBI and SANDRONI [5], by KOVNER [6] and by SOURNIA [7] but in poor agreement with those of KATON and LIPPINCOTT for $C_{12}D_{10}$ [8].

Vibrational frequencies were calculated for a planar configuration and for dihedral angles of 30° , 60° and 90° . A regular hexagonal geometry was assumed for the rings and the force field was as given in [1]. The results are given in Tables 1 and 2.

The computed frequencies for the planar D_{2h} structure are in good accord with the in-plane frequencies calculated by ZERBI and SANDRONI [9]. The latter used a Urey-Bradley field which had been obtained by a minimum least squares fit to the assigned frequencies of biphenyl and d_{10} biphenyl [10]. Since the field of Zerbi and Sandroni was derived from their assignments of these molecules the agreement of the computed frequencies, even for the partially deuterated systems, cannot

[10] G. ZERBI and S. SANDRONI, Spectrochim. Acta 24A, 511 (1968).

^[3] R. E. BUCKLES and N. G. WHEELER, Org. Syn. 31, 29 (1951).

^[4] R. G. JONES and H. GILMAN, Org. Reactions 6, 352 (1951).

^[5] G. ZERBI and S. SANDRONI, Spectrochim. Acta 24A, 483 (1968).

^[6] M. A. KOVNER, Optik. i. Spektrosk. 1, 742 (1956).

^[7] A. SOURNIA, Thesis for the degree of Doctor of Physical Sciences, University of Perpignan, (1972).

^[8] J. E. KATON and E. R. LIPPINCOTT, Spectrochim. Acta 15, 627 (1959).

^[9] G. ZEBBI and S. SANDRONI, Spectrochim. Acta 26A, 1951 (1970).

The vibrational spectra of d_{10} and $4,4' d_2$ biphenyl

Table 1.	Calculated and	observed	frequencies	(cm^{-1})	for	various	dihedral	angles
			(biphenyl d	d ₁₀)				

					Observed fr	equencies	- 6 3
Cal	lculated f	frequencie	38	solid	aman melt	disc	solution
A sp	ecies (D	A_{g} , - A_{g} , .	A _u)				· · · · · · · · ·
-for e	a 11						
A. 8							
2201				n m	2273 w. n*		_
2280				n.m.	2010 11, 1		
1878				1562 vst	1563 vat (0.36)	· —	_
1457				1411 8	14158 (0.16)	—	
1198				1186 vs	1190 vs (0.11)		
951				965 vs	962 vs (0.06	· -	
862				882 s	872 s (0.04)		
840				846 s	842 m (0·34)	— —	
699				690 m	691 ms (0.04)		
261				312 m	299 m (0·12)) —	
Au							
780				—	786 w (0·25)) —	782 m
648				—	652 ms† (0·48))	652 m†
358				<u> </u>	348 m† (0·4 0)) —	352 w†
$\theta = 0^{\circ}$	30°	60°	90°				
B_1 species	$(D_{2\lambda} - D_{2\lambda})$	B _{1g} , B _{1u})					
2281	2281	2281	2281	n.m.	n.m.		
2279	2279	2279	2279	n.m.	n.m.		
1054	1083	1001	1080	10/0 8	10/28		
1304	1077	1294	1209	104/ W 1990	1343 VW	concident w	
1277	1097	1099	1470	1200 Ш	1410 W		1203 W
940	840	240 240	840	850 1		helieved coin	aident with h and
010	010	010	010	000 #		a, in liquid	l.
822	822	822	821	831 m	828 w		
583	583	585	587	583 m	588 m	coincident wi	th b. fundamental
319	302	276	254			_	334 m
B ₁₄							
820	820	891	821	_	_	813 **	815 st
729	731	737	746			742 8	744 8
613	616	623	631		_	620 s	624 s
539	539	542	545			538/541 vs	542 vs
387	404	430	446		<u> </u>	410 m	437 s
85	85	85	85	<u> </u>		73 m	73 s
B, species	$(D_{2\lambda}$	B21, B25)					
B_1.					_		
2281	2281	22 81	2281	n.m.	n.m.)	_
2278	2278	2278	2279	n.m.	n,m,	}2295-2250	complex.
1582	1581	1580	1580	<u> </u>		1522 m	1525 m
1297	1296	1292	1289	—	_	1317 s	1314 s
1262	1264	1269	1278		—	1260 m	1263 m
1016	1018	1022	1028	—		10 24 w	1024 vw
841	841	841	840		<u> </u>	854 s	860 w
822	822	821	821	—		818 w	825 m
596	594	591	587	_	597 w	594 w	596 w
89	88	87	85			112 s	106 s

* Frequency reported by Sandroni and Geiss. No measurements made by present authors in v_{CD} region.

Frequency reported by Samitha and Gens. At measurements made by present success in your prese

2

Table 1 (contd)

				Observed frequencies					
				Ram	an	Ini	frared		
Calculated frequencies			s	solid	melt	disc	solution		
B _{2g}									
826	826	825	822	816 w		coincident with	1 b _{1u} , b _{3u} , b _{3u}		
759	758	753	746		<u> </u>	_			
629	630	632	631	660/658/654 m	$652 \text{ ms}^{\dagger} (0.48)$		652 m†		
549	548	547	543	544 vw	551 w	<u> </u>	550 m sh.		
450	450	451	446	46 5 vw			464 s		
221	226	237	254	225 m	243 m		247 m		
B_{3u} . All θ									
2287				n.m.	n.m.				
2285				n.m.	n.m.	2295-2260 c	omplex.		
2280				n.m.	n.m.)			
1591						1566§	1565 vs		
1320						1343 vs§	1344 vs		
988					—	981 m§	981 s		
947						949 w§	950 m		
855					<u> </u>	844 ms	842 ms		
823				_	_	813 s§†	815 s		
590				coincident with b_{1g}		583 m§	587 m		
B _{3g}									
780					786 w† (0·25)	—	$782 m^{+}$		
648				660/658/654 m	652 ms† (0.48)		652 m †		
358				coincident with a.		363 w	352 w^{\dagger}		

Table 2. Calculated and observed frequencies (cm⁻¹) for various dihedral angles (4,4' biphenyl $d_2)$

-				Observed frequencies						
				F	Raman		Infi	ared		
Calculated frequencies				solid	m	elt	solid melt	solution		
A species	$(D_{2h} - A)$ all θ	I_g, A_u								
A.										
3072				n.m.	n. :	m.				
3072				n.m.	n. :	m.				
2283				2272 m	$2272 \mathrm{m}$	(0.25)				
1687				1600 vs	1607 vs	(ca 0·6)				
1516				1501 s	1501 s	(0.30)				
1338				1273 vs	1286 vs	(0.21)				
1192				1207 m	1187 s	(0.14)		-		
1024				1028 s	1027 s	(0.07)	_	—		
978				986 vs	986 vs	(0.12)	—	—		
738				732 s	735 vs	(0.09)		_		
269				322 s	310 vs	(0.31)	—	305 w		
A _u										
963				—	966 m	(0.09)		<u> </u>		
833					838 m	(0.29)				
409					405 s*	(0.35)		(403* s)		
$\theta = 0^{\circ}$	3 0°	6 0°	90°							
B_1 species	(D _{2h})	B _{1g} , B _{1u})								
B _{1g}										
3070	3070	3070	3070	n.m.	n. 1	m.		n.m.		
3069	3069	3069	3069	n.m.	n. :	m.		n.m.		
1608	1606	1604	1603	1593 vs	1584 s					
1404	1401	1395	1388	—	_	-	_	1375 m		

Table 2 (contd)

				Observed frequencies					
Calculated frequencies			98	Raman solid melt		Infrared solid melt solution			
	<u>, </u>				<u> </u>				
D_{1g} (contract	,	1015	1017				1990		
1320	1319	1317	1310	-	1949		1330 W !		
1280	1281	1283	1280	(1110 m	1107 m	aoinaidan	t with h		
1095	1094	1092	1091	1117 m	1107 m	contracta	te with ogu.		
868	868	888	867	873 m	869 m		868 w		
804	605	606	607	601 m*	603 s*	coincide	nt with h.		
340	390	201	967				359 w-m		
010	020	201	201				000 11		
B ₁₁									
050	050	050	950		_	954 w	953 w		
898	898	898	830	coincid	ent with a	840 va	842 vs		
806	608	703	709			715 8	720 8		
615	615	616	618	_	_	609 va*	610 vs*		
407	430	465	492	_		447 m	477 m hr		
	400	80	402			n.m.	n.m.		
30	00	00	00						
B ₂ species B _{2u}	(D ₂₁	B _{2u} , B _{2g})							
3070	3070	3070	3070	n.m.	n.m.	n.m.	n.m.		
3069	3069	3069	3069	n.m.	n.m.	n.m.	n.m.		
1605	1604	1603	1603			1554 m			
1377	1378	1381	1388			1393 vs	1394 vs		
1312	1312	1313	1315			1322 m	1308 m		
1290	1290	1289	1286		—	1261 m	1263 m		
1088	1088	1089	1091			(1131 s			
2000	1000	1000				11114 8	1110 s		
865	865	866	867			861 8	859 s		
619	619	619	618		617 m	609 vs*	610 vs*		
95	94	92	90	n.m.	n.m.	n.m.	n.m.		
00	•-	•=							
B,,									
950	950	950	950			954 w	953 w		
831	831	830	830	overla	id by b. ?				
708	710	711	709	741 m	741 m	(737 m)	(736 m)		
619	611	800	607	601 m*	605 a*	(10111)	(
519	511	506	492	538 w	535 m		533 m		
939	237	249	267		259 w	236 m	262 8		
202	201	210	20.		200 11	200			
All θ B_{s} species	(D _{2h} —	B _{3u} , B ₃₀)							
84									
3072				—	—	n.m.	n.m.		
3072						n.m.	n.m.		
2282					—	2296 m†	2297 m		
1603				—	_	${1596 m}^{+}$	1595 s		
						(1587 m†	1586 s		
1478						1471 vs†	1471 vs		
1193				—		1180 8	1178 m		
1035					—	1033 s†	1038 s		
1019					—	1006 s†	1007 s		
976						—	978 m		
604				coincid	ent with b_{1g}	604 vs†	605 w		
B 39									
0.00				975 w	(966 m* (0·09))		964 w		
963									
963 833				845 w	(838 m* (0·29))	coincide	nt with b,,		

† Intensities relatively less in crystallized melt than in disc due to molecular orientation effects.

be taken as firm evidence for the correctness of their assignments. It is encouraging therefore that we do agree so well. The field used here is primarily determined from the force field of benzene and, with the exception of a few constants involving the inter ring bond, is independent of biphenyl assignments [1]. The only significant errors in the calculated frequencies, as far as the scope of the present investigation is concerned, are in the highest frequency ring modes. As has been shown in a perturbation treatment these errors are due to neglect of the interaction constants involving the inter ring stretch [2].

DISCUSSION

The spectra of d_{10} biphenyl have been discussed earlier by KOVNER and PEREGUDOV (K-P) [6, 11], KATON and LIPPINCOTT (K-L) [8], and ZERBI and SANDRONI (Z-S) [5, 9], and recently the infrared active species have been the subject of a thesis by SOURNIA (S) [7]. We shall not tabulate all the assignments of the earlier works, but rather focus attention on the extent to which the current work concurs and differs from results of the earlier studies. The basis of assignments was as for biphenyls. In solution all fundamentals including those derived from the a_{μ} modes of the planar structure, appeared as strongly polarized Raman bands. In the a_{g} class the assignments of K-P and Z-S are in complete accord with the present. The actual frequencies quoted by K–P agree to within 2 cm^{-1} with ours. There is also no disagreement with earlier work on the a_{u} frequencies as they appear in the solution state. b_{3u} fundamentals of the solid state D_{2h} structure were generally strong and easily identified by their reduction in absorption intensity on going from a K Br disc (random crystal orientation) to a solidified melt on an alkali halide plate (long axes of molecules oriented almost perpendicular to plate) [12, 5]. There is some confusion however near 800 cm⁻¹. There are ten fundamentals predicted to lie between 850 and 800 cm⁻¹. Of the five i.r. active bands only two assignments seem unequivocal. The 813 and 854 cm⁻¹ bands must be b_{3u} and b_{2u} respectively on the basis of intensities and frequencies. b_{1u} and b_{2u} modes are also expected near 820 cm^{-1} . Our assignments at 818 and 825 cm^{-1} are rather tentative. This leaves only the 844 cm⁻¹ band to be correlated with the remaining $b_{a_{\mu}}$ vibration. The failure to see a significant intensity increase in going from disc to solution does throw some doubt on this assignment, but Z-S considered that their measurements on a single crystal justified inclusion of this frequency in the b_{3u} list [5]. Sournia selects the b_{2u} fundamentals at 860 and 845 cm⁻¹ and b_{3u} at 830 and 815 cm⁻¹ (liquid state frequencies) on the basis of relative intensities in solution and solid [7], but these pairs seem too close in frequency. As has been noted earlier [5, 12] there ought to be a reasonable correlation between the a_1 and b_2 frequencies of the pentadeutero phenyl halides and the b_3 and b_2 frequencies of d_{10} biphenyl. The agreement is indeed very good [5]. Of special note is the fact that there are a_1 frequencies of 843 and 813 cm⁻¹ and b_2 frequencies of 863 and 818 cm⁻¹. These are in reasonable accord with our choice for d_{10} biphenyl. Our b_{3u} assignments are in complete agreement with those of Z-S. The b_{3g} fundamentals are calculated to

^[11] G. V. PEREGUDOV, Optik i. Spektrosk 7, 155 (1960).

^[12] D. STEELE and E. R. LIPPINCOTT, J. Mol. Spectrosc. 6, 238 (1961).

be coincident with the a_u . Separate bands could not be identified. In solution all of these b_3 and a frequencies are predicted to be unchanged from their solid state values. This means, of course, that the intra-molecular forces are unaltered. In fact there are three significant shifts. The lowest a_g mode obtains 32% of its energy from distortion of the inter-ring bond. As for biphenyl there is a marked decrease in the frequency of the mode, of 15 and 13 cm⁻¹ respectively for d_{10} and d_2 . This is almost certainly due to a weakening of the inter-ring bond on rotation of the rings away from planarity.

For d_2 biphenyl shifts are also observed in the bands at 1274 and 1209 cm⁻¹ in the solid. These move to 1281 and 1187 cm⁻¹. An analogous shift has been noted earlier in biphenyl in which the shifts are 1276–1285 and 1205–1192 cm⁻¹, and explained as due to changes in the steric interactions between the 2,2' hydrogen atoms [12, 1]. The shifts for d_{10} are less dramatic, presumably due to the lower amplitudes of motion of the deuterium atoms as compared to the protons.

The b_{2u} bands are fairly readily identified once the b_{3u} bands have been located. The present assignments receive good support from the vapour phase band contours and analysis of SOURNIA [7], with whom we differ only on the fundamental near 820 cm⁻¹ as mentioned earlier. We differ in several cases from Z-S [5, 9]. Note that as for biphenyl no dramatic frequency shifts are predicted or observed in going to solution. The $b_{2\sigma}$ class vibrations are characterized by their appearance in the solution state of infrared bands coincident with the Raman due to mixing with b_{2u} modes. The lowest frequency also shows a marked shift. There is a rather high density of fundamentals between 900 and 600 cm⁻¹ and it is not certain that all fundamentals have been correctly located. Some multiple assignments have been necessary. On the basis of the calculations however it seems unlikely that any of the quoted frequencies are more than 20 cm⁻¹ out.

It is in the b_1 class that the most dramatic frequency shifts are predicted and seen to occur. Thus for d_2 biphenyl an absorption band is seen to move from $449-477 \text{ cm}^{-1}$ with a marked intensity enhancement, and a new band appears at 359 cm^{-1} which is readily assigned to the formerly b_{1g} mode. The other b_{1g} modes present difficulties. As has been noted earlier the Raman bands associated with these are either very weak or cannot be observed. Those assignments which are made rely heavily on the computed frequencies.

In the remaining i.r. active class, the b_{1u} , the highest mode was not assigned by Z-S [5]. We agree on v_2 to v_4 , but differ on the last two. The assignment of v_1 to v_5 agree well with those for C_6D_5X (X = halogen). Thus for X = Br the b_1 frequencies are 817, 743, 614, 543, 403 and 172 cm⁻¹. The lowest frequency of $C_{12}D_{10}$ is much lower than is its C_6D_5Br counterpart, and this seems to be firmly supported by the present calculations.

The only assignment studies of $4,4' d_2$ biphenyl are by SANDRONI and GEISS [13] and by ZERBI and SANDRONI [9]. Sandroni and Geiss were mainly interested in tracing the frequency changes with deuterium substitution, rather than producing a complete assignment set. As the work leans heavily on Z-S results for $C_{12}H_{10}$ and $C_{12}D_{10}$ no detailed comparison with the new assignment will be made.

^[13] S. SANDRONI and F. GEISS, Spectrochim. Acta 22, 235 (1966).

The experimental frequencies agree well and where they have made assignments they are largely in accord with ours.

The conclusions of the more detailed study [10], which unfortunately is restricted to the in-plane fundamentals, are in good accord with those of the present work. A weak Raman band at 845 cm⁻¹ is assigned by Z-S as b_{1g} but this we believe to be b_{3g} . A second Raman band at 869 cm⁻¹ fits our predictions better and is in superior accord with our biphenyl assignment [1]. A number of additional assignments are made by us on the basis of the observed changes in frequencies and intensities accompanying a change from solution to solid state.

Conclusion

Some of the intensity and frequency changes which occur with change of state are quite dramatic. For example in biphenyl d_2 strong polarized Raman bands exist for solutions at 966, 838 and 405 cm⁻¹. These have no counterparts in the solid state. Frequency shifts with increase in spectral activity occur for bands at 322 (a_g) , 447 (b_{1u}) , 538 (b_{2g}) , 236 (b_{2g}) , 978 (b_{3u}) and 408 cm⁻¹ (b_{3g}) . The quoted frequencies are as measured for the solid state. All of the observed changes are readily understood by comparison with the calculated frequencies for various dihedral angles and on the basis of the lower molecular symmetry existing in solution. These effects have been discussed in detail for biphenyl and 4,4' diffuorobiphenyl [1] and we shall not duplicate the arguments here.

There are clearly several dubious or unknown fundamentals for the deuterated biphenyls, particularly in the b_1 class. However the evidence for the bulk of the fundamentals is now firm and the spectral frequency shifts may confidently be used in further studies aimed at studying the dihedral angle change in solution.

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