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The Vibrational Spectra and Molecular Structure of 4,4′-Difluoro-, Dicyano-, Dichloro-, Dibromo-, and Diiodobiphenyl

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The IR spectra of 4,4′-difluoro-, dicyano-, dichloro-, dibromo-, and diiodobiphenyl were recorded between 4000 and 50 cm^{-1} as solids and between 4000 and 200 cm^{-1} in solution. Raman spectra of the solids and their saturated solutions were obtained and semi-quantitative polarization measurements carried out. Force fields for the five molecules were derived, largely by transferring force constants from biphenyl.

The vibrational spectra have been interpreted in terms of a planar conformation in the crystal (D_{2h}) becoming twisted (D_2) in solution. Tentative assignments of the fundamental frequencies are presented.

It is well established by Bastiansen *et al.*[1] from electron diffraction measurements that biphenyl and various substituted derivatives are non-planar in the vapour phase. Biphenyl appears planar in the crystalline state,[2] whereas *ortho* substituted biphenyls are definitely non-planar[3] in the crystal. Moreover, certain biphenyls substituted in the 3,3′- and 4,4′-positions crystallize in distinctively non-planar conformations.[4,5]

The geometry of biphenyl and various derivatives in solution is subject to much more uncertainty. Molar Kerr constant measurements[6] indicate a planar conformation, the NMR data[7] are inconclusive, whereas ESR[8] and UV[9–11] spectra support a twisted structure in solution. Several authors have recorded the IR and Raman spectra of biphenyl; the references to the earlier work have been listed by Pasquier and Lebas.[12] Later Zerbi and Sandroni have obtained new data for biphenyl-d_0 and biphenyl-d_{10}, including spectra of vapour, melt, solution, powder, and single crystals and made new assignments,[13] checked by normal coordinate analysis and including some partly deuterated biphenyls.[14] Most recently new Raman data for biphenyl, including measurements on single crystals, have been published.[15]

In view of the extensive studies reported on biphenyl we decided to investigate a series of *para*-substituted symmetric biphenyls, including difluoro- (DFBP), dicyano- (DCNBP), dichloro- (DCBP), dibromo- (DBBP), and diiodobiphenyl (DIBP). A few IR bands of these compounds have been reported,[16,17] but to our knowledge they have not been thoroughly studied neither in the vapour phase, in solution nor in the crystalline state. These molecules should belong to the same point groups as biphenyl (D_{2h} or D_2) and we would expect a close resemblance with the spectra of biphenyl.

The present work was somewhat restricted by the low volatility and limited solubility of these compounds, preventing the recording of vapour spectra and making the Raman solution spectra and polarization measurements incomplete. With the aid of force constant calculations based upon our earlier force field for biphenyl [18] tentative assignments of the fundamental frequencies are presented in terms of a planar (D_{2h}) model.

EXPERIMENTAL

Chemicals. Commercial products of DFBP (Aldrich) were recrystallized from dichloromethane, DBBP (K & K Laboratories) was recrystallized from dichloromethane and purified by sublimation while DIBP (Aldrich) was purified by successive sublimation *in vacuo*. The remaining compounds DCBP and DCNBP were synthesized from benzidine and purified by sublimation.

A variety of solvents were employed for the recordings, including chloroform, dichloromethane, benzene, and heptane. These solvents (spectrograde Uvasole from Merck) were used without further purification.

The crystalline samples were studied as KI tablets and Nujol mulls ($4000-200$ cm^{-1}) and as Rigidex pellets ($270-50$ cm^{-1}) in the infrared region. A variety of sealed cells of thickness $0.1-0.5$ mm, having windows of KBr, CsI, and polyethylene, were employed for the solutions. Raman spectra of the solids and the saturated solutions were recorded in the 180° illumination mode.

Instrumental. The infrared spectra in the region $4000-200$ cm^{-1} were recorded with a Perkin-Elmer model 225 spectrometer. A Michelson interferometer, RIIC model FS-520, equipped with a low frequency transmission filter of NaF suspended in polyethylene was employed in the region $270-50$ cm^{-1}, and the interferograms were Fourier transformed on a GIER computer.

A Cary model 81 Raman spectrometer equipped with a Spectra Physics model 125 helium-neon laser was used for the Raman recordings. Semiquantitative polarization measurements of the saturated solutions were obtained in the 180° mode and the values calibrated against the 220 and 459 cm^{-1} bands of carbon tetrachloride. The limitations of this procedure is well known, but sufficient band intensities could not be achieved by the 90° illumination.

The ultraviolet spectra were recorded on a Beckman DK-1 spectrometer in standard 1 cm absorption cells.

RESULTS AND DISCUSSION

The infrared and Raman spectra of DCBP in the crystalline state are shown in Figs. 1 and 2, whereas the corresponding curves for the other compounds are not given for the sake of brevity. The observed infrared and Raman frequencies (solid state and solution) are listed in Tables $1-5$, for DFBP, DCNBP, DCBP, DBBP, and DIBP, respectively. These tables have been restricted to the fundamental regions around 3000 cm^{-1} and below 1650 cm^{-1} and the weakest bands of the solids have not been included.

Table 1. Observed vibrational frequencies of 4,4′-difluorobiphenyl.

Infrared		Raman			Interpretation	
Solid KI pellet	Solution CCl_4	Solid	Solution CCl_4			
3095 w,sh[a]					1,2,21,22	A_g,B_{3g}
3061 w	3071 m	3084 w	3080 s	P		
					35,45	B_{1u},B_{2u}
3041 w	3045 s				36,46	B_{1u},B_{2u}
1645 w						
1640 w	1638 w		1642 w,sh		23	B_{3g}
	1631[b] vw	1625 w,sh				
1612 s	1615 w,sh				47	B_{2u}
1599 s	1600 s	1603 vs	1608 vs	P	37,3	B_{1u},A_g
1586 m,sh	1587 m,sh					
			1553 vw		4	A_g
		1529 m	1524 s	D	24	B_{3g}
1498 vs	1499 vs				38	B_{1u}
1473 m,sh	1476 s				48	B_{2u}
1450 w,sh	1459 m		1452 vw			
1420 vw	1420 vw		1426 vw		25	B_{3g}
1394 m	1396 m					
	1355 w					
1319 m	1303 m	1320 w	1320 m	P	39,5	B_{1u},A_g
		1278 vs	1288 vs	P	6	A_g
1240 vs	1230 vs	1257 m,sh	1241 m	D	49,26	B_{2u},B_{3g}
1160 s	1156 s	1169 s	1164 s	P	40,7	B_{1u},A_g
1123 w	1122 vw				50	B_{2u}
1108 m	1097 s	1098 w	1097 w		51	B_{2u}
1016 m	1019 m	1017 vw	1017		27	B_{3g}
1007 m	1009 s				41	B_{1u}
955 w	952 w		957 w		12,15	B_{1g},B_{2g}
935 w	932 m				55	B_{3u}
893 vw	881 vw					
	849 s	846 s	845 m	P	42,8	B_{1u},A_g
822 vs	822[b] vs		827 vw		9,13,56	A_g,B_{1g},B_{3u}
805 s	806 s		816 vw		16	B_{2g}
	726[b] w	723 m	729 m	D	17	B_{2g}
701 w	704 w				57	B_{3u}
		660 m	660 m	D	18	B_{2g}
	630 vw	628 m	632 s	D	10,28	A_g,B_{3g}
519 vs	543 s				43,52	B_{1u},B_{2u}
506 s	517 vs				58	B_{3u}
	455 m				44	B_{1u}
411 m	422 m		424 m,sh		53,14,29	B_{2u},B_{1g},B_{3g}
		386 m	392 s	D	19,30	B_{2g},B_{3g}
279 w		278 s	265 m	P	59,11	B_{3u},A_g
			180 m,sh		20	B_{2g}
118[c] s,b					54	B_{2u}
85[c] w						
		79 m				
61[c] w					60	B_{3u}

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; P, polarized; D, depolarized. Bands in the regions 4000–3100 and 3000–1650 cm^{-1} are omitted.

[b] Solutions in CS_2.

[c] Polyethylene (Rigidex) pellets were used below 250 cm^{-1}.

Table 2. Observed vibrational frequencies of 4,4′-dicyanobiphenyl.

Infrared		Raman				Interpretation
Solid KI pellet	Solution $CHCl_3$	Solid	Solution $CHCl_3$			
3073 w[a]		3067 vw			1,2,21,22 35,36,45,46	A_g,B_{3g} B_{1u},B_{2u}
2225 vw	2229 vs	2229 vs	2232 m	P		A_g,B_{1u}
1696 w	1703 m				47	B_{2u}
1660 w	1658 w					
1604 s	1604 vs	1609 vs	1609 s	P	37,3	B_{1u},A_g
1515 vw		1518 w			4	A_g
1503 vw	1503 vw				38	B_{1u}
1491 s	1493 vs				48	B_{2u}
1447 vw	1447 vw	1453 w			24	B_{3g}
1397 s	1394 s					
1312 m	1309 m				49	B_{2u}
1282 w	1285[b] w	1285 s	1287 m	P	6	A_g
1269 w	1265[b] w	1265 w				
		1238 vw				
1196 w						
1180 s	1179 m	1182 s	1181 m	P	39,5	B_{1u},A_g
		1161 w			26	B_{3g}
1126 w	1123 w	1118 m			7	A_g
1110 w	1110 m				40,50	B_{1u},B_{2u}
1089 vw	1092 w				51	B_{2u}
	1073 vw					
		1043 w				
1027 vw		1023 vw				
1006 m	1006 s	1009 w			41	B_{1u}
		997 m			27	B_{3g}
971 w		975 vw			12,15	B_{1g},B_{2g}
952 w	953 w					
	910 vw					
859 m	858 s				55	B_{3u}
842 w	842 m	848 vw			8,42	A_g,B_{1u}
		834 vw			13	B_{1g}
818 vs	823 vs	814 w			56,16	B_{3u},B_{2g}
		789 m			9	A_g
768 w		773 vw				
737 w		738 w				
696 w	696 w	688 vw			57,17	B_{3u},B_{2g}
	660 w					
641 w	641 vw	642 w			52,18	B_{2u},B_{2g}
		618 w			10	A_g
		604 vw			28	B_{3g}
568 m	568 w				43	B_{1u}
556 m	557 m	556 w				
544 s	545 m				58	B_{3u}
518 w	518 w	520 w				
458 m	458 w				44	B_{1u}
		411 m,sh			29	B_{3g}
		403 m	405 w	D	14	B_{1g}
		376 vw			19	B_{2g}
275 vw		280 w			30	B_{3g}
225 vw?					59	B_{3u}

Table 2. Continued.

Infrared		Raman		Interpretation	
Solid KI pellet	Solution $CHCl_3$	Solid	Solution $CHCl_3$		
200[c] s					
184[c] s		186 w		11	A_g
150[c] m,b		158 w		20	B_{2g}
135[c] m,b				54	B_{2u}
61[c] w		65 m		60	B_{3u}
56[c] vw					

[a] For abbreviations and regions listed, see Table 1.
[b] Solution in CS_2.
[c] Polyethylene (Rigidex) pellets were used below 200 cm^{-1}.

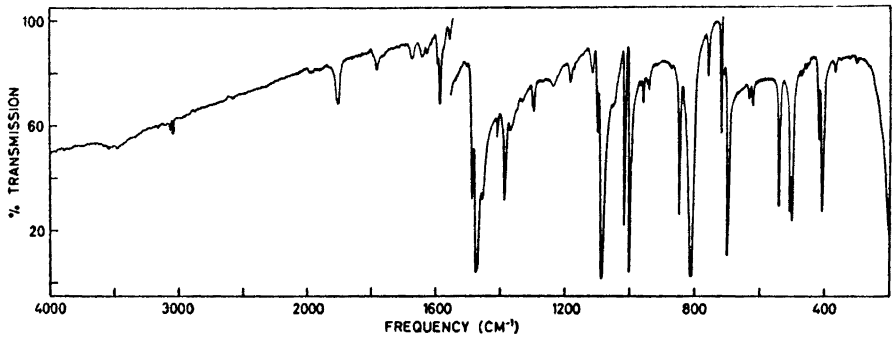


Fig. 1. IR spectrum (4000 – 200 cm^{-1}) of 4,4′-dichlorobiphenyl as KI pellet.

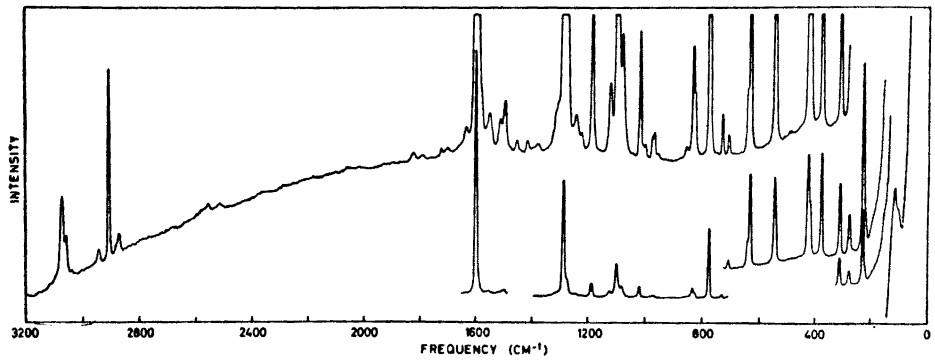


Fig. 2. Raman spectrum of solid 4,4′-dichlorobiphenyl.

Table 3. Observed vibrational frequencies of 4,4′-dichlorobiphenyl.

Infrared		Raman				
Solid KI pellet	Solution CS_2	Solid	Solution CS_2		Interpretation	
3074 s[a]	3081 m				45	B_{2u}
3063 w	3062 w	3068 m	3068 m	P	1,2,21,22	A_g,B_{3g}
					35,36,46	B_{1u},B_{2u}
1625 w,sh	1631 m	1632 w			47,23	B_{2u},B_{3g}
	1602 w,sh					
1596 m	1597 m	1598 vs	1600 vs	D	37,3	B_{1u},A_g
1504 vw	1505[b] w,sh	1514 w			4	A_g
1490 s	1485[b] vs	1494 m			38	B_{1u}
1476 vs	1474[b] vs				48	B_{2u}
1456 m,sh	1450 m	1452 w				
1412 w	1411 w	1414 w			24	B_{3g}
1390 m	1390 w					
1372 w	1360[b] w	1377 vw			25	B_{3g}
1330 w	1322[b] vw		1313 vw			
1299 m	1300 m				49	B_{2u}
	1289 w	1287 vs	1285 vs	P	6	A_g
	1241 w	1242 w				
1238 w	1225 m	1223 vw	1226 vw			
1186 w	1179 m	1184 s	1188 m	P	42,7	B_{1u},A_g
1102 m	1114 m	1120 m	1123 m		50,26	B_{2u},B_{3g}
1089 vs	1092 vs	1096 vs	1099 s	P	40,8	B_{1u},A_g
			1086 w		31	A_g
		1078 m	1078 w		27	B_{3u}
1049 m,sh	1042 w					
1021 s	1020 s	1015 s	1017 m	P	51,10	B_{2u},A_g
1004 vs	1005 vs	1005 vw			41	B_{1u}
995 m,sh		997 w				
969 vw		972 m				
962 w	956 m	966 m	958 vw		12	B_{1g}
851 s	843 s	851 vw			55,15	B_{3u},B_{2g}
822 m,sh	828 m,sh	829 m	828[c] w		16	B_{2g}
		823 w,sh			13	B_{1g}
813 vs	812 vs	773 s	775 w	P	56,9	B_{3u},A_g
762 w	757 m					
724 m	721 m	726 m	722 w		43,10	B_{1u},A_g
703 s	704 vs	705 w			57,17	B_{3u},B_{2g}
638 w	637 w	638 m,sh			18,52	B_{2g},B_{2u}
625 w	626 w	628 s	628[c] w	D	28	B_{3g}
545 s	538 s	541 s	544 m	P?	44,5	B_{1u},A_g
505 s	502 vs				58	B_{3u}
421 m		421 s			29	B_{3g}
412 s	414 s	414 m,sh	412 s	D	14,39	B_{1g},B_{1u}
370 w		374 s	371 m	D	19	B_{2g}
307 w		308 s	308 w		30,53	B_{3g},B_{2u}
271 vw		274 m	273 w			
		228 s	225 s	P	11	A_g
216[d] w					59	B_{3u}
158[d] w						
		117 s			20	B_{2g}
108[d] w,sh		105 m				
96[d] s					54	B_{2u}
88[d] m						
63[d] w		57 m			60	B_{3u}

[a] For abbreviations and regions listed, see Table 1. [b] Solution in CCl_4. [c] Solution in CH_2Cl_2. [d] Polyethylene (Rigidex) pellets were used below 250 cm^{-1}.

Table 4. Observed vibrational frequencies of 4,4′-dibromobiphenyl.

Infrared		Raman			
Solid KI pellet	Solution CS_2	Solid	Solution CS_2		Interpretation
3075 vw[a]	3077 m			35,45	B_{1u},B_{2u}
3057 w,sh	3061 w	3066 s	3065 s P	1,2,21,22	A_g,B_{3g}
				36,46	B_{1u},B_{2u}
1668 w	1661 m			47	B_{2u}
		1640 vw	1646 vw	23	B_{3g}
1631 w	1627 m	1630 vw		37	B_{1u}
			1617 w,sh		
1585 w,sh	1587 s	1592 vs	1594 vs P?	3	A_g
1582 m					
		1498 s	1501 s	4	A_g
1485 s	1487[b] s	1490 m	1485 w	38	B_{1u}
	1482[b] s				
1470 vs	1472[b] s			48	B_{2u}
1450 m,sh	1448[b] m,sh	14444 w		24	B_{3g}
1405 w	1400 w	1410 vw			
1382 s	1382 s	1375 w		25	B_{3g}
1361 w	1356 m				
		1285 vs	1286 vs P	6	A_g
	1240 w,sh				
1231 w	1225 w	1228 w	1228 m D?	49,26	B_{2u},B_{3g}
1187 vw	1185 w,sh	1188 s	1189 s P	42,7	B_{1u},A_g
	1174 w				
1164 w	1160 vw				
	1125 w,sh				
1114 w	1112 m	1107 vw		50	B_{2u}
1100 m	1099 m			40	B_{1u}
1076 m,sh	1079 s	1087 m	1080 sv P	8	A_g
1067 vs	1070 vs	1072 s	1071 s D	51,27	B_{2u},B_{3g}
1049 w,sh	1057 m				
1001 vs	1001 vs			41	B_{1u}
984 w,sh		987 w,sh		12	B_{1g}
960 w	956 w	965 w	960 w D	15	B_{2g}
			880 w	32	A_u
847 s	841 s	847 vw	847 vw	16,55	B_{2g},B_{3u}
828 w,sh		828 s	828[b] s	10	A_g
822 w,sh		823 w,sh		13	B_{1g}
809 vs	808 vs			56	B_{3u}
	770 vw				
761 vw	757 w	761 s	762 s P	9	A_g
720 s	719 m	725 vw		43,17	B_{1u},B_{2g}
671 s	673 s	671 vw		57	B_{3u}
635 m	635 m	637 w,sh		52,18	B_{2u},B_{2g}
630 w,sh		627 m	626[b] w D	28	B_{3g}
623 m	623 w				
542 s	537 s	544 vw	540 w	44	B_{1u}
499 s	497 s		496 w	53,58	B_{2u},B_{3u}
		467 s	471 s P	5	A_g
		420 s		29	B_{3g}
410 s	411 m	413 m,sh	410 s D	14	B_{1g}
355 w		358 s	357 s	19	B_{2g}
313 s	316[c] m			39	B_{1u}
271[d] vw		273 m	273 m	30	B_{3g}

Table 4. Continued.

Infrared		Raman				
Solid KI pellet	Solution CS_2	Solid	Solution CS_2			Interpretation
236[d] vw		240 w	238 w		59	B_{3u}
190[d] w						
166[d] vw		169 m	164 m	P	11	A_g
144[d] w						
132[d] vw						
		116 s			20	B_{2g}
105[d] vw		101 w				
87[d] m						
73[d] w		73 vw			54	B_{2u}
		56 vw				

[a] For abbreviations and regions listed, see Table 1.
[b] Solution in CCl_4.
[c] Solution in C_6H_6.
[d] Polyethylene (Rigidex) pellets were used below 280 cm^{-1}.

Crystalline state. The 60 normal modes of the 4,4'-dihalobiphenyl (66 in DCNBP) will distribute themselves between the various symmetry species as listed in Table 6. In the planar conformation (D_{2h}) there will be mutual exclusion between the *u*-modes (IR active) and the *g*-modes (Raman active). With the exception of the 15 A vibrations, all the fundamentals will be IR as well as Raman active in the non-planar D_2 model. We have not considered the D_{2d} model with a 90° twisting angle since this conformation has not been detected among the biphenyls. Because of the loose coupling between the benzene rings the spectra can also be interpreted [20] in terms of a pseudo C_{2v} symmetry as in monosubstituted benzene. Consequently, the A_u and B_{1u} modes will be in-phase and out-of-phase parallel vibrations, respectively, whereas B_{3g} and B_{2u} are the in-phase and out-of-phase perpendicular in-plane modes. The out-of-plane fundamentals can be described as the B_{1g} (in-phase) and A_u (out-of-phase) and B_{2g} (in-phase) and B_{3u} (out-of-phase).

As a consequence of the weak coupling between the benzene rings the various in-phase and the appropriate out-of-phase vibrations should be quite closely spaced. For biphenyl, calculations [13] have shown that the separation between the A_g and the B_{1u} vibrations is highly depending upon the C–C force constant, the other corresponding in-phase and out-of-phase modes being rather insensitive to the central bond strength. These results and our own force constant calculations reveal that each IR band will have a neighbouring Raman band and *vice versa* in the D_{2h} conformation, exceptions being the three B_{1g} modes (the A_u modes are inactive) and the single A_g C–C stretching vibration. Therefore, apparent IR and Raman coincidences do not necessarily exclude the D_{2h} conformation, but can be interpreted as neighbouring in-phase and out-of-phase modes.

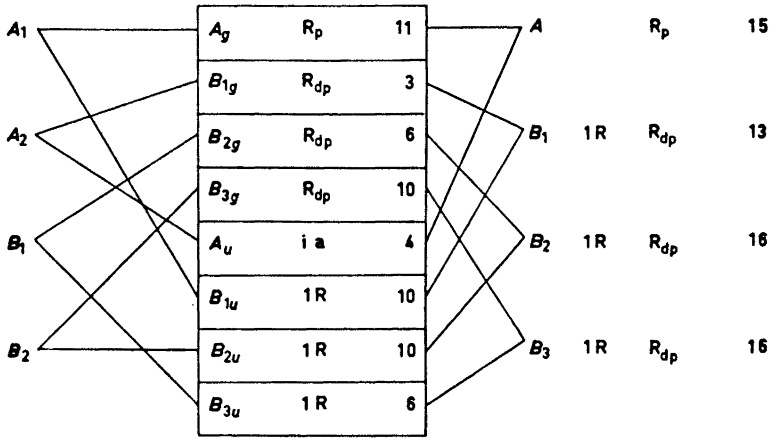
It appears from Tables 1–5 that for each of the present molecules a fair number of IR-Raman coincidences were observed in the solid spectra. These

Table 5. Observed vibrational frequencies of 4,4′-diiodobiphenyl.

Infrared		Raman				
Solid KI pellet	Solution CS_2	Solid	Solution CS_2		Interpretation	
3079 w[a]	3073 m				35,45	B_{1u},B_{2u}
3058 w	3055 w	3068 w	3058 m		1,2,21,22	A_g,B_{3g}
					36,46	B_{1u},B_{2u}
1616 w	1623 m				47	B_{3u}
			1606 w		23	B_{3g}
1582 m	1581[c] w	1584 vs	1589 vs	P	3,37	A_g,B_{1u}
		1500 vw			4	A_g
1486 vw	1482[b] s				38	B_{1u}
1471 s	1471[b] vs				48	B_{2u}
	1390[c] w,sh					
1378 m	1379 s					
	1302 vw					
	1282 m	1277 vs	1285 vs	P	6	A_g
	1222 w	1216 m			49,26	B_{2u},B_{3g}
		1187 s	1191 s	P	7	A_g
	1180 w				42	B_{1u}
1101 vw	1096 w				50	B_{2u}
		1075 m	1076 m	D	27	B_{3g}
1065 s	1063 vs		1064 s	P	40,8	B_{1u},A_g
	1010 m					
	1006 m	1005 m	1002 s	P	51	B_{3u}
995 s	997 vs		997 vw		41	B_{1u}
	992 w,sh					
	956 w		958 m		12,15	B_{1g},B_{2g}
	940 w					
	838 s	837 w			55,13,16	B_{3u},B_{1g},B_{2g}
805 vs	803 vs				56	B_{3u}
		753 s	753 s	P	9	A_g
			723 vw		32	A_u
718 vw	715 w	712 vw			43,17	B_{1u},B_{2g}
652 m	655 s				57	B_{3u}
637 w	635 w				52	B_{2u}
	623 vw	621 m			18	B_{2g}
	537 m	539 w	537 vw	D	28,44	B_{3g},B_{1u}
485 vw	495 s				58	B_{3u}
463 m					53	B_{2u}
		453 s	437 s	P	5,14,29,33	A_g,B_{1g},B_{3g},A_u
		330 w	341 m	D	19	B_{2g}
			246 w		30,34	B_{3g},A_x
225[c] vw					39,59	B_{1u},B_{3u}
		133 s			11	A_g
118[c] m						
		106 m			20	B_{2g}
95[c] w					60	B_{3u}
		79 w				

[a] For abbreviations and regions listed, see Table 1.
[b] Solution in CCl_4.
[c] Polyethylene (Rigidex) pellets were used below 250 cm^{-1}.

Table 6. Correlations between C_{2v} (monosubstituted benzene), D_{2h} and D_2 (4,4′-dihalobiphenyl).



numbers varied somewhat and were larger in DCBP than in DFBP and DIBP, but an equally large number of non-coincidences were found. Although certain 4,4′-disubstituted biphenyls (4,4′-diamino-3,3′-dimethylbiphenyl,[4] and bitolyl [5]) are twisted in the crystalline state, our spectral data are best interpreted in terms of a planar structure in the solid, although a twisted form (D_2) in one or all the molecules cannot be completely excluded.

Solution. It appears from Tables 1 – 5 that except for the slightly soluble DCNBP as many IR or Raman bands were observed in solution as in the solid state. The majority of the bands in solution were shifted only a small distance from the corresponding solid bands. However, for each compound IR or Raman bands were observed in solution which were not present in the solid IR or Raman spectra, although the IR solution bands may have Raman counterparts and *vice versa*.

The new bands appearing in solution strongly suggest that the molecular geometry in solution is different from that of the crystal, thus relaxing the D_{2h} selection rules. Thus, the present parasubstituted biphenyls are very probably twisted in solution in accordance with the results from vibrational [12,13,20] and UV [9–11] spectra and calculations [21] on the parent molecule biphenyl.

The vibrational frequencies of the D_{2h} point group will not change drastically with the twisting angle. This was verified by making a force constant calculation of DIBP in the D_2 point group imposing a twisting angle of 45°, and comparing the frequencies with those of Table 7. No frequency shifts were calculated for $A = A_g + A_u$ or $B_1 = B_{1g}$ whereas average shifts of 5.5 cm^{-1}

and 11.2 cm^{-1} were calculated for $B_2 = B_{2g} + B_{2u}$ and $B_3 = B_{3g} + B_{3u}$, respectively. No shifts larger than 18 cm^{-1} were calculated for the the B_2 frequencies. The fundamental No. 58 (out-of-plane ring def.) of species B_3 was shifted 59 cm^{-1} after twisting. Therefore, with a few exceptions the "twisting" shift is of the same order of magnitude as the general liquid-solid frequency shift.

Apart from the A-fundamentals only active in Raman, all the fundamentals in the D_2 point group are IR and Raman active giving rise to spectral coincidences. However, also in the D_2 point group the "in-phase" and "out-of-phase" vibrations will be close, making real coincidences or accidental degeneracy fortuitous.

In the Tables 1 – 5 we detected, respectively, 14, 3, 5, 7, and 18 IR or Raman bands in solution which were absent in the appropriate solid spectra. If present in the complimentary spectra they can be real IR or Raman coincidences in solution of species B_1, B_2, or B_3.

Raman bands observed in solution without any counterpart in IR can be interpreted as A modes. If corresponding Raman bands are present in the solid they should correlate with A_g, if absent they may be A_u fundamentals.

Force constant calculations. Due to the large number of fundamental vibrations in the biphenyls, a force constant calculation for each molecule was essential for interpreting the spectra. These calculations were based upon the planar conformation (D_{2h}) in each of the molecules, the valence and symmetry coordinates have been described elsewhere.[22] The following structural parameters were used: C – H = 1.09; C – C (ring) = 1.395; C – C (inter-ring) = 1.50, and C – X (X = F, CN, Cl, Br, I) = 1.33, 1.40, 1.70, 1.85, 2.05 Å and all angles equal to 120°.

Force constants previously derived for biphenyl [18] were used as a starting set with individual values for the C – X stretching constants. The CN stretching and bending frequencies in DCNBP were not calculated, but the CN considered as one atom. The calculated frequencies combined with the previous work on biphenyl [12,13,15,20] were used as a guide for the vibrational assignments. Considering the very approximate force fields the agreement between observed and calculated frequencies were satisfactory. The initial force constants were refined to give a better fit between the observed and calculated frequencies, keeping corresponding force constants in the five molecules at the same value except the C – X stretching constants. Obviously, it is a very crude approximation to keep the various ring stretching and bending force constants for these molecules invariable, and in particular the C – X in-plane and out-of-plane bending force constants will undoubtedly vary with the substituent X. However, this procedure was adopted to prevent an excessive number of parameters and the resulting frequencies are listed in Table 7. Furthermore, the observed IR and Raman frequencies listed in Table 7 are whenever possible taken from the solution spectra. Although a contradiction (the calculated frequencies based upon D_{2h} and the observed frequencies upon D_2 symmetry) this procedure was justified by the relatively small observed shifts for most of the bands.

Table 7. Tentative vibrational fundamentals and calculated frequencies of the 4,4′-dihalo(or dicyano)biphenyls.

Approx. descr.	No.	DFBF Obs.	DFBF Calc.	DCNBF Obs.	DCNBF Calc.	DCBF Obs.	DCBF Calc.	DBBF Obs.	DBBF Calc.	DIBF Obs.	DIBF Calc.
A_g											
C–H str.	1	3071	3067	3067	3067	3068	3067	3065	3067	3058	3067
C–H str.	2	3071	3061	3067	3061	3068	3061	3065	3061	3058	3061
C–H def.	3	1608	1579	1609	1575	1600	1575	1594	1575	1589	1575
C–C str.	4	1553	1555	1518	1534	1514	1529	1501	1528	1500	1527
C–X str.	5	1320	1405	1182	1203	544	540	471	483	437	452
C–C inter-ring str.	6	1288	1286	1287	1336	1285	1327	1286	1324	1285	1323
C–H def.	7	1164	1093	1118	1088	1188	1145	1189	1126	1191	1114
C–C str.	8	845	877	848	871	1099	1079	1080	1069	1064	1052
C–C str.	9	827	805	789	784	775	770	762	763	753	757
Ring def. (breath)	10	632	648	618	594	722	867	828	866		864
Inter-ring def.	11	265	249	186	230	225	208	164	153	133	122
B_{1g}											
C–H O.p.b.	12	957	951	975	951	958	951	987	951	958	951
C–H O.p.b.	13	827	826	834	826	823	826	823	826	837	826
Ring def. (O.p.)	14	424	410	405	410	412	410	410	410	437	410
B_{2g}											
C–H O.p.b.	15	957	860	975	861	851	864	960	866	958	870
C–H O.p.b.	16	816	822	814	822	828	824	847	825	837	827
Inter-ring def. (O.p.)	17	729	666	688	667	705	670	725	673	712	677
Ring def. (O.p.)	18	660	655	642	654	638	658	637	659	621	660
Ring def. (O.p.)	19	392	358	376	353	371	347	357	344	341	343
C–X O.p.b.	20	180	173	158	161	117	143	116	128	106	121
B_{3g}											
C–H str.	21	3071	3072	3067	3072	3068	3072	3065	3072	3058	3072
C–H str.	22	3071	3059	3067	3059	3068	3059	3065	3059	3058	3059
C–C str.	23	1642	1700		1699	1631	1699	1646	1699	1606	1699
C–C str.	24	1524	1493	1453	1492	1414	1491	1444	1490		1490
C–C str.	25	1426	1391		1391	1377	1393	1375	1393		1395
C–H def.	26	1241	1196	1161	1195	1123	1193	1228	1192	1216	1192
C–H def.	27	1017	1078	997	1078	1078	1078	1071	1078	1076	1079
Ring def.	28	632	614	604	613	628	612	626	612	537	612
C–X def.	29	424	463	411	448	421	439	420	432	437	431
Inter-ring def.	20	392	313	280	295	308	267	273	239	246	227
A_u											
C–H O.p.b.	31		981		981	1086	981		981		981
C–H O.p.b.	32		733		733		733	880	733	723	733
Ring def. (O.p.)	33		416		416		416		416	437	416
Inter-ring torsion	34		242		242		242		242	246	242
B_{1u}											
C–H str.	35	3071	3063	3073	3063	3062	3063	3077	3063	3073	3063
C–H str.	36	3045	3060	3073	3060	3062	3060	3061	3060	3055	3060
C–C str.	37	1600	1598	1604	1589	1597	1588	1627	1588	1581	1588
C–H def.	38	1499	1567	1503	1539	1485	1530	1487	1528	1482	1525
C–X str.	39	1303	1324	1179	1188	414	405	316	327	225	284
C–H def.	40	1156	1090	1110	1083	1092	1067	1099	1052	1063	1034

Table 7. Continued.

Approx. descr.	No.	DFBF Obs.	DFBF Calc.	DCNBF Obs.	DCNBF Calc.	DCBF Obs.	DCBF Calc.	DBBF Obs.	DBBF Calc.	DIBF Obs.	DIBF Calc.
C–C str.	41	1009	988	1006	987	1005	987	1001	986	997	986
C–C str.	42	849	805	842	776	1179	1133	1185	1119	1180	1110
Ring def.	43	543	639	568	589	721	759	719	751	715	744
Inter-ring def.	44	455	462	458	440	538	547	537	524	537	510
B_{2u}											
C–H str.	45	3071	3072	3073	3072	3081	3072	3077	3072	3073	3072
C–H str.	46	3045	3059		3059	3062	3059	3061	3059	3055	3059
C–C str.	47	1615	1689	1703	1689	1631	1688	1661	1688	1623	1688
C–C str.	48	1476	1477	1493	1476	1474	1476	1470	1476	1471	1475
C–C str.	49	1230	1302	1309	1301	1300	1301	1225	1301	1222	1303
C–H def.	50	1122	1106	1110	1106	1114	1105	1112	1105	1096	1105
C–H def.	51	1097	1075	1092	1075	1020	1075	1070	1075	1006	1075
Ring def.	52	543	628	641	628	637	627	635	627	635	627
C–X def.	53	422	419		390	307	360	497	333	463	324
Inter-ring def.	54	118	94	135	87	96	77	73	63		55
B_{3u}											
C–H O.p.b.	55	932	832	858	832	843	831	841	830	838	826
C–H O.p.b.	56	822	806	823	807	812	816	808	820	803	832
Ring def. (O.p.)	57	704	655	696	655	704	660	673	662	655	666
Ring def. (O.p.)	58	517	489	545	489	502	489	497	489	495	489
C–X O.p.b.	59	279	297	225	286	216	272	236	262	225	258
Inter-ring def(O.p.)	60	61	74	61	66	63	56		43	95	37

The diagonal valence force constants * used in the potential fields are given in Table 8. Certain off-diagonal elements not given had considerable influence on the calculated frequencies. Since the present symmetry coordinates [22] were constructed without redundancies the derived force constants should not be transferred to similar types of molecules without great care.[22,23,24]

The approximate descriptions of the atomic motions in Table 7 generally agree with the accepted group frequency correlations for benzene derivatives [25] and the present potential energy distribution (PED) among the symmetry co-ordinates. Our PED have not been given for the sake of brevity, but they reveal that most of the vibrations are highly delocalized. The C–H deformation modes are mixed with the ring stretching modes and these are again mixed with the ring bending modes. Apart from the localized C–H stretching vibrations, the C–C inter-ring stretching mode is highly localized for all the molecules. However, the calculated frequencies vary considerably in relation to the observed strong Raman bands which for all the molecules are situated close to the frequency in biphenyl [12,13,15] at 1285 cm^{-1}.

Vibrational assignments. The assigned fundamentals listed in Table 7 should be considered as highly tentative due to the complexity of the

* The complete set of symmetrized force constants can be obtained from the authors on request.

Table 8. Valence force constants (in mdyn/Å) used in the calculations.

C – C stretch (ring), $f_d{}^a = f_s = f_u = 6.0$
C – C stretch (inter-ring), $f_w = 6.2$
C – H stretch, $f_t = f_v = 5.1$
CCC bend (ring), $f_\alpha = 1.5$
CCC bend (inter-ring), $f_\phi = 1.0$
C – X wag, $f_\omega = 1.0$
CCH (in-plane bend), $f_\varepsilon = f_\varphi = 0.60$
CCCC torsion (ring), $f_\delta = 0.48$
Out-of-plane def. (ring), $f_\sigma = 0.44$
Out-of-plane def. (middle bond), $f_\tau = 0.24$
C – X bend (out-of-plane), $f_\vartheta = 0.36$
C – H bend (out-of-plane), $f_\varrho = f_\gamma = 0.19$
C – X stretch (X = F, CN, Cl, Br, O), $f_r = 7.0, 4.9, 3.8, 3.4, 2.8$

[a] The meaning of the indices is defined in Ref. 22.

vibrational spectra. Throughout this work the biphenyls have been listed according to molecular weight, and apart from DCNBP, this order corresponds to decreasing electronegativity of the halogens. Most of the assigned fundamental frequencies vary monotonically in this order. For DCNBP the data are less complete and the additional six fundamentals have not been considered except the A_g and B_{1u} C≡N stretching modes, practically coinciding at 2229 cm^{-1}. In principle the biphenyls (except DCNBP) should have 13 polarized Raman bands in solution below 1650 cm^{-1}, species A, of which 9 should correlate with A_g and 4 with A_u in the solid. Fewer polarized Raman bands were observed, and the solution bands corresponding to the inactive A_u fundamentals will probably be very weak.

The IR spectra below 200 cm^{-1} were recorded as polyethylene pellets only and the Raman solution spectra rarely gave clearcut bands below 200 cm^{-1}. Therefore the observed IR and Raman frequencies in the low frequency region can be lattice modes and the assignments are particularly uncertain.

Ultraviolet spectra. Biphenyl has a strong band at 247 nm in heptane solution shifted to longer wave length in the solid [9] and interpreted [9,10] as a result of increased conjugation in the planar conformation. We observed the following absorption peaks and extinction coefficients: biphenyl 247 (17.5); DFBP 245 (15.0); DCNBP 270 (?); DCBP 259 (29.4); DBBP 262 (24.2); and DIBP 269 nm (33.8×10^3 l mol^{-1} cm^{-1}). For comparison the 2,2′-dihalobiphenyls reveal bands close to 230 nm [10] probably as a result of larger twisting angles and reduced conjugation. The present data indicate a considerable conjugation between the benzene rings in solution, suggesting a twisting angle far from 90°. In spite of the bathochromic shift observed with more electronegative substituents in the 4,4′-dihalobiphenyls no definite conclusions can be drawn about the relative values of the twisting angle since the perturbation of the halogens on the biphenyl electron system is not well known.

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Note adedd in proof. While this paper was in press Barrett and Steele (Barret, R. M. and Steele, D. *J. Mol. Struct.* **11** (1972) 105) published the vibrational spectra of DFBP, DCBP and DBBP in good agreement with the present data. They interpreted their spectra in terms of planar DFBP and twisted DCBP and DBBP in the crystal, all the molecules being twisted in the melt.

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