ture trap and the mixture refluxed until water no longer separated in the trap. The time required was 18 hr. The benzene and dioxane were distilled and the residue was treated with 100 ml. of 1% aqueous sodium hydroxide and the solution extracted twice with 50-ml. portions of ether. The ether was evaporated leaving a liquid which was distilled to give 13 g. (60%) of a colorless material, b.p. 259–261° (atmosphere); 170–174° (14 mm.); $n^{25}D$ 1.4640.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.12; H, 8.24.

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORY, DOJINDO & CO., LTD.]

Polyazobenzenes. III. Infrared Absorption Spectra of Some Polyazobenzenes

BY KEIHEI UENO

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Infrared absorption frequencies from 4000 to 650 cm.$^{-1}$ are reported for seventeen polyazobenzenes including their nitro, amino and hydroxy derivatives. Frequencies are assigned in most cases to bond or group vibrations, and the results are discussed in relation to their structure. Tentative assignment was made for the N=N bond at 1400 and 1455 cm.$^{-1}$.

Introduction

Le Fèvre and his co-workers[1] have investigated some 43 aromatic diazonium and azo compounds and found common absorption bands at around 1406 and 1577 cm.$^{-1}$. However, their result was not conclusive, and more fundamental information on the infrared absorption spectra of aromatic azo compounds is badly needed from both theoretical and practical standpoints. It is the purpose of this investigation to analyze the infrared absorption spectra of polyazobenzenes and their nitro, amino and hydroxy derivatives, as well as polyazostilbenes, which can be considered as model structures of commonly used azo dye molecules. The result of such a study should be of importance in connection with the infrared analysis of azo dyes of more complicated structures.

Experimental

Compounds chosen for this investigation are identical with those which were previously synthesized for our ultraviolet absorption study, and details of their syntheses have been described.[2] Since it was almost impossible to prepare solid samples of stereochemically pure isomers for most of the compounds, the infrared absorption measurements were carried out on samples neglecting their stereochemical purity, although they are believed to consist mainly of *trans* isomers.

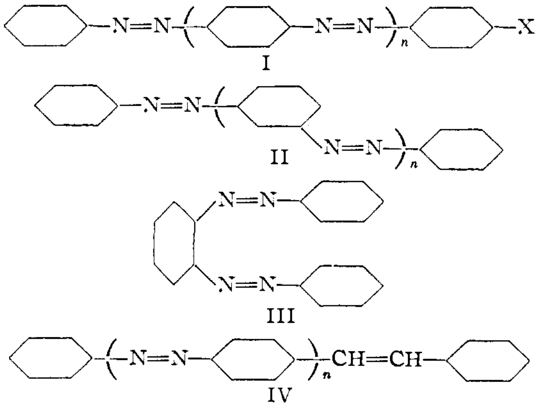
A Perkin-Elmer model 21 double beam spectrophotometer equipped with sodium chloride optics was used for the measurements, and samples were run both as Nujol mulls and as potassium bromide disks. For most of the samples, the Nujol run and the potassium bromide disk run gave almost the same absorption spectra; however, better resolution was observed in the latter technique, and additional bands were found in the region where the Nujol bands overlap.[3]

Result and Discussion

The significant absorption bands observed below 1650 cm.$^{-1}$ are presented in Table II, along with the assignments to the group vibrations wherever possible.

TABLE I

LIST OF THE COMPOUNDS INVESTIGATED



Compound no.	Name of compound	Structural description Type	*n*	X
1	Azobenzene	I	0	H
2	4-Phenylazo-azobenzene	I	1	H
3	4,4'-Bis-(phenylazo)-azobenzene	I	2	H
4	4-Hydroxy-azobenzene	I	0	OH
5	4-Hydroxy-4'-phenylazo-azobenzene	I	1	OH
6	4-Phenylazo-4'-(*p*-hydroxyphenylazo)-azobenzene	I	2	OH
7	4-Aminoazobenzene	I	0	NH_2
8	4-Phenylazo-4'-aminoazobenzene	I	1	NH_2
9	4-Phenylazo-4'-(*p*-aminophenylazo)-azobenzene	I	2	NH_2
10	4-Nitroazobenzene	I	0	NO_2
11	4-Phenylazo-4'-nitroazobenzene	I	1	NO_2
12	4-Phenylazo-4'-(*p*-nitrophenylazo)-azobenzene	I	2	NO_2
13	3-Phenylazo-azobenzene	II	1	
14	3,3'-Bis-(phenylazo)-azobenzene	II	2	
15	2-Phenylazo-azobenzene	III		
16	4-Styryl-azobenzene	IV	1	
17	4-Styryl-4'-phenylazo-azobenzene	IV	2	

In general, the absorption patterns of each set of polyazobenzenes are found to be almost identical but become broader and more diffuse when the number of azo linkages increases. The same tendency was reported for the amino acids and the corresponding polypeptides.[4]

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[1] R. J. W. Le Fèvre, M. F. O'Dwyer and R. L. Werner, *Australian J. Chem.*, **6**, 341 (1953).

[2] K. Ueno, THIS JOURNAL, **74**, 4508 (1952); K. Ueno and S. Akiyoshi, *ibid.*, **76**, 3667 (1954).

[3] Infrared absorption spectra of some of these compounds have been published in the Sadtler Infrared Catalog: however, their spectra were taken by the Baird double beam spectrophotometer of linear wave length on Nujol mull samples. Since our spectra were recorded in linear wave number with potassium bromide technique, more precise investigation was possible, especially in the 3000 and 1600 cm.$^{-1}$ regions.

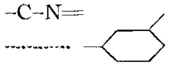
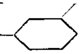
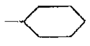
[4] E. Ellenbogen, THIS JOURNAL, **78**, 366 (1956).

TABLE II

INFRARED ABSORPTION SPECTRA OF POLYAZOBENZENES

Compound^a																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Assignment
						1621s	1617s	1613s									N-H deform. of $-NH_2$
									1607m	1610m	1609m				1612m		
1575m	1585m	1589s	1600s	1594s	1590s	1601s	1598s	1598s	1590m	1589m	1590m	1585s	1585m	1584s	1595s	1585m	Phenyl ring vibration
			1587s	1565w	1570m	1582m	1586m	1587m	1562w	1565w	1562w				1573m	1565m	
									1525s	1522s	1525s						NO_2 stretch.
	1525w			1520m													
		1502m	1506m	1504s	1502s	1508m	1505s	1505s							1501m	1501w	
1485s	1485m	1484m	1468m	1477m	1485m				1480w	1484m	1482m	1490m		1487s	1485w	1483m	Phenyl ring vibration
												1471s	1470s	1469s			
1455s	1461m	1463m	1456m	1469m	1462w	1465m	1451w	1457w	1467w	1455w	1460w	1460w	1460w	1452s	1462w	1462w	$-N=N-$ stretch.?
	1441m	1440s		1440m	1439w	1450w	1440w	1436w	1455m	1436m	1430w	1457s	1446s	1440s	1450s	1441m	
1395w	1398w	1400m	1417m	1425w		1420m	1417w	1417w	1408w	1411w	1410w	1420w	1420w		1414m	1405w	$-N=N-$ stretch.?
								1402w									
	1382w	1363s	1378m	1379m	1380w					1370w	1371w			1380w	1363w		
					1345w												
									1345s	1341s	1340s						NO_2 stretch.
	1312m		1315w				1316w	1315m	1327m	1322s	1315m	1318w	1318w		1331m		
1298s	1303s	1304s		1305m	1303m	1309s	1300w	1300s	1302m	1306m	1305m	1302m	1303m	1305m	1300m	1302s	$-C-N=$
						1300m	1276s	1273m									C-N stretch. of $C-NH_2$
								1240w					1268w	1258m	1265w		
			1278s		1288m												O-H deform.
			1240s	1240s													
1220m	1208m	1212s	1230m	1215m	1212s		1214m	1215s	1212w	1213m	1210m	1227m	1232m	1216m	1220m	1210s	
												1202m	1190w		1190w		
1156m	1166w	1170m	1165m	1162m	1177w		1171m	1175w	1158w	1160w	1170w				1178w		
			1155m								1159w			1157m	1153m		
1150m	1136m	1139m	1143s	1145s	1140m	1141s	1145s	1146s	1138m	1147w	1145w	1149s	1142s	1146s	1140w	1140w	$-C—N=$
							1136s	1133m		1128w	1118w						
						1125m	1120w	1120m									
		1110s	1114w		1112s		1110w										
	1099s	1100s		1100m	1100s		1100w	1100m	1102m	1104m	1101m	1101m	1103s	1095s	1103m	1098m	
1069s	1065m	1069m	1075w	1070w		1068w	1066w	1068w	1068w	1070w	1068w	1075s	1070s	1070s	1068m	1068m	
															1023w		
1018m	1015m	1016m		1017w	1015w	1020w	1017w	1015w				1016m	1015m	1016m	1015w	1015w	
997m	995m	998m	1000w	997w	997w		998w	1000w	997w	997w	997w	997w	995m	996w	998w	996w	
981m												985w		982w	980w		
												967w		957m	966s	962w	C-H deform. of $-CH=CH-$
		965w	940w												952s		

TABLE II (*continued*)

Compound[a] 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Assignment
924s	917m	914m	916w	912w	915w	920w	920w	920w	925w	929w	925w	923s	915s	918s	923w		–C–N=
												907s	900s				
															914w	914w	
	856s	861s		851s	860m		860s	865m	856s	856s	856s				867m	855s	
845w		852s		845m	852s			858s									
		825m	837s	831m	835m	834s	835m	835m									
			790w		797w		806w		800w	729m	784w				825s	825m	
												803s	800s				
772s	763s		765m	757m	760m	770m	769m	767m	771s	772s	770s	758s	760s	764s			
	760s	758s					765m		747w	751s	752m				745s		
		730m	718w	728w	731w	722w	715w			735w	732w					732m	
				708w													
684s	680s	677s	680m	677s	678s	689s	680m	684m	684s	683s	681s	680s	680s	679s	684s	681s	

[a] Compound number refers to Table I.

As would be expected, there are several strong absorptions arising from the phenyl rings, which are indicated in the table. For the *p*-hydroxy, *p*-amino and *p*-nitro compounds, there are additional bands due to these substituents. Of these absorption bands, the hydroxy and the amino groups should give rise to absorptions in the 3300 cm.$^{-1}$ region.

For *p*-hydroxyazobenzene, an O–H stretching absorption band is found at 3140 cm.$^{-1}$ [5]; however, for the corresponding polyazo compounds no well defined absorption band can be observed. The bathochromic shift of this band from the normal position of the 3590–3650 cm.$^{-1}$ region is due to the intermolecular hydrogen bonding as was indicated by Hadzi.[6]

The hydroxy group is also expected to give absorptions at the lower frequency regions which are caused by the O–H bending and C–O–H deformation vibrations. For the compounds investigated, two common absorptions are observed, one at 1378–1380 cm.$^{-1}$ and the other at 1240–1288 cm.$^{-1}$. Hadzi assigned the 1280 cm.$^{-1}$ band of *p*-hydroxyazobenzene to the O–H bending vibration which was confirmed by a deuteration study.[6] Thus it is probable that the 1240–1288 cm.$^{-1}$ band is responsible for this mode of vibration. Hadzi also assigned the 1230 cm.$^{-1}$ band to the C–O–H in-the-plane deformation vibration. However, the corresponding band with comparable intensity is observed in many other polyazo compounds, and it cannot be said with any certainty that the 1230-1212 cm.$^{-1}$ band of *p*-hydroxypolyazobenzene is caused purely by C–O–H deformation vibration.

It is interesting to find three absorption bands in the 3300 cm.$^{-1}$ region for *p*-amino compounds. The frequencies of these bands are listed in Table III.

TABLE III

ABSORPTION BANDS OF *p*-AMINOPOLYAZOBENZENE IN 3300 CM.$^{-1}$ REGION

	Frequencies in cm.$^{-1}$ Overtone	–NH$_2$ stretch.	
Monoazo	3220	3400	3510
Disazo	3220	3350	3440
Trisazo	3210	3380	3480
Aniline		3395	3481

The bands are clear in the monoazo compound, but they become broader and more diffuse in polyazo compounds. The primary amine usually gives rise to two absorption bands in this region; for instance, aniline gives absorptions at 3481 and 3395 cm.$^{-1}$ [7a] which are assigned to the N–H stretching modes of vibration. Thus, of the three absorption bands of aminoazo compounds, two corresponding bands at the higher frequency side can be assigned to the N–H stretching vibration. With regard to the remaining band at 3220 cm.$^{-1}$, which is the weakest in intensity of these three bands, one can reasonably explain it as an overtone of the 1620

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[5] No corresponding band can be observed for *o*-hydroxyazobenzene, where strong intramolecular hydrogen bonding exists; *cf.* K. Ueno, THIS JOURNAL, **79**, 3066 (1957).

[6] D. Hadzi, *J. Chem. Soc.*, 2143 (1956).

[7] (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 214; (b) p. 249; (c) p. 31.

cm.$^{-1}$ band. Since this strong band at 1620 cm.$^{-1}$ is characteristic of the aminoazo compound and since the frequency is in a region where the N–H deformation band of primary amines appears, this band can be assigned to N–H deformation mode of vibration. In this connection, it is noteworthy that the trisazo compound (compound 9) which has the lowest N–H deformation band (1613 cm.$^{-1}$) also has the lowest overtone band at 3210 cm.$^{-1}$. An additional band at the lower frequency region of 1300–1273 cm.$^{-1}$ can likewise be assigned to the C–N stretching vibration of the *p*-amino group.

For the nitro derivatives, two strong bands at 1525 and 1345 cm.$^{-1}$ are observed in addition to the absorption bands of the non-substituted polyazobenzenes, and these two bands are, without doubt, due to the NO_2 group.[7b]

With regard to the absorption bands due to the azo linkage, no conclusive result has been reported, although Le Fèvre and his co-workers assigned two bands near 1406 and 1577 cm.$^{-1}$ to the —N=N— linkage.[1] The main difficulty is that the azo absorptions are expected to appear in the double bond region, so that they may well be merged with the stronger aromatic ring absorptions. For the compounds under investigation, two common absorption bands at around 1455 and 1400 cm.$^{-1}$ are observed. The former band probably was overlooked by Le Fèvre, because the region is overlapped by a Nujol band. Although it is not clear which band is responsible for which mode of vibration of —N=N— bonding, these two bands can tentatively be assigned to the azo linkage.

Azo compounds are also expected to give rise to other bands at lower frequency regions, which originate in the C—N= linkage. The assignments for these bands in the literature are rather confusing, spreading over the range of 900–1325 cm.$^{-1}$.[8] However, according to Le Fèvre, three bands of aromatic azo compounds in the regions of 900, 1150 and 1300 cm.$^{-1}$ were assigned to the C–N linkage. For the polyazobenzenes under investigation, three bands at 920, 1140 and 1300 cm.$^{-1}$ regions correspond to those assigned by Le Fèvre, and these three bands are tentatively assigned to the —C—N= linkage.

As was reported in the previous papers,[2] the frequencies of absorption maxima in the ultraviolet region were related to the number of azo linkages and with the relative position of azo linkages against the phenyl ring. However, there is no simple relationship between the infrared absorption frequencies of the —N=N— or —C—N= linkage and the number of azo groups. Although some differences in the double bond region of the infrared spectra of *p*-, *m*- and *o*-polyazobenzenes were observed, no clear-cut rule was found for these absorption spectra.

For the polyazostilbenes, the steric configuration of the C=C bond is understood to be *trans*,[2,9] so that the C=C stretching absorption would be too weak to be observed, and moreover it may well overlap with the aromatic ring vibrations. Thus, the only characteristic absorptions of these compounds are to be observed in the —CH=CH— deformation region, and the C–H out-of-plane deformation vibration is expected to appear in a region of 970–960 cm.$^{-1}$.[7c] The observed band of the polyazostilbenes at 960–962 cm.$^{-1}$ can accordingly be assigned to this mode of vibration.

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KUMAMOTO-SHI, JAPAN

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(8) H. W. Thompson, *J. Chem. Soc.*, 328 (1948); N. V. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950); W. West and R. B. Killingsworth, *J. Chem. Phys.*, **6**, 1 (1938); S. Imanishi and Y. Kanda, *J. Sci. Res. Inst. Tokyo*, **43**, 17 (1949); H. Stammreich, *Experientia*, **6**, 225 (1950); W. J. C. Thomas, *Chemistry & Industry*, **23**, 567 (1953).

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