THE EFFECT OF HYDROGEN BONDING ON THE ELECTRONIC SPECTRA OF ORGANIC MOLECULES

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(Received 1 August 1962)

Abstract-1. The effect of hydrogen bonding upon the spectra of ionic and non-ionic compounds is examined.

2. It is found that:

a. when hydrogen bonding increases the polarity of the solute molecule, the absorption spectra moves to longer wavelengths, and

b. when the polarity of the molecule is decreased the absorption spectra tends to move to shorter wavelengths. In both cases the extent being determined, in part, by the effect of solvent polarity.

3. The "blue-shift" of the Merocyanines in solvents of high polarity (which can hydrogen bond) can be explained by a reduction in solute polarity caused by solute-solvent hydrogen bonding.

4. The structure of the sydnones is discussed in relation to the movement of their absorption spectra in hydrogen and non-hydrogen bonding solvents.

INTRODUCTION

THE hypsochromic shift displayed by many organic compounds on moving from a polar solvent to a non-polar solvent has been shown by many workers to be a general effect dependent upon the relative polarities of the solvents.

However, some compounds, notably the merocyanine types of dye, have been shown by Brooker¹ to have anomalous behaviour in that they, unlike the majority of previously investigated compounds, display a bathochromic shift under the same circumstances. In order to explain this behaviour Brooker assumed that the dyes form dipolar resonance structures which are stabilized by the polar solvent and, due to the stabilized zwitterion structure, so the energy of excitation increases leading to the bathochromic shift of the absorption spectrum. This theory is supported mathematically by Simpson².

However, later work has cast doubt upon this explanation. Bayliss and McRae³ showed when one of Brooker's merocyanines was dissolved in solvents of increasing polarity, the bathochromic shift of the maxima of the absorption spectra bore no relationship to the variation in polarity of the solvent. They pointed out that some sort of relationship should have been apparent if Brooker's theory were correct, and also said that there were two other significant factors:

a. An increase in the molecular size of the solvent caused the absorption spectra of the solute to display a bathochromic shift.

b. When the solvent molecule had a hydrogen atom that could form a hydrogen bond, the absorption spectra of the solute displayed a hypsochromic shift relative to its position in a non-hydrogen bonding solvent.

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- ¹ L. G. S. Brooker et al., J. Amer. Chem. Soc. 73, 5332, 5350 (1951).
- ² W. T. Simpson, J. Amer. Chem. Soc. 73, 5359 (1951).
- ⁸ N. S. Bayliss and E. G. McRae, J. Amer Chem. Soc. 74, 5803 (1952).

It appeared probable that this latter suggestion was the more important. Consequently, the investigation was initiated in order to establish, if possible, that hydrogen bonding was responsible for this anomaly and to determine whether there was a general case to answer.

Related and parallel work by Burawoy and other on the effects of the hydrogen bond on the absorption spectra of phenol and its derivatives, which is an essential precourser to the following discussion, is fully reported elsewhere.⁴⁻¹¹

It is assumed throughout that the hydrogen bond is of an electrostatic nature since this view is most strongly supported.¹²⁻³¹

THE MODIFICATION OF SOLUTE ABSORPTION SPECTRA BY SOLUTE-SOLVENT HYDROGEN BONDING

The modification of the absorption spectra of a simple molecule by substituent and solvent effects will be considered before the general case.

a. Phenol Derivatives and the Hydrogen Bond

The effect of the introduction of electron donating, bonding and non (or very weakly) bonding groups may now be studied conveniently with a compound such as 4-phenylbiphenyl and its derivatives. Table 1 shows the expected bathochromic shift of the K-Band of this compound on the introduction of electron donating groups.

The K-Bands of the 4-hydroxy- and 4-methoxy- compounds suffer a further bathochromic shift on solution in solvents of greater polarity, as illustrated in Table 2.

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- ¹⁴ A. Burawoy et al., J. Chem. Soc. 4793 (1952).
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- ²¹ R. Hofstadter et al., J. Chem. Phys. 6, 531 (1938).
- ²² J. Karle and L. O. Brockway, J. Amer. Chem. Soc. 66, 594 (1945).
- ²³ R. Mecke, Nature, Lond. 328 (1945).
- ²⁴ T. S. Moore and T. F. Winmill, J. Chem. Soc. 101, 1635 (1912).
- ⁸⁵ S. Nagacura and M. Goutermann, J. Chem. Phys. 25, 881 (1957).
- ²⁴ L. Pauling, Nature of the Chemical Bond Cornell (1940).
- ²⁷ L. Pauling, J. Amer. Chem. Soc. 57, 2680 (1935).
- ³⁸ C. Reid, p. 128. Excited States in Chemistry and Biology London (1957).
- ³⁹ V. Schomaker and J. M. O'Gorman, J. Amer. Chem. Soc. 69, 2638 (1947).
- ³⁰ A. Tsubomura, Bull. Chem. Soc. Japan 27, 445 (1954).
- ³¹ E. O. Wollan et al., Phys. Rev. 75, 1348 (1949).

The effect of hydrogen bonding on the electronic spectra

TABLE 1.	MAXIMA (IN	Å) of K	- BANDS OF	COMPOUNDS					
Substituent	Solvent	λ	e	$D\lambda(H \rightarrow X)$					
x									
—H	hexane	2750	32000						
-OH	hexane	2810	32500	60					
-OMe	hexane	2854	34000	104					

The larger shift shown by the 4-hydroxy- derivative is due to two superposed effects, the influence of a polar solvent, general solvation, and the result of hydrogen bonding with a hydrogen donating solute, specific solvation.

x	-	IN HEXANE AND ETHANOL		
Substituent	Solvent	λ	£	$D\lambda$ (Hex \rightarrow Eth)
x		· · ·		
-OMe	hexane	2854	34000	
—OMe	ethanol	2875	33000	21
OH	hexane	2810		
—OH	ethanol	2890	31000	80

TABLE 2. MAXIMA (IN Å) OF K- BANDS OF COMPOUNDS

In the introduction it was shown that, as a result of this type of hydrogen bonding, the oxygen atom of the phenolic hydroxyl group becomes more electronegative relative to its non-bonded state, and as a consequence there is a bathochromic shift of the K- Band. This is shown in Table 2, although it is not possible to give a precise figure for the shift due to hydrogen bonding between solvent and a solute hydrogen atom, for a *strict* comparison cannot be drawn between the phenol and its methyl ether.

The small negative charge induced on the phenolic oxygen atom by hydrogen bonding will reach a maximum value on the formation of the phenolate ion.

Consequently, it would be expected that the K- Band would suffer a strong bathochromic displacement. This is in fact so (cf. Table 3), where the effect, on the K-Band, of the introduction of progressively more electron repelling groups is clearly shown

> TABLE 3. MAXIMA (IN Å) OF K-BANDS OF COMPOUNDS IN ETHANOL Substituent Solvent λ $D\lambda(H \rightarrow X)$ € х ---H ethanol 2769 32000 -OMe ethanol 2875 33000 106 -OH ethanol 2890 31000 121 ---0cthanol 3270 33000 501

Solutions of the phenolate ion in hydrogen bonding solvents do not, as did solutions of the corresponding phenol, display a bathochromic shift, relative to solutions in non hydrogen bonding solvents. On the contrary, there is a strong hypsochromic shift (cf. Table 4). This shift can only be attributed to a reduction in the electron repelling power of the terminal group, since this group acts as hydrogen acceptor on the formation of a solute-solvent hydrogen bond. The hypsochromic shift shows that the energy required for excitation is increased.

TABLE 4. N X-	Лахіма (in Å	A) OF K-1 IN PYRI	BANDS OF	COMPOUNDS
Substituent	Solvent	λ	E	$D\lambda(H \rightarrow bond)$
Х —О ⁻ —О ⁻ ··· НОЕt —О ··· НОН	pyridine ethanol water	3675 3270 3140	20560 33000 32000	- 405 - 535

The effect due to hydrogen bonding is even greater than the figures in Table 4 would indicate, for the bathochromic shift due to solvent polarity is opposed to the shift due to solute hydrogen accepting hydrogen bonding. There is, unfortunately, no way of accurately correcting the figures.

b. The general case—The Functional Group and the Hydrogen Bond

Solute molecules which may contain more than one hydrogen bonding group, hydrogen accepting or donating can be examined more clearly if they are divided into the six following groups:

- 1. Compounds containing only one, relatively strong, hydrogen bonding group
 - (i) ionic
 - (ii) non ionic
- 2. Compounds containing more than one hydrogen bonding group
 - (i) ionic
 - (ii) non ionic
- 3. Compounds containing
 - (i) nitro groups
 - (ii) nitroso groups.

1. (i) Ionic compounds containing only one relatively strong hydrogen bonding group

Table 5 shows the values for the K- Bands of the ions of 4-hydroxy-4-phenylbiphenyl, *trans* 4-hydroxy-azobenzene, *trans* 4-hydroxy- γ -stilbazole and 4-hydroxybiphenyl in solutions of pyridine, ethanol, water-pyridine (50:50) and water.

A strong hypsochromic shift is observed on the transfer to the more polar hydrogen bonding solvent. As solvents, the effect of water is always the greatest while that of ethanol and of aqueous pyridine are roughly the same (about 75% of that caused by water). Polar solvents normally give bathochromic shifts which, in this case,

lons of	Solvent	1.max	E	vmax	$D\lambda(P \rightarrow solv)$	$D\nu(P \rightarrow solv)$
4-Hydroxy-	(P)yridine	4790	38680	20880		
azobenzene	(E)thanol	4060	29080	24630	-730	3750
	(W)ater	4000	28200	25000	- 790	4120
	P/W	4350	—	22990	-440	2110
4-Hydroxy-	Р	4270	25960	23420		
2-	E	3850	21550	25970	-420	2550
stilbazole	w	3600	22000	27780	-670	4360
	P/W	3860	21180	25910	-410	2490
4-Hydroxy-	Е	2970	23000	33670	_	_
biphenyl	W	2915	20350	34306	_	—
4-Hydroxy-	Р	3675	20560	27210		
4'-phenyl	E	3270	33000	30580	- 405	3370
biphenyl						
	w	3140	_	31850	- 535	4640
	P/W	3265	22380	30630	-110	3420

TABLE 5. MAXIMA OF K- BANDS IN Å AND CM^{-1}

Compounds	Solvent	λ _{max}	£	vmax	$D\lambda(P \rightarrow solv)$	$D\nu(P \rightarrow solv)$
4-Dimethyl-	Р	4190	28000	23866		
amino-	Ε	4075	29360	24539	-115	673
azobenzene	w	4500	21500	22222	310	-1644
4-Amino-y-	Р	3735	28160	26774		_
stilbazole	E	3697	27120	27047	- 38	273
	w	4060		24631	325	-2143
	W*	3395	27540	29444	-340	2670
4-Aminoazo-	Р	3982	20880	25113	_	
benzene	E	3883	25300	25750	99	637
	W	3760	20350	26596	- 222	1483
4-Amino-	Е	2805	19000	35652		
biphenyl	W	2755	19350	36295	—	
4-Amino-4'-	Р	3185	27150	31307	_	
nhenvl-	Ē.	3040	32000	37895		1405
biphenyl	w†	2805	-	35652	- 380	4255

TABLE 6. MAXIMA OF K- BANDS IN Å AND CM^{-1}

* Water + 1% 2 N Na₂CO₃ or 1% 2 N NaOH † Due to insolubility this figure is very doubtful and should only be regarded as a general indication of the shift.

since we are dealing with polar solutes, would be quite appreciable, and consequently the effect of hydrogen bonding is much greater than the figures would indicate.

(ii) Non ionic compounds containing only one, relatively strong, hydrogen bonding group

Table 6 shows the values for the K- Bands of trans 4-dimethylaminoazobenzene, trans 4-amino- γ -stilbazole, trans 4-aminoazobenzene, 4-aminobiphenyl and 4-amino-4'-phenylbiphenyl.

4-dimethylaminoazobenzene and 4-amino- γ -stilbazole are very sensitive to acid, their ionization in aqueous solution shown by their spectra, was prevented by the addition of alkali (cf. Table 6). This addition precipitated the azobenzene and consequently the position of its K- Band could not be determined.

With this exception, one observes a strong hypsochromic displacement due to the formation by the amino-group, of a hydrogen accepting hydrogen bond which causes the consequent reduction in the polarity of the terminal group. Again, the true shift cannot be ascertained, since it is partially masked by the bathochromic shift caused by increase in solvent polarity.

2. (i) Ionic compounds containing more than one hydrogen bonding group

Table 7 shows the values for the K- Bands of the ions of 1-formyl-4-hydroxy-1,3-butadiene, 4-hydroxybenzaldehyde, 4-hydroxybenzophenone, 4,4'-dihydroxybenzophenone, 4,4'-dihydroxytriphenylmethane carbinol, 4-phenol-phthalein, 4phenolindophenol, 4-phenolindophenol-N-oxide, 4-aminoindophenol, and 4-nitrosoaniline.

The compounds in this group display a hypsochromic shift on being transferred from pyridine to water, though here it is of a smaller order than that shown in Tables 5 and 6. This small shift depends upon the fact that the compounds, which are all homologues of structures I and II, contain two groups, both in the same conjugated system, and both capable of hydrogen bonding.

$$I \qquad O = CH - (CH = CH)_n - O^-$$

$$II \qquad O = CH - (CH = CH)_n - NH^- \checkmark$$

$$NH = CH - (CH = CH)_n - O^- \checkmark$$

The terminal groups in I and II are hydrogen acceptors and consequently on bonding they suffer similar changes in polarity. As the groups are at opposite ends of the molecule, the overall effect is quite small and is due to the nett change in solute polarity. Consequently, only relatively small hypsochromic shifts are observed.

No comment may be made on the shift of the aliphatic compound, due to lack of comparative data. It is interesting to note that the shifts of these closely related compounds, except for 4,4'-dihydroxybenzophenone and 4-phenolindophenol-Noxide, are very similar, and the expected displacement of the K- Band caused by the introduction of further groups is observed.

A comparison of the data for the ions of 4-hydroxy- and 4,4'-dihydroxybenzophenone shows that the hypsochromic shift of the latter, in water, is less than that of the former, and indeed of all the other compounds listed.

This apparent anomaly is due to two factors:

- (a) The effects of general solvation.
- (b) The influence of a second $-O^-$ in the side chain

Ions of	Solvent	λ_{max}	E	Vmax	$D\lambda(P \rightarrow solv)$	$Dr(P \rightarrow solv)$
1-Formyl-4-	Р	3675	43300	27210		_
hydroxy-1,3-	Е	3655	54150	27359	-20	149
butadiene	w	3635	49750	27510	-40	300
4-Hydroxy-	Р	3520	35940	28410		_
benzaldehyde	E	3370	30900	39670	-150	1260
•	w	3305	28450	29850	-215	1440
	P/W	3385	27420	29540	-135	1130
4-Hydroxy-	Р	3665	23120	27390	_	
benzophenone	E	3500	25600	28570	-165	1180
•	w	3465	22720	28940	-200	1550
	P/W	3530	20300	28330	-130	940
4,4'-Di-	Р	3675	32775	27210	_	_
hydroxy	E	3550	36800	28169	-125	959
benzophenone	w	3590	27500	27855	-85	645
	P/W	3643	27450	27450	-32	240
4,4'-Di-						
hydroxy-	Р	6025	1756†	16600	—	—
triphenyl-	E	5835	1660†	17140	-1 90	540
methane-	w	5800	1388†	17240	-225	680
carbinol	P/W	5850	1740†	17090	-175	490
4-Phenol-	Р	5725	3960†	17470	_	
phthalein	E	5630	17120	17760	-95	290
-	w	5525	24250	18100	-200	630
	P/W	5650	4065	17700	75	230
4-Phenol-	Р	6550	64800	15270		—
indophenol	E	6465	52760	15470	85	200
	w	6275	29820	15940	-275	670
	P/W	6515	48200	15350	-35	80
4-Phenol-	Р	6940	61960	14409		
indophonol	E	6700	34600	14925	-240	516
N-oxide	w	6165	19280	16221	-775	1812
4-Amino-	Р	6105	37240	16380	_	
indophenol	E	5725	24040	17468	- 380	1088
	W	5425	14740	18433	-680	2053
4-Nitroso-	Р	407 0 *	25720	24570		
aniline	Е	3930	22050	25445	-140	875
	w	3545	29820	28209	- 525	3639

TABLE 7. MAXIMA OF K- BANDS IN Å AND CM^{-1}

* This figure should only be regarded as an indication of the general trend, for the alkali required to form the ion caused, in addition, the decomposition of the compound.

† The extinction coefficient is small due to the formation of the leuco compound.

The former factor is, of course, always present, but it is more noticeable here because the second factor causes, in a highly polar and strongly hydrogen bonding solvent, water, an increase in the polarity of the molecule.

A similar situation is observed with the ion of 4-methoxy-4'-carboxybiphenyl, where hydrogen bonding at the carboxylate group tends to increase the polarity of the absorbing system, while the weak bonding at the methoxy group^{10,32} tends to decrease the polarity of the system. This is illustrated in Table 8.

14000 011			
Ions of	Solvent	Âmax	e
4-Methoxy-4'- carboxybiphenyl	E W	2765 2825	20700 23560

TABLE 8. MAXIMA OF K- BANDS IN Å

Indophenol-N-oxide is interesting because it displays hypsochromic shifts which are almost three times as great as those of indophenol itself. It is suggested that the most probable explanation is that the compound can exist as a zwitter ion and that in a hydrogen bonding solvent this ion is stabilized by hydrogen bonding at the three terminal oxygen atoms and by specific solvation of the nitrogen atom as illustrated in III.



This concept of five molecules in association is allowed by molecular models. The overall result is that the polarity of the molecule is decreased and, in addition to causing bigger shifts, the absorption spectra of indophenol-N-oxide is observed to approximate to that of indophenol itself.

(ii) Non ionic compounds containing more than one hydrogen bonding group

Table 9 shows the values for the K- Bands of 4-aminobenzaldehyde, 4-aminobenzophenone, 4,4'-diaminobenzophenone and 4-aminoindophenol.

Unlike the compounds discussed previously, the compounds in this group display a predominantly bathochromic shift. This is because the hydrogen bonding groups are non ionic and when, as here, their individual effects are in opposition the overall change in solute polarity, due to the more strongly bonding group, is small relative to the effect of general solvation. The influence of the more strongly bonding solvent, water, is illustrated in all compounds by a smaller bathochromic shift in water than in ethanol and, in the case of 4-aminobenzaldehyde, a slight hypsochromic shift, although water is the more polar solvent.

³² R. A. Morton and A. L. Stubbs, J. Chem. Soc. 1347 (1940).

Compound	Solvent	Âmax	€	Vmax	$D\lambda(P \rightarrow solv)$	$D\nu(P \rightarrow solv)$
4-Amino-	Р	3290	28600	30395		
benzaldehyde	Е	3315	26350	30166	25	-229
2	w	3275	21540	30533	-15	138
	Hexane*	2955	20750	33840		
4-Amino-	Р	3315	21660	30166		_
benzophenone	Е	3365	18000	2 9717	50	- 449
Ĩ	w	3330	16755†	30030	15	-136
4,4'-Diamino-	Р	3370	31290	29674	_	_
benzophenone	Ε	3425	29460	29198	55	-476
1	W	3390	25530	29499	20	-175
4-Amino-	Р	5710	19280	17513		
indophenol	E	5875	21380	17021	165	492
I.	W	5510	—	18149	_	_

TABLE 9. MAXIMA OF K-BANDS IN Å AND CM-1

* This compound is difficult to purify and the spectra in hexane was done to check purity.

† This figure is only approximate.

It is interesting to note that the comparative figures for 4-amino- and 4,4'-diaminobenzophenone are very similar, unlike those of their corresponding hydroxy ions. This similarity is due to the fact that the more weakly bonding, non ionic, side chain amino group has, as would be expected, little effect on the spectra.

The value for aminoindophenol in water does not concur with the rest of the Table. It is thought that this discrepancy is caused by the sensitivity of the compound to small changes in pH.

3. (i) Compounds containing nitro groups

These compounds may be conveniently divided into three sections:

(a) Nitro- compounds containing only one strongly hydrogen bonding group.

(b) Nitro- compounds containing more than one strongly hydrogen bonding group.

(c) Nitrophenolates and related compounds.

Ions of	Solvent	λ_{max}	E	vmax	$D\lambda(P \rightarrow solv)$	$Dv(P \rightarrow solv)$
4-Nitro-	Р	3395	23560	29544		
azobenzene	Ε	3305	25840	30258	-90	714
	w	3390	22520	29499	-5	45
4-Nitro-y-	Р	3380	19700	29586		
stilbazole	E	3300	26000	30303	-80	717
	w	3390	25350	29499	10	-87
4-Nitro-4'-	Р	3405	25320	29370	_	-
phenylbiphenyl	E	3265	19320	30627	-140	1257
	W		insoluble			

TABLE 10. MAXIMA OF K- BANDS IN Å AND CM^{-1}

(a) Nitro- compounds containing only one strongly hydrogen bonding group

Table 10 shows the values for the K- Bands of 4-nitroazobenzene, 4-nitro- γ -stilbazole and 4-nitro-4'-phenylbiphenyl.

The results listed in Table 10 appear at first sight to be anomalous, since from the previous discussion it would be expected that the absorption spectra of compound IV in either ethanol or water, would show a bathochromic shift relative to its position in a pyridine solution.

IV H-(CH=CH),-NO

This is, however, not so, although the highly polarizable nature of the nitro group affords an explanation similar to that used to rationalize the large hypsochromic shift of indophenol-N-oxide.

Three solvation effects must now be considered:

- (i) General solvation.
- (ii) Hydrogen bond formation.

(iii) Specific solvation at the nitrogen atom of the terminal nitro group and the influence of steric hindrance.

(i) General solvation will give a bathochromic shift in all cases in the order:

pyridine
$$<$$
 alcohol $<$ water.

(ii) Hydrogen bond formation will increase solute polarity in the order:

pyridine
$$<$$
 ethanol \sim water.

It is doubtful whether the increase in solute polarity, due to solvent hydrogen bond formation with the readily polarized nitro group, is any greater in water than it is in ethanol.

(iii) Specific solvation at the nitrogen atom, shown by models to be possible for water and ethanol, is greater in the case of ethanol.

A possible explanation of the anomaly is that specific solvation at the nitrogen atom, which is electron deficient as a result of hydrogen bonding, is causing, despite the opposition of other solvent effects, a nett decrease in solute polarity.

It is interesting to note that Tanekazu Kubota³³ found that the absorption spectrum of pyridine-N-oxide was hypsochromically displaced in ethanol and water relative to its position in carbontetrachloride. He claims that this shift is due to hydrogen bonding, though if it is, it is anomalous and the possible explanation may well be similar to that suggested for the nitro- compounds in this sub-section.

(b) Nitro- compounds containing more than one strongly hydrogen bonding group

The values for the K- Bands of 4-nitroaniline, 2-nitroaniline and 2,4,6-trinitroaniline are shown in Table 11. It is not possible to undertake a detailed analysis of

** Tanekazu Kubota, J. Pharm. Soc. Japan 74, 831 (1954).

Compound	Solvent	2.max	e	vmax	$D\lambda(P \rightarrow solv)$	$D\nu(P \rightarrow solv)$
4-Nitro-	Р	3790	17820	26390		
aniline	Ε	3725	16800	26846	-65	56
	W	3820	12960	26180	30	-210
2-Nitro-	Р	4115*	5500	24300	<u> </u>	
aniline	E	4050*	6100	24690	-65	390
	w	4130*	4372	24210	15	90
	Ε	2777	4900	36101	_	
	w	2825	5280	35399	_	
2,4.6-Tri-	Р	4285	7870	23336	_	
nitroaniline	Ε	4190	8340	23866	-95	530
	w	4260	8440	23474	-25	138

TABLE 11. MAXIMA OF K- BANDS IN Å AND CM⁻¹

*B-Band

the spectra of these compounds in solution, since hydrogen bonding occurs at several points and specific solvation is possible on at least the nitrogen atom of the nitro group. However, an examination of Table 11 would indicate that the changes in solute polarity caused by hydrogen bonding at the nitro and amino groups almost cancel each other out and, as a consequence, solvent polarity is an important factor. The nett result is either a small hypsochromic or bathochromic shift.

The observation that there is a small bathochromic or hypsochromic shift can be interpreted as showing that the degree of specific solvation of the nitrogen atom of the nitro group is small. This is not surprising for the electron repelling nature

Ions of	Solvent	λmax	ε	v_{max}	$D\lambda(P \rightarrow solv)$	$D\nu(P \rightarrow solv)$
 4-Nitro-	 P	5050*	_	19802		
thiophenol	E	4210		23753	- 840	3951
•	W	4075	—	24539	975	4737
4-Nitro-	Р	4312	32680	23190		
phenol	Е	4010	24000	24940	-302	1750
•	w	3990	19000	25060	-412	1870
	P/W	4100	21200	24390	-212	1200
2.4.6-Tri-	Р	3820	17430	26180	_	
nitrophenol	Е	3650	14120	27400	-170	1220
1	w	3580	14125	27930	-240	1750
	P/W	3720	14925	26880	-100	700
2-Nitro-	Р	4470	7920	22370	_	
phenol [†]	E	4230	5790	23640	240	1270
	w	4140	4940	24160	-330	1790
	P/W	4250	5560	23530	-220	1160

TABLE 12. MAXIMA OF K- BANDS IN Å AND CM⁻¹

* This figure is ± 25 Å.

† B- Band.

of the amino group will make up any electron deficiency of the nitrogen atom. The results also infer that the decrease in solute polarity due to bonding at the amino group is somewhat greater than the increase due to bonding at the nitro group. Consequently, it is possible that the amino group forms stronger hydrogen bonds than the nitro group.

(c) Nitrophenolates and related compounds

Table 12 shows the values for the K- Bands of the ions of 4-nitrothiophenol, 4-nitrophenol, 2,4,6-trinitrophenol, and the B- Band of sodium 2-nitrophenolate.

The compounds in this group display a hypsochromic shift of similar order to that of the majority of the compounds in Table 7. This similarly is due to the fact that the molecule contains two groups both of which form hydrogen bonds, but the change in solute polarity due to one is much greater than that due to the other. The exceptions are the ions of 4,4'-dihydroxytriphenylmethane carbinol and phenolphthalein, whose displacements are much smaller than those of the other compounds in the two groups. This discrepancy may be explained by the formation of stronger hydrogen bonds by quinonoid groups relative to those formed by either nitro or carbonyl groups.

It is interesting to note (cf. Table 13) that the energy relationships of the B- Band of 2-nitrophenolate are of a similar order to those of the K- Bands of related substances. This need not be so if the bonding groups were not in the terminal position of the absorbing system which corresponds to the B- Band.

	K- E Solv	lands cents	B- B Solv	ands ents
	ethanol	water	ethanol	water
Âmax	3370	3305	2400	2380
vmax	29670	29850	41667	42017
$D\lambda(E \rightarrow W)$	-65		-20	
$D\nu(E \rightarrow W)$	180		50	

Table 13. Maxima of K- and B- bands of 4-hydroxybenzaldehyde ion in Å and \mbox{cm}^{-1}

It is not possible to give a figure for the maximum in pyridine in this or other investigated compounds, since the position of absorption of pyridine masks the region usually occupied by **B**- bands.

The Burawoy formulation for the type of transition corresponding to the B- Band offers an explanation, since this would imply that the two groups involved are the terminal groups of the absorption system involved in the transition.³⁴ Thus, although both bands display a hypsochromic shift, that of the B- Band is much smaller than that of the K- Band.

Although it is not possible, due to the instability of the solute, to give the K- Band maximum of the ion of 4-nitrothiophenol in pyridine within 25 Å, it is obvious that

84 A. Burawoy, Tetrahedron 2, 122 (1958).

there is a very large hypsochromic shift $(P \rightarrow W)$ for this solute, a shift which is due to the greater electron polarizability of the terminal $-S^-$ as compared to a terminal $-O^-$. This is also illustrated in Table 14 which is a comparative table of water and ethanol as solvents, and of the ions of thiophenol, phenol and 4-nitrothiophenol and 4-nitrophenol as solutes.

Table 14.* Maxima (in Å and cm^{-1}) of the K- bands of the compounds X—(—)—Y in water and ethanol

	Substi	tuent			Solver	nts	
x	Y	wa	ater	et	hanol		
		2.max	*max	λ _{max}	vmax	$D\lambda(E \rightarrow W)$	$D\nu(E \rightarrow W)$
н	0-	2345	42646	2374	42123	-29	523
н	S	2620	38168	2680	37313	-60	855
NO2	O -	3990	25063	4010	24938	-20	125
NO ₂	S -	4075	24539	4210	23753	-135	786

* Values due to Burawoy et al.35

The greater hypsochromic shift exhibited by the more polarizable group $-S^-$ is illustrated by the comparison of the maximum of the phenolate ion with that of thiophenol. In addition, the polarizability of the $-S^-$ group is so great, unlike that of the $-O^-$ group, that on the introduction of a hydrogen bonding 4-nitro group

Ions of			So	lvents		
	w	ater	eth	anol		
	λ _{max}	Vmax	λ _{max}	Vmax	$D\lambda(E \rightarrow W)$	D <i>v</i> (E · + W)
4-Amino- phenol	2430	41152	2452	40783	-22	369
4-Amino- thiophenol	2657	37636	2702	37024	-45	612

TABLE 15.* MAXIMA OF K- BANDS IN Å AND CM-1

* Values due to Burawoy et al.35

the hypsochromic shift of the thiophenolate derivative, relative to that of the phenolate, is hardly affected. A comparison of the data for the ions of 4-aminothiophenol and 4-aminophenol (cf. Table 15) show that even with an electron donating group the same conclusions may still be drawn.

(ii) Compounds containing nitroso groups

Table 16 shows the K- Band maxima for 4-nitrosobiphenyl, 4-nitrosoaniline and 4-dimethylaminonitrosobenzene.

³⁵ A. Burawoy, J. P. Critchley and Thompson, *Tetrahedron* 4, 403 (1958).

Compound	Solvent	λ _{max}	£	Vmax	$D\lambda(P \rightarrow solv)$ or $(H \rightarrow solv)$	$D\nu(P \rightarrow solv)$ or $(H \rightarrow solv)$
4-Nitroso-	H*	3275	13800	30533		
biphenyl	E	3402	14340	29403	127	-1136
. ,	H†	2285	9790	43763	_	_
	E†	2315	9490	43198	30	- 565
4-Nitroso-	Р	4025	29750	24845		—
aniline	E	4050	28480	24691	25	-154
	W	4145	29820	24126	100	- 565
4-Dimethyl-	Р	4235	31860	23613	_	
aminonitroso-	Ε	4200	30400	23810	35	197
benzene	w	4400	32820	22727	165	- 886

TABLE 16. MAXIMA OF K- BANDS IN Å AND CM⁻¹

* H = hexane

† B- Band

Since comparative data is not available, it is not possible to comment upon the bathochromic shifts of the K- and B- Bands of nitrosobiphenyl. However, in the case of the two amino compounds the situation is essentially the same as that for the nitro anilines (cf. iii, (1), (b)).

CONCLUSIONS

The experimental results obtained in the previous section allow the following observations to be made:

1. The general case of hydrogen bonding has been verified, i.e. the shift of the absorption spectrum will be either bathochromic or hypsochromic dependent on whether the polarity of the molecule is increased or decreased respectively by hydrogen bonding.

2. The change in solute polarity with hydrogen bonding varies from series to series; it is very large in many of the compounds investigated, and is greatest in the phenolate and thiophenolate ions.

3. The strength of the hydrogen bond formed is in the order:

$$_{S^-} > _{O^-} > _{NH_2} > = C = O$$
 quinonoid $> _{NO_3} \sim C = O > _{N=N_2} \sim N$

\$

4. The amino group forms hydrogen accepting hydrogen bonds.

In conclusion, it can be said that the hypsochromic shift shown by merocyanines is but an instance of a reduction of solute polarity caused by the formation of hydrogen bonds. The reverse concept, that all similar hypsochromic shifts observed may be explained by Brooker's¹ theory of solvent stabilized zwitter ions, is not tenable for many of the compounds investigated cannot be resolved into the imidic structures (V) required for resonance.



The phenolate and other ions examined may not, within the bounds of reasonable energy requirements, form zwitter ions at all.

Subsequent to the commencement of this work, publications by McRae^{36,37} showed that, for merocyanines at least, the difference in frequency on transfer from one polar solvent to another (both non-hydrogen bond forming) was a function of both the dielectric constant and the refractive index of the solvent. Certainly, in all the merocyanines he investigated, the absorption spectrum in nitrobenzene (dielectric constant(35) was at longer wavelengths than that in pyridine (12.4) and ethanol(36) whereas, if Brooker's theory were correct, the reverse observation should have been made.



It has been claimed by McRae that the formation of a single hydrogen bond by the merocyanine dyes, VI and VII cannot account for the very large hypsochromic shifts observed. It has been suggested by Pimentel³⁸ and McRae³⁶ that this shifts may be due to the formation of a double hydrogen bond VIII.

Compounds		Solvents				
	pyridine	ethanol	water	$D\nu(P \rightarrow E)$	$D\nu(P \rightarrow W)$	$D\nu(E \rightarrow W)$
4-Amino- biphenyl		35652	36298			646
4-Hydroxy- biphenyl*	_	33670	34306	-		636
4-Amino-4'- phenylbiphenyl	31397	32895	35652	1498	4255	2757
4-Hydroxy-4'- phenylbiphenyl*	27210	30580	31850	3370	4640	1270
Merocyanine (VI)	16380	18050	21320	1670	4940	3270

TABLE 17. MAXIMA OF K- BANDS IN CM⁻¹

* Ions.

³⁴ McRae, Spectrochim Acta 12, 192 (1958).

³⁷ McRae, J. Phys. Chem. 61, 562 (1957).

⁸⁸ Pimentel, J. Amer. Chem. Soc. 79, 3323 (1957).

Compound		Solv	/ents						
	pyridine	ethanol	water	ethanol*	water*	$D\nu(P \rightarrow E)$	$D\nu(P\to W)$	D#(P -+ E*)	$D\nu(P\to W^{\bullet})$
Lamino-4'- ohenyl- oiphenyl	31397	32895	35652	35714	1	1498	4255	4317	1
Lnitro- hio- shenolate	19802	23753	24539	31496	ļ	3951	4737	11694	I
4-nitro- shenolate	26390	26846	26180	31746	ł	456	-210	5356	Ι
mero- yanine VII)	17680	18110	20280	23330	I	430	2600	5650	l
nero- yanine VI)	16380	18650	21320	ļ	24800	2270	4940		8420
 Protonated 					1				

Table 18. Maxima of K- bands in cm^{-1}

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However, this explanation is not required for the shift is only of a similar order to that of many of the compounds investigated by the authors. In particular, this holds for the amino compounds where the formation of two hydrogen accepting hydrogen bonds on the amino group is rather unlikely. The hypsochromic shift is a measure not only of the strength of the hydrogen bond, but of the decrease in polarity and polarizability of the molecule; thus, the more polar the molecule, the greater the possible decrease. This factor is illustrated in Table 17, where a comparison is made between the hypsochromic shifts obtained from the more polar of the compounds investigated by the authors and those of the merocyanine VI, which must be one of the most polar of the non-ionized organic molecules.

The ultimate degree of hydrogen bonding, proton addition, may cause a very considerable reduction in the polarity of the molecule, and may even reverse it, giving as a result the largest of all the hypsochromic shifts observed. Thus the largest hypsochromic shift shown by merocyanines is observed on protonation though it is still only of the same order and comparable with that of other less complex protonated compounds, as is illustrated in Table 18.

The sydnones have presented a structure problem for some little time. It was felt that the effect of hydrogen bonding solvents on the absorption spectra of these compounds might possibly confirm or refute their postulated structures.

THE STRUCTURE OF THE SYDNONES

Baker *et al.*³⁹ concluded, after a consideration of both spectroscopic and chemical data, that the sydnones could be considered as compounds, exhibiting aromatic characteristics, which can be represented only as resonance hybrids of a large number of contributing ionic forms. It is impossible to represent this type of compound by



any one covalent formula, or as a hybrid of a few covalent forms. They suggested that the structure might well be represented by diagram IX, and if this were so, then the compound ought to have a considerable dipole moment due to the sum of the prevailing ionic forms X.



They synthesized a number of the compounds and showed them to possess a dipole as required by X.

This means that the sydnones exist as zwitter ions and consequently ought, as do phenolate ions, to display hypsochromic shifts when, as solutes, their polarity is

³⁹ W. Baker, W. D. Ollis and V. D. Poole, J. Chem. Soc. 307 (1949).

reduced by hydrogen bonding. Such a shift is, in fact, observed (cf. Table 19) and consequently it can be concluded, at least in solution, that the structure proposed by Baker *et al.* is further supported.

					•
Compound	Sc	olvents			
	pyridine λ _{max}	ethanol λ _{max}	water λ_{\max}	$D\lambda(P \rightarrow E)$	$D\lambda(P \rightarrow W)$
Benzyl sydnone		2920	2875	_	_
N-phenyl sydnone	3200	3130	3015	- 70	185
N,C-diphenyl sydnone	3410	3340	3280	-70	-130

TABLE 1	19.	Maxima	IN	Ż

EXPERIMENTAL

Spectra were determined with a Hilger Uvispek Photoelectric Spectrophotometer, using quartz cells. Maxima above 4000 Å were determined with a glass prism, those below, with a quartz prism.

All solvents were purified and their absorption spectra checked against published values.

i. The absorption spectra of unstable compounds were determined by making up and maintaining solutions under appropriate oxidizing-reducing and pH conditions and, when necessary, in the dark.

ii. Weak acids were ionized by the addition of aqueous sodium hydroxide.

iii. Care was taken to ensure that deliberate pH changes did not have any adverse effect upon the absorption spectrum of the compound concerned, cf. i, ii.

i. 4-Aminobenzaldehyde

4-Nitrotoluene (10 g) hydrated sodium sulphide (6 g) sulphur (2.5 g) (a ratio of 1 g mole of 4nitrotoluene to 0.33 g mole of sodium polysulphide), ethanol (60 ml), water (120 ml) and sodium hydroxide (4.5 g) were mixed and refluxed for 50 min. The ethanol and 4-toluidene were steam distilled off. The mother liquor, contained in the steam vessel, was chilled quickly and left for 24 hr at 0°. The preparation took one of 3 courses.

1. No precipitate formed. An ether extract of the mother liquor was concentrated, dried and refluxed with activated charcoal. The filtrate was seeded and crystallized to give large white rhomboids.

2. A crystalline precipitate formed. The crystals are pure except for a thin surface coating of the polymer (cf. 3). They may only be purified as above.

3. A red sludge formed. The sludge, a polymer of the aldehyde⁽⁴⁰⁾, in hydrochloric acid (0.05 N, 1000 ml) was heated to 70° and filtered hot. Precipitation with aqueous sodium hydroxide (5N) gave small yellow crystals which were purified as above.

m.p. 77-78°; (Beard and Hodgson⁴¹; Jance⁴³, 71-72°; Critchley⁴³, 77-78°: yield, varies, (cf. 1-3) but up to 74%.

ii. 4-Aminoindophenol

Solutions of 4-aminoaniline (21.5 g, 0.2 mole) in water (500 ml), phenol (24 g, 0.255 mole) in water (1250 ml), disodium hydrogenphosphate (50 g) and sodium carbonate (35 g) in water (750 ml),

- ⁴⁰ Friedlander, 4, 136, 139.
- 41 H. G. Beard and H. H. Hodgson, J. Chem. Soc. 44 (1944).
- ⁴² L. C. Jance, Rec. Trav. Chim. 40, 286 (1921).
- ⁴³ J. P. Critchley, Private communication.

were mixed, cooled (7°) and well stirred. A paste of lead dioxide (100 g, 0.42 mole) in water was added and stirring continued for 20 min. The mixture was filtered, washed with cold water (0°), extracted with hot water (70°), the extract cooled (0°), when short blue needles were formed.

The purification of the crystals as described by Heller is unsatisfactory.

The crude product (0.25 g) was boiled in light petroleum (100 ml, 60–80°) and just enough chloroform added to dissolve almost all of the solute. Activated charcoal was added and the mixture shaken and filtered immediately. This was repeated 4 times, that is, until fine coppery blue needles were obtained on at least two successive occasions, m.p. 118–119°, (Heller,⁴⁴ 105–106°, water of crystallization?); yield, 6 g of crude. (Found: C, 73·2; H, 5·1; N, 13·8; C₁₉H₁₀N₂O₁: requires: C, 72·75; H, 5·05; N, 14·2%).

iii. 4,4'-Dihydroxytriphenylmethane carbinol (Benzaurin)

The methods quoted in the literature are unsatisfactory, (yields 0-2% with heavy contamination). The preparation below is a much modified version of that given by Illari.⁵²

A solution of phenol (37.6 g, 0.4 mole) in ether (500 ml) was stirred with a powerful downbeating motion. Aluminium trichloride (52.9 g, 0.4 mole) was added slowly and the mixture cooled, a slow current of dry air being drawn through the reaction flask. The temp was slowly raised to, and maintained at 40°, until no more hydrogen chloride was evolved (about 9 hr). Light petroleum (60-80°, 250 ml) and fresh benzaldehyde (21 g, 0.2 mole) were added dropwise to the cooled (20°) white slurry. The mixture was slowly heated to, and maintained at, 90° for a further 9 hr, when the hydrazine reaction for aldehydes was negative. The red sludge was cooled (0°) , and excess cold (0°) concentrated hydrochloric acid added with constant stirring. A brilliant orange suspension and a granular white mass were formed and separated by decantation. The suspension was filtered and washed with water and dissolved in aqueous sodium hydroxide (10%). The solution was filtered and carbon dioxide bubbled through when a red/brown solid was precipitated. Solution and reprecipitation were repeated. The precipitate was dried and extracted with chloroform. Sufficient glacial acetic acid, to prevent tar formation, was added to the chloroform extract and the chloroform was removed by distillation. The acid solution was then added dropwise to well stirred distilled water, when the benzaurin precipitated as feathery particles, was filtered off and dried, m.p. 199-200° sintering at 173°; yield, 18.5 g, 33%. (Found: C, 83.45; H, 5.15; C₁₀H₁₄O₂ requires: C, 83.4; H, 5.15%).

iv. 4-Hydroxy-y-stilbazole

The preparation of this compound has not been reported in the literature. Two methods were developed.

a. 4-Amino- γ -stilbazole (0.5 g. 0.0025 mole) was diazotized and urea added until no more nitrogen was evolved. The solution was poured with stirring into dil sulphuric acid (200 ml) and warmed (50–60°) for 30 min. The solution was neutralized with sodium carbonate, the yellow-brown precipitate filtered, dissolved in ethanol, dried and treated with activated charcoal and crystallized, to give yellow needles, m.p. 271° (0.24 g, 50%).

b. This method is a development of the preparation of 4-nitro- γ -stilbazole by Ming-Chien Chiang and Hartung.⁴⁵

4-Hydroxybenzaldehyde (2.44 g, 0.02 mole), γ -picoline (0.9 g, 0.02 mole) and acetic anhydride (2 g, 0.02 mole) were refluxed for 5 hr. The acetate produced was hydrolyzed with dil hydrochloric acid. The acid solution was neutralized with sodium carbonate and the precipitate filtered off and dried.

Crystallization from aqueous ethanol gave pale yellow needles, m.p. 271° . No depression when mixed with the product of method (a), (2.8 g, 70%). (Found: C, 78.9; H, 5.4; N, 7.3; C₁₈H₁₁N₁O₁ requires: C, 78.2; H, 5.4; N, 7.1%).

v. 2-Methoxybenzonitrile

2-Methoxyaniline (12.3 g, 0.1 mole) was diazotized, and poured into a solution of potassium cyanide (32.5 g, 0.5 mole) and nickel chloride (13.0 g, 0.1 mole) in water (200 ml). The mixture was heated (100°) until decomposition had taken place. Steam distillation formed an oil and water

44 Heller, Liebigs Ann. 344, 46.

⁴⁵ Ming-Chien Chiang and Hartung, J. Org. Chem. 10, 21 (1945).

emulsion which after salting was ether extracted. The extract was distilled under red press to give a light yellow oil, crystallization from ethanol gave small white rhomboids, m.p. 21.5–22°, (Korczynski, 4° gives an oil only) yield, 10.5 g, 80%.

vi. 4-Nitrosobiphenyl

1. 4-hydroxylaminebiphenyl. Methyl cellasolve (35 ml), water (10 ml) and ammonium chloride (1.5 g) were added with stirring to 4-nitrobiphenyl (20 g, 0.1 mole) in hot ethanol (75 ml, 60°). The mixture was refluxed gently and zinc dust (12 g, 0.18 mole) added over 20 min. After a further 5 min the mixture was filtered hot and the filtrate precipitated with water. The precipitate was dried yielding 18 g crude product.

Mijs⁴⁷ did not isolate the hydroxylamine; Brocklehurst *et al.*⁴⁸ and the authors failed to isolate the nitroso compound if the hydroxylamine was left in solution.

2. 4-nitrosobiphenyl. Aqueous chromium trioxide (2.7 g, 50 ml, 0.027 mole) was added dropwise to a suspension of 4-hydroxylaminebiphenyl (5 g, 0.027 mole) in water (100 ml, 20°). Methyl cellasolve (10 ml) was added to an etherial extract and the mixture steam distilled. (The cellasolve aids selective distillation of the nitrosobiphenyl).

The distillation was continued until the green distillate took on a yellow brown cast. The distillates of several runs were combined and the compound further steam distilled. Crystallization from ethanol and activated charcoal gave greeny gold needles, m.p. 70°, (Vorlander,⁴⁹ 84°; Mijs,⁴⁷ 74°): yield, varies, about 5%. (Found: C, 76·8, 76·89; H, 4·5, 4·6; C₁₂H₀N₁O₁ requires: C, 78·68; H, 4·97%; C₁₂H₀N₁O₂ requires: C, 75·78%). Spectra, R— Band R max in Å. ethanol 7687 ϵ , 33·75; hexane 7750 ϵ , 33·5.

These maxima were confirmed by Liversedge⁵⁰ who had lower ϵ values due to greater contamination. Mijs, λ in Å. chloroform 7500; ϵ , 46.1.

vii. Phenolindophenol (Indophenol)

Carbon dioxide was bubbled through a saturated solution of the sodium salt of phenolindophenol (ex. B.D.H. Ltd.) in an acetone-water mixture (100:1) until the colour of the solution changed from green to red. The solution was filtered and three quarters of the acetone distilled off. An equal part of light petroleum (60-80°) was added and the solution distilled until crystallization commenced. The flask was cooled very slowly. Recrystallization with activated charcoal gave red-black rhomboids, m.**p**. 160°, Lit.^{\$1}, 160°: yield, quantitative. (Found: C, 72·4, 72·5; H, 4·7, 4·86; N, 6·9, (fresh) 6·5 (after 14 days); $C_{12}H_{4}N_{1}O_{2}$ requires: C, 72·35; H, 4·55; N, 7·03 %).

As the sample became older so the m.p. fell, in addition although the maxima of the solution remained the same the intensity fell off with each solution made up. Solutions for spectra were always made up with freshly crystallized samples.

Spectroscopic analysis shows that the compound is also formed in solution by the reduction of indophenol N-oxide in sodium ethoxide.

Acknowledgements—The authors wish to thank Professors H. N. Rydon and R. N. Haszeldine for the facilities provided in the College and the laboratory staff for their unfailing assistance.

A special tribute is due to the late Dr. A. Burawoy who supervised this work, in which he was actively engaged before his sudden and untimely death.

⁴⁶ A. Korczynski and B. Frandrich, C. R. Acad. Sci. Paris 183, 421 (1926).

- 47 W. J. Mijs et al. Rec. Trav. Chim. 77, 750 (1958).
- ⁴⁸ P. Brocklehurst, F. Liversedge and J. P. Critchley. Private communication.
- 49 D. Vorlander, Ber. Disch. Chem. Ges. 58, 1893 (1925).
- ⁵⁰ F. Liversedge, Private communication.
- ⁵¹ Chem. Zentr. 2, 315 (1905).
- 52 G. Illari, Gazz. Chim. 77, 597 (1947).