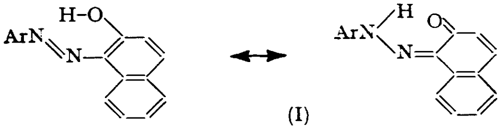
The Nature of the Internal Hydrogen Bond. Part III. Tautomeric Equilibria of 2-Nitrosophenols.*

By A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge,
and A. R. Thompson.

[Reprint Order No. 6385.]

The electronic spectra of 2-nitrosophenol, 5-methoxy-2-nitrosophenol, and 5-dimethylamino-2-nitrosophenol in various solvents are determined and compared with those of the corresponding 2-nitrosoanisoles and 6-methoxyimino*cyclo*hexa-2 : 4-dienones. It is shown that these compounds contain an internal hydrogen bond and that, in spite of it, the methoxy- and dimethylamino-derivatives exist as solvent-dependent tautomeric equilibria. This confirms that an internal hydrogen bond cannot be interpreted as a non-localised bond, such as in (I) or (II). In all solvents, the parent compound is observed only as the true 2-nitrosophenol tautomer. The participation of the nitroso-group in an internal hydrogen bond is responsible for a strong displacement of the *R*-band to shorter wavelengths (800—1200 Å).

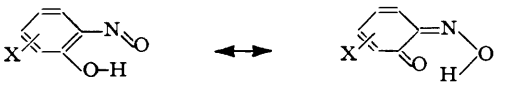
An investigation of the electronic spectra of 1-phenylazo-2-naphthol and its derivatives in various solvents has established that these compounds exist as solvent-dependent tautomeric equilibria (Burawoy, Salem, and Thompson, *Chem. and Ind.*, 1952, 668; Part I *; Burawoy and Thompson, *J.*, 1953, 1443). This is conclusive evidence that an internal hydrogen bond, as present in both tautomers of these compounds, cannot be interpreted as a non-localised bond, *e.g.*, as a resonance hybrid such as (I).

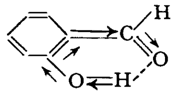

(I)

Simultaneously, we have carried out an examination of the electronic spectra of 2-nitrosophenol, 5-methoxy-2-nitrosophenol, and 5-dimethylamino-2-nitrosophenol in various solvents, in order to ascertain whether these compounds exist as true nitroso-compounds, as *o*-benzoquinone monoximes, as tautomeric equilibria, or as resonance hybrids such as (II).

The ability of 2-nitrosophenols to form stable complex salts, which have application in inorganic analysis and as colouring matters, already indicates that they contain an internal hydrogen bond, but an additional aim of this investigation has been to obtain direct spectroscopic evidence for its presence and, possibly, to obtain information of the effect of this bond on the *R*-band (of the nitroso-group).

It has already been shown (Morton and Stubbs, *J.*, 1940, 1347; Burawoy and Chamberlain, *J.*, 1952, 2310, 3734) that an internal hydrogen bond displaces the *B*- and the *K*-bands


(II)


(III)

of phenols to longer wavelengths, undoubtedly because the polarity of the absorbing system (in the ground state) is increased by polarisation (cf. III). Thus, these bands in the spectra in hexane of 4-hydroxydiphenyl, 2-hydroxydiphenyl, 3-methoxybenzaldehyde, and 4-hydroxyazobenzene appear at slightly shorter wavelengths than in the spectra of the corresponding methyl ethers, whereas those of salicylaldehyde, which

---

* Parts I and II, *J.*, 1952, 4793; preceding paper.

contains an internal hydrogen bond, are observed (in hexane) at longer wavelengths than the corresponding bands of 2-methoxybenzaldehyde (for data see Table 1). This is also true for 2-hydroxy-5-methylazobenzene and 2-nitrophenol, but in these examples the blue-shift of the *B*- and *K*-bands of the corresponding methyl ethers is considerably greater, being enhanced by the intramolecular steric interaction between the methoxy-group and the azo- and nitro-group, respectively.

An additional and, for the following discussion, important criterion for the presence of an internal hydrogen bond is the characteristic effect of solvents. The *B*- and *K*-bands of the former phenols are displaced to longer wavelengths approximately as the dielectric constant of the solvent increases. This is shown in Table 1 for hexane and ethanolic solutions and is due mainly to the increasing polarity of the absorbing system resulting partly from the dielectric effect of the solvent and partly from the formation of a true (stoicheiometric) external hydrogen bond in ethanol. On the other hand, the bands of salicylaldehyde, 2-hydroxy-5-methylazobenzene, and 2-nitrophenol are almost unchanged, partly because the formation of an external hydrogen bond with the solvent is inhibited. Some of these bands in ethanol are even displaced to slightly shorter wavelengths, indicating the contribution of an additional factor probably arising from a weakening of the internal hydrogen bond in solvents of higher dielectric constant.

TABLE 1. B- *and* K-*Bands of phenols and their methyl ethers.**

	Phenol								Methyl ether			
	In hexane				In ethanol				In hexane			
	B-Band		*K*-Band		*B*-Band		*K*-Band		*B*-Band		*K*-Band	
	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
1 : 4-$C_6H_5·C_6H_4·OH$	—	—	2558	25,000	—	—	2612	22,500	—	—	2596	27,000
1 : 2-$C_6H_5·C_6H_4·OH$	2825	5750	2442	12,500	2880	5500	2470	13,500	2835	6200	2460	15,500
1 : 3-$HO·C_6H_4·CHO$	3050	2700	2480	12,000	3155	3000	2537	9500	3050	3000	2488	10,000
1 : 4-$C_6H_5·N{:}N·C_6H_4·OH$	—	—	3365	28,500	—	—	3510	29,000	—	—	3380	24,700
1 : 2-$HO·C_6H_4·CHO$	3285	3230	2550	10,000	3250	3000	2550	10,000	3100	5620	2465	12,000
1 : 5 : 2-$C_6H_5·N{:}N·C_6H_3Me·OH$	3935	9800	3230	25,000	3935	9600	3235	25,000	3590	9000	3090	13,500
1 : 2-$HO·C_6H_4·NO_2$	3460	3900	2710	7600	3435	3600	2730	6600	3172†	2850	2585	3450

* Cf. Burawoy and Chamberlain, *loc. cit.* † In ethanol.

No investigation of the effect of an internal hydrogen bond on *R*-bands has been reported. These bands, in contrast to *B*- and *K*-bands, are known to be displaced to *shorter* wavelengths by influences (substituents, solvents, proton addition) increasing the polarity of the chromophoric double bonds (for references, cf. Part II, *loc. cit.*). It would, therefore, be expected that the participation of the groups in an internal hydrogen bond would show a similar effect.

TABLE 2. *Spectra of* 2-*nitrosophenol.*

	R-Band			*B*-Band			*K*-Band *	
Solvent	$\lambda_{max.}$	ε	*D* †	$\lambda_{max.}$	ε	*D* †	$\lambda_{max.}$	ε
C_6H_{14}	6975	47	—	3950	2000	—	2995	8200
CCl_4	6975	65	−795	4000	2600	+310	3000	10,900
Et_2O	7025	44	−745	3910	2650	+195	3020	8900
C_6H_6	6975	60	−785	4025	2200	+270	3060	8700
$CHCl_3$	6850	55	−810	4060	2250	+260	3060	10,900
EtOH	7150	53	−460	3890	3400	+120	3040	7800
H_2O	6730	31	—	3990	2300	+80	3080	6300

* Owing to fine structure of the *K*-band of 2-nitrosoanisole, no accurate values of *D*(Me ⟶ H) can be given.

† *D* refers to *D*(Me ⟶ H) in all cases, measured in Å.

2-*Nitrosophenol.*—Data for the spectra of 2-nitrosophenol in various solvents and the displacements [*D*(Me ⟶ H)] of the *R*- and *B*-bands as compared with the corresponding bands of 2-nitrosoanisole are shown in Table 2. The spectra in hexane and ethanol together with those of 2-nitrosoanisole and 6-methoxyimino*cyclo*hexa-2 : 4-dienone in ethanol are reproduced in Fig. 1. In all solvents, 2-nitrosophenol exhibits the characteristic *R*-band of the nitroso-group (λ 6730—7150 Å; ε 31—65), thus establishing the presence of this compound in solution as a true nitroso-compound. The *R*-band is observed in all solvents at considerably shorter wavelengths than that of 2-nitrosoanisole (λ 7440—7770 Å; ε 23—54) and, in contrast to the normal effect of solvents as, *e.g.*, shown by 2-nitrosoanisole (cf. Part II), appears at the longest wavelength in ethanol. These facts afford experimental evidence for the presence of an internal hydrogen bond in 2-nitrosophenol and show that this bond is responsible for a considerable blue-shift of the *R*-band (700—800 Å) which is comparable with the opposite one observed for *B*- and *K*-bands, *e.g.*, of salicylaldehyde (cf. Table 1) and of 2-nitrosophenol itself (cf. Table 2).

As shown in Part II, the ultraviolet spectra of 2-nitrosoanisole and 6-methoxyimino*cyclo*hexa-2 : 4-dienone (consisting of *B*- and *K*-bands) are surprisingly similar, but, fortunately, the *K*-band system of the methoxyimino-compound is displaced by approximately 200 Å to longer wavelengths. The *K*-band of 2-nitrosophenol, which in contrast to that of the ethers consists of only one peak of greater intensity, has in all solvents an intermediate position (cf. *e.g.*, Fig. 1 for the spectra in ethanol). Since the methylation of a hydroxy-group participating in an internal hydrogen bond displaces a *K*-band to shorter wavelengths, this band must be attributed to the true nitrosophenol tautomer. The presence of an internal hydrogen bond is supported by the red-shift of the *B*-band in all solvents (λ 80—310 Å) as compared with the *B*-band of 2-nitrosoanisole (as well as of the methoxyimino*cyclo*hexadienone) and by the characteristic blue-shift of its maximum in ethanol (and water). The electronic spectra show that 2-nitrosophenol exists in solution as the true nitrosophenol tautomer, although they cannot exclude the presence of small, but undetectable, amounts of the oxime tautomer.

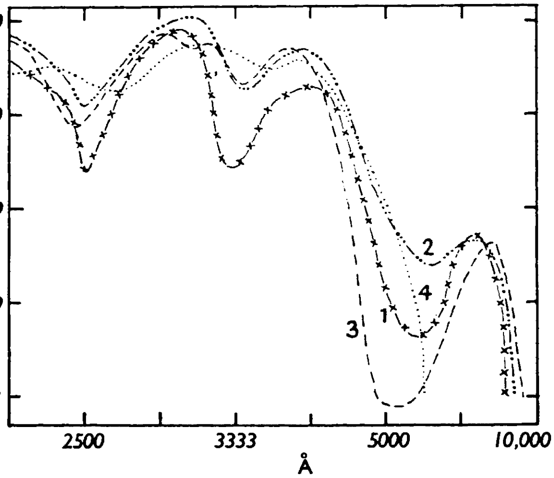
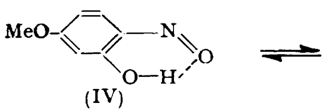


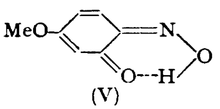
FIG. 1.

1, *2-Nitrosophenol in hexane.*
2, *2-Nitrosophenol in ethanol.*
3, *2-Nitrosoanisole in ethanol.*
4, *6-Methoxyimino*cyclo*hexa-2:4-dienone in ethanol.*

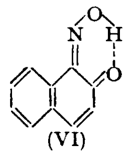
5-Methoxy-2-nitrosophenol.—Henrich and Eisenach (*J. prakt. Chem.*, 1904, **70**, 332) have shown that 5-methoxy-2-nitrosophenol crystallises from benzene as green dichroic prisms and from ethanol as yellowish-brown prisms. The former changed into the brown form below the melting point. They suggested that these two forms represent the 2-nitrosophenol and *o*-quinone oxime tautomers (IV and V), respectively. We have confirmed these observations and found that in solution both forms give an identical spectrum.



(IV)



(V)



(VI)

Powder photographs of the solid forms taken by Dr. G. W. R. Bartindale reveal very different X-ray patterns. Data of the spectra in various solvents are collected in Table 3, and a few diagrams are reproduced with those of 2 : 4-dimethoxy-1-nitrosobenzene and 3-methoxy-6-methoxyiminocyclohexa-2 : 4-dienone in ethanol in Figs. 2 and 3.

The spectra of 5-methoxy-2-nitrosophenol exhibit in all solvents the characteristic R-band of the nitroso-group (λ 6100—6460; ε 10—35), but it always appears at appreciably shorter wavelengths and is much less intense than that of 2 : 4-methoxy-1-nitrosobenzene (λ 6990—7525; ε 48—59). This shows that 5-methoxy-2-nitrosophenol contains an internal hydrogen bond and suggests that it is only partly present as the nitrosophenol tautomer (IV), the concentration of which is smaller in ethanol and water than in ether, benzene, and chloroform.

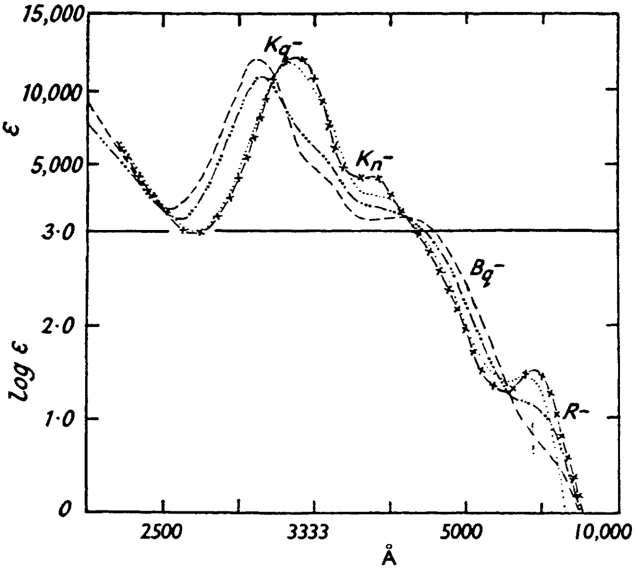


FIG. 2. *5-Methoxy-2-nitrosophenol in*
— × — × — *ethyl ether.*
. . . . *chloroform.*
—. . . —. . . — *ethanol.*
— — — — — — *water.*

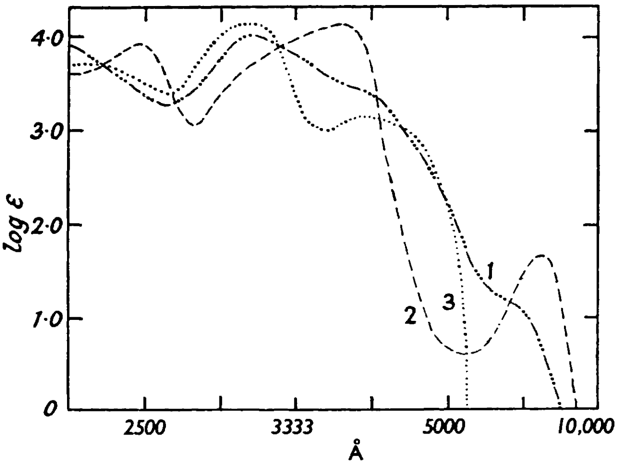


FIG. 3.
1, *5-Methoxy-2-nitrosophenol.*
2, 2 : *4-Dimethoxy-1-nitrosobenzene.*
3, *6-Methoxyiminocyclohexa-2 : 4-dienone. In ethanol.*

This interpretation is supported by the appearance of a band or inflexion at about 3750 Å (ε <4400) which can only correspond to the K-band appearing in 2 : 4-dimethoxy-1-nitrosobenzene at slightly shorter wavelengths (λ 3600—3740 Å; ε 11,000—12,000), *i.e.*, it is due to the K-band of the nitrosophenol tautomer (K_n). Again, its intensity in all solvents is appreciably lower than that of the anisole and decreases approximately in the same order of solvents as does the R-band due to the nitroso-group.

This band (or inflexion) cannot be due to the B-band of the 4-methoxy-*o*-quinone 1-oxime tautomer (B_q). The latter would be expected to be at longer wavelengths and of lower intensity than that of the methoxyimino-compound (λ 3760—4110 Å; ε <2000), just as the B-bands of salicylaldehyde and 2-nitrosophenol lie at longer wavelengths and are less intense than those of their methyl ethers (cf. Table 1 and Fig. 1, respectively). It is, indeed, observed as an inflexion superposed on the red slope of the K_n-band at about 3750 Å, its intensity increasing from ether to water, *i.e.*, in the opposite order of solvents. This results in a broad absorption region at 4000 Å in water which is due to the superposition of both the K_n- and B_q-bands (cf. Fig. 2).

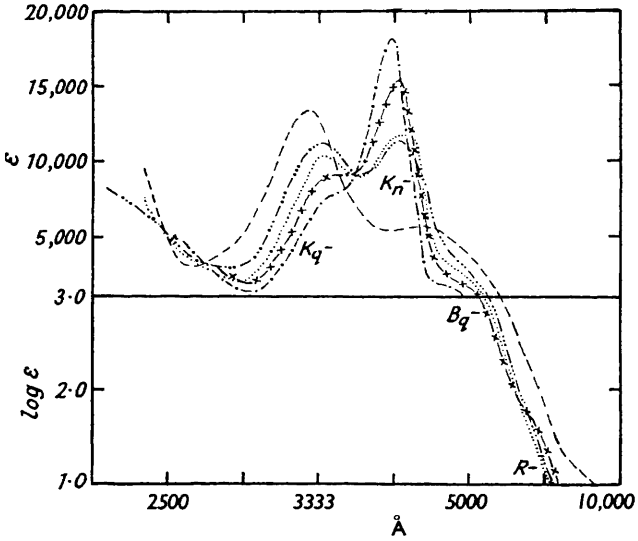


FIG. 4.
5-Dimethylamino-2-nitrosophenol in
— · — · — · — *carbon tetrachloride.*
· · · · · · · · · · · · *chloroform.*
— — — — — — *water.*
— × — × — *benzene.*
— · · · — · · · — *ethanol.*

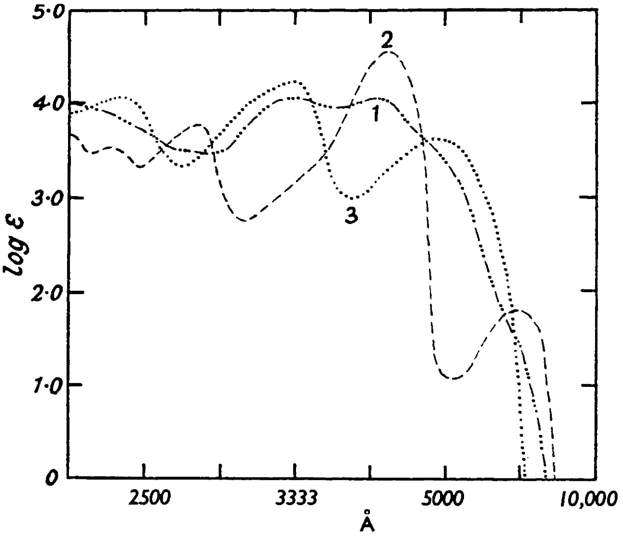


FIG. 5.
1, *5-Dimethylamino-2-nitrosophenol.*
2, *5-Dimethylamino-2-nitrosoanisole.*
3, *3-Dimethylamino-6-methoxyimino-*cyclo*hexa-2 : 4-dienone.* In ethanol.

The presence of the *o*-quinone oxime tautomer is unambiguously confirmed by the appearance in all solvents of its expected K-band (K_q) in the region 2960—3230 Å (ε 11,000—12,300) which corresponds to the K-band of the 3-methoxy-6-methoxyimino*cyclo*hexadienone at 2940—3060 Å (ε 12,200—16,600). An internal hydrogen bond is indicated by the appreciable red-shift in non-hydroxylic solvents as compared with the methyl ether and by the characteristic blue-shift approximately following the order of increasing dielectric constant of the solvent (cf. Table 3).

TABLE 3. *Spectra of* 5-*methoxy*-2-*nitrosophenol.*

	R-Band			K_n-Band			K_q-Band		
Solvent	$\lambda_{max.}$	ε	*D* *	$\lambda_{max.}$	ε	*D* *	$\lambda_{max.}$	ε	*D* *
CCl_4	—	—	—	3750	4000	+145	3225	12,300	+240
Et_2O	6460	32	−1065	3740	4400	+130	3225	11,900	+285
C_6H_6	6430	35	−1045	3750 †	3800	+ 90	3230	11,600	+220
$CHCl_3$ ...	6220	29	−1140	3750 †	3500	+ 40	3175	12,100	+165
EtOH ...	6140	15	−1110	3700 †	3050	+ 10	2990	11,000	− 20
H_2O	6100 ‡	10	− 890	4000 §	2050	—	2960	12,000	−100

* *D* refers to *D*(Me ⟶ H), measured in Å. † Inflexion. ‡ Ethanol–water (1 : 1).
§ Broad band resulting from superposition of K_n- and B_q-bands, the latter appearing as a steep inflexion also in the spectra of the other solutions.

The latter displacements (240 Å from benzene to ethanol) are greater than those observed for the *B*- and/or *K*-bands of salicylaldehyde, 2-nitrophenol, and 2-nitrosophenol (cf. Tables 1 and 2). This appears to be characteristic of the *o*-quinone oxime system, since it is also observed in the spectra of 1-nitroso-2-naphthol which exists in all solvents as 1 : 2-naphthaquinone 1-oxime (VI), the *R*-band due to the nitroso-group being absent in the visible spectral region. The spectra of 1-nitroso-2-naphthol show a high-intensity band at 2630—2800 Å (ε 10,800—13,500) and a band of lower intensity (ε 5000—6000) at longer wavelengths (3725—3820 Å) which should be comparable with the *K*- and *B*-bands, respectively, of the benzenoid *o*-benzoquinone oximes (cf. Table 4). The *K*-band in ethanol is displaced by 110 and 170 Å to shorter wavelengths as compared with that in hexane and benzene, respectively.

TABLE 4. *Spectra of* 1 : 2-*naphthaquinone* 1-*oxime.*

		C_6H_{14}	Et_2O	CCl_4	C_6H_6	$CHCl_3$	EtOH
B-Band	$\lambda_{max.}$, Å	3750	3740	3775	3790	3820	3725
	ε	5700	5700	6000	5700	5800	5000
K-Band	$\lambda_{max.}$, Å	2740	2735	2755	2800	2745	2630
	ε	12,400	10,800	12,600	12,000	13,500	12,200

We have considered the possibility that the hypsochromic displacement of the *B*- and *K*-bands of phenols containing an internal hydrogen bond in solvents such as ethanol and water might be due to a partial replacement of this bond by an external hydrogen bond with the solvent, but this view cannot easily be reconciled with the observation that the *K*-band of 4-methoxy-*o*-quinone 1-oxime in water and ethanol appears at even shorter wavelengths than that of its methyl ether, 3-methoxy-6-methoxyimino*cyclo*hexadienone. This matter requires further elucidation.

The spectra of 5-methoxy-2-nitrosophenol show the existence of a tautomeric equilibrium in all solvents and the presence of an internal hydrogen bond in both tautomers. The complexity of the spectra due to the considerable overlap of the absorbing systems of the tautomers in the middle region does not allow a more quantitative analysis. An *X*-ray analysis of the solid forms is at present being carried out by Dr. G. W. R. Bartindale.

5-Dimethylamino-2-nitrosophenol.—As shown in Part II, 5-dimethylamino-2-nitrosoanisole in various solvents exhibits the *R*-band of the nitroso-group (λ 5450—7340 Å; ε 60—80) and a *K*-band (λ 4000—4210 Å; ε 28,000—35,000), whereas 3-dimethylamino-6-methoxyimino*cyclo*hexadienone exhibits a *B*-band (λ 4700—4900 Å; ε 2600—5000) and a *K*-band (λ 3200—3300 Å; ε 14,000—19,000). The spectra of 5-dimethylamino-2-nitrosophenol in all solvents show the presence of each of the four band systems, confirming its existence as a tautomeric equilibrium (VII $\rightleftharpoons$ VIII). Data of spectra in various solvents are collected in Table 5. A few spectra are shown together with those of the two methyl ethers in ethanol in Figs. 4 and 5.

The *K*-bands (or inflexions) of the 2-nitrosophenol tautomer (VII) and the *o*-benzoquinone oxime tautomer (VIII) are observed at 3960—4100 Å (ε 5600—18,500) and at

TABLE 5. *Spectra of* 5-*dimethylamino*-2-*nitrosophenol.*

Solvent	B_q-Band *	K_n-Band			K_q-Band		
	ε 5000 Å	$\lambda_{max.}$	ε	D †	$\lambda_{max.}$	ε	D †
CCl_4	780	3960	18,500	− 55	3400 *	7500	+185
Et_2O	1130	4000	17,300	− 0	3400 *	9200	+175
C_6H_6	1450	4035	15,400	− 35	3475	9000	+240
$CHCl_3$	1920	4080	11,800	−100	3360	10,300	+ 85
EtOH	2230	4040	11,400	−170	3340	11·100	+ 50
H_2O	3390	4225 ‡	5600	—	3245	13,400	− 65

* Inflexion. † D refers to $D(Me \longrightarrow H)$, measured in Å.
‡ Broad band resulting from superposition by B_q-band.

3245—3475 Å (ε 7500—13,400), respectively. The intensity of the former decreases and that of the latter increases in the solvent order: carbon tetrachloride, ether, benzene, chloroform, ethanol, and water. Little importance can be attached to the small displacements of the maxima as compared with those of the corresponding methyl ethers owing to the considerable overlap of these band systems.

(VII)

(VIII)

The B_q-band corresponding to that of the 3-dimethylamino-6-methoxyimino*cyclo*hexa-2 : 4-dienone appears as an inflexion overlapping the red slope of the K_n-band. In aqueous solution, a very broad band at 4225 Å (ε 5600) is observed. Its considerable width is due to superposition of the B_q-band on the K_n-band, which in this solvent reach the highest and lowest intensity, respectively. In agreement with this interpretation, in all other solvents this broad band divides into its components, the K_n-band at 3960—4100 Å and an inflexion at about 5000 Å corresponding to the B_q-band (cf. Fig. 4). The intensity of the former band increases and that of the latter (similar to the K_q-band) decreases in the solvent order: water, alcohol, chloroform, benzene, ether, and carbon tetrachloride.

As already shown, owing to the presence of an internal hydrogen bond, the R-bands of 2-nitrosophenol and its 5-methoxy-derivative are displaced by approximately 800 and 1050 Å, respectively, to shorter wavelengths, compared with those of their methyl ethers. A similar or slightly greater shift could, therefore, be expected for the R-band of the 5-dimethylamino-2-nitrosophenol tautomer which would place the maximum in the region of 6000—6200 Å. This is indeed the case, but owing to the overlap with the more intense B_q-band in this region it is observed only as an inflexion which is particularly well defined in ether, benzene, and carbon tetrachloride.

The existence of 5-methoxy- and 5-dimethylamino-2-nitrosophenol as solvent-dependent equilibria between the corresponding nitrosophenol and quinone oxime tautomers, both tautomers containing an internal hydrogen bond, confirms that this bond is of an essentially electrostatic nature and cannot be interpreted as a non-localised bond.

EXPERIMENTAL

Spectra were determined with a Hilger Uvispek Photoelectric Spectrophotometer. The concentrations used varied between 0·005 and 0·03M for the R-bands and 0·0002 and 0·0005M for the B- and K-bands. In view of the difficulty of isolating the very volatile 2-nitrosophenol (cf. Baudisch, *Ber.*, 1912, **45**, 1164; 1915, **48**, 1660), its solutions were prepared by adding potassium hydrogen sulphate and a very small drop of distilled water to suspensions or solutions respectively of its sodium salt (cf. Part II), shaking the mixture for a few minutes, and filtering it (except for the aqueous solution). The reported spectra of 5-methoxy-2-nitrosophenol in ethanol and water have been determined in the presence of a small amount of sulphuric acid (to inhibit dissociation), although the effect has been found to be negligible.

COLLEGE OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, May 4th*, 1955.]