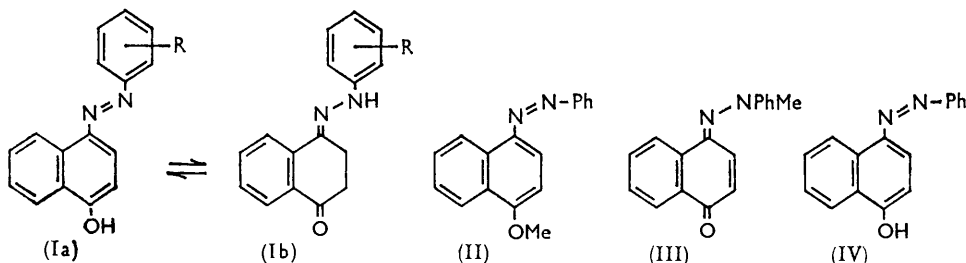


409. Infrared Spectra and Structure of Arylazonaphthols.

By K. J. MORGAN.

Infrared spectra show the presence of an azo-hydrazone tautomerism (*e.g.*, Ia \rightleftharpoons Ib) both in the solid and in solutions of 1-aryldazo-2-naphthols and 4-aryldazo-1-naphthols. The position of equilibrium moves towards the hydrazone in polar solvents and under the influence of electron-withdrawing substituents in the aryl group.

THE structure of the compounds formed by condensation of diazonium salts with phenols has provoked many investigations. Chemical evidence¹ has been used to support the formulation of the products as hydroxyazo-compounds (*e.g.*, Ia) and as hydrazones (*e.g.*, Ib). More valid evidence is provided by physical properties, notably of their electronic spectra. Strong presumptive evidence for the presence of tautomerism in the hydroxyazo-compounds was first provided by Kuhn and Bär.² The ultraviolet spectrum of 4-phenylazo-1-naphthol* (I; R = H) shows bands at 410 and 460 m μ which correspond in position to bands found in the *O*-methyl (II) and *N*-methyl derivative (III), respectively. The relative intensity of the bands in the spectrum of the parent compound changes with solvent, and in the more polar solvents (acetic acid, nitrobenzene) only the longer-wavelength band is seen. Similar effects have been detected in the ultraviolet spectra of substituted 4-phenylazo-1-naphthols.^{3,4} 1-Phenylazo-2-naphthol and the isomeric 2-phenylazo-1-naphthol show analogous effects.⁵



The existence of an equilibrium in the solutions of the azonaphthols is clearly demonstrated⁵ by the formation of an isosbestic point by the spectral curves measured in a variety of solvents. Kuhn and Bär² suggested that this equilibrium was that of a keto-enol tautomerism (Ia \rightleftharpoons Ib) and subsequent work³⁻⁸ has supported this conclusion. Despite the loss of a fully aromatic ring in the hydrazone, the total bond energies of the

* The designation "arylazonaphthol" is used throughout this paper for convenience; it is not intended to define the structure of the compound.

¹ See, *e.g.*, (a) McPherson, *Amer. Chem. J.*, 1899, **22**, 364; (b) Fierz-David, Blangey, and Streiff, *Helv. Chim. Acta*, 1946, **29**, 1718.

² Kuhn and Bär, *Annalen*, 1935, **516**, 143.

³ Burawoy and Thompson, *J.*, 1953, 1443.

⁴ Shingu, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 1938, **35**, 78.

⁵ Burawoy, Salem, and Thompson, *J.*, 1952, 4793.

⁶ Ospenson, *Acta Chem. Scand.*, 1951, **5**, 491.

⁷ Savicki, *J. Org. Chem.*, 1957, **22**, 743.

⁸ Badger and Buttery, *J.*, 1956, 614.

two forms are comparable⁶ and from recent results⁹ it follows that the hydrazone (Ib; R = H) cannot be destabilised relative to the azo-form by more than 2 kcal./mole. It has recently^{9,10} been shown that the existence of *cis*-4-phenylazo-1-naphthol (IV) is too transient at room temperatures to permit any possibility that the tautomerism involves a *cis*-*trans*-conversion about the azo-link. No evidence for a tautomeric equilibrium is found in the spectra of hydroxyazobenzenes or hydroxyazoanthracenes: the former behave spectrally as phenolic compounds,¹¹ the latter as hydrazones.^{4,6}

Investigation of the infrared spectra of hydroxyazo-compounds, which can in principle provide direct evidence of the structure, has been restricted to some isolated spectra¹²⁻¹⁵ and to a more detailed examination of the phenylazonaphthols as solids.¹⁶ A more complete examination of the infrared spectra appeared desirable; accordingly, spectra of 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols substituted in the phenyl ring have been measured.

EXPERIMENTAL

Azo compounds were prepared by the usual diazo-coupling reactions with α - and β -naphthols and were purified chromatographically and by crystallisation to constant m. p. The following m. p. were observed: 4-arylozo-1-naphthols (I), R = H, 208°; *o*-MeO, 177—178°; *m*-MeO, 159°; *p*-MeO, 173°; *o*-Me, 162—163°; *m*-Me, 200°; *p*-Me, 211.5°; *o*-Cl, 189.5—190.5°; *m*-Cl, 227.5—228° (decomp.); *p*-Cl, 229.5° (decomp.); *o*-NO₂, 256—257°; *m*-NO₂, 242—242.5° (decomp.); *p*-NO₂, 281—282° (decomp.); 1-arylozo-2-naphthols (VII), R = H, 133—134°; *o*-MeO, 187—188°; *m*-MeO, 149°; *p*-MeO, 142°; *o*-Me, 132—133°; *m*-Me, 141—142°; *p*-Me, 133—134°; *o*-Cl, 171—173°; *m*-Cl, 164—165°; *p*-Cl, 165—166°; *o*-NO₂, 217—219°; *m*-NO₂, 197—198°; *p*-NO₂, 259—260°. These values agree with those in the literature.

1-Methoxy-4-phenylazonaphthalene, m. p. 80°, was prepared by methylation of the naphthol;¹⁷ 1,4-naphthaquinone methylphenylhydrazone, m. p. 121—122°, was prepared from the quinone with methylphenylhydrazine.¹

Spectra of the solids were obtained from mulls with Nujol and Fluorolube and from discs with potassium bromide; no significant differences could be detected between the spectra of the mulls and of the discs. Spectra of solutions were determined at sufficient dilution (0.005—0.007M) to be free from intermolecular hydrogen-bonding.¹⁸ The low solubility of some compounds, notably the derivatives of α -naphthol, entailed the use of lower concentrations, and several compounds proved insufficiently soluble in the less polar solvents to yield useful spectra. Bromoform containing 4% (w/w) ethanol was used; other solvents were of "Spectro" grade.

Spectra were measured with a Perkin-Elmer Model 21 spectrophotometer equipped with rock-salt optics.

RESULTS AND DISCUSSION

The infrared spectra of the tautomeric forms of the hydroxyazo-compounds should show significant differences.¹⁹ Bands characteristic of the hydroxyl and azo-groupings should appear in the spectrum of the azo-form and be replaced by amino- and carbonyl bands in the spectrum of the hydrazone. Changes in the position of the tautomeric equilibrium should be accompanied by changes in the intensity of these bands. Some characteristic hydroxy-, amino-, and carbonyl-band frequencies and apparent extinction coefficients are given in the accompanying Tables. [The extinction coefficient, ϵ_{ν}^{α} , is defined by $\epsilon_{\nu}^{\alpha} = (1/cl) (\log T_0/T)_{\nu}$, and is not corrected for the use of finite slit widths.]

⁹ Fischer and Frei, *J.*, 1959, 3159.

¹⁰ Brode, Gould, and Wyman, *J. Amer. Chem. Soc.*, 1952, **74**, 4641; 1953, **75**, 1856.

¹¹ Burawoy and Chamberlain, *J.*, 1952, 3734.

¹² Druckrey, Schmähl, and Dannenberg, *Naturwiss.*, 1952, **39**, 393.

¹³ Le Fèvre, O'Dwyer, and Werner, *Austral. J. Chem.*, 1953, **6**, 341.

¹⁴ Kendall, *Analyt. Chem.*, 1953, **25**, 382.

¹⁵ Dolinsky and Jones, *J. Assoc. Offic. Agric. Chemists*, 1954, **37**, 197.

¹⁶ Hadži, *J.*, 1956, 2143.

¹⁷ Charrier and Casale, *Gazzetta*, 1914, **44**, 228.

¹⁸ Putnam, *J.*, 1960, 487.

¹⁹ Cf. Tanner, *Spectrochim. Acta*, 1959, **15**, 20.

The apparent half band width ($\Delta\nu_{1/2}$) (width at half-peak absorbance) of all the bands listed increases with the polarity of the solvent. In these circumstances the extinction coefficient provides a poor estimate of the intensity of the absorption, and in the present case the triangular area, $t = 10^{-3}\epsilon^{\alpha} \cdot \Delta\nu_{1/2}^{\alpha}$, is a more useful, if approximate, measure of the band intensity as it takes account of the variation in band width; values of t are listed in the Tables. Similar expressions have been proposed²⁰ for the calculation of true band intensities.

An attempt was made to locate in the spectra characteristic bands other than those listed in the Tables; this was to some extent hampered by the opacity of the solvents over much of the spectral range. Typical aromatic bands and C-H deformation bands characteristic of the various substitution patterns were observed.²¹ Hadži¹⁶ assigned bands near 1250 and 1540 cm^{-1} in the spectra of the phenylazonaphthols to in-plane

TABLE I. *Hydroxyl and amino-stretching bands in the spectra of 4-arylazo-1-naphthols.*

Substituent R in (I) H	Amino (N-H) bands						Hydroxyl (O-H) bands				
	Solid	C ₆ H ₁₂	C ₂ Cl ₄	CCl ₄	CH ₂ Cl ₂	CHCl ₃	C ₆ H ₁₂	C ₂ Cl ₄	CCl ₄	CH ₂ Cl ₂	CHCl ₃
	3140	—	—	—	3360	3360	—	—	—	3580	3570
	3260	—	—	—	40	45	—	—	—	90	70
<i>t</i>										3.2	—
<i>o</i> -MeO	3320	3380	3370	3370	3350	3340	0	0	0	0	0
		75	95	110	130	130					
<i>t</i>		1.8	2.4	2.7	4.0	4.2					
<i>m</i> -MeO	3130	—	—	—	3350	3350	—	—	—	3560	3560
	3250	—	—	—	55	55	—	—	—	60	45
<i>t</i>					2.3	—				2.6	—
<i>p</i> -MeO	3130	—	—	—	3340	3340	—	—	—	3575	3570
	3250	—	—	—	30	35	—	—	—	105	105
<i>t</i>					—	—				5.8	—
<i>o</i> -Me	3300	0	0	3380	3360	3360	3610	3610	3600	3570	3570
	3240	—	—	30	40	40	145	110	108	70	65
<i>t</i>				0.7	—	—	3.6	3.3	3.2	3.1	—
<i>m</i> -Me	3140	—	—	—	3340	3340	—	—	—	3580	3575
	3250	—	—	—	40	45	—	—	—	80	60
<i>t</i>					1.4	—				3.2	—
<i>p</i> -Me	3140	—	—	—	3350	3350	—	—	—	3580	3570
	3270	—	—	—	40	40	—	—	—	85	70
<i>t</i>					1.6	—				3.2	—
<i>o</i> -Cl	3340	3370	3370	3370	3350	3340	0	0	0	0	0
		55	105	105	75	70					
<i>t</i>		1.4	2.1	2.1	2.6	2.8					
<i>m</i> -Cl	3280	—	—	—	3350	3340	—	—	—	3580	3570
					50	55	—	—	—	60	25
<i>t</i>					2.3	—				1.5	—
<i>p</i> -Cl	3220	—	—	—	—	—	—	—	—	—	—
	3170	—	—	—	—	—	—	—	—	—	—
<i>o</i> -NO ₂	3320	—	3330	—	3320	3300	—	0	—	0	0
			120	—	115	90					
<i>t</i>			3.0	—	3.4	3.4					
<i>m</i> -NO ₂	3280	—	—	—	—	3330	—	—	—	—	0
						75					
<i>t</i>						—					
<i>p</i> -NO ₂	3280	—	—	—	—	—	—	—	—	—	—

bending modes of the hydroxyl and amino-group; similar bands were detected but proved of little diagnostic value. A band near 1450 cm^{-1} in the spectrum of many azo-compounds has been assigned^{13,22} to the $-\text{N}=\text{N}-$ stretching frequency; comparison of the spectra of the *N*-methyl (III) and *O*-methyl (II) compounds showed that the latter contained a very

²⁰ Fox and Martin, *Proc. Roy. Soc.*, 1938, *A*, **167**, 257; Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

²¹ Randle and Whiffen, "Molecular Spectroscopy," Institute of Petroleum, 1954, p. 111; Hawkins, Ward, and Whiffen, *Spectrochim. Acta*, 1957, **10**, 105.

²² Le Fèvre, Sousa, and Werner, *Austral. J. Chem.*, 1956, **9**, 151; Le Fèvre and Werner, *ibid.*, 1957, **10**, 26.

weak band at 1445 cm^{-1} not found in the former. Similar bands occur in the spectra of the *p*-hydroxyazobenzene and of many of the arylazonaphthols; in all cases they are weak and no significant changes in intensity could be detected.

4-Arylazo-1-naphthols.—The infrared spectrum of solid 4-phenylazo-1-naphthol shows bands in the single-bond stretching region at 3140 and 3260 cm^{-1} . In spectra of solutions these are replaced by bands near 3360 and 3580 cm^{-1} which may best be ascribed to N-H and O-H stretching frequencies.²³ Similar bands are found in the spectra of a number of substituted derivatives (Table 1) and establish the presence of a tautomeric mixture both in solution and in the solid. The intensity of the bands varies both with solvent and with the substituent carried by the phenyl group. In general the intensity of the amino-band increases and that of the hydroxyl band decreases as the polarity of the solvent is increased. Further, the presence of electron-withdrawing groups on the phenyl ring increases the intensity of the amino-band at the expense of the hydroxyl band. This effect will be discussed in more detail below.

The spectrum of solid 4-phenylazo-1-naphthol shows only one band near the carbonyl stretching region, at 1625 cm^{-1} . This frequency is low: benzophenone and anthrone²⁴ absorb at 1650 cm^{-1} , and 1,4-naphthaquinone at 1664 cm^{-1} . However, the carbonyl band in the spectrum of the *N*-methyl derivative (III) appears at 1632 cm^{-1} , and consequently the band in the spectrum of the parent compound can confidently be ascribed to a carbonyl vibration. The low frequencies of these bands must be due in part to the electron-releasing character of the hydrazone group, and in part to intermolecular interactions. Low values have also been reported²⁴ for 2-amino-anthraquinones and related compounds. Similar bands appear in the spectra of the phenyl-substituted derivatives (Table 2) and confirm the presence of the hydrazone tautomer in the solid state. No such band is found in the spectrum of the *O*-methyl derivative (II).

In solution the band moves to higher frequencies (Table 2). The position is dependent both on solvent and on substituent: higher frequencies are shown in the less polar solvents and by compounds containing electron-withdrawing substituents. The quantitative dependence of the frequency on the electron-withdrawing ability of the substituent can be seen in the linear variation of frequency with the Hammett substitution constant (σ) (Fig. 1). The displacement of the band by solvents is that typical of a carbonyl band.²⁵ The correlation of these shifts has been systematised by Bellamy *et al.*²⁶ by plotting relative frequency shifts ($\Delta\nu/\nu$) against those of a standard compound. Similar plots for those 4-arylazo-1-naphthols yielding sufficient data, with the *N*-methyl compound (III) as standard, are essentially linear (Fig. 2): this further substantiates the assignment of this band to a carbonyl stretching frequency and so confirms the presence of the hydrazone tautomer.

The intensity of the carbonyl absorption also varies with both solvent and substituent. In the more polar solvents the intensity of the band increases. (Examination of the extinction coefficients does not reveal this: the apparent band width increases faster than the band intensity, and the extinction coefficients actually decrease.) A similar increase in intensity is found in the carbonyl band of the *N*-methyl compound but the ratio $t_{\text{hydrazone}}/t_{N\text{-Me}}$ (where hydrazone = Ib, R = *o*-MeO, *o*-Me, *o*-Cl, *o*-NO₂) also increases on passing from the less to the more polar solvents. This, together with the corresponding changes in intensity shown by the amino- and hydroxyl bands, strongly suggests that as the solvent is changed the amount of hydrazone tautomer increases in the order: cyclohexane < tetrachloroethylene < carbon tetrachloride < methylene chloride < chloroform < bromoform. and so confirms the findings of Burawoy and Thompson³ from the

²³ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

²⁴ Flett, *J.*, 1948, 1441.

²⁵ See, *e.g.*, Bayliss, Cole, and Little, *Austral. J. Chem.*, 1955, **8**, 26; Archibald and Pullin, *Spectrochim. Acta*, 1958, **12**, 34; Thompson and Jewell, *ibid.*, 1959, **13**, 254.

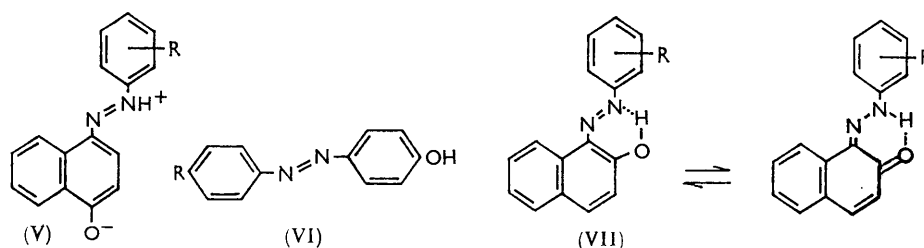
²⁶ Bellamy, Hallam, and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120; Bellamy and Williams, *ibid.*, 1959, **55**, 14.

ultraviolet spectra. A similar order is found²⁷ for the effect of solvents on simple keto-enol tautomerism. Solvents can affect the position of equilibrium in two ways. Stabilisation of the hydrazone form is provided by the ability of the solvent to interact directly

TABLE 2. Carbonyl bands in the spectra of 4-arylazo-1-naphthols.

Substituent R in (I)	Solid	Solvent					
		C ₆ H ₁₂	C ₂ Cl ₄	CCl ₄	CH ₂ Cl ₂	CHCl ₃	CHBr ₃
H	1625	—	—	—	1641 370 7·1	1634 320 —	1629 190 5·4
H	1632	1653 750 10·9	1649 800 12·0	1648 705 12·3	1636 560 13·4	1633 540 14·0	1629 490 11·7
(N-methyl deriv., III) o-MeO	1639	1650 745 5·6	1649 710 9·7	1648 700 10·5	1643 580 11·0	1641 445 10·8	1628 390 9·8
m-MeO	<i>t</i> 1630	—	—	—	1642 410 7·2	(1636) 380 —	1630 — —
p-MeO	<i>t</i> 1625	—	—	—	1639 120 3·7	1630 104 —	1626 — —
o-Me	<i>t</i> 1625	1648 120	1647 180	1647 170	1642 365	1638 290	1626 280
m-Me	<i>t</i> 1620	1·2	2·4	2·7	6·2	7·3	—
p-Me	<i>t</i> 1625	—	—	—	1641 455 6·8	1639 360 7·9	1628 — —
o-Cl	<i>t</i> 1625	—	—	—	1640 310 6·2	1633 210 —	1627 — —
m-Cl	<i>t</i> 1630	1653 480 6·7	1652 710 7·1	1650 730 7·3	1644 632 8·9	1642 590 10·0	1636 365 9·1
p-Cl	<i>t</i> 1627	—	—	—	1643 350 —	1640 515 8·8	1635 — 1633
o-NO ₂	1640	—	1655 610 6·4	—	1651 650 10·4	1647 520 10·4	1643 450 10·9
m-NO ₂	1627	—	—	—	1648 340 —	1643 455 9·1	1638 — —
p-NO ₂	1628	—	—	—	—	—	—

with the carbonyl group, probably through a weak hydrogen-bond;²⁶ additionally, an increase in dielectric constant stabilises the charge separation that accompanies the hydrazone tautomer, *i.e.*, stabilises the zwitterionic form (V). Both effects act to reduce



the carbonyl frequency and to displace the tautomeric equilibrium towards the hydrazone form. Direct solvent-solute interaction accounts most satisfactorily for the frequency shifts of simple carbonyl compounds,²⁶ and although the greater charge separation

²⁷ See, *e.g.*, Meyer, *Ber.*, 1912, **45**, 2843; Mecke and Funk, *Z. Elektrochem.*, 1956, **60**, 1124; Wilde Delvaux and Teyssié, *Spectrochim. Acta*, 1958, **12**, 289.

generated in this system may increase the contribution due to the change in dielectric constant, it seems possible that direct solvent-solute interaction is of paramount importance here also. This is supported by the results obtained from the isomeric 1-aryl-azo-2-naphthols (see below).

Superimposed on the solvent effect is that due to the substituents in the phenyl group. *meta*- and *para*-Substituents exert simple electron-donor and -acceptor forces on the hydrazono-azo-system. An sp^2 hybridised nitrogen atom is essentially more electro-negative than one having sp^3 hybridisation;²⁸ additionally, while the lone pair in the azo-grouping lies close to the plane of the aromatic ring, in the hydrazone it is correctly orientated for interaction with the conjugated system. In consequence, the relatively electron-withdrawing azo-grouping ($p\text{-C}_6\text{H}_5\text{-N=N-}$, $\sigma_p = +0.64$ ²⁹) is stabilised by electron-donating substituents and the position of equilibrium shifts accordingly. As a corollary it follows that the electron-donating properties of the hydrazono-group in the tautomer are

FIG. 1. Correlation of the Hammett substitution constant (σ), with the frequency (ν) of the carbonyl band in the spectra of 1-arylozo-4-naphthols (I) in bromoform \times , chloroform \circ , and methylene chloride \bullet .

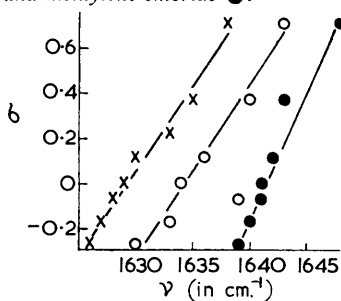
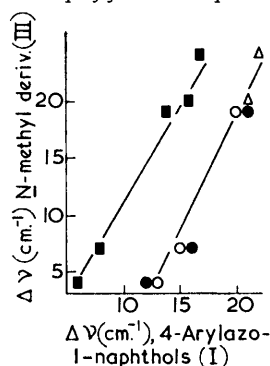


FIG. 2. Correlation of frequency shifts ($\nu_{\text{CHBr}_3} - \nu_{\text{solv.}}$) of 4-arylozo-1-naphthols (I, R = *o*-Me \bullet , *o*-OMe \circ , *o*-Cl \blacksquare) with those for naphthoquinone methylphenylhydrazone (III). Δ denotes overlap of filled and open circles.



increased by donor substituents and give lower carbonyl frequencies. Substituents in the *ortho*-position show rather different effects. The methoxy-, chloro-, and nitro-substituted derivatives all exist mainly in the hydrazone form. This is undoubtedly due to additional stabilisation of the hydrazone by internal hydrogen bonding; no such effect is shown by the *o*-tolyl derivative. It is noted that the solubility of the *ortho*-substituted derivatives is markedly higher than that of the *meta*- and *para*-isomers: this may be due to shielding of the polar nitrogen atoms by the *ortho*-substituent.

With the assumption that the intensity of the carbonyl band provides an approximate measure of the concentration of hydrazone in the tautomeric mixture, the hydrazone content increases in the order: *p*-MeO < *o*-Me \approx *p*-Me < *m*-Me < H < *m*-MeO < *m*-Cl < *m*-NO₂ < *o*-MeO \approx *o*-NO₂; a similar order is derived from the data on the amino- and hydroxyl bands; it closely resembles the order established^{3,4} from ultraviolet spectra.

A brief examination of the spectra of some *p*-hydroxyazobenzenes (VI; R = MeO, NO₂, H) confirmed that these are correctly represented as azo-compounds: neither amino- nor carbonyl bands could be detected.

1-Arylozo-2-naphthols.—Neither in the solid nor in solution do the spectra of *o*-hydroxyazo-compounds show distinct bands in the hydroxyl stretching region.^{15,16,30} In the spectra of the 1-arylozo-2-naphthols (VII) a series of weak, broad bands can be detected

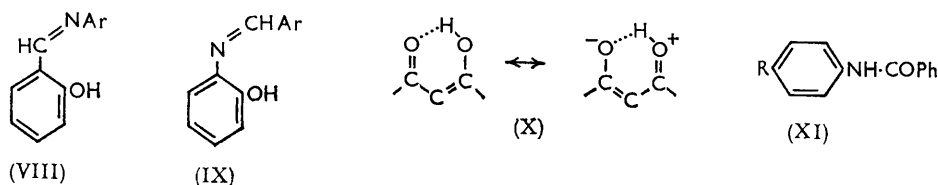
²⁸ Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60; Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166.

²⁹ Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188.

³⁰ Henricks, Wulf, Hilbert, and Liddel, *J. Amer. Chem. Soc.*, 1936, **58**, 1991.

in the range 2400—3100 cm^{-1} and may be ascribed to a chelate hydrogen-bonded system. A similar effect is found in hydroxy-naphtha-³¹ and -anthra-quinones²⁴ and in some Schiff's bases (VIII)³⁰ [but not in the isomeric compounds³² (IX)]. These bands are of little use for diagnostic purposes.

A band appears in the spectra of the azo-compounds derived from β -naphthol near 1620 cm^{-1} (Table 3). This value can be compared with the frequency of the carbonyl bands found in the spectra of 1-hydroxy- and 1-amino-anthraquinones and anthrones²⁴ (1614—1633 cm^{-1}) and of the corresponding naphthaquinones³¹ (1623 cm^{-1}) and there can be little doubt that it is correctly assigned to a carbonyl stretching frequency. The reduction of this frequency below that found in the derivatives of α -naphthol must be ascribed to strong internal hydrogen bonding:³³ confirmation of this is provided by the small shifts which accompany changes in solvent and indicate that the environment of the carbonyl group remains largely unaltered. The small changes that do occur may be indicative of the contribution made by dielectric changes to the larger shifts found in the 1,4-derivatives.



The intensity of the carbonyl band in the spectra of 1-arylazo-2-naphthols (Table 3) is considerably less than that of the 1,4-derivatives. As no adequate model compound is available for comparison, it is not immediately apparent whether the reduction in intensity is to be ascribed to a lower hydrazone concentration. The intensity of carbonyl bands has been correlated³⁴ with the availability of a charge-separated electronic configuration. In agreement with this, enolisable β -diketones³⁵ (X) and their amino-analogues³⁶ show intense carbonyl bands. A similar effect operates with both the 1,4- and the 1,2-azo-naphthols and will be differentiated only by the presence of internal hydrogen-bonding in the latter. This might be expected to increase the intrinsic intensity of the band, but comparison of the carbonyl bands in the spectra of *o*-hydroxy- and *o*-amino-benzaldehydes and -benzoates³⁷ with those of the unsubstituted and *para*-substituted compounds³⁸ shows that the former are slightly weaker. This effect clearly requires further investigation. It is possible that in the hydrazone some coupling of the carbonyl and aromatic C=C stretching modes near 1600 cm^{-1} occurs, but if so this cannot account for the reduction in intensity of the carbonyl band, for the aromatic band is in general weaker in the spectrum of the 1,2-compounds than the corresponding band in the spectrum of the 1,4-isomer.

The ultraviolet spectra were originally thought to indicate that the 1-arylazo-2-naphthols were largely present as hydrazones.^{2,39} This was based on comparisons with inadequate model compounds,¹¹ and further examination suggested that comparable amounts of hydrazone are formed from both the 1,4- and the 1,2-derivatives.⁵⁻⁸ Conversely, the weight of infrared evidence suggests that part at least of the diminution

³¹ Josien, Fuson, Lebas, and Gregory, *J. Chem. Phys.*, 1953, **21**, 331.

³² Baker and Shulgin, *J. Amer. Chem. Soc.*, 1959, **81**, 1523.

³³ Cf. Hunsberger, *J. Amer. Chem. Soc.*, 1950, **72**, 5626.

³⁴ Richards and Burton, *Trans. Faraday Soc.*, 1949, **45**, 874; Barrow, *J. Chem. Phys.*, 1953, **21**, 2008.

³⁵ Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068; Hergert and Kurth, *ibid.*, 1953, **75**, 1622.

³⁶ Cromwell, Miller, Johnson, Frank, and Wallace, *J. Amer. Chem. Soc.*, 1949, **71**, 3337.

³⁷ Krueger and Thompson, *Proc. Roy. Soc.*, 1959, *A*, **250**, 22.

³⁸ Thompson, Needham, and Jameson, *Spectrochim. Acta*, 1957, **9**, 208.

³⁹ Burawoy and Markowitsch, *Annalen*, 1933, **503**, 180.

in carbonyl intensity must be ascribed to a decrease in hydrazone concentration, and it may well be that the ultraviolet evidence overestimates the amount of hydrazone present.

TABLE 3. Carbonyl bands in the spectra of 1-arylozo-2-naphthols.

Substituent R in (VII)	Solvent					
	Solid	C ₆ H ₁₂	C ₂ Cl ₄	CCl ₄	CH ₂ Cl ₂	CHCl ₃
H	1622	1624	1623	1622	1622	1621
		190	195	200	215	230
<i>o</i> -MeO	<i>t</i> 1615	2·7	2·7	2·8	3·0	3·1
		1625	1624	1622	1622	1622
		265	280	285	295	370
<i>m</i> -MeO	<i>t</i> 1622	3·4	3·7	3·8	4·0	4·1
		1625	1623	1623	1621	1621
		195	195	210	225	250
<i>p</i> -MeO	<i>t</i> 1612	—	—	—	—	—
		1624	1624	1623	1622	1622
		185	185	190	205	210
<i>o</i> -Mc	<i>t</i> 1618	—	—	—	—	—
		1624	1622	1621	1621	1621
		150	190	190	205	260
<i>m</i> -Mc	<i>t</i> 1620	1·9	2·5	2·6	2·7	2·9
		1624	1623	1623	1622	1622
		190	195	195	220	260
<i>p</i> -Mc	<i>t</i> 1617	—	2·7	2·7	2·9	3·0
		1624	1623	1622	1621	1620
		170	185	190	200	220
<i>o</i> -Cl	<i>t</i> 1617	2·2	2·6	—	2·8	2·9
		1623	1623	1622	1622	1621
		225	220	245	275	275
<i>m</i> -Cl	<i>t</i> 1620	3·2	3·3	3·3	3·7	3·9
		1625	1623	1623	1621	1622
		215	215	220	275	280
<i>p</i> -Cl	<i>t</i> 1620	3·0	3·0	3·1	3·4	3·5
		1625	1623	1623	1622	1622
		210	205	210	230	235
<i>o</i> -NO ₂	<i>t</i> 1622	2·8	2·8	2·9	3·2	3·3
		—	1628	—	1624	1622
		—	285	—	290	285
<i>m</i> -NO ₂	<i>t</i> 1615	—	—	—	—	—
		—	1625	—	1624	1621
		—	285	—	305	305
		—	3·7	—	—	3·9
<i>p</i> -NO ₂	<i>t</i> 1625	—	—	—	1624	1624
		—	—	—	275	250
		—	—	—	—	—

It may be noted that in the 1-arylozo-2-naphthols internal bonding O—H ··· N will stabilise the azo-form by a mechanism not available to the 1,4-compounds. This bonding, and that in the complementary O ··· H—N system, involves orbitals in the plane of the aromatic rings and hence not directly linked to the conjugated system. It is to be expected that the more acidic phenolic form will be bonded the more strongly and in consequence be relatively stabilised.

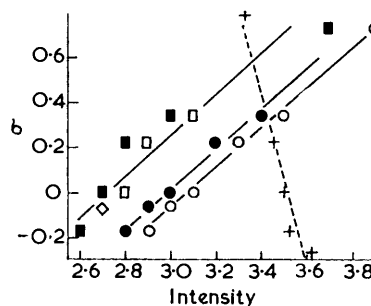
The effect of both solvents and substituents on the intensity of the carbonyl band is analogous to that found for the 1,4-derivatives. The same solvent order is found, but the change in intensity is smaller and may be due largely to change in dielectric constant⁴⁰ since direct carbonyl-solvent interaction is inhibited. The effect of substituents also follows an order closely similar to that of the 1,4-derivatives. The greater solubility of the 1-arylozo-2-naphthols enables sufficient data to be collected to justify plots of intensity against Hammett substitution constants (σ). These plots (Fig. 3) are linear and demonstrate the quantitative dependence of the carbonyl intensity on the electron-withdrawing properties of the substituents. It is well known^{37,38,41} that band intensities in

⁴⁰ Cf. Taft, Glick, Lewis, Fox, and Ehrenson, *J. Amer. Chem. Soc.*, 1960, **82**, 756.

⁴¹ Thompson and Jameson, *Spectrochim. Acta*, 1958, **13**, 236.

many non-tautomeric compounds can be represented as linear functions of substitution constants. To examine whether a similar effect was responsible for the intensity changes here, a series of benzanilides (XI; R = H, MeO, Me, Cl, NO₂) was examined (the arylazonaphthols can be regarded as vinylogues of amides). The plot (Fig. 3) of the intensity of their carbonyl bands shows a small negative gradient (a similar result is provided by the data of Thompson and Jameson⁴¹) and confirms that the changes in intensity in the spectra of 1-arylazo-2-naphthols are due to changes in hydrazone concentration.

FIG. 3. Correlation of the Hammett substitution constant (σ) with the intensity (I) of the carbonyl band in the spectra of 1-arylazo-2-naphthols (VII) (in chloroform \circ , methylene chloride \bullet , carbon tetrachloride \square , tetrachloroethylene \blacksquare) and (I)₃ of the amides (XI) (in chloroform $-|$). \diamond denotes overlap of filled and open squares.



Structure of the Arylazonaphthols.—It was suggested⁴² that the arylazonaphthols could be adequately represented by zwitterionic formulæ (e.g., V). Such structures alone are incapable of interpreting the ultraviolet and infrared spectroscopic evidence and can be discounted. The presence of a tautomeric azo-hydrazone mixture in both 1-arylazo-2-naphthols and 4-arylazo-1-naphthols is clearly indicated, but the infrared spectra show that the structure of the hydrazones must contain some electronic displacement, *i.e.*, significant contribution from a zwitterionic canonical structure (e.g., V). Equally to be discounted is the suggestion^{1b,4,30} that no distinction can be drawn between the azo- and hydrazono-forms of the 1-arylazo-2-naphthols. The interaction between the mobile hydrogen atom and the adjacent oxygen and nitrogen atoms is best described in terms of a hydrogen bond whose potential-energy curve shows a double rather than a single minimum.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

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⁴² Kuhn, *Naturwiss.*, 1932, **20**, 622.