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The Diffuse Reflection Spectra of 1-Arylazo-2-naphthols Diluted with Sodium Chloride

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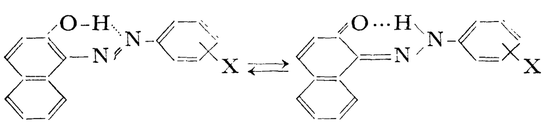
The diffuse reflection spectra of sixteen 1-arylazo-2-naphthols diluted with sodium chloride were measured at concentrations of 1, 0.1, and 0.01% in the range from 350 to 700 mμ. The spectra indicate the coexistence of the azo and hydrazone tautomers in this solid, two-component system. Moreover, the spectra were found to be markedly modified in many cases by elevating the temperature, especially at a concentration of 0.01%. These changes were shown to be thermally reversible and were attributed to the movement of the tautomeric equilibrium. The direction depends upon the kind and position of the substituents, *e.g.*, towards the hydrazone tautomer in the case of the *p*-Cl and *o*-NO_2 derivatives and towards the azo tautomer in the case of the *p*-NO_2 and *o*-OH derivatives. It was suggested that the present systems are not simple mixtures of pulverized 1-arylazo-2-naphthols and sodium chloride, but that some fraction of the organic components is well dispersed and adsorbed on the highly polar surface of the alkali halide.

A large number of studies have been carried out to elucidate the structure of 1-arylazo-2-naphthols,*2 which may exist as true azo compounds (I) or as β-naphthoquinone hydrazones (II).[1)]



(I) (II)

On the basis of the electronic spectra in various solvents, Burawoy *et al.* have clearly demonstrated that they exist in solution as tautomeric equilibria.[2)] For example, the spectrum of 1-phenylazo-2-naphthol in hexane shows an absorption region consisting of two coalescent bands at about 420 and 460 mμ, whereas in alcohol, chloroform, and 50% alcohol the intensity of the former band is consistently reduced, and that of the latter, increased. The two bands correspond to the azo and the hydrazone tautomers respectively, the former being present in an appreciable quantity only in a hexane solution.

A few years later Hadzi discovered that the electronic spectrum of solid 1-phenylazo-2-naphthol

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[*2] This designation is used throughout this paper for convenience; it is not intended to define the structure of the compounds.

1) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York (1961), p. 322.

2) A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, **1952**, 4793.

pressed with potassium bromide into a disc consists of two bands, at 410 and 486 mμ.[3] The first maximum was assigned to the azo tautomer, and the second, to the hydrazone tautomer. His finding was rather surprising, as Hadzi himself noted. To the best of our knowledge, compounds exhibiting tautomerism in solution are known to be in one form only in the crystalline state. Therefore, Hadzi suggested that the two types of molecules have very similar bond lengths, that the proton changes its position from oxygen to nitrogen with time, and that thus the two types of molecules give, on the time-average, a single set of bond dimensions. It is noteworthy that the general character of the electronic spectrum of the solid corresponds to that of solutions in polar solvents. Recently Bansho *et al.* extended the spectral measurement by the same technique to cover a number of derivatives.[4] By comparing the extinctions in the regions from 410 to 420 mμ and from 480 to 500 mμ, they concluded that 60 to 70% of the molecules in the solids exist as hydrazones. Further evidence for the presence of the tautomerism in solid 1-arylazo-2-naphthols has been provided by the infrared spectra examined by Morgan and also by the fluorescence studied by Rau.[5,6]

If the compounds exist as tautomeric equilibria in solids, the temperature dependence of the electronic spectra may be observed. To confirm this expectation, we started measurements of the diffuse reflection spectra. As our preliminary attempts indicated that the spectra, which are much better resolved than the transmission spectra presented by Hadzi, depend appreciably on the degree of dilution, concentrations of 1, 0.1, and 0.01% were used throughout this work.

Experimental

Materials. The compounds were prepared by the usual diazo-coupling reactions with 2-naphthol. The derivatives carrying one of the following substituents in the *o*-, *m*-, or *p*-position on the phenyl ring were included in the present work: methyl, chloro, hydroxy, methoxy, and nitro. They were recrystallized twice from appropriate solvents selected from among methanol, benzene, toluene, and acetic acid, and were finally sublimed in *vacuo*.

Measurements. The compounds were diluted with dried sodium chloride in the desired concentrations. The well-ground mixture was mounted on a brass block in which a 60-W heater is embedded. The temperature near the surface of the mixture was monitored by a copper-constantan thermocouple and was kept constant with the aid of a Chino temperature-indicating controller, Type E 500. The difference in reflectance between the mixture heated to a desired temperature and pure sodium chloride kept at room temperature was recorded in the range from 350 to 700 mμ by a Beckman DK 2A spectroreflectometer. The spectra were then plotted using the Kubelka-Munk function $f(R)=(1-R)^2/2R$, where R is the reflectance. The measurements were carried out at three different temperatures, namely, room temperature (about 20°C), the highest temperature selected (at least 50°C below the melting point of each compound), and one between these two. As the reflectance is strongly affected by the thermal dispersion of the compound as the temperature rises, only the spectra measured as the temperature fell were employed in our considerations. The room-temperature spectra are those recorded after cooling by storage in a desiccator over silica gel. Even with these precautions, the absorption intensity depends somewhat upon how the mixture was heated and cooled; therefore, the maximum was arbitrarily taken as 1.00 in each spectrum.

Results and Discussion

1-Phenylazo-2-naphthol (Fig. 1). The room-temperature spectra at concentrations of 1, 0.1, and 0.01% are presented in Fig. 1. There are a broad band covering the region from 350 to 425 mμ and a sharp strong doublet appearing at 480 and 525 mμ. The former band is assigned to the azo tautomer, and the latter, to the hydrazone tautomer. In the present case, the spectra at the three concentrations are rather similar to each other. As the compound is strongly absorbing, the deviation from the Kubelka-Munk theory due to regular reflection may be considered to be the cause of the apparent flattening of the spectra at high concentrations. However, the spectral change observed in the case of the *p*-NO_2 derivative (shown in Fig. 9) undoubtedly indicates that the deviation from the theory cannot be the sole cause of the concentration dependence of the spectra. The marked depression in the relative

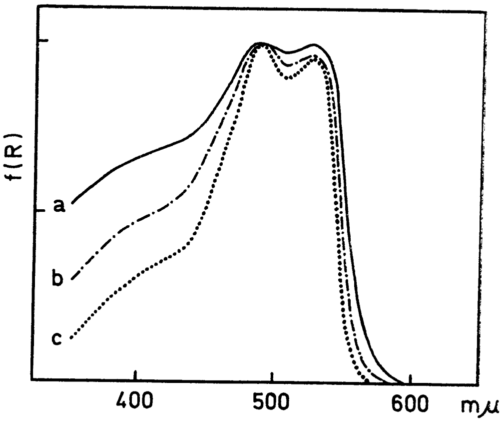

Fig. 1. Spectra of 1-phenylazo-naphthol diluted with sodium chloride; (a) 1%, (b) 0.1% and (c) 0.01% at room temperature.

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[3] D. Hadzi, *ibid.*, **1956**, 2143.

[4] I. Saito, Y. Bansho, and A. Kakuta, *Kogyo Kagaku Zasshi*, **70**, 1715 (1967).

[5] K. J. Morgan, *J. Chem. Soc.*, **1961**, 2151.

[6] H. Rau, *Ber. Bunsenges. Phys. Chem.*, **72**, 637 (1968).

intensity of the broad band by dilution found in Fig. 1 may be partially attributed to the movement of the equilibrium towards the hydrazone tautomer. We do not expect such movements if the samples are simple mixtures of pulverized substances. Therefore, the contribution from the molecules adsorbed on the surface of the diluent to the observed spectra should be taken into consideration. Even if the concentration is as high as 1%, the spectrum may still not be that of a true solid, but, on the other hand, it may not be far from that. Our spectrum at a concentration of 0.01% is in good agreement with the one reported by Rau, who measured it by the same technique and at the same concentration.

When the temperature was raised to 75°C, no change occurred in the spectrum at any of the concentrations examined except for a small broadening of the doublet.

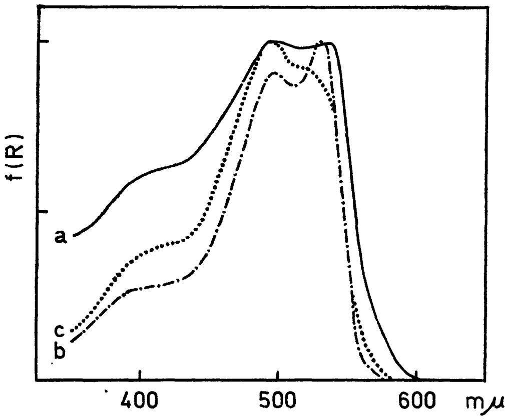

Fig. 2. Spectra of 1-(*o*-tolylazo)-2-naphthol diluted with sodium chloride; (a) 1%, (b) 0.01% at room temperature and (c) 0.01% at 75°C.

1-Tolylazo-2-naphthols (Fig. 2). The spectra of these compounds are almost identical with that of 1-phenylazo-2-naphthol (presented in Fig. 1). Although the relative intensity in the region from 350 to 450 mμ cannot be directly correlated with the amount of the azo tautomer, it is interesting to note that the intensity at a concentration of 1% increases in this order of substituents: *o*-Me$\sim$H$<$*m*-Me$<$*p*-Me. This order is nearly the same as that found in an ethanolic solution by Burawoy *et al.*: *o*-Me$<$*m*-Me$\sim$H$<$*p*-Me.[2]

A change in the spectrum upon an elevation of the temperature was observed in the case of the *o*-Me derivative, most clearly at 0.01%. As is shown in Fig. 2, the intensities in the region from 350 to 500 mμ measured at 75°C are higher than those at room temperature. This observation indicates that the equilibrium moves towards the azo tautomer at high temperatures. The change in the spectrum upon dilution is also illustrated in this figure. In the case of the *m*-Me derivative, none of the spectra recorded at 75°C were found to be different from those at room temperature. The spectrum of the *p*-Me derivative is modified a little bit only at 0.01% when the temperature is raised to 75°C. The direction of the change is the same as that found in the *o*-Me derivative.

1-Chlorophenylazo-2-naphthols (Figs. 3 and 4). The spectra of the *o*-Cl and *m*-Cl derivatives are shown in Fig. 3. No temperature dependence was observed in these cases; however, a movement of the equilibrium towards the hydrazone tautomer upon heating to 75°C was found in the *p*-Cl derivative. It must be added that this movement is in the direction opposite to that observed in the *o*-Me and *p*-Me derivatives. At a concentration of 1%, the presence of a doublet due to the hydrazone tautomer is clearly noted only in the *m*-Cl derivative. In the other two cases, the

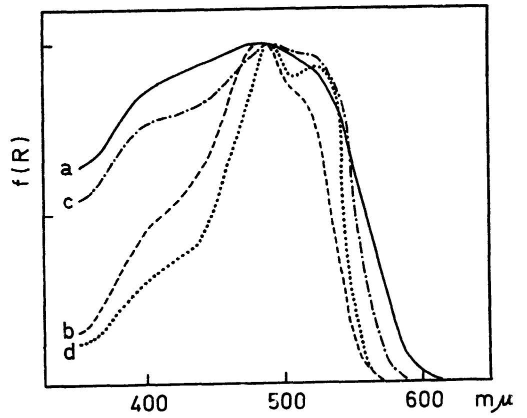

Fig. 3. Spectra of 1-(*o*-chlorophenylazo)-2-naphthol; (a) 1% and (b) 0.01% and those of 1-(*m*-chlorophenylazo)-2-naphthol; (c) 1% and (d) 0.01% at room temperature.

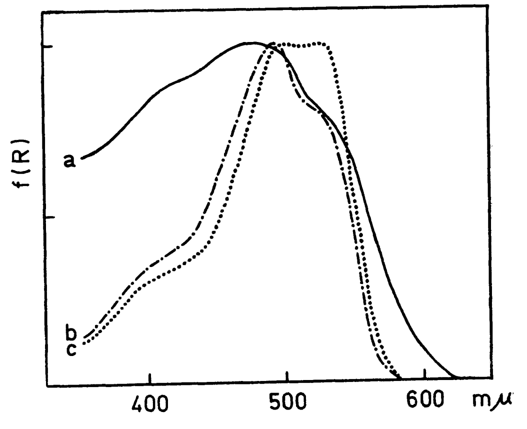

Fig. 4. Spectra of 1-(*p*-chlorophenylazo)-2-naphthol diluted with sodium chloride; (a) 1%, (b) 0.01% at room temperature and (c) 0.01% at 75°C.

absorptions in the region from 350 to 450 mμ are so high that the sharp peaks due to the hydrazone tautomers cannot be resolved. The relative intensities measured at 1% in the above-mentioned region increase in this order: H<*m*-Cl<*p*-Cl∼*o*-Cl, an order which is not in accordance with that drawn from the data obtained in an ethanolic solution: *o*-Cl<*m*-Cl<*p*-Cl∼H.[2] When the compounds are much more diluted with sodium chloride, the relative intensities in the region from 350 to 450 mμ are drastically decreased, as is generally found in a solid, two-component system. Nevertheless, the order remains essentially the same: H<*m*-Cl<*o*-Cl<*p*-Cl. Therefore, the effect of chlorine substitution on the tautomeric equilibrium in our system is apparently very different from that observed in solution by Burawoy *et al.*

1-Hydroxyphenylazo-2-naphthols (Figs. 5 and 6). The *o*-OH derivative is one of the compounds showing a very pronounced temperature dependence in the spectra. In Fig. 5 the spectra measured at room temperature and at 100°C are presented. The room-temperature spectrum at 1% is very similar to that of 1-phenylazo-2naphthol examined under the same conditions. However, the whole spectrum is shifted to the long-wavelength side. The doublet to be assigned to the hydrazone tautomer is located at 500 and 540 mμ. It is apparent that the equilibrium moves towards the azo tautomer when the temperature is elevated. Contrary to the case of the *o*–OH derivative, the absorption due to the azo tautomer is dominant in the spectrum of the *m*–OH derivative at a concentration of 1%. A small movement of the equilibrium towards the hydrazone tautomer is noted upon heating to 100°C only at 0.01%. The spectra of the *p*–OH derivative shown in Fig. 6 bear some similarity to those of the *o*–OH derivative, but the change upon an elevation of the temperature is in the opposite direction.

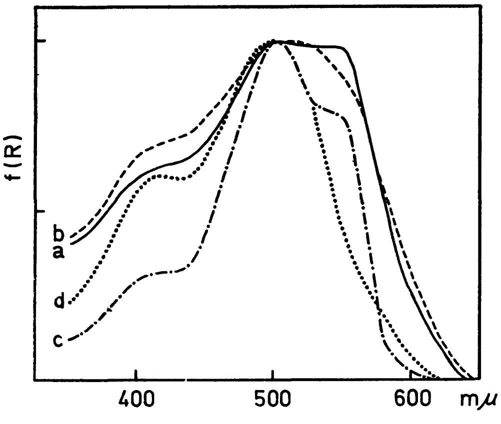

Fig. 5. Spectra of 1-(*o*-hydroxyphenylazo)-2-naphthol diluted with sodium chloride; (a) 1% at room temperature, (b) 1% at 100°C, (c) 0.01% at room temperature and (d) 0.01% at 100°C.

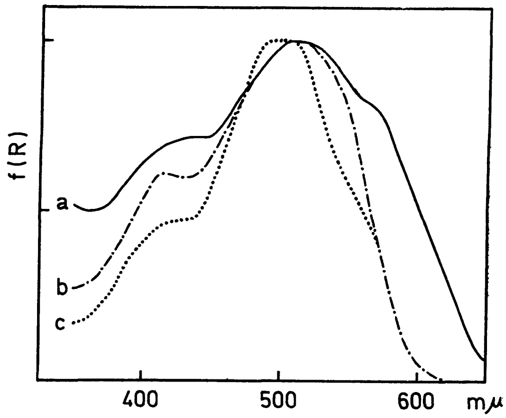

Fig. 6. Spectra of 1-(*p*-hydroxyphenylazo)-2-naphthol diluted with sodium chloride; (a) 1%, (b) 0.01% at room temperature and (c) 0.01% at 100°C.

1-Anisylazo-2-naphthols (Fig. 7). The doublet to be assigned to the hydrazone tautomer is located at 500 and 540 mμ in the spectrum of the *o*–MeO derivative. By heating to 100°C, the peak at the longer wavelength disappears. The equilibrium seems to move slightly towards the azo tautomer upon an elevation of the temperature. The *m*–MeO derivative shows a spectrum similar to that of the *o*-MeO derivative; however, no temperature dependence was detected in this case. The spectrum of the *p*-MeO derivative shown in Fig. 7 suggests that a fairly large amount of the azo tautomer is present, even at a concentration of 0.01%. The change caused by heating discloses that high temperatures favor the hydrazone tautomer. The spectrum examined as a potassium bromide disc by Bansho *et al.* is like ours measured at 0.01%. The concentration of the azo tautomer in solution was reported by Burawoy *et al.* to increase in this order: *o*-MeO

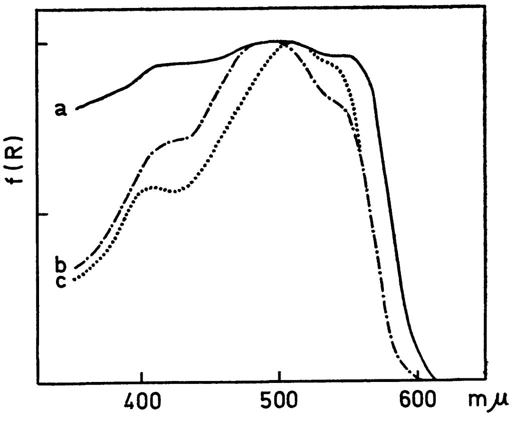

Fig. 7. Spectra of 1-(*p*-anisylazo)-2-naphthol diluted with sodium chloride; (a) 1%, (b) 0.01% at room temperature and (c) 0.01% at 75°C.

<*m*-MeO<H<*p*-MeO.[2] In our solid, two-component system, the effect of the substituent on the equilibrium is quite different from theirs. The relative intensity in the region between 350 and 450 mμ is found to be in this order: H< *m*-MeO∼*o*-MeO<*p*-MeO at a concentration of 1%.

1-Nitrophenylazo-2-naphthols (Figs. 8 and 9). As is shown in Fig. 8, the spectrum of the *o*-NO_2 derivative at room temperature is dominated by the broad absorption assigned to the azo tautomer. The change upon an elevation of the temperature is well demonstrated, even at a concentration of 1%. Apparently the amount of the hydrazone tautomer increases at high temperatures. In the spectra of the *m*-NO_2 derivative, the doublet due to the hydrazone tautomer can be seen in this case, but only weakly, at a concentration of 1%. As the absorption assigned to the azo tautomer at 100°C is stronger than that at room temperature, the hydrazone tautomer appears to be more stable than the azo tautomer.

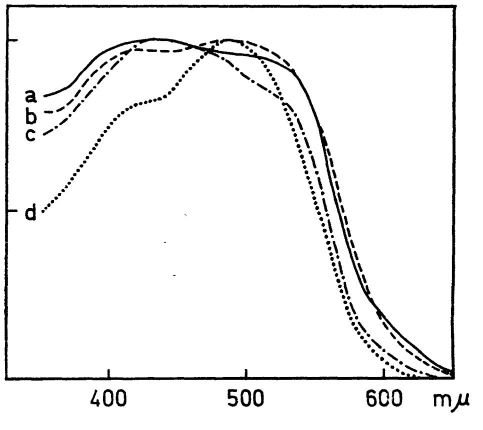

Fig. 8. Spectra of 1-(*o*-nitrophenylazo)-2-naphthol diluted with sodium chloride; (a) 1% at room temperature, (b) 1% at 125°C, (c) 0.01% at room temperature and (d) 0.01% at 125°C.

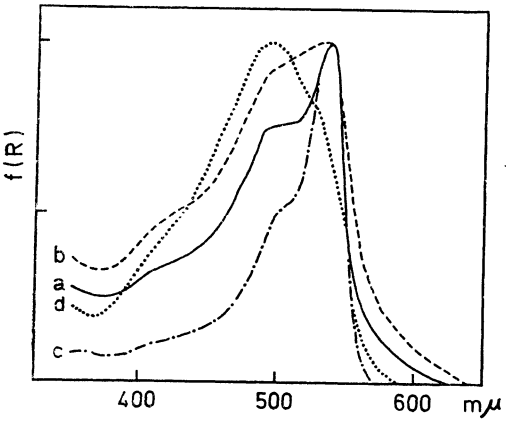

Fig. 9. Spectra of 1-(*p*-nitrophenylazo)-2-naphthol diluted with sodium chloride; (a) 1% at room temperature, (b) 1% at 150°C, (c) 0.01% at room temperature and (d) 0.01% at 150°C.

The most pronounced temperature dependence of the spectrum has been observed with the *p*-NO_2 derivative. There is a sharp peak at 538 mμ, with a shoulder around 500 mμ. Upon heating to 150°C, the shoulder is appreciably intensified. Especially at a concentration of 0.01%, the change is quite remarkable. The peak at 538 mμ, which is supposed to be assigned to the hydrazone tautomer, is nearly completely obscured by a strong absorption appearing at 500 mμ. The latter may be assigned to the azo tautomer. Our high-temperature spectrum obtained at 0.01% closely resembles the one reported by Bansho *et al.*[4] It must be pointed out that the high-temperature spectrum at 0.01% differs greatly from that at 1%. This observation confirms the dependence of the tautomeric equilibrium on the degree of dilution. Burawoy *et al.* stated that the concentration of the hydrazone tautomer in these nitro derivatives is the highest among the 1-arylazo-2-naphthols examined.[2] However, the spectra of the *o*-NO_2 derivative given in Fig. 8 are not consistent with their finding.

General Remarks. Since the true maxima and intensities of the bands of the individual tautomers are not known, a quantitative analysis of the equilibria cannot be made. Bansho *et al.* reported that 60 to 70% of the molecules in solid 1-arylazo-2-naphthols exist as hydrazone tautomers, regardless of the kind and position of the substituents examined, *i.e.*, Me, MeO, Cl, and NO_2.[4] In their estimations, the relative intensities of the bands due to the azo and hydrazone tautomers were assumed to be constant throughout the derivatives examined and were taken to be equal to those of 4-(*o*-chlorophenylazo)-1-naphthol in solution. The temperature dependence of the electronic spectra reported in the present work indicates that some of the Bansho estimations are too high.

The effects of the temperature on the tautomeric equilibria are summarized in Table 1. There are five derivatives for which the temperature dependence of the electronic spectra could not be detected. Such cases may occur when the azo and hydrazone tautomers have nearly the same energy or when the energy difference between the two tautomers is so large that the amount of the minor one is too small to affect the spectrum. In the present system, the former situation seems to be likely. If the magnitude of the energy difference is in the order of thermal energy, the electronic spectrum may be modified by the temperature change. The direction of the movement of the equilibrium upon an elevation of the temperature should be towards the minor tautomer. Thus, more than 50% of the molecules in the *o*-Me, *p*-Me, *o*-OH, *o*-MeO, *m*-NO_2, and *p*-NO_2

TABLE 1. THE MOVEMENT OF THE EQUILIBRIUM BY ELEVATING TEMPERATURE; TOWARDS THE AZO TAUTOMER (+) OR THE HYDRAZONE TAUTOMER (−)
The number in parenthesis is Hammett substituent constant.

Substituent	Position		
	ortho	meta	para
None		not detectable (0.00)	
Methyl	+	not detectable (−0.07)	+ (−0.17)
Chloro	not detectable	not detectable (0.37)	− (0.23)
Hydroxy	++	− (0.12)	− (−0.37)
Methoxy	+	not detectable (0.12)	− (−0.27)
Nitro	−−	+ (0.71)	++ (0.78)

derivatives are expected to exist as hydrazone tautomers in the present two-component system. On the other hand, the situation must be reversed in the *p*-Cl, *m*-OH, *p*-OH, *p*-MeO, and *o*-NO_2 derivatives. This conclusion is in serious conflict with the estimations made by Bansho *et al.* On the basis of this disagreement, we have to conclude that the relative intensities of the bands of the tautomers are not independent of the kind and position of the substituents. Although the distribution of the substituents in the above-discussed three groups reveals the general tendency for the hydrazone tautomer to be favored in the derivatives carrying substituents with large Hammett constants, no simple correlation can be established in the present system.

The electronic and vibrational spectra examined as potassium bromide discs have been considered like those of solid samples.[3-5] However, our observation that the spectra depend greatly upon the degree of dilution casts some suspicion on the technique. As has been mentioned earlier, the spectral changes caused by dilution may be attributed not only to a decreasing deviation from the Kubelka-Munk theory, but also, at least in part, to the movement of the equilibrium towards the hydrazone tautomer. As a matter of fact, Rau has considered his spectrum of 1-phenylazo-2-naphthol, measured at a concentration of 0.01%, as that of the species adsorbed on the diluent.[6] These pieces of evidence suggest that the spectra obtained by the potassium-bromide-disc method are also not free from the influence of the diluent. It has been pointed out by Burawoy *et al.* that the relative stability of the hydrazone tautomer increases in this order of the solvents: hexane< ethanol<chloroform<water.[2] The observed trend of the movement of the equilibrium upon dilution with sodium chloride seems reasonable, since more and more molecules of 1-arylazo-2-naphthol are dispersed and adsorbed on the highly polar surface of the alkali halide. As has been discussed earlier, measurements at higher concentrations may provide the spectra of true solids, but they will be very much distorted. At a maximum concentration of 1% or higher, the reflectance spectra are expected to be flattened because of an increasing regular reflection.

The authors wish to express their thanks to Mr. Nobuhiko Miyajima for his collaboration throughout the course of this work.