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Tautomerism in 1-Arylazo-2-naphthols as Studied by Fluorescence

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Earlier we examined the diffuse reflection spectra of sixteen 1-arylazo-2-naphthols[1] diluted with sodium chloride and concluded that the azo and hydrazone tautomers coexist in this solid, two-component system.[2] In many cases, the spectra were found to be markedly modified by elevating the temperature. These changes were thermally reversible and were attributed to the movement of the tautomeric equilibrium. A few years ago, Rau studied the fluorescence of hydroxyazo compounds, mostly at 77°K, and concluded that the hydrazone tautomer is the emitting species.[3] Solid 1-phenylazo-2-naphthol was noted by him to be weakly fluorescent at room temperature. Therefore, the examination of the fluorescence in our samples seemed to be a useful means of checking the validity of our earlier conclusions.

The samples of 1-arylazo-2-naphthols diluted with sodium chloride were those used in our previous work.[2] The fluorescence spectra were recorded on a Hitachi Model MPF-2A spectrophotometer. The samples, packed into quartz capillaries, were examined at room temperature and also at the temperature of liquid nitrogen. The wavelength of the exciting light, selected on the basis of experiments on the excitation-dependence of the fluorescence spectra, was 400 or 470 mμ. It is well known that fluorescence spectra are usually mirror-images of the corresponding absorption spectra when plotted on a frequency scale. Unfortunately, the present spectra are located in the region where the sensitivity of the detector decreases drastically; therefore, the attempts at calibration were not successful. In spite of this shortcoming, it is certain that the peak with the longest wavelength in the reflection spectrum arises from the hydrazone tautomer.

Whether or not the samples at a concentration of 1% are fluorescent is summarized in Table 1. Six among the sixteen examined are not fluorescent; however, the following three become fluorescent when diluted more: the *p*-NO_2 derivative at a concentration of 0.1%, and the *p*-Cl and *o*-OH derivatives at 0.01%. In the last column of Table 1, we show which is the major tautomer in the samples diluted with sodium chloride. This information, obtained from the temperature-dependence of the reflection spectra, is cited from one of our earlier works.[2] There is a fairly good parallelism between the detection of fluorescence at 1% and the presence of an appreciable amount of the hydrazone tautomer. The only exceptions are the *o*-OH and *p*-NO_2 derivatives mentioned above. The detection at 0.1 or 0.01% is in accordance with one of our conclusions that the higher the degree of dilution, the more molecules in the hydrazone form. In the case of the *p*-NO_2 derivative, a reexamination of the reflec-

Table 1. The detection of fluorescence in 1-arylazo-2-naphthols diluted with sodium chloride

Substituent	Concentration		Major tautomer[a]
	1%	0.1 or 0.01%	
None	+	+	Comparable
o-Methyl	+		Hydrazone
m-Methyl	+		Comparable
p-Methyl	+		Hydrazone
o-Chloro	+		Comparable
m-Chloro	+		Comparable
p-Chloro	—	+	Azo
o-Hydroxy	—	+	Hydrazone
m-Hydroxy	—	—	Azo
p-Hydroxy	—	—	Azo
o-Methoxy	+		Hydrazone
m-Methoxy	+		Comparable
p-Methoxy	+		Azo
o-Nitro	—	—	Azo
m-Nitro	+		Hydrazone
p-Nitro	—	+	Hydrazone[b]

a) Determined by the temperature-dependence of the reflection spectra with the samples diluted with sodium chloride, see Ref. 2.

b) The azo tautomer may be the major one when the concentration is high.

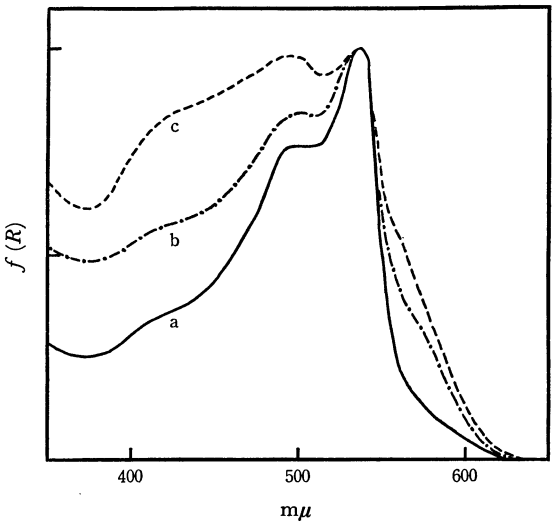

Fig. 1. Diffuse reflection spectra of 1-(*p*-nitrophenylazo)-2-naphthol diluted with sodium chloride at a concentration of 1%; (a) stored for one day after the temperature-dependence measurement, (b) after storage over one year, (c) prepared by grinding at room temperature only. The maximum is arbitrarily taken as 1.00 in each spectrum.

1) This designation is used throughout this paper for convenience; it is not intended to define the structure. The substituents are on the phenyl ring.

2) C. Dehari, Y. Matsunaga, and K. Tani, This Bulletin, **43**, 3404 (1970).

3) H. Rau, *Ber. Bunsenges. Phys. Chem.*, **72**, 637 (1968).

tion spectra revealed that a large change occurred at a concentration of 1% during prolonged storage at room temperature. As is shown in Fig. 1, the sharp peak appearing at 538 mμ is relatively strong when examined one day after the temperature-dependence measurement, but was much weaker after storage for one year. A sample prepared by grinding at room temperature gives the spectrum shown by Curve c. Thus, the hydrazone tautomer of this derivative seems to be less stable than we thought earlier. However, the peak is dominant at concentrations of 0.1 and 0.01% even after storage for nearly two years. It must be noted that the absence of fluorescence cannot be considered as an indication of the absence of the hydrazone tautomer. Nevertheless, fluorescence is not detected at a 1% dilution in most of the cases where the azo tautomer is the major one. All the compounds which are fluorescent at a concentration of 1% are also fluorescent without dilution with sodium chloride. In such cases, it is very likely that the two tautomeric forms exist together, even in crystals.

Cooling brings about a marked increase in the intensity of the fluorescence at the short-wavelength end of the spectrum. In the cases of 1-phenylazo-2-naphthol and the *m*-Cl derivative, the appearance of a fine structure is noted. With the *m*-Me, *p*-Me, *m*-MeO, and *m*-NO_2 derivatives, the change in the relative intensity is so great that the low-temperature fluorescence seems to be shifted to the short-wavelength side by 15—20 mμ.

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