(32) J. M. Harris, D. L. Mount, M. R. Smith, and S. P. McManus, *J. Am. Chem. Soc.*, **99,** 1283 (1977).

(33) This force field, referred to as either the Schleyer, Engler, or Schleyer-Engler force field, gives somewhat better results for polycylic systems than alternative force fields:[2c] T. Clark, T. McO. Knox, H. Mackle, M. A. McKervey, and J. J. Rooney, *J. Am. Chem. Soc.*, **97,** 3835 (1975); T. Clark, T. McO, Knox, H.Mackle, and M. A. McKervey, *J. Chem. Soc., Chem. Commun.*, 666 (1975).

(34) The input geometry determines which rotamer in eq 2 or 3 is calculated. Even though the minimization program used[2a] contains a "group rotation" routine, it would not cross energy barriers.

(35) L. P. Hammett, "Physical Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1970, p 133 ff.

(36) P. v. R. Schleyer and C. W. Woodworth, *J. Am. Chem. Soc.*, **90,** 6528 (1968).

(37) A priori, there is no reason to postulate that a correlation be linear, since second-order effects might intervene.

(38) R. O. Klaus, H. Tobler, and C. Ganter, *Helv. Chim. Acta*, **57,** 2517 (1974); H. Tobler, R. O. Klaus, and C. Ganter, *ibid.*, **58,** 1455 (1975); D. P. G. Hamon and G. F. Taylor, *Tetrahedron Lett.*, 155 (1975); *Aust. J. Chem.*, **29,** 1721 (1976); D. P. G. Hamon, G. F. Taylor, and R. N. Young, *Tetrahedron Lett.*, 1623 (1975); J. S. Poley and R. K. Murray, Jr., *J. Org. Chem.*, **41,** 3294 (1976); T. Sasaki, S. Eguchi, and Y. Hirato, *ibid.*, **42,** 2981 (1977); M. Kawanishi, T. Imakawa, R. Yamaguchi, T. Katsushima, Y. Fujimoto, and S. Ryu, Japanese Patent 76-101,966; *Chem. Abstr.*, **86,** 43293r (1977); Japanese Patent 76-101,967; *Chem. Abstr.*, **86,** 43294s (1977); L. A. Paquette, P. B. Lavrik, and R. H. Summerville, *J. Org. Chem.*, **42,** 2659 (1977).

(39) Cf. ref 19, p 281.

(40) P. v. R. Schleyer in "Reaction Transition States", J. E. Dubois, Ed., Gordon and Breach, New York, N.Y., 1972, p 197 and 210.

(41) (a) J. A. Bone and M. C. Whiting, *J. Chem. Soc., Chem. Commun.*, 115 (1970); (b) See the discussions and references in: J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *J. Am. Chem. Soc.*, **96,** 4484 (1974).

(42) Thus, it was stated that "unlike the secondary protoadamantyl and 2-adamantyl series, the bridged ion (i.e., **2b**) dominates the chemistry of" **1b** and the tertiary protoadamantyl substrates.[16c]

(43) For the reaction of tertiary substrates,[13c,27] the steric effect observed was also that of β and γ substituents, since the variable substituent was CRR′R″, with R = R′ = R″ = H for the "parent" compound.

(44) Following our previous article (ref. 14) and the solvolysis study on optically active **1b**, the original workers in the field describe presently this system as involving a weakly bridged ion **2b** (ref 19), in contrast to a model nonclassical ion "which behaves according to textbook expectations", as was stated originally (ref 16c).

(45) With the exception of the parent peak, only the peaks with an intensity (in parentheses) higher than 15% of the intensity of the base peak are listed.

(46) The conditions used for the present GLC-MS experiments (5% silicone SP2250, 3 m × 3 mm o.d., at 170 °C with 30 mL/min He as carrier gas) ensured a more uniform elution of each component from the column (broader, yet well-resolved peaks) than in the previous work.[14] Whenever the relative intensities of fragment ions differ from those reported,[14] it is believed that the present values are more reliable.

Tautomerism and Dissociation of 4-Arylazo-1-naphthols in Various Solvents[1]

Satoshi Kishimoto,*[2a] Shinya Kitahara,[2a] Osamu Manabe,[2b] and Hachiro Hiyama[2a]

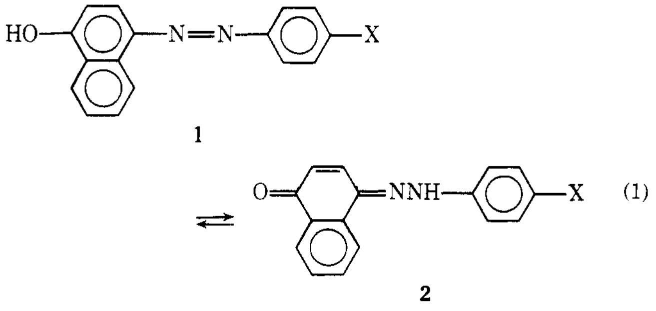
Osaka Municipal Technical Research Institute, Ogimachi, Kita-ku, Osaka-shi, 530, Japan

Received February 23, 1977

The tautomerism of 4-(4′-substituted-phenylazo)-1-naphthol [azo form (1) vs. hydrazone form (2)] is estimated by means of electronic spectra in various solvents. With electron-donating substituents the azo form is stabilized, while electron-withdrawing ones stabilize 2. The azo form is stabilized in pyridine, acetone, ethanol, and methanol, while the hydrazone form predominates in chloroform and acetic acid based on the equilibrium in benzene as standard. The equilibrium fits the Yukawa–Tsuno equation, $\log K/K_0 = \rho(\sigma^0 + r\Delta\bar{\sigma}_R{}^+)$, r and ρ values being determined in the solvent system mentioned above. The proton-donating solvent (chloroform) gives a larger r value; the values for the proton-acceptor solvents are smaller than that of benzene, the standard solvent. In polar aprotic solvents such as dimethyl sulfoxide and *N,N*-dimethylformamide 4-(4′-substituted-phenylazo)-1-naphthol is found to be present as a dissociated form.

Introduction

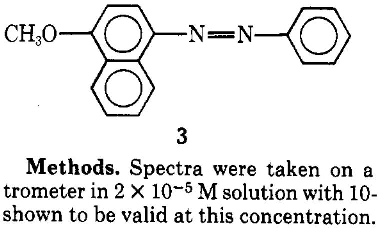
The physical properties of azo dyestuff (e.g., tone, color) are closely related with the tautomerism of the dyes. 4-(4′-Substituted-phenylazo)-1-naphthols (4-azo dyes) prepared by the coupling reaction of 4-substituted benzenediazonium salts with 1-naphthol are profoundly interesting as fundamental azo compounds. They may have two tautomeric isomers, 1 and 2, as shown in eq 1. The tautomeric equilibration is found to depend upon their substituents as well as on solvents.[3-5] Every study reported so far has been qualitatively treated. In this paper we wish to describe experimental results on the tautomerism investigated quantitatively by means of electronic spectra and to discuss the effects of substituents and solvents.



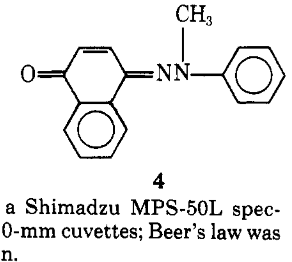
X = OCH_3, CH_3, H, Cl, NO_2

Experimental Section

Materials. The 4-azo dyes[6,7] 1-methoxy-4-phenylazonaphthalene (3)[8] and 1,4-naphthoquinone-*N*-methylphenylhydrazone (4)[9] were prepared according to the literature.



3



4

Methods. Spectra were taken on a Shimadzu MPS-50L spectrometer in 2×10^{-5} M solution with 10-mm cuvettes; Beer's law was shown to be valid at this concentration.

The 1/2 ratios were estimated by assuming that 3 and 4 represent the extreme forms for 1 and 2 and that the spectral shape of 1 and 2 and the ratios of the molecular extinction coefficients of 1 and 2 at the maximum absorptions are constant irrespective of the kinds of substituents when recorded in the same solvent.

Results and Discussion

Figure 1a exhibits the electronic spectra of 4-(4′-methox-

0022-3263/78/1943-3882$01.00/0

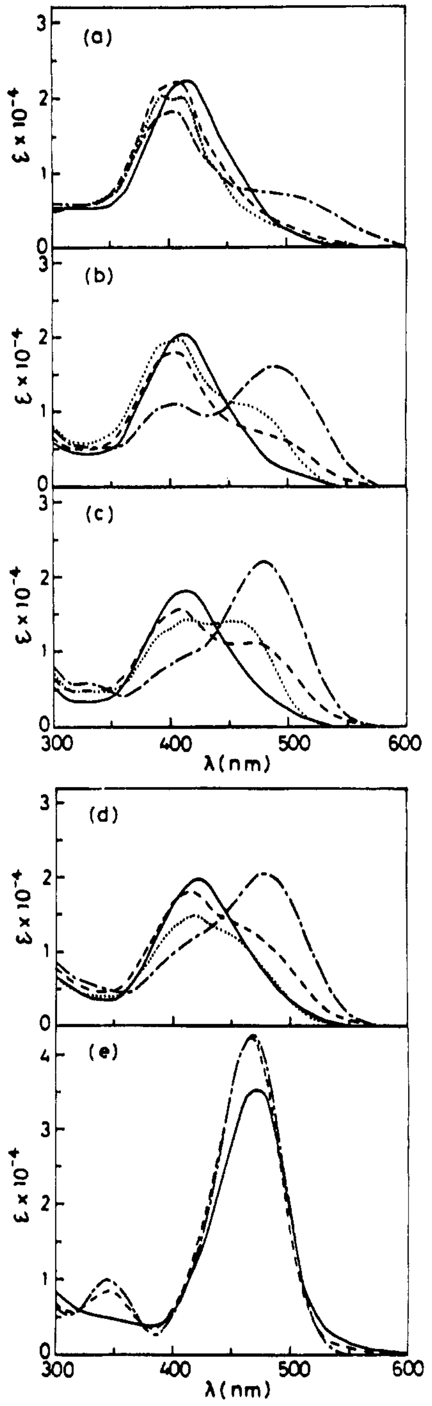


Figure 1. Electronic spectra of 4-(4′-substituted-phenylazo)-1-naphthols: (a) 4′-OCH_3 derivative; (b) 4′-CH_3 derivative; (c) H derivative; (d) 4′-Cl derivative; (e) 4′-NO_2 derivative. Solvents: — C_5H_5N; - - - CH_3OH; ··· C_6H_6; -·-·- CH_3COOH.

yphenylazo)-1-naphthol (4′-OCH_3 derivative) in typical solvents. In pyridine, methyl alcohol, or benzene the sole band appeared at about 410 nm ascribable to the azo form (1);[10] the absorption (~480 nm) due to the hydrazone form (2) was virtually negligible. In acetic acid form 1 was still favored, though the latter peak was observed slightly. The electronic spectra of 4-(4′-methylphenylazo)-1-naphthol (4′-CH_3 derivative) is shown in Figure 1b. Small absorptions at ~480 nm were recognized in methyl alcohol and benzene, whereas in acetic acid this was preferred. The unsubstituted compound, 4-phenylazo-1-naphthol (H derivative), gave the spectra shown in Figure 1c. The band at 480 nm was observed even in methyl alcohol. In benzene the absorbance at 410 nm was approximately equal to that at 480 nm. In acetic acid the longer wavelength absorption predominated. The 4′-chloro derivative gave the spectra exhibited in Figure 1d. The 480-nm absorption appeared as a discernible shoulder even in pyridine. The nitro derivative showed the absorption near 480 nm only in every solvent used (Figure 1e).

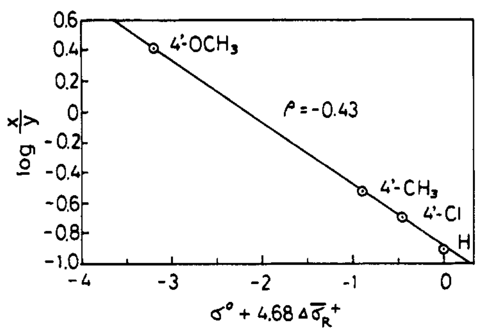


Figure 4. Relation of log K to $(\sigma^0 + r\Delta\bar{\sigma}_R^+)$ in CH_3COOH.

The spectrum of 3 (see Figure 2 of supplementary material) in various solvents exhibits the absorption maximum at 393–405 nm corresponding to the azo form (1); on the other hand the absorption maximum of 4 (460–469 nm, see Figure 3 of supplementary material) may be related to the hydrazone form (2).

Tables I and II exhibit the molecular extinction coefficients (ϵ_{410} and ϵ_{480}) and wavelengths (λ_{410} and λ_{480}) at the absorption maxima of 4-azo dyes, and the ratios of the molecular extinction coefficients ($\epsilon_{410}/\epsilon_{480}$), respectively. From the $\epsilon_{410}/\epsilon_{480}$ values, the 1/2 ratios were determined in the following way.

If the molecular extinction coefficients of 1 (or 2) at about 410 and 480 nm in each solvent are expressed by ϵ_{410}^{azo} and ϵ_{480}^{azo} (or ϵ_{410}^{hyd} and ϵ_{480}^{hyd}), and the mole fractions of 1 and 2 by x and y, respectively, then eq 2 should be:

$$\frac{\epsilon_{410}}{\epsilon_{480}} = \frac{x\epsilon_{410}^{azo} + y\epsilon_{410}^{hyd}}{x\epsilon_{480}^{azo} + y\epsilon_{480}^{hyd}} = \frac{\frac{x}{y}\epsilon_{410}^{azo} + \epsilon_{410}^{hyd}}{\frac{x}{y}\epsilon_{480}^{azo} + \epsilon_{480}^{hyd}} \qquad (2)$$

Substituting a, b, and c for $\epsilon_{410}^{azo}/\epsilon_{480}^{azo}$, $\epsilon_{410}^{hyd}/\epsilon_{480}^{hyd}$, and $\epsilon_{410}^{azo}/\epsilon_{480}^{hyd}$, respectively, eq 2 yields the equation

$$\frac{\epsilon_{410}}{\epsilon_{480}} = \frac{\frac{x}{y}\epsilon_{410}^{azo} + b\epsilon_{480}^{hyd}}{\frac{1}{a}\frac{x}{y}\epsilon_{410}^{azo} + \epsilon_{480}^{hyd}} = \frac{c\frac{x}{y} + b}{\frac{c}{a}\frac{x}{y} + 1} = a - \frac{a - b}{\frac{c}{a}\frac{x}{y} + 1} \qquad (3)$$

Figure 1 shows that the 4′-OCH_3 derivative exists almost 100% as 1 in pyridine, acetone, ethanol, methanol, or benzene. Similarly, the 4′-CH_3 derivative takes only the azo form (1) in pyridine. In this case the $\epsilon_{410}/\epsilon_{480}$ ratio (Table II) is equal to a ($= \epsilon_{410}^{azo}/\epsilon_{480}^{azo}$). On the other hand, the hydrazone form (2) is completely formed for the 4′-nitro derivative (Figure 1e). Therefore, $\epsilon_{410}/\epsilon_{480}$ (Table II) is equal to b ($= \epsilon_{410}^{hyd}/\epsilon_{480}^{hyd}$) in every solvent. The value for chloroform and acetic acid was estimated to be 5.2, the average value for other solvents.[11]

The ratio of the molecular extinction coefficients of 3 to 4 (Table III), $\epsilon_{410}^{azo}/\epsilon_{480}^{hyd} = c$, is listed in Table IV as well.

On the assumption that a, b, and c values are independent of the kind of substituents in the same solvent the 1/2 ratio can be calculated according to eq 3 (Table V). The assumption is valid in the case of 4′-OCH_3 and 4′-CH_3 derivatives in pyridine (Table II).

The logarithm of the equilibrium constant K ($= x/y$) was plotted against the substituent constant to give a linear relationship satisfying the Yukawa–Tsuno equation:[12]

Table I. Molecular Extinction Coefficients (ϵ_{410} and ϵ_{480}) and Wavelengths (λ_{410} and λ_{480}) at the Absorption Maxima of Azo and Hydrazone forms of 4-(4′-Substituted-phenylazo)-1-naphthols in Various Solvents

	substituent									
	4′-OCH$_3$		4′-CH$_3$		H		4′-Cl		4′-NO$_2$	
solvent	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm
pyridine	22.5	418	20.6	413	18.2	414	19.8	423	8.2	410[b]
	4.7	480[a]	4.3	480	6.1	470	9.4	470	34.6	475
acetone	23.0	412	22.0	408	19.0	408	19.1	418	10.5	405[c]
	3.5	480[a]	5.5	480	9.1	470	10.0	470	49.0	462
ethyl alcohol	22.6	413	18.0	410	17.4	410	18.0	420		410[b]
	4.8	480[a]	5.9	480	9.8	470	9.4	470		467
methyl alcohol	22.2	410	17.9	406	15.6	408	18.0	415	9.4	410[b]
	4.6	480[a]	7.3	480	11.2	470	12.4	470	42.2	470
benzene	20.3	412	19.8	408	14.2	412	15.0	412		400[c]
	3.8	480[a]	10.6	470	12.9	470	9.7	470		457
chloroform	18.5	410	11.9	412	11.0	410	13.3	410		405[c]
	6.8	475	13.4	475	20.0	467	17.0	463		463
acetic acid	18.2	408	11.0	410	9.2	410	10.9	410	9.5	410[b]
	7.2	490	16.2	490	22.0	480	20.5	480	42.4	470

[a] The average value (480 nm) of λ_{max} in chloroform and pyridine. [b] The average value (410 nm) for other derivatives in various solvents is listed. [c] The estimated value is shifted according to the absorption of the hydrazone form.

Table II. Ratios of Molecular Extinction Coefficients ($\epsilon_{410}/\epsilon_{480}$) at the Absorption Maxima of Azo and Hydrazone Forms of 4-(4′-Substituted-phenylazo)-1-naphthols in Various Solvents

	substituent				
solvent	4′-OCH$_3$	4′-CH$_3$	H	4′-Cl	4′-NO$_2$
pyridine	4.79	4.79	2.98	2.11	0.237
acetone	6.57	4.00	2.09	1.91	0.214
ethyl alcohol	4.71	3.05	1.78	1.91	0.240[a]
methyl alcohol	4.83	2.45	1.39	1.45	0.223
benzene	5.34	1.87	1.10	1.55	0.250[a]
chloroform	2.72	0.888	0.550	0.782	0.236[a]
acetic acid	2.53	0.679	0.418	0.532	0.224

[a] Values were obtained at arbitrary concentrations because of slight solubility.

Table III. Molecular Extinction Coefficient (ϵ) and Wavelength (λ_{max}) at the Absorption Maximum of 1-Methoxy-4-phenylazonaphthalene and 1,4-Naphthoquinone-*N*-methylphenylhydrazone in Various Solvents

	1-methoxy-4-phenylazo-naphthalene		1,4-naphtho-quinone-*N*-methylphenyl-hydrazone	
solvent	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max} nm
pyridine	11.5	405	9.2	460
acetone	10.3	395	8.8	452
ethyl alcohol	11.0	395	9.8	462
methyl alcohol	11.6	393	10.6	460
benzene	9.8	400	7.1	460
chloroform	10.9	398	8.5	461
acetic acid	19.0	395	10.8	469

$$\log K/K_0 = \rho(\sigma^0 + r\Delta\bar{\sigma}_R{}^+) \qquad (4)$$

where K_0 is the equilibrium constant of the H derivative and ρ and r are arbitrary constants. The $\Delta\bar{\sigma}_R{}^+$ value in eq 4 is defined as $\sigma^+ - \sigma^0$ where the σ^+ value is that given by Brown and Okamoto[13] and σ^0 by Taft et al.[14] For example, Figure 4 exhibits the relation in acetic acid, in which r and ρ were calculated to be 4.68 and −0.43, respectively. Similar relations were obtained for other solvents; r and ρ values for each solvent are listed in Table VI. The log ($-\rho$) was plotted against the log r to give a very good linear inverse correlation.

Table IV. The Values *a*, *b*, and *c* in Various Solvents

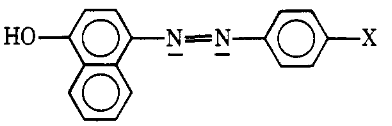
solvent	*a*	*b*	*c*
pyridine	4.79	0.237	1.25
acetone	6.57	0.214	1.17
ethyl alcohol	4.71	0.240	1.12
methyl alcohol	4.83	0.223	1.09
benzene	5.34	0.250	1.38
chloroform	52.[a]	0.236	1.28
acetic acid	5.2[a]	0.224	1.76

[a] The average of the first five values in the column.

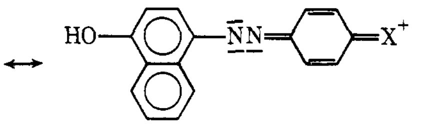
As shown in Table V, the percentage of 1 increased in the following order (eq 5) in each solvent system.

$$4'\text{-NO}_2 < \text{H} \approx 4'\text{-Cl} < 4'\text{-CH}_3 < 4'\text{-OCH}_3 \qquad (5)$$

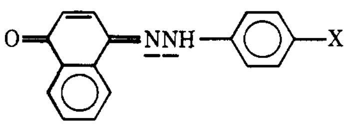
This trend can be explained in terms of the following discussion. The azo group (-N=N-) in 1 is an electron acceptor and the imino group (-NH-) in 2 is an electron donor, so that 1 is stabilized by the more electron-donating 4′-substituent, while an electron-accepting group stabilizes 2. Furthermore, the good linear relation of the equilibrium constant K to sub-



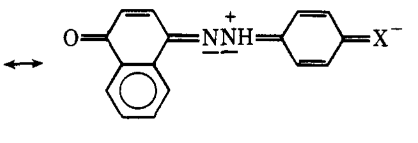
1



(6)



2



(7)

Table V. Ratio (1/2) and Percentage of 1 of 4-(4′-Substituted phenylazo)-1-naphthols in Various Solvents

	substituent									
	4′-OCH$_3$		4′-CH$_3$		H		4′-Cl		4′-NO$_2$	
solvent	1/2	% of 1	1/2	% of 1	1/2	% of 1	1/2	% of 1	1/2	% of 1
pyridine	∞	100	∞	100	5.80	85	2.67	73	0	0
acetone	∞	100	8.28	89	2.36	70	2.05	67	0	0
ethyl alcohol	∞	100	7.11	88	2.21	69	2.51	71	0	0
methyl alcohol	∞	100	4.15	81	1.50	60	1.61	62	0	0
benzene	∞	100	1.81	64	0.777	44	1.33	57	0	0
chloroform	4.07	80	0.611	38	0.271	21	0.499	33	0	0
acetic acid	2.56	72	0.300	23	0.123	11	0.198	17	0	0

Table VI. The Values *r* and *ρ* in Various Solvents

solvent	*r*	*ρ*
acetone	1.45	−1.41
ethyl alcohol	2.07	−1.06
methyl alcohol	1.94	−0.96
benzene	6.85	−0.29
chloroform	17.23	−0.11
acetic acid	4.68	−0.43

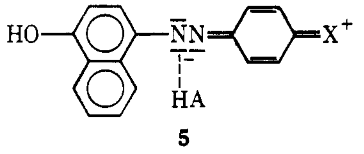
stituent constant as well as the relatively high *r* value suggest a relatively large contribution of the resonance form. That is to say, with an electron-donating group (X) the stability of 1 is increased by the resonance shown in eq 6. On the other hand, the resonance shown in eq 7 raises the stability of 2 on the electron acceptor, such as a nitro group.

The percentage of 1 increased in the following order of solvents.

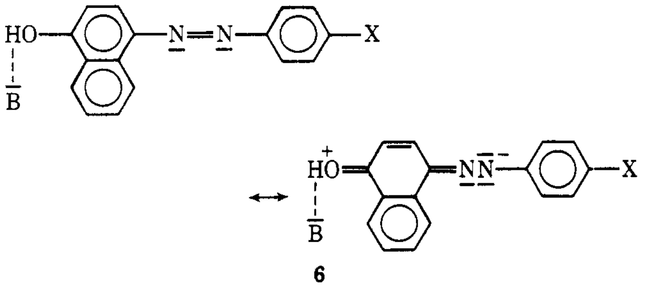
$$\text{acetic acid} < \text{chloroform} < \text{benzene} < \text{methyl alcohol} < \text{ethyl alcohol} \approx \text{acetone} < \text{pyridine} \quad (8)$$

We considered this effect as follows. The tautomeric equilibria are influenced considerably by the ability of external hydrogen bonds between each tautomer and suitable solvents; the tautomers are stabilized to differing degrees by such bonds. The hydroxy group (–OH) in 1 is capable of stronger hydrogen bonding than the imino group (–NH–) in 2 in the proton-acceptor solvents such as pyridine, acetone, and alcohols as compared with benzene.[15] The imino group (–NH–) in 2 is so basic that 2 is more stabilized in the proton-donor solvents such as acetic acid and chloroform than in the proton-acceptor solvents.

The value *r* varied over a wide range depending on the solvent. The proton-donor solvent (HA), chloroform, showed a larger *r* value than benzene. The effect can be ascribed to the stabilization of 1 by the solvation indicated in 5. On the other hand, in the proton-accepting solvent (B) the resonance (6) stands against that of eq 6, therefore the *r* value has become smaller than on benzene.



5



6

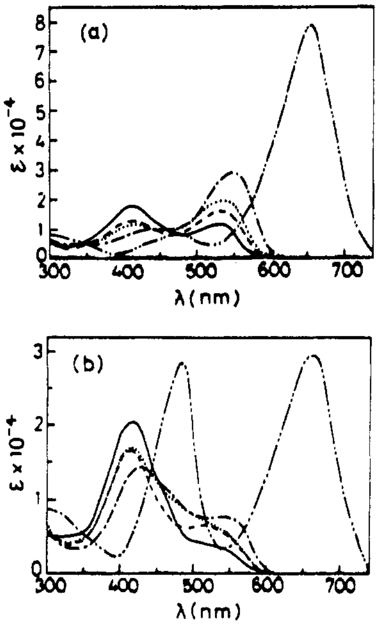
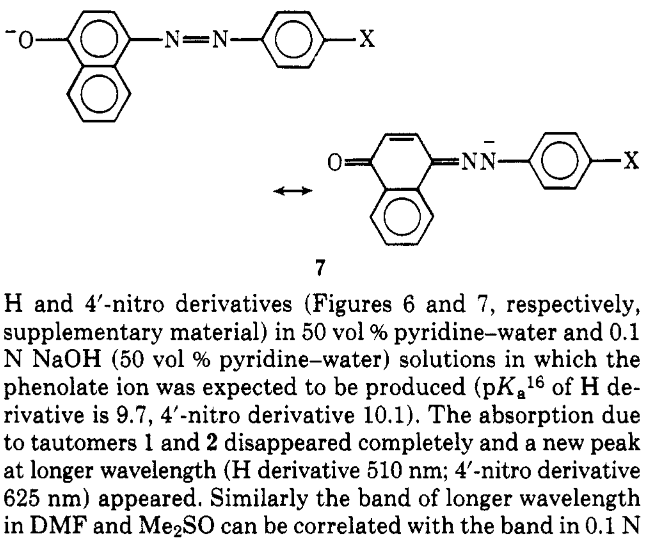


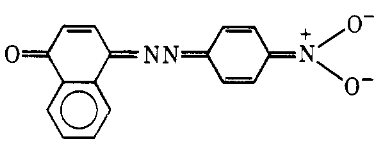
Figure 5. Electronic spectra of 4-(4′-substituted-phenylazo)-1-naphthols in (a) DMF and (b) Me$_2$SO: — 4′-OCH$_3$ derivative; - - - 4′-CH$_3$ derivative; ··· H derivative; –·–· 4′-Cl derivative; –··–·· 4′-NO$_2$ derivative.

The electronic spectra of 4-azo dyes in DMF and Me$_2$SO (Figure 5), respectively, possess the absorption band at comparably longer wavelength than those in the above mentioned seven solvents. In particular the band appeared remarkably well in DMF: 4′-OMe, 530 nm; 4′-Me, 532 nm; H, 535 nm; 4′-Ch, 550 nm; 4′-nitro, 654 nm. These bands may be ascribed to the anionic form 7. Therefore we measured the spectra of H and 4′-nitro derivatives (Figures 6 and 7, respectively, supplementary material) in 50 vol % pyridine–water and 0.1 N NaOH (50 vol % pyridine–water) solutions in which the phenolate ion was expected to be produced (pK_a[16] of H derivative is 9.7, 4′-nitro derivative 10.1). The absorption due to tautomers 1 and 2 disappeared completely and a new peak at longer wavelength (H derivative 510 nm; 4′-nitro derivative 625 nm) appeared. Similarly the band of longer wavelength in DMF and Me$_2$SO can be correlated with the band in 0.1 N NaOH (50 vol % DMF–water) and 0.1 N NaOH–DMF solutions (H derivative, see Figure 8 of supplementary material;



7

4′-nitro derivative, see Figure 9 of supplementary material), and 0.1 N NaOH (50 vol % Me_2SO–water) and 0.1 N NaOH–Me_2SO solutions (H derivative, see Figure 10 of supplementary material; 4′-nitro derivative, see Figure 11 of supplementary material). The remarkable red shift of the band of the 4′-nitro derivative can be ascribed to the lengthening of the conjugated system in the form **8**. Thus, the 4-azo dyes dissolved in DMF and Me_2SO are converted to the phenolate ion (**7**) probably due to the high dielectric constant and high basicity of the solvent. The discussion may be supported from the absorption maximum of the electronic spectra (see Figure 12 of supplementary material) of **3** and **4** in DMF and Me_2SO, which are quite different from the spectra in Figure 5. The longer wavelength absorption is not due to **1** or **2**.



8

Registry No.—1 (X = OCH_3), 3009-53-8; 1 (X = CH_3), 5098-99-7; 1 (X = H), 3651-02-3; 1 (X = Cl), 7252-64-4; 1 (X = NO_2), 5290-62-0; 2 (X = OCH_3), 32159-06-1; 2 (X = CH_3), 36853-51-7; 2 (X = H), 19059-71-3; 2 (X = Cl), 36853-56-2; 2 (X = NO_2), 36853-60-8; **3**, 24390-69-0; **4**, 66881-37-6.

Supplementary Material Available: Figures 2, 3, and 6–12 of electronic spectra of compounds mentioned in the text (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Studies on Coupling Reaction of 1-Naphthol. 6. Part 5: S. Kishimoto, S. Kitahara, O. Manabe, and H. Hiyama, *Nippon Kagaku Zassi*, 1962 (1974).

(2) (a) Osaka Municipal Technical Research Institute; (b) Nagasaki University.

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

(4) A Burawoy, and A. R. Thompson, *J. Chem. Soc.*, 1443 (1953).

(5) E. Fischer and Y. Frei, *J. Chem. Soc.*, 3159 (1959).

(6) S. Kishimoto, T. Hirashima, O. Manabe, and H. Hiyama, *J. Chem. Soc. Jpn.*, **71**, 1195 (1968).

(7) S. Kishimoto, O. Manabe, H. Hiyama, and N. Hirao, *Nippon Kagaku Zassi*, 2132 (1972).

(8) N. Woroshzow, *Chem. Zentralbl.*, 261 (1916).

(9) M. Pherson, *Am. Chem. J.*, **22**, 379 (1899).

(10) R. Kühn and F. Bär, *Justus Liebigs Ann. Chem.*, **516**, 143 (1935).

(11) The estimation seems reasonable based on the Yukawa–Tsuno relation (Figure 4).

(12) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **39**, 2274 (1966).

(13) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). σ^+: OCH_3, −0.778; CH_3, −0.311; H, 0; Cl, +0.114; NO_2, + 0.790.

(14) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959); R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959). We used the following values for σ^0: OCH_3, −0.12; CH_3, −0.15; H, 0; Cl, +0.27; NO_2, +0.82.

(15) Benzene forms π-type hydrogen bonds, being a proton-acceptor solvent, but the bond energy is very small and can be neglected as compared with that of a common hydrogen bond; therefore, benzene was used as a standard solvent.

(16) H. Ikegami and H. Hiyama, *Kagaku To Kogyo* (*Osaka*), **27**, 328, 330 (1953).

Photolysis and Thermolysis of Di-*n*-butylmalonyl Peroxide. Evidence for α-Lactone Intermediates[1]

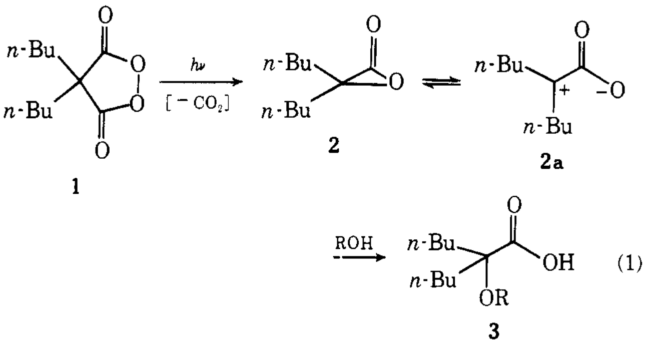
Waldemar Adam*[2] and Rudolf Rucktäschel

Department of Chemistry, University of Puerto Rico, Río Piedras, Puerto Rico 00931

Received April 10, 1978

Photolysis and thermolysis of di-*n*-butylmalonyl peroxide (**1**) afford α-lactone **2** as a reaction intermediate. In a nonprotic solvent such as benzene or *n*-hexane, the α-lactone **2** polymerizes to polyester **5**, while in methanol or ethanol it is trapped nucleophilically in the form of α-alkoxy acid **3**. Some of the α-lactone decarbonylates into 5-nonanone (**4**), but only small amounts decarboxylate to give 4-nonene (**12**), presumably via its carbene. In the thermal decomposition of the malonyl peroxide **1** in methanol and ethanol, α-lactone formation is competed for by solvolytic reaction, leading to a complex product mixture of malonic half-ester **6** and its decarboxylated ester **7**, α, β-unsaturated ester **8**, α-hydroxy ester **9**, malonic acid **10**, and its decarboxylated acid **11**. This solvolytic process predominates over α-lactone formation in the thermolysis of the malonyl peroxide **1** in ethanol.

Several years ago we communicated[3] that photodecarboxylation of di-*n*-butylmalonyl peroxide (**1**) leads to α-lactones **2** as intermediates which can be trapped through their dipolar form **2a** with protic nucleophiles (eq 1). Subsequently, we showed[4] that in a matrix isolated form these elusive reaction intermediates can be preserved to enable infrared characterization. By means of bis(trifluoromethyl) substitution at the α carbon, it was possible to isolate a stable α-lactone by discouraging formation of the dipolar form **2a** through electronic destabilization.[5] Other papers on the chemistry of malonyl peroxides include their vapor phase thermolysis[6] and their solvolysis with primary and secondary alcohols.[7] In this paper, we give a full account of the photo- and thermodecarboxylation of di-*n*-butylmalonyl peroxide.



(1)

Results and Discussion

When a 0.15 M solution of the malonyl peroxide **1** in benzene or *n*-hexane is irradiated at 350 nm in a Pyrex vessel, within 15–20 h its characteristic sharp carbonyl band at 1783 cm^{-1} is replaced by a broad carbonyl band at 1740 cm^{-1}. Removal of the solvent by distillation at reduced pressure afforded a solid residue, mp 138.5–140.5 (benzene) and 146–146.5 °C (*n*-hexane), identified as poly-3,3-di-*n*-butyloxi-

0022-3263/78/1943-3886$01.00/0