TABLE I

THEORETICAL AND EXPERIMENTAL HYPERFINE SPLITTING CONSTANTS (IN GAUSS), CALCULATED CHARGE DENSITIES, AND S-ORBITAL SPIN DENSITIES FOR 2-FURANYLMETHYL RADICAL

		Position of hydrogen				
		3	4	5	6	6
Experimental hfs		8.79 ± 0.03	1.28 ± 0.02	7.87 ± 0.03	13.32 ± 0.03	13.01 ± 0.03
Calculated (INDO)	*a*	9.40	3.29	6.44	14.79	14.67
	b	8.23	2.93	5.59	16.59	16.49

	Atom					
	1	2	3	4	5	6
s-Orbital spin density	0.0011	−0.0180	0.0217	−0.0120	0.0153	0.0340
Charge density[c]	−217.0	+217.9	−43.9	−29.4	+164.9	−97.6

[a] Calculated using the 2–6 bond distance of 1.40 Å; this was the minimum energy calculation. [b] Calculated using the 2–6 bond distance of 1.46 Å. [c] Charge densities × 10^3.

TABLE II

THE *g* VALUES FOR BENZYL, 2-THENYL, AND 2-FURANYLMETHYL RADICALS IN SOLUTION

Radical	Average value of *g*, G[a]
Benzyl	2.00252
2-Furanylmethyl	2.00269
2-Thenyl	2.00312

[a] These values are the average of six individual determinations, with an approximate error of ±0.0001 G.

lated values of the hyperfine splittings summarized in Table I compare very closely with the observed spectrum and emphasize the inequivalence of the methylene protons. Table I also lists the s-orbital spin densities and atomic charge densities in I. The charge densities illustrate oxygen's high electronegativity, and adjacent carbons, 2 and 5, bear significant positive charge. As predicted by valence-bond theory, the largest amount of spin density is concentrated on carbons 6, 3, and 5. This is in agreement with the short 2–6 bond length of 1.40 Å, which indicates the existence of significant 2–6 double bond character and suggests that a large rotational barrier should exist. The calculated π-bond orders (shown in Figure 2) further substantiate this view. The 2–3 and 4–5 bonds have the highest π-bond order (see Ia), but the large π-bond order of the 2–6 bond indicates that resonance hybrids Ib and Ic may be correctly invoked in portraying a valence bond structure. Furthermore, the moderately high π-bond order of the 3–4 bond supports the use of Ic.

The barrier to rotation about the 2–6 bond was calculated. The planar conformation was found to be 25.16 kcal/mol more stable than the conformation in which the plane of the methylene group is perpendicular to the plane of the ring.[16] This large rotational barrier explains the observed spectral inequivalence of the methylene protons at −30° and further demonstrates the strong electronic interaction of the methylene group with the ring.

In conclusion, the inequivalence of the methylene protons in the 2-furanylmethyl radical has been explained, and good agreement with the esr hyperfine splittings has been obtained using an INDO molecular orbital calculation based on the experimental microwave structural data of furan providing that the 2–6 bond (methylene) distance has been optimized.

(16) As expected, the methylene protons become equivalent in this perpendicular conformation.

Registry No.—2-Furanylmethyl, 31902-01-9; benzyl, 2154-56-5; 2-thenyl, 25879-26-9.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through Grant PRF-1495-G2, to the University of Alabama Computing Center for a generous amount of computer time, to Dr. Richard Fessenden of Carnegie-Mellon Radiation Labs for several discussions and circuit diagrams on the nmr tracking system used in this study, to Dr. Paul Krusic for valuable discussions, and to the National Science Foundation for a matching equipment grant for purchase of the Varian E-12 esr spectrometer and Varian Data machine's 620/i computer.

Polar Tautomer Dimerization of Ionic Arylazonaphthols in Water

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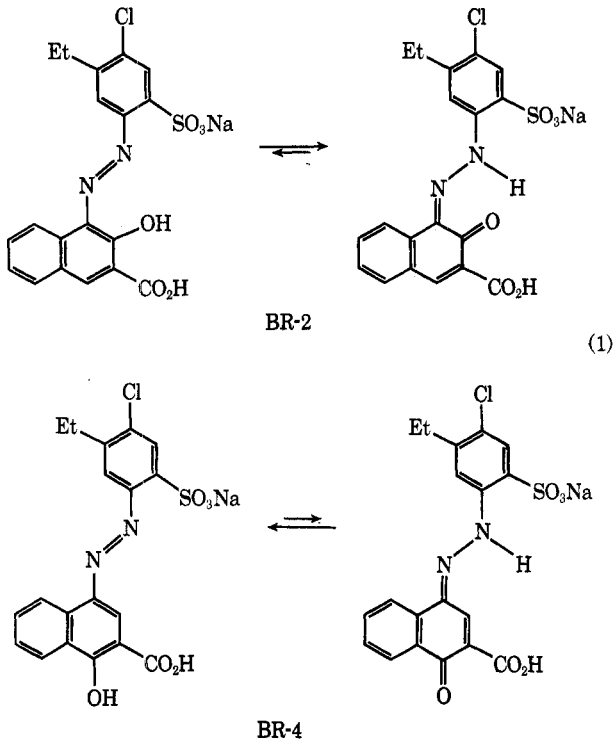
Recent spectroscopic investigations[1] on the aggregation of ionic 1-phenylazo-2-naphthols in aqueous and methanolic solutions have shown the existence of monomer–dimer equilibria in the 10^{-6}–10^{-4} *M* concentration range. The absorption spectra of the ionic hydroxy azo dyes with increasing dye concentration clearly indicate a decrease in the absorptive strength of the main absorption band accompanied by a hypsochromic shift in the peak maxima. The dimer spectra for several ionic 1-arylazo-2-naphthols show a strong H band on the high energy side of the monomer band and a weaker J band on the low energy side of the monomer transition. A study of the aggregation of this class of compounds is complicated by the fact that the molecules can exist in a quinone–hydrazone ⇌ azo–enol tautomeric equilibrium.

In this note we report on the dimerization processes involving the tautomeric species involved in eq 1. The BR-2 compound is a common ionic arylazonaphthol compound known as Bonadur Red. It has recently been spectroscopically shown to exist as a quinone–

(1) (a) A. R. Monahan and D. F. Blossey, *J. Phys. Chem.*, **74**, 4014 (1970); (b) A. R. Monahan, N. J. Germano, and D. F. Blossey, *ibid.*, **75**, 1227 (1971).



hydrazone species.[1] The BR-4 compound favors azo–enol tautomer formation, as do most 1-phenylazo-4-naphthols. The reasons for the shift in position of the tautomeric equilibrium are very complex and it is not the purpose of this note to explain them in detail. However, factors such as solvent stabilization of the 4-OH azo species and lower quinone stability (relative to the 2-OH quinone) of the respective hydrazone species[2,3] tend to favor azo-tautomer formation for the 4-OH dye.

The visible absorption spectra in aqueous acidic solution were measured in the concentration range 10^{-6}–10^{-4} M for the BR-2 and BR-4 molecules. The spectra were analyzed using previously reported computer techniques[1] which separate the monomer and dimer contributions to the spectra at each concentration along with a best fit equilibrium constant, where $K_{eq} = c_d/c_m^2$. Raman spectroscopy was used to determine the relative concentrations of tautomers in each dye system. Hence, the dramatic difference noted in the relative affinities of the two tautomers toward dimerization could be definitively proven for the first time. Possible reasons for the differences are discussed.

Experimental Section

BR-2 and BR-4 were prepared by standard preparative procedures[1b] from 2-amino-4-ethyl-5-chlorobenzenesulfonic acid (American Cyanamid) and 2-hydroxy-3-naphthoic acid (Eastman Organic Chemicals) or 1-hydroxy-2-naphthoic acid (Eastman Organic Chemicals). Purification of the starting materials was as reported previously.[1a] The isolated dyes were recrystallized twice from isopropyl alcohol–water solution, and subsequently vacuum dried prior to use.

Anal. Calcd for BR-2 ($C_{19}H_{13}N_2Na_2O_6SCl \cdot H_2O$): C, 45.8; H, 3.0; S, 6.4; Cl, 7.1; N, 5.6. Found: C, 46.0; H, 2.7; S, 6.2; Cl, 7.0; N, 5.9.

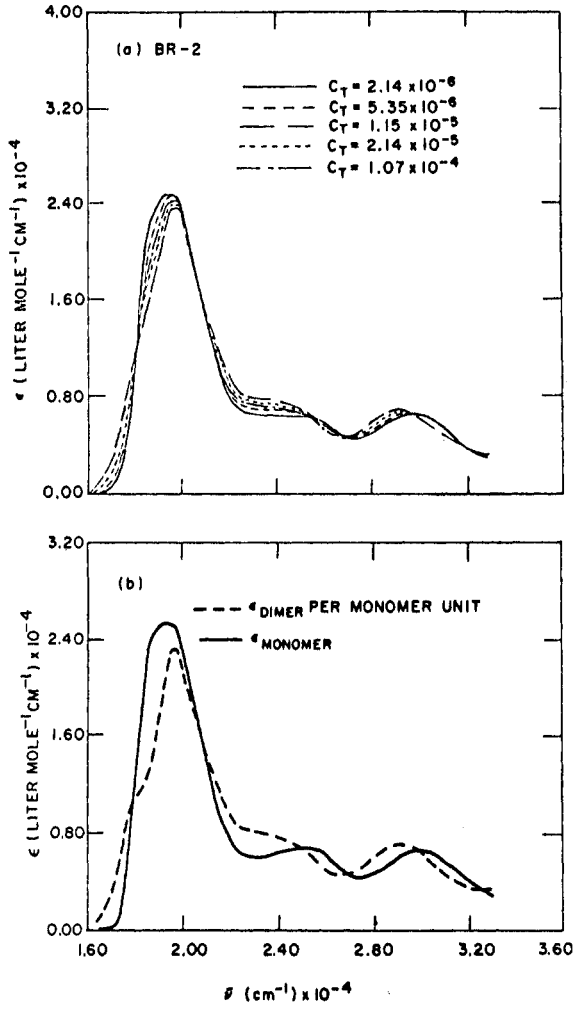


Figure 1.—(a) Concentration-dependent spectra of BR-2 in water at 22°; (b) calculated absorption spectra of pure monomer and dimer species of BR-2 in water.

Anal. Calcd for BR-4 ($C_{19}H_{13}N_2Na_2O_6SCl \cdot H_2O$): C, 45.8; H, 3.0; S, 6.4; Cl, 7.1; N, 5.6. Found: C, 45.7; H, 3.4; S, 6.3; Cl, 6.9; N, 5.5.

All spectroscopic measurements were performed using dye–water solutions having a pH of 3.15 ± 0.05 (10^{-3} M HCl). This pH was chosen in order to maintain a constant ionic strength in addition to ensuring precisely defined monomeric species of BR-2 and BR-4. At a pH of ~3 only the sulfonic acid group remains ionized in both compounds. Further details pertaining to pH effects on the nature of the dye monomer were presented in a previous publication.[1b] Solutions of both dyes in the 10^{-6}–10^{-4} M concentration range were run on a Cary Model 14R automatic spectrophotometer using 0.1-, 1-, 2-, 5-, and 10-cm matched quartz cells.

The molecular configurations existing in the hydrated crystalline phases of the sodium salts of Bonadur Red and its 4-hydroxy analog were determined by Raman spectroscopy. It was not possible to obtain the relative concentrations of the two tautomers in liquid media. Spectra were excited by 6328-Å radiation from a Spectra Physics Model 125 He-Ne laser operating cw at 90 mW. The sample, ~0.1 g of polycrystalline powder enclosed in a small Pyrex bottle, was mounted in a configuration allowing 45° incidence of the exciting light and normal collection of the scattered light. Spectra were analyzed by a Spex 1400 double grating monochromator and detected by a S-20 response photomultiplier. Signal was amplified by conventional phase-sensitive techniques and recorded on a strip chart.

Results and Discussion

The concentration dependence of the absorption spectra of BR-2 and BR-4 are shown in Figures 1a and

(2) G. Gabor, Y. F. Frei, D. Gegiou, M. Kaganowitch and E. Fischer, *Israel J. Chem.*, **5**, 193 (1967).
(3) A. Burowoy and A. R. Thompson, *J. Chem. Soc.*, 1443 (1953).

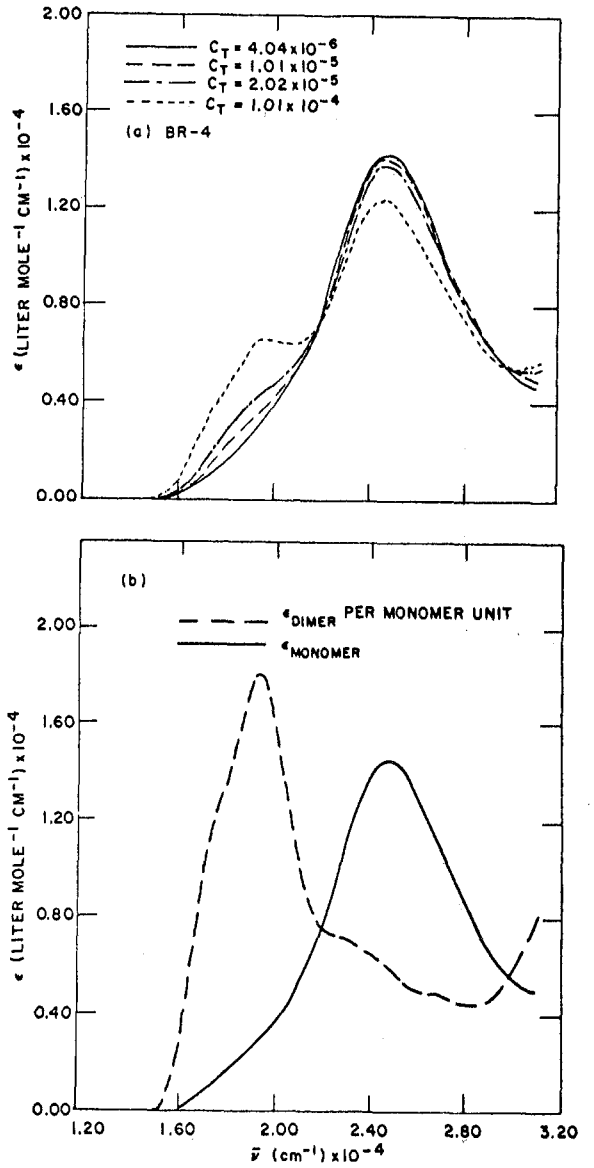


Figure 2.—(a) Concentration-dependent spectra of BR-4 in 22°; (b) calculated absorption spectra of pure monomer and dimer species of BR-4 in water.

2a, respectively. At very dilute concentrations (*ca.* 10^{-6} *M*), BR-2 is characterized by an intense hydrazone transition at 19,400 cm^{-1}. In agreement with previous work[4] on 1-arylazo-4-naphthols, the BR-4 compound in dilute aqueous media shows a band at 24,600 cm^{-1} which is assignable to that of the azo-enol tautomer. The measured concentration dependences of the two compounds under comparable conditions are quite different. With increasing dye concentration, BR-4 shows a decrease in observed extinction coefficient (ϵ) in the region of the azo-monomer transition. This is accompanied by an increase in ϵ near 20,000 cm^{-1}. Isosbestic points appear at 21,900 and 29,800 cm^{-1}. The concentration dependence of BR-2 has been reported previously.[1b] For BR-2, a slight blue shift of the hydrazone monomer transition occurs with increasing concentration. This is accompanied by a measurable decrease in the apparent extinction coefficient of the peak maximum. Isosbestic points appear at 17,900 and 20,600 cm^{-1}.

From each set of data, the pure monomer spectrum, pure dimer spectrum, and the equilibrium constant can be calculated using a least-squares fit computer procedure.[1] In the analysis, it is initially assumed that the monomer concentration c_m and dimer concentration c_d follow the law of mass action

$$K_{eq} = c_d/c_m^2 \quad (2)$$

where K_{eq} is the association (equilibrium) constant for dimer formation. This assumption is valid in the concentration range studied.[1a] The monomer concentration in the calculation is initially assumed to be pure hydrazone for BR-2 and pure azo for BR-4. The best fit was obtained at equilibrium constants of $K_{eq} = (5.55 \pm 0.39) \times 10^4$ l. mol^{-1} for BR-2 and $K_{eq} = (2.05 \pm 0.22) \times 10^3$ l. mol^{-1} for BR-4. The above equilibrium constants are calculated for the overall "pool" of azo plus hydrazone forms. The best fit monomer and dimer spectra are shown in Figures 1b and 2b for the hydrazone tautomeric system and the azo-rich system, respectively. The calculated dimer spectrum for BR-2 has been previously interpreted[1b] in terms of molecular excitation theory which predicts that the energy levels of the monomer species are split in the dimer species. Thus, BR-2 shows a strong H band at 19,700 cm^{-1} and a weaker J band at 18,000 cm^{-1} on the low energy side of the monomer band (19,500 cm^{-1}). The resolved dimer of BR-4 also shows bands at 19,600 cm^{-1} and a shoulder at *ca.* 18,000 cm^{-1}. The striking similarities in the two dimer spectra suggested that only the hydrazone component of the BR-4 molecule was active in the aggregation process. Raman spectroscopy was used to determine how much, if any, hydrazone tautomer existed in BR-4.

The solid state Raman spectra of Bonadur Red and its 4-hydroxy analog are shown in Figure 3 on traces A and B, respectively. The spectrum of azobenzene, trace C, is included for comparison. Inspection of traces B and C reveals a near correspondence in the two dominant Raman frequencies of both materials in the neighborhood of 1140 and 1440 cm^{-1}, respectively. Additional work indicates that this spectral signature is invariant for a wide variety of substituted azobenzenes, azophenols, and azonaphthalenes. Bassignana and Cogrossi[5] have assigned these lines on the basis of infrared spectroscopy of arylazo compounds to a stretching vibration associated with arylazo conjugation and to a stretching vibration of the -N=N- bond, respectively. Accordingly, the spectral signature comprising the intense lines near 1140 and 1440 cm^{-1} is assigned to the azo linkage. This spectral signature does not appear in trace A, the spectrum of BR-2, *i.e.*, there is a weak line near 1440 cm^{-1}, but the complementary line at 1140 cm^{-1} is missing. Furthermore, there are strong lines in the region below 500 cm^{-1} in trace A which do not appear in the spectra of typical arylazo compounds. This lack of an azo linkage spectral signature for Bonadur Red implies that this compound exists as the hydrazone modification in the crystalline state. Conversely, the dominance of the characteristic azo group frequencies in the spectrum of BR-4 is taken to indicate that this compound exists primarily as the azo modification. However, a small (10 ± 5%) hydrazone contribution to the spectrum of

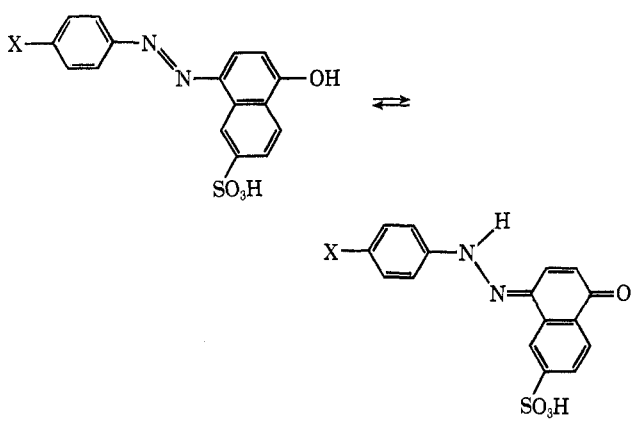
(4) E. Fischer and Y. F. Frei, *J. Chem. Soc.*, 3159 (1959).

(5) P. Bassignana and C. Cogrossi, *Tetrahedron*, **20**, 2361 (1964).

the 4-hydroxy dye is indicated since the lines near 1220, 1360, 1400, 1490, and 1550 cm^{-1} correspond closely with the more intense lines found in the spectrum of the 2-hydroxy compound.

The results using Raman spectroscopy seem to be an accurate indication of the molecular configuration of these compounds in aqueous media (*i.e.*, 10 ± 5% of BR-4 is hydrazone and 100% of BR-2 is hydrazone). If the assumption is made that only 10% of BR-4 (*i.e.*, only the hydrazone) aggregates, then a value of *ca.* 10^4 l. mol^{-1} is obtained for the hydrazone equilibrium constant (K_{eq}^{H}) for dimerization of the BR-4 compound. Differences in K_{eq}^{H} for the hydrazones of BR-2 and BR-4 were not within the scope of this investigation. This is due to the fact that the tautomeric concentrations from the Raman work are highly approximate. However, the approximate nature of the Raman spectra and equilibrium constant calculation are significant in light of the similar dimer spectra for BR-2 and BR-4.

It is somewhat surprising that such a dramatic difference in the capability toward aggregation exists for the two tautomers, and even more surprising perhaps that it has never been previously noted. Zollinger[6] in 1928 qualitatively observed dimer formation in H_2O in molecules of the type



In the concentration range 10^{-6}–10^{-4} *M*, increasing proportions of the above dye, at any concentration, were in the associated form as the electron-withdrawing nature of group X was increased. When X was $-NO_2$, the hydrazone absorption at 20,900 cm^{-1} was preceded by another band at 22,200 cm^{-1} as the concentration was increased from 5.0×10^{-6} to 4.0×10^{-4} *M*. The interpretation of this result, based on our study, is that withdrawing groups favor hydrazone[2] and therefore the molecule containing the NO_2 group (strong withdrawer) allows dimerization to be readily observed.

Reasons as to why this difference in aggregation tendency for the two tautomers exists are highly speculative at present. However, one possible reason for the difference in aggregation tendency for the two species is that there is a dramatic increase in negative charge density or ground-state charge transfer on the naphthyl moiety in going from the azo to the hydrazone tautomer. Therefore, the electrostatic interaction is probably stronger for hydrazone dimer formation relative to azo dimer formation. The extensively reported fact that

(6) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, pp 311–360.

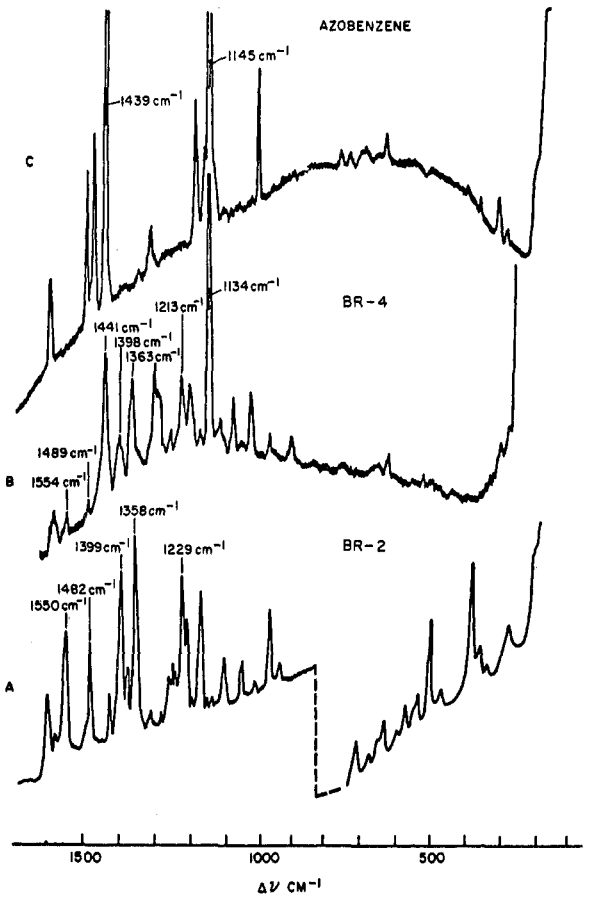


Figure 3.—Solid-state Raman spectra of azobenzene, BR-2, and BR-4.

the hydrazone tautomer is highly favored over the azo tautomer in polar solvents supports the large difference in dipole moment between the two molecules.[2] Past studies have indicated that hydrogen bonding may be important in dimer formation.[1a] This type of bonding would favor hydrazone aggregation, since a C=O · · · HN or =N · · · HN bond is probably stronger than a =N · · · HO bond in the case of the azo tautomer.[7]

Strong support for our result that the polar tautomer is preferential in the self-association of azo dyes can be found in the literature. For example, most of the work to date on the aggregation of azo dyes involves molecules having arylazonaphthol structures containing OH or NH_2 moieties either ortho or para to the azo linkage. Dyes such as Congo Red,[8] Solochrome Violet R,[9] Benzopurprine 4B,[10] and Sky Blue FF[11] fit into this category. On the other hand, Chrysophenine G,[8] which is a large planar ionic "pure" azo dye, does not aggregate to as great an extent. This is apparently because a polar hydrazone tautomer is nonexistent for the Chrysophenine molecule.

Registry No.—BR-2 hydrazone, 30425-34-4; BR-4, azo-enol, 32044-59-0; BR-4 hydrazone, 32044-57-8; water, 7732-18-5.

(7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 499.

(8) E. Coates, *J. Soc. Dyers Colour.*, **85**, 355 (1969).

(9) E. Coates and B. Rigg, *Trans. Faraday Soc.*, **57**, 1637 (1961).

(10) S. E. Sheppard and A. L. Geddes, *J. Amer. Chem. Soc.*, **66**, 1995 (1944).

(11) M. N. Inscoe, J. H. Gould, M. E. Corning, and W. R. Brode, *J. Res. Nat. Bur. Stand., Sect. A*, **60**, 65 (1958).

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Tautomeric Behavior Comparison of 4-Phenylazo-1-naphthol and 1-Phenylazo-2-naphthol Systems by Nuclear Magnetic Resonance

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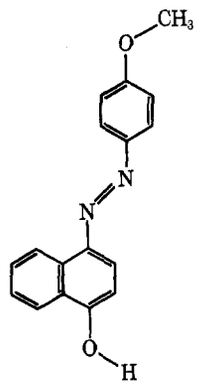
Azo–hydrazone tautomerism of arylazonaphthols has been the topic of many investigations[1-13] subsequent to Zincke's original observations in 1884.[14] However, to date the large difference between the tautomeric behavior of the 4-phenylazo-1-naphthol and 1-phenylazo-2-naphthol systems, which exist in solution predominantly as azo and hydrazone, respectively,[6,7,9,10,13] we believe has not been adequately explained. In this note we give the results of a thermodynamic study designed to provide an incisive explanation for this unusual difference in tautomeric behavior.

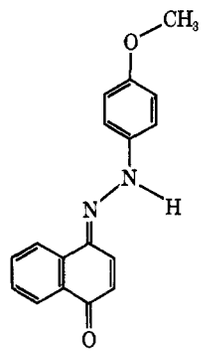
Since inter- and intramolecular proton exchange processes for 4-(*p*-methoxyphenylazo)-1-naphthol (**1**) and 1-(*p*-methoxyphenylazo)-2-naphthol (**2**) (in acetone-d_6) are sufficiently slow so that lifetimes of protons on oxygen and nitrogen are long compared to $1/(\nu_{OH} - \nu_{NH})$,[15] equilibrium constants, as a function of temperature, can be determined for the azo $\rightleftarrows$ hydrazone equilibrium process for these two compounds by nuclear magnetic resonance (nmr).

The proton nmr spectrum of 4-(*p*-methoxyphenylazo)-1-naphthol (**1**) at 10° (acetone-d_6) shows mobile proton resonances at δ 10.19 and 3.59 ppm downfield from tetramethylsilane. On the other hand, the nmr spectrum of 1-(*p*-methoxyphenylazo)-2-naphthol (**2**) at 38°, in the same solvent, shows a single acidic proton resonance at δ 16.2 ppm.

Assignment of the azo OH in **1a** and hydrazone NH in **1b** resonances were made on the basis of the temperature dependence[16] of the azo (~400 mμ) and hydrazone (~480 mμ) electronic transitions, which have been clearly established.[1,4] We found that the transition at ~480 mμ increased in intensity relative to the band at ~400 mμ (in acetone) with decreasing temperature. From this we conclude that the signals at δ 10.19 and 3.59 ppm are due to the hydrazone NH and azo OH protons, respectively.



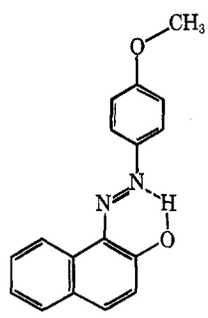
1a



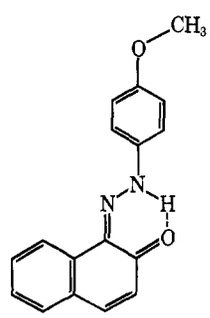
1b

The δ 16.2 ppm resonance in **2** possessed an integrated intensity considerably less than one proton using the time-averaged peri naphthalene proton as an internal standard. Assignment of this signal to the azo OH in **2a** was made on the basis of the visible spectrum temperature dependence using electronic transitions at ~420 and ~500 mμ for monitoring the relative concentrations of azo and hydrazone species,[3,4,11] respectively, as described for **1**.

The intensity of the band at ~500 mμ increased relative to that at ~400 mμ as the temperature was decreased, confirming earlier observations.[10] This temperature-induced equilibrium change indicates the resonance at δ 16.2 ppm to be from the azo OH proton.



2a



2b

Integration of the NH and OH proton resonances in **1** allowed direct evaluation of equilibrium constants for the tautomerization process. In the case of the 1-phenylazo-2-naphthol derivative (**2**), the hydroxyl proton resonance was integrated with respect to the time-averaged peri naphthalene proton (δ 8.65 ppm) for equilibrium constant evaluation. Table I presents

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(2) H. Shingu, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **35**, 78 (1938).
(3) A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).
(4) A. Burawoy and A. R. Thompson, *ibid.*, 1443 (1953).
(5) D. Hadzi, *ibid.*, 2143 (1956).
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(12) V. Bekarek, J. Dobas, J. Socha, P. Vetesnik, and M. Vecera, *Collect. Czech. Chem. Commun.*, **35**, 1406 (1970).
(13) R. L. Reeves and R. S. Kaiser, *J. Org. Chem.*, **35**, 3670 (1970).
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