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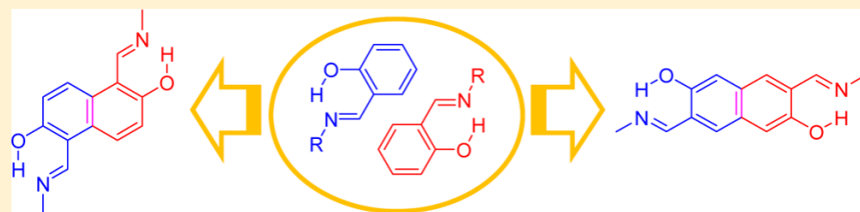
# Mutual Interference between Intramolecular Proton Transfer Sites through the Adjoining $\pi$ -Conjugated System in Schiff Bases of Double-Headed, Fused Salicylaldehydes

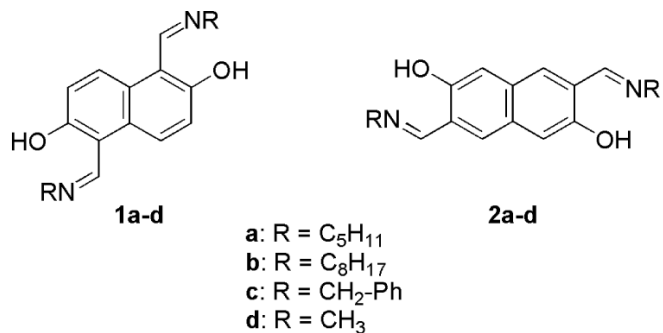
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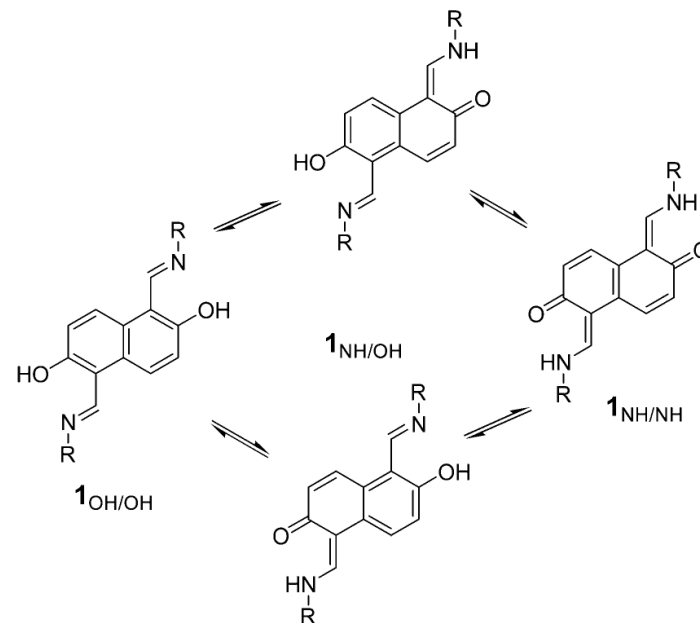
**ABSTRACT:** We synthesized two constitutionally isomeric bis(iminomethyl)-2,6-dihydroxynaphthalenes, namely,  $\alpha,\alpha$ -diimines **1** and  $\beta,\beta$ -diimines **2**, which can be formally represented as fused salicylaldimines with resonance-assisted hydrogen-bonding sites. Spectroscopic data show that the OH/OH, NH/OH, and NH/NH forms of **1** were in equilibrium in solution and that the proportion of the NH-bearing tautomers increased as the solvent polarity increased. The UV spectra of thin solid films of **1** with various types of hydrogen-bonding networks differed from one another, and the spectral profiles were markedly temperature dependent, whereas the spectra of **1** in the molten state showed quite similar profiles. In contrast, **2** existed predominantly as the OH/OH form irrespective of the solvent polarity or crystal packing. Quantum chemical calculations suggest that the difference between the probabilities of intramolecular proton transfer in **1** and **2** can be explained in terms of the interplay between the resonance-assisted hydrogen-bonding sites and the adjoining  $\pi$ -conjugated system.



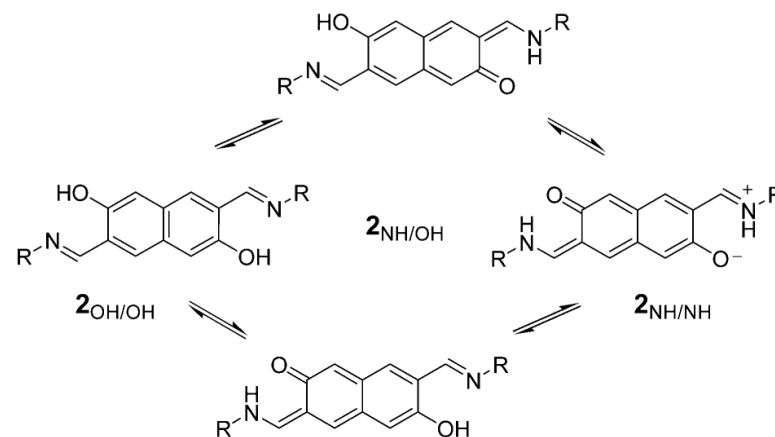
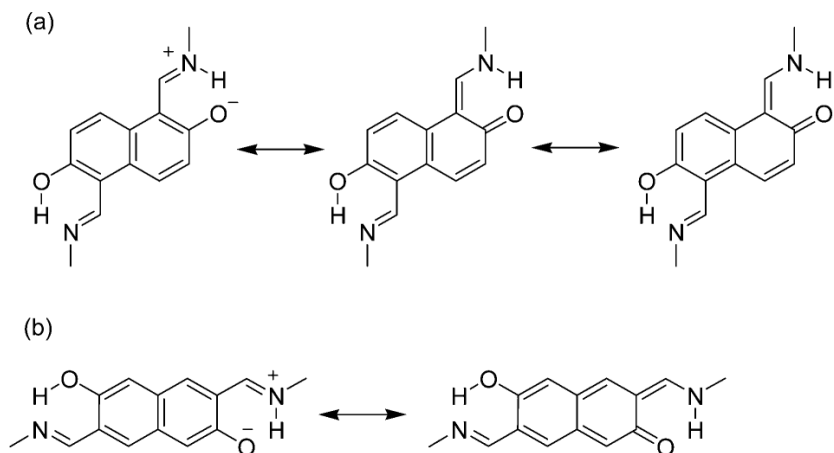


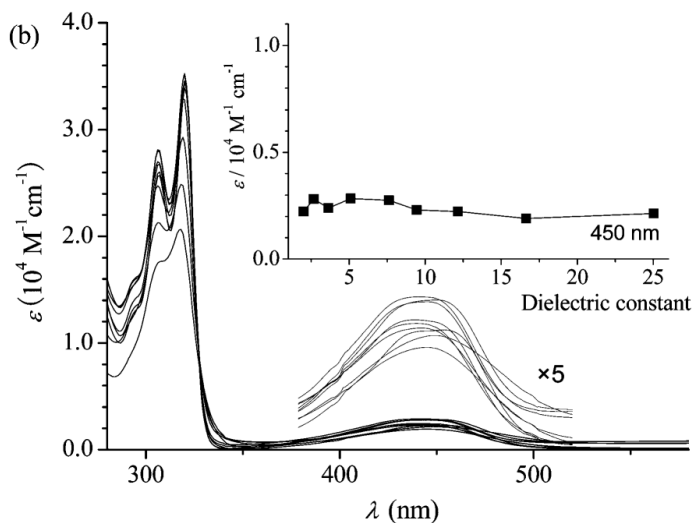
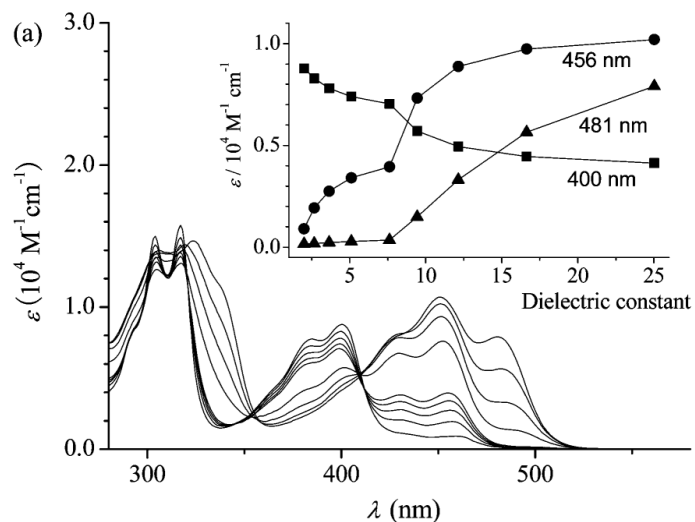
**Figure 1.** Structures of  $\alpha,\alpha$ -diimines **1** and  $\beta,\beta$ -diimines **2**.

**Scheme 1.** Possible Tautomers of  $\alpha,\alpha$ -Diimines **1** and  $\beta,\beta$ -Diimines **2**

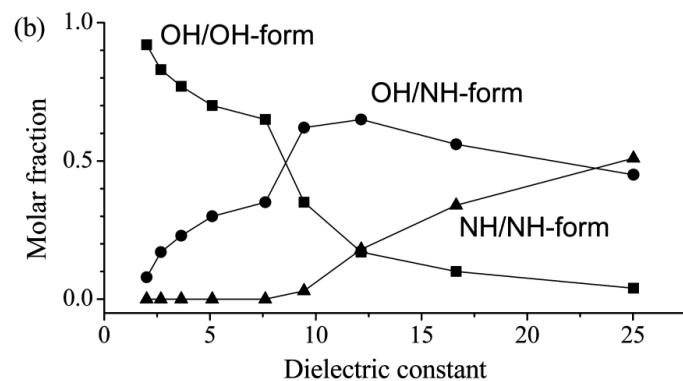
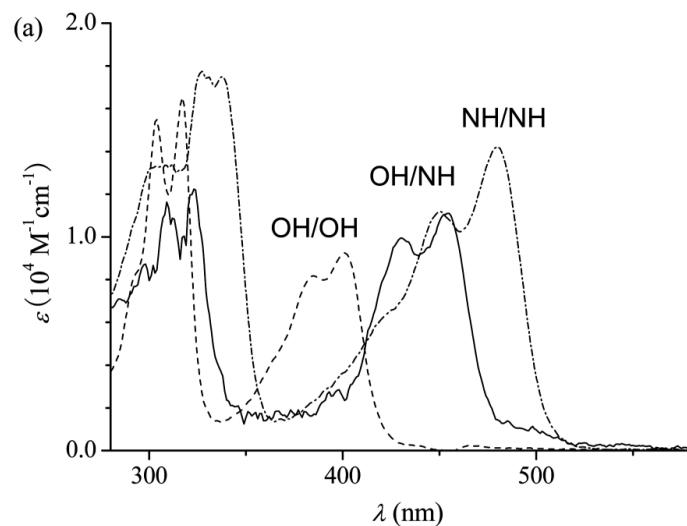


**Scheme 2.** Resonance Hybridization Schemes for the NH/OH Forms of (a)  $\alpha,\alpha$ -Diimines **1** and (b)  $\beta,\beta$ -Diimines **2**





**Figure 2.** UV-vis absorption spectra of (a) **1b** and (b) **2b** in methylcyclohexane, tetrahydrofuran, ethanol, 75/25, 50/50, and 25/75 mixtures of methylcyclohexane and tetrahydrofuran, and 75/25, 50/50, and 25/75 mixtures of tetrahydrofuran and ethanol. Each inset shows the absorbance at selected wavelengths as a function of the dielectric constant of the solvents used.



**Figure 3.** (a) Ideal spectra of the OH/OH, NH/OH, and NH/NH forms of **1b**. (b) Solvent dependence of the molar fraction of each tautomer, calculated on the basis of the ideal spectra.

In contrast, in pure ethanol ( $\epsilon = 25$ ), **1b**<sub>NH/NH</sub> was the major component and the **1b**<sub>OH/OH</sub>/**1b**<sub>NH/NH</sub> and **1b**<sub>NH/OH</sub>/**1b**<sub>NH/NH</sub> population ratios were 0.08 and 0.88, respectively. The difference in solvent composition dependence between **1b**<sub>NH/OH</sub> and

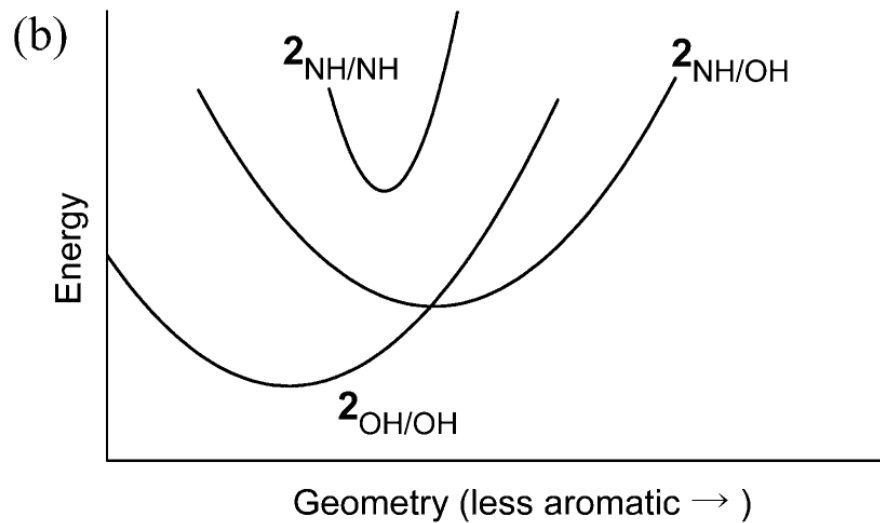
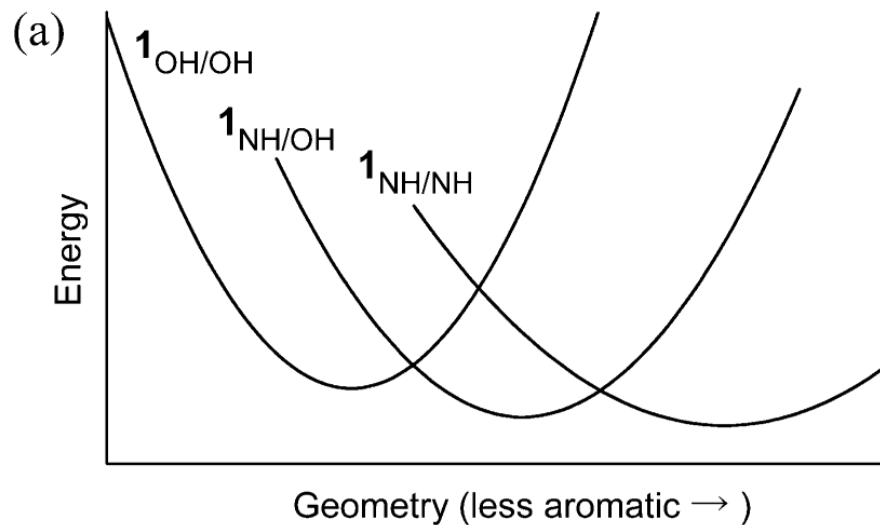
**Table 1. Energies of Tautomers of Aldimines Calculated at the B3LYP/6-311G\*\* Level**

	energy (kJ/mol)		$\lambda_{\max}$ (nm)		$\langle \text{HOMA} \rangle^a$	
	$\epsilon = 1$	$\epsilon = 25$	$\epsilon = 1$	$\epsilon = 25$	$\epsilon = 1$	$\epsilon = 25$
$\mathbf{1}_{\text{OH/OH}}$	(0.0)	(0.0)	360	358	0.70	0.70
$\mathbf{1}_{\text{NH/OH}}$	+6.9	-7.7	396	396	0.39	0.46
$\mathbf{1}_{\text{NH/NH}}$	+20.4	-9.9	441	446	0.00	0.19
$\mathbf{2}_{\text{OH/OH}}$	(0.0)	(0.0)	431	413	0.78	0.77
$\mathbf{2}_{\text{NH/OH}}$	+45.1	+21.2	599	578	0.36	0.60
$\mathbf{2}_{\text{NH/NH}}$	+89.8	+51.9	950	912	0.67	0.66
$\mathbf{3}_{\text{OH}}$	(0.0)	(0.0)	290	286	0.98	0.98
$\mathbf{3}_{\text{NH}}$	+22.8	+4.2	355	360	0.19	0.46

<sup>a</sup>Harmonic oscillator model of aromaticity index averaged over the two six-membered rings.

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{\text{opt}} - R_i)^2$$

mol, respectively; as a result, the relative stabilities of the two tautomers were opposite those observed under in vacuo conditions. We calculated the energetic difference between  $\mathbf{1}_{\text{NH/OH}}$  and  $\mathbf{1}_{\text{NH/NH}}$  to be 2.18 kJ/mol, and from this value, we calculated the  $\mathbf{1}_{\text{NH/OH}}/\mathbf{1}_{\text{NH/NH}}$  population ratio to be 0.83 (at 298 K) when we correctly included the statistical weight of the tautomers. The  $\mathbf{1}_{\text{OH/OH}}/\mathbf{1}_{\text{NH/NH}}$  population ratio was calculated to be 0.02. These values were in good agreement with the observed values (0.88 and 0.08, respectively); therefore, we concluded that this level of calculation was sufficient.



**Figure 10.** Approximate quadratic potential curves for the tautomers of (a) **1** and (b) **2**. Energy is plotted against a geometrical parameter related to the loss of aromaticity.