Solvent Polarity and Hydrogen Bonding Effects on Steric Inhibition of Resonance[1a]

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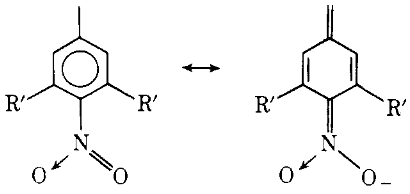
Abstract: Angles of twist from planarity with the ring, θ, in a number of solvents are calculated for the nitro groups in 3,5-dimethyl-4-nitroaniline (**3**) and N,N,3,5-tetramethyl-4-nitroaniline (**4**) from the Braude–Sondheimer relationship $\epsilon/\epsilon_0 = \cos^2 \theta$, where ϵ_0 values are molar absorbancy indexes for the planar reference analogues, 4-nitroaniline (**1**) and N,N-dimethyl-4-nitroaniline (**2**). Angles of twist are shown to decrease with increasing solvent polarity, with type B hydrogen bonding by the amine protons of **3** to HBA (hydrogen bond acceptor) solvents, and with type A hydrogen bonding by HBD (hydrogen bond donor) solvents to the nitro oxygens of **3** and **4**. The solvatochromic comparison method is used to unravel the various effects and determine their magnitudes.

We wish to describe solvent polarity and hydrogen bonding effects on steric inhibition of resonance in some 3,5-dimethyl-4-nitroaniline derivatives. Resonance effects associated with the [$^+R_2N{=}C(1) \rightarrow C(4){=}NO_2^-$] chromophore are maximized when the atoms lie in a common plane, allowing for maximum overlap of p and π orbitals; such effects fall off rapidly as coplanarity decreases. Conversely, steric strains are relieved most easily by rotating the nitro group from planarity with the ring, so that the average angle of twist, θ, is determined by the free-energy balance between these competing forces. Braude and Sondheimer[2] have suggested that the angles of noncoplanarity can be estimated from the relationship

$$\epsilon/\epsilon_0 = \cos^2 \theta \qquad (1)$$

where ϵ is the molar absorbancy index of the sterically hindered compound and ϵ_0 that of a planar reference analogue. Substituent effects on θ in hindered nitrobenzenes and nitroanilines have been described in a classical series of papers by Wepster and co-workers.[3]

In the present study, we have used 4-nitroaniline (**1**) and N,N-dimethyl-4-nitroaniline (**2**) as planar analogues of 3,5-dimethyl-4-nitroaniline (**3**) and N,N,3-5-tetramethyl-4-nitroaniline (**4**). The angles of twist of the nitro groups in **3** and **4** depend on how substituents and solvents influence the relative contributions of canonical structures **3a, 4a** and **3b, 4b** to the total resonance hybrids. The greater the contribution of the quinoidal structures, the greater is the driving force toward coplanarity. Extinction coefficients for **1-4** in a number of representative solvents are assembled in Table I, together with θ values calculated through eq 1, and $\Delta\theta$ values relative to CCl_4.



a b

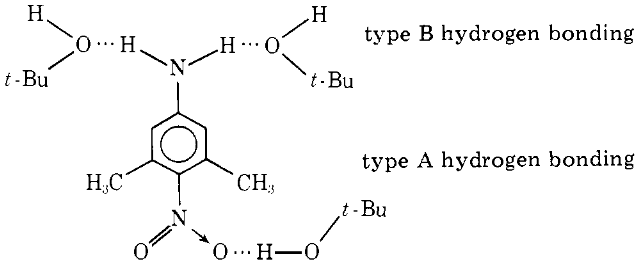
1. R = R′ = H
2. R = CH_3; R′ = H
3. R = H; R′ = CH_3
4. R = R′ = CH_3

Considering first the relative effects of the para substituents in non-hydrogen-bond acceptor (non-HBA) solvents, it is seen that $\theta(4)$ is 6.7° lower than $\theta(3)$ in CCl_4 and 5.9° lower in 1,2-dichloroethane (DCE). The effects are proportional, the $\theta(3)/\theta(4)$ ratio being 1.11 in both solvents. The smaller angles of twist for the nitro of **4** relative to **3** are consonant with the $-N(CH_3)_2$ substituent ($\sigma_p^+ = -1.67$) being a better mesomeric electron donor than $-NH_2$ ($\sigma_p^+ = -1.47$),[4] so that (in valence bond nomenclature) structure **4b** is a more important resonance contributor than **3b**.

The $-5.2°\ \Delta\theta$ (3) and $-4.4°\ \Delta\theta$ (4) in DCE ($\pi^* = 0.807$) relative to CCl_4 ($\pi^* = 0.294$)[5] reflect the effects of solvent polarity-polarizability on steric inhibition of resonance. The rationale here is that increased solvation stabilization of charge-separated canonical structures **3b** and **4b** relative to **3a** and **4a** in the more polar solvent leads to greater contributions of the former structures to the resonance hybrids, with consequently lowered angles of twist.

Type B hydrogen bonding[6] by the amine protons of the hydrogen bond donor (HBD) **3** to HBA solvents can also serve to stabilize canonical structure **3b** by delocalization of the positive charge on the amine nitrogen. Hence, coplanarity of **3** is favored in N-methylpyrrolidone solvent (NMP, $\pi^* = 0.921$, $\beta = 0.741$)[5,7] relative to CCl_4 by virtue of both enhanced polarity and solvent hydrogen bonding effects. Using the concepts of the solvatochromic comparison method,[7] and comparing θ values for **3** and its similarly sterically hindered non-HBD analogue, **4**, we can unravel the multiple solvent effects on $\theta(3)$ as follows.

The effect of increasing solvent polarity is to lower $\theta(4)$ from 59.1° in CCl_4, to 54.7° in DCE, to 54.0° in NMP, a progression which is consistent with the solvent π^* values.[8] From the constant $\theta(3)/\theta(4)$ ratio of 1.11 in CCl_4 and DCE, we can estimate that $\theta(3)_{\mathrm{NMP}}^{\mathrm{ex\text{-}HB}}$ (the hypothetical angle of twist which would be expected for **3** if type B hydrogen bonding to NMP were excluded) should be 59.9°, i.e., 1.11 × 54.0°. Subtracting from this the $\theta(3)_{\mathrm{NMP}}^{\mathrm{obsd}}$ value of 55.8° (obtained from the extinction coefficients and eq 1), we arrive at $\Delta\Delta\theta(3\text{-}4)^{\mathrm{B}}{}_{\leftarrow \mathrm{H_2N}} = -4.1°$ (the hydrogen bonding effect).[9]



hydrogen bonding between
3 and *tert*-butyl alcohol

Table I. Extinction Coefficients and Angles of Twist

1, 4-nitroaniline
2, *N*,*N*-dimethyl-4-nitroaniline
3, 3,5-dimethyl-4-nitroaniline
4, *N*,*N*,3,5-tetramethyl-4-nitroaniline

Solvent	$\epsilon(\mathbf{3})/\epsilon(\mathbf{1})$	$\theta(\mathbf{3})$	$\Delta\theta(\mathbf{3})$	$\epsilon(\mathbf{4})/\epsilon(\mathbf{2})$	$\theta(\mathbf{4})$	$\Delta\theta(\mathbf{4})$
Carbon tetrachloride ($\pi^* = 0.294$)	2410/14 300	65.8°		5320/20 200	59.1°	
1,2-Dichloroethane ($\pi^* = 0.807$)	3630/15 100	60.6°	−5.2°	7250/21 700	54.7°	−4.4°
N-Methylpyrrolidone ($\pi^* = 0.921$, $\beta = 0.742$)	6230/19 700	55.8°	−10.0°	7470/21 600	54.0°	−5.1°
tert-Butyl alcohol ($\pi^* = 0.534$, $\beta = 1.014$, $\alpha = 0.436$)	4990/15 800	55.8°	−10.0°	6240/18 400	54.4°	−4.7°

Table II. Solvent Polarity and Hydrogen Bonding Effects on Angles of Twist

	$-\Delta\theta$ relative to CCl_4 attributable to			
Indicator (solvent)	Increased solvent polarity	Type B hydrogen bonding	Type A hydrogen bonding	Total
3 in DCE	5.2°			5.2°
4 in DCE	4.4°			4.4°
3 in NMP	5.9°	4.1°		10.0°
4 in NMP	5.1°			5.1°
3 in *t*-BuOH	2.4°	4.9°	2.7°	10.0°
4 in *t*-BuOH	2.0°		2.7°	4.7°

The situation in *tert*-butyl alcohol (*t*-BuOH, $\pi^* = 0.534$, $\beta = 1.014$, $\alpha = 0.436$)[5,7,10] is more complex still, since this solvent, in addition to acting as a type B hydrogen bond acceptor at the amine site of **3**, can serve as a type A hydrogen bond donor at the nitro site. As with type B bonding by the amine function, type A bonding to the nitro group stabilizes the quinoidal resonance contributors, with the mechanism here being by delocalization of the negative charge on oxygen.[11]

Again considering first the solvent effect on the angle of twist of the nitro group in **4**, we can evaluate solvent polarity and type A hydrogen bonding effects as follows. From the progression of $\theta(\mathbf{4})$ with π^*,[8] we estimate that $\theta(\mathbf{4})^{\text{ex-HB}}_{t\text{-BuOH}} = 57.1°$. Subtracting from this the observed $\theta(\mathbf{4})$ value of 54.4°, we obtain as the type A hydrogen bonding effect, $\Delta\Delta\theta(\mathbf{4}\text{-}\pi^*)^{\text{A}}{}_{\rightarrow O_2N} = -2.7°$.[9]

We can now use the above results for **4** to unravel solvent polarity and type A and B hydrogen bonding effects on θ (**3**) by evaluating the following additive terms.

$$\theta(\mathbf{3})^{\text{obsd}}_{t\text{-BuOH}} = \theta(\mathbf{3})^{\text{ex-HB}}_{t\text{-BuOH}} + \Delta\Delta\theta(\mathbf{3}\text{-}\pi^*)^{\text{A}}{}_{\rightarrow O_2N} + \Delta\Delta\theta(\mathbf{3}\text{-}\mathbf{4})^{\text{B}}{}_{\leftarrow H_2N} \quad (2)$$

Estimating again that $\theta(\mathbf{3})^{\text{ex-HB}}_{t\text{-BuOH}} = 1.11\theta(\mathbf{4})^{\text{ex-HB}}_{t\text{-BuOH}}$, we obtain 63.4° for the former term. From the observed $\theta(\mathbf{3})$ value of 55.8°, and on the reasonable assumption that type A hydrogen bonding effects are the same for **3** and **4** [i.e., $\Delta\Delta\theta(\mathbf{3}\text{-}\pi^*)^{\text{A}}{}_{\rightarrow O_2N} = \Delta\Delta\theta(\mathbf{4}\text{-}\pi^*)^{\text{A}}{}_{\rightarrow O_2N} = -2.7°$], we obtain by difference the effect of type B hydrogen bonding, $\Delta\Delta\theta(\mathbf{3}\text{-}\mathbf{4})^{\text{B}}{}_{\leftarrow H_2N} = -4.9°$. This value accords well with the −4.1° type B effect estimated earlier for **3** in NMP and the relative HBA basicities (NMP, $\beta = 0.741$; *t*-BuOH, $\beta = 1.014$).[7]

Magnitudes of the various polarity and hydrogen bonding effects on $\theta(\mathbf{3})$ and $\theta(\mathbf{4})$ are summarized in Table II. These estimates are consistent with relative solvent π^* and β values, and with the contributions of solvent polarity and hydrogen bonding terms to effects of steric inhibition of resonance on other solvatochromic properties, such as frequency shifts between solvents.[12]

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References and Notes

(1) (a) Part 7 in the series "The Solvatocromic Comparison Method"; (b) Naval Surface Weapons Center; (c) University of California; (d) Visiting Scientist, UCI, 1976–1977; (e) Federal Junior Fellow, NSWC.

(2) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

(3) Summarized by B. M. Wepster in "Progress in Stereochemistry", Vol. 2, W. Klyne and P. B. D. de la Mare, Ed., Butterworths, London, 1958.

(4) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, N.Y., 1975, p 72.

(5) Solvent polarities in the π^* scale range from 0.000 for cyclohexane to 1.000 for Me_2SO: M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977).

(6) In type B hydrogen bonding, the solvent is HBA base, the indicator is HBD acid. The converse applies in type A hydrogen bonding.

(7) Solvent HBA basicities in the β scale range from 0.000 for non-HBA solvents to 0.990 for hexamethylphosphoramide: M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976); T. Yokoyama, R. W. Taft, and M. J. Kamlet, *ibid.*, **98**, 3233 (1976).

(8) A plot of θ (**4**) in the three solvents vs. solvent π^* values is nicely linear. The regression equation is θ (**4**) $= -8.27\pi^* + 61.51°$, with $r = 0.999$ and SD = 0.2°.

(9) Following the nomenclature system used throughout this series,[1] $\Delta\Delta\theta$ represents an enhanced change in the angle of twist attributable to hydrogen bonding; (**3**–**4**) indicates that the effect is for compound **3** relative to **4** as reference; (**4**–π^*) indicates that the effect is for **4** relative to the π^* scale as reference; the superscript A or B denotes the type of hydrogen bonding which causes the effect;[6] the subscript $\leftarrow H_2N$ indicates that the bonding is by the amine protons of the indicator to the solvent; the subscript $\rightarrow O_2N$ indicates that the bonding is by solvent proton to nitro oxygen of the indicator. This nomenclature system is most useful when unraveling multiple solvent–solute hydrogen bonding effects as in eq 2.

(10) Solvent HBD acidities in the α scale range from 0.000 for non-HBD solvents to 0.980 for MeOH: R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 2886 (1976).

(11) M. J. Kamlet, E. G. Kayser, J. W. Eastes, and W. H. Gilligan, *J. Am. Chem. Soc.*, **95**, 5210 (1973).

(12) For example, we will show in a future paper that the $-\Delta\nu_{\text{max}}$ from CCl_4 to NMP is 0.485 μm^{-1} for **1** and 0.320 μm^{-1} for **3**, i.e., steric inhibition of resonance causes a 0.165 μm^{-1} reduction in the total solvatochromic shift from CCl_4 to NMP. From the solvatochromic equations relating ν_{max} to the solvatochromic parameters, $\nu(\mathbf{1})$ (in μm^{-1}) $= 3.110 - 0.314\pi^* - 0.324\beta$, and $\nu(\mathbf{3})$ (in μm^{-1}) $= 2.866 - 0.180\pi^* - 0.214\beta$, and from the solvent π^* and β values, this 0.165 μm^{-1} can be apportioned as ~0.084 μm^{-1} in the $\Delta s\pi^*$ term and ~0.082 μm^{-1} in the $\Delta b\beta$ term. Hence, considering the approximations involved, the ratio of polarity and hydrogen bonding contributions to the effect of steric inhibition of resonance on the $\Delta\nu$ between the two solvents is not very dissimilar from the ratio of contributions to the $\Delta\theta(\mathbf{3})$ (Table II).