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The Solvatochromic Comparison Method. 3. Hydrogen Bonding by Some 2-Nitroaniline Derivatives

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Abstract: Enhanced solvatochromic shifts in hydrogen-bond acceptor (HBA) solvents for 2-nitroaniline, 2-nitro-*p*-toluidine, and 2-nitro-*p*-anisidine relative to their *N,N*-dimethyl derivatives show good linear correlation with the β-scale of solvent HBA basicities. Reciprocally, the new experimental results are used to expand the data base which supports the β-scale. Solvatochromic comparison between *N*-methyl- and *N,N*-dimethyl-2-nitro-*p*-toluidine shows hydrogen bonding in the former compound to be *intra*molecular in all solvents studied.

In documenting solute-solvent hydrogen-bonding interactions by the solvatochromic comparison method,[2] three important conditions need to be met. (a) First, a plot of corresponding ν_{max} values (or other appropriate spectroscopic or free-energy properties) for two solutes of differing hydrogen-bonding ability in a series of solvents of varying polarity, but wherein hydrogen bonding is excluded, should show a linear relationship with a statistically acceptable correlation coefficient; this establishes how the spectra are influenced by changing solvent polarity. (b) Next, data points representing solvents in which hydrogen bonding occurs should be displaced from the regression line (all in the same direction) by statistically significant amounts; the deviations are presumed to reflect specific solute–solvent interaction effects. (c) Finally, the direction of the displacements should be consistent with the chemistry involved, and the relative magnitudes should reflect a reasonable order of solvent hydrogen-bond donor (HBD)[3] strengths in the case of solvent to solute (type A)[4] bonding or solvent hydrogen-bond acceptor (HBA) strengths where the effects derive from solute to solvent (type B)[4] hydrogen bonds.

In an earlier paper,[5] we employed the method to evaluate the spectral effects of type-B hydrogen bonding by 4-nitroaniline and 4-nitrophenol to a series of HBA solvents and to provide data toward the formulation of a β-scale of solvent hydrogen-bond acceptor basicities. We shall now use the solvatochromic comparison method and the β-scale to assess hydrogen bonding and solvent polarity effects on the electronic spectra of several 2-nitroaniline derivatives.

Hydrogen Bonding by 2-Nitroaniline. Values of ν_{max} in 25 solvents for the $[>^{+}N{=}C(1) \rightarrow C(2){=}NO_2^{-}]$ electronic transitions of 2-nitroaniline (**1**) and *N,N*-dimethyl-2-nitroaniline (**2**) are assembled in Table I and plotted against one another in Figure 1. Compound **1**, but not **2**, can act as an HBD solute. The solvents are of three types: nine which are considered to be neither HBD's or HBA's (or such weak acceptors that their pK_{HB}'s would be anticipated to be lower than -0.5)[6] are represented by open circles in the figure; seven hydrogen-bond bases (p$K_{HB} > 0.7$)[6] are represented by filled circles; and nine amphiprotic R-OH solvents (capable of acting as HBD acids or HBA bases) are represented by triangles.

It is seen that the results fulfill the first requirement for solvatochromic comparison in that excellent linear regression is observed for the data in the nine non-hydrogen-bonding solvents. The least-squares correlation equation is

$$\nu(\mathbf{1})_{max} = 0.874\nu(\mathbf{2})_{max} + 4.51 \text{ kK} \qquad (1)$$

with $n = 9$, r (the correlation coefficient) = 0.991, and SD (the standard deviation) = 0.08 kK [kK (kilokaysers) = cm^{-1}/1000].

Condition b (above) is also easily satisfied by the results in the HBA and amphiprotic solvents. Displacements from the regression line are all in the direction of lower transition energies for the HBD substrate **1** relative to the non-HBD substrate **2** and range from 2.1 to 12.6 SD's of eq 1. The enhanced bathochromic shifts attributable to hydrogen bonding by **1** to the HBA solvents, $-\Delta\Delta\nu(\mathbf{1{-}2})^{B}{}_{\leftarrow H_2N}$,[7] calculated from

$$-\Delta\Delta\nu(\mathbf{1{-}2})^{B}{}_{\leftarrow H_2N} = \nu(\mathbf{1})_{max}{}^{calcd,\ eq\ 1} - \nu(\mathbf{1})_{max}{}^{obsd} \qquad (2)$$

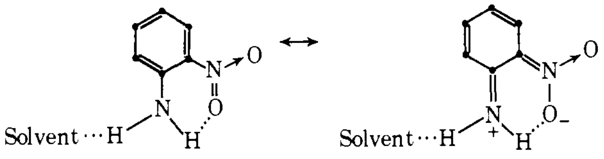
are included in Table I.

An electronic transition from a ground state resembling **1a** to an excited state more like **1b** should lead to strengthening of the type B hydrogen bond in the electronic excitation, so that the bathochromic effect of association between **1** and HBA solvents is as anticipated. The ordering of the $-\Delta\Delta\nu$ values for the amphiprotic solvents, 2-methyl-2-propanol (solvent 101) > 2-propanol (102) > 1-butanol (103) > ethanol (104) > methanol (105) > water (111) confirms that in these solvents also we are dealing *primarily* with type B hydrogen bonding phenomenology, rather than a type A effect (like **1c**).[8]

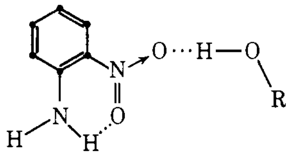
Table I. Solvatochromic Comparisons of Ultraviolet Spectral Data: 2-Nitroaniline (**1**) vs. *N,N*-Dimethyl-2-nitroaniline (**2**); 2-Nitro-*p*-toluidine (**3**) vs. *N,N*-Dimethyl-2-nitro-*p*-toluidine (**4**); 2-Nitro-*p*-anisidine (**5**) vs. *N,N*-Dimethyl-2-nitro-*p*-anisidine (**6**)

Solvent	$\nu(\mathbf{2})_{max}$ kK	$\nu(\mathbf{1})_{max}$		$-\Delta\Delta\nu$ (**1–2**), kK	$\nu(\mathbf{4})_{max}$, kK	$\nu(\mathbf{3})_{max}$		$-\Delta\Delta\nu$ (**3–4**), kK	$\nu(\mathbf{6})_{max}$, kK	$\nu(\mathbf{5})_{max}$		$-\Delta\Delta\nu$ (**5–6**), kK
		Obsd	Calcd[a]			Obsd	Calcd[b]			Obsd	Calcd[c]	
Non-Hydrogen-Bonding Solvents												
1a. Pentane	25.39	26.73			25.00	25.91			23.93	24.39		
1b. Hexane	25.38	26.71			24.88	25.84			23.87	24.33		
2. Cyclohexane	25.23	26.46			24.81	25.71			23.71	24.24		
6. CCl_4	24.67	26.12			24.15	25.19			22.99	23.77		
10. $Cl_2C{=\!=}CHCl$	24.33	25.83			23.84	24.94			22.56	23.56		
20. $ClCH_2CH_2Cl$	23.75	25.32			23.13	24.45			22.00	23.04		
21. CH_2Cl_2	23.81	25.27			23.10	24.36			21.99	23.06		
14. Benzene	24.13	25.57			23.67	24.75			22.42	23.20		
8. Toluene	24.39	25.67			23.80	24.81			22.62	23.38		
Hydrogen-Bond Acceptor Solvents												
11. Ethyl acetate	24.27	25.28	25.72	0.44	23.77	24.45	24.89	0.44	22.62	23.00	23.47	0.47
9. Dioxane	24.11	25.19	25.58	0.39	23.59	24.43	24.74	0.31	22.48	22.98	23.37	0.39
13. Tetrahydrofuran	24.20	25.06	25.66	0.60	23.66	24.21	24.80	0.59	22.62	22.81	23.47	0.59
25. Dimethylformamide	23.41	24.35	24.97	0.62	22.87	23.53	24.15	0.62	21.86	22.38	22.94	0.56
29. Dimethyl sulfoxide	23.18	24.04	24.77	0.73	22.79	23.36	24.09	0.73	21.45	21.96	22.65	0.69
28. *N*-Methylpyrrolidone	23.40	24.24	24.96	0.72	22.87	23.47	24.15	0.68	21.78	22.20	22.88	0.68
19. Triethyl phosphate	23.83	24.65	25.34	0.69	23.30	23.83	24.50	0.67	22.31	22.49	23.25	0.76
Amphiprotic Solvents												
105. Methanol	23.96	24.86	25.45	0.59	23.39	24.04	24.58	0.54	22.45	22.70	23.34	0.64
104. Ethanol	24.16	24.84	25.67	0.79	23.70	24.10	24.83	0.73	22.63	22.76	23.48	0.72
103. 1-Butanol	24.24	24.75	25.70	0.95	23.64	23.98	24.78	0.80	22.67	22.67	23.50	0.83
102. 2-Propanol	24.29	24.81	25.74	0.93	23.84	24.00	24.94	0.94	22.68	22.62	23.51	0.89
101. 2-Methyl-2-propanol	24.27	24.71	25.72	1.01	23.81	23.90	24.92	1.02	22.63	22.53	23.48	0.95
107. Ethylene glycol	23.28	24.37	24.86	0.49	22.68	23.53	24.00	0.47	21.67	22.24	22.80	0.56
106. 2-Phenylethanol	23.47	24.44	25.02	0.58	22.88	23.59	24.16	0.57	21.75	22.28	22.86	0.58
109. Benzyl alcohol	23.27	24.41	24.85	0.44	22.68	23.59	24.00	0.41	21.65	22.26	22.79	0.53
111. Water	22.97	24.42	24.59	0.17	22.49	23.70	23.84	0.14	21.46	22.38	22.65	0.27

[a] Eq 1. [b] Eq 4. [c] Eq 5.



1a **1b**



1c

Finally, we demonstrate that the effects reported here are completely consistent with the chemistry involved (condition c above) by relating the magnitudes of the enhanced solvatochromic effects to the β-scale of solvent HBA basicities.[5] The plot is shown in Figure 2.

It is seen that the $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})^{B}{}_{\leftarrow H_2N}$ results show good linear correlation with the $\beta_{1\text{-}5}$ values.[5,10] The least-squares regression equation is

$$-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})^{B}{}_{H_2N} = 1.017\beta_{1\text{-}5} - 0.025\text{ kK} \qquad (3)$$

with $n = 16$, $r = 0.959$, and SD = 0.065 kK. Considering that the $-\Delta\Delta\nu$ values are based on *differences* between observed values and values calculated from the earlier correlation equation, it deserves mention that the standard deviation from eq 3 is not much more than the probable experimental error in a ν_{max} determination. The low value of the intercept (0.025 kK, compared with 0.065 kK SD of eq 3 and 0.08 kK SD of antecedent eq 1) is also noteworthy. It lends reassurance that the experimental results do indeed reflect a *direct proportionality* between the enhanced spectral shifts and the corresponding solvent HBA strengths.

2-Nitro-*p*-toluidine and 2-Nitro-*p*-anisidine as Hydrogen-Bond Donors. Exactly parallel effects to the above are seen in solvatochromic comparisons of 2-nitro-*p*-toluidine (**3**) with *N,N*-dimethyl-2-nitro-*p*-toluidine (**4**) and of 2-nitro-*p*-anisidine (**5**) with *N,N*-dimethyl-2-nitro-*p*-anisidine (**6**) (data in Table I). As before, the results in the non-hydrogen-bonding solvents show excellent linear regression; the least-squares correlation equations are

$$\nu(\mathbf{3})_{max} = 0.813\nu(\mathbf{4})_{max} + 5.56\text{ kK} \qquad (4)$$

with $n = 9$, $r = 0.996$, and SD = 0.06 kK and

$$\nu(\mathbf{5})_{max} = 0.702\nu(\mathbf{6})_{max} + 7.57\text{ kK} \qquad (5)$$

with $n = 9$, $r = 0.990$, and SD = 0.08 kK.

Also as before, deviations of the results in HBA and amphiprotic solvents from the non-hydrogen-bonding solvent correlation equations ($-\Delta\Delta\nu$ values also assembled in Table I) are statistically significant, amounting to 2.3 to 17 SD's of eq 4, and 3.4 to 12 SD's of eq 5, respectively.

The $-\Delta\Delta\nu(\mathbf{3}\text{–}\mathbf{4})^{B}{}_{\leftarrow H_2N}$ and $-\Delta\Delta\nu(\mathbf{5}\text{–}\mathbf{6})^{B}{}_{\leftarrow H_2N}$ results are plotted against $\beta_{1\text{-}5}$ values in Figure 3. Again linear correla-

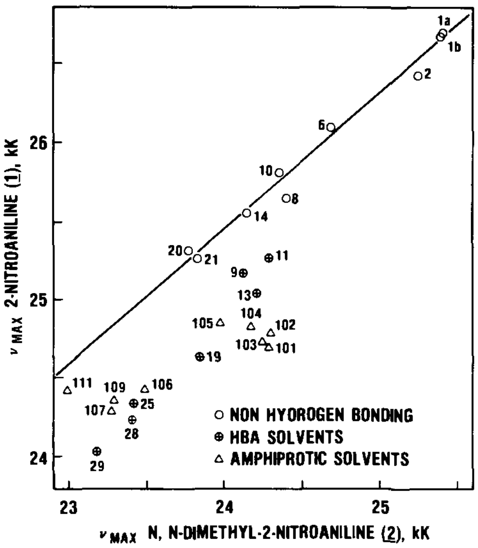


Figure 1. Spectral data for 2-nitroaniline (**1**) plotted against results in corresponding solvents for *N,N*-dimethyl-2-nitroaniline.

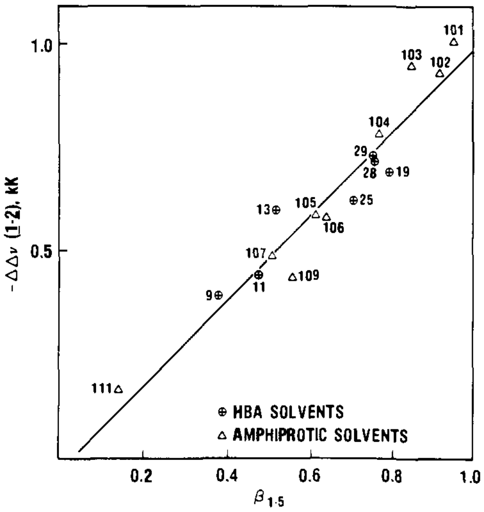


Figure 2. Enhanced solvatochromic shifts for 2-nitroaniline (**1**) relative to *N,N*-dimethyl-2-nitroaniline (**2**) plotted against $\beta_{1\text{-}5}$ values for HBA solvents.

tions are good; the least-squares regression equations are

$$-\Delta\Delta\nu(\mathbf{3\text{–}4})^{B}{}_{\leftarrow H_2N} = 1.025\beta_{1\text{-}5} - 0.06\ \text{kK} \qquad (6)$$

with $n = 16$, $r = 0.963$, and SD = 0.063 kK and

$$-\Delta\Delta\nu(\mathbf{5\text{–}6})^{B}{}_{\leftarrow H_2N} = 0.812\beta_{1\text{-}5} + 0.11\ \text{kK} \qquad (7)$$

with $n = 16$, $r = 0.959$, and SD = 0.05 kK. In these instances also, the regression lines are sufficiently close to the origin to lend confidence that the experimental results reflect direct proportionality.

These findings for the 2-nitroaniline derivatives correspond quite closely to the pattern reported earlier in the solvatochromic comparison of 4-nitroaniline with its *N,N*-diethyl derivative.[5] We believe this to be the first demonstration of solvent effects on an $[^{+}X{=}C(1) \rightarrow C(2){=}Y^{-}]$ electronic transition which parallel those on the corresponding $[^{+}X{=}C(1) \rightarrow C(4){=}Y^{-}]$ transition.

Hydrogen Bonding in *N*-Methyl-2-nitro-*p*-toluidine. In addition to showing the presence of such effects, the solvatochromic comparison method can also serve to demonstrate the absence of significant solvent-solute hydrogen-bonding interactions. In Figure 4, spectral data for *N*-methyl-2-nitro-*p*-toluidine (**7**) are plotted against $\nu_{\max}$ values for the *N,N*-dimethyl derivative **4** in the same solvents as before.

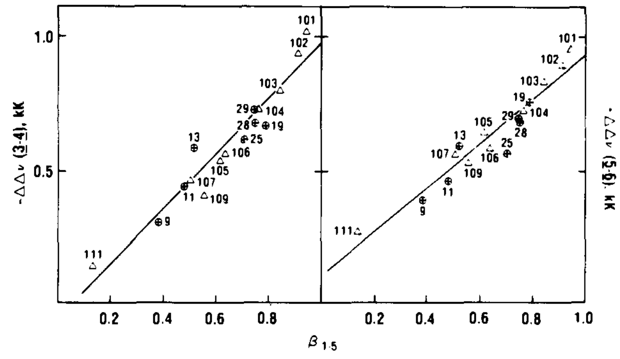


Figure 3. Enhanced solvatochromic shifts for 2-nitro-*p*-toluidine (**3**) and 2-nitro-*p*-anisidine (**5**) relative to their *N,N*-dimethyl derivatives **4** and **6** plotted against $\beta_{1\text{-}5}$ values for HBA solvents.

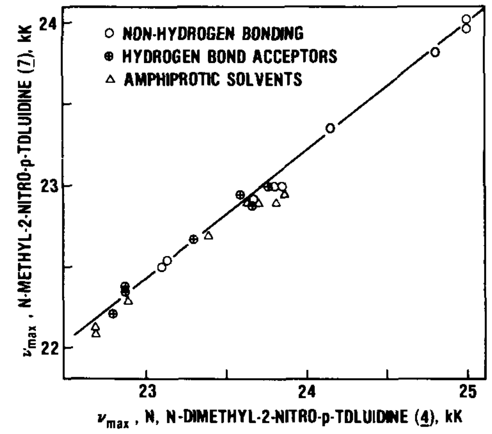


Figure 4. Spectral data for *N*-methyl-2-nitro-*p*-toluidine (**7**) plotted against results in corresponding solvents for *N,N*-dimethyl-2-nitro-*p*-toluidine.

Table II

Property	Correlation eq	Eq for β
Series 6. Enhanced solvatochromic shift for 2-nitroaniline relative to *N,N*-dimethyl derivative	3	$\beta_6 = [-\Delta\Delta\nu(\mathbf{1\text{-}2}) + 0.025]/1.017$
Series 7. Enhanced solvatochromic shift for 2-nitro-*p*-toluidine relative to *N,N*-dimethyl derivative	6	$\beta_7 = [-\Delta\Delta\nu(\mathbf{3\text{-}4}) + 0.06]/1.025$
Series 8. Enhanced solvatochromic shift for 2-nitro-*p*-anisidine relative to *N,N*-dimethyl derivative	7	$\beta_8 = [-\Delta\Delta\nu(\mathbf{5\text{-}6}) - 0.11]/0.812$

It is seen that, in marked contrast to the earlier examples, the data points for the non-hydrogen-bonding solvents (open circles) and the HBA solvents (filled circles) are essentially colinear. The least-squares correlation equation for these 16 data points is

$$\nu(\mathbf{7})_{\max} = 0.782\nu(\mathbf{4})_{\max} + 4.32\ \text{kK} \qquad (8)$$

with $r = 0.997$ and SD = 0.04 kK. The data points for the amphiprotic solvents (triangles) show minor displacements toward lower $\nu(\mathbf{7})_{\max}$ values. Although not statistically sig-

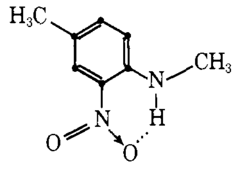
Table III. The β-Scale of Solvent HBA Basicities

Solvent	$\beta_{1\text{-}5}$	(n)	β_6	β_7	β_8	$\beta_{1\text{-}8}$	(n)
9. Dioxane	0.386 ± 0.006	(4)	0.408	0.361	0.344	0.379 ± 0.018	(7)
11. Ethyl acetate	0.481 ± 0.005	(5)	0.457	0.488	0.443	0.474 ± 0.014	(8)
13. Tetrahydrofuran	0.523 ± 0.013	(5)	0.615	0.634	0.591	0.556 ± 0.042	(8)
25. Dimethylformamide	0.710 ± 0.009	(4)	0.634	0.663	(0.554)[a]	0.690 ± 0.027	(6)
29. Dimethyl sulfoxide	0.752 ± 0.035	(5)	0.742	0.771	0.714	0.749 ± 0.029	(8)
28. *N*-Methylpyrrolidone	0.754 ± 0.019	(5)	0.732	0.722	0.702	0.741 ± 0.023	(8)
19. Triethyl phosphate	0.797 ± 0.042	(4)	0.703	0.712	0.800	0.772 ± 0.052	(7)
101. 2-Methyl-2-propanol	0.95	(1)	1.018	1.054	1.034	1.014 ± 0.032	(4)
102. 2-Propanol	0.92	(1)	0.939	0.976	0.961	0.949 ± 0.020	(4)
103. 1-Butanol	0.85	(1)	0.958	0.839	0.887	0.884 ± 0.032	(4)
104. Ethanol	0.77	(1)	0.801	0.771	0.751	0.773 ± 0.014	(4)
105. Methanol	0.62	(1)	0.604	0.585	0.652	0.615 ± 0.020	(4)
106. 2-Phenylethanol	0.64	(1)	0.595	0.615	0.579	0.607 ± 0.020	(4)
107. Ethylene glycol	0.51	(1)	0.506	0.517	0.554	0.522 ± 0.016	(4)
109. Benzyl alcohol	0.56	(1)	0.457	0.458	0.517	0.498 ± 0.040	(4)
111. Water	0.14	(1)	0.192	0.195	0.197	0.181 ± 0.020	(4)

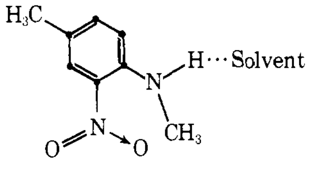
[a] Datum not included in average.

nificant, these may reflect a small but real $-\Delta\Delta\nu(\mathbf{7}\text{-}\mathbf{4})^{A}{}_{\rightarrow O_2N}$ effect.[7,9]

These results indicate that hydrogen bonding in **7** is essentially intramolecular (**7a**) with little evidence of intermolecular bonding to strong HBA solvents (**7b**) as suggested earlier.[11]



7a

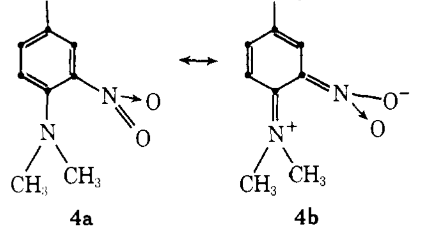


7b

On this basis, the $-\Delta\Delta\nu$ values reported above for **1**, **3**, and **5** are considered to reflect one inter- and one intramolecular hydrogen bond. In this respect the *o*-nitro derivatives differ from 4-nitroaniline, for which enhanced solvatochromic shifts were shown to result from two roughly equal-strength hydrogen bonds to HBA solvent molecules.[13]

Solvent Polarity Effects. The present solvatochromic comparisons illustrate a further effect which merits discussion. From the slopes in eq 4 and 8, the influences of changing solvent polarity on electronic transition energies for 2-nitro-*p*-toluidine (**3**), its *N*-methyl derivative (**7**), and its *N,N*-dimethyl derivative (**4**) are in the ratio 0.813:0.781: 1.000; i.e., $\nu(\mathbf{4})_{\max}$ shifted significantly more to the red in more polar non-hydrogen-bonding solvents than $\nu(\mathbf{3})_{\max}$ or $\nu(\mathbf{7})_{\max}$. The similar dependences on solvent polarity for **3** and **7** probably derive from the fact that strong intramolecular hydrogen bonds keep the amine and nitro groups very nearly coplanar in all solvents. In **4**, however, the ortho substituents are twisted from planarity, as evidenced by $\epsilon(\mathbf{4})_{\max}/\epsilon(\mathbf{3})_{\max}$ values of 0.39 to 0.56,[11] with the exact angles of twist determined by competing steric and resonance effects in the various solvents.

Canonical structures like **4b**, contributing more to the **4a–4b** resonance hybrid in the more polar solvents, could lead to lower angles of twist. Superimposed on the normal effect of increasing solvent polarity whereby charge-separated electronic excited states are stabilized relative to ground states, the decreasing angles of twist could account for the accentuated polarity effect on $\nu(\mathbf{4})_{\max}$.



4a **4b**

Expanding the Data Base for the β-Scale of Solvent HBA Basicities. In addition to using the β values to rationalize hydrogen-bonding effects on the properties which we correlate in the present series of papers, we will attempt to use the new experimental information reciprocally to expand the data base which supports the β values. Hence, as additional properties are correlated, they will lend increasing reliability to the β-scale of solvent HBA basicities.

Toward this end, we calculate for each $-\Delta\Delta\nu$ datum in the present paper an individual $\beta_n{}^m$ value[14] which would cause that datum to lie directly on the regression line correlating the $-\Delta\Delta\nu$ values with β. If the regression line in series n, for example, is defined by the correlation equation $-\Delta\Delta\nu = A(\beta_{1\text{-}5}) + B$, then the β value for solvent m is given by $\beta_n{}^m = (-\Delta\Delta\nu - B)/A$. Results from five series of properties were averaged to obtain the β values in Part I;[5] series 6 to 8 are shown in Table II. Individual β values are assembled in Table III, together with the new averages which we represent by $\beta_{1\text{-}8}$.

The additional data in Table III for the amphiprotic solvents are of particular importance to our construction of the β-scale because, of the very many sets of properties we have correlated, there have been relatively few where the $\Delta\Delta$ values in the R-OH solvents reflect differential hydrogen-bond acceptor, but not differential hydrogen-bond donor abilities of the solvents.[15] The fact that the amphiprotic solvent data points in Figure 4 lie so close to the non-HBD solvent correlation line suggests that type-A hydrogen bonding effects by protic solvents to *o*-nitro oxygens are either nil or quite similar for 2-nitroanilines and their *N*-alkyl and *N,N*-dialkyl derivatives [i.e., $-\Delta\Delta\nu(\mathbf{3}\text{-}\mathbf{4})^{A}{}_{\rightarrow O_2N} \approx 0$]. In choosing a preferred set of β values for the R-OH solvents in our previous paper,[5] we assumed that there were no effective differential type-A effects between 4-nitroaniline and *N,N*-diethyl-4-nitroaniline. The close correspondence between this earlier set and the current β values supports that earlier assumption.

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References and Notes

(1) (a) Toyama University; (b) University of California; (c) N.S.W.C.
(2) Part II: R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 2886 (1976).

(3) There has been some confusion in the hydrogen-bonding literature as to whether the terms *donor* and *acceptor* refer to the proton or the electron pair. In the present series of papers, HBD (hydrogen-bond donor) and HBA (hydrogen-bond acceptor) refer to donation or acceptance of the proton.

(4) M. J. Kamlet, E. G. Kayser, R. R. Minesinger, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, **36**, 3852 (1971). In type-A hydrogen bonding the solvent acts as proton donor and the solute as proton acceptor; the converse applies in type-B bonding.

(5) Part I: M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).

(6) R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *J. Am. Chem. Soc.*, **91**, 4801 (1969).

(7) The notation $-\Delta\Delta\nu(\mathbf{1}\text{–}\mathbf{2})^{B}{}_{\leftarrow H_2N}$ signifies a bathochromic displacement for **1** relative to **2**, caused by type-B hydrogen bonding *by* the amine proton to the solvent. See footnote 8 of part I[5] for an outline of this system, which makes nomenclature much less confusing and cumbersome when several types of hydrogen bonding with concomitant spectral effects occur simultaneously.

(8) Strengthened type-A hydrogen bonds by the R–OH solvents to the nitro oxygens of **1** compared with **2** (like **1c**) could also account for bathochromic displacements,[9] but where hydroxylic solvents participate in type-A effects, the converse $-\Delta\Delta\nu$ ordering is observed, with the greater solvatochromic displacements in methanol and water and the lesser shifts in 2-methyl-2-propanol and 2-propanol.[2,4]

(9) Such enhanced hydrogen bonding to nitro has been demonstrated for *N,N*-diethyl-4-nitroaniline relative to 4-nitroanisole.[4] However, solvatochromic comparisons of **4** and **7** with 4-nitroanisole suggest that hydrogen bonding to the *o*-nitro group of **4** or **7** is very much weaker than to the *p*-nitro group of *N,N*-diethyl-4-nitroaniline.

(10) The subscript indicates that data from five sets of properties were averaged to obtain the β value.

(11) T. Yokoyama, *Aust. J. Chem.*, **27**, 915 (1974). This earlier work illustrates the pitfall in using our previously reported method[12,13] for finding $\Delta\Delta\nu$ values where solvent polarity effects are not similar for the substrates being compared.

(12) M. J. Kamlet, R. R. Minesinger, and W. H. Gilligan, *J. Am. Chem. Soc.*, **94**, 4774 (1972).

(13) R. R. Minesinger, E. G. Kayser, and M. J. Kamlet, *J. Org. Chem.*, **36**, 1347 (1971).

(14) In the term, $\beta_n{}^m$, the superscript indicates that we are dealing with solvent *m* (solvent numbering is the same in all papers of this series); the subscript indicates that we are dealing with property series *n*.

(15) For example, the $-\Delta\Delta\nu$ value for 4-nitrophenol (**8**) relative to 4-nitroanisole (**9**) probably includes a term due to hydrogen bonding by the phenol proton to the R–OH oxygen and a term due to bonding by the R–OH proton to the phenol nitro group, i.e., $-\Delta\Delta\nu(\mathbf{8}\text{–}\mathbf{9})_{\text{total}} = [-\Delta\Delta\nu(\mathbf{8}\text{–}\mathbf{9})^{B}{}_{\leftarrow HO}] + [-\Delta\Delta\nu(\mathbf{8}\text{–}\mathbf{9})^{A}{}_{\rightarrow O_2N}]$.[5]

Phenolic and Ketonic Tautomers in Polycyclic Aromatic Hydrocarbons[1]

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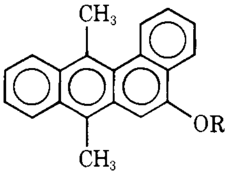
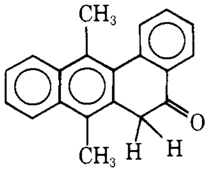
Abstract: 5-Hydroxy-7,12-dimethylbenz[*a*]anthracene (**2**) has been shown to exist as a mixture with the tautomer, 7,12-dimethylbenz[*a*]anthracen-5(6*H*)-one (**3**). By chromatography almost pure **2** and **3** have been isolated and their spectral properties recorded. The tendency of a number of other hydroxy derivatives of polycyclic aromatic hydrocarbons to either exist as, or react as, their ketonic counterparts is described. Steric hindrance due to intramolecular overcrowding is postulated to account for the stability of the keto form. The tendencies of a number of hydroxy compounds to react with methanolic hydrogen chloride at room temperature to form methyl ethers and with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones are used as a measure of the relative reactivity of the keto forms. The possibility that keto forms of polycyclic aromatic hydrocarbons may be metabolites of importance in understanding the carcinogenic activities of the hydrocarbons is raised. Improved syntheses of a number of methoxy derivatives in the benz[*a*]anthracene series are described as well as a new method of cleaving these methoxy compounds to phenols by heating with sodium sulfide.

In a recent communication[3] the synthesis of 5-methoxy-7,12-dimethylbenz[*a*]anthracene[4] (**1**) and its conversion into a mixture of 5-hydroxy-7,12-dimethylbenz[*a*]anthracene (**2**) and its ketonic tautomer, 7,12-dimethylbenz[*a*]anthracen-5-(6*H*)-one (**3**) was described.[5] In the present paper improved syntheses of **1**, 5-methoxybenz[*a*]anthracene[6] (**4**), 5-methoxy-7-methylbenz[*a*]anthracene[7] (**5**), and 5-methoxy-12-methylbenz[*a*]anthracene[8] (**6**) are described, as are the syntheses of 6-methoxy-7,12-dimethylbenz[*a*]anthracene (**7**) and 6-methoxy-12-methylbenz[*a*]anthracene (**8**) and their conversion to the corresponding hydroxy compounds, **7a** and **8a**. In addition, the general question of the existence of ketonic forms of phenols of polycylic aromatic hydrocarbons is discussed, as well as the possible involvement of the keto forms in the carcinogenic activity of DMBA.



1 (R = CH_3)
2 (R = H)



3

The syntheses of the required methoxy compounds, **1**, **4**, **5**, and **6**, were carried out as indicated in Scheme I.

The syntheses of **10** and **11** proceeded in almost quantitative yield by reaction of 1-methoxynaphthalene with **9** and **9a** as described.[9] The reduction of lactones such as **10** and **11** has been effected by many different reducing agents. To summarize our experience in this area, we recommend reduction with zinc and formic acid[10] as generally the most reliable for small- and large-scale reactions. In the present cases, almost quantitative yields of **12** and **13** were obtained.

The yields on conversion of acids **12** and **13** via **15** and **17** to **4** and **6**, respectively, were very high. Thus, the overall route is superior to previous routes which involved cyclization of acids to benzanthrones followed by reduction of the latter to benz[*a*]anthracenes.[11] Big improvements (especially in large-scale runs) in the conversions of **12** and **13** to **1** and **5**, respectively, were also made,[11,12] largely because higher yields of the methyl ketones **18** (82%) and **19** (97%) were obtained by two modifications in the reactions of carboxylic acids with methyllithium: in one, the addition of methyllithium was made to the acid instead of the reverse;[11,12] in the other, the reaction mixtures thus obtained were added to water instead of the reverse. Each of these factors cuts down on the tendency to form tertiary alcohol instead of the desired methyl ketone.

The synthesis of **7** is outlined in Scheme II. The requisite, 2,4-dibromo-1-naphthylamine[13] (**20**) was converted by diazotization into 4-bromonaphth[1,2-*d*][1,2,3]oxadiazole[14] (**21**) (shown in ionic form in Scheme II for convenience), which was