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Substituent Effects on Spectral Properties of Protonated Azo Compounds

G. L. EIAN and Charles A. KINGSBURY

Department of Chemistry, University of Nebraska, Lincoln, Nebraska, U.S.A.

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The effect of a remote substituent upon the NMR and visible spectra, and upon hydrogen-deuterium exchange in certain phenylazophenol systems is reported. Electron donating substituents uniformly lower the NMR chemical shift function, $\Delta\delta$, cause bathochromic shifts in the visible spectra, and increase the rate of deuterium exchange. Correlations between the above measurements and also with Hammett constants are reported. In particular the logarithm of $t_{1/2}$ is linear with δ_o, the chemical shift of the position adjacent to the position attacked by deuterium.

Correlations involving the nuclear magnetic resonance (NMR) parameters with the several types of linear free energy parameters have been successful for many classes of organic compounds.[1] In recent years the substituent effects on NMR spectra have been reported for pyridines,[2,3] anilines,[4] amines,[5] aldoximes,[6] phenols,[7,8] alkylbenzenes,[9] styrenes,[10] stilbenes,[11] diphenylethylenes,[12]

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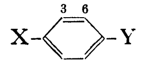
phenylacetylenes,[13a] esters,[13b] phosphines,[14] acetophenones,[15] pyrazoles[16] and other heterocycles,[17] metalocenes,[18,19] protonated benzophenones,[20] and carbonium ions.[21] In other works, the effect of substituent upon coupling constants in various fluorine systems has been investigated.[22,23]

In particular, the NMR spectra of many types of cations have been investigated, principally by Olah and co-workers.[24] In other work, the chemical shift of the proton donated to the various substituted acetophenones has been correlated with σ^+ parameters.[25]

The deshielded character of certain chemical shifts in carbonium ion systems has been related to the charge delocalization of the ion.[26] In cyclopropenium ions additive ring current effects also have a profound effect on the chemical shifts of the various groups.[27]

One salient feature of the NMR spectrum of *para* substituted benzene derivatives is illustrated in Scheme I.[28]



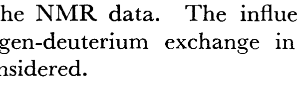
X	Y	δH_A	δH_B	$\Delta\delta$
NO_2	CH_2CN	8.25	7.57	−0.68
NO_2	$NH\text{-}CH_3$	8.10	6.55	−1.55
CH_3O	CH_3	6.80	7.05	+0.25
CH_3	CHO	7.02	7.83	+0.81

Scheme I

As noticed by many of the workers cited above, when there is a significant resonance interaction between X and Y, the difference in chemical shift between H_a and H_b (hereafter termed $\Delta\delta$) is large. Little resonance interaction produces a much smaller $\Delta\delta$.

Corio and Dailey[29] have interpreted the chemical shifts of the various ring protons in terms of the same resonance and inductive parameters of a given substituent which enhance or detract from aromatic substitution rates. Jackman[30] however considers the anisotropy of the various groups to be important.

The subject of this work is a series of 4-phenylazophenols (**1**), and their protonated analogues (**1H**). The effect of the remote substituent (ring B)



(**1**)

on the chemical shift function ($\Delta\delta$) of ring A is of interest. In this context if should be noticed that any anisotropy effects of X will have little effect on the NMR spectrum of ring A. In other cases the visible spectra in system **1H** will be compared to the NMR data. The influence of X on the hydrogen-deuterium exchange in ring A will also be considered.

Results and Discussion

Table I lists the NMR data for the series of azophenols (**1**). The function $\Delta\delta$(ring A) is rather small for electron donating substituents and is largest for $X{=}NO_2$, but the total change is small, and rather irregular. The effect of substituent of the protons of its own immediate ring are of course much larger. In the two extreme cases, $X{=}CH_3O$ and $X{=}NO_2$, $\Delta\delta$(ring B) is large and of opposite sign.

The chemical shift of the *ortho* protons of both rings is relatively constant at δ *ca.* 7.8. This absorption, however, occurs rather far downfield compared to certain stilbenes, in which analogous protons absorb at δ *ca.* 7.0—7.3. Similarily, the chemical shifts of methyls substituted in the 2′

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Table 1. Proton chemical shifts of substituted phenylazophenols[a] (**1**)

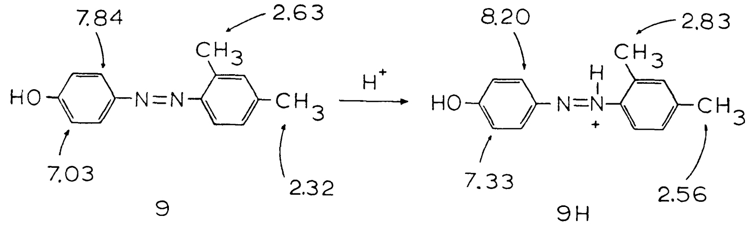
Compd.	X	Ring A			Ring B			CH_3
		δ_o[b]	δ_m[c]	$\Delta\delta$	δ_o[b]	δ_m[c]	$\Delta\delta$	
2	4'-OCH_3	7.86	7.04	0.82	7.83	7.02	0.81	
3	4'-CH_3	7.89	7.06	0.83	7.86	7.24	0.62	2.35
4	H	7.92	7.06	0.86		complex		
5	4'-Br	7.89	7.06	0.83	7.92	7.78	0.14	
6	4'-NO_2	7.86	6.99	0.87	7.87	8.24	−0.37	
7	3'-CH_3	7.90	7.05	0.85				2.41
8	2'-CH_3	7.89	7.04	0.85				2.67
9	2',4'-$(CH_3)_2$	7.84	7.03	0.81				2.63; 2.32
10	2',5'-$(CH_3)_2$	7.85	7.01	0.84				2.60; 2.32
11	2',6'-$(CH_3)_2$	7.83	7.02	0.81				2.30

a) Spectra were made of 5 mol% solutions in acetone. Chemical shifts are in ppm downfield from an internal TMS standard.
b) δ_o refers to the protons *ortho* to the azo group.
c) δ_m refers to the protons *meta* to the azo group.

Table 2. NMR[a] and visible[b] spectral parameters of the protonated phenylazophenols (**1H**)

	X	Ring A			Ring B			δ_{CH_3}	λ_{max} (mμ)	ε ($\times 10^{-4}$)
		δ_o[c]	δ_m	$\Delta\delta$	δ_o[c]	δ_m	$\Delta\delta$			
2H	4'-OCH_3	8.14	7.30	0.84	8.21	7.34	0.87		488	4.28
3H	4'-CH_3	8.22	7.32	0.90	7.99	7.52	0.47	2.53	472	4.16
4H	H	8.28	7.35	0.93		complex			461	3.42
5H	4'-Br	8.30	7.37	0.93	7.97	7.86	0.11		477	4.28
6H	4'-NO_2	8.42	7.42	1.00	8.29	8.59	−0.30		473	5.11
7H	3'-CH_3	8.27	7.35	0.92				2.53	466	3.46
8H	2'-CH_3	8.25	7.33	0.92				2.83	472	3.36
9H	2',4'-$(CH_3)_2$	8.20	*ca.* 7.33	*ca.* 0.87				2.83; 2.56	481	3.60
10H	2',5'-$(CH_3)_2$	8.26	*ca.* 7.36	*ca.* 0.90				2.81; 2.52	481	3.05
11H	2',6'-$(CH_3)_2$	8.26	*ca.* 7.38	*ca.* 0.88				2.67	464	2.79

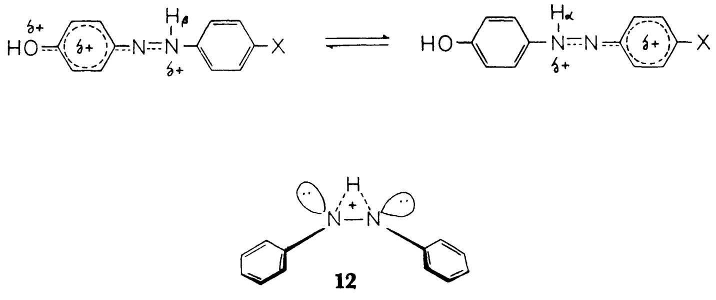
a) Solutions were prepared by dissolving 100 mg of substrate in 1 m*l* of trifluoroacetic acid containing 29.4% sulfuric acid by weight. Chemical shifts are taken relative to tetramethylsilane as 0 ppm.
b) The same solvent mixture was used for the visible spectra (*vide supra*).
c) δ_o refers to the aromatic protons *ortho* to the azo group, in ppm.



position (ring B) occur considerably downfield of the methyls in the 3' or 4' positions. The azo group may be somewhat electron withdrawing compared to the unsaturated carbon analogue in the stilbene system, but more likely the anisotropy of the azo group has a deshielding influence on the neighboring *ortho* protons.

The data for the protonated azophenols are listed in Table 2. Relevant chemical shifts for a typical compound and its conjugate acid are given above. The particular position of protonation is given for illustration purposes only.

Every group in the cation is deshielded compared to its counterpart in the unprotonated structure, as the result of the interplay of resonance, inductive and anisotropy effects. The downfield absorption of the 2' methyl in **9H** compared to the 4' methyl is suggestive that the anisotropy of the azo function persists in the cation form. Other types of cations shown the opposite trend, the 4' methyl



Scheme II

being downfield compared to the 2′ methyl.[20)]

As Table 2 shows the change in $\Delta\delta$ (ring A) is now larger and quite regular. The increased electron demand of the cationic system renders it more sensitive to the various substituents. Moving from electron donating substituents X to electron withdrawing substituents involves a steady increase in $\Delta\delta$. In fact a plot of $\Delta\delta$ *vs.* σ^+ of the remote substituent is reasonably linear (Fig. 1).

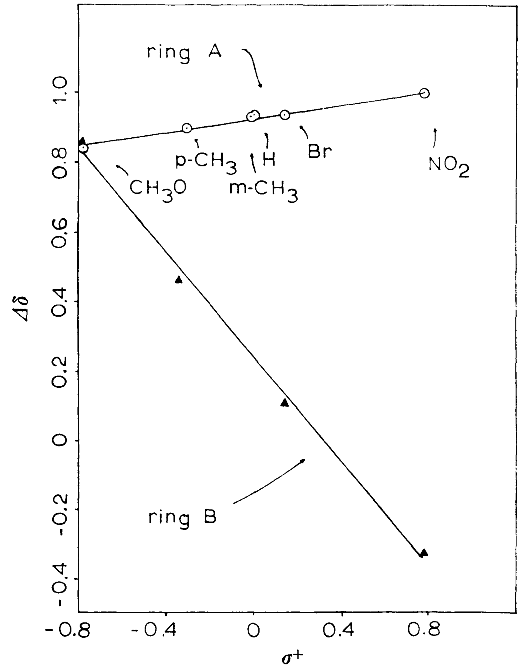


Fig. 1. A plot of the NMR chemical shift function, $\Delta\delta$ *vs.* Okamoto-Brown σ^+ constants.

For ring B, again the effect of the substituent is much greater. The trend of $\Delta\delta$ is now the opposite from that in ring A. Electron withdrawing substitutents produce smaller values of $\Delta\delta$. A plot of $\Delta\delta$ *vs.* σ^+ is again reasonably linear.[31)] In ring B the anisotropy of the substituents would be expected to affect the chemical shift of the *meta* protons, thus a linear plot was somewhat unexpected.

The position of protonation of the azo structure remains a question of interest. One likely possibility is that the acid attacks one of the non-bonded pairs on nitrogen. This type of protonation would leave the pi orbitals of the system essentially undisturbed. An equilibrium between structures in which the proton has attacked the α nitrogen and structures resulting from β nitrogen attack seems likely. With electron withdrawing substituents the former structure would seem less probable due to the instability of the resonance froms involving a charge in ring B. In either case the transmission of electronic effects from substituent X through the pi system to affect ring A would be possible.

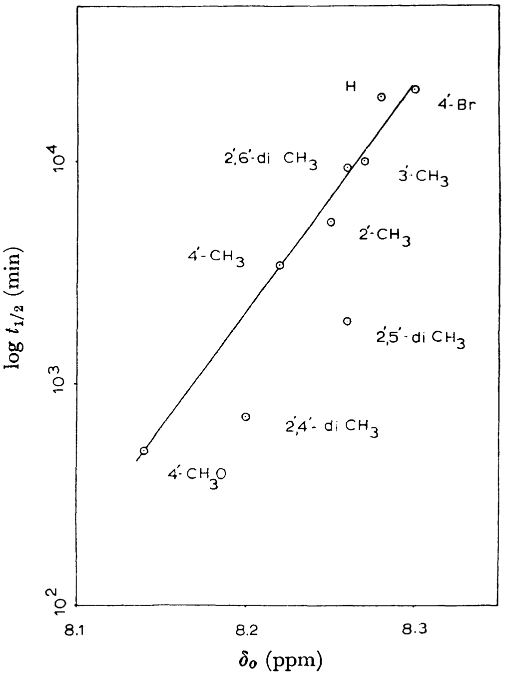


Fig. 2. A plot of log half-life of hydrogen-deuterium exchange in the *meta* position (ring A) *vs.* the chemical shift of the *ortho* proton (ring A) for the various remote substituents indicated.

The symmetrically protonated structure **12** does

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not appear to be generally accepted.[32]

For comparison purposes, two model systems have been investigated. The first system, *para* substituted anilinium ions[33] in trifluoroacetic acid, illustrated the effect of a localized charge on a nitrogen attached to one ring. The $\Delta\delta$ values vary with substituent as follows: CH_3O, 0.30; CH_3, *ca.* 0.0; Br, -0.33; $CH_3\overset{O}{\overset{\|}{C}}$, -0.54; NO_2, -0.65. Quite similar values result when small amounts of sulfuric acid are added to the solvent mixture.

The second model system of interest is that of the *para* substituted benzenediazonium chlorides, in which some delocalization of charge from a two nitrogen system into a single ring is possible. The $\Delta\delta$ values vary with substituent as follows: CH_3O, 0.74; Br, 0.32; and NO_2, $|0.21|$.

Although a strict comparison is not possible due to solvent differences, ring B of system **1H** seems somewhat closer to the anilinium ion model (taking into consideration the anisotropy of the protonated azo function). Thus in the equilibrium between α and β nitrogen protonation, the latter would seem somewhat more important for most substituents.

The visible spectral parameters for the cations **1H** are given in Table 2. The λ_{max} and ε decrease as the electron donating character of X diminishes, in the order **2H**>**3H**>**4H**. However, these parameters increase for **5H** and **6H**. The absorption bands are rather broad and possibly result from the superposition of two or more bands.[34] One band may undergo a bathochromic shift for electron donating substituents X whereas the other band undergoes a bathochromic shift for electron withdrawing substituents. Changes in the site of protonation also would affect λ_{max}, but the direction of change is difficult to predict.

Compound **11H** (2′,6′ dimethyl) exihibits a significantly lower λ_{max} and ε compared to **9H** and **10H**. Although $\Delta\delta$ value is similar, the chemical shifts of the 2′ and 6′ methyl groups occur upfield from the 2′ methyl groups in all other compounds. Ring B in this case (**11H**) appears to be somewhat out-of-plane.

In deuteriotrifluoroacetic acid - deuteriosulfuric acid mixtures, hydrogen-deuterium exchange occurred smoothly in the meta positions of ring A. The half-lives of exchange are recorded in Table 3. It is noteworthy that 4′-electron donating substituents markedly accelerate exchange in the *meta* position (ring A) even though no resonance form can be written in which the 4′ substituent stabilizes the σ complex intermediate. Thus, methyl groups in the 2′ or 4′ of ring B accelerate the exchange in ring A by a factor of 4—5 compared to the case where X=H. A methyl group in the 3′ position is less effective however. The 2′ substituent does not appear to hinder coplanarity of ring B to any great extent, in agreement with the spectral data.

However, the slowness of exchange in ring A of **11H** compared to **9H** is consistent with the out-of-plane character of the former, in which the activating effect of the methyls is reduced. However in ring B, **11H** exchanges much faster than **9H**. Although other explanations are possible, some exchange through a dication intermediate may be in effect. Since ring B of **11H** is not planar with the rest of the pi system, ring B would be less deactivated than the planar system **9H**.

Two aspects of the data in Table 3 are particularly interesting. One aspect concerns compound **7H**. In this case ring B exchanges more rapidly than the much more highly activated ring A. Again exchange directly on the protonated form **7H** may be in effect, rather than exchange *via* the small amount of **7** present in equilibrium with **7H**.

TABLE 3. EXCHANGE HALF-LIVES FOR SUBSTITUTED PHENYLAZOPHENOLS (**1H**) IN TRIFLUOROACETIC ACID-d - 29.4% SULFURIC ACID-d_2 AT 30°C

	X	Ring A	Ring B
2H	4′-CH_3O	500 min	*ca.* 500
3H	4′-CH_3	3400	
4H	H	19000	
5H	4′-Br	21000	
6H	4′-NO_2	very slow[a]	
7H	3′-CH_3	10000	1700[b]
8H	2′-CH_3	5300	
9H	2′,4′-$(CH_3)_2$	700	
10H	2′,5′-$(CH_3)_2$	*ca.* 1900	[c]
11H	2′,6′-$(CH_3)_2$	*ca.* 9200	*ca.* 9200[b]

a) No exchange was observed in 30 days.
b) Three protons exchange.
c) The degeneration of the spectrum over a period of time was probably indicative of sulfonation.

The second aspect worthy of comment is shown in Fig. 2. Although plots of the log exchange half-life ($t_{1/2}$) *vs.* δ_m (ring A) or $\Delta\delta$ are reasonably linear for monosubstituted ring B compounds, the best correlation occurs by plotting log $t_{1/2}$ *vs.* δ_o (ring A). The remote substituent can supply or withdraw electrons from the *ortho* position by resonance. The modified electron density will in turn affect the chemical shift. However, the effect of the electron donation by X to the *ortho* position on hydrogen-deuterium exchange in the adjacent *meta* position is considered to be an inductive effect.

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Experimental

Preparation of 4-Phenylazophenols (1). The phenylazophenols were prepared by the coupling reaction of the appropriately substituted diazonium chloride with phenol. A typical procedure is the preparation of **10**. The diazotization was carried out by dissolving 2,5-dimethylaniline (6.0 g, 0.05 mol) in a solution of 12.5 m*l* of concd. hydrochloric acid in 50 m*l* of water. This solution was cooled in an ice bath and an aqueous solution of sodium nitrite was added until a positive test for nitrous acid was obtained. Sodium hydroxide (4.8 g, 0.12 mol) and phenol (4.6 g, 0.05 mol) in 30 m*l* of water was placed in a three necked flask, equipped with stirrer, *etc.* The diazonium salt was added to the cooled phenoxide solution. The resulting bright orange mixture was filtered and the filtrate acidified with hydrochloric acid. The product was filtered off, thoroughly washed, and recrystallized from benzene, mp 98—100°C, 7.2 g, 65% yield.

Found: C, 74.21; H, 6.25%. Calcd for $C_{14}H_{14}ON_2$: C, 74.31; H, 6.24%.

Compound **11** was prepared similarly, mp 147—148°C.

Found: C, 74.17; H, 6.25%. Calcd for $C_{14}H_{14}ON_2$: C, 74.31; H, 6.24%.

The following were literature preparations: **2**, mp 136—137°C, (lit,[35) 142°C): **3**, mp 150—151°C (lit,[36) mp 151°C); **4**, mp 150—151°C (lit,[37) 152°C); **5**, mp 160—161°C (lit,[38) 162°C); **6**, mp 206—207°C (lit,[39) mp 211°C); **7**, mp 142—143°C (lit,[40) 141°C); **8**, mp 101—102°C (lit,[41) mp 102—103°C); **9**, mp 134—135°C (lit,[35) mp 134°C).

The anilines from which the diazonium salt NMR data were taken were commercial products recrystallized twice, usually from ethanol. In each case the literature melting point was obtained.

Sulfuric acid-d_2 was obtained from Merck, Sharp and Dohme of Canada and was used as received. Trifluoroacetic acid-d was prepared from the anhydride (Mathieson) by the procedure of Taylor and Templeman.[42) On distillation the fraction boiling at 71°C was collected. The isotopic purity was greater than 96%.

The NMR data were taken on a Varian-A-60 instrument. The chemical shift data (taken *vs.* tetramethylsilane or *vs.* tetramethylammonium bromide in acid solutions) are considered good to ±0.03 ppm, and the $\Delta\delta$ values to ~0.01 ppm. The latter are less sensitive to concentration than the chemical shifts. The NMR solvents 29.4% sulfuric acid-d_2 in trifluoroacetic acid-d were made up by weight. Stronger acid solutions showed rather diffuse peaks whereas weaker solutions did not appear to protonate the substrate fully in all cases. For the diazonium salt runs, the solvent was 18% hydrochloric acid in water.

The ultraviolet data were taken on a Cary Model 14 instrument. The λ_{max} data are considered good to ±2—3 mμ due to rather broad peaks in some cases.

The rate solutions were made up and run as described previously.[20)

This work was begun at Iowa State University.

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