

Linear Free Energy Relationships of the ^{13}C NMR chemical shifts in 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones

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Abstract

The ^{13}C NMR chemical shifts of the C2 carbon atom in the heteroaromatic nuclei of seventeen 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones were determined in deuterated DMSO solution. For quantitative assessment of the substituent effects on the ^{13}C NMR chemical shifts simple and extended Hammett equations and Swain-Lupton equation were used. The mode of transmission of substituent effects have been discussed in a relation to the geometry of investigated molecules. The geometry data were obtained using semiempirical MNDO-PM6 energy calculations. The observed ^{13}C NMR substituent chemical shifts were correlated with literature ^{13}C NMR data for the corresponding 3- and 4-substituted-2',6'-dimethylazobenzenes and 3- and 4-substituted azobenzenes. A good linear dependence obtained in this way, provided a basis to discuss the influence of the *ortho*-methyl groups on the degree of coplanarity of azobenzene and pyridone systems, and on the efficiency of transmission of electronic substituent effect from one ring to the other one.

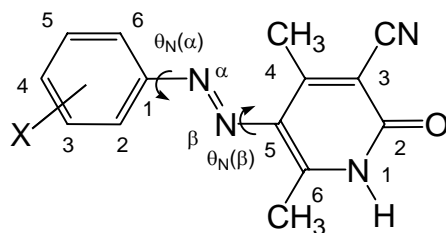
Keywords: LFER models, arylazo pyridone dyes, substituent effects, azo linking group, MNDO-PM6 and DFT-*ab initio* calculations

Introduction

It has been known for many years that azo compounds are the most widely used compounds in various fields such as the dyeing of textile fibers, the coloring of different materials, colored plastic, and polymer, in biological-medical studies, and advanced application in organic synthesis.¹⁻⁴ The success of azo colorants is due to the simplicity of their synthesis by

diazotization and azo coupling, to the almost innumerable possibilities presented by variation on the diazo compounds and coupling components, to the generally high molar extinction coefficient, and to the medium to high light and wet fastness properties.⁵ The arylazo pyridone dyes are very important class of colorants and several investigations on substituted arylazo pyridones were carried out and reviewed.⁶⁻⁸ In our previous work,⁹ absorption spectra of seventeen 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones in different solvents were examined.

In this work, the same series of compounds⁹ (Figure 1) has been studied using ¹³C substituent chemical shifts (SCS). The observed ¹³C NMR chemical shifts confirm the existence of the only one tautomeric form of the investigated dyes. The intention of the present investigation was to study the effects of substituents at the azobenzene ring on the ¹³C NMR chemical shifts of the C2 carbon atom in the heteroaromatic ring of investigated 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones to get an insight into the factors determining chemical shifts. The SCS(C2) were correlated using a few different linear free energy relationship (LFER) models, based on the mono and the dual substituent parameter (MSP and DSP, respectively) treatments. Since the quantum chemical calculations suggest that the investigated dyes prefer *trans*-2-pyridone tautomeric form, the mode of transmission of substituent effects in **1** were discussed in relation to such molecular geometry.



1

X = 4-OCH₃, 3-OCH₃, 4-CH₃, 3-CH₃, 4-C₂H₅, 3-C₂H₅, H, 4-Cl, 3-Cl, 4-Br, 3-Br, 4-I, 4-COCH₃, 4-CN, 3-CN, 4-NO₂ and 3-NO₂

Figure 1. The structure of studied 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones with added nuclei labels used for ¹³C NMR data and torsion angles labels.

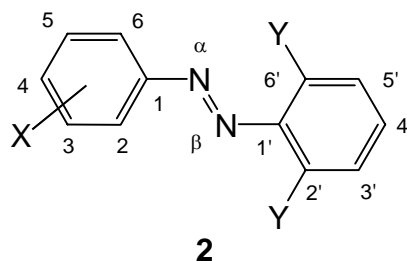


Figure 2. Structure of azobenzene (**2-H**; Y = H) and its 2',6'-dimethyl derivative (**2-Me**; Y = Me) with added nuclei labels used for ^{13}C NMR data. (X substituents are the same as in Figure 1.)

Numerous previous investigations of molecular structure of azobenzenes^{10,11} show that the introduction of alkyl substituents into 2'- and 6'-positions of the azobenzene system would be likely to result in a significant decrease in the tendency towards planarity. A number of spectroscopic and structure studies, both in the solid state and in solution¹²⁻¹⁵ pointed out the existence of a greater non-planarity in these systems in relation to azobenzene. C. J. Byrne *et al.*¹⁶ have previously studied the ^{13}C NMR substituent chemical shifts of a number of 3- and 4-substituted-2',6'-dimethylazobenzenes and a comparison of the effect of substituents on the ^{13}C NMR chemical shift for C4' carbon atom (Figure 2) with that for the corresponding azobenzenes has been used as a probe for exploring the influence of the two introduced *ortho*-methyl groups on the degree of coplanarity of the azobenzene system. The results of C. J. Byrne *et al.*¹⁶ supported previous studies that have suggested that the methyl groups have a striking effect on the (non)planarity of the system, but surprisingly, suggested that such loss of planarity has a relatively little effect on the efficiency of transmission of both polar and resonance effects between the two rings.

The observed SCS(C2) for 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones are compared with previously reported literature data¹⁶ for the corresponding 3- and 4-substituted-2',6'-dimethylazobenzenes (**2-Me**) and 3- and 4-substituted azobenzenes (**2-H**) as a probe for exploring the influence of the *ortho*-methyl groups on the degree of coplanarity of azobenzene and pyridone systems and the efficiency of transmission of electronic substituent effects from one ring to the other.

Results and Discussion

The ^{13}C NMR chemical shifts of both the C2 carbons for the 17 compounds in the series of 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones, **1**, and C4' carbons in **2** are given in Table 1 in terms of the substituent chemical shifts with respect to the parent compound.

Table 1. ^{13}C substituent chemical shifts (SCS) in **1** and **2**

Compound	1	2-Me	2-H
Substituent/SCS	C2 ^a	C4' _{2-Me} ^b	C4' _{2-H} ^b
H ^c	161.35	128.08	130.98
4-OMe	-1.18	-0.53	-0.62
4-Me	-0.11	-0.29	-0.3
4-Et	-0.45	—	—
4-Cl	0.95	0.4	0.27
4-Br	1.07	0.45	0.31
4-I	0.16	—	0.31
4-Ac	1.84	1.01	0.77
4-CN	2.40	1.54	1.22
4-NO ₂	2.92	1.84	1.42
3-OMe	0.62	0.03	0.02
3-Me	0.42	-0.15	-0.13
3-Et	0.31	—	—
3-Cl	1.35	0.64	0.51
3-Br	1.49	0.65	0.52
3-CN	1.82	1.31	1.06
3-NO ₂	2.08	1.45	1.14

^a ^{13}C Chemical shifts (in ppm) expressed relative to the unsubstituted compound. Downfield shifts are positive. Solvent is DMSO-*d*₆.

^b Data from Ref. 16. ^{13}C Chemical shifts (in ppm) expressed relative to the unsubstituted compound. Downfield shifts are positive. Solvent is CDCl₃-*d*₆. See Figure 2 for labeling of nuclei and compounds.

^c Chemical shifts of the parent compound relative to Me₄Si.

Inspection of the SCS data in Table 1 shows that the effects of the azobenzene ring substituents on the chemical shifts of C2 carbon in **1** are electronic in origin. While the electron-donor substituents influence the upfield shifts of the values of the NMR chemical shifts of C2, the electron-acceptor substituents cause the downfield shifts.

For the quantitative assessment of the substituent effects on the SCS(C2) in **1**, we used three conventional LFER models, based on MSP and DSP treatment. All the substituent constants needed were taken from the literature.^{17,18}

The first LFER model is MSP equation, so called simple Hammett equation, which we used in the following form:

$$SCS(C) = \rho\sigma_{m/p} + h \quad (1)$$

where $SCS(C)$ is the change in chemical shift induced by the substituent X, and $\sigma_{m/p}$ is the substituent parameter reflecting the electronic effects. Parameters h (the intercept on the ordinate) and ρ (measure of the sensitivity of the chemical shift to the electronic effects of the substituents), are obtained by the regression analysis.

The second one is the DSP equation, so called extended Hammett equation, which we used in the following form:

$$SCS(C) = \rho_I \sigma_I + \rho_R \sigma_R + h \quad (2)$$

where σ_I and σ_R are substituent parameters reflecting the polar and resonance electronic effects, respectively. Parameters ρ_I and ρ_R (measure of the sensitivity of the chemical shift to the polar and resonance electronic effects of the substituents, respectively), are obtained by the regression analysis.

The third one is the DSP equation, so called Swain-Lupton equation, which we used in the following form:

$$SCS(C) = fF + rR + h \quad (3)$$

where F and R are substituent parameters reflecting the field and resonance electronic effects, respectively. Parameters f and r (measures of the sensitivity of the chemical shift to the field and resonance electronic effects of the substituents, respectively), are obtained by the regression analysis.

Application of MSP analysis to the $SCS(C2)$ in **1** using Equation (1) yields good results that are shown in Figure 3 and given in Table 2.

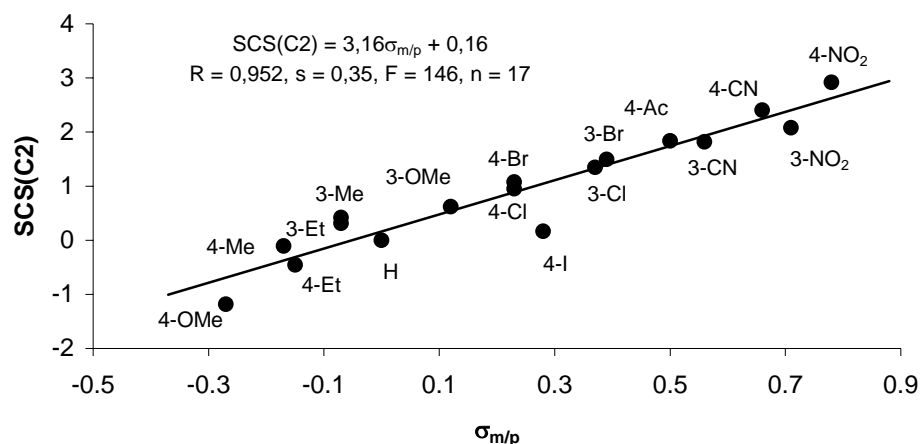


Figure 3. Plot of $SCS(C2)$ for 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones versus Hammett σ constants.

Table 2. Results of the correlations of SCS(C) with Equation (1) for **1** (C2) and **2** (C4'_{2-Me} and C4'_{2-H})

ρ^a	h^b	R^c	s^d	F^e	n^f
Compound 1					
Series <i>para</i>					
3.53 (± 0.34)	0.02 (± 0.14)	0.964	0.37	106	10
Series <i>meta</i>					
2.50 (± 0.25)	0.38 (± 0.09)	0.972	0.20	101	8
Compound 2-Me^g					
Series <i>para</i>					
2.21 (± 0.10)	0.01 (± 0.04)	0.994	0.10	546	8
Series <i>meta</i>					
2.16 (± 0.18)	-0.08 (± 0.07)	0.982	0.13	137	7
Compound 2-H^h					
Series <i>para</i>					
1.85 (± 0.09)	-0.09 (± 0.04)	0.992	0.09	445	9
Series <i>meta</i>					
1.73 (± 0.15)	-0.07 (± 0.06)	0.981	0.11	128	7

^a Weighting coefficients for appropriate equation.

^b Intercept.

^c Correlation coefficient.

^d Standard error of estimate for the SCS.

^e F test for significance of regression.

^f Number of points in the set.

^g The SCS data were not available for 4-I, 4-Et and 3-Et substituted **2-Me**.

^h The SCS data were not available for 4- and 3-Et substituted **2-H**.

Much better correlation for SCS(C2) was obtained with DSP Equations 2–3. The corresponding relationships are shown in Tables 3 and 4. It should be noted that all the DSP correlations are of satisfactory precision. The pattern of the weighting factors (ρ_L , ρ_R and f , r) indicates a dominant polar effect and the minor resonance effect in the *meta* series of **1**, while two substituent effects are balanced in the *para* series.

Table 3. Results of the correlations of SCS(C) with Equation (2) for **1** (C2) and **2** (C4'_{2-Me} and C4'_{2-H})

ρ_I ^a	ρ_R ^b	ρ_R/ρ_I ^c	h ^d	R ^e	s ^f	F ^g	n ^h
Compound 1							
Series <i>para</i>							
3.20 (±0.46)	3.71 (±0.54)	1.16	0.15 (±0.21)	0.971	0.36	57	10
Series <i>meta</i>							
2.45 (±0.28)	0.42 (±0.37)	0.17	0.29 (±0.14)	0.972	0.21	44	8
Compound 2-Meⁱ							
Series <i>para</i>							
2.15 (±0.16)	2.11 (±0.16)	0.98	0.01 (±0.07)	0.994	0.11	215	8
Series <i>meta</i>							
1.90 (±0.07)	0.98 (±0.08)	0.52	0.01 (±0.04)	0.998	0.05	583	7
Compound 2-H^j							
Series <i>para</i>							
1.70 (±0.10)	1.88 (±0.11)	1.12	-0.03 (±0.05)	0.996	0.07	356	9
Series <i>meta</i>							
1.52 (±0.04)	0.78 (±0.04)	0.51	0.01 (±0.02)	0.999	0.02	1235	7

^a Weighting coefficients for appropriate equation.

^b Weighting coefficient ratio.

^c Intercept.

^d Correlation coefficient.

^e Standard error of estimate for the SCS.

^f F test for significance of regression.

^g Number of points in the set.

^h The SCS data were not available for 4-I, 4-Et and 3-Et substituted **2-Me**.

ⁱ The SCS data were not available for 4- and 3-Et substituted **2-H**.

Table 4. Results of the correlations of SCS(C) with Equation (3) for **1** (C2) and **2** (C4'_{2-Me} and C4'_{2-H})

f ^a	r ^b	r/f ^c	h ^d	R ^e	s ^f	F ^g	n ^h
Compound 1							
Series <i>para</i>							
3.24 (±0.40)	3.96 (±0.41)	1.22	0.19 (±0.16)	0.983	0.27	102	10
Series <i>meta</i>							
2.74 (±0.28)	0.57 (±0.32)	0.21	0.28 (±0.12)	0.979	0.19	57	8
Compound 2-Meⁱ							
Series <i>para</i>							
2.22 (±0.18)	2.20 (±0.16)	0.99	0.01 (±0.08)	0.995	0.10	228	8
Series <i>meta</i>							
2.03 (±0.10)	1.11 (±0.10)	0.54	0.02 (±0.04)	0.997	0.06	373	7
Compound 2-H^j							
Series <i>para</i>							
1.74 (±0.12)	1.95 (±0.11)	1.12	-0.02 (±0.05)	0.995	0.08	317	9
Series <i>meta</i>							
1.62 (±0.09)	0.89 (±0.09)	0.55	0.02 (±0.04)	0.996	0.05	271	7

^a Weighting coefficients for appropriate equation.

^b Weighting coefficient ratio.

^c Intercept.

^d Correlation coefficient.

^e Standard error of estimate for the SCS.

^f F test for significance of regression.

^g Number of points in the set.

^h The SCS data were not available for 4-I, 4-Et and 3-Et substituted **2-Me**.

ⁱ The SCS data were not available for 4- and 3-Et substituted **2-H**.

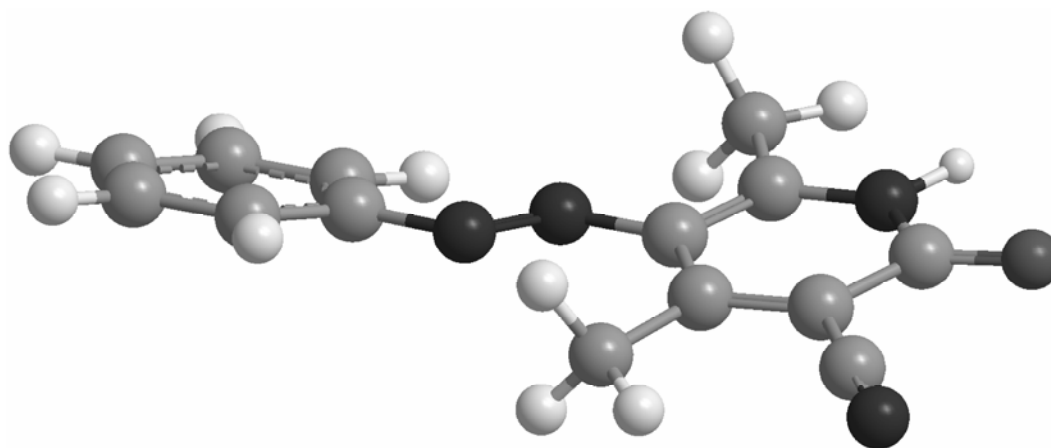


Figure 4. Stable *trans*-conformer of 5-phenylazo-4,6-dimethyl-3-cyano-2-pyridone. Corresponding calculated heat of formation, ΔH^0 : **1-H**, 45.094 kcal mol⁻¹. (The geometries correspond to the energy minimum in DMSO).

In the studied series of 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones (Figure 1) the *para* and *meta* substituted phenyl ring is linked to the azo group bearing heteroaromatic ring with the two *ortho*-methyl groups. The semi-empirical, MNDO-PM6, and *Ab initio*, RB3LYP/6-311++G, calculations suggest that **1** have non-planar molecular geometry (the aromatic rings are twisted in respect to the azo group linkage) (Figure 4). Computed energy, and torsion angles for both the stable *trans*-conformer of 5-phenylazo-4,6-dimethyl-3-cyano-2-pyridone and its less stable 2-hydroxypyridine tautomer, are given in Tables 5 and 6.

Table 5. Computed energy and torsion angles for stable *trans*-conformer of 5-phenylazo-4,6-dimethyl-3-cyano-2-pyridone

Type of calculation	Heat of formation	$\theta_{N(\alpha)}$ [°]	$\theta_{N(\beta)}$ [°]	θ_{Ph-Pyr}^a [°]
HF (PM6) COSMO	45.094 [kcal mol ⁻¹]	42.0	3.6	33.8
HF (DFT)	-834.876 [a.u.]	7.2	12.5	19.7
HF (DFT) SCRF	-834.908 [a.u.]	6.9	16.0	22.5

^a Torsion angle phenyl ring plane–heteroaromatic ring plane.

Table 6. Computed energy and torsion angles for not detected 2-hydroxypyridine tautomer of 5-phenylazo-4,6-dimethyl-3-cyano-2-pyridone

Type of calculation	Heat of formation	$\theta_{N(\alpha)}$ [°]	$\theta_{N(\beta)}$ [°]	θ_{Ph-Pyr}^a [°]
HF (PM6) COSMO	58.012 [kcal mol ⁻¹]	-40.1	63.2	30.3
HF (DFT)	-834.865 [a.u.]	6.1	18.5	23.6
HF (DFT) SCRF	-834.890 [a.u.]	6.6	27.7	32.4

^a Torsion angle phenyl ring plane–heteroaromatic ring plane.

It is well known that any significant deviations from coplanarity will have an effect on the degree of π electron delocalization of the system. While the existence of the former does not require the system to be completely planar, the more planar the system, the greater should be the efficiency with which polar and (especially) resonance effects are related from one ring to another. In a system with non-planar molecular geometry like **1**, one would expect a decrease in the ability of the azo linkage to relay the π -inductive effects (effect of charged or dipolar group on an isolated π -electron system) and resonance effects from one ring to the other relative to that existing in more planar azobenzene (**2-H**). In an effort to obtain confirmation for that, we compared the observed ¹³C NMR substituent chemical shifts (Table 1; **1**) with literature ¹³C NMR data¹⁶ for 3- and 4-substituted-2',6'-dimethylazobenzenes (**2-Me**) and 3- and 4-substituted azobenzenes (**2-H**) (Table 1; **2-Me** and **2-H**). If both, the literature ¹³C SCS of carbon C4' in **2-Me** and **2-H**, are intercorrelated with the same data set of SCS of carbon C2 in **1**, the following relationships were obtained:

$$SCS(C4'_{2-Me}) = 0.65(\pm 0.05)SCS(C2) - 0.13(\pm 0.08) \quad (4)$$

(R = 0.964, s = 0.21, F = 156, n = 14)

$$SCS(C4'_{2-H}) = 0.54(\pm 0.04)SCS(C2) - 0.17(\pm 0.06) \quad (5)$$

(R = 0.973, s = 0.15, F = 215, n = 14)

Satisfactory intercorrelations shown above, imply that the electron distribution in system **1** is very similar to that in **2-Me** and **2-H** systems. Further evidence for this is obtained from the comparison of the results of the DSP analysis for SCS(C2) with those for SCS(C4'_{2-Me}) and SCS(C4'_{2-H}) that are summarized in Tables 4 and 5. Examination of the results in Tables 4 and 5 reveals that in the *meta* series of **1** and **2** polar effects dominate, resonance effects playing only a minor part (as expected), whereas in the *para* series the two substituent effects are being related to the NMR probe nuclei with roughly equal efficiencies.

D. Christoforou et. al.¹⁹ have shown by application of the DSP Eq. 2 to the ¹³C NMR substituent chemical shifts of C4' carbons of fifteen 4- and fifteen 3-substituted azobenzenes (**2-H**) that there is an excellent correlation with σ_R^{BA} (*meta* series $\rho_I = 1.5$, $\rho_R = 0.8$, s.d./r.m.s. =

0.11, $n = 15$ in CDCl_3 solvent; *para* series $\rho_I = 1.7$, $\rho_R = 1.9$, s.d./r.m.s. = 0.10, $n = 15$ in CDCl_3 solvent). It was found there that polar effects are transmitted to the remote ring from the *meta* and *para* positions with equal efficiencies and polarize the phenyl group independently of the rest of the molecule. Resonance interaction is greatest when the substituent is *para* to the azo linking group. Our results shown in Table 4 for **2-H** (with the limited range of substituents) are consistent with those from the literature¹⁹ indicating that an adequate number of the substituents are involved for justification of DSP analysis of the data.

The results of the correlations of $\text{SCS}(\text{C4}'_{2-\text{Me}})$ with DSP Equations 2 and 3 (Tables 4 and 5) support the previous studies¹⁶ which have suggested that the non-planarity of **2-Me** (as a result of introducing two flanking methyl groups) has relatively little effect on the efficiency of the transmission of electronic effects from the substituted phenyl ring to the side-chain ring. The **2-Me** set appears to be formally at least as efficient as planar azobenzene (**2-H**) in transmitting of electronic effects.

Since the electron distribution in the phenylazo group in **1** is very similar to that of **2-H**, the efficiency of transfer of both polar and resonance substituents effects, as far as the β azo nitrogen is concerned, (see Figure 1) should, therefore, be the same in these systems. Although the heteroaromatic ring bears *ortho*-methyl groups that reduce coplanarity in the part involving azo linkage–pyridone ring, **1** appears to be at least as efficient as planar azobenzene (**2-H**) in transmission of the electronic substituent effects from one ring to another.

The phenylazo group is generally recognized as an electron-withdrawing group in most circumstances. In view of its strong $-\text{M}$ character it is surprising to find the evidence that, under suitable conditions, it can act as an overall electron-donor. For instance, in **2-Me** system where the side-chain aromatic ring is perpendicular to approximately planar phenylazo group, the π orbitals of the aromatic ring are overlapping with lone pair on the β azo nitrogen rather than the π orbital of the azo linkage that results in electronic character change of the phenylazo group.¹⁶ It appears that a similar mechanism of transmission through a π system could operate due to geometric relationship between the heteroaromatic ring and the azo linkage in **1**.

Conclusions

Seventeen 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones have been studied using ^{13}C NMR chemical shifts. Application of simple and extended Hammett equations and Swain-Lupton equation to the SCS of the C2 carbon atom gave good results. The validity of the used LFER models is confirmed by the fact that the calculated molecular geometry in general allows accurate prediction of the ^{13}C NMR data. The observed ^{13}C NMR substituent chemical shifts for 5-(3- and 4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones were correlated with literature ^{13}C NMR data for the corresponding 3- and 4-substituted-2',6'-dimethylazobenzenes and 3- and 4-substituted azobenzenes. These results support previous

studies¹⁶ that the major pathway for the transmission of substituent effects from one ring to the other, in investigated systems, is through field and π -inductive effects.

Experimental Section

Synthesis of the compounds

All of the investigated azo pyridone dyes were synthesized by the diazotization-coupling reaction, starting from acetylacetone and arendiazonium salt, followed by condensation with cyanoacetamide using modified literature procedure²⁰ as reported previously.⁹ The chemical structure and the purity of the azo dyes were confirmed by melting points, ¹H NMR, FTIR and UV spectra.⁹

NMR Spectra

The ¹³C NMR spectra were determined on a Varian Gemini-200 instrument and checked on a Bruker DMX 500 spectrometer, with tetramethylsilane as an internal standard. The spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-d₆) in 5mm tubes.

Method of Calculation

In our work we used the MNDO-PM6 method that proved to be highly reliable for investigating the molecular properties of molecules, ions,²¹⁻²⁹ and zwitterions.³⁰ The MOPAC program package, Version 7.01 was used. The initial structures of compounds were generated by PC MODEL, version 4.0,³¹ that involves an MMX force field^{32,33} and were saved as MOPAC input files for MNDO-PM6 semi-empirical calculations.^{23,24} The geometries of all molecular species, corresponding to the energy minima in DMSO, were optimized by the PM6 method. When needed, the structures obtained were refined by Bartel's method (Non-Linear Least Squares gradient minimization routine - NLLSQ), and further proved by vibrational analysis showing no negative vibration. The simulation of polar medium was performed using COSMO facility.^{34,35} A DFT *ab initio* calculations were done, too. The structures were preliminary optimized by semiempirical PM6 method. The GUSSIAN03 program package³⁶ involving B3LYP Hamiltonian was used at 6-311++G level. The solvent was simulated using SCRF method, as a C-PCM model, with built-in DMSO dielectric constant.

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