# Fluorescence and Absorption Spectra of Phenylazopyrazolone Dyes

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The absorption and fluorescence spectra of some arylazopyrazolone dyes have been investigated. The emission is assigned to their hydrazone form. A very good linear correlation is obtained between the $\sigma$ Hammett constants and the differences of the absorption maxima of the hydrazone form and the anion. Quantum chemical calculations indicate to a charge migration upon excitation.

The electron donor substituents cause bathochromic and hypsochromic shifts in the absorption and in the fluorescence maxima resp., while the acceptor substituents shift bathochromically both maxima. All compounds studied except the p-$N(CH_3)_2$ derivative show an anomalously large Stokes shift in nonpolar solvents.

The compounds studied are a class of widely used azo dyes for synthetic and natural textiles. They may exist in one of two tautomeric forms, the hydrazone form IH or the azoenol form IA (Fig. 1); both forms have the same anion ($I^{\ominus}$) in common. Under normal conditions phenylazopyrazolone and its derivatives are almost totally in the form IH and only in strongly alkaline conditions (pH $\geqq$ 11) do they transform into the common anion $I^{\ominus}$ [1–4]. For the similarly structured phenylazonaphthols (II, III and IV, Fig. 1), a displaced equilibrium between the azo and quinonehydrazone tautomeric form is observed [5–8]. Bearing in mind Fischer's suggestion [6, 9] that the quinonehydrazone structure is responsible for the emission of the phenylazonaphthols, we found it of interest to study the fluorescence and absorption spectra of the phenylazopyrazolone dyes and to observe the effect of substituents and solvents on their spectral properties.

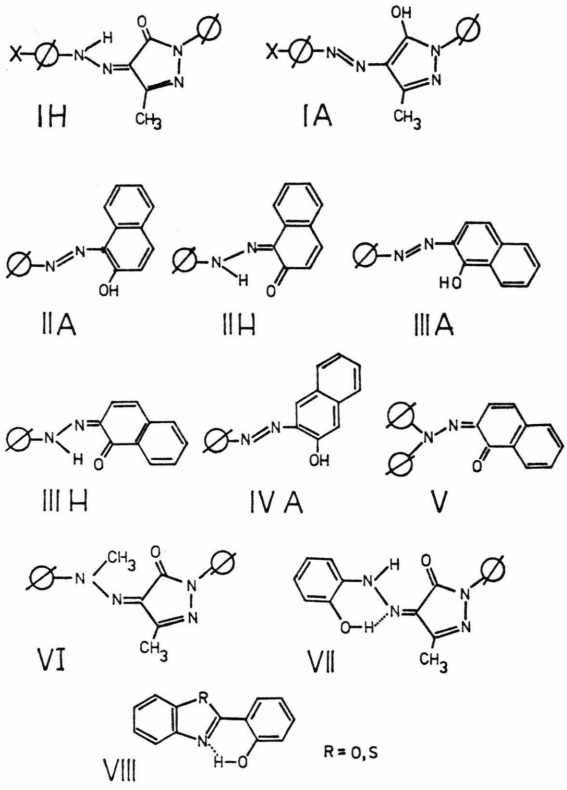


Fig. 1. 1-Phenyl-3-methyl-4-arylazopyrazolone (I) and several structural analogues in their azoenol (A) and quinonehydrazone (H) forms.

## Experimental

The compounds studied were obtained by the standard procedure [10] of diazotization of the corresponding substituted anilines and subsequent coupling in alkaline solution with 1-phenyl-3-

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methyl-pyrazolone-5. The compounds were recrystallised repeatedly until a constant melting point was obtained, and their purity was verified chromatographically and spectrally (UV, VIS). The corrected fluorescence and excitation spectra were recorded on a Perkin-Elmer MPF-44 B spectrofluorimeter. The absorption spectra were recorded on Specord UV/VIS (Carl Zeiss, Jena). Solvents used were of fluorescence grade.

## Results and Discussion

### *1. Absorption, Fluorescence and Excitation Spectra*

In Table 1 the absorption and fluorescence characteristics of phenylazopyrazolone and 9 derivatives are given. Figure 2 shows the absorption and the corrected fluorescence spectra of 3 representative compounds of the series: X=H, p-$NH_2$, and p-CN. Vertical lines specify the position and intensity of the computed electron transitions, taking into account all singly excited configurations within the framework of the SCF-CI-PPP method [4, 8]. The maximal difference between the experimental and theoretical values for the calculated transitions does not exceed 0.2 eV.

The quantum-chemical results assign the 400 nm absorption maximum which determines the colour of the compound as a $S_0 - S_1$ transition; the 250 nm absorption maximum is $S_0 - S_6$.

All compounds studied show a weak fluorescence with a quantum yield in the range of $10^{-1}$ to $10^{-2}$ in the 600 nm vicinity at room temperature and in non-polar solvents (cyclohexane, hexane); some fluorescence in polar solvents as well (Table 1). In accordance with King's suggestion [11], we also observed that the quantum yield of the fluorescence decreases with increasing $\sigma$ values of the substituents. No fluorescence is obtained from the anions formed by the addition of KOH to the ethanolic solution.

As previously mentioned, in the ground state all compounds are totally in the hydrazone form. The compound IH(X=H) and its N-methyl homologue VI, which possesses no mobile hydrogen atom, have their absorption and fluorescence maxima at nearly the same respective positions. This, as well as the mirror symmetry of the absorption and emission bands (Fig. 2), shows that no change from IH to IA form take place upon excitation. This conclusion is supported by the coincidence of the excitation spectra with the longest wavelength absorption band of the IH form for all compounds investigated and also by the absence of emission from the anions; further, it is in agreement with Fischer's suggestions [6, 9] that the fluorescence of the phenylazonaphthols (II—V) is due to their H form.

### *2. Effect of Substituents*

It is seen from Table 1 that for the H-form, electron donor substituents lead to a strong bathochro-

Table 1. Experimental spectral characteristics. The frequencies $\nu$ of the maxima are given in $10^3$ $cm^{-1}$; $[\varepsilon] = 10^3$ $mol^{-1}$ $cm^{-1}$. (DMSO ... dimethylsulfoxide, HMPA ... hexamethylphosphorustriamide; 0 ... no measurements, / ... no fluorescence observed.)

| | | Cyclohexane | | | | EtOH | | | | EtOH + 0.1 n KOH | | $CHCl_3$ | | | DMSO | | | HMPA | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N° | X | $\nu_{Abs}$ | $\varepsilon$ | $\nu_{Fl}$ | $\Delta\nu_{St}$ | $\nu_{Abs}$ | $\varepsilon$ | $\nu_{Fl}$ | $\Delta_{St}\nu$ | $\nu_{Abs}$ | $\varepsilon$ | $\nu_{Abs}$ | $\nu_{Fl}$ | $\Delta\nu_{St}$ | $\nu_{Abs}$ | $\nu_{Fl}$ | $\Delta\nu_{St}$ | $\nu_{Abs}$ | $\nu_{Fl}$ | $\Delta\nu_{St}$ |
| 1 | p-$N(CH_3)_2$ | 21.2 | 26.4 | 17.7<br>17.0 | 3.5<br>4.2 | 20.0 | 26.8 | 16.0 | 4.0 | 23.0<br>24.8 | 25.4<br>23.2 | 20.2 | 16.4 | 3.8 | 21.1 | 16.7 | 5.4 | 19.8 | 15.8 | 4.0 |
| 2 | p-$NH_2$ | 22.0 | 21.4 | 17.4 | 5.4 | 21.1 | 23.2 | 16.4 | 4.7 | 23.6<br>25.6 | 21.1<br>21.8 | 21.7 | 16.9 | 4.8 | 20.8 | 16.0 | 4.8 | 19.2 | 16.0 | 3.2 |
| 3 | p-$OCH_3$ | 24.0 | 25.8 | 16.6 | 7.4 | 23.6 | 23.9 | / | / | 25.8 | 20.0 | 23.5 | 16.6 | 6.9 | 23.5 | 16.6 | 6.9 | 23.5 | 16.6 | 6.9 |
| 4 | o-$OCH_3$ | 24.3 | 23.0 | 16.6 | 7.7 | 23.8 | 21.3 | 16.6 | 7.2 | 25.1 | 17.0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | o-OH | 23.8 | | 16.6 | 7.2 | 23.2 | 21.4 | 17.5 | 5.7 | 0 | 0 | 23.8 | 16.6 | 7.2 | 23.2 | 17.5 | 5.7 | 23.2 | 17.5 | 5.7 |
| 6 | H | 25.3 | 23.8 | 16.6 | 8.7 | 25.3 | 21.9 | / | / | 26.7 | 18.2 | 25.0 | 16.6 | 8.4 | 25.0 | 19.6 | 5.4 | 25.0 | 19.8 | 5.2 |
| 7 | p-Cl | 25.0 | 25.6 | 16.6 | 8.4 | 25.1 | 25.4 | / | / | 25.2 | 21.0 | 25.0 | 16.6 | 8.4 | 24.5 | 20.0 | 4.5 | 25.0 | / | / |
| 8 | p-CN | 25.2 | 28.7 | 16.1 | 9.1 | 25.2 | 29.2 | / | / | 22.8 | 25.5 | 25.2 | 16.4 | 8.8 | 25.0<br>21.5 | / | / | 25.0<br>21.5 | / | / |
| 9 | p-$NO_2$ | 25.2 | 34.6 | 15.8 | 9.4 | 25.2 | 34.8 | / | / | 20.3 | 27.0 | 24.7 | 16.6 | 8.1 | 24.1 | 16.6 | 7.5 | 24.1 | 15.9 | 8.2 |
| 10 | o-COOH | 25.6 | | 16.6 | 9.0 | 25.1 | 25.7 | 16.6 | 8.5 | 25.4 | 18.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

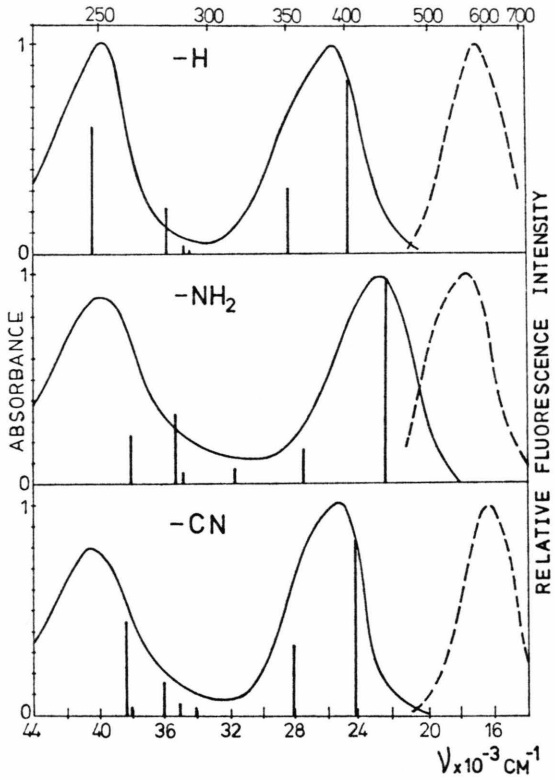


Fig. 2. Absorption (——) and fluorescence (- - -) spectra of IH(X=H, p-$NH_2$, p-CN) in cyclohexane at $T=20$ °C. Vertical lines indicate calculated electron transitions [4, 8].

mic shift in the $S_0 - S_1$ transition while electron acceptor substituents exert no significant influence.

The theoretical analysis by the method of Sukhorukov et al. [12] shows that the 1-phenyl ring takes almost no part in the electron excitation $S_0 - S_1$, i.e., when considering the longest wavelength absorption band, we can neglect this phenyl ring. The remainder of the molecule has two groups between which charge transfer could take place. These groups are —C=O, which is always an electron acceptor A, and X-Ph which, depending on the nature of the substituent X, can be an electron donor D′ or an electron acceptor A′. This conclusion is supported by quantum-chemical calculations of the net charge $\xi$ on both groups in $S_0$ and $S_1$ (Table 2).

If the group X—Ph is a donor [X=p-$N(CH_3)_2$, p-$NH_2$, p-$OCH_3$, etc.], the molecule behaves as a donor-acceptor conjugated system (D′—A) and, indeed, the absorption spectra show a strong bathochromic shift as expected. When the group X—Ph is an acceptor, there should be no significant charge transfer between the two groups neither in $S_0$, nor in $S_1$, i.e. the transition $S_0 - S_1$ does not have a marked CT character. In agreement with this, Table 2 shows that a strong electron acceptor group like CN has only relatively small effects on the charges $\xi$; therefore, only small spectral shifts are to be expected. Indeed, the absorption maxima or the unsubstituted compound and its derivatives with electron acceptor substituents lie in a small spectral range (Table 1). This is also confirmed by the linear correlation of $\nu_{Abs}$(IH) with the $\sigma$-Hammett constants (Figure 3, H).

The spectral substituent shifts of the anion ($I^{\ominus}$) can be interpreted analogously. In this case, the C=O group transforms into its ionised form C—$O^{\ominus}$ and behaves as a strong electron donor with $\xi_{C-O^{\ominus}}(X=H) = 0.132$. Then, electron acceptor substituents in the fragment X—Ph(X=p-CN, p-$NO_2$, etc.) should lead to the formation of an A′—D system with a significant charge transfer, thus explaining the observed bathochromic shift of the longest wavelength absorption maxima of the anions (Table 1). For an electron donor substituent X in the fragment X—Ph, $\xi_{X-Ph}(X=p\text{-}NH_2) = 0.046$, so the anion behaves as a D′—D system without a marked CT effect in contrast to the IH form.

The differences in the slopes of the dependencies of $\nu_{Abs}$ upon $\sigma$ for $\sigma \geqq 0$ and $\sigma \leqq 0$ for the IH and $I^{\ominus}$ forms (Fig. 3, H and A) corroborate the above conclusions concerning the different substituent effect in the two forms.

| X | —H | | —CN | | —$NH_2$ | |
|---|---|---|---|---|---|---|
| state | $S_0$ | $S_1$ | $S_0$ | $S_1$ | $S_0$ | $S_1$ |
| $\xi$ X—Ph | − 0.104 | − 0.042 | − 0.113 | − 0.072 | + 0.080 | + 0.144 |
| $\xi$ C=O | − 0.176 | − 0.169 | − 0.174 | − 0.169 | − 0.184 | − 0.210 |

Table 2. Net electron charges $\xi$ on the groups X—Ph and C=O.

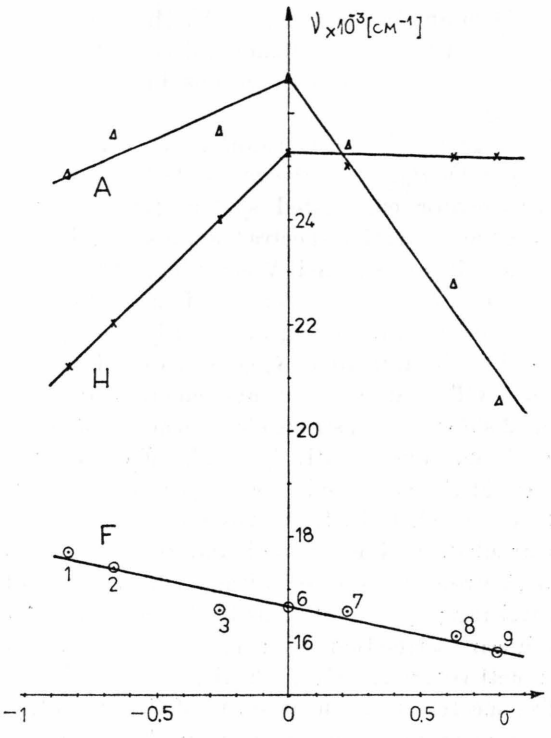


Fig. 3. Dependency of the spectral minima upon the $\sigma$ Hammett constants. The numbering of the points corresponds to those in Table 1. A ... absorption of the anion I$^{\ominus}$ ($\Delta$), H ... absorption of IH form (x), F ... fluorescence of IH form ($\odot$).

In accordance with the results of Griffiths [13] on similar systems, we also found a very good linear correlation (Fig. 4) between $\sigma$ and the experimental

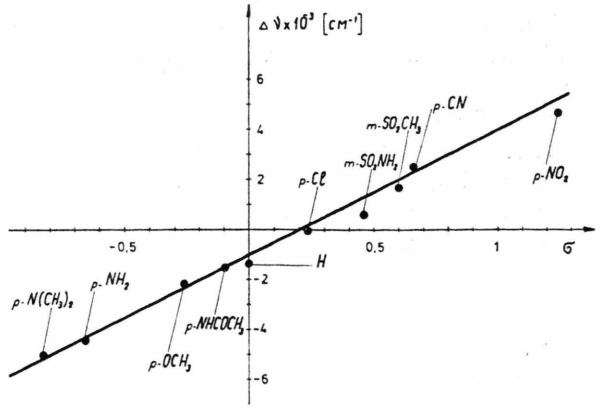


Fig. 4. Dependency of $\Delta\nu = \nu_{Abs}(H) - \nu_{Abs}(I^{\ominus})$ upon the $\sigma$ Hammett constants (only for X = p-$NO_2$ $\sigma^-$ value is used). $\Delta\nu = a\,\sigma + b$, where $a = -1180$ cm$^{-1}$, $b = 4750$ cm$^{-1}$; $r^2 = 0.996$.

values $\Delta\nu = \nu_{Abs}(IH) - \nu_{Abs}(I^{\ominus})$. Although the absorption maxima of the two forms correlate with different slopes for $\sigma \leqq 0$ and $\sigma \geqq 0$, their differences correlate with one and the same slope in both regions. Further, the above mentioned quantum-chemical estimation of the properties of the electron donors/acceptors, constructed from pairs of the groups X—Ph, C—O$^{\ominus}$, and C=O, confirms and generalizes the hypothesis of Griffiths [13] on the charge migration in azoquinonehydrazone tautomeric systems.

For most organic compounds donor and acceptor substituents cause the same shift in fluorescence as well as in absorption bands. Such behaviour was observed for the IH form of the compounds studied with electron acceptor substituents ($\sigma \geqq 0$); the influence of these substituents on the fluorescence spectrum is more marked (Fig. 3, H and F). The electron donor substituents ($\sigma \leqq 0$), however, display a two-directional effect, i.e. a strong bathochromic shift of the absorption bands and a significantly weaker hypsochromic shift of the fluorescence maxima (Fig. 3, H and F). In passing it is worthwile to note that the fluorescence maxima correlate to a single line in the whole range of the $\sigma$ constants, like $\Delta\nu$ as mentioned above.

A more detailed analysis on the basis of [14] shows that the $S_0 - S_1$ energy gap is lessened by substituents in general, but that the steepness of both potentials ($S_0$ and $S_1$) is decreased by electron donor substituents and increased by electron acceptor substituents.

The use of the dual substituent parameter equation does not improve the correlations shown in Figure 3. The dual equation cannot be applied in the whole range of the substituents. Only the separate treatment of donating and accepting substituents achieves acceptable correlations for the spectral substituent shift $\Delta\nu$ ($\Delta\nu$ denotes the difference in the maxima of the spectra of the substituted and nonsubstituted compound):

| | Donors | Acceptors |
|---|---|---|
| $\Delta\nu$ (Abs, H form): | $7.3\,\sigma_I + 5.3\,\sigma_R$ | $-0.32\,\sigma_I + 0.67\,\sigma_R$ |
| $\Delta\nu$ (Fl, H form): | $-1.7\,\sigma_I + 0.88\,\sigma_R$ | $-0.74\,\sigma_I - 1.5\,\sigma_R$ |
| $\Delta\nu$ (Abs, I$^{\ominus}$ form): | $8.0\,\sigma_I + 5.0\,\sigma_R$ | $-6.9\ \sigma_I - 7.3\,\sigma_R$ |

For all substituents the product $\varrho_I\sigma_I$ is comparable with $\varrho_R\sigma_R$. This is in contradiction to

King's conclusions [11] that the fluorescence maxima should be independent of the inductive effects.

### 3. *Stokes Shift*

The Stokes shift $\Delta\nu_{St} = \nu_{Abs} - \nu_{Fl}$ for all compounds studied is given in Table 1. Using Nurmukhametov's classification concerning aromatic compounds [15] to the effect that a shift is anomalously great when it exceeds 5000 $cm^{-1}$, it can be asserted that with the exception of the p-$N(CH_3)_2$ compound, all monosubstituted compounds manifest an anomalously large Stokes shift. For X=p-$NO_2$, $\Delta\nu_{St}$ has a value of 9400 $cm^{-1}$, near that observed by Weller [17] for salicyclic acid.

Stokes shifts of the magnitudes observed are usually caused by an proton transfer in the excited state. As mentioned above, such a proton transfer can be excluded in our case by the similarity of the absorption and the fluorescence spectra of IH(X=H) and VI. A possible explanation of the anomalous magnitude of the Stokes shifts is offered by its proportionality to the change of Iulg's degree of aromaticity [16] upon the $S_0 - S_1$ transition (Table 3).

Since in the field of aromatic compounds, usually $A(S_1) - A(S_0) = \Delta A \leqq 0.1$, the critical value of 5000 $cm^{-1}$ for the normal Stokes shifts [15] corresponds to such a value of $\Delta A$; in case of non aromatic compounds, a greater magnitude of the critical value should be expected.

Benzazole VIII [18] and the corresponding bisbenzazole [19], both having hydrogen bridges of the form O—H...N=C, exhibit a very large Stokes shift due to a proton transfer in the excited state. o-Hydroxyphenylazopyrazolone (VII = N° 5 in Table 1) has an analogous structure. Therefore, its anomalous Stokes shift could also be due to a proton transfer. However, the o-methoxy derivative (N° 4 in Table 1), which has no mobile proton, shows a larger Stokes shift than VII; therefore, the proton transfer could not be the reason for the anomalous magnitude of the Stokes shift of VII. A similar situation might exist in the case of the o-carboxy derivative (N° 10 in Table 1).

### 4. *Solvent Effect*

Cyclohexane, chloroform, ethanol, dimethylsulfoxide, and hexamethylphosphorustriamide have been used as solvents. In the $10^{-3}$ to $10^{-6}$ M interval, no concentration effects were observed on the positions of the maxima in the excitation, absorption, and fluorescence spectra. The increase of the polarity of the solvent leads to a bathochromice shift of the longest wavelength absorption maximum for the electron donor substituents, while for electron acceptor substituents the effect is negligible.

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Table 3. Julg's degree of aromaticity [16] and comparison of $\Delta A = A(S_1) - A(S_0)$ with $\Delta\nu_{St}$. The contributions to $A$ upon bonds and charges are taken into account by $A_1$ and $A_2$, respectively.

| | X | $S_0$ | | | $S_1$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $A_1$ | $A_2$ | $A$ | $A_1$ | $A_2$ | $A$ | $\Delta A$ | $\Delta\nu_{St}$ |
| IH | —CN | 0.769 | 0.285 | 0.219 | 0.839 | 0.541 | 0.451 | 0.232 | 9.1 |
| IH | —H | 0.771 | 0.288 | 0.224 | 0.843 | 0.541 | 0.455 | 0.231 | 8.7 |
| IH | $-NH_2$ | 0.770 | 0.300 | 0.231 | 0.833 | 0.475 | 0.396 | 0.165 | 5.4 |
| IIIH | H | | | | | | | 0.067 | 2.8 |

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