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Abstract

Full Text

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On the Connection Between Color and the Structure of the Products of the Janovsky Reaction

(Presented by Academician A. N. Terenin, 3 February 1962)

Acetone solutions of aromatic dinitro compounds in the presence of alkali, as Janovsky showed ([1]), form intensely colored products. Despite a number of studies of the Janovsky reaction ([2–5]) and its broad analytical application, the structure of these products has not been clarified up to the present time. In studying their absorption spectra we established ([6,7]) that dinitro derivatives of the aromatic series form two colored complexes of the quinoid type: monosalt I with a short-wavelength absorption maximum (550—573 mμ) and monosalt II with a long-wavelength absorption maximum (600—688 mμ).

$$\underset{\text{Monosalt I}}{\left[\text{ quinoid structure with } X,\ RO,\ H,\ NO_2,\ NO_2^-\ \right]K^+} \qquad \underset{\text{Monosalt II}}{\left[\text{ quinoid structure with } X,\ H,\ OR,\ NO_2,\ NO_2^-\right.}$$

where

$$OR = -O - C\begin{matrix}=CH_2\\ \backslash CH_3\end{matrix}.$$

In the absorption spectra of most dinitro derivatives, considerable shifts of both absorption maxima were observed in comparison with *m*-dinitrobenzene. The results of measurements ([6,7]) show that the introduction of a substituent X in place of a hydrogen atom leads to hypsochromic shifts of the absorption maximum irrespective of the electron-donor or electron-acceptor nature of the substituent.

The effect of the substituent on the position of the absorption maximum apparently consists in its influence on the conjugation chain. In monosalts I and II, conjugation is effected between two nitro groups, one of which bears the negative charge of the anion and is therefore electron-donating. Interaction of the donor and acceptor nitro groups leads to a uniform distribution of this charge along the conjugation chain. Introduction of a substituent disrupts the uniform distribution of the anion charge along the conjugation chain and creates in it an asymmetry of electron density. This changes the energy of the ground

(unexcited) state of the molecule and leads to the corresponding shift of the absorption maximum. Disruption of the symmetry of the conjugation chain may be caused both by electron-donor and by electron-acceptor groups, as a result of which they will shift the absorption maximum in the same direction. A similar phenomenon was observed by Kiprianov and co-workers for thiocyanine dyes ([8]), and by Gerzon and Heilbronner for phenyl-azo-azulenes ([9]).

The study of the absorption spectra of the monosalts of derivatives of *m*-dinitrobenzene makes it possible to investigate simultaneously two cases of the arrangement

the substituent relative to the conjugation chain: 1) the substituent is bonded to a carbon atom of the conjugation chain through a single *C*—*C* bond (monosalt I, short-wavelength maximum); 2) the substituent is directly bonded to a carbon atom of the conjugation chain (monosalt II, long-wavelength maximum).

Fig. 1
Fig. 1. Relation between the value σ_m and the shift of the absorption maximum for monosalt I

Fig. 2
Fig. 2. Relation between the value $\sigma_n - \sigma_1$ and the shift of the absorption maximum for monosalt II

In monosalt I, the action of the substituent is due to its ability to withdraw electrons and enter into competition with the electron-acceptor nitro group, which decreases the magnitude of the charge in the conjugation chain.

Indeed, for most of the substituents studied, the shift of the absorption maximum corresponds to the strength of their negative inductive effect. This is seen from Fig. 1, where a linear dependence is observed fairly well between the shift of the absorption maximum and the Hammett value σ_m ([10]), which expresses, basically, the magnitude of the inductive effect of the substituent. The exception is the iodine atom, which leads to a much smaller $\Delta\lambda_{\max}$ than is required by the value of σ_m. Electron-donor substituents also lead to hypsochromic shifts of $\lambda_{\max}$. The electron-donor substituents we studied may be arranged in the following series:

X	NH_2	$O—CH_2—CH_2—O^-$	$N\begin{matrix}/H\\ \backslash O^-\end{matrix}$
$-\Delta\lambda_{\max}$	51	80	83

Fig. 3
Fig. 3. Relation between the value $\mu_{\mathrm{ArX}} - \mu_{\mathrm{AlkX}}$ and the shift of the absorption maximum for monosalt II

Their action probably consists in a decrease in the strength of the electrophilic nitro group owing to partial transfer to it of their negative charge. In the case of monosalt II, the conjugation chain can be represented schematically as

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shown in Fig. 2. Here the influence of the substituent apparently consists in displacement of the lone pair of electrons toward the electronophilic nitro group, which leads to a decrease in its electron-acceptor strength. Its interaction takes place along the conjugation chain indicated by dotted arrows. Such an action of substituents, leading to a decrease in the degree of conjugation between the nitro groups, is equivalent to a "shortening" of the conjugation chain and should lead to a hypsochromic shift of λ_{max}. It is evidently determined by the magnitude of the conjugation effect of the substituents.

Convincing confirmation of this fact is provided by the linear dependence between the shifts of the absorption maximum and the quantities $\sigma_n - \sigma'$ (according to Roberts and Moreland(11)) and $\mu_{ArX} - \mu_{AlkX}$(12), which, as is known, quantitatively characterize the magnitude of the conjugation effect of substituents (Figs. 2 and 3). The influence of the methyl group should be noted in particular: owing to σ, π-conjugation(13), it exhibits the same electron-donor properties as the bromine atom.

The nitro group ($-\Delta\lambda_{max} = 32$ mμ) cannot take part in the above-mentioned conjugation, and its action is possibly due to a negative inductive effect. The results presented above constitute a quantitative confirmation of the explanation we have proposed for the influence of substituents on the position of the absorption maximum of the complexes. At the same time, on the basis of the linear dependences obtained (Figs. 1, 2, 3), knowing the shift of both absorption maxima, one can determine the magnitude of both σ_m and σ_n for a given substituent without resorting to kinetic measurements.

Thus, measurement of the absorption spectra of the colored products of the Janovsky reaction provides a sufficiently simple and reliable method for the separate quantitative estimation of the magnitude of the inductive influence of a substituent (short-wavelength maximum) and the strength of its conjugation effect (long-wavelength maximum).

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CITED LITERATURE

1. J. V. Janowsky, *Ber.*, **10**, 2155 (1886).

2. A. I. Shatenshtein, Ya. M. Varshavskii, *ZhFKh*, **22**, 529 (1948).

3. T. Canbäck, *Farmac. Rev.*, **48**, 153 (1949); **48**, 217 (1949).

4. M. J. Newlands, F. Wild, *J. Chem. Soc.*, 1956, 3696.

5. J. P. Heotis, J. W. Cavett, *Anal. Chem.*, **31**, 1977 (1959).

6. S. S. Gitis, G. I. Oksengendler, A. Ya. Kaminskii, *ZhOKh*, **29**, 2983 (1959).

7. S. S. Gitis, A. Ya. Kaminskii, *ZhOKh*, **30**, 3810 (1960).

8. A. I. Kiprianov, I. K. Ushenko, *ZhOKh*, **15**, 207 (1945).

9. F. Gerson, E. Heilbronner, *Helv. Chim. Acta*, **42**, 1877 (1959).

10. H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

11. *Steric Effects in Organic Chemistry*, Izd. Inostrannoi Literatury, 1960, p. 595.

12. K. K. Ingold, *Mechanism of Reactions and Structure of Organic Compounds*, Izd. Inostrannoi Literatury, 1959, p. 88.

13. A. N. Nesmeyanov, *Scientific Notes of Moscow University*, issue 132, book 7, 1 (1950).

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