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SIGMA COMPLEXES IN THE PYRIMIDINE SERIES.

4.* INVESTIGATION OF THE ELECTRONIC ABSORPTION SPECTRA OF ANIONIC SIGMA COMPLEXES OF 5-NITROPYRIMIDINE

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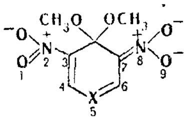
The electronic absorption spectra of sigma complexes of the Meisenheimer type, viz., the anions of potassium salts of 4H-5-nitro-4-acetonylpyrimidines, were investigated. The 5-nitropyrimidine molecule and its sigma complex involving the 4 position were subjected to quantum-chemical calculation by the simple MO LCAO method. It is shown that it is expedient to use the Forster—Dewar—Knott rule for the study of the electronic spectra of the indicated sigma complexes.

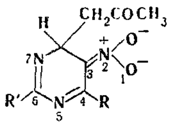
It is known that 5-nitropyrimidines, like di- and trinitrobenzenes, add nucleophilic reagents, viz., potassium methoxide [1, 2] and potassium derivatives of acetone and acetophenone [3, 4], to give colored sigma complexes of the Meisenheimer type [5].

The absorption spectra of these complexes have not been previously examined from the point of view of the general principles of the theory of chromaticity of organic compounds and have not been compared with the spectra of the similarly constructed Meisenheimer complexes of the benzene series. It was recently shown [6] that it is expedient to use the Forster—Dewar—Knott (FDK) rule [7-9] for the study of the spectra of anionic sigma complexes.

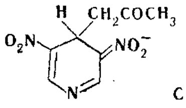
This rule makes it possible to qualitatively explain the shift of the absorption bands when substituents with different electronic natures are introduced in the polymethine chromophore. In addition, a quantitative correlation relationship between the absorption frequencies and the σ_I and σ_R substituent constants can often be found. For example, the following relationship has been found [6] for sigma complexes of the I type, where X is the methylidyne carbon atom with substituent R:



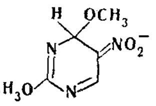
I



II



III



IV

I a $X = \rangle C-H$; b $X = \rangle C-NO_2$; c $X = \rangle N$; II a $R=R'=H$; b $R=OCH_3$, $R'=H$;
c $R=H$, $R'=OCH_3$; d $R=R'=OCH_3$; e $R=H$, $R'=C_6H_5$

$$\nu = 16\,864 + 2567(\sigma_I + 3.20\sigma_R).$$

According to the FDK rule, the presence of electron-acceptor substituents attached to the odd-numbered carbon atoms in the chromophore (see formula I) or replacement of these atoms by more electronegative nitrogen atoms should lead to a shift in the absorption band to the short-wave region (a hypsochromic effect). Thus σ complex Ia has a λ_{max} band at 586 nm, while σ complex Ib has a λ_{max} band at 492 nm [in dimethylformamide (DMF)] [10]. Sigma complex Ic displays another large hypsochromic effect with λ_{max} at 455 nm (in

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*See [16] for Communication 3.

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TABLE 1. Electronic Absorption Spectra of σ Complexes II and IV

Compound	λ_{max} ($\varepsilon \cdot 10^{-4}$)	$\Delta\lambda$
IIa	244 (0,29) sh; 360 (0,51), 454 (0,66)	
IIb	254 (0,72), 405 (0,84)	−49
IIc	234 (0,24), 397 (0,27)	−57
IId	249 (0,57), 385 (2,14)	−69
IIe	263 (0,48), 406 (0,11)	−48
IV*	403 DMSO	

*Described in [2].

methanol) [1, 11]. This is not only in qualitative agreement with the FDK rule but is also quantitatively close to the maximum at 483 nm found from the equation presented above if it is assumed that $\sigma_R = 0.24$ [12] and $\sigma_I = \sigma_p - \sigma_R = 0.72$ (found from $\sigma_p = 0.96$) [13] for the nitrogen atom. Thus the FDK rule makes it possible to qualitatively and quantitatively determine the effect of the nitrogen atoms in anionic σ complexes of dinitropyridine on their electronic absorption spectra.

The present research was devoted to a study of the electronic absorption spectra of the anionic σ complexes of 5-nitropyrimidine derivatives II [4]. (IIe has not been previously described.)

The absorption maxima of the σ complexes depend not only on the chromophore π-electron system but also on the groups bonded to the nodal carbon atom. These groups have an inductive effect on the chromophore. Since the nodal carbon atom is bonded to odd-numbered (3 and 7) carbon atoms of the chromophore, from the FDK rule it might be expected that electron-acceptor groups attached to this atom would have a hypsochromic efffect. The absorption bands of the sigma complexes obtained by the addition of the $CH_3COCH_2^-$ anion to the nitro compounds are therefore found in a longer-wave region than the absorption bands of anionic sigma complexes I. For example, complex III has a λ_{max} band at 519 nm [in dimethyl sulfoxide (DMSO)] [14], while complex Ic has a λ_{max} band at 455 nm. A comparison of the absorption maxima of complexes III and IIa shows that replacement of the carbon atom with the terminal nitro group of the chromophore by a nitrogen atom shifts the absorption maximum 65 nm to the short-wave region.

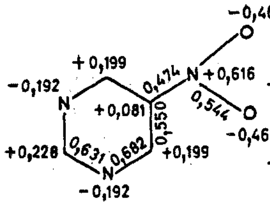
According to the FDK rule, electron-donor substituents attached to even-numbered carbon atoms of the chromophore should also have hypsochromic effects. This is confirmed in the case of σ complexes IIb-d. The phenyl group in the 2 position of complex IIe also affects the spectrum like an electron-donor substituent.

The close values of the absorption maxima of sigma complexes IV and IIc indicate the presence of an identical conjugation chain in these compounds.

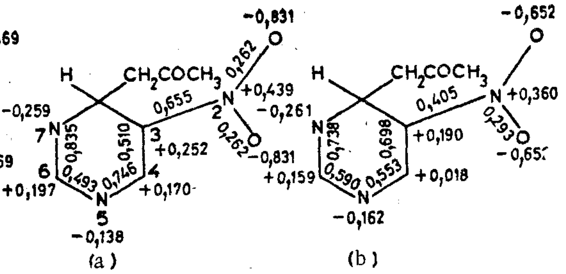
We subjected the 5-nitropyrimidine molecule and its sigma complex involving the 4 position to quantum-chemical calculation by the simple MO LCAO method within the Hückel approximation, for which we used the parameters for the heteroatoms presented in [15].

The charges of the atoms and the orders of the π bonds of the 5-nitropyrimidine molecule in the ground state and its σ complex involving the 4 position in the ground and excited states are presented.

The positive charge in the 2 position (+0.228) of 5-nitropyrimidine is greater than in the 4 position (+0.199). A strong nucleophilic reagent such as $AlkO^-$ therefore adds to the 2 position [2]. The sigma complex involving the 4 position is evidently more stable, since its π-electron energy (+15.194β) is greater than for the σ complex involving the 2 position (+15.117β). A more stable σ complex involving the 4 position is therefore formed by the action of a weaker and milder nucleophilic agent, viz., the acetonyl anion, on 5-nitropyrimidine [4]. According to the results of a calculation of the excited state of the σ complex obtained in the case of nucleophilic attack by the acetonyl anion on the 4 position of 5-nitropyrimidine, the electron density increases in the even-numbered positions (for example, the 4 and 6 positions) of the chromophore. Electron-donor substituents increase the energy of the excited state and thereby have a hypsochromic effect, in con-



Ground state of 5-nitropyrimidine



(a)

(b)

Ground (a) and excited (b) states of the σ complex of 5-nitropyrimidine with the acetonyl anion

formity with the FDK rule, i.e., the calculated values are in agreement with the experimental values.

Thus the FDK rule makes it possible to explain the effect of the nitrogen atom and the substituents on the absorption spectra of σ complexes of pyrimidine derivatives.

EXPERIMENTAL

The electronic spectra of solutions (on the order of 10^{-4} mole/liter) of the compounds in methanol were recorded with a Specord UV-vis spectrophotometer. Sigma complexes IIa-d were obtained by the method in [4].

5-Nitro-2-phenyl-4H-4-acetonylpyrimidine Potassium Salt (IIe). A 0.14-g (2.5 mmole) sample of finely ground potassium hydroxide was added with vigorous stirring to a suspension of 0.5 g (2.5 mmole) of 5-nitro-2-phenylpyrimidine in 20 ml of acetone, during which a dark-red coloration that became deeper with time developed. After 75 min, 0.07 g of KOH was added, and another 0.07 g of KOH was added after 50 min. Twenty minutes after the last addition the reaction mixture was filtered to remove the unchanged KOH, the filtrate was evaporated to a volume of 3-4 ml, and dark-red shiny crystals of σ complex IIe were precipitated by the addition of diethyl ether. The yield was 0.59 g (80%). PMR spectrum (in d_6-DMSO): 8.63 (1H, s, 6-H), 7.60-8.26 (5H, m, phenyl protons), 5.50 (1H, dt, 4-H), 3.00 (2H, m, CH_2—4-H), and 2.43 ppm (3H, s, CH_3). Found: C 52.6; H 4.4; K 13.1; N 16.0%. $C_{13}H_{12}KN_3O_3$. Calculated: C 52.5; H 4.0; K 13.3; N 16.1%.

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