ELECTRONIC ABSORPTION SPECTRA OF NITROANILINES

Viktor ŘEHÁK[a] and Vladimír KADEŘÁBEK[b]

[a] *Department of Organic Technology and*
[b] *Department of Chemical Technology of Paper and Cellulose,*
Institute of Chemical Technology, 532 10 Pardubice

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Electronic absorption spectra of N-alkyl- and N-arylsubstituted 2,4-dinitro- and 2,6-dinitroanilines are discussed in the terms of energy and intensity of the energetically lowest absorption transitions and molecular structure (intramolecular hydrogen bond, sterical effects, hyperconjugation and increase of the π-electronic system of the molecule).

Murrel[1] interpreted satisfactorily spectral properties of *o*-, *m*- and *p*-nitroanilines in the terms of locally excited and charge-transfer (CT) configurations. Inductive effect of amino and nitro groups operating in the aromatic nucleus was shown to have decisive influence on energy and intensity of the electronic transitions. The $2p_a$ AO of the nitrogen atom plays an important role in the transfer of charge to the electron-deficient aromatic nucleus. On the basis of the quantum chemical calculations using the MIM method (molecules in molecules)[2] and localized orbitals at the amino and nitro groups and benzene nucleus it was possible to calculate energies and intensities of transitions showing a good agreement with experiment. Both the CT and the locally excited configurations were found to contribute to the first absorption band to different extent.

In this communication absorption spectra of N-alkyl- and N-arylsubstituted 2,4-dinitro- and 2,6-dinitroanilines are discussed in the terms of energy and intensity of the energetically lowest absorption transitions, intramolecular hydrogen bond and sterical effects.

EXPERIMENTAL

For references to preparations of the measured substances and their published and found melting points see our paper[3]. Purity of the compounds was checked by TL chromatography on silica gel and by paper chromatography[3]. The electronic absorption spectra were measured at the room temperature by the standard method using a double-beam recording spectrophotometer Specord UV VIS (Zeiss, Jena) in the medium of spectroscopically pure ethanol. Suitable concentration was $5 \cdot 10^{-5}$M. The spectrum was measured and read within the range 217 to 500 nm.

RESULTS AND DISCUSSION

2,4-*Dinitroanilines* (2,4-DNA). The long-wavelength absorption band of 2,4-dinitroaniline (Table I, 23000 to 32000 cm^{-1}) is composed of two electronic transitions.

TABLE I

Electronic Absorption Spectra of N-Substituted 2,4-Dinitroanilines

Aniline	$\nu . 10^{-3}$ cm^{-1}	ε_{max}	$\nu . 10^{-3}$ cm^{-1}	ε_{max}	$\nu . 10^{-3}$ cm^{-1}	ε_{max}	$\nu . 10^{-3}$ cm^{-1}	ε_{max}
2,4-Dinitro-	26·00	6 900	29·57	14 200	38·65	9 850	44·00	11 000
N-Methyl-2,4-dinitro-	24·80	6 250	28·50	16 250	38·30	9 120	—	—
N,N-Dimethyl-2,4-dinitro-	—	—	27·00	17 300	—	—	—	—
N-Ethyl-2,4-dinitro-	24·80[a]	6 400[a]	28·60	16 200	38·20	8·750	—	—
N,N-Diethyl-2,4-dinitro-	—	—	26·60	16 000	—	—	—	—
N-Propyl-2,4-dinitro-	24·80[a]	6 500[a]	28·60	16 900	38·17	9 300	—	—
N-Isopropyl-2,4-dinitro-	24·80[a]	6 800[a]	28·60	17 800	38·15	9 550	—	—
N-Butyl-2,4-dinitro-	24·80[a]	6 700[a]	28·60	17 100	38·30	9 400	—	—
N-Isobutyl-2,4-dinitro-	24·80[a]	6 400[a]	28·60	16 500	38·30	9 400	—	—
N-Cyclohexyl-2,4-dinitro-	24·70[a]	6 200[a]	28·60	17 200	38·10	8 800	—	—
N-Phenyl-2,4-dinitro-	—	—	28·15	8 800	38·35[a]	11 000[a]	43·10	14 200
N-2′,4′-Dinitrophenyl-2,4-dinitro-	27·70	22 600	27·70	17 600	—	—	—	—
N,N-Diphenyl-2,4-dinitro-	24·70	12 000	—	—	—	—	40·50	17 800
N-Methyl-N-phenyl-2,4-dinitro-	—	—	26·40	15 200	—	—	40·70	15 400
N-2′-Aminophenyl-2,4-dinitro-	—	—	28·70	17 800	—	—	—	—
N-1-Naphthyl-2,4-dinitro-	—	—	28·50	16 500	—	—	—	—
N-2′,4′-Dinitrophenyl-N-phenyl-2,4-dinitro-	24·10	4 100	28·05	4 750	—	—	41·90	18 900
N,N-Bis(2,4-dinitrophenyl)-2,4-dinitro-	—	—	27·20	5 200	—	—	—	—

[a] Inflection.

Theoretical calculations show[2] that the transition with the maximum at 26000 cm^{-1} has predominantly the character of the locally excited configuration Λ_1. The CT configurations of the nitro groups at 2 and 4 positions contribute with a substantially lower weight ($75\Lambda_1$, $13T_1^{A_2}$, $9T_2^{A_4}$), out of them the most significant being the CT configuration bound to *o*-nitro group. The energetically higher transition (max. 29570 cm^{-1}) has (according to theory) predominantly the character of the CT configuration bound to *p*-nitro group ($78T_1^{A_4}$). This interpretation also agrees with rough comparison of spectra of *o*-nitroaniline and *p*-nitroaniline with those of 2,4-dinitroaniline[4].

The energetically higher transitions above 35000 cm^{-1} have the character of considerably mixed CT configurations.

Monoalkyl substitution results in bathochromic shift of the long-wavelength absorption bands by 1000 to 1200 cm^{-1} and simultaneous intensity increase of the transitions (Table I).

N-Aryl substitution causes bathochromic shift of the second absorption band by 1400 cm^{-1} and intensity increase of the transition, the half-width of the absorption band being simultaneously increased to such an extent that the first transition is overlapped. Similar changes (even though to a lesser extent) can be found in region of higher energies (above 34000 cm^{-1}).

N,N-Dialkyl substitution has, at first sight, a similar effect as the N-aryl substitution (bathochromic shift by 2560 to 3000 cm^{-1} and intensity increase), the reason being, however, of quite a different nature (see below).

The combined N-alkyl-N-aryl substitution has a similar effect as the dialkyl substitution, the transition intensity being smaller than that for N,N-dialkyl derivative and higher than that for the N-phenyl derivative.

N,N-Diaryl substitution results in a strong bathochromic shift (by 4870 cm^{-1}) of the absorption band, its broadening (from 4500 cm^{-1} to 6600 cm^{-1}) and intensity decrease (Table I).

2,6-*Dinitroanilines* (2,6-DNA). The long-wavelength absorption band (Table II, 20000 to 28000 cm^{-1}) involves, according to theoretical prediction[2], only one vibronic transition with predominant CT character with the same contributions of the both nitro groups ($32\Lambda_1$, $20T_1^{A_6}$, $20T_1^{A_2}$). Also theory predicts well the relatively large energy interval (12910 cm^{-1}, experiment 16400 cm^{-1}) between transitions to the S_1 and S_3 states. The second singlet excited state is probably situated in the short-wavelength part of the first absorption band.

N,N-Dialkyl substitution first of all affects markedly the transitions intensity, their energy being changed less than that of 2,4-DNA. A still greater intensity decrease is encountered with the N-phenyl derivative, the energy of transition maximum being, however, unchanged.

N,N-Dialkyl substitution results in drastic intensity decrease of the first absorption band; a weak bathochromic shift takes place (1000 cm^{-1}).

The observed changes can theoretically be interpreted on the basis of cooperation of the following factors: *a*) formation of intramolecular hydrogen bond, *b*) steric effects, *c*) effect of hyperconjugation, *d*) extension of conjugation to another aromatic system.

Nitro and amino groups at *o*-position form intramolecular hydrogen bond[5]; in the opinion of several authors[6] this H-bond forms an additional pseudoaromatic ring enabling partial delocalization of the free electron pair of amino group, which increases planarity of the whole system[7]. The $2p_z$ AO of the amino nitrogen atom is oriented perpendicularly to the plane of the molecule, and its interaction with the whole π-electron system of the molecule is significant. These two energy contributions (delocalization energy) along with the induction component lower the energy of the $2p_z$ AO at the amino nitrogen atom, the CT transition of the $2p_z \rightarrow \pi^*$ type will have the highest energy within the series of the N-substituted compounds.

The N-substitution introduces disturbances in the molecular system (steric hindrance, hyperconjugation effects of alkyl groups). Both these effects concordantly increase the π-electron density at the amino nitrogen and, hence, also energy of the $2p_z$ AO.

Mono-N-alkyl substitution of 2,4-DNA probably has no marked effect on the intramolecular hydrogen bond, the steric effect being of little importance here, too, thus the observed spectral shifts (which are roughly the same for all alkyl groups) can be assigned to the hyperconjugation effect predominantly. This is manifested almost equally in CT transitions connected with both *o*-nitro- and *p*-nitro groups.

TABLE II

Electronic Absorption Spectra of N-Substituted 2,6-Dinitroanilines[a]

Aniline	$\nu \cdot 10^{-3}$ cm^{-1}	ε_{max}	$\nu \cdot 10^{-3}$ cm^{-1}	ε_{max}	$\nu \cdot 10^{-3}$ cm^{-1}	ε_{max}
2,6-Dinitro-	23·50	9·400	39·90	11 400	44·90	24 100
N-Methyl-2,6-dinitro-	23·40	7 000	38·00	5 600	43·20	21 600
N,N-Dimethyl-2,6-dinitro-	24·40	760	—	—	42·60	13 000
N-Ethyl-2,6-dinitro-	23·40	6 800	37·80[b]	5 800[b]	43·15	23 000
N,N-Diethyl-2,6-dinitro-	24·20	730	—	—	43·00	11 350
N,N-Dipropyl-2,6-dinitro-	30·10[b]	640[b]	34·30	1 660	—	—
N-Cyclohexyl-2,6-dinitro-	23·45	5 900	—	—	42·90	22 400
N-Phenyl-2,6-dinitro-	23·50	1 280	39·15	4 900	—	—

[a] Morpholino-2,6-dinitrobenzene: $\nu \cdot 10^{-3} = 26 \cdot 30$, $\varepsilon_{max} = 1\ 440$.

A different situation is encountered with N,N-dialkyl substitution, where there is no hydrogen bond, and bulky groups at amino nitrogen cause deviations from coplanarity. With respect to the bathochromic shift of the second absorption band (2,4-DNA) and its intensity increase it can be presumed that rather the *o*-nitro group is deviated from coplanarity, its electron-acceptor effect being strongly decreased.

In the case of 2,6-DNA effects of N-substitution are still more marked. Formation of two hydrogen bonds stabilizes the whole molecule considerably, the planar structure being energetically the most advantageous. The both nitro groups are completely equivalent in their effects. N-Alkyl substitution eliminates one hydrogen bond and causes an intensity decrease of the long-wave absorption band and increase of its half-width. The intensity decrease can be explained by deviation of nitro group from coplanarity rather than by that of alkylamino group, the latter being fixed by hydrogen bond. From the change of the transition intensity it is possible to calculate (in rough approximation) the relative angle of deviation according to Webster's considerations[8] from the equation $\varepsilon_{\text{subst}}/\varepsilon_{\text{unsubst}} = \cos^2 \alpha$, where ε is molar absorption coefficient of the substituted and the reference unsubstituted derivatives. The calculated values are given in Table III.

N,N-Dialkyl substitution has a drastic effect on intensity of the long-wavelength absorption band as well as on those in the region of higher energies. The overall structure of spectrum is strongly blurred. The hydrogen bonds do not exist, and coplanarity of the molecule is considerably disturbed. The calculated deviations from coplanarity (Table III) are more than doubled as compared with N-alkyl substitution. This fact quite agrees with theoretical presumption, since the deviation from coplanarity concerns all the three substituents, the calculated angle being most probably sum of all the deviation angles. Interesting relatively small shifts of absorption maxima of the alkyl and dialkyl derivatives are observed as compared with 2,6-DNA. It would suggest that the relative energy shifts $2p_z$ AO, π and π^* MO are practically

TABLE III

Deviations from Coplanarity[a] with 2,6-DNA

N-Substituent	α^0	N-Substituent	α^0
CH_3-	30	$(CH_3)_2$-	73
C_2H_5-	31	$(C_2H_5)_2$-	70
C_6H_{11}-	38	$(C_3H_7)_2$-	75
C_6H_5-	68		

[a] Morpholino-2,6-dinitrobenzene: $\alpha = 67°$.

maintained, or that the $2p_z$ AO energy remains unchanged, and, hence, also its delocalization in π-molecular system is maintained, which would mean that amino group remains in the plane of the molecule, and nitro groups are deviated (predominantly).

N-Aryl substitution of 2,4-DNA causes bathochromic shift of long-wavelength absorption band and intensity decrease. These facts can be explained by extension of π-molecular conjugated system and greater delocalization of $2p_z$ AO electrons of the amino nitrogen. In case of 2,6-DNA N-phenyl substitution only lowers intensity of the long-wave absorption band, position of the maximum being maintained and almost identical with that of N-cyclohexyl and other N-alkyl derivatives. It means that extension of the π-electronic conjugated system and increased delocalization of $2p_z$ AO into the phenyl ring do not make themsevles felt in this case. It can be presumed that deviation from complanarity concerns both nitro group and phenyl ring.

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